Online Issn : 2249 - 4626
Print Issn : 0975 - 5896

GLOBAL JOURNAL

OF SCIENCE FRONTIER RESEARCH : B

CHEMISTRY

DISCOVERING THOUGHTS AND INVENTING FUTURE

HIGHLIGHTS

- Non Rigid Tetraphenylporphyrin
- facile Multicomponent Synthesis
- Plectranthus tenuiflorus (Shara)
- Trichlorom Ethane Solutions

Volume 12 | Issue 1 | Version 1.0

ENG

Global Journal of Science Frontier Research: B
Chemistry

Global Journal of Science Frontier Research: B
Chemistry

Volume 12 Issue 1 (Ver. 1.0)

Open Association of Research Society

© Global Journal of Science Frontier Research .2012 .

All rights reserved.

This is a special issue published in version 1.0 of "Global Journal of Science Frontier Research." By Global Journals Inc.

All articles are open access articles distributed under "Global Journal of Science Frontier Research"

Reading License, which permits restricted use. Entire contents are copyright by of "Global Journal of Science Frontier Research" unless otherwise noted on specific articles.

No part of this publication may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopy, recording, or any information storage and retrieval system, without written permission.

The opinions and statements made in this book are those of the authors concerned. Ultraculture has not verified and neither confirms nor denies any of the foregoing and no warranty or fitness is implied.

Engage with the contents herein at your own risk.

The use of this journal, and the terms and conditions for our providing information, is governed by our Disclaimer, Terms and Conditions and Privacy Policy given on our website http://globaljournals.us/terms-and-condition/menu-id-1463/

By referring / using / reading / any type of association / referencing this journal, this signifies and you acknowledge that you have read them and that you accept and will be bound by the terms thereof.

All information, journals, this journal, activities undertaken, materials, services and our website, terms and conditions, privacy policy, and this journal is subject to change anytime without any prior notice.

Incorporation No.: 0423089
License No.: 42125/022010/1186
Registration No.: 430374
Import-Export Code: 1109007027
Employer Identification Number (EIN):
USA Tax ID: 98-0673427

Global Journals Inc.

*(A Delaware USA Incorporation with "Good Standing"; **Reg. Number: 0423089**)*
Sponsors: *Open Association of Research Society*
Open Scientific Standards

Publisher's Headquarters office

Global Journals Inc., Headquarters Corporate Office,
Cambridge Office Center, II Canal Park, Floor No.
5th, ***Cambridge (Massachusetts)***, Pin: MA 02141
United States
USA Toll Free: +001-888-839-7392
USA Toll Free Fax: +001-888-839-7392

Offset Typesetting

Open Association of Research Society, Marsh Road,
Rainham, Essex, London RM13 8EU
United Kingdom.

Packaging & Continental Dispatching

Global Journals, India

Find a correspondence nodal officer near you

To find nodal officer of your country, please email us at *local@globaljournals.org*

eContacts

Press Inquiries: *press@globaljournals.org*
Investor Inquiries: *investers@globaljournals.org*
Technical Support: *technology@globaljournals.org*
Media & Releases: *media@globaljournals.org*

Pricing (Including by Air Parcel Charges):

For Authors:
22 USD (B/W) & 50 USD (Color)
Yearly Subscription (Personal & Institutional):
200 USD (B/W) & 250 USD (Color)

Editorial Board Members (HON.)

John A. Hamilton,"Drew" Jr.,
Ph.D., Professor, Management
Computer Science and Software Engineering
Director, Information Assurance Laboratory
Auburn University
Dr. Henry Hexmoor
IEEE senior member since 2004
Ph.D. Computer Science, University at Buffalo
Department of Computer Science
Southern Illinois University at Carbondale
Dr. Osman Balci, Professor
Department of Computer Science
Virginia Tech, Virginia University
Ph.D.and M.S.Syracuse University, Syracuse, New York
M.S. and B.S. Bogazici University, Istanbul, Turkey
Yogita Bajpai
M.Sc. (Computer Science), FICCT
U.S.A.Email:
yogita@computerresearch.org

Dr. T. David A. Forbes
Associate Professor and Range Nutritionist
Ph.D. Edinburgh University - Animal Nutrition
M.S. Aberdeen University - Animal Nutrition
B.A. University of Dublin- Zoology

Dr. Wenying Feng
Professor, Department of Computing & Information Systems
Department of Mathematics
Trent University, Peterborough,
ON Canada K9J 7B8

Dr. Thomas Wischgoll
Computer Science and Engineering,
Wright State University, Dayton, Ohio
B.S., M.S., Ph.D.
(University of Kaiserslautern)

Dr. Abdurrahman Arslanyilmaz
Computer Science & Information Systems Department
Youngstown State University
Ph.D., Texas A&M University
University of Missouri, Columbia
Gazi University, Turkey
Dr. Xiaohong He
Professor of International Business
University of Quinnipiac
BS, Jilin Institute of Technology; MA, MS, PhD,. (University of Texas-Dallas)

Burcin Becerik-Gerber
University of Southern California
Ph.D. in Civil Engineering
DDes from Harvard University
M.S. from University of California, Berkeley & Istanbul University

Dr. Bart Lambrecht
Director of Research in Accounting and FinanceProfessor of Finance
Lancaster University Management School
BA (Antwerp); MPhil, MA, PhD (Cambridge)

Dr. Carlos García Pont
Associate Professor of Marketing
IESE Business School, University of Navarra
Doctor of Philosophy (Management), Massachusetts Institute of Technology (MIT)
Master in Business Administration, IESE, University of Navarra
Degree in Industrial Engineering, Universitat Politècnica de Catalunya

Dr. Fotini Labropulu
Mathematics - Luther College
University of ReginaPh.D., M.Sc. in Mathematics
B.A. (Honors) in Mathematics
University of Windso

Dr. Lynn Lim
Reader in Business and Marketing
Roehampton University, London
BCom, PGDip, MBA (Distinction), PhD, FHEA

Dr. Mihaly Mezei
ASSOCIATE PROFESSOR
Department of Structural and Chemical Biology, Mount Sinai School of Medical Center
Ph.D., Etvs Lornd University
Postdoctoral Training,
New York University

Dr. Söhnke M. Bartram
Department of Accounting and FinanceLancaster University Management SchoolPh.D. (WHU Koblenz)
MBA/BBA (University of Saarbrücken)

Dr. Miguel Angel Ariño
Professor of Decision Sciences
IESE Business School
Barcelona, Spain (Universidad de Navarra)
CEIBS (China Europe International Business School).
Beijing, Shanghai and Shenzhen
Ph.D. in Mathematics
University of Barcelona
BA in Mathematics (Licenciatura)
University of Barcelona

Philip G. Moscoso
Technology and Operations Management
IESE Business School, University of Navarra
Ph.D in Industrial Engineering and Management, ETH Zurich
M.Sc. in Chemical Engineering, ETH Zurich

Dr. Sanjay Dixit, M.D.
Director, EP Laboratories, Philadelphia VA Medical Center
Cardiovascular Medicine - Cardiac Arrhythmia
Univ of Penn School of Medicine

Dr. Han-Xiang Deng
MD., Ph.D
Associate Professor and Research Department Division of Neuromuscular Medicine
Davee Department of Neurology and Clinical NeuroscienceNorthwestern University
Feinberg School of Medicine

Dr. Pina C. Sanelli
Associate Professor of Public Health
Weill Cornell Medical College
Associate Attending Radiologist
NewYork-Presbyterian Hospital
MRI, MRA, CT, and CTA
Neuroradiology and Diagnostic
Radiology
M.D., State University of New York at
Buffalo,School of Medicine and
Biomedical Sciences

Dr. Roberto Sanchez
Associate Professor
Department of Structural and Chemical
Biology
Mount Sinai School of Medicine
Ph.D., The Rockefeller University

Dr. Wen-Yih Sun
Professor of Earth and Atmospheric
SciencesPurdue University Director
National Center for Typhoon and
Flooding Research, Taiwan
University Chair Professor
Department of Atmospheric Sciences,
National Central University, Chung-Li,
TaiwanUniversity Chair Professor
Institute of Environmental Engineering,
National Chiao Tung University, Hsin-chu, Taiwan.Ph.D., MS The University of
Chicago, Geophysical Sciences
BS National Taiwan University,
Atmospheric Sciences
Associate Professor of Radiology

Dr. Michael R. Rudnick
M.D., FACP
Associate Professor of Medicine
Chief, Renal Electrolyte and
Hypertension Division (PMC)
Penn Medicine, University of
Pennsylvania
Presbyterian Medical Center,
Philadelphia
Nephrology and Internal Medicine
Certified by the American Board of
Internal Medicine

Dr. Bassey Benjamin Esu
B.Sc. Marketing; MBA Marketing; Ph.D
Marketing
Lecturer, Department of Marketing,
University of Calabar
Tourism Consultant, Cross River State
Tourism Development Department
Co-ordinator , Sustainable Tourism
Initiative, Calabar, Nigeria

Dr. Aziz M. Barbar, Ph.D.
IEEE Senior Member
Chairperson, Department of Computer
Science
AUST - American University of Science &
Technology
Alfred Naccash Avenue – Ashrafieh

PRESIDENT EDITOR (HON.)

CHIEF AUTHOR (HON.)

DEAN & EDITOR-IN-CHIEF (HON.)

Contents of the Volume

Global Journal of Science Frontier Research
Chemistry
Volume 12 Issue 1 Version 1.0 January 2012
Type : Double Blind Peer Reviewed International Research Journal
Publisher: Global Journals Inc. (USA)
Online ISSN: 2249-4626 & Print ISSN: 0975-5896

Synthesis of poly (ε-caprolactone-co-propylene oxide) by a green catalyst, Maghnite

By Abdelghani Bouchama , Mohammed Issam Ferrahi ,
Mohamed Belbachir

Université d'Oran Es-Sènia, Oran, Algerie

Abstract - In the present work the copolymerization of ε-caprolactone (CL) with propylene oxide (PO) uses proton exchanged Montmorillonite clay as initiator is reported. The effects of the amounts of Maghnite -H+ and the temperature on the synthesis of poly (ε-caprolactone-co-propylene oxide) were studied. The copolymer obtained was characterized by 1H-NMR spectroscopy.

Keywords : Epichlorohydrin, Epsilon - caprolactone, Maghnite, Montmorillonite, Ring opening polymerization.

GJRE Classification : FOR Code: 030305

SYNTHESIS OF POLY -CAPROLACTONE-CO-PROPYLENE OXIDE BY A GREEN CATALYST, MAGHNITE

Synthesis of poly (ε -caprolactone-co-propylene oxide) by a green catalyst, Maghnite

Abdelghani Bouchama [α], Mohammed Issam Ferrahi [Ω] ,Mohamed Belbachir [β]

Abstract - I the present work the copolymerization ε of - caprolactone (CL) with propylene oxide (PO) uses proton exchanged Montmorillonite clay as initiator is reported. The effects of the amounts of Maghnite -H+ and the temperature on the synthesis of poly (ε-caprolactone-co-propylene oxide) were studied. The copolymer obtained was characterized by 1H-NMR spectroscopy.

Keywords : Epichlorohydrin, Epsilon - caprolactone, Maghnite, Montmorillonite, Ring opening polymerization.

I. INTRODUCTION

Polycaprolactone (PCL) is one of the most important biodegradable polymers due to its biodegradability, biocompatibility, non-toxicity and good permeability to drug [1–3]. Many copolymers of CL with other monomers such as lactide (LA) [4, 5], 5-methyl-5 benzyloxycarbonyl-1,3-dioxane-2-one (MBC) [6,7], 1,3-dioxane-2-one (TMC) [8–10], glycolide (GA) [11,12],tetrahydrofuran(THF)[13] and poly (ethylene glycol) (PEG) [14,15] have been extensively investigated in order to expand applications of PCL, but most of the cationic initiators used in the synthesis of these copolymers are expensive. They may be poisoned by products of the reaction or impurities present in the monomer feed, and contain heavy metals, such as chromium, mercury, antimony, etc., that presents environmental disposal problems for the user. Frequently, these initiators require the use of very high or very low temperature and high pressures during the polymerization reaction.

The separation of the initiators from the polymer is not always possible. Therefore, the presence of toxic initiators presents problems in the manufacture of polymers used especially in medical and veterinary procedures.

There is still a great demand for heterogeneous catalysis under mild conditions and in environmentally friendly processes. Montmorillonite, a class of inexpensive and noncorrosive solid acids, have been used as efficient catalysts for a variety of organic reactions. The reactions catalyzed by montmorillonite are usually carried out under mild conditions with high yields and high selectivities, and the workup of these reactions is very simple; only filtration to remove the catalyst and evaporation of the solvent are required. Montmorillonite catalysts are easily recovered and reused [16, 17].

The purpose of this paper is to study the copolymerization of ε-caprolactone with tetrahydrofyran, catalyzed by Maghnite -H^+ [18], a proton exchanged Montmorillonite clay. This new non-toxic cationic catalyst has exhibited higher efficiency via the polymerization of vinylic and heterocyclic monomers [19, 20].

The effects of the amounts of the Maghnite -H^+ and the temperature on the synthesis of poly (ε-caprolactone-co- propylene oxide) are also discussed.

II. EXPERIMENTAL

a) General

The 1H-NMR spectra were recorded on Bruker Avance-300 spectrometer in deuterochloroform. Chemical shifts are shown in δ values.

b) Materials

ε-Caprolactone (grade 99%) was used as purchased from Aldrich. Propylene oxide was purified by fractional distillation. Chloroform was dried on CaH_2 anhydrous and distilled before use. Raw-Maghnite: Algerian Montmorillonite clay was procured from BENTAL (Algerian Society of Bentonite).

c) Preparation of "Maghnite -H^+ 0.25M"

Maghnite-H+ was prepared according to the process similar to that described by Belbachir et al. [20]. Raw-Maghnite (20 g) was crushed for 20 mn using a prolabo ceramic balls grinder. It was then dried for 2 hours at 105° C the Maghnite was placed in an Erlenmeyer flask together with 500 ml of distilled water. The Maghnite/water mixture was stirred using a magnetic stirrer and combined with 0.25 M sulfuric acid solution, until saturation was achieved over 2 days at room temperature, the mineral was then washed with distilled water to became sulfate free and then dried at 105°C.

d) Copolymerization and products characterization

The bulk copolymerizations were carried out in stirred flasks at 25°C for 24 hours. The catalyst was dried in a muffle furnace at 120°C overnight and then transferred to a vacuum desiccator containing P_2O_5. After cooling to room temperature under vacuum, the mineral was added to the ε-caprolactone (0.026mol), propylene oxide (0.026mol) mixtures previously kept in the stirred flask at 25°C. After the required time was reached, an aliquot of the reaction mixture was then removed in such a manner as to exclude any clay

---

Author [α Ω β] : Laboratoire de Chimie des Polymères, Département de Chimie, Faculté des Sciences, Université d'Oran Es-Sènia BP N° 1524 El M'Naouar, 31000 Oran, Algerie. (Email : elatik@hotmail.fr)

mineral, and then dried by evaporation to remove solvent and remaining monomer.

III. RESULT AND DISCUSSION

a) Copolymerization and products characterization

The result of bulk copolymerization experiment of ε - caprolactone (0.026mol), with propylene oxide (0.026mol) induced by "Maghnite-H+ 0.25M" is reported in Table 1.

For all these experiments the temperature was kept constant at 23°C for 24 hours.

Table.1. Copolymerizations of ε - caprolactone with propylene oxide induced by"Maghnite-H^+0.25M"

Experiment	Mag-H^+ 0.25M (%)	Time (Hours)	Yield %	Mn *	Mw **	Mw/Mn ***
1	10	24	56.12	613	3702	6.04
2	5	24	41.63	682	4317	6.33

** Mn:The Number Average Molecular Weight.*
*** Mw:The Weight Average Molecular Weight.*
**** Mw/Mn:polydispersity index (PDI).*

b) Effect of temperature on copolymerization

The effect of temperature on the copolymerization of ε - caprolactone (0.026mol) with propylene oxide (0.026mol) initiated by Maghnite-H^+(5% by weight) for 5 hours, is shown in Fig. 1.The copolymerization yield reach maximum value around 90-100°C. On the other hand, with the increase in the reaction temperature above 90°C the molecular weight of the obtained copolymer decrease progressively, suggesting the possible occurrence of thermal degradation. On the basis of these results, subsequent copolymerizations were carried out at 90°C.

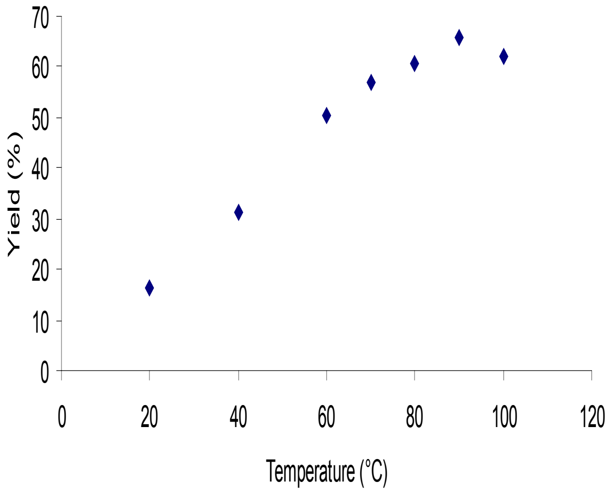


Fig.1. Effect of temperature on copolymerization of ε - caprolactone (0.026mol), with propylene oxide (0.026mol).

c) Effect of the amount of Maghnite -H^+ on the copolymerization

Fig. 2 shows the effect of the amount of Maghnite-H^+ on the copolymerization yield of ε - caprolactone with propylene oxide. Indeed, using various amounts of Maghnite-H^+, 1, 2, 3, 5, 7.5, and 10% by weight, this copolymerization was carried in bulk at 90°C, for 5 hours. The copolymerization yield increased with the amount of Maghnite-H^+, thus clearly showing the effect of Maghnite-H^+ as a catalyst. This phenomenon is probably the result of an increase in the number of "initiating active sites" responsible of inducing polymerization, a number that is pro rata to the amount of catalyst used in reaction.

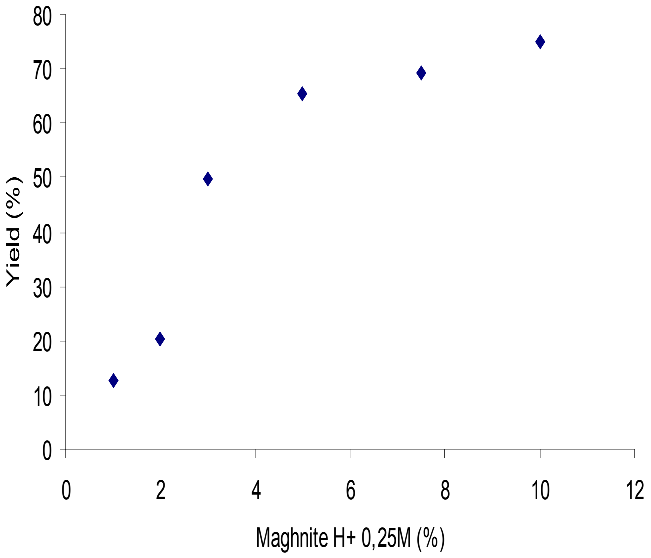
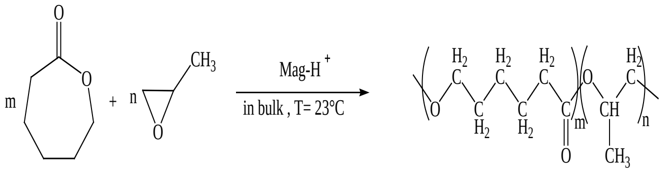


Fig.2. Effect of the amount of the catalyst on copolymerization of ε -caprolactone (0.026mol), with propylene oxide (0.026mol).

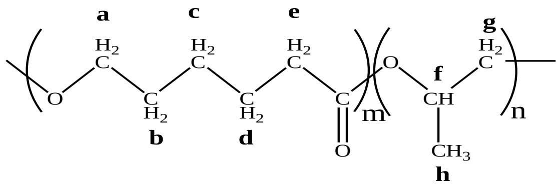
d) Characterization of products

The formation of the copolymer was confirmed by ^1H NMR spectroscopy at 300 MHz (Figure 4). The reaction taking place is shown in the following scheme:



CL PO poly (CL-co-PO)

Table.2. Results of products analysis by ^1H NMR spectroscopy.

Proton type	a	b c d	e	f	g	h
δ in ppm	4.21	1.41–1.78	2.24	4.98	3.63	1.20
						

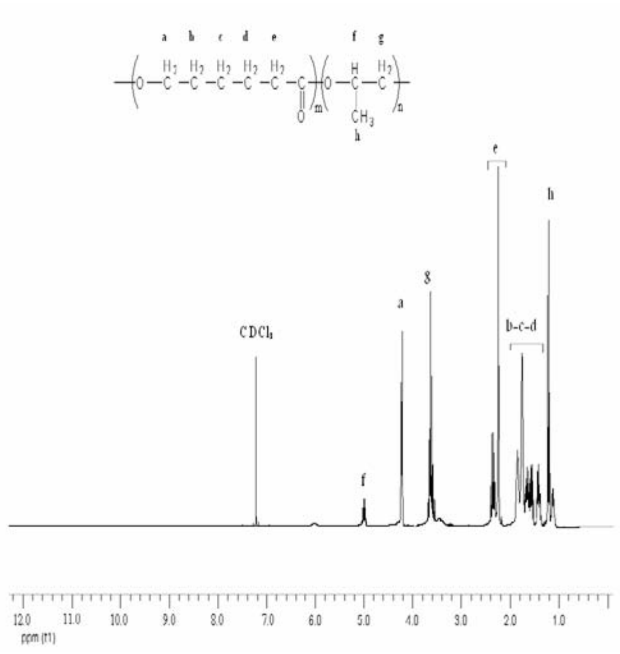


Fig.3. ^1H NMR spectrum of poly (ε-caprolactone-co-propylene oxide) in CDCl 3.

^{1}HMNR spectroscopy at 300 MHz (Solvent deuterated $CHCl_3$) (Fig4) showed different peaks, the three methylene in position 3, 4 and 5 of ε -caprolactone ($-O-CH_2-CH_2-CH_2-CH_2-CH_2-CO-$), lie between δ = 1.41ppm and δ = 1.78 ppm, the proton carried by the carbon in position 2 and 6 of ε-caprolactone ($-O-CH_2-CH_2-CH_2-CH_2-CH_2-CO-$),($-O-CH_2-CH_2-CH_2-CH_2-CH_2-CO-$) at δ = 4.21 ppm and δ = 2.24 ppm respectively, the methylene in position 3 of PO ($-O-CH(CH_3)-CH_2-$) at δ = 3.63ppm, the proton carried by the carbon in position 2 of OP at 4.98 ppm and the Methyl group of OP at 1.20 ppm.

IV. CONCLUSION

Maghnite-H^+,a proton exchanged montmorillonite clay is effective as an acidic catalyst for the copolymerization of ε-caprolactone with propylene oxide. The balance of copolymerization moves towards the formation of copolymer with the rise in the temperature and the increase in the quantity of catalyst. The copolymerization proceeds smoothly, and a simple filtration is sufficient to recover the catalyst.

REFERENCES

1. Chen. J. H., Huang. C. X.and Chen. Z. L., (2000).Study on the biocompatibility and toxicology Of biomaterials poly(ε-caprolactone).J Biomed Eng.17:380–382.
2. Le Ray. A. M., Chiffoleau. S., Iooss. P.,Grimandi. G., Gouyette. A., Daculsi. G. and Merle. C. (2003). Vancomycin encapsulation in biodegradable poly(epsilon-caprolactone) microparticles for bone implantation. Influence of the formulation process on size, drug loading, in vitro release and cytocompatibility. Biomaterials. 24:443–449.
3. Pitt. C. G., Jeffcoat. A. R., Zweidinger. R. A. and Schindler. A. (1979). Sustained drug delivery systems I. The permeability of poly(epsilon-caprolactone), poly(DL-lactic acid), and their copolymers. J Biomed Mater Res. 13: 497–507.
4. Ye. W.P., Du. F.S., Jin. W.H., Yang. J.Y.and Xu. Y.(1997).In vitro degradation of poly(caprolactone), poly(lactide) and their block copolymers: Influence of composition, temperature and morphology. React Funct Polym.32:161–168
5. Yavuz. H., Babac. C., Tuzlakoglu. K.and Piskin. E. (2002). Preparation and degradation of l-lactide and unknowing caprolactone homo and copolymer films. Polym. Degrad. Stab. 75:431–437
6. Storey. R.F., Mullen. B.D.and Melchert. K.M. (2001). Synthesis of novel hydrophilic poly(ester-carbonates) containing pendent carboxylic acid groups. J. Macromol. Sci. Pure. Appl. Chem.38:897– 917.
7. Guan. H.L., Xie. Z.G., Tang. Z.H., Xu. X.Y., Chen. X.S. and Jing. X.B. (2005). Preparation of block copolymer of epsilon-caprolactone and 2-methyl-2-carboxyl-propylene carbonate. Polymer. 46:2817–2824.
8. Pêgo. A.P., Luyn. M.J.A.V., Brouwer. L.A., Wachem. P.B.V., Poot. A.A. and GrijiPma. D.W. (2003). In vivo behavior of poly(1,3-trimethylene carbonate) and

copolymers of 1,3-trimethylene carbonate with D,L-lactide or e-caprolactone:Degradation and tissue response. J.Biomed.Mater.Res . 67(A):1044–1054.

9. Albertsson. A.C. and Eklund. M. (1995). Influence of molecular structure on the degradation mechanism of degradable polymers: In vitro degradation of poly(trimethylene carbonate), poly(trimethylene carbonate-co-caprolactone), and poly(adipic anhydride). J. Appl. Polym. Sci.57:87–103.
10. Barakat. I., Dubois. Ph.,Grandfils. Ch.and Jêrôme, R. (2001). Poly(e-caprolactone-b-glycolide) and poly(D,L-lactide-b-glycolide) diblock copolyesters: Controlled synthesis, characterization, and colloidal dispersions. J.Polym. Sci. Part A:Polym. Chem. 39: 294–306.
11. Bero. M., Czapla. B., Dobrzynski. P., Janeczek. H. and Kasperczyk. J. (1999). Copolymerization of glycolide and ε-caprolactone, 2. Random copolymerization in the presence of tin octoate. Macromol. Chem. Phys. 200: 911–916.
12. Dzhavadyan. E.A., Rozenberg. B.A.and Yenikolopyan. N.S. (1973). Kinetics of the copolymerization of tetrahydrofuran with ε-caprolactone. polymer. Science.U.S.S.R.15: 2235-2242.
13. Ge. H., Hu. Y., Jiang. X., Cheng. D.,Yuan. Y., Bi. H. and Yang. C. (2002) Preparation, characterization, and drug release behaviors of drug nimodipine-loaded poly (epsilon-caprolactone)-poly(ethylene oxide)-poly(epsilon -caprolactone) amphiphilic triblock copolymer micelles. J. Pharm. Sci. 91:1463–1473.
14. He. F., Li. S., Vert. M., Zhuo. R.(2003) Enzyme-catalyzed polymerization and degradation of copolymers prepared from ε-caprolactone and poly(ethylene glycol). Polymer. 44: 5145–5151.
15. Brown. D.R., Carpathica. G. (1994) Clays as catalyst and reagent supports.. Ser.Clays. 45: 45.
16. Laszlo. P. (1987). Preparative Chemistry Using Supported Reagents. Academic. Press. San Diego.
17. Belbachir. M. and Bensaoula. A. (2006).Composition and method for catalysis using bentonites . US Patent 6,274,527 B1.
18. Harrane. A., Meghabar. R. and Belbachir. M.(2002). A Protons Exchanged Montmorillonite Clay as an Efficient Catalyst for the Reaction of Isobutylene Polymerization. Int. J. Mol. Sci. 790-800.
19. Meghabar. R., Megherbi. A., and Belbachir, M.(2003). an ecocatalyst for cationic polymerization of N-vinyl-2-pyrrolidone. Polymer.2397.

GLOBAL JOURNAL OF SCIENCE FRONTIER RESEARCH
CHEMISTRY
Volume 12 Issue 1 Version 1.0 January 2012
Type : Double Blind Peer Reviewed International Research Journal
Publisher: Global Journals Inc. (USA)
Online ISSN: 2249-4626 & Print ISSN: 0975-5896

Adsorption Of Mn(II) Ions From Wastewater Using Activated Carbon Obtained From Birbira (Militia Ferruginea) Leaves

By Alemayehu Abebaw Mengistie, T. Siva Rao, A. V. Prasada Rao

Ambo University, Ambo Town, Western Shoa, Ethiopia

Abstract - The adsorption of manganese (II) onto activated carbon derived from the leaf an indigenous Ethiopian plant, namely Birbira (Militia ferruginea), was investigated using flame atomic absorption spectrometer. The effects of contact time, adsorbent dose, Mn (II) initial concentration, pH and temperature were investigated. The maximum adsorption occurred after 2 hrs. There was 95.8% of Mn^{2+} adsorption at pH of 4.0. The positive value of ΔH shows that the adsorption of manganese ions on the adsorbent is an endothermic process. The values of free energy (ΔG) were negative. The decrease in ΔG value with increasing temperature reveals that adsorption of the ion on the adsorbent becomes favorable at higher temperature. The calculated value of ΔH is 16.05 $kJmol^{-1}$ and ΔS is 99.13$JK^{-1}mol^{-1}$. The two theoretical adsorption isotherms, namely, Langmuir and Freundlich were used to describe the experimental results. The Freundlich adsorption isotherm best fits and adsorption capacity was calculated to be 3.41 mg of Mn (II) per g of adsorbent. The adsorption followed the first order kinetics and was found to be pH dependent being maximum at pH 4.0. Reuse of the desorbed bio-adsorbent is possible. The effect of foreign ions on the removal of Mn (II) has been investigated. The removal of Mn (II) from industrial wastewater sample was also tested and showed that more than 93% removal is possible. The results showed that activated carbon prepared from Birbira (Militia ferruginea) leaves can be used for the removal of Mn (II) from wastewater.

Keywords : *Industrial wastewater, Manganese removal, adsorbent, Militia ferruginea, adsorption isotherm, kinetics of adsorption and flame atomic absorption spectrometer (FAAS).*

GJRE Classification : *FOR Code: 090409*

Adsorption Of Mn(II) Ions From Wastewater Using Activated Carbon Obtained From Birbira *(Militia Ferruginea)* Leaves

Alemayehu Abebaw Mengistie[α], T. Siva Rao[Ω], A. V. Prasada Rao[β]

Abstract - The adsorption of manganese (II) onto activated carbon derived from the leaf an indigenous Ethiopian plant, namely Birbira (Militia ferruginea), was investigated using flame atomic absorption spectrometer. The effects of contact time, adsorbent dose, Mn (II) initial concentration, pH and temperature were investigated. The maximum adsorption occurred after 2 hrs. There was 95.8% of Mn^{2+} adsorption at pH of 4.0. The positive value of ΔH shows that the adsorption of manganese ions on the adsorbent is an endothermic process. The values of free energy (ΔG) were negative. The decrease in ΔG value with increasing temperature reveals that adsorption of the ion on the adsorbent becomes favorable at higher temperature. The calculated value of ΔH is 16.05 $kJmol^{-1}$ and ΔS is 99.13$JK^{-1}mol^{-1}$. The two theoretical adsorption isotherms, namely, Langmuir and Freundlich were used to describe the experimental results. The Freundlich adsorption isotherm best fits and adsorption capacity was calculated to be 3.41 mg of Mn (II) per g of adsorbent. The adsorption followed the first order kinetics and was found to be pH dependent being maximum at pH 4.0. Reuse of the desorbed bio-adsorbent is possible. The effect of foreign ions on the removal of Mn (II) has been investigated. The removal of Mn (II) from industrial wastewater sample was also tested and showed that more than 93% removal is possible. The results showed that activated carbon prepared from Birbira (Militia ferruginea) leaves can be used for the removal of Mn (II) from wastewater.

Keywords : Industrial wastewater, Manganese removal, adsorbent, Militia ferruginea, adsorption isotherm, kinetics of adsorption and flame atomic absorption spectrometer (FAAS).

I. INTRODUCTION

Heavy metals are generally present as pollutants in a variety of industrial effluents. Industries such as metal plating, metal finishing, rubber processing, fertilizers, mining, as well as agriculture release these heavy metals into the surface and ground water [1]. At least 20 metals are classified as toxic and half of these are released into the environment in quantities that pose risks to human health [2-5]. The increasing contamination of urban and industrial wastewaters by toxic metal ions is a serious environmental problem. These inorganic micro-pollutants are of considerable concern because they are non-biodegradable and highly toxic [6]. The toxic actions of these trace elements are due to their bioaccumulation in the tissues of living organisms [7-10]. On the other hand, the Groundwater that contains an appreciable amount of iron or manganese or both is always devoid of dissolved oxygen and high in carbon dioxide content [11]. As far as is known, humans suffer no harmful effects from drinking water containing manganese. However, manganese interferes with laundering operation, imparts objectionable stains to plumbing fixture, and causes trouble in distribution systems by supporting growths of iron bacteria. For these reasons public water supplies should not contain more than 0.05 mg/L of manganese according to the U.S.E.P.A. secondary standard [11]. According to WHO the maximum permissible limit (MPL) of manganese in drinking water is 0.5 mg/L [11-13].

At present, a number of technologies can be used to remove heavy metals from the contaminated waste water such as filtration, adsorption, chemical precipitation, ion exchange, membrane separation and electro remediation methods. However, most of this method might not be efficient in removing heavy metals at very low concentrations, and could be relatively expensive. These methods are also not effective due to their secondary effluent impact on the recipient environment [14-17]. For this reason, the uses of some low-cost materials for sorbent/adsorbent of metals from contaminated wastewater have been popular.

Randall et al. worked on removal of heavy metals using various barks and eventually expanded their work to peanut skins [18,19]. Others researchers also used bagasse, acacia bark, husk, paddy straw, wheat flour, and waste peanut [20, 21]. More recently, great effort has been contributed to develop new adsorbents and improve existing adsorbents. Studies of removal of heavy metal ions using low-cost abundantly available adsorbents from agricultural and solid wastes such as tea waste, coffee and nut shells [22], saw dusts, bark and bin [23], palm kerner husk [24], rice hulls [25], cactus leaves and charcoal [26], were performed. In our earlier studies we have used leaves of a plant for the removal of heavy metals [27, 28]. The aim of the present investigation is to propose new biomaterial involving applications of an Ethiopian

---

Author [α] : Department of Chemistry, Ambo University, P.O. Box. 19, Ambo Town, Western Shoa, Ethiopia
E-mail : alemayehuabebaw@yahoo.com

Author [Ω] [β]: Department of Inorganic and Analytical Chemistry, School of Chemistry, Andhra University, Vishakhapatnam, Andhra Pradesh, India.

indigenous plant material leaves, Militia ferruginea also known in the vernacular as birbira, in the removable of heavy metals from synthetic wastewater (spiked with manganese) and subsequently its application to industrial wastewater. For environmental degradation industries are not the only contributors but deforestation of indigenous trees for agriculture does also contribute. It is therefore of great value to solve this problems simultaneously. The search for indigenous biomaterials especially, those with high social value and economically important trees for tackling both deforestation and environmental pollution are sounding. Selection of these indigenous trees for this application will increase the farmer's attention towards planting the trees since the value of these trees will increase in terms of economy.

II. MATERIALS AND METHODS

a) *Preparation of carbon from the bio-adsorbent*

After it was authenticated by an expert, the leaves of Birbira *(Militia ferruginea)* were collected, dried in air and powdered. The homogenous powder was treated with concentrated sulfuric acid (sp.gr. 1.84) in a weight ratio of 2:1 (powder: acid). The resulting black product was kept in an air-free oven monitored at 195 ± 5°C for three hours, followed by several washings with distilled water until free of excess acid and drying at 105 ± 5°C. The carbon obtained was ground and the portion retained between 90 and 125 μm sieves was used for the metal adsorption experiments. The yield of the carbon was about 38% of the starting powder.

b) *Preparation of synthetic wastewater*

Synthetic wastewater samples were prepared by using analytical grade manganese dioxide ($MnCl_2.4H_2O$) (Loba Chemie) and doubly distilled water. The stock solution was prepared in a concentration of 1000 ppm. Working solutions of 5, 10, 20, 50, 60 and 100 ppm were prepared by dilution.

c) *Sampling of Industrial effluent*

The metal polishing industrial effluent sample was collected in polyethylene bottles. pH, electrical conductivity were measured with portable pH meter and electrical conductivity meter. Samples were filtered and preserved at 4°C. Trace metals were determined by flame atomic absorption spectrometer (FAAS) and soluble cations, anions and other parameters were determined by standard analytical methods [12].

d) *Batch adsorption experiments*

Each batch experiment was performed with 50 ml of a working solution and the desired adsorbent does, shaking time pH, and temperature. The solution was transferred into a 250 ml conical flask and shaken in a mechanical Gemmy orbit shaker (model: VRN-480) at 250 rpm for a definite period. Adsorbent dose, shaking time, pH, and temperature were optimised by continuous variation method (studying one, keeping the other parameters constant). After equilibrating, the system was allowed to settle for 20-30 minutes, filtered and analysed for manganese. The pH of the original solution and the filtrate was determined using HANNA instruments pH meter (pH 209 model).

The difference in the manganese content before and after adsorption experiment represents the amount of manganese adsorbed by the bio-adsorbent. All experiments were performed at room temperature ($23^oC \pm 2^oC$) except for the samples used for study of the temperature effect. The free ion concentration of Mn^{2+} in the test solution was measured by atomic absorption spectrometer model AA-6200, Shimadzu Japan. The concentration was measured at the wavelength of 279.5 nm with slit width of 0.2 nm for the photon hollow cathode lamp system in AAS. Each experiment was carried out in triplicate and mean values were taken for calculation.

The percent removal of metal ions can be calculated by using the formula:

$$\%\,\mathrm{Re}\,moval = \frac{C_i - C_f}{C_i} 100 \qquad (1)$$

Where C_i is the initial concentration in the aqueous solution and C_f is the final concentration in the aqueous solution after adsorption procedures carried on and equilibrium is achieved.

e) *Temperature Study*

The effect of temperature was studied using 50 ml of 10, 20, 40 and 60 ppm of Mn^{2+} solution for 2hr at adsorbent dose of 4.0 gm. The temperature was set at 23°, 30°, 35°, 40°, 45°, 50° and 60°C.

III. RESULTS AND DISCUSSION

a) *Effect of adsorption time*

The effect of adsorption time using 4.0 g of the adsorbent and 50 mL of test solution containing 5, 10, 20 and 100 ppm of Mn (II) ions is shown in Figure 1. It is evident from the figure that the removal of metal ion increases at adsorption time increases. Initially the rate of uptake is fast. However, equilibrium is attained in 2 hr. Hence, in further studies the adsorption time of 2hr was used.

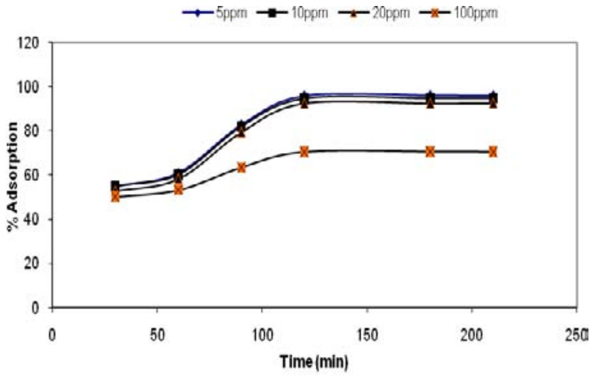


Figure 1. Effect of adsorption time

pH = 4.0, Adsorbent dose = 4.0 g

b) *Effect of Adsorbent dose*

Figure 2 shows the effect of carbon dosage on Mn (II) ion removal from aqueous solutions. Each test solution (50 mL) contained 20 ppm of manganese ions. The adsorption of manganese ions is observed to increase as the amount of adsorbent is increased from 0.25 g to 4.5 g. The maximum adsorption is obtained from the adsorbent dose of 4.0 g which is 92.6% for 20 ppm of initial concentration. A further increase of the adsorbent up to 4.5 g seems to give no more adsorption. About 4.0 g of the adsorbent were thus sufficient to adsorb the maximum ions under the experimental conditions. The increase in the removal efficiency as adsorbent dose increases is due to the availability of more adsorbing sites at higher doses. At constant initial concentration once equilibrium between adsorption desorption is reached the percent adsorption remains constant.

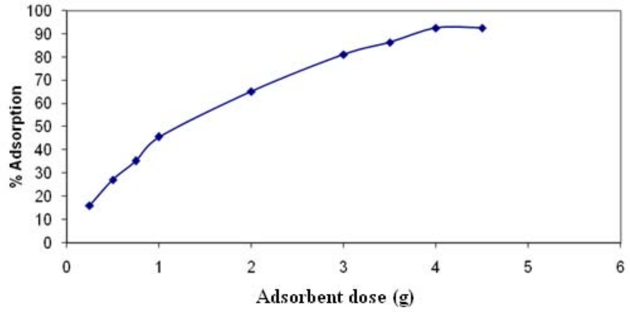


Figure 2. Effect of adsorbent dose

pH = 4.0, Initial concentration = 20 ppm

c) *Effect of initial concentration of Manganese ions*

Removal of Mn (II) ions from the aqueous solution was studied for the metal ion concentrations ranging from 5 to 100 ppm. The percentage adsorption of Mn (II) ions from 50 mL solutions of different initial ion concentrations (equilibrated with 4.0 g of adsorbent) is shown in Figure 3. As can be seen from the figure the removal of the metal ions is found to decrease with increase in initial concentration. At the experimental conditions of 4.0 g dose of adsorbent and at pH 4 maximum adsorption is obtained for concentrations of 5 – 10 ppm.

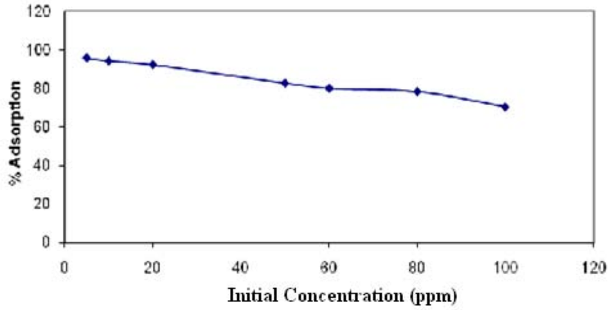


Figure 3. Effect of initial concentration

pH = 4.0, Adsorbent dose = 4.0 g

d) *Effect of pH*

The pH of a solution is an important controlling parameter in the adsorption process, and the initial pH value of the solution has more influence than the final one. The influences of pH are on both the adsorbent surface of the metal binding sites and the metal chemistry in water [29, 30]. In this experiment, the pH effect was studied in the range of 2.0-7.0. Removal of Mn^{2+} onto the activated carbon is pH dependent as shown in Figure 4. The maximum adsorption is obtained at pH 3.5 for both 10 and 50 ppm solutions. At pH < 2.0, H^+ ions compete with Mn (II) ions for the surface of the adsorbent, which would hinder Mn (II) ions from reaching the binding sites of the sorbet. At pH > 7.0, the Mn (II) gets precipitated due to hydroxide anions forming a manganese hydroxide precipitate. The highest efficiency was 94.2% at a pH of 4.0 for 10 ppm and 82.8% for 50 ppm. A change in the pH of the solution after adsorption was observed in this study. In all cases the pH of the solution decreases after equilibrium was achieved. The larger the adsorbent dose the greater the decrease in pH. It was presumed that adsorption of the metal ions on the surface could result in the release of more H^+ ions from the surface by ion exchange mechanism.

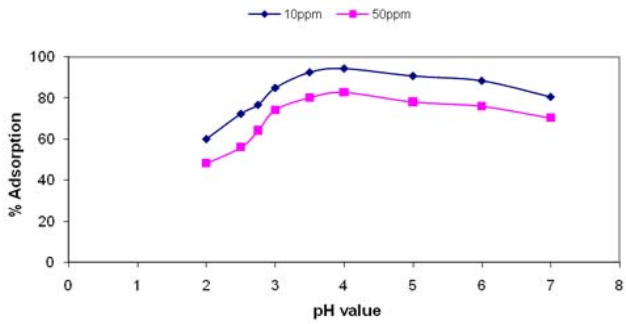


Figure 4. Effect of pH

Adsorbent dose = 4.0 g

e) Effect of Temperature

The extent of manganese ion adsorption on the activated carbon at various temperatures is given in Figure 5. As can be seen from the figure as the temperature of the system is increased, there was an increase in the percent removal of the metal. The enhancement of the adsorption capacity on increasing the temperature may be due to increase in the mobility and diffusion of ionic species. Since diffusion is an endothermic process, it would be expected that an increased solution temperature would result in the enlargement of pore size due to 'activated diffusion' causing the micro-pores to widen and deepen and create more surface for adsorption.

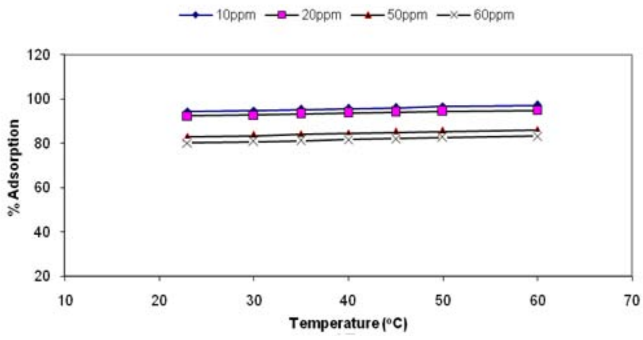


Figure 5. Effect of Temperature

Adsorbent dose = 4.0 g, pH = 4.0

Calculation of thermodynamic parameters

The value of ΔH and ΔS were calculated from the slope and intercept of the linear van't Hoff plot respectively, using the relation:

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (2)$$

Where: ΔS = entropy change for the process
ΔH = enthalpy change for the process
R = gas constant
T = absolute temperature

The distribution coefficient (K_d) of the activated charcoal surface was calculated using the equation,

$$K_d = \frac{C_i - C_e}{C_e}\frac{V}{m} \qquad (3)$$

Where C_i = the initial concentration of the metal ion
C_e = the equilibrium concentration of the metal ion
V = the volume of the solution equilibrated in mL
m = mass of the adsorbent in g

The change in free energy (ΔG) for the specific adsorption has also been calculated using the equation

$$\Delta G = -RT \ln K_d \qquad (4)$$

Where, the symbols have their usual significance.

The thermodynamic quantities ΔH, ΔS, ΔG of manganese ion adsorption on activated carbon were calculated from the K_d values using Eqs. (3) and (4). The values of ΔH and ΔS were computed from the slope and intercept of the linear variation of ln K_d with the reciprocal of temperature (Figure 6) and was found to be 16.05 kJ mol^{-1} and 99.13 JK^{-1}mol^{-1} respectively (Table 1). The values of free energy of specific adsorption, ΔG at various temperatures were calculated by using Eq. (4) and are listed in Table 1. The positive value of ΔH shows that the adsorption of manganese ions on the adsorbent is an endothermic process. The values of free energy (ΔG) are negative as expected for a spontaneous process. The decrease in ΔG value with increasing temperature reveals that adsorption of the ion on the adsorbent becomes favorable at higher temperature. The positive value of ΔS reveals the increase in randomness at solid solution interface during the fixation of manganese ions on active site of the adsorbent.

Table 1. Adsorption Studies of Mn^{2+} Ions on Activated Carbon as a Function of Temperature

T (K)	1/T (K^{-1} x 10^{-3})	K_d (mLg^{-1})	ΔG (kJ mol^{-1})	lnk_d
296	3.38	232.01	-13.41	5.45
303	3.30	255.25	-13.95	5.54
308	3.25	277.26	-14.39	5.62
313	3.19	303.17	-14.85	5.71
318	3.14	342.85	-15.41	5.83
323	3.09	393.87	-16.03	5.97
333	3.0	478.32	-17.08	6 .17

Amount adsorbent: 4.0g shaking time 2hrs, volume equilibrated 50 ml, pH of the solution 4.0, and concentration of Mn (II) 20 ppm.

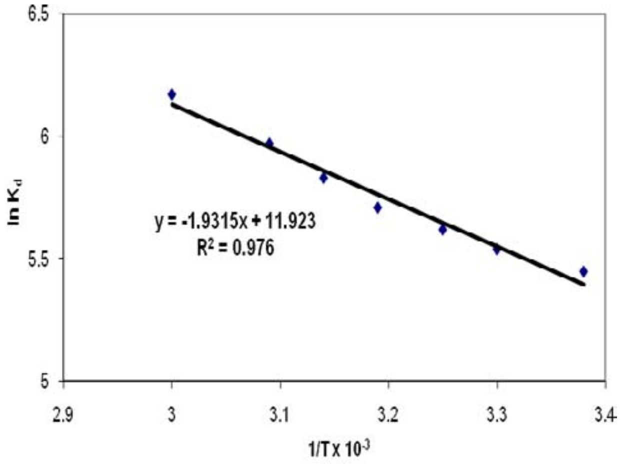


Figure 6. Plot of ln K_d vs 1/T

Initial concentration = 20 ppm, pH = 4.0 g

f) Effects of anions and cations

The effect of anions such as F^-, Cl^-, NO_3^{-2}, SO_4^{-2} and $PO4^{-3}$ as well as the effect of cations such as Fe^{+2}, Ca^{+2}, Na^+ and K^+ on the Mn^{2+} adsorption efficiency of the bio-adsorbent was studied. There is no significant reduction in the adsorption of Mn^{2+} when the concentration of the above ions increases up to 80 ppm in the synthetic water. It is evident that with the proper treatment of the wastewater; it is possible to adsorb Mn^{2+} ions on the surface.

g) Adsorption isotherm

Equilibrium batch adsorption experiments resulted in points of the adsorption isotherm, which were approximated by the Langmuir model,

$$q = \frac{q_{\max} b C_{\max}}{1 + b C_{eq}} \tag{5}$$

where, $q_{\max}$ is the maximum adsorbate uptake and b is the Langmuir constant related to energy of adsorption, which quantitatively reflects the affinity between the adsorbent and the adsorbate. The evaluation of the specific uptake q was performed according to

$$q = \frac{V\left(C_i - C_{eq}\right)}{m} \tag{6}$$

where, V is the volume, C_i , initial concentration of the metal ion, C_{eq} is the metal ion concentration remaining in the solution after adsorption has taken at equilibrium and m is mass of the biomaterial.

The Langmuir parameters were obtained by fitting the experimental data to linearized equation derived from Eq. (7),

$$1/q = \frac{1}{q_{\max}} + \frac{1}{\left(C_{eq} q_{\max} b\right)} \tag{7}$$

The Freundlich isotherm can be derived from the Langmuir isotherm by assuming that there exists a distribution of sites on the adsorbent that have different affinities for different adsorbates with each site behaving according to the Langmuir isotherm. According to Freundlich, adsorption from solution can be expressed by the equation

$$q = KC^{1/n} \tag{8}$$

where K is the measure of the capacity of the adsorbent (mass of adsorbate/mass of adsorbent) and n is a measure of how affinity for the adsorbate changes with changes in adsorption density. The expression n > 1 indicates that the affinities decrease with increasing adsorption density. Evaluation of the coefficients K and n can be accomplished using the linearized form of equation 8,

$$\log q = \log K + \frac{1}{n}\log C \tag{9}$$

The Freundlich parameters as well as the correlation coefficient are listed in Table 2. From the values obtained for these parameters the theoretical Freundlich curves were calculated and plotted (Figure 7). It can be observed that the experimental data fit the isotherm adequately. The applicability of the Freundlich model to the experimental data indicates monolayer coverage on heterogeneous adsorbent surface by each of the Mn (II) ions. For comparison the Langmuir adsorption isotherm is also given in Figure 8.

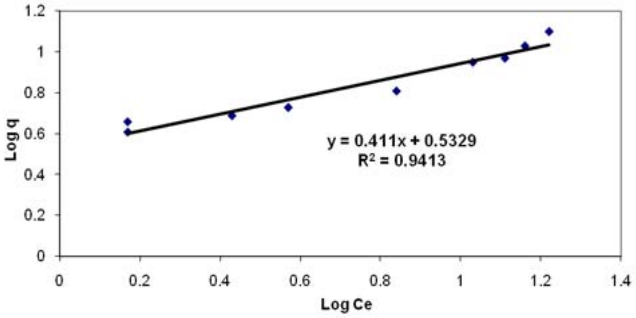


Figure 7. Freudlich adsorption isotherm of Mn (II)

Initial concentration = 20 ppm, pH = 4.0 g

Table 2. Freundlich Isotherm Parameters

Equation	K (mg/g)	n	R2
Log q =0.411 Log Ce + 0.5329	3.41	2.43	0.94

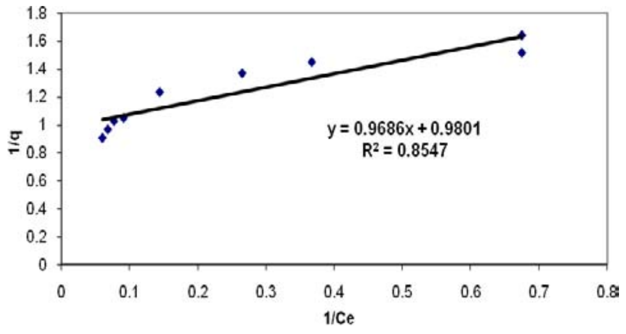


Figure 8. Langmuir adsorption isotherm of Mn (II) *Initial concentration = 20 ppm, pH = 4.0 g*

h) Order of reaction of manganese ion adsorption

The rate constant (K) of the manganese ion adsorption at the adsorbent surface was calculated at 25°C with equilibration time (t) of 120 min using the following equation [31],

$$K = \frac{1}{t}\ln(C_o/C_e) \qquad (10)$$

Here C_o and C_e are the initial and equilibrium concentrations of manganese ions respectively. The values of C_e and the rate constant for the adsorption process at different initial concentrations of manganese ions (C_o) were calculated. The plot of rate constant (K) versus In (C_o/C_e) is observed to be a straight line as shown in Figure 9. The result indicates that the adsorption process of manganese ions at the surface of the adsorbent follows first order reaction kinetics.

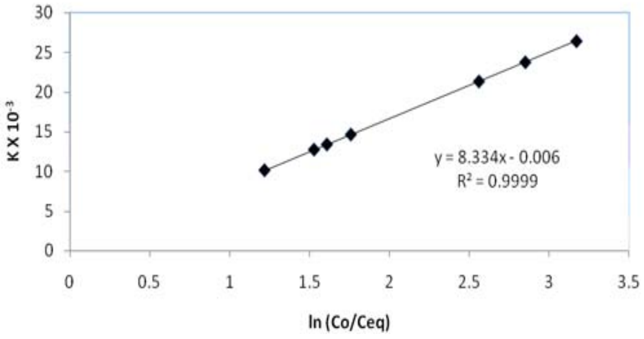


Figure 9 : Kinetics of Adsorption of Mn^{2+}

i) Treatment of industrial wastewater

The suitability of the bio-adsorbent material for the removal of Mn (II) was tested with a metal polishing industrial wastewater sample. The composition of the wastewater is given in Table. 3. pH of the wastewater sample was maintained between 3.5.-4.0. Using the adsorbent dose of 4.0 g to 50 ml of 20 ppm Mn (II) the effect of adsorption time is shown in Figure 10. It was found in this experiment that the treatment of Mn (II) ion in industrial wastewater was quite satisfactory: almost 94% removal of the metal ion from the wastewater was possible. Thus, the result was in good agreement with those obtained from batch experiments conducted for Mn (II) removal in synthetic wastewater samples. However, a preliminary treatment of the industrial wastewater is recommended before the application of activated carbon of the bio-adsorbent.

Table 3. Determined composition of metal polishing industrial effluent

Parameters	Results
pH	3.5
Electrical conductivity (μ mhos/cm)	4367.75
Total dissolved solids (mg/L)	6846
Turbidity (NTU)	1.25
COD (mg/L)	33
Chloride (mg/L)	468
Sulphate (mg/L)	1228
Iron (mg/L)	38
Manganese (mg/L)	32.6
Cadmium (mg/L)	964
Calcium (mg/L)	86
Sodium (mg/L)	177
Potassium (mg/L)	32

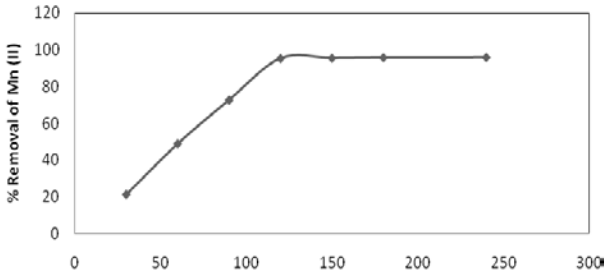


Figure 10. Effect of adsorption time *pH = 4.0, Adsorbent dose = 4.0 g*

j) Desorption studies

The adsorbent (50 mg) that was used for the adsorption of the Mn^{2+} ion in solutions of 5, 10, 20, 40, 50, and 80 ppm from determination of effect of initial concentration experiment was separated from the solution by filtration. The Mn^{2+} loaded adsorbent was filtered using Whatman filter paper and washed gently with distilled water to remove the unadsorbed Mn^{2+}, and the water was immediately removed. Then the adsorbent was mixed with 50 ml of distilled water, adjusted to a pH value in the range 2.0-9.0 using dilute HCl/ NaOH and agitated for 3 hours longer period than the equilibrium time. The desorbed Mn^{2+} was estimated as before. The adsorbent after desorption of the ions the ions was checked for further adsorption capacity. The reuse of regenerated activated carbon was found to be efficient. The desorption results are shown in Figure 11.

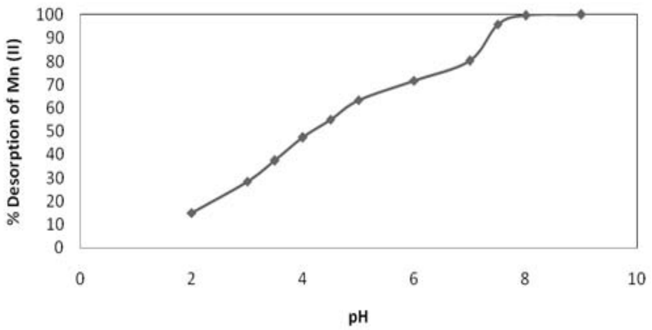


Figure 11. Desorption of Manganese ions from the spent adsorbent

IV. CONCLUSIONS

The removal of Mn (II) ion in synthetic wastewater as well as industrial effluent by activated carbon obtained from the leaves of Birbira plant has been studied. The prepared activated carbon is an efficient biomaterial for removal of manganese (II) ions from industrial wastewater. The adsorption of Mn (II) is a monolayer according to Freundlich adsorption isotherm. The percent removal of Mn (II) under the conditions employed; here is 94.2% for initial concentration of 10 ppm. Adsorption efficiency increased with increasing pH showing a maximum at pH 4.0 and then decrease at higher pH, greater than pH 9 desorption is complete. Adsorption equilibrium for the metal is reached in about 2 hrs and is endothermic in nature. The adsorption is first order in kinetics. This methodology can be applied to the removal of toxic metals from wastewater efficiently. Reuse of the regenerated bio-adsorbent is also possible.

REFERENCES RÉFÉRENCES REFERENCIAS

1. B. Southichak, K. Nakano, M. Normura, N. Chibia and O. Nishmura. "Pharagmites australis: a novel bio-adsorbent for the removal of heavy metals from aqueous solution", *Water Res.,* 2006, 40, 2295-2302.
2. A.Kortenkamp, M. Casadevall, S. P. Faux, A. Jenner, R. O. J. Shayer, N. Woodbridge and P. O'brien, "A role for molecular oxygen in the formation of DNA damage during the reduction of the carcinogen chromium (VI) by alutathione", *Arch. Biochem. Biophys.,* 1996, 329(2), 199-208.
3. S. M. Ross, "Toxic Metals in Soil Plant System", John Wiley and Sons, Chichester, 1994, 3-26.
4. M. K. John, V. Laerhoven and C. H. Cross, "Cadmium, Lead and zinc accumulate in soils nearer a smother complex", *Environ. Lett.,* 1975, 10, 25-35.
5. K. Y. Tiller, "Heavy metals in soil and their environmental significance" *Adv. soil sci.,* 1989, 9, 113-142.
6. G. Cimino, A. Passerini and G. Toscano, "Removal of toxic cations and Cr (VI) from aqueous solution by hazelnut shell", *Water Res.,* 2000, 34 (II), 2955-2962.
7. A.Kebede and T. Wondimu, "Distribution of trace elements in muscle and organs of tilapia, *Oreochromis niliticus,* from lakes Awassa and Ziway, Ethiopia", *Bull. Chem. Soc. Ethiop.,* 2004, 18(2), 119-130.
8. E. J. Underwood, "Trace Elements in Human and Animal Nutrition", 4th Edn., Academic press, New York, 1977.
9. W. Kaim and B. Schwedski, "Bio-inorganic Chemistry", John Wiley and Sons, Chichester. 1994.
10. K. C. Pillalli, "Heavy Metals in Aquatic Environment" Wiley Eastern Limited, New Delhi, 1985, 74-93.
11. C. N. Sawyer, P. L. McCarty and G. F. Parkin "Chemistry for Environmental Engineering and Science" Tata McGraw-Hill Publishing, New Delhi 5th Edn., 2003, 660-661 and 717.
12. D. A. Kumar, "Environmental Chemistry", New Age International, New Delhi, 5th Edn., 2004, 280.
13. A. Celik and A. Demirabas. "Removal of heavy metal ions from aqueous solutions via adsorption onto modified lignin wastes", *Energy Sources,* 2005, 27, 1167-1177.
14. J. Muslehiddinojlu, Y. Uludag, H. O. Ozbelege and Z. Yilmaz, "Determination of heavy metal concentration in feed and permeate streams of polymer enhanced ultrafilitration process." *Talanta.,* 1998, 46(6), 1557-1565.
15. K. J. Kim, V. Chen and A. G. Fane, "Characterization of clean and fouled membranes using metal colloids", *Membr. Sci.,* 1994, 88, 93-101.
16. D. C. Sharma and C. F. Forster, "A preliminary examination into the adsorption of hexavalent chromium using low cost adsorbents." *Biores. Technol.,* 1994, 47, 257-264.
17. C. Namasiuvayam and D. Sangeetha, "Removal of chromium (VI) by ZNCl2 activated coir pith carbon." *Toxicol. Environ. Chem.,* 2006, 88(2), 219-233.
18. J. M. Randall, R. L. Bermann, V. Garret and A. C. Waiss, "Use of bark for removal of heavy metal ions from waste solution". *For. Prod. J.,* 1974, 24, 80-84.
19. J. M. Randall, F. W. Reuter and A. C. Waiss, "Removal of cupric ions from solution with peanut skins", *J. Appl. Polym. Sci.,* 1975, 19, 1563-1571.
20. S.Babel and T.A. Kurniawan. "Low cost adsorbents for heavy metals uptake from contaminated water, a review" *J. Hazard. Mater.,* 2003,B97, 219-243
21. P. Kumar and S. S. Dara, "Binding heavy metal ions with polymerized onion skin", *J. Appl. Polym.. Sci.,* 1981, 19, 397-402.

22. Y. Orhan and H. Bűyűkgűngör, "The removal of heavy metals by using agricultural wastes", *Water Sci. Technol.,* 1993, 28, 247-255.
23. G. Vazquez, J. Gonzalaez-Alvarez, S. Freire, M. Lopez-Lorenzo and G. Antorrena, "Removal of cadmium and mercury ions from aqueous solution by sorption on treated Pinus pinaster bark: kinetics and isotherms", *Bio. reso. Technol.,* 2002, 82, 247-251.
24. J. A. Omgbu and V. I. Iweanya, "Dynamic sorption of Pb2+ and Zn2+ with palm *(Eleasis Guineensis)* kernel husk", *J. Chem. Ed.,* 1990, 67, 800-801.
25. K. S. Low, C. K. Lee and A.Y. Ng, "Column study on the sorption of Cr (IV) using quaternized rice hulls", *Bio Reso. Technol.,* 1999, 68, 205-208.
26. M. Dakiky, M. Khamics, A. Manassra and M. Mer'eb, "Selective adsorption of chromium (VI) in industrial wastewater using low-cost abundantly available adsorbents", *Adv. Environ. Res.,* 2002, 6, 533-537.
27. M. Singanan, V. Singanan and A. Abebaw, "Phytoremediation of heavy metals from industrial wastewater by using indigenous biomaterial", *Indian J. Environ. Prot.,* 2006, 26(5), 385-391.
28. M. Singanan, V. Singanan and A. Abebaw, "Removal of cadmium from industrial waste water by using bio-materials". *Ethiopia J. Health Sci.,* 2006, 16(1), 59-69.
29. P. Waranusantigul, P. Pokethityook, M. Kruatrachue and E. S. Upatham, "Kinetics of basic dye (methylene blue) bio-sorption by giant duckweed *(spirodela polyrrhiza)", Environ. Pollut.,* 2003, 1, 385-392.
30. H. Hasar, "Adsorption of nickel (II) from aqueous solution onto activated carbon prepared from almond husk", *J. Hazard. Mater.,* 2003, B 97, 49-57.
31. G. Raj, "Chemical Kinetics in Advanced Physical Chemistry", Geol Publishing House Meerut, 2001, 669-676 and 149-150.

Global Journal of Science Frontier Research
Chemistry
Volume 12 Issue 1 Version 1.0 January 2012
Type : Double Blind Peer Reviewed International Research Journal
Publisher: Global Journals Inc. (USA)
Online ISSN: 2249-4626 & Print ISSN: 0975-5896

Computing Group Theory and Character Table of Non Rigid Tetraphenylporphyrin H2 (Tpp) and Metalloporphyrin Mii (Tpp)

By M. Eslami Moghadam,T. Karimi, M. Farrokhi D. G.
University of Payam Noor, Fariman, Iran

Abstract - The studies on symmetry of Metalloporphyrins are very important due to better understanding of their spectra. Also, the non rigid molecule group theory, in which the dynamical symmetry operations are defined as physical operations, is a new field of chemistry. In this paper, by a simple method, we calculate character table for symmetry group of non rigid porphyrin molecule consisting of four phenyl groups attached to a rigid framework. We apply the group theory package, GAP, to compute the symmetry of Tetraphenylporphyrin, H_2(TPP), and Metalloporphyrin, M^{II}(TPP), with symmetry groups D_{2h} and D_{4h}, respectively. We prove that the full non rigid of these molecules are seen be the group of order 64 which has 16 conjugacy classes and order 128 which has 20 conjugacy classes, respectively.

Keywords : Character table; Conjugacy classes; GAP; Non-rigid group; Tetraphenylporphyrin.

GJRE Classification : FOR Code: 030799

COMPUTING GROUP THEORY AND CHARACTER TABLE OF NON RIGID TETRAPHENYLPORPHYRIN H2 TPP AND METALLOPORPHYRIN MII TPP

Computing Group Theory and Character Table of Non Rigid Tetraphenylporphyrin H2 (Tpp) and Metalloporphyrin Mii (Tpp)

M. Eslami Moghadam [α], T. Karimi [Ω], M. Farrokhi D. G. [β]

Abstract - The studies on symmetry of Metalloporphyrins are very important due to better understanding of their spectra. Also, the non rigid molecule group theory, in which the dynamical symmetry operations are defined as physical operations, is a new field of chemistry. In this paper, by a simple method, we calculate character table for symmetry group of non rigid porphyrin molecule consisting of four phenyl groups attached to a rigid framework. We apply the group theory package, GAP, to compute the symmetry of Tetraphenylporphyrin, H_2(TPP), and Metalloporphyrin, M^{II}(TPP), with symmetry groups D_{2h} and D_{4h}, respectively. We prove that the full non rigid of these molecules are seen be the group of order 64 which has 16 conjugacy classes and order 128 which has 20 conjugacy classes, respectively.

Keywords : Character table; Conjugacy classes; GAP; Non-rigid group; Tetraphenylporphyrin.

I. INTRODUCTION

The study of porphyrins has received increased interest in recent years. Metalloporphyrin complexes play significant roles in many biological and catalytic systems. The diversity of their functions is due in part to the variety of metals that bind in the "pocket" of the porphyrin ring system. The study of porphyrins is well suited to college and university laboratories because of their importance and several other reasons. Specifically, interpretation of their spectra offers an introduction to molecular orbital and molecular symmetry (1,2).Group theory for non-rigid molecules is becoming increasingly relevant and its numerous applications to vibrational spectroscopy of small molecules are appearing in the literatures (3,9). As it is well known, group theory for non-rigid molecules was essentially developed for two points of view: i) The molecular symmetry group theory (MSG) of permutation inversion groups constructed by permutations and permutation-inversions of identical particles (The MSG group is formed by all feasible permutations); ii) The full and restricted non-rigid group theory built up with physical operations, expressed in terms of internal coordinates that transform one conformation into another iso-energetic one (10).

In a series of paper Ashrafi and coauthors computed full non-rigid groups of some molecules such as tetraammine platinum(II) (11), cis- and transdichlorodiammine platinum(II) and trimethylamine (12), tetraammine platinum(II) with C_{2v} and C_{4v} point group (13,14), tetraamine platinum(II) as a wreath product (15), tetra-tertbutyltetrahedrane (16), tetramethylethylene (17), hexamethylbenzene (18) and melamine (19).

In this paper the full non-rigid groups of Tetraphenylporphyrin, H_2(TPP), and Metalloporphyrin ,M^{II}(TPP), are computed. Firstly, the algebraic structures of the full non-rigid group of these molecules are specified. Then, based on the structure of the group, a useful programming language, namely GAP (20), is applied and the character Tables of f-NRG of these molecules are computed. The GAP package is used to find many properties of the groups (21,22). We determine the order of the f-NRG of two porphyrin molecules and conjugacy classes of them. Finally, we calculate the character tables of them.

II. THEORETICAL METHOD

Our computations were carried out using the "Groups, Algorithms and Programming" (GAP) system (20). GAP is a free and extensible software package for computation in discrete abstract algebra, in which you can write your own programs in the GAP language, and use them in the same way the programs which form part of the system are used. More information on the motivation and development of GAP to date can be found on the GAP web page (http://www.gapsystem.org/).

First of all, we consider the point group of Tetraphenylporphyrin, H_2(TPP), and Metalloporphyrin, M^{II}(TPP), in the case of rigid state (see Figures. 1(A) and (B) where the structures are optimized using PM3 method of the chemistry package Hyperchem (23)) and determine the point groups of full non-rigid group of these molecules with symmetry groups D_{2h} and D_{4h}, which denoted

---

Author [α] : Department of Chemistry, University of Payam Noor, Fariman, Iran.
Author [Ω] : Department of Mathematics, University of Payam Noor, Fariman, Iran.
Author [β] : Department of Mathematics, Ferdowsi University of Mashhad, Mashhad, Iran.

by G and K, respectively. Then we apply G and K to compute their conjugacy classes and character tables.

III. GAP PROGRAM

The group theory of H_2(TPP) and M^{II}(TPP) can be computed using the GAP function Group() for D_{2h} and D_{4h} point group, respectively. Also the conjugacy classes and the character table of each of these groups can be computed using the GAP functions Conjugacy Classes() and Irr(), respectively.

IV. RESULTS AND DISCUSSION

Determination of conjugacy classes and character table

Tetraphenylporphyrin, H_2(TPP) with D_{2h}: Now, we consider the point group D_{2h} of the f-NRG of tetraphenylporphyrin. From the Figure 1(A), it follows that the elements $\alpha_1 = (1,2)$, $\alpha_2 = (3,4)$, $\alpha_3 = (5,6)$ and $\alpha_4 = (7,8)$, which permutes hydrogens in either of phenyl cases. We assume that these operations are all feasible, that barrier to rotation of the phenyl group is low. Also there are five elements:

$$\alpha_5=(1,5)(2,6)(3,7)(4,8)(9,13)(10,14)(11,15)(12,16),$$

$$\alpha_6=(1,4)(2,3)(5,8)(6,7)(9,14)(10,13)(11,12)(15,16),$$

$$\alpha_7=(1,8)(2,7)(3,6)(4,5)(9,10)(11,16)(12,15)(13,14),$$

$$\beta_1=(1,2)(6,5),$$

$$\beta_2=(3,4)(7,8),$$

Which correspond to $C_2(z)$, $C_2(y)$, $C_2(x)$, σ (xz) and σ (xy), respectively. These nine permutations generate the group G and a simple GAP program shows that G is a group of order 64 with 16 conjugacy classes. The conjugacy classes of G can be computed.

The representative for conjugacy classes of G is given in Table I. Also the character table of G can be easily computed using GAP function Irr(G). From conjugacy classes of the groups G, we able to compute the irreducible character table of them. The values of the irreducible character $\chi_i\,(1 \le i \le 16)$ for D_{2h} symmetry is shown in Table II.

We know the 22 p_z orbitals in the free-base porphyrin are the basis of set of orbitals combined to create the π molecular orbitals of the porphyrin ring (1). The point group is D_{2h}. This gives the reducible representation:

$D_{2h\ \text{(rigid)}}$	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
$\Gamma_{\Pi porphyrin}$	22	0	-2	0	0	-22	0	2

Which reduces to $5B_{2g} + 6B_{3g} + 4A_u + 6B_{1u}$. None of these states are degenerate. But the configuration with $D_{2h(\text{non-rigid})}$ symmetry possesses some rotations of phenyl groups with the symmetry representations:

$D_{2h\ \text{(Non-rigid)}}$	1(1a)	4(2a)	2(2b)	2(2c)	2(2d)	4(2e)	1(2f)	4(2g)	8(4a)	4(4b)	4(2h)	8(4c)	4(4d)	4(2i)	8(4e)	4(f)
$\Gamma_{\Pi porphyrin}$	22	22	22	22	22	22	22	0	0	0	0	0	0	2	2	2
$\Gamma_{\Pi phenyl}$	24	20	16	16	16	12	8	0	0	0	0	0	0	0	0	0

Thus, the skeletal modes of a porphyrin derivative can be classified, according to the D_{2h} symmetry, as

$$\Gamma_{\Pi por} = 6\chi_1 + 6\chi_6 + 5\chi_7 + 5\chi_8$$

$$\Gamma_{\Pi ph} = 4\chi_1 + 4\chi_6 + 4\chi_7 + 4\chi_8 + 2\chi_{16}$$

Metalloporphyrin, M^{II}(TPP) with D_{4h}: After metalation the symmetry is D_{4h}, as all nitrogens are equivalent. Whereas during metalation the $d\pi$ metal orbital overlap with the π system of the porphyrin ring, the change in the porphyrin spectrum on metalation is due to increased symmetry relative to the free-base porphyrin.

Similar mentioned method, by figure 1(B) we have four rotations $\alpha_1 = (1,2)$, $\alpha_2 = (3,4)$, $\alpha_3 = (5,6)$ and $\alpha_4 = (7,8)$ in the D_{4h} symmetry, which permutes hydrogens in either of phenyl cases. Also, we have rotation and reflections,

$$\alpha_5 = (1,3,5,7)(2,4,6,8)(9,11,13,15)(10,12,14,16),$$

$$\beta_1=(1,2)(3,8)(4,7)(5,6)(9,12)(10,11)(13,16)(14,15),$$

$$\beta_2=(1,6)(2,5)(3,4)(7,8)(9,16)(10,15)(11,14)(12,13),$$

$$\beta_3=(1,4)(2,3)(5,8)(6,7)(9,14)(10,13)(11,12)(15,16),$$

$$\beta_4=(1,8)(2,7)(3,6)(4,5)(9,10)(11,16)(12,15)(13,14),$$

for D_{4h} point group.The permutations α_1, α_2, α_3, α_4, β_1, β_2, β_3 and β_4 generate the group K. GAP program shows that K is group of order 128 with 20 conjugacy classes. The representative for conjugacy classes and character table of K are shown in Table III and IV.

In rigid conformation, the resulting basis set consists of the $24\ p_z$ orbitals (1).

$D_{4h\ \text{(rigid)}}$	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_v$
$\Gamma_{\Pi porphyrin}$	24	0	0	-2	-2	0	0	-24	2	2

Which reduces to $6E_g + 3A_{1u} + 3A_{2u} + 3B_{1u} + 3B_{2u}$.

But the configuration with $D_{4h\text{(non-rigid)}}$ symmetry possesses some rotations of phenyl groups with the symmetry representations:

$D_{4h\ \text{(non-rigid)}}$	1(1a)	4(2a)	4(2b)	2(2c)	4(2d)	4(2e)	4(4a)	8(2f)	8(4b)	1(2g)
$\Gamma_{\Pi porphyrin}$	24	24	24	24	24	2	2	2	2	24
$\Gamma_{\Pi phenyl}$	24	20	16	16	12	4	4	4	4	8

$D_{4h\ \text{(non-rigid)}}$	4(2h)	4(4c)	8(2i)	16(4d)	8(4e)	16(4f)	16(8a)	4(2j)	8(4g)	4(4h)
$\Gamma_{\Pi porphyrin}$	2	2	2	2	2	0	0	0	0	0
$\Gamma_{\Pi phenyl}$	4	4	0	0	0	0	0	0	0	0

$$\Gamma_{\Pi por} = 4\chi_1 + 2\chi_6 + 3\chi_7 + 3\chi_8 + 6\chi_9$$

$$\Gamma_{\Pi ph} = 3\chi_1 + \chi_6 + \chi_7 + 3\chi_8 + 4\chi_9 + \chi_{19} + \chi_{20}$$

We know the change in the spectrum on metalation is due to increased symmetry relative to the free-base porphyrin. The two hydrogens on the nitrogen atoms in the free base porphyrin reduce the ring symmetry from square (for Metalloporphyrins) to rectangular- that is from D_{4h} to D_{2h}. In general, a more symmetrical molecule gives a simpler spectrum.

V. CONCLUSIONS

The method described in this paper appears to be more efficient in dealing with the construction to the character table of the symmetry group of the molecule. First, all the permutations and inversions which don't change the whole framework of the molecule should be examined. We have considered the point groups of Tetraphenylporphyrin, H_2(TPP), and Metalloporphyrin, M^{II}(TPP), in the case of non-rigid state and calculated the conjugacy classes of full non-rigid groups of H_2(TPP) and M^{II}(TPP) with symmetry groups D_{2h} and D_{4h} which denoted by G and K, respectively. Then using the GAP package the character table of the f-NRG group is computed. This method is usually very useful for calculating symmetries of the molecule, when the numbers of vertices are at most 30. It is hoped that the present study would help to interpret Raman and IR spectra of full non-rigid porphyrin derivatives and another molecules in future.

ACKNOWLEDGEMENT

We would like to thank Fariman university of Payam Noor for financial support for this research.

REFERENCES RÉFÉRENCES REFERENCIAS

1. D. F. Marsh, L. M. Mink, *J. Chem. Edu.* 73 (12), 1188 1190 (1996).
2. L. C. Xu, Z. Y. Li, W. Tan, T. J. He, F. C. Liu, D. M. Chen, *Spectrochimica Acta Part A* 62, 850–862 (2005).
3. P. R. Bunker, *Mol. Phys.* 8, 81-91(1964).
4. S. L. Altmann, *Induced Representation in Crystal & Molecules,* Academic Press, London (1977).
5. G. S. Ezra, *Symmetry Properties of Molecules,* Lecture Note in Chemistry 28, Springer (1982).
6. J. Maruani and J. Serre (Eds.), *Symmetries and Properties of Non-Rigid Molecules,* Elsevier, Amsterdam (1983).
7. Y. G. Smeyers, M. L. Senent, V. Botella, and D. C. Moule, *J. Chem. Phys.* 98, 2754-2767 (1993).
8. Y. G. Smeyers, M. Villa, and M. L. Senent, *J. Mol. Spect.* 191, 232-238 (1998).
9. A.Vivier-Bunge, V. H. Uct, and Y. G. Smeyers, *J. Chem. Phys.* 109, 2279-2286 (1998).
10. H. C. Longuet-Higgins, *Mol. Phys.* 6, 445-460 (1963).
11. A.R. Ashrafi, M. Hamadanian, *Croat. Chem. Acta* 76, 299-303 (2003).
12. M. Hamadanian, A. R. Ashrafi, *Croat. Chem. Acta* 76, 305-312 (2003).
13. A.R. Ashrafi, M. Hamadanian, J. *Appl. Math. & Computing* 14, 289-303 (2004).
14. G. Moghani, A. Ashrafi, M. Hamadanian, *J. Zhejiang Univ. Sci.* 6, 222-226 (2005).
15. M. R. Darafsheh, Y. Farjami and A. R. Ashrafi, *Bull. Chem. Soc. Jpn.* 78, 996-1000 (2005).
16. M. R. Darafsheh, A. R. Ashrafi, A. Darafsheh, *Int. J. Quantum Chem.* 105, 485-492 (2005).
17. M. R. Darafsheh, A. R. Ashrafi, A. Darafsheh, *Acta Chim. Slov.* 52, 282-286 (2005).
18. M. R. Darafsheh, A. R. Ashrafi, A. Darafsheh, *Chem. Phys. Lett.* 421, 566-570 (2006).
19. A.R. Ashrafi, M. Hamadanian, *J. Iran. Chem. Soc.* 2, 135-139 (2005).
20. The GAP Group, *GAP-Groups, Algorithms, and Programming,* Version 4.4.12 (http://www.gap-system.org/)(2008).
21. T. Karimi, M. Eslami Moghadam, M. Farrokhi D. G., M. Aghaei, The full non-rigid group theory for trimethylborane with C3v, C3h and CS point groups, *J. Argent. Chem. Soc,* in press, (2011).
22. A.R. Ashrafi, M. Ghorbani, *J. Serb. Chem. Soc.* 75 (3) 361-368 (2010).
23. Hyperchem, Version 8.0.7 (http://www.hyper.com/) (2009).

Table I

The representatives of conjugacy classes of the group G (D_{2h})

No.	Representative	Size	Name	Symmetry
1	()	1	1a	E
2	(7,8)	4	2a	α_4
3	(5,6)(7,8)	2	2b	$\alpha_3\alpha_4$
4	(3,4)(7,8)	2	2c	$\alpha_2\alpha_4$
5	(3,4)(5,6)	2	2d	$\alpha_2\alpha_3$
6	(3,4)(5,6)(7,8)	4	2e	$\alpha_2\alpha_3\alpha_4$
7	(1,2)(3,4)(5,6)(7,8)	1	2f	$\alpha_1\alpha_2\alpha_3\alpha_4$
8	(1,3)(2,4)(5,7)(6,8)(9,14)(10,13)(11,12)(15,16)	4	2g	$\alpha_1\alpha_2\alpha_3\beta_1\alpha_3$
9	(1,3)(2,4)(5,7,6,8)(9,14)(10,13)(11,12)(15,16)	8	4a	$\alpha_1\alpha_2\alpha_3\beta_1$
10	(1,3,2,4)(5,7,6,8)(9,14)(10,13)(11,12)(15,16)	4	4b	$\alpha_1\alpha_3\beta_1$
11	(1,5)(2,6)(3,7)(4,8)(9,13)(10,14)(11,15)(12,16)	4	2h	α_5
12	(1,5)(2,6)(3,7,4,8)(9,13)(10,14)(11,15)(12,16)	8	4c	$\alpha_5\alpha_2$
13	(1,5,2,6)(3,7,4,8)(9,13)(10,14)(11,15)(12,16)	4	4d	$\alpha_3\alpha_5\alpha_2$
14	(1,7)(2,8)(3,5)(4,6)(9,10)(11,16)(12,15)(13,14)	4	2i	$\alpha_1\alpha_2\alpha_3\beta_2\alpha_1$
15	(1,7,2,8)(3,5)(4,6)(9,10)(11,16)(12,15)(13,14)	8	4e	$\alpha_1\alpha_2\alpha_3\beta_2$
16	(1,7,2,8)(3,5,4,6)(9,10)(11,16)(12,15)(13,14)	4	4f	$\alpha_1\alpha_2\beta_2$

Table II

The representatives of conjugacy classes of the group K (D_{4h})

No.	Representative	Size	Name	Symmetry
1	()	1	1a	E
2	(7,8)	4	2a	α_4
3	(5,6)(7,8)	4	2b	$\alpha_3\alpha_4$
4	(3,4)(7,8)	2	2c	$\alpha_2\alpha_4$
5	(3,4)(5,6)(7,8)	4	2d	$\alpha_2\alpha_3\alpha_4$
6	(3,7)(4,8)(9,12)(10,11)(13,16)(14,15)	4	2e	$\alpha_1\alpha_2\alpha_3\alpha_4\beta_1$
7	(3,7,4,8)(9,12)(10,11)(13,16)(14,15)	4	4a	$\alpha_1\alpha_2\alpha_3\beta_1$
8	(3,7)(4,8)(5,6)(9,12)(10,11)(13,16)(14,15)	8	2f	$\alpha_1\alpha_2\alpha_4\beta_1$
9	(3,7,4,8)(5,6)(9,12)(10,11)(13,16)(14,15)	8	4b	$\alpha_1\alpha_2\beta_1$
10	(1,2)(3,4)(5,6)(7,8)	1	2g	$\alpha_1\alpha_2\alpha_3\alpha_4$
11	(1,2)(3,7)(4,8)(5,6)(9,12)(10,11)(13,16)(14,15)	4	2h	$\alpha_2\alpha_4\beta_1$
12	(1,2)(3,7,4,8)(5,6)(9,12)(10,11)(13,16)(14,15)	4	4c	$\alpha_2\beta_1$
13	(1,3)(2,4)(5,7)(6,8)(9,14)(10,13)(11,12)(15,16)	8	2i	$\alpha_1\alpha_2\alpha_3\alpha_4\beta_3$
14	(1,3)(2,4)(5,7,6,8)(9,14)(10,13)(11,12)(15,16)	16	4d	$\alpha_1\alpha_2\alpha_3\beta_3$

15	(1,3,2,4)(5,7,6,8)(9,14)(10,13)(11,12)(15,16)	8	4e	$\alpha_1\alpha_3\beta_3$
16	(1,3,5,7)(2,4,6,8)(9,11,13,15)(10,12,14,16)	16	4f	α_5
17	(1,3,5,7,2,4,6,8)(9,11,13,15)(10,12,14,16)	16	8a	$\alpha_4\alpha_5$
18	(1,5)(2,6)(3,7)(4,8)(9,13)(10,14)(11,15)(12,16)	4	2j	α_5^2
19	(1,5)(2,6)(3,7,4,8)(9,13)(10,14)(11,15)(12,16)	8	4g	$\alpha_4\alpha_5^2$
20	(1,5,2,6)(3,7,4,8)(9,13)(10,14)(11,15)(12,16)	4	4h	$\alpha_3\alpha_4\alpha_5^2$

Table III

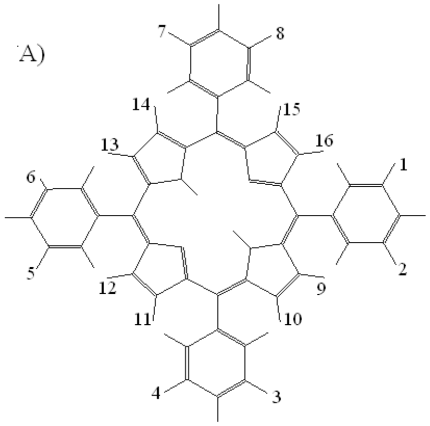
The character table of the group G (D_{2h})

D_{2h}	1a	2a	2b	2c	2d	2e	2f	2g	4a	4b	2h	4c	4d	2i	4e	4f
χ_1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
χ_2	1	-1	1	1	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1
χ_3	1	-1	1	1	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1
χ_4	1	-1	1	1	1	-1	1	1	-1	1	-1	1	-1	-1	1	-1
χ_5	1	-1	1	1	1	-1	1	1	-1	1	1	-1	1	1	-1	1
χ_6	1	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1	1
χ_7	1	1	1	1	1	1	1	-1	-1	-1	1	1	1	-1	-1	-1
χ_8	1	1	1	1	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1
χ_9	2	0	-2	2	-2	0	2	0	0	0	-2	0	2	0	0	0
χ_{10}	2	0	-2	2	-2	0	2	0	0	0	2	0	-2	0	0	0
χ_{11}	2	0	-2	-2	2	0	2	0	0	0	0	0	0	-2	0	2
χ_{12}	2	0	-2	-2	2	0	2	0	0	0	0	0	0	2	0	-2
χ_{13}	2	0	2	-2	-2	0	2	-2	0	2	0	0	0	0	0	0
χ_{14}	2	0	2	-2	-2	0	2	2	0	-2	0	0	0	0	0	0
χ_{15}	4	-2	0	0	0	2	-4	0	0	0	0	0	0	0	0	0
χ_{16}	4	2	0	0	0	-2	-4	0	0	0	0	0	0	0	0	0

Table IV

The character table of the group K (D_{4h})

D_{4h}	1a	2a	2b	2c	2d	2e	4a	2f	4b	2g	2h	4c	2i	4d	4e	4f	8a	2j	4g	4h
χ_1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
χ_2	1	-1	1	1	-1	-1	1	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1	1
χ_3	1	-1	1	1	-1	-1	1	1	-1	1	-1	1	1	-1	1	-1	1	1	-1	1
χ_4	1	-1	1	1	-1	1	-1	-1	1	1	1	-1	-1	1	-1	-1	1	1	-1	1
χ_5	1	-1	1	1	-1	1	-1	-1	1	1	1	-1	1	-1	1	1	-1	1	-1	1
χ_6	1	1	1	1	1	-1	-1	-1	-1	1	-1	-1	-1	-1	-1	1	1	1	1	1
χ_7	1	1	1	1	1	-1	-1	-1	-1	1	-1	-1	1	1	1	-1	-1	1	1	1
χ_8	1	1	1	1	1	1	1	1	1	1	1	1	-1	-1	-1	-1	-1	1	1	1
χ_9	2	2	2	2	2	0	0	0	0	2	0	0	0	0	0	0	0	-2	-2	-2
χ_{10}	2	-2	2	2	-2	0	0	0	0	2	0	0	0	0	0	0	0	-2	2	-2
χ_{11}	2	0	-2	2	0	2	0	0	-2	2	2	0	0	0	0	0	0	2	0	-2
χ_{12}	2	0	-2	2	0	-2	0	0	2	2	-2	0	0	0	0	0	0	2	0	-2
χ_{13}	2	0	-2	2	0	0	-2	2	0	2	0	-2	0	0	0	0	0	-2	0	2
χ_{14}	2	0	-2	2	0	0	2	-2	0	2	0	2	0	0	0	0	0	-2	0	2
χ_{15}	4	0	0	-4	0	0	0	0	0	4	0	0	-2	0	2	0	0	0	0	0
χ_{16}	4	0	0	-4	0	0	0	0	0	4	0	0	2	0	-2	0	0	0	0	0
χ_{17}	4	-2	0	0	2	-2	2	0	0	-4	2	-2	0	0	0	0	0	0	0	0
χ_{18}	4	-2	0	0	2	2	-2	0	0	-4	-2	2	0	0	0	0	0	0	0	0
χ_{19}	4	2	0	0	-2	-2	-2	0	0	-4	2	2	0	0	0	0	0	0	0	0
χ_{20}	4	2	0	0	-2	2	2	0	0	-4	-2	-2	0	0	0	0	0	0	0	0



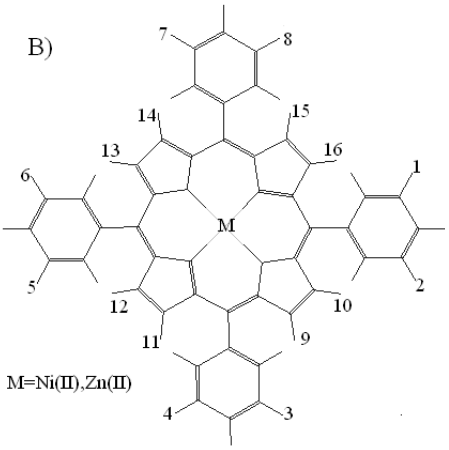


Figure 1. Top-view diagram of the structures of (A) Tetraphenylporphyrin, H_2(TPP), and (B) Metalloporphyrin, M^{II}(TPP).

This page is intentionally left blank

Global Journal of Science Frontier Research
Chemistry
Volume 12 Issue 1 Version 1.0 January 2012
Type : Double Blind Peer Reviewed International Research Journal
Publisher: Global Journals Inc. (USA)
Online ISSN: 2249-4626 & Print ISSN: 0975-5896

Synthesis and Antibacterial Activities of Bimetallic Complexes of Cobalt (II) and Nickel (II) Acetophenolate

By A.O.Aliyu , H.Adamu, DB Maikaje"s
Nigerian Defence Academy, Kaduna

Abstract - Bimetallic complexes of cobalt (II) and nickel (II) acetophenone with tin chloride were synthesized and characterized by elemental analyses, conductivity measurement, magnetic and spectral data. The complexes are 1:2 adducts and non-electrolytes in solution. The ligands and their complexes were screened for antibacterial activities against Staphyloccus aureus and Escherichia coli. Cobalt (II) bimetallic complexes were found active against the tested microorganisms.

Keywords : Synthesis, antibacterial activities and bimetallic complexes.

GJRE Classification : FOR Code: 030499

SYNTHESIS AND ANTIBACTERIAL ACTIVITIES OF BIMETALLIC COMPLEXES OF COBALT II AND NICKEL II ACETOPHENOLATE

Strictly as per the compliance and regulations of:

Synthesis and Antibacterial Activities of Bimetallic Complexes of Cobalt (II) and Nickel (II) Acetophenolate

A.O.Aliyu[α] , DB Maikaje"s[Ω]

Abstract - Bimetallic complexes of cobalt (II) and nickel (II) acetophenone with tin chloride were synthesized and characterized by elemental analyses, conductivity measurement, magnetic and spectral data. The complexes are 1:2 adducts and non-electrolytes in solution. The ligands and their complexes were screened for antibacterial activities against *Staphyloccus aureus* and *Escherichia coli*. Cobalt (II) bimetallic complexes were found active against the tested microorganisms.

Keywords : Synthesis, antibacterial activities and bimetallic complexes

I. INTRODUCTION

Acetophenone is a viscous colourless aromatic ketone. It is used as a precursor in resins and fragrances (Hardo and Manfred, 2002). It has a melting and a boiling point of 19-20°C and 220°C respectively. In industry, acetophenone is used in the production of propylene oxide [1].

Acetophenone occurs naturally in many foods such as apple, cheese, apricot, banana, beef and cauliflower [2]. It is a polymerization catalyst for the manufacture of olefin and an intermediate for pharmaceutical, agrochemical and other organic compounds. It has been used as a drug to induce sleep and as teargas in warfare [3].

Schiff bases and it's metal chelates have played an important role in the development of chemical industries through catalysis, substrate carrier and dyes[4].Tucareso, a schiff base forming immunomodulator is currently undergoing pilot phase 1\11 clinical trials as an immunopotentiator in chronic hepatitis B virus infection, HIV infection and malignant melanoma [5].

These ligands are widely studied because of their coordinating properties and abilities [6,7]..The ligands are important compounds in medicinal and pharmaceutical field. They show biological activities including antibacterial, antifungal, anticancer, and herbicidal activities[8].Schiff base are utilized as starting materials in the synthesis of industrial and biological compounds[9].

The work is aimed at carrying out syntheses, conductivity measurement and electronic spectral of biologically active bimetallic complexes of cobalt (II) and nickel (II) of acetophenone and their antibacterial activities.

II. MATERIALS AND METHODS

The reagents used are of analytical grade and were used without further purifications. Metal complexes of cobalt (II) and nickel (II) acetophenolate were prepared according to well established methods in literature [10].

a) Preparation of cobalt (II) acetophenolate

1.25g of cobalt (II) chloride was weighed into a 100cm^3 beaker and 10cm^3 of acetophenone was added. The mixture was heated to 90°C on a hot water bath and was stirred continuously. Temperature was maintained for 15 minutes with stirring. The mixture was cooled in an ice bath and on cooling the dark pink product formed was vaccum-filtered and air dried for 15 minutes. The product was later dried in a descicator over a silica gel, weighed and its percentage yield determined (56%).

$$CoCl_2.6H_2O + 2C_6H_5C\,(O)CH_3 \rightarrow [Co(C_6H_5OC(O)CH_3)_2Cl_2]^{2+} + 6H_2O$$

Similar method was used for the preparation of nickel (II) acetophenolate.

$$NiCl_2 6H_2O + 2C_6H_5C(O)CH_3 \longrightarrow [Ni(C_6H_5C(O)CH_3)_2CI_2]^{2+} + 6H_2O$$

b) Preparation of the bi metallic complexes [4]

A general method has been used for the preparation of the binuclear complexes by the reaction of the metal salts and the Schiff base ligand at a metal to ligand molar ratio of 2:1.The mixture was heated on water bath to ensure complete dissolution of the metal salt. To this solution the ligand (2.2g, 5mmol dissolved in 10cm^3 ethanol) was added gradually. The reaction mixture was were filtered, washed with ethanol and dried in over an hydrous calcium chloride (62%). The procedure was used to prepare and isolate the ML^1.

$$L + SnCl_4 \longrightarrow LSn + 4Cl$$

Author [α] *: Department of Chemistry, Nigerian Defence Academy, P.M.B 2109 Kaduna. E-mail : salimatadetutu@yahoo.co*
Author [Ω]*:* Depertment of Biological Sciences ,Nigerian Defence Academy,Pmb 2109.Kaduna,Nigeria

c) *Evaluation of antimicrobial activities[12]*

The antimicrobial activities of the test compounds were assayed against two micro organisms *Staphylococus aureus and Escberichia coli* regarded as pathogen to man and animal. All media and bacteria suspension were prepared using a suitable method. The *in-vitro* evaluation of antimicrobial activities was performed according to the diffusion technique .The bacterial including *staphylococcus aureus and Escherichia coli* were grown in nutrient broth at 37°C for 24 hours. The ligands and their complexes were tested using diffusion on solid media . Sterile (5mm) diameter sensitivity paper disc were impregnated with concentration of dimethyl formamide (DMF), ligands and their bimetallic complexes at concentration of 50µg/cm^3 and placed in the nutrient agar. The plates were then incubated for 24 hours. Additionally antibiotics disc for cephalosporin were tested as positive control. The results were recorded by measuring the growth inhibition surrounding the disc.

d) *Physical measurement*

The infrared spectra of the complexes were measured as KBr disc on Perkin Elmer FTIR Paragon 1000 spectrometer in the range 4000-400cm^{-1}while the electronic spectra in chloroform were recorded on Perkin Elmer λ 20.The elemental analyses (C and H) were determined. Nickel and Cobalt were determined titrimetrically [13]. .Magnetic susceptibilities were measured on Johnson Matthey magnetic susceptibility balance and diamagnetic corrections were calculated using Pascal's constants [14].Melting point were determined using a Stuart scientific melting point SMPI machine. Molar conductivity at room temperature was measured in water using ELCOM-CM-82 conductivity machine using 10^{-3}mol dm^{-3} stock solution of the complexes.

III. RESULTS AND DISCUSSION

All complexes are coloured and amorphous in nature. Acetophenone complexes of nickel (II) $[Ni(Acet)_2]$ is greenish yellow while its cobalt (II) complexes $\{Co(Acet)_2\}$ are pinkish and are all soluble in polar solvents such as dimethlyformanide (DMF), dimethylsulfoxide (DMSO), methanol, ethanol and water, but insoluble in chloroform, diethyl ether and petroleum ether. The elemental analyses showed the complexes as 1:2 adducts and the conductivity data suggest non-electrolytic behavior (Table 1).

a) *Molar conductance*

The molar conductance of the metal complexes in DMSO were observed below 14.0 ohm^{-1} cm^2 mol^{-1} showing that they were non-electrolyte. A value of 60-115 ohm^{-1} cm^2 mol^{-1} is expected for 1:1 electrolyte.

b) *Electronic Spectra*

Nickel (II) complexes are known to have a range of coordination numbers from six (octahedral) to four(square planar/tetrahedral).Their electronic spectra are typically characterized by the existence complexes of complicated equilibra involving this structural type [15].The electronic spectra of the complexes of $[Ni(Acet)_2CI_2].H_2O$ has three characteristic absorption at 14,000, 25,000 and 33,000cm^{-1} bands while its bimettalic counterpart has characteristic band at around 24,000 cm^{-1} indicative of octahedral stereochemistry (Table I). These signals are assigned to $^3A_2 g$ to Tig (F),v_1 ,v_2, v_4 and ^3A_2g to $^3T_I g(P)$, V_3 respectively. Octahedral nickel (II) complexes exhibit another transition from ^3A_2g to $^3T_{2g}$ at approximate 900cm^{-1} but this may not be determined when the splitting constant is nearly unity and the v_2 transition appears as a well-defined doublet due to the spin forbidden level ^1E_g spinning intensity through configuration interaction with the $^3T_{1g}(E)$ level [16,17]. Therefore the presence of the two characteristic band v_2 and v_3 confirmed that the stereochemistry of the complexes as octahedral and has not changed from its bimetallic complex.

The electronic data of $[Co(Acet)_2CI_2].H_2O$ and its bimetallic complexes(Table 2).The metal complex exhibit a multiple band at 15,748cm^{-1} The band is assigned to the $^4T_{1g}(F)$ to$^4T_{2g}(P)$ transition and its bimetallic complex exhibits a band at 19,230cm^{-1} and band was assigned $^4T_{1g}(F)$ to$^4T_{2g}(P)$ The electronic spectra indicate that cobalt in bimetallic complexes remains in an octahedral environment [16,18].

c) *Magnetic moment*

The magnetic moment of nickel (II) in a cubic field falls between 2.8 - 4.2B.M,tetrahedral complexes have moment in the range 3.20 -4.10 B.M while in octahedral field falls between 4.2- 5.1 B.M. The nickel complexes reported in this work are diamagnetic and consequently octahedral geometry. $[Co(acet)_2CI_2].H_2O$ and its bimetallic complex has magnetic moments between (4.37 – 4.75)BM. These together with the electronic spectra data are suggestive of an octahedral geometry. [16,18].

d) *Infrared spectra*

A comparison of the infrared spectra of the complexes with the parent ligand in DMSO solution shows the conformity with what was reported in literature on similar system[16,18,19].Table 3.The broad band at(3350-3490)cm^{-1} in the metal and bimetallic complexes was observed and assigned to υ (O-H) stretching frequencies. The strong band, which are very prominent at (957-729)cm^{-1} are attributed to υ (C-H) bands of phenyl ring. The υ(C=O)in the parent ligand is shifted to lower region in the complexes by (60-44) cm^1, thus indicating coordination through the carbonyl oxygen of the ketone. The weak bands around 530-540 cm^{-1} has been assigned to υ(M-O) stretching frequencies in metal carbonyl complexes. Also, the bands observed at around 680-575 cm^{-1} was assigned to υ(M-M) in the complexes. The strong band observed in the ligand at around 2850 cm^{-1} is shifted to a lower region in the complexes by (50-40)cm^{-1},thus showing coordination through the cabanion (methyl hydrogen) in the acetophenone [20].

e) Antibacterial Activity

Acetophenone and its metal and bimetallic complexes were screened for their antibacterial activity and the results have been presented in Tables 4 and 5. The bimetallic complexes of cobalt (II) showed good activity against gram positive *Staphylococcus aureus* and least activity against gram negative *Escherichia coli*. While on the other hand the bimetallic complexes of nickel (II) showed least activity against the gram positive and gram negative bacteria. The enhance activity of the complexes over ligands can be explained in terms of chelation theory [21]. Although chelation is not the only criteria for antibacterial activity, some important factor such as nature of the metal ion, metal ion coordinating site, hydrophilicity, hypophilicity and presence of co-ligands have considerable influence on the antibacterial activity. The chelate complexes deactivated various cellular enzymes which play vital role in various metabolic pathways of these microorganisms. Other factors such as solubility, conductivity and dipole moment affected by the presence of metal ions, may be the reasons for increasing the biological activities of the metal complexes compared to the corresponding ligands. Therefore the antibacterial activity of the metal complexes cannot be ascribed to chelation alone but it's an intricate blend of all of the above contributions.

IV. CONCLUSION

The ligand acts as bidentate with carbonyl oxygen atom and carbon as donors. The antibacterial activity of the acetophenone is enhanced upon complexation with metal ions particularly for cobalt (II).

Table 1: Analytical data and physical properties of the complexes

COMPOUND	FW(gmol^1)	COLOUR	%YIELD	% M		M.P	Ohm^{-1}cm^{-1}mol^{-1}
				Found	Calculated		
$[Ni(C_6H_5COCH_3)_2CI_2].H_2O$	389.99	Greenish	64.00	15.07	15.05	256	20
$Ni(C_6H_5COCH_3)_2Sn].H_2O$	579.68	Light green	71.60	10.14	10.13	226	36
$C_6H_5COCH_3)_2CI_2].H_2O$	390.21	Pink	76.00	15.12	15.10	245	32
$[Co(C_6H_5COCH_3)_2CI_2].H_2O$	579.90	Light pink	81.00	10.18	10.16	234	40

Table 2: Magnetic moments and electronic spectra (cm^{-1}) of the complexes.

Compound	μ_{eff}B.M	Elecronic spectra (cm^{-1})
$[Ni(L_2CI_2].H_2O$	0	14,000;25,000;30,000
$[Ni(L_2Sn].H_2O$	0	24,000
$[Co(L_2CI_2].H_2O$	4.75	15,748
$[Co(L_2Sn].H_2O$	4.37	19,230

Table 3 : Diagnostic infrared spectra for the complexes (cm^{-1})

Compounds	υ(O-H)	υ(C- H)	υ(C=O)	Δ(C=O)	υ(C-H)	ΔH(C-H)	υ(M-M)	υ(M-O)
L	-	870m,747s	1689	-	2850		-	-
$[Ni(L_2CI_2].H_2O$	3490	870m,749s	1639	50	2803	47	-	530
$[Ni(L_2Sn].H_2O$	3350	890m,750s	1630	59	2802	48	575	535
$[Co(L_2CI_2].H_2O$	3517	950m,729s	1645	44	2804	46	-	540
$[Co(L_2Sn].H_2O$	3428	957m,766s	1640	49	2802	48	680	532

Table 4a. Diameter of zones of inhibition (Aliyu & Nwabueze, 2009)

Diameter of inhibition (mn)	Symbol	Comments
12-15	+	Insignificant activity
16-20	++	Minimum activity
21-25	+++	Moderate activity
26-35	++++	Maximum activity

Key: + = activity

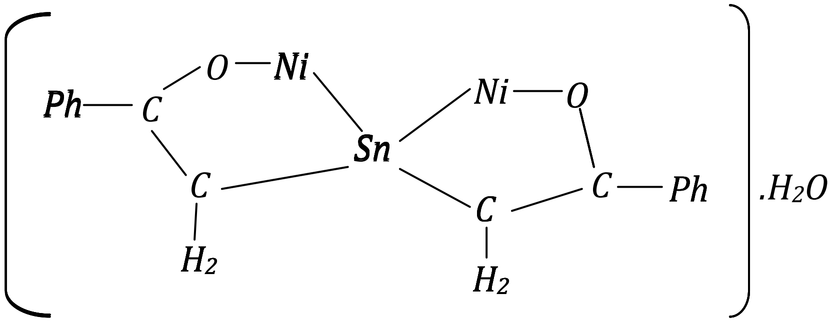
Table 4b. Biological test on *Escherichia coli* (gram negative) $50\mu g/cm^3$.

Complexes/Ligands	Diameter of zone of inhibition(mm)	Symbol	Comments
Acetophenone	13	+	Insignificant activity
$[Ni(acet)_2CI_2].H_2O$	12	+	Insignificant activity
$[Ni(acet)_2.Sn]].H_2O$	14	+	Insignificant activity
$[Co(acet)_2CI_2].H_2O$	17	++	Minimum activity
$[Co(acet)_2.Sn].H_2O$	16	++	Minimum activity
DMF(Solvent control)	-	-	No activity
Cephalosporin(positive control)	23	+++	Moderate activity

Table 5: Microbial Tests on *Staphylococcus aureus* (gram positive) $50\mu g/cm^3$

Complexes/Ligands	Diameter of zone of inhibition(mm)	Symbol	Comments
Acetophenone	17	++	Minimum activity
$[Ni(acet)_2CI_2].H_2O$	12	+	Insignificant activity
$[Ni(acet)_2.Sn_4].H_2O$	13	+	Insignificant activity
$[Co(acet)_2CI_2].H_2O$	23	+++	Moderate activity
$[Co(acet)_2.Sn].H_2O$	21	+++	Moderate activity
DMF(Solvent control)	-	-	No activity
Cephalosporin (positive control)	28	++++	Maximum activity

Proposed structure for the Bimetallic complexes of acetophenone.



References Références Referencias

1. Hardo, S., Manfred, E. (2002) 'Ketones' in Ullman's Encyclopedia of Industrial Chemistry, Willey-VCH.Wienheim.
2. Gadamasetti, K. and Tamin, B. (2007) Process Chemistry in the Pharmaceutical Industry. *Anal.Chem*.69(6): 1167-1173.
3. U. S. Environmental Protection Agency. Health and Environmental effects. Documents for Acetophenone. ECAO-CIN-G001. Environmental Criteria and Assessment office of Research and Development, Cincinnati, OH. (1987).
4. Aderoju A.Osowole (2008) Studies on some VO (IV),Ni (II) and Cu (II) Complexes of non-symetrical tetradentate Schiff – Bases Bull. Chem. Soc.Ethiop.22(2),219-224.
5. Chen.H.;Rhodes.J (1996) Schiff base forming drugs: mechanisms of immune potentiation and therapeutic potential. J Mol Med (Berl). 74(9):497-504.
6. Singh,R.V.;Fahmi,N.;Biyala,M.K(2005) Complexes of Cu(II) and Ni(II) with Bis(phenylthiosemi carbazone): Synthesis, Spectral, EPR and *in vitro* - Antibacterial and Antioxidant Activity*J.Chem.Soc.*Iran.2,40
7. Denoon, C. E. Jr. (1984). Acetylacetone .*Organic Synthesis Coll*. 3:1
8. Abou-Melha, K.S and Farook,H (2008) Bimetallic complexes of schiff base Bis-[4-hydroxycuomarin-3-N^{5}N thiocarbohydrazone as a potential dibasic pentadentate ligand,synthesis, spectra and antimicrobial properties.*J.Iran. Chem. soc.,*5(1);122-134.
9. Stefan France, Harald Wack, Ahmed M. Hafez, Andrew E. Taggi, Daniel R. Witsil, and Thomas Lectka*(2002) Bifunctional Asymmetric Catalysis: A Tandem Nucleophile/Lewis Acid Promoted Synthesis of â-Lactams.Organic letters,4(9);1603-1605
10. Divarkar, M. C., Biradar, N. S. and Aminabhavi, T. M. (1984) Biologically Active Complexes formed from Acetylacetonates of copper, cobalt and nickel. *Inorganica Chemical Acta*, 92: 99-105.
11. Aliyu, A.O and Nwabueze,J.N.(2009) Studies on complexation of Cobalt(II) with isonicotinohydroxamic acid and it's microbial sensitivity.*Reserch journal of medical sciences*.3(5);170-174.
12. Ferrari, M. B., Capacchi, S., Pelosi, G., Tarasconi, P., Alberitini, R. (1999).Synthesis,structural characterization and antiproliferative and toxic bioactivities of Copper(II) and nickel(II) citonellal-N4 ethylmorpholine thiosemicarbazonates. *Inorganic Chemical Acta,*73,(1-2);7-15
13. Bassett.J; Denney,R.C.; Jeffery.G.H.; Mendham. J(1979) Vogel"s text book of qualitative inorganic analysis 4th edition,ELBS; London p 325
14. Earnshaw.A(1980) The introduction of magnetochemistry. Academic press:London:1980 p 80.
15. Lever,A.B.P (1980) Inorganic Spectroscopy; 4th Ed., Elsevier, London. P481
16. Nicholls, David (1974) complexes and first row transition element, Macmillan, London ,UK, Pp 89-95.
17. Maryama Lashanizadegan[1], Saeed Rayati[2,*], Zeinab Dejparvar Derakhshan(2011) Heterogeneous Green Catalyst for Oxidation of Cyclohexene and Cyclooctene with Hydrogen Peroxide in the Presence of Host (Nanocavity of Y-zeolite)/Guest (N4-Cu(II) Schiff Base Complex) Nanocomposite Material. Chinese journal of Chemistry.29(11);2213-2565.DOI: 10.1002/cjoc.201180414
18. Bennett, M. A. and Mitchell, T. R. B. (1976). Carbon bonded 2, 4, Pentanedionato Complexes of

Trivalent Iridium, *Inorganic Chemistry*, 15:2936-8. Doi-10.1021/ic50165a079.

19. Nwabueze J.N (1996) complexes of cyclocarbohydroxamic acids with cobalt (II), Nickel (II), and Copper (II). *Transition Met. Chem*. 22;123.
20. El-sayed, B. A., Abo Aly, M. M. Emara, A. A. A., Khalil, S. M.E. (2002). Synthesis and Structural Study of the Ligands O-OH acetophenone azine and its Cu (II), Co (II) and Zn (II) Complexes.*Inorganic Chemical Acta*,1;1 41:139
21. Rama Krishna, R. K., Suneetha, P., Karigar, C. S., Manjunath, N. H. and Mahendra, K. N. (2008) Cobalt (II), Nickel (II), Copper (II), Zinc (II), Cadmium (II), Mercury (II), Uranium Oxide (IV) and Thorium (IV) from Onnn Schiff Ligand, *Journal of the Chlean Chemical Society*, 53:1653-1657.

GLOBAL JOURNAL OF SCIENCE FRONTIER RESEARCH
CHEMISTRY
Volume 12 Issue 1 Version 1.0 January 2012
Type : Double Blind Peer Reviewed International Research Journal
Publisher: Global Journals Inc. (USA)
Online ISSN: 2249-4626 & Print ISSN: 0975-5896

An Expedient and facile Multicomponent Synthesis of β-Acetamido Ketones by Using Various Green Solvents

By S. S. Patil , Deepak. M. Nagrik, Rameshwar S. Dhamak,
D.M.Ambhore , J.B.Devhade

Amravati University, Amravati, India

Abstract - Multicomponent reactions (MCRs) are emerged as one of the most imperative synthesis route in organic synthesis due to their wide application range in pharmaceutical chemistry. A variety of **β** - acetamido ketones were readily prepared in good to excellent yield (50.-95%) via four component reaction of aromatic aldehydes, enolizable ketones and acetonitrile in presence of stoichiometric amount of acetyl chloride. Here water, methanol, ethanol, perchloroethylene, xylene, and 1,1,1 trichloroethane were used as green solvent. The corresponding compounds were obtained in good to excellent yield, under mild conditions and ambient temperature.

Keywords : β-acetamido carbonyl compounds, Multicomponent synthesis, Green Chemistry, Enolizable ketones.

GJRE Classification : FOR Code: 030306,030504

AN EXPEDIENT AND FACILE MULTICOMPONENT SYNTHESIS OF -ACETAMIDO KETONES BY USING VARIOUS GREEN SOLVENTS

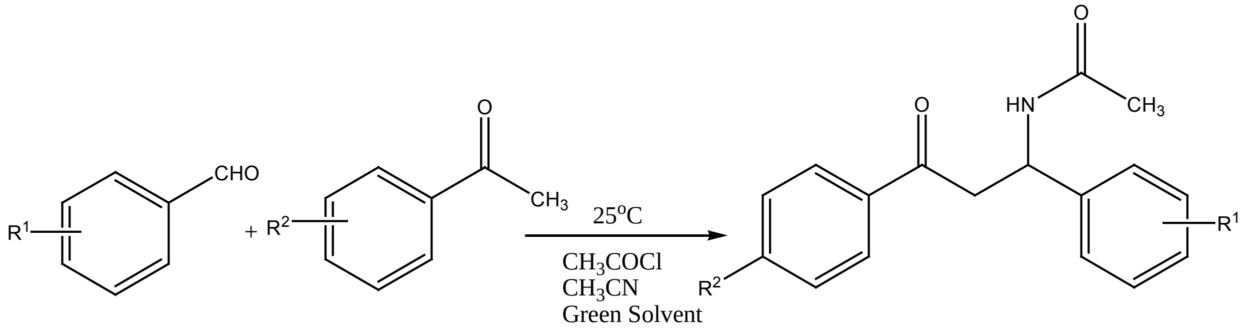
An Expedient and facile Multicomponent Synthesis of β-Acetamido Ketones by Using Various Green Solvents

S. S. Patil[α], Deepak. M. Nagrik[Ω], Rameshwar S. Dhamak[β], D.M.Ambhore , J.B.Devhade[¥]

Abstract - Multicomponent reactions (MCRs) are emerged as one of the most imperative synthesis route in organic synthesis due to their wide application range in pharmaceutical chemistry. A variety of **β**- acetamido ketones were readily prepared in good to excellent yield (50.-95%) via four component reaction of aromatic aldehydes, enolizable ketones and acetonitrile in presence of stoichiometric amount of acetyl chloride. Here water, methanol, ethanol, perchloroethylene, xylene, and 1,1,1 trichloroethane were used as green solvent.

The corresponding compounds were obtained in good to excellent yield, under mild conditions and ambient temperature.

Keywords : β-acetamido carbonyl compounds, Multicomponent synthesis, Green Chemistry, Enolizable ketones.



R^1=H,Cl,Me,OH,NO_2,OCH_3,$OCOCH_3$,
R^2=H,Me,Cl,4-NO_2,3-OMe,4-Cl,4-Br

I. INTRODUCTION

Multicomponent reactions (MCRs) provide useful products in a single step without isolation of any intermediates; they are preferred over the other reactions. The MCRs constitutes to single step procedures and non isolation of intermediate moiety which leads to the synthetic route representing saving of both energy and raw materials.[1] These reaction (MCRs) have emerged as one of the most useful tool for synthetic transformation in organic synthesis due to their wide application in pharmaceutical chemistry for production of structural scaffolds and combinatorial libraries for drug discovery. One of the important reason for up growing vitality of MCRs is their key role in organic chemistry in generation of high complex structure by simple one pot process.[2] MCRs owed to the requirements of an environmentally friendly process by reducing the number of synthetic steps, energy consumption and waste production. The transformation of this useful technology into a most efficient and economic tools for combinatorial and parallel synthesis is done by many researchers.[3,4] The multicomponent synthesis have attracted considerable interest due to its automated nature and exceptional synthetic efficiency from the point of view of synthesis of new chemicals along with the term green chemistry.[5] Actually when we move through the period of evolution then its seems that, this concept is not unknown for us.

Adenine is a major constituent in basic unit in all living things i.e. nucleic acids viz.DNA and RNA was formed prebiotically by condensation of molecules of HCN in prebiotic atmosphere, under the influence of catalytic nature of NH_3.[6] Since from this event, many MCRs have been developed over the years includes Strecker synthesis,[7] Biginelli reaction[8] and Mannich reaction.[9] These MCRs are valuable because they leads to conversion of simple starting molecules to complex

---

Author [α] [β] : Department of Chemical Technology SGB Amravati University, Amravati-444602, M.S., India.
E-mail : drsspatil199@yahoo.co.in, Tel: +91 9423424204
Author [Ω] : Department of Chemistry, PLIT and MS Buldana-443001, M.S., India. E-mail : dmnagrik@gmail.com, Tel : +91 9970837347 Fax: +91 0721 2662135
Author [¥] : P.G.Department of Chemistry, Jijamata Mahavidyalaya Buldana-443001, M.S., India

species in single step. This allow for quick approach to variant set of compounds.[10] More transformations being carried out in a single step results in less waste product (i.e. solvent) and purification time.[11] More economical protocol is resulted upon optimization of these factors.[12]

Many factors are responsible for successful journey of a multicomponent reactions; that mainly includes the appropriate starting material, temperature conditions, solvents, catalytic conditions etc.[13] Out of these, solvents plays important role throughout the chemical transformations of initial components.[14] Obviously the use of green solvents highlights the challenges on various occasion, particularly with the toxicity and environment persistence.[15] In response to these challenge, green solvents being designed for low toxicity and low biodegradability. However, any process solvent should be evaluated in terms of overall environmental impact of process.[16] It is quite eventual that if the use of a more hazardous solvents gave significant improvement to the total environmental impact of the overall process than a less hazardous alternative, then a greener choice is former.[17] The thermodynamic and kinetics of reaction carried out in green solvents are different from those in conventional molecular solvent, then the chemistry is different and unpredictable.[18] That means green solvents have many characteristic fascinating properties which make them attract fundamental interest to many chemist and thus forms the cause for their successful use in synthesis and preparation of material, catalyst, fuel cell and electrodeposition of metal.[19,20] Following points underlines the general characteristics of green solvents;[21-24] 1)Ability to dissolve a wide range of inorganic and organic compounds which is important for dissolving district combination of reagents into same phase. 2) Low or negligible vapour pressure and non-flammable. The non-flammable nature of solvents play vital role in exothermic reaction.3) Lower melting point, stability with respect to air and water. This relates with the scope of electrochemical reactions.4) High electrochemical stability and ion conductivity, it permit study of electrochemical processes that are previously beyond solvents limits and can be used instead of traditional solvent-based electrolytes.5) Thermal stability and wide liquid range .These properties of green solvents allows them to wider temperature range and tremendous kinetic control of chemical or electrochemical processes than that attained by traditional solvents. The separation techniques such as extraction, precipitation or crystallization are temperature dependent. Hence the said characteristic possesses importance in these regards too.

The use of green solvents for the synthesis of industrially important and biologically active molecules seems to be an important tool for elevating the status of synthetic organic chemistry. One of the most important chemical species in the list of novel hetero compounds is β-acetamido ketones. The novelty of this compounds reflects through their biological and pharmaceutical properties.[25,26] β-acetamido ketones serves as an important starting material in the preparation of antibiotic drug such as nikkomycin or neopolyoxines.[27,28] The ideal route for the synthesis of this class of compounds is Dakin-West reaction,[29] in which the condensation of α-amino acid with acetic anhydride in presence of base provides the α-acetamido ketones via an azalactone intermediate is explained.[30] From the review of literature it reveals that the synthetic evaluation of β-acetamido ketones under green condition, especially by using green solvents is still lacking.

Therefore, it was thought of interest for our research group to carry out an efficient multicomponent synthesis of β-acetamido ketones by using water, methanol, ethanol, perchloroethylene, xylene, toluene, and 1, 1, 1 trichloroethane as green solvents.

II. EXPERIMENTAL

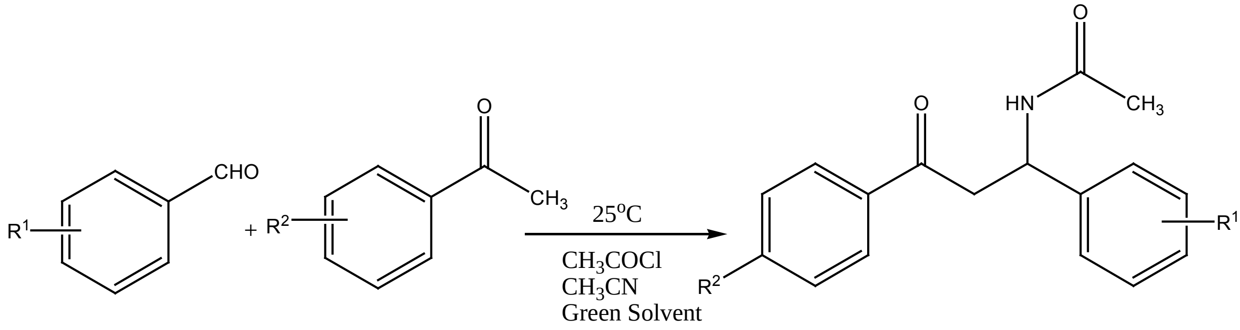
a) General

All commercially available chemicals and reagents were purchased from Aldrich and used without further purification. The melting points of all the synthesized compounds were recorded in precision digital melting point apparatus, Model MP-D and are uncorrected.

The IR spectra of the synthesized compounds were recorded on Nicolet Instruments Corporation, USA make MAGNA 550 spectrometer. The PMR spectra were recorded on Varian, USA make Mercury plus-300 MHz NMR spectrometer. The GC-MS analysis of synthesized compounds was performed on Hewlett Packard make GCD-1800A EI source analyzer at Sophisticated Analytical Instrument Facility (SAIF), IIT Bombay, Powai, Mumbai, India.

b) Typical Experimental Procedure For The Preparation of β-acetamido ketones

In typical synthesis of β-acetamido ketones, mixture of aromatic aldehyde (10 mmol), enolizable ketone (10 mmol), acetyl chloride (10 mmol) and acetonitrile (10 mmol) was well stirred (Scheme : 1) in presence of green solvents at 25° C for the appropriate time (as mentioned in Table-2). The progress of reaction was monitored by TLC. After completion of reaction, the reaction mixture was extracted with ethyl acetate. Purification of product was carried out on silica gel before evaporation of solvent.



R^1=H,Cl,Me,OH,NO_2,OCH_3,$OCOCH_3$,
R^2=H,Me,Cl,4-NO_2,3-OMe,4-Cl,4-Br

Scheme 1 : Synthesis of β-acetamido ketones

III. RESULTS AND DISCUSSION

In order to explore our interest for the application of Green Solvents in organic synthesis, we herein present a simple and efficient one-pot synthesis of β-acetamido ketones from enolizable ketones, aromatic aldehydes, acetonitrile and acetyl chloride in presence of green solvents viz. water, methanol, ethanol, perchloroethylene, xylene, and 1,1,1 trichloroethane at room temperature (Scheme: 1). The present protocol provide a variety of β- acetamido ketones which are obtained in good to excellent yields.(%)

In our initial endeavor, the reaction was studied with different green solvents and the best salvation activity of green solvents was optimized to room temperature and any excess of the solvent did not show further increase in terms of conversion and yield. According to this procedure, the reaction proceeded smoothly at room temperature to afford the corresponding β-acetamido ketones in good yields (Table: 2)

Table No.1 : List of β- acetamido ketone compounds synthesized by four component *reaction.

No.	Compounds	Name of compounds	M.P.(°C)
1	a	β-Acetamido-β-(phenyl) propiophenone	100-102
2	b	β-Acetamido-β-(4-methylphenyl) propiophenone	110-112
3	c	β-Acetamido-β-(3-nitrophenyl) propiophenone	114-116
4	d	β-Acetamido-β-(4-nitrophenyl) propiophenone	145-147
5	e	β-Acetamido-β-(4-chlorophenyl) propiophenone	142-144
6	f	β-Acetamido-β-(phenyl) - 4-chloropropiophenone	110-112
7	g	β-Acetamido-β-(4-chlorophenyl)-4-chloropropiophenone	138-140
8	h	β-Acetamido-β-(4-nitrophenyl)-4-chloropropiophenone	120-122
9	i	β-Acetamido-β-(phenyl)-4-methylpropiophenone	115-117
10	j	β-Acetamido-β-(Acetoxyphenyl) -propiophenone	117-119
11	k	β -Acetamido- β-(3-methoxy, 4-acetoxy-phenyl) propiophenone	90-92
12	l	β -Acetamido- β-(2-methoxy)-4-nitro propiophenone	145-146
13	m	β -Acetamido- β-(2-chloro)-3-methoxy propiophenone	102-104
14	n	β -Acetamido- β-(2-chloro)-4-chloro propiophenone	167-169
15	o	β -Acetamido- β-(3-chloro)-4-nitro propiophenone	171-172
16	p	β-Acetamido-β-(2-chloro)-4-bromo propiophenone	191-192

*Reaction conditions: aromatic aldehyde=10mmol, enolizable ketone=10mmol, acetyl chloride =10mmol and acetonitrile=10mmol, green solvent (5ml), temp. = 25°C, All compounds are well characterized by spectroscopic techniques such as IR, NMR, GC-MS.

Table No.2 : *Synthetic evaluation of β - acetamido ketones

Solvent → **Compound ↓**	water		Methanol		Ethanol		1,1,1 Trichloroethane		Perchloroethylene		Xylene	
	Yield (%)	Time (h)	Yield (%)	Time (h)	Yield (%)	Time (h)	Yield (%)	Time (h)	Yield (%)	Time (h)	Yield (%)	Time (h)
a	62	3	86	4	78	5	85	5.5	75	5	60	6
b	65	3.5	74	2.5	75	2.5	81	3	85	6	55	5.5
c	70	4	85	3	84	3.5	80	4	71	7	80	4
d	72	4.5	65	4	86	2.5	87	2.5	95	7.5	70	5
e	60	2.5	95	3.5	80	3	75	3	86	5.2	65	5
f	55	2.5	84	5	70	4	90	4	73	4.5	75	4
g	50	4	75	4	90	3	85	3.5	78	3	65	3
h	65	2.5	78	2.5	95	5	76	4	70	5	74	2.5
i	70	5	80	3	82	6	68	3	80	4	80	3
j	69	3	84	4.5	65	3.5	84	5	90	6	65	4
k	66	8	58	9	77	6	85	10	74	5.5	68	9.5
l	85	6	94	6.5	90	10	65	8	75	7	60	5
m	90	7	80	8	72	12	71	5	68	6.5	90	6.5
n	87	7.5	80	6	75	8	77	8	65	4	90	7
o	68	4	75	6	84	5	90	6	75	8	80	4.5
p	71	6.5	78	5	80	6	70	7.5	94	10	85	9

*Reaction conditions: aromatic aldehyde=10mmol, enolizable ketone=10mmol, acetyl chloride =10mmol and acetonitrile=10mmol, green solvent (5 ml), temp.=25oC,All compounds are well characterized by spectroscopic techniques such as IR,NMR,GC-MS.

The representative data of few compounds:

1) β-acetamido-β-(2-methoxy)-4-nitro propiophenone (Table-2, Entry l):

1HNMR($CDCl_3$, 300MHz): δ2 (s, 3H), 3.55 (dd, J =6.9 and 17.5 Hz, 1H), 3.6 (dd, J = 6.5 and 17.5 Hz, 1H), 3.9(s, 3H), 5.7 (dd, J = 6.9 and 16 Hz, 1H), 6.7 (d, J = 6.9 Hz,1H), 6.9 (m, 2H), 8.1 (m, 3H), 8.3 (m, 3H); IR (KBr, cm-1)3260, 1684, 1637, 1545, 1510, 1337, 1234, 837, 742; MS(m/z,%) 344 (M+2+, 1.87), 342 (M+, 10.65), 299 (100), 150(85), 107 (25), 77 (17.8), 43 (27.6, CH_3-CO^+).

2) β-acetamido-β-(2-chloro)-3-methoxy propiophenone (Table-2,Entry m):

1HNMR($CDCl_3$, 300MHz): δ 2 (s, 3H), 3.45 (dd, J =17 and 5.7 Hz, 1H), 3.77 (dd, J = 17 and 6 Hz, 1H), 3.84 (s,3H), 5.82 (dd, J = 15 and 6 Hz, 1H), 6.93 (dbr, J = 6.7 Hz,1H), 6.9-7.5 (m, 8H). IR (KBr, cm-1) 3265, 1681, 1643,1547, 1284, 1002, 747; MS (m/z, %) 332 (M+, 3.75), 296 (83), 135 (100), 107 (49), 77 (94), 43 (73, CH_3-CO^+).

IV. Conclusions

In conclusion, we have reported an efficient procedure for the synthesis of β-acetamido ketones using green solvents. The major advantage of this method is that the ease of work-up, i.e. the products can be isolated without column chromatography. This method also offers some other merits such as clean synthesis, high yields of products, shorter reaction times and use of various substrates, which make it useful and attractive strategy for the synthesis of β-acetamido ketones.

Acknowledgement

We are thankful to Head, SGB Amravati University, Amravati-444602, M.S., India and Sophisticated Analytical Instrument Facility(SAIF), Indian Institute of Technology, Bombay(M.S.), India, for availing the spectral data.

References References Referencias

1. Zhu, J.; Bienayme, H. Multicomponent Reactions, Wiley: Weinheim, 2005.
2. Timmons, C.; Kattuboina, A.; Banerjee, S.; Li, G. *Tetrahedron* 2006, *62*, 7151.
3. Dömling, A. Chem. Rev.2006, 106, 17–89.
4. Beck, B.; Hess, S.; Dömling, A. *Bioorg. Med. Chem. Lett.* 2000, *10*, 1701.
5. Fayol, A.; Zhu, J. *Org. Lett*. 2005, *7*, 239.
6. Leslie,E.O. *Crit. Rev. Biochemi.Mole.Bio*.2004,39, 99,123.
7. Strecker,A.*Liebigs ann.Chem*.1850,75,27.
8. Biginelli,P.*Ber.Dtsch. Chem.Ges*.1891,24,1317.
9. Mannich,C.; Kroschl,*Arch.Phar*.1912,250,647.
10. Armstrong, R. W.; Combs, A.P.; Tempest, P. A.; Brown, S. D.; Keating, T. A. *Acc. Chem*. 1996, 29, 123–131.
11. Ramon, D. J.; Yus, M. Angew. Chem., Int. Ed. 2005, 44,1602–1634.
12. Chapman, C. J.; Frost, C. G. Synthesis 2007, 1–21.
13. Puri,S.;Kaur,B.;Parmar,A.;Kumar,H. *ISRN Organic Chemistry* 2011 1,16,211-215.
14. Shahnaz,R.;Ali,M.A.;Gholam,H.M.;Hamid,S.;Samira, E. *Synthesis* 2010,8, 1356-1360.
15. Romero, A.; Santos, A.; Tojo, J.; Rodríguez, A. *J. Haz.Mat*. 2008,1,151, 268-273.
16. Martyn, J. E.;Kenneth, R. S. *Pure Appl. Chem*. 2000 ,72, 7, 1391–1398.
17. Welton, T. *Green Chem*. 2011, 13, 225-225.
18. Singh,G.;Kumar,A.*Ind.J.Chem*. 2008,47A,495-503.
19. Seda,K.; Defne,K.T.;Ugur,A.;Oner, H. *J.Sup.Fluids* 2007 43,150–180.
20. Roger, A.S. *Green Chem*. 2005, 7, 267-278.
21. William,M.N. *ACS Symposium Series*, 2000, 767, 313–328.
22. Nelson, W. M. *Green Solvents for Chemistry: Perspectives and Practice*, Oxford University Press: Oxford, 2003.
23. Maria, J.H.; Andres, R. A.; Jose, I. G.; Jose, V. S. *Chem.Eur.* J. 2010, 16, 31, 9422–9437.
24. Mieczyslaw, M. *Pure Appl. Chem*. 2000,72,7,1399–1403.
25. Casimir, J. R.; Turetta, C.; Ettouati, L.; Paris, *J. Tetrahedron Lett*. 1995, 36, 4797.
26. Godfrey, A.G.; Brooks, D. A.; Hay, L. A.; Peters, M.; McCarthy, J. R.; Mitchell, D. *J. Org.Chem*. 2003, *68*, 2623.
27. Dahn, U.; Hagenmaier, H.; Hohne, M.; Konig, W. A.; Wolf, G.; Zahner, H. *Arch. Microbiol*.1976, *107*, 249.
28. Kobinata, K.; Uramoto, M.; Nishii, M.; Kusakabe, H.; Nakamura, G.; Isono, K. *Agric. Biol.Chem*. 1980, *44*, 1709.
29. Dakin, H. D.; West, R. *J. Biol. Chem*. 1982, 78, 745.
30. Bhatia, B.; Reddy, M. M.; Iqbal, J. *J. Chem. Soc. Chem. Commun*. 1994, 713.

This page is intentionally left blank

GLOBAL JOURNAL OF SCIENCE FRONTIER RESEARCH
CHEMISTRY
Volume 12 Issue 1 Version 1.0 January 2012
Type : Double Blind Peer Reviewed International Research Journal
Publisher: Global Journals Inc. (USA)
Online ISSN: 2249-4626 & Print ISSN: 0975-5896

Application Of A New Ph-Metric Method To The Kinetic Study Of Copolymerization Of Polysaccharides Fucan N1 With PMMA In Presence Of Cerium Ce^{+4}

By El-Bahri Sakri
University of ANNABA, Algeria

Abstract - The copolymerization of a Poly-Acrylic PMMA with polysaccharide, Fucan N1 and Dextran T70,in presence of a ceric salt used as initiator in acidic medium ,was carried out under the following conditions : Fucan N1=0,5 g ; $[CAN] = 3{,}6.10^{-3}M$, $[HNO_3] = 0{,}2M$; temperature =40°C with a relative ratio between the initiator and the monomer , initiator/monomer =1/10. Besides a pH study of the reaction medium , an infrared spectroscopy (IR) proved the appropriatness of these best conditions of synthesis , and this by showing the presence of a characteristic peak of the carbonyl grouping situated at $1733 cm^{-1}$ for the copolymer Fucan PMMA in respect to the individual PMMA spectra and Fucan N1. In addition , a ^{13}C NMR study has been conducted on the copolymer. A viscosimetry study of two Fucan fractions was performed in aqueous medium (H_20), and also of the obtained copolymer in DMSO. An outcome of this work allows for us the suggestion of a plausible reaction mechanism , of which the copolymerization rate -Rp- is first order dependant to the monomer concentration, and to the square –concentration of both the initiator and the polysaccharide .

Keywords : poly-acrylic, copolymerization, polysaccha-ride with ceric initiator .

GJRE Classification : FOR Code: 030305

Application Of A New Ph-Metric Method To The Kinetic Study Of Copolymerization Of Polysaccharides Fucan N1 With PMMA In Presence Of Cerium Ce^{+4}

El-Bahri Sakri

Abstract - The copolymerization of a Poly-Acrylic PMMA with polysaccharide, Fucan N1 and Dextran T70,in presence of a ceric salt used as initiator in acidic medium ,was carried out under the following conditions : Fucan **N1=0,5 g;** $[CAN] = 3{,}6.10^{-3} M$, $[HNO_3] = 0{,}2M$; temperature =40°C with a relative ratio between the initiator and the monomer , initiator/monomer =1/10. Besides a pH study of the reaction medium , an infrared spectroscopy (IR) proved the appropriatness of these best conditions of synthesis , and this by showing the presence of a characteristic peak of the carbonyl grouping situated at 1733cm^{-1} for the copolymer Fucan PMMA in respect to the individual PMMA spectra and Fucan N1. In addition , a ^{13}C NMR study has been conducted on the copolymer. A viscosimetry study of two Fucan fractions was performed in aqueous medium (H_20), and also of the obtained copolymer in DMSO. An outcome of this work allows for us the suggestion of a plausible reaction mechanism , of which the copolymerization rate -Rp- is first order dependant to the monomer concentration, and to the square – concentration of both the initiator and the polysaccharide .

Keywords : poly-acrylic, copolymerization, polysaccharide with ceric initiator.

I. INTRODUCTION

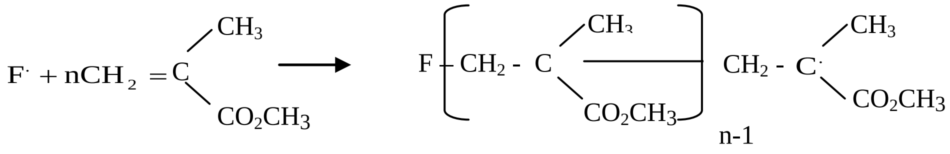
The essential aim of this work is to apply the pH-metric measuring method to the study of the PMMA copolymerization with polysaccharides Fucan N1 and Dextran T70 (Fucan N1 is a sulfated polysaccharide extracted from a brown seaweed of the Ascopohyllum nodosum kind) , in presence of ceric ions ce^{4+} in nitric acidic medium pH=1 , at a temperature 4OC° during 40mn , under argon atmosphere[1-5] (Chowdhury and Pal, 1999; Dalton *et al.* , 2002; Masci *et al.*, 2004; Fuoss and Cathers, 1949; Costa and Vasconcelos, 2002) , with a relative ratio between the initiator and the monomer $\frac{initiator}{monomer} = \frac{1}{10}$.

The reaction is conducted in suspension ,and initiated by the ions ce^{4+} (Hexanetratace rate of ammonium $(NH_4)_2\ [Ce(NO_3)_6]$ "Acros" leading first to the formation of a white- milky complex that disappears immediately , giving a radical (F) of Fucan to a proton (H^+) and an ion Ce^{3+} ,as it is shown in the following reaction equation :

Initiation :

$$F - H + Ce^{4+} \rightarrow [complex] \rightarrow F^{\cdot} + Ce^{3+} + H^{+}$$

Propagation :



The kinetic study of this copolymerization , of which the polymerization rate measure is performed by pH metric measuring method -that we had put in evidence - and with comparison to the method of extraction by soxhelt with acetone.

II. EXPERIMENTAL WORK

a) *Products*

Dextran of different molecular weights (MW= 10, 40, 70, 80.7, and 264 kg/mol) were purchased from

---

Author : Department of chemistry, Faculty of Sciences, University of ANNABA, ALGERIA. E-mail : sakribahri@yahoo.fr

Sigma for molecular weight assessment. Dextran (70 kg/mol) was also used for synthesis. It was dried in a vacuum oven at 60°C for 24h. Methyl methacrylate monomers were obtained from Acros France and were purified by washing with 5% NaOH and 20% NaCl, followed by distilled water. Ammonium cerium (IV) nitrate (Acros France) was dried at 80°C under vacuum for 24h. Solvents were of the highest commercially available purity.

Fucan N1 and Fucan BBP-2 , having a mass of 95500g/mol and 46600g /mol respectively, are two fractions of Fucan obtained by HPLC chromatography on a S 5300 HR gel after an acidic extraction followed by an acidic hydrolysis[6], (see Figure 1).

The Dextran is , like the Fucan, soluble in water , whereas its copolymer with PMMA is soluble in the water /THF (20/ 80 v/v) mixture and in the dimethylsulfoxide (DMSO).

The polymerization of the methyl methacrylate « MMA »with Fucan N1 and Dextran T-70 depends closely on the concentration of the initiator [7-8] of the monomer (MMA) and the concentration of the used polysaccharide.

This polymerization is performed by cycle – opening forming active radicals F or D that are likely to be bound by covalent links to the methyl poly-methacrylate (PMMA) forming Fucan copolymer(PMMA) and Dextran (PMMA).

This copolymerization is conducted in a highly acidic medium to avoid a possible formation of the ceric hydroxide ,which can take place at a medium in which pH=4 to 5 . In such a medium , the IR spectrum shows no anomaly .

The kinetic polymerization is performed by applying the PH- Metric measuring method ,as an experimental technique , we know that the variation of the PH in the medium is linked to the initiator concentration at instant "t", with the equation :

$$[M]_t = [M]_0 \left(1 - \frac{\Delta C_t^H}{\Delta C_\infty^H} \right) \qquad (1)$$

Where: ΔC_t^H , et ΔC_∞^H - variation of the hydrogen concentration during the synthesis .

$$\Delta C_t^H = 10^{-pH_t} - 10^{-pH_0}$$

$$\Delta C_\infty^H = 10^{-pH_\infty} - 10^{-pH_0}$$

So we can write the equation (1) as follows :

$$[M]_t = [M]_0 \left(1 - \frac{10^{-pH_t} - 10^{-pH_0}}{10^{-pH_\infty} - 10^{-pH_0}} \right). \qquad (2)$$

With pH_0 ; pH_t and pH_∞ are respectively the variation of the pH at the instant "t=0" , at time t (we take t=30mn) and the instant when the whole monomer will be converted into copolymer ($pH_\infty = pH_{cons\tan t}$).

The equation (2) permits to determine directly the polymerization rate –Vp- ; monitoring the variation of the monomer concentration in function of pH, and time . We have also determined the polymerization rate by applying the extraction by soxhlet with the acetone method . We determined the percentage (P_g %) of the PMMA grafting , the grafting rate (Vg) of the copolymerization , polymerization , the homo – polymerization (V_h), and the total rate (V_P) of the polymerization that are calculated from the weight of the grafted poly-acrylic of the obtained products [10].

$$P_g \% = \frac{grafted\ \ weight\ \ of\ \ PMMA \times 100}{weight\ \ of\ \ polysaccharide} \qquad (3)$$

$$V_g = \frac{grafted\ \ weight\ \ of\ \ PMMA \times 1000}{M\overline{w}\ de\ \ MMA \times reaction\ time(s) \times volume\ (ml)\ of\ \ reaction} \qquad (4)$$

$$V_h = \frac{weight\ of\ \ homo-\ PMMA \times 1000}{M\overline{w}\ de\ \ MMA \times reaction\ time(s) \times volume\ (ml)\ of\ reaction} \qquad (5)$$

The total rate of the polymerization is :

$$V_p = V_g + V_h \qquad (6)$$

We have determined the polymerization rate-V_P- by applying two methods independent the one from the other (equations 2 and 6) (table III) , for a comparison purpose .

b) Synthesis and Reaction of the copolymerization

In a (250 ml) reactor equipped with three flasks , we take a polysaccharide mass of 0,5 to 1g (Fucan N1 or Dextran)dissolved in HNO_3 at 0,2M. after 10minutes of agitation under an atmosphere of Argon (or N_2) at a temperature of 40 ± 1°C , we add at the same time 3,6.10^{-3} M/L of cerium and 0,5M of MMA (of which the relative ratio $\frac{initiator}{Monomer} = \frac{1}{10}$), The time variation of the pH is measured at a sampling interval of 5mn . The reaction is considered finished when the pH does not change any more , and this is the case after 30 minutes of reaction ($pH_\infty = pH_{const}$).

The obtained product is poured into 500ml of methanol with the PH adjusted to a volume of 8, and NaOH at 10M. After that we concentrate the solution to a volume of 20/30ml approximately. We decant the solution into a spectra-membrane of a diameter of $\phi = 20{,}4mm$ to be cleaned /washed in EDTA solution at 0,05 M during 72hours , under permanent agitation . Then, the solution is put under lyophilization , and later on in a vacuum dryer till a constant weight .

First of all, we have monitored pH evolution in time of the reaction medium of the copolymerization.This pH variation is generally not higher than the unity ,as it is shown on Figure (2) bellow.

c) *Extraction of Homo-polymer of PMMA*

We weight exactly 2,00gr of each raw product-mentioned above – that was extracted with the acetone by soxhlet during 24 h, to eliminate the homo-polymer-poly (Methyl Methacrylate). The pure copolymer is dried at 50°C till a constant weight.

III. CHARACTERIZATION

a) *Preparation OF Three- Dimensional Structures*

We prepared discs or films by using dried homopolymer PMMA (15 mg) solubilized in THF. Copolymer DM was dissolved in 1 ml of THF/H_2O (80/20) that was treated in an ultrasonic bath for 1 h . Dextran gave any 3D structures. To obtain discs, solutions were poured in Petri dishes for 24 h at room temperature in a satured atmosphere of THF and in the presence of $CaCl_2$ to absorb water. Thin films were stripped from the mold and were dried in an oven at 30°C. A morphological analysis of the cross section of films was carried out by the of a Leica S-440scanning electron microscope(SEM) . All 3D structures were extensively washed with before any biological assays.

b) *NMR Analysis*

^{13}C NMR spectra of dextran, PMMA and copolymer DM were recorded by the use of a Varian Gemini 200 Mhz spectrometer in deutered dimethyl sulfoxide-d_6 at ambient temperature. Tetramethylsilane (TMS) was used as an internal standard. Before use, all products were lyophilized twice with deuterium oxide (D_2O).

c) *Copolymers Analysis by Infrared Spectroscopy*

This technique allows us to identify some chemical groupings that may be present in the polymers and the copolymers . Tablets of 150mg of potassium bromide (KBr) , with infrared quality(Fluka) . The sample is mixed in the KBr, ground and then vacuum dried at 45°C during 6hours , pressed under 10 tons for 2minutes , and then stored at a 45°C in a humidity- free environment . These tablets are analyzed by means of a Fourier transform based infrared spectrophotometer (Perklin Elmer ,1600) .Every spectrum is taken to be an average of the cumulus of 16 increments, in order to decrease the effect of background noise. Figure 3 shows the spectra of MMA, and Dextran taken individually , in addition to that of the synthesized Dextran-PMMA copolymer .Curve (A) presents many strips characteristic of the PMMA : one at about 2953cm^{-1} which is assigned to the (CH_2) group, another strip is situated at 1732cm^{-1} which represents the carbonyl ($\rangle c = 0$) group and a third band is located at 1380cm^{-1} assigned to the(CH_3) Methyl group .Curve (B) presents strips that are specific for Dextran T70 : the presence of the radical (OH)is attested by the absorption band that appears at about 3400 cm^{-1} , the strip at 2930cm^{-1} is assigned to the methylene group (CH_2), the strip arround1650corresponds to the grouping (OH) of the Dextran T70.Curve (C) illustrates the spectrum of the product obtained by copolymerization of the Dextran and the MMA monomer by Cerium (Ce^{4+}). This spectrum presents strips that are common to both the Dextran and PMMA . We can notice an important intensity at 1733Cm^{-1} that corresponds to the carbonyl grouping ($\rangle c = 0$) .Figure 4 shows that the individual Fucan N1 spectrum in curve (A) is identical to curve (B)with a concentration o f cerium $\left[Ce^{4+}\right] = 1{,}8.10^{-5}\,M/L$. Yet, when we increase the concentration of this latter 200 times, i.e. at $\left[Ce^{4+}\right] = 3{,}6.10^{-3}\,M/L$,by keeping the same concentration of monomer and polysaccharide ,we notice the formation of a copolymer Fucan PMMA characterized by a peak located at 1725cm^{-1} for PMMA with respect to the spectrum of Fucan N1alone , as shown on curve (C) .

d) *Viscosity Measurements*

In order to determine the molar mass of the different obtained products , we have measured the viscosity of Fucan N1 , BBP-2 solutions as well as the viscosity of copolymer solutions for different cerium (Ce^{4+}) concentrations. In this technique, we use a well adapted viscometer (the Ubbelohde Viscometer) with a capillary diameter of 0,7mm, was used for two different polysaccharides ; Fucan N1 and Fucan BBP-2 having a mass 95500 g/mol and 46600g/mol respectively We determine $\left(\frac{ln\eta_2}{C}\right) = \left[\frac{ln(t/t_0)}{C}\right]$ and the specific viscosity $\frac{\eta_{sp}}{C} = (t - t_0)/t_0 C$ for a set of an increasing concentration in the percentage of Fucan N1 and BBP-2 dissolved in water , as follows (0% , 0, 45 %, 0,65%, 0, 75% , 1,0% , 1,25% , 1,45% , 1,65%, and 2 %).

On the same graph ($\frac{ln\,\eta_r}{C}$), we have simultaneously plotted the specific viscosity ($\frac{\eta_{sp}}{C}$) in function of polysaccharide concentration. The intrinsic viscosity $[\eta]$ is obtained by extrapolation and intersections of these two curves at a zero-point concentration .On the other hand , this intrinsic viscosity is related to the molar mass through the formula of Mark Houwkin: $[\eta] = K.M^a$, where a and K are constants .

As for the two fractions of Fucan N1 and BBP-2 with known mass, the values of the constants were deduced from measures of the intrinsic viscosity $[\eta]$ at a zero-point concentration . For example, as concerns the first fraction $[\eta_1] = 0{,}252$ and $[\eta_2] = 0{,}086$, we find Fucan values as follows :

$$\begin{vmatrix} a = 1{,}49 \\ K = 8{,}8.10^{-9}\,dl/g \end{vmatrix}$$

And for the Dextran T70 (with a mass=73 000g/mol), in water and in DMSO, we have found the following values:

$$\left| \begin{array}{l} a = 0{,}50 \\ K = 98{,}8.10^{-5}\, dl / g \end{array} \right.$$

The difference in values of ‘a’ for the Dextran T70 and Fucan , is present only in aqueous solutions , the Dextran is manifested therefore , more flexible than the Fucan.

e) Viscosity and mass measurements of the obtained copolymers

The measurement of the molar mass by applying the viscometric method is performed through measuring the intrinsic viscosity by extrapolation of the two curves at $[\ln\eta_2]/C$ and $\frac{\eta_{sp}}{C}$ at a zero –point concentration. This is why we have synthesized tow Fucan PMMA copolymers ; one with no monomer ; the other with the presence of 0,4% of monomer MMA, keeping the same concentration values in the initiator and the polysaccharide (0,5 of Fucan) , soluble in the mixture water/ THF (20/80 v/v) at T° = 40°C.

We found the intrinsic viscosity equal to 0,16 dl/g for the first copolymer , but equal to 0,244 dl/g , for the second copolymer .The viscometric mass Mv corresponding to the viscosity could be formulated through the following equation:

$$\ln[\eta] = \ln\left[8{,}8.10^{-9}\right] + 1{,}49 \ln \bar{M} \qquad (7)$$

Where $[\eta] = 0{,}244; \quad \bar{M} = 98900\, g/mol$

$[\eta] = 0{,}16; \quad \bar{M} = 64800\, g/mol$

We notice that the increase of the viscosimetric mass is due to the increase of PMMA formed in shapes of grafted connections on the polysaccharide , on the one hand , and this prove the effective formation of a copolymer between the Fucan and PMMA for Dextran T70 , on the other hand. We can use the following formula:

$$\ln[\eta] = \ln\left[98{,}8.10^{-5}\right] + 0{,}50 \ln \bar{M} \qquad (8)$$

By the same manner , knowing $[\eta]$ we can deduce the molar mass $\bar{M}$.

f) Determination of the obtained copolymers by HPLC in function of initiator concentration [CAN] ½

$\bar{M}_v$ determination of the obtained copolymers by HPLC chromatography on a S 5300 HR gel , shows that those ones decrease as the initiator concentration increases ,i.e. :

For $[CAN]^{1/2} = 3.10^{-2}\, M/L$ we have $\bar{M} = 1{,}28.10^5\, g/mol$ And for $[CAN]^{1/2} = 6.10^{-2}\, M/L$ $\bar{M} = 0{,}59.10^5\, g/mol$ We can interpret these results on Figure 5.

As for the case of Dextran , the Fucan mass decreases because of an acid hydrolysis of the macromolecular chains during the different stages of synthesis . we can notice clearly that this mass variation could be interpreted in the following formula:

$$\bar{M} = \frac{3{,}74.10^3}{\left[Ce^{+4}\right]^{1/2}} \qquad (9)$$

$[CAN]^{1/2}.10^2\, mol/l$: 0,9 ; 3 ; 3,46 ; 4,59 ; 6, 00

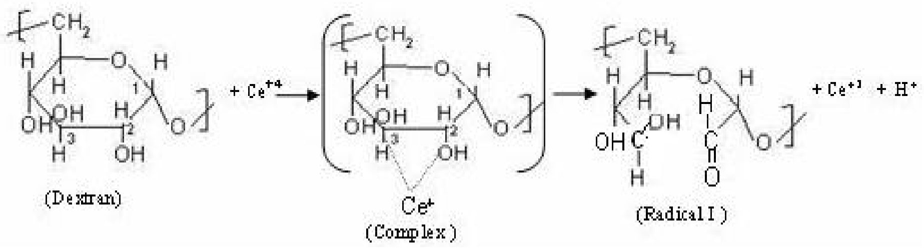
$\bar{M} : g/mol$: 4,0.10^5 ; 1,28 .10^5 ; 1,047.10^5 ; 0,87.10^5 ; 0,59.10^5

IV. Results and Discussion

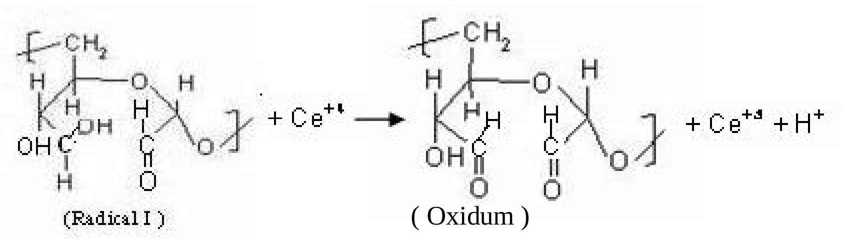
This research consists of applying the pH-metric measuring method in the kinetic study the MMA polymerization of the methacrylate methyl, with the polysaccharides Fucan N1 and Dextran T70 , in presence of ceric ions (Ce^{4+}) in the best conditions .We must take the quantity of the initiator and the monomer in a reactor we have found equal to 1/10.

The infrared analysis (IR)of the copolymers obtained after radical synthesis , shows that the polymerization depends on the nature of each polysaccharide , and on the concentration of the cerium (Ce^{4+}), and the monomer used ; the reaction of the polysaccharide / poly acrylic synthesis is performed through several stages , as depicted on the following graph [9]:

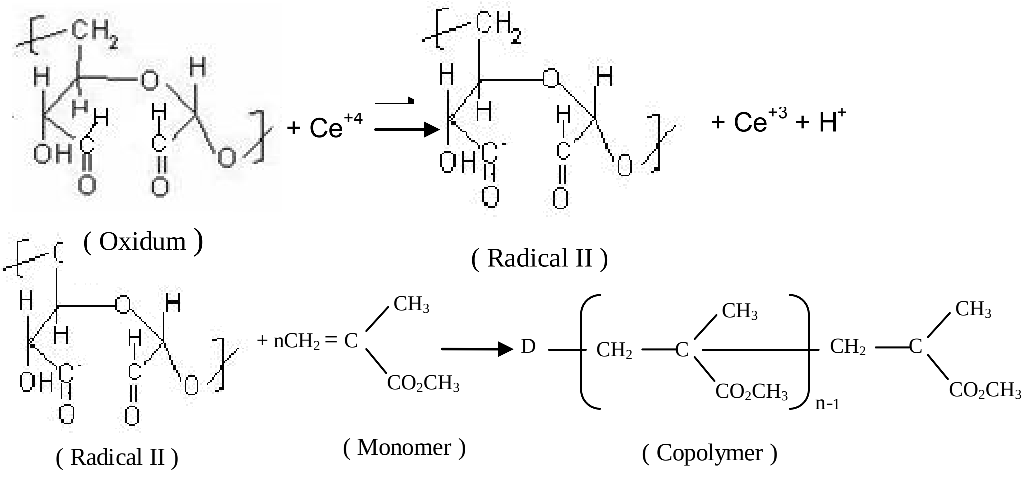
Stage 1 : Formation of radical I



Stage 2 : Formation of the Oxidum



Stage 3 : Formation of radical II



The radical II is chained to the monomer and engendering copolymers. The first stage consists of forming a complex between the polysaccharide and the cerium $\left(Ce^{4+}\right)$.This complication is performed between the cerium $\left(Ce^{4+}\right)$and hydroxide groups in position 2and 3 of the Polysaccharide. After a laps of time, it is decomposed giving a Radical I , ion Ce^{3+} and a proton H^{+} . The second stage, however, consists of forming an oxydium from a radical I with the cerium, making the appearance of aldhydic groups in position 2 and 3 of the polysaccharide , an ion Ce^{4+} and a proton H^{+}. As concerns the third stage , it consists of forming a radical II , which is Dextran radical (D or F) responsible for the propagation with the monomer $\left(D^{\cdot}+M_{n}\rightarrow DM_{n}^{\cdot}\right)$ this radical $\left(D^{\cdot}\right)$ is generated by the reaction between Oxidium and Cerium (Ce^{4+}).

The termination is achieved by classical termination .

$$DM^{\cdot}+DM^{\cdot}\rightarrow Copolymer$$

Or : $FM^{\cdot}+FM^{\cdot}\rightarrow Copolymer$

The analysis of ^{13}C NMR spectrum (Fig. 6.) suggests a chemical structure of Dextran-PMMA polymer as indicated in [12].

Under the light of the obtained results and the discussion we have led , we may establish that our polymerization follows a reactional mechanism a little complex ; the stages of which are governed by the following reaction equation :

Initiation:

$$F-H+Ce^{4+}\xleftrightarrow{K}[Complex]\xrightarrow{k_0}F^{\cdot}+Ce^{3+}+H^{\cdot} \quad (10)$$

$$F^{\cdot}+M\xrightarrow{k_0}FM \quad (11)$$

$$M+Ce^{4+}\xrightarrow{k_1}M^{\cdot}+Ce^{+3}+H^{+} \quad (12)$$

$$F^{\cdot}+Ce^{4+}\xrightarrow{k_2}F-OX+Ce^{3+}+H^{+} \quad (13)$$

$$F-OX+Ce^{4+}\xrightarrow{k_3}F^{\cdot}+Ce^{3+}+H^{+} \quad (14)$$

Propagation :

$$FM^{\cdot} + M_n \xrightarrow{k_p} FM_{n+1} \qquad (15)$$

$$M^{\cdot} + M_n \xrightarrow{k_p} M^{\cdot}_{n+1} \qquad (16)$$

Termination :

$$FM^{\cdot}_n + FM^{\cdot}_m \xrightarrow{k_t} FM_{n+m}F \qquad (17)$$

$$FM^{\cdot} + M^{\cdot} \xrightarrow{k_{t_1}} FM_{n+1} \qquad (18)$$

$$M^{\cdot}_n + M^{\cdot}_m \xrightarrow{k_{t_2}} M_{n+m} \qquad (19)$$

To put in evidence this polymerization mechanism ,we should suppose that the states between the following different initiating species ,are quasi-stationary . That is to say:

$$\frac{d[F^{\cdot}]}{dt} = K\,k_0[F][Ce^{4+}] + k_3[Ce][F-OX] - k_a[F^{\cdot}][M] - k_2[F^{\cdot}][Ce] = 0 \qquad (20)$$

$$\frac{d[FM^{\cdot}]}{dt} = k_a[F^{\cdot}][M] - k_k[FM^{\cdot}]^2 - k_{t_1}[FM^{\cdot}][M^{\cdot}] = 0 \qquad (21)$$

$$\frac{d[M^{\cdot}]}{dt} = k_1[Ce][M] - k_{t_1}[FM^{\cdot}][M^{\cdot}] - k_{t_2}[M^{\cdot}]^2 = 0 \qquad (22)$$

$$\frac{d[F-OX]}{dt} = k_2[F^{\cdot}][Ce^{4+}] - k_3[Ce^{4+}][F-OX] = 0 \qquad (23)$$

By summing together the equations (20to23) and ignoring the equation (22) which is less likely to take place; because we did not notice any considerable attack by the cerium (Ce^{4+}) on the monomer . By assuming that the termination constants are equal to the global $k_t\left(k_t = k_{t_1} = k_{t_2}\right)$ [9], we obtain that:

$$Kk_0[F][Ce^{4+}] - k_t[FM^{\cdot}]^2 - 2k_t[FM^{\cdot}][M] - k_t[M^{\cdot}]^2 = 0$$

$$Kk_0[F][Ce^{4+}] = k_t\left([FM^{\cdot}] + [M^{\cdot}]\right)^2$$

We deduce :

$$[FM^{\cdot}] + [M^{\cdot}] = \left(Kk_0[F][Ce^{4+}]/k_t\right)^{1/2} \qquad (25)$$

The polymerization rate Rp of the Fucan N1 or Dextran in presence of a ceric initiator , is expressed in this formula :

$$R_p = k_p[FM^{\cdot}][M] + k_p[M\ ][M] = k_p\left([FM^{\cdot}] + [M^{\cdot}]\right)[M] \qquad (26)$$

By substituting the expression of eq.(25) into eq.(26) , we obtain :

$$R_P = k_P\left(\frac{Kk_0}{k_t}\right)^{1/2} .[F]^{1/2}[Ce^{4+}]^{1/2}[M] \qquad (27)$$

The expression of the polymerization rate Rp of the Fucan N1 and Dextran T70 with the MMA in presence of a ceric salt used as initiator , in acidic medium a simple ratio between Rp and the order equal to the concentration unity of the monomer MMA , and to the square –root of both the polysaccharide and initiator (Figures 7 to 10).

And also, the speed of polymerization is :

$$R_h = R_p/2 + K[Ce^{+4}]_{max} \qquad (28)$$

The grafting speed is expressed as:

$$R_g = R_p/2 - K[Ce^{+4}]_{max} \qquad (29)$$

Consequently, the rate of grafting is given by :

$$PG\% = (A R^2_P + B R_P + C) . 100 \qquad (30)$$

Where A, B ,C and K are constants which can be determined ultimately.

We also know that the speed of polymerization 'R_p' is proportional to the square-root of initiator concentration $R_P = K'[Ce^{+}4]^{1/2}$, and the same relationship is found for the quantities R_h , R_g and PG.

The method applied in measuring the polymerization rate (Rp) is the PH-metric measuring method, compared to the extraction by soxhlet with the acetone (method of " Le Poutre and Hui [10] (see Table III).

V. RELIABILITY CONTROL OF THE PH-METRIC METHOD

In order to control the reliability of the PH-metric method, we compared it to a more exact and precise method ; which is the "extraction by soxhlet with the acetone method. By comparing these two methods, we can see that same values of PG, V_g , V_h and the universal constants A ,B ,C and K are exactly found by both methods. The variation of PG reaches the same maximum for a maximal speed of R_p =3,39 .10^{-5} mol.l^{-1}.s^{-1} and a initiator concentration [CAN] =1,197. 10^{-3} M for both methods . The obtained results are given in the following table (see Table III). We notice that the pH-metric method is in good concordance with the extraction by soxhlet with the acetone method, at strong concentration values of the initiator.

$R_p^{(a)}$, $R^{(a)}_h$, $R^{(a)}_g$ and $PG^{(a)}$ polymerization rate determined by the pH-metric method , that we have worked out . As Figures (7 -10) show , the quantity kp $(kk_0/k_t)^{1/2}$ is equal to =5,32 ; 10,22 and to 13,71 for soluble starch (Mansor and Haron , 2000) ; as concerns Dextran T70 and Fucan N1 respectively . This quality varies increasingly with a rate of nearly 2.5 when going from the soluble starch to the Fucan and this in proportion with the mass of each polysaccharide used , namely :

M_n = $(164{,}4)_n$g / mol For the soluble starch; 73000g/ mol for the Dextran T70 ,and finally 95500g/ mol for the Fucan N1 .

VI. CONCLUSION

We can summarize the obtained results in the following points :

Polymerization between polysaccharides and poly-acrylics is generally achieved through opening the polysaccharide cycle. This kinetic polymerization is considered to be a complex one . The pH-metric method used to determine Rp is found to be very precise and with great concordance with the extraction by the acetone method . The infrared spectroscopy shows that the copolymer can't be formed if the initiator concentration is less than $[CAN]=1{,}8.10^{-5}M/l$,but when this latter is increased to 200 times ,we notice the formation a copolymer characterized by a peak situated at 1725cm^{-1} for PMMA on the polysaccharide spectrum alone , with an $[MAM]=0{,}4\%$. The viscometry shows the effective formation of a copolymer between the polysaccharide and the PMMA, due to the intrinsic viscosity increase of 0,16 dl/g to 0,244dl/g in absence and presence of 0,4 % of monomer . The polymerization rate Rp of polysaccharide / poly-acrylic depends on a kinetic complex , first order ,equal to the concentration of the monomer and , and to the square-root of the initiator and polysaccharide.

The grafting rate of PMMA (PG%) on the polysaccharide increases with the increase of (CAN) concentration , it reaches a maximum concentration equal to : [CAN] =1,197 . 10^{-3} Mol/l, and realizes 196,.60% (this maximum value is found to be equal to 260% at 0.5.10^{-3} M/l ceric ion).

Regarding difficulties that may face researchers for determining the speed of polymerization R_P, we propose to use the pH-metric method because it is simple and precise, and also does not require sophisticated means. In addition, it opens doors for great perspectives in this domain of research.

REFERENCES RÉFÉRENCES REFERENCIAS

1. Chowdhury P, Pal CM. (1999), European Polymer Journal, 35: 2207-2213.
2. Dalton Paul. D, Flynn L, Shoichet M. (2002), Biomaterials, 23: 3843-3851.
3. Masci G, Bentempo D, Tiso N, Diociaiuti M, Mannina L, Capitani D, Crescenzi V. (2004), Macromolecules, 37 : 4461-4473.
4. O.R Costa R, Vasconcelos W. L. (2002), Journal of Non-Crystalline Solids; 304 : 84-91.
5. Fuoss,RM, Cathers,G.I . Journal. Polym. Sci. (1949); 4: 97.
6. Hoppe HA. (1979), Marine algae and their products and constituents in pharmacy: in Hoppe HA ,Levring T, Tanak Y, editors. Berlin: Walter de Gruyter ,. p. 25 –119.
7. Colliec- Jouault S. Boisson- Vidal C. , Jozefonvitz J. (1993), Low molecular weight fucoidane fraction from Pelvetia canaliculata . Phytochemistry (under press),.
8. Mulloy, B,Mourao PAS. , Gray E. (2002), Structure/ function and studies of anticoagulant sulphated polysaccharides using NMR. Journal of Biotechnology,; 77: 123-135.
9. Lepoutre P, Hui SH. (1975), Jnl appl. Polym. Sci.; 19: 1257
10. Mansor A, Haron MDJ. (2000), Kinetics and Mechanism of Free Radical Grafting of Methyl Acrylate onto Sago Starch. Journal of Applied Science ; 77:784-791.
11. Okiemen EF, Eghrevba FE. (1992), Graft Copolymerization of Methyl Acrylate on Dextrin, European Polymer Journal; 28 (4): 415-417.
12. Chauvièrre C, Labarre D, Couvreur P, Vauthier C. (2003), Radical Emulsion Polymerization of Alkylcyanoacrylates Initiated by the Redox System Dextran-Cerium(IV) under Acidic Aqueous Conditions. Macromolecules; 36: 6018-6027.

$$\text{seaweed (Thalles)} \xrightarrow{(1)} \text{Parietal material} \xrightarrow{(2)} \text{Raw acidic extract} \xrightarrow{(3)} \text{Fucans.}$$

1- Preprocess , Extraction.

2- Hydrolysis .

3- Deterioration , fractioning.

Figure 1 : Simplified flow- chart of Fucans

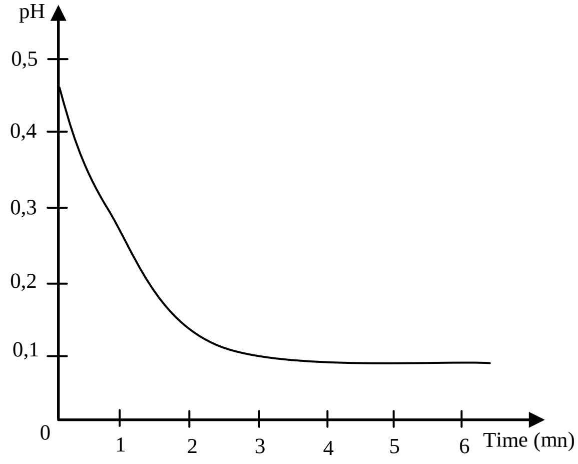


Figure 2 : pH evolution during synthesis reaction of the copolymer Fucan PMMA; Temperature :40°C ; solvation HNO_3 at 0,2 M.

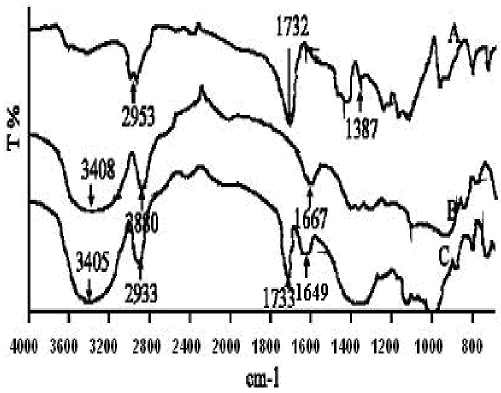


Figure 3 : Infrared spectrum of copolymer Dextran –PMMA ; Curve (A) PMMA alone; Curve (B) Dextran alone ; Curve(C) copolymer of Dextran ; 0,5g ; MMA 2% ; Cerium $3{,}6.10^{-3}$ M.

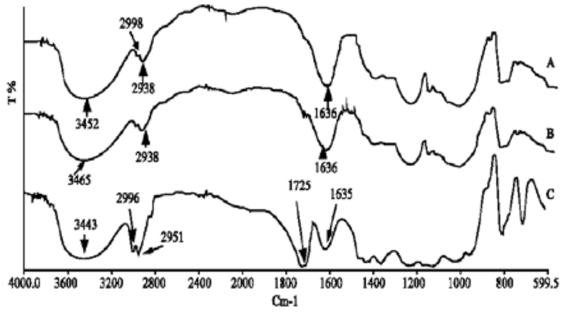


Figure 4 : Infrared spectrum of copolymer Fucane –PMMA ; Curve (A) Fucane alone; Curve (B) 0,5 g of Fucane, 0,2% of MAM ,Ce^{+4} 1,80.10^{-5} g/mol; Curve(C) 0,5g of Fucane, 0,2% of MMA, Ce^{+4} 3,6.10^{-3} g /mol

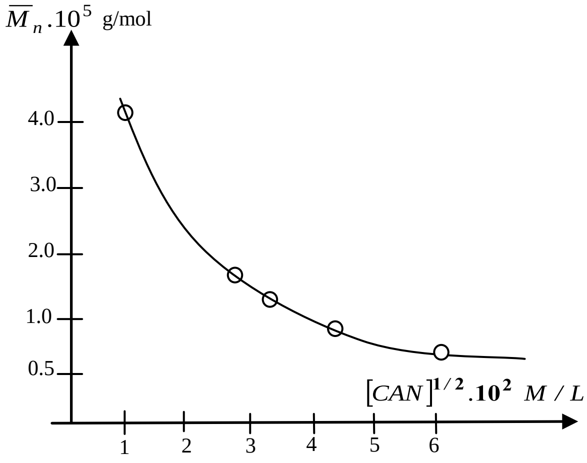


Figure 5 : Variation of the copolymer mass obtained by HPLC in function of the monomer concentration $[CAN].10^2\ M/L$

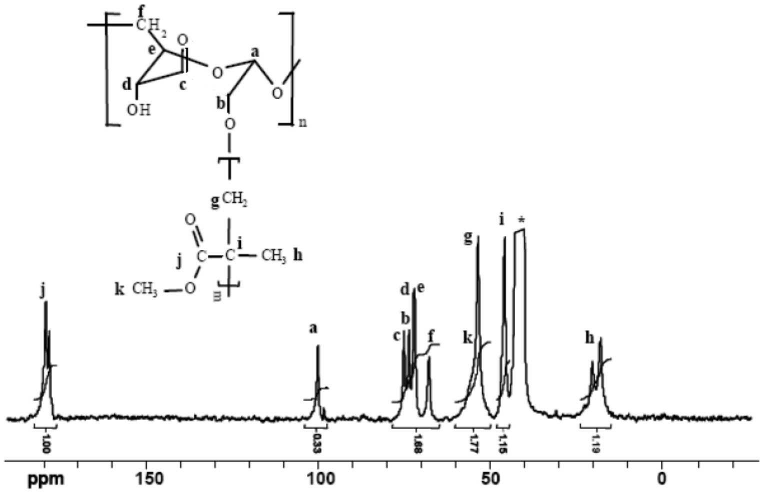


Figure 6 : The ^{13}C NMR spectrum of DEXTRAN-PMMA in deutered DMSO. Carbon atoms and corresponding peaks are identified by a literal.

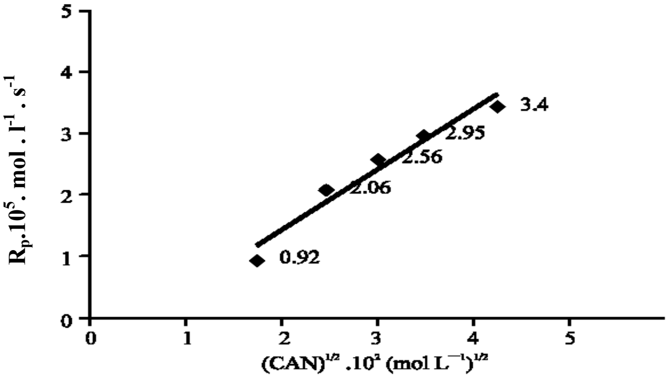


Figure 7 : Polymerization rate (Rp) of Fucan in function of the square-root of CAN; MMA=0,0742M ; (Fu)=00417g; (HNo3)= 0,2M ; temperature =40°.

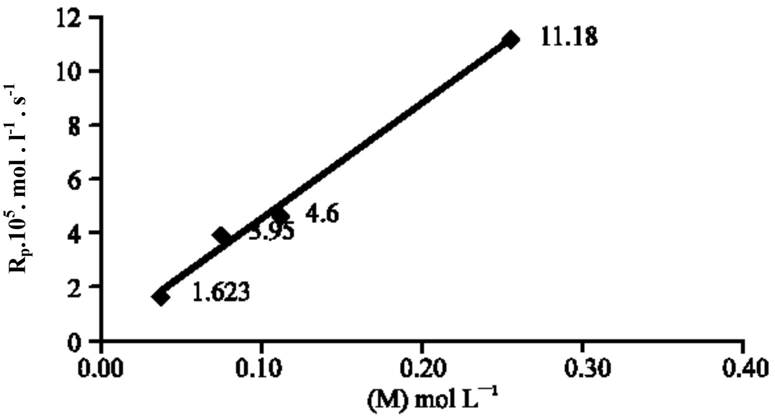


Figure 8 : Polymerization rate (Rp) of fucan N1 with MMA in function of monomer; (Fu) =00417g ; (CAN)=0,503.10^{-3}M, (HNo_3)= 0,2M , temperature = 40°C.

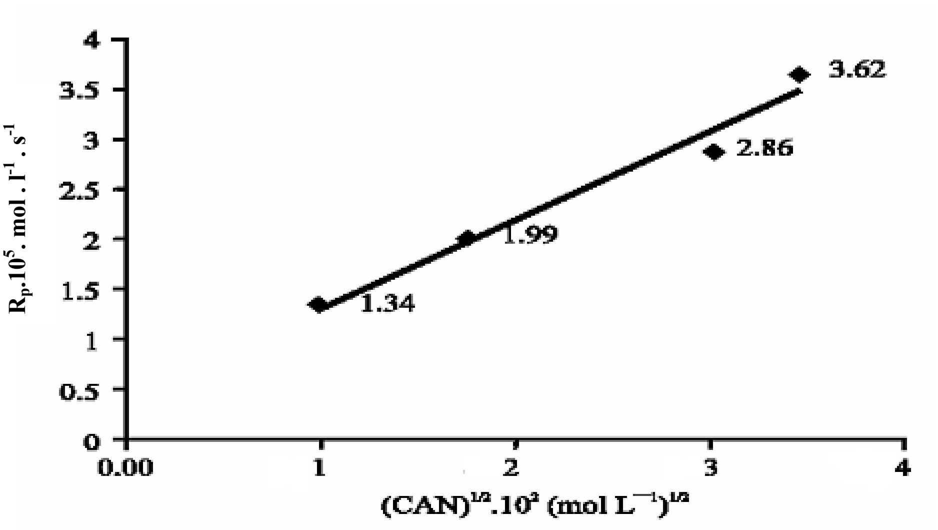


Figure 9 : Polymerization rate (Rp) of fucan N1 with MMA in function of the square root of the initiators (CAN), Dextran= 0,0318g ; (MMA) = 0,0742M (HNO_3) = 0,2M Température = 40°C.

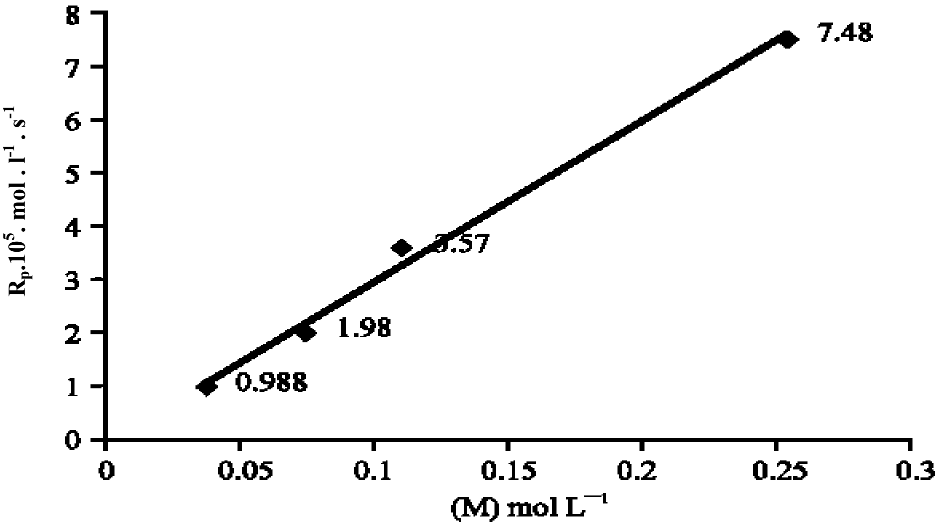


Figure 10 : Polymerization rate (Rp) of fucan N1 with MMA in function of monomer concentration (M), Dextrane= 0,0318g ; (CAN) = 0,503.10^{-3} M, (HNO$_3$) = 0,2M Temperature = 40°C.

Table I : Measurement of the relative viscosity $\left(\frac{\ln \eta_r}{C}\right)$ and specific viscosity $\left(\frac{\eta_{sp}}{C}\right)$ of Fucane N1 in function of its concentration percentage in the solvent H_2O at a temperature T°=40°C.

$[Fucan\ N1]\%$	0	0,45	0,65	0,75	1,0	1,25	1,45	1,65	2,0
$\frac{\ln \eta_r}{C}$	0,252	0,260	0,265	0,280	0,300	0,305	0,310	0,320	-
$\frac{\eta_{sp}}{C}$	0,252	0,280	0,320	0,340	0,350	0,360	0,380	0,410	-

Table II : Measurement of the relative viscosity $\left(\frac{\ln \eta_r}{C}\right)$ and specific viscosity $\left(\frac{\eta_{sp}}{C}\right)$ BBP-2 in function of its concentration percentage in the solvent H_2O at a temperature T°=40°C.

$[BBP-2]\%$	0	0,45	0,65	0,75	1,0	1,25	1,45	1,65	2,0
$\frac{\ln \eta_r}{C}$	0,086	0,10	0,11	0,12	0,13	0,14	0,15	0,165	-
$\frac{\eta_{sp}}{C}$	0,086	0,11	0,12	0,13	0,14	0,16	0,17	0,185	-

Table III : Comparative table of the two (Vp) measuring methods : the pH- metric method and the extraction by soxhlet with the acetone method .

$[\mathrm{CAN}]^{1/2}.10^{2}\,\mathrm{M/l}$	2	3	3,46	4,59	5,99
PG%	145,30	163,05	218,10	201,.20	16,220
$R_h.10^5 mol/l^{-1}s^{-1}$	/	1,476	1,504	2,272	3,084
$R_g.10^5 mol/l^{-1}s^{-1}$	/	1,004	1,256	1,868	2,436
$R_p = \left(R_h + R_g\right).10^5 mol.l^{-1}s^{-1}$	/	2,480	2,760	4,140	5,518
$R_p^{(a)}$. 10^5 mol.l^{-1}.s^{-1}	2,25	2,660	3,040	4,000	5,520
PG$^{(a)}$%=(-4,084.10^{9}R$^2{}_P$+2,774.10^{5}R$_P$-2,698). 100 or = K$^{'}$[Ce^{+4}] +K$^{''}$[Ce^{+4}]$^{1/2}$ + K$^{'''}$	147,75	179,31	196,29	186,68	17,58
R$^{(a)}{}_g$=(R$_P$/2 - 2,71 . 10^{-3}[Ce^{+4}]$_{max}$). 10^5 Mol. L^{-1}. s^{-1}	/	1,006	1,196	1,676	2,436
R$^{'a)}{}_h$=(R$_p$/2 + 2,71 . 10^{-3}[Ce^{+4}]$_{max}$) . 10^5 mol.l^{-1}.s^{-1}	/	1,654	1,844	2,324	3,084

GLOBAL JOURNAL OF SCIENCE FRONTIER RESEARCH
CHEMISTRY
Volume 12 Issue 1 Version 1.0 January 2012
Type : Double Blind Peer Reviewed International Research Journal
Publisher: Global Journals Inc. (USA)
Online ISSN: 2249-4626 & Print ISSN: 0975-5896

Voltammetric Behaviour of Carbonyl Group Containing Pesticides Topramezone, Fenomidone and Methiocarb

By Sarvareddy Rajasekhar Reddy, Neelam Y.Sreedhar, Kukkambacum Chandra mohan, Maddela Nagaraju

S.V. university,Tirupati AP,India

Abstract - In this work the effect of functional groups (substuents) on the reduction potentials of carbonyl group containing pesticides topramezone ,fenomidone and methiocarb were studied. Deferential pulse adsorptive stripping voltammetry, cyclic voltammetry, millicoulometry and controlled potential electrolysis were used for the determination of reduction potentials and electrode mechanisms. HMDE (Hanging mercury drop electrode) used as working electrode and universal buffer used as supporting electrolyte.

Keywords : Topramezone, fenomidone and methiocarb,.defferentialpulse adsorptive stripping voltammetry,cyclic voltammetry,millicoulometry and controlled potential, HMDE ,Universal buffer.

GJRE Classification : FOR Code: 030503, 040204

VOLTAMMETRIC BEHAVIOUR OF CARBONYL GROUP CONTAINING PESTICIDES TOPRAMEZONE, FENOMIDONE AND METHIOCARB

Strictly as per the compliance and regulations of:

Voltammetric Behaviour of Carbonyl Group Containing Pesticides Topramezone, Fenomidone and Methiocarb

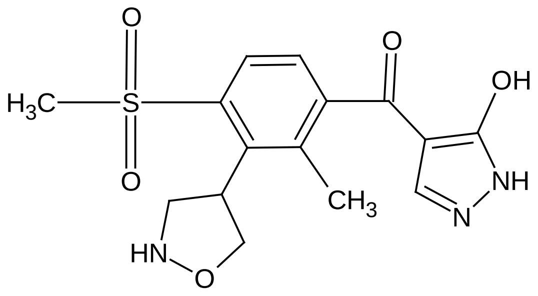
Sarvareddy Rajasekhar Reddy [α], Neelam Y.Sreedhar [Ω], Kukkambacum Chandra mohan [β], Maddela Nagaraju [ψ]

Abstract - In this work the effect of functional groups (substuents) on the reduction potentials of carbonyl group containing pesticides topramezone ,fenomidone and methiocarb were studied. Deferential pulse adsorptive stripping voltammetry, cyclic voltammetry, millicoulometry and controlled potential electrolysis were used for the determination of reduction potentials and electrode mechanisms. HMDE (Hanging mercury drop electrode) used as working electrode and universal buffer used as supporting electrolyte.

Keywords : Topramezone, fenomidone and methiocarb,.defferentialpulse adsorptive stripping voltammetry,cyclic voltammetry,millicoulometry and controlled potential, HMDE ,Universal buffer.

I. INTRODUCTION

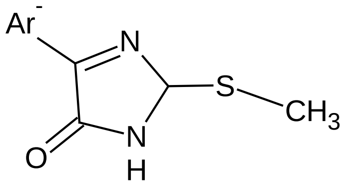
Topramezone [3-(4,5-dihydro-1,2-oxazol-3-yl) 4-mesyl-*o*-tolyl](5-hydroxy-1-methylpyrazol-4-yl) methanone] is broad spectrum compound used for seed treatment and for the protection of fruits and vegetables.



Most of the methods reported in the literature for the determination of the topramezone is based on the several techniques. Fungicides are widely used for crops that lack natural resistance to the fungal species involved. These chemicals are used to treat foliage diseases of some crops. Seeds for damping off, soil in seed beds for root and to control turf and transplant diseases. Kruvea et al.[1] reported potential washing methods with LC-ESI-MS to determine pesticide residues in oranges. Chandra mouli et al.[2] reported GC/LC-MS method for rapid screening of 250 pesticides including methiocarb in aqueous matrices.

Kateina et al.[3] evaluated the suitability of organic solvent for GC analysis of pesticides. A solid-phase micro extraction method and HPLC with diode array detection of fungicide in wine was developed by Millan et al.[4]. Gimeno et al.[5] monitored antifouling agents in water samples by on-line solid phase extraction liquid chromatography-atmospheric pressure chemical ionization mass spectrometry method. Dimitral et al.[6] determined fungicides in natural water using SPME and GC coupled with electron-capture and mass spectrometric detection. Carabias maltinez[7] developed a procedure for analysis of pesticide residue in matrices with high lipid contents by membrane separation coupled online HPLC system. HPLC-DAD [8-10] with multivariate calibration, partial least squares calibration and with spectrograms for the quantification mixtures of pesticides. Application of solid phase disc extraction,[11] dispersion extraction,[12] and partition cartridges followed by gas and liquid chromatography for the determination of fungicides in environmental water, oranges, vegetable samples.

Fenamidone((*S*)-1-anilino-4-methyl-2methyl thio-4-phenylimidazolin-5-one) is imidazole fungicide.It is broad spectrum pesticide used to protect crops from fungel diseases.



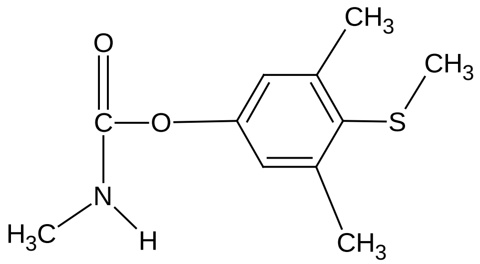
Susana et al.[13] reported GC/MS for analysis of fenamidone in grapes and wine. De mello et al.[14] reported LC with diod array

---

*Author [α] : Electro analytical lab, department of chemistry, S.V. university,Tirupati AP,India. *corresponding auther, tel:9493234699 E-mail : sarvareddyraja@gmail.com*

detection (DAD) method for screening of pesticides including fenamidone in grapes and wines. Danion et al.[15] reported solid phase extractin method coupled with LC/MS for isolation of fenamidone from plants. Luigi et al.[16] analised three fungicide residues including fenamidone by applying pseudo first order kinetics and half life method in wine. Schreiber et al.[17] reported triple quadropole mass spectroscopy with liquid chromatographic (LC/MS/MS) method for analysis of fenamidone residues in food stuffs. Lutz alder et al.[18] reported GC/MS, LC/ MS/ MS, GC/ EI/ MS and LC/ ESI/ MS/MS methods for analysis of 500 high priority peticide residues including fenamidone. Donbroun[19] reported GC/MS/MS and LC/MS/MS methods for analysis of pesticide residues in fruits and vegitables. Lambropoulou et al.[20] reported coupling of head space solid space micro extraction with ultra sonic extraction for determination of fenamidone residues in birds by using GC.

Methiocarb (4-methylthio-3,5-xylyl methyl carba mate) is registered as acaricide for the control or kill mites in agricultural fields. Due to the continuous increase in the application of such pesticide, the necessity of water analysis is always growing. The traditional techniques used for such purpose are liquid chromatography and gas chromatography with electron capture detection, which is one of the most adequate due to the very low value obtainable for the detection limit.



Yang et al.[21] reported chromatographic methods ie HPLC-,GC,super critical fluid chromatography and TLC to determine methyl carbamate pesticide residues in water, soil and plant tissues. Chiron et al.[22] employed on line solid phase extraction LC/MS to investigate methiocarb residues in water samples. Alvarez et al.[23] performed the spectrophotometric determination of carbamates including methiocarb. Msahiro et al.[24] determined methyl carbamaete pesticide residues in foods by using accelerated solvent extraction ASE and HPLC with post column fluorescence.

Parilla et al.[25] reported SPE and HPLC/DAD method to determine pesticide residues in water. Richerd[26] employed HPLC method to determine N-methyl carbamate recidues using post column hydrolysis electro chemical detection. Aulakh et al.[27] reported solid phase micro extraction HPLC for analysis of pesticides. Tomomi et al.[28] devoloped anew analytical method for determination of nine pesticide residues including methiocarb in fruits and vegtables using ESI-LC/MS/MS with direct sample injection into a short column. Davia osselton et al.[29] reported GLC, HPLC/DAD and TLC for determination of 51 common pesticides including methiocarb. Parilla et al.[30] employed SPE and HPLC photo diod array detection for determination of pesticide residues in water samples. Leejeong et al.[31] reported HPLC with UV detection method using super critical fluid exractin to determine methyl carbamates from spicked matricies. Wang et al.[32] reported SMPE/HPLC method for analysis of pesticide residues from straw berries. Feride kocl et al.[33] employed HPLC wth post column derivatisation and flurascence detectin for analysis of methiocarb in honey. Jose fernondo et al.[34] reported HPLC with chemiluminiscence detection for determination of carbamates. Moore et al.[35] reported multi residue analytical method for analysis of pesticides in water using SPE and LC/MS.

II. Materials and METHODS

a) Apparatus

The electrochemical measurements were carried outwith model Metrohm 757 VA computrace. Three electrodesystems consisting of hanging mercury electrode (HMDE) as working electrode, Ag/AgCl (salt KCl) wasused as a reference electrode and a platinum wire as an auxiliary electrode which displays negative potential range. Eli co Li-129 model glass calomel combined electrode was employed for measuring pH values.

b) Reagents

All reagents used were of analytical reagent grade. Double distilled water was used throughout the analysis. In the present investigation universal buffers of pH range 2.0 to 6.0 are used as supporting electrolytes and are prepared by using

0.2 M boric acid, 0.05M citric acid and 0.1M trisodium orthophosphate solutions, pesticide samples obtained from Rankem.

III. RESULT AND DISCUSSION

In case of metheocarb the carbonyl group is present in open chain it has the rich electronic environment because of nitrogen attached to carbonyl carbon due to this the reduction of metheocarb is some what difficult but at the same time oxygen present on carbonyl carbon suppress the electron density and facilitate to reduction when compared to the carbonyl groups present in other two compounds under observation that is fenomidone and topramezone which has one carbonyl group for each methiocarb redueses at higher negative potentials.

In topramezone the carbonyl group is present in in between two rings it has the poor electronic environment because of electron with drawing nature of aromatic rings attached to carbonyl carbon due to this the reduction of topramezone is some what easy when compared to the carbonyl group present in fenomidone. topramezone redueses at lower negative potentials.

Though there is a carbonyl group which is present in the ring fenomedone reduces at greater negative potentials than topramezone because of the electron donating nitrogen adjacent to carbonyl carbonyl carbon.

a) Differential pulse-adsorptive stripping voltammetric studies

The DP-Adsv behaviour of topramezone, fenomidone and methiocarb (1x 10^{-5}M) was investigated over pH range 2.0 to 6.0 at the HMDE. The Faradic response exhibited is an adsorptive reduction peak (Fig. 1) which corresponded to the reduction of carbonyl group (>C = 0) of topramezone, fenomidone and methiocarb.

b) Effect of pH

The position of peaks is strongly pH dependent in that it shifts to more negative potentials with increasing pH. No reduction was observed in basic medium pH < 8.0.

c) Characterization of waves / peaks

All the three compounds exhibits only one voltammetric wave / peak over the pH range 2.0 to 6.0 with all techniques. This wave / peak is attributed to the reduction of carbonyl group involving 2 electrons. Typical cyclic voltammogram are shown in Fig. 2. No reduction peak is observed in basic medium ($8 \leq pH \leq 12$) for carbonyl groups due to the precipitation of electroactive species.

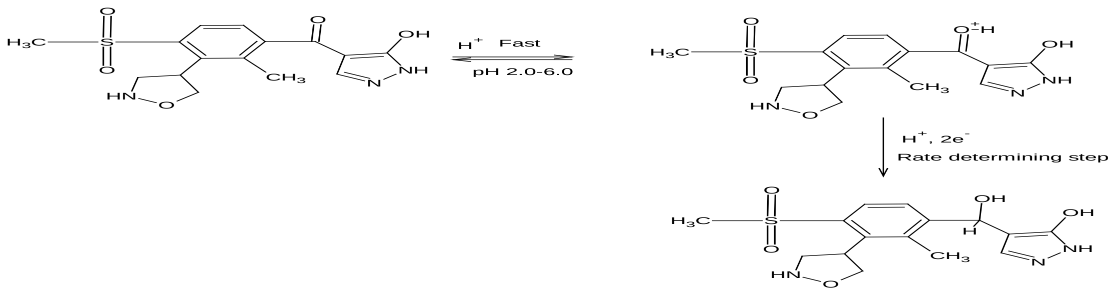
d) Recommended analytical procedure

A stock solution (1.0 x 10^{-3}M) of samples prepared by dissolving the appropriate amount of the electro active species in dimethyl formamide. One ml of the standard solution is transferred into the voltammetric cell and made upto 9 ml with the supporting electrolyte to get the required concentration and then deoxygenated by bubbling nitrogen gas for 10 min. After recording the voltammograms, small increments of the standard solution are added and the voltammograms are recorded for each addition under similar conditions.Optimum conditions for this analysis are pH 4 concentration:1x10 $^{-5}$ M, and scan rate : 45 mVs^{-1}

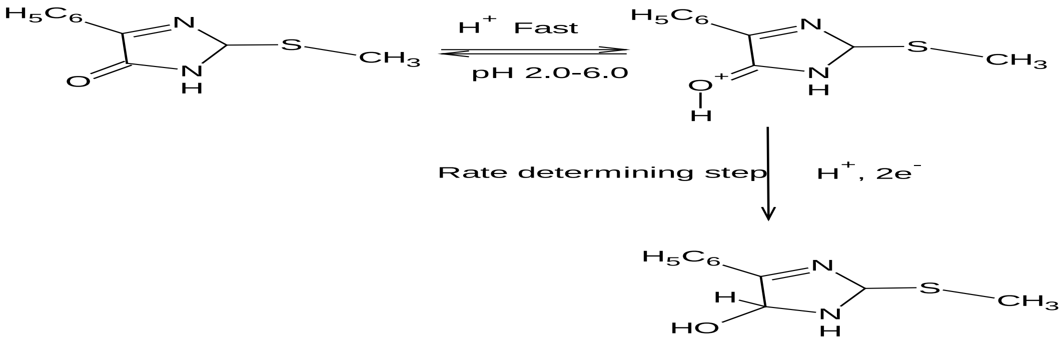
e) Kinetic data

The values obtained for diffusion coefficient, transfer coefficient and heterogeneous forward rate constant are given in Tables 1,2 and 3. The diffusion coefficient values evaluated from cyclic voltammetry is in good agreement indicating the diffusion controlled and adsorption at the electrode surface. The variation of diffusion current with the pH of the supporting electrolyte influences the diffusion coefficient values also to vary in the same manner. The reason for slight variation in diffusion coefficient values with increase in pH may be attributed to the decrease in the availability of protons with increase in pH of the supporting electrolyte. The rate constant values are in general found to decrease with increase in pH indicating that the electrode reaction tends to become more and more irreversible with change in pH. Based on the experimental results obtained from all the techniques employed, a possible electrochemical reduction mechanism of the three compounds under investigation has been suggested on the basis of protons and electrons involved in the reduction as shown in scheme1,2 and 3.

Scheme 1 : Reduction mechanism of topramezone



Scheme 2 : Reduction mechanism of fenomidone



Scheme 3 : Reduction mechanism of methiocarb

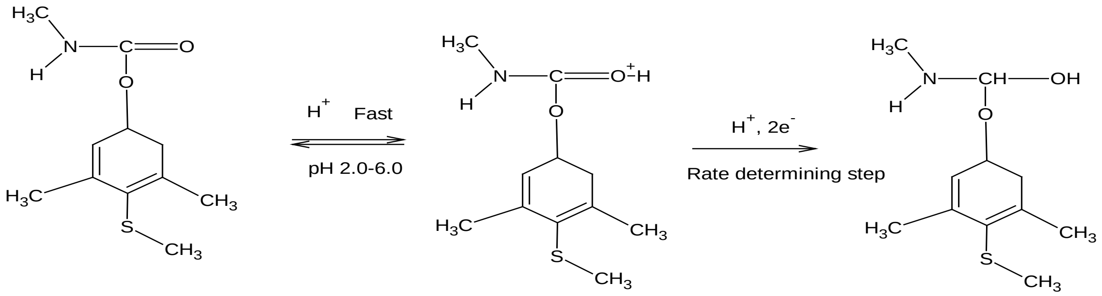


Table 1 : Typical cyclic voltammetric data of topramezone

pH	**$-E_p$ / V**	**i_p / µA**	**$\alpha\ n_a$**	**D x 10^6 / $cm^2\ s^{-1}$**	**$k^0_{f,h}$ / $cm\ s^{-1}$**
2.0	0.153	7.4	0.327	7.621	3.149×10^{-3}
4.0	0.201	5.9	0.366	6.994	7.072×10^{-4}
6.0	0.301	4.9	0.318	4.971	2.542×10^{-4}

Table 2 : Typical cyclic voltammetric data of fenamidone

pH	$-E_p$ V	i_p μA	$\alpha\ n_a$	$D\ x\ 10^6$ $cm^2\ s^{-1}$	$k^0_{f,h}$ $cm\ s^{-1}$
2.0	0.16	9.3	0.62	2.82	8.20 x 10^{-2}
4.0	0.36	5.7	0.60	2.60	4.32 x 10^{-3}
6.0	0.38	8.2	0.61	2.30	3.89 x 10^{-6}

Table 3 : Typical cyclic voltammetric data of methiocarb

pH	$-E_p$ V	i_p μA	$\alpha\ n_a$	$D\ x\ 10^6$ $cm^2\ s^{-1}$	$k^0_{f,h}$ $cm\ s^{-1}$
2.0	0.36	5.81	0.99	5.66	2.60 x 10^{-6}
4.0	0.41	6.0	0.92	5.49	1.57 x 10^{-7}
6.0	0.61	5.55	0.88	5.22	6.47 x 10^{-9}

IV. CONCLUSION

In the above investigation highly potent carbonyl group containing pesticides had selected to get detailed information on the reduction behaviour of carbonyl group and electrode kinetics concerned employing cyclic voltammetry, differential pulse adsorptive stripping voltammetry, controlled potential electrolysis and millicoulometric techniques. The method shows a good reproducibility and high accuracy compared with spectrophotometric, spectrofluorimetric and chromate - graphic methods of analysis.

REFERENCES RÉFÉRENCES REFERENCIAS

1. Anneli Kruvea, Andrea Lamosb, Jekaterina Kirillovab, and Koit Herodesa, Proc.Estonian Acad. Scie. Chem, ,56 (2007) 3.
2. Bharat Chandramouli, Donald Harvan, Scott Brittain, Ronald Hass, Organohalogen compounds, 66 (2004) 246.
3. Katerina Mastovska and Steven J. Lehotay, J. Chromatogr. A, 1040 (2) (2004) 259.
4. S. Millan, M.C. Sampedro, N. Unceta, M.A. Goicolea, E. Podriguez and R.J. Barri, J. Chromatogr. A, 995(1-2) (2005)135.
5. R.A. Gimeno, C. Aguilar, M. Marece and F. Borrull, J. Chromatogr. A,1-2 (2001) 139.
6. A.Dimitra, Lambropoulou, K. Ioannis, Konstantinou and Triantfullos, Albanis, J. Chromatogr. A, 893,1 (2000)143.
7. R. Carabias-Martinez, E. Rodriguez-Gonzalo, P.H. Paniagua-Marcos and J. Hernadez Mendez, J. Chromatogr. A, 869 ,1-2 (2000) 427.
8. M. Martimez Galera, J.L. Martinez Vidal, A. Garridofreni chand, M.D. Gilgercia, J. Chromatogr. A, , 778,(1-2), (1997) 139.
9. A.Garridofrenich, J.L. Martinez Vidal, P. Parrilla and M. Martinez Galera, J. Chromatogr. A, , 778 ,(1-2) (1997)183.
10. M.D. Gilgarcia, A. Garrido Frenich, J.L. Martinez Vidal, M. Martinez Galera, A. Munozde La Pena and F. Salinas, Anal. Chim. Acta, 348(1-2), (1997) 177.
11. S. Jaume, Salau, Rosi Alonso, Gloria Batllo and Damia Barcelo, Anal. Chim. Acta, , 293 (1994) 109.
12. C.M. Torres, Y. Pico, M.J. Redondo and J. Manes, J. Chromatogr. A, 719, (1996) 95.
13. Susana de Melo Abreu; Paulo Herbert; Pierluigi Caboni; Paolo Cabras,Arminda Alves; Vincenzo Luigi Garau, Journal of Environmental Science and Health, Part B, 42(2007) 7.
14. De Melo Abreu S, Caboni P, Cabras P, Garau VL, Alves A., Anal Chim Acta., 291(2006)7.
15. Anne Danion, Jean Disdier Chantal Guillard,Olivier Païssé, and Nicole Jaffrezic-Renault, Applied Catalysis B: Environmental, 62 (2006)3-4.
16. Vincenzo Luigi Garau, Susana De Melo Abreu, Pierluigi Caboni, Alberto Angioni, Arminda Alves and Paolo Cabras, J. Agric. Food Chem. 57(2009)6.
17. André Schreiber, Yuriko Ozeki, Applied bio systems 2008.

18. Lutz Alder, Kerstin Greulich, Günther Kempe, Bärbel Vieth Mass Spectrometry Reviews, 25(2006)6.
19. Don Brown,Bodycote LawLabs – Birmingham, UK2005.
20. Lambropoulou, Dimitra A; Konstantinou, Ioannis K; Albanis, Triantafyllos A Analytica Chimica Acta, (2006).
21. S. S. Yang, A. I. Goldsmith and I. Smetena, Journal of Chromatography A,754, 1-2 (1996)22.
22. S. Chiron; J. A. Torres; A. Fernandez-alba; M. F. Alpendurada; D. Barcelo, International Journal of Environmental Analytical Chemistry, 65 (1996) 1-4 .
23. L. Alvarez-Rod´ıgueza, Ll. Monferrer-Ponsa, J. S. Esteve-Romeroa M. C, Analyst,122, (1997).
24. Masahiro Okihashi, Hirotaka Obana and Shinjiro Hori, Analyst, 123(1998).
25. P. Parrilla; J. L. Martínez Vidal, Analytical Letters, 30 (1997)9.
26. Richard T. Krause, Journal of Chromatography A, 442 (1988).
27. J. S. Aulakh; A. K. Malik; Varinder Kaur; Philippe Schmitt-Kopplin, Critical Reviews in Analytical Chemistry, 35(2005) 1.
28. Tomomi Goto, Yuko Ito, Sadaji Yamada Hiroshi Matsumoto, Hisao Oka and Hisamitsu Nagase, Analytica Chimica Acta,,555 (2006)2.
29. Michael David Osselton and Robert Duncan Snelling, Journal of Chromatography A ,368(1986).
30. P. Parrilla; J. L. Martinez-Vtdal; A. R. Fernandez-Alba, Journal of Liquid Chromatography and related Technologies, 16 (1993)18.
31. Mijeong Lee Jeong and David J. Chesney,Analytica Chimica Acta, ,1-3 (1999) 14.
32. Zhi Wang; Bernard Hennion; Louise Urruty; Michel Montury, Food Additives & Contaminants: Part A, 17 (2000)11.
33. Feride Koc1, Yusuf Yigit, Yavuz Kursad Das, Yasemin Gure and Cevdet Yarali, Journal of Food and Drug Analysis, 16 (2008) 3.
34. Jose Fernando Huertas-Perez and Ana María Garcia-Campana, Analytica Chimica Acta, 630, 2 (2008)23.
35. Keith M. Moore, Susan R. Jones and Carole James, Water Research, 29(1995) 5.

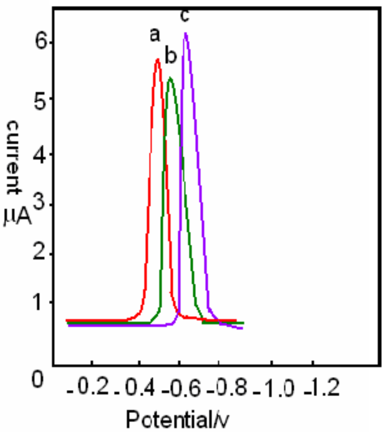


Fig 1: Stripping voltammograms at pH 4

A=Topramezone
B=Fenomidone
C=Methiocarb

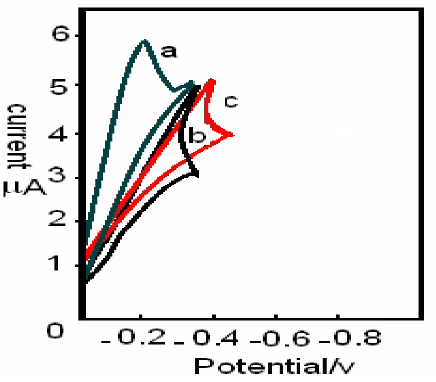


Fig 2 : cyclic voltammograms at pH 4

A=Topramezone
B=Fenomidone
C=Methiocarb

GLOBAL JOURNAL OF SCIENCE FRONTIER RESEARCH
CHEMISTRY
Volume 12 Issue 1 Version 1.0 January 2012
Type : Double Blind Peer Reviewed International Research Journal
Publisher: Global Journals Inc. (USA)
Online ISSN: 2249-4626 & Print ISSN: 0975-5896

Removal of Mn^{+2} and Fe^{+3} Ions from Waste Water and Underground Water Using Calcium Silicate (CS)

By Wael A. El-Helece
Jazan University, Jazan, KSA

Abstract - The determination of heavy metal ions are limited by two difficulties, very low concentration of heavy metal ions which may be lower than the detection limit of many traditional analytical techniques such as atomic absorption spectrometry, colorimetric, and voltametry. And the interfering effects of the matrix. Calcium silicate (CS) is obtained as mentioned in the literature, This synthesized material, which have many applications in various walks of life will be under study in this research. In a new area of the most important areas of life and the environment, a water treatment and removal of some heavy ions such as Mn+2 and Fe+3 ions present in waste water and underground water were efficiently removed by (CS).

Keywords : *Calcium silicate, removal of heavy metals, elemental analysis.*

GJRE Classification : *FOR Code: 030207*

Removal of Mn^{+2} and Fe^{+3} Ions from Waste Water and Underground Water Using Calcium Silicate (CS)

Wael A. El-Helece

Abstract - The determination of heavy metal ions are limited by two difficulties, very low concentration of heavy metal ions which may be lower than the detection limit of many traditional analytical techniques such as atomic absorption spectrometry, colorimetric, and voltametry. And the interfering effects of the matrix. Calcium silicate (CS) is obtained as mentioned in the literature, This synthesized material, which have many applications in various walks of life will be under study in this research. In a new area of the most important areas of life and the environment, a water treatment and removal of some heavy ions such as Mn^{+2} and Fe^{+3} ions present in waste water and underground water were efficiently removed by (CS).

Keywords : Calcium silicate, removal of heavy metals, elemental analysis.

I. INTRODUCTION

Determination of heavy metals became one of the important water quality control measurements; human beings cannot deal with the surrounding environment safely without affirmative information about the level of different hazards. This is attributed to the harmful effects caused by the accumulation of heavy metals in human tissues through daily contact with the polluted environment [1].

Iron removal from water is mostly carried out in drinking water preparation, because mineral water contains high amounts of iron ions. These influence water color, odour and turbidity.

Iron is present in all wastewaters. Iron removal from wastewater may be achieved by oxidation of binary iron to tertiary iron. Hydrolysis subsequently causes flake formation, and flakes can be removed by sand filtration. Oxidation may be achieved by adding oxygen or other oxidants, such as chlorine or potassium permanganate. The reaction rate depends upon pH values, and is slower under acidic than under alkalic conditions. To speed up the reaction under acidic conditions, the water may be aerated for carbon dioxide removal and pH recovery. The total reaction causes acid formation and thereby diminishes itself. Iron is often reduced together with manganese. Applying ion exchangers for iron trace removal from drinking water and process water is another option, but this is not very suitable for removing high iron concentrations. Iron compounds are applied in wastewater treatment, usually as coagulants. One example is iron sulphate application in phosphate removal [3 - 6].

Calcium silicate is a known material and has many uses and diverse in many areas of life, for example Rice husk ash when ground with hydrated lime is being successfully used as mortar. Activated carbon and furfural are the two important chemicals which can be derived from rice husk [7].

A literature survey on the uses of the ash remained after firing agricultural residues showed that the following are the most abundant uses all over the world [8-12].

- As aggregate for insulating and light weight concerts.
- In making light weight, refractory and heat – insulating bricks.
- In rubber compounding (reinforcing fillers for rubber compounds).
- Preparation of activated carbon and sodium silicate.
- Making hydraulic cements and glasses.
- As effective agent in disposing of oil spills.
- In insecticides as anticaking.
- Manufacture of silicon tetrachloride.
- Manufacture of silicon carbide and silicon nitride.
- As growing media and fertilizer.
- As moulds for molten steel ingots.
- As filter aid and filter media in water purification.

The following summarizes some technical commercial opportunities for agricultural residues, ash and char utilization. Pure silicon used for making semi-conductors is yet another expensive material, which can be obtained from rice husk [13].

Silicon carbide and, silicon nitride are also very costy and useful materials obtainable from rice husk [14]. Rice husk can also be used for production of acetic acid, proprionic acid, and phenol, cresol…etc by destructive distillation or xylos and glucose through hydrolysis [15].preparation of CSH by the reaction between pure silica and calcium hydroxide had been extensively studied [16, 17]. On the other hand preparation of CSH from the ash remained after firing rice straw or other agricultural wastes [18].The aim of the present work was to use calcium silicate to remove heavy metals ions from waste water and underground water.

Author : Chemistry Department, Faculty of Science, Jazan University, Jazan, KSA. E-mail: waelaboola@yahoo.com

a) *Experimental*

Underground water samples were collected from different locations within the Delta region. All samples were filtered off and acidified with concentrated HCl to pH2 then introduced into plastic vessels at a temperature of 20-25 °C. Suspended matters were determined by filtering 1000 cm^3 of the untreated water sample using a sintered glass G4 and weighing the residue after drying at 120 °C for 2 hrs.

Dissolved oxygen (DO) was determined by Winkler method [19]; dissolved oxygen was stabilized in field using manganese sulfate solution in presence of ammonia buffer. The compound formed was treated with H_2SO_4 and KI and the liberated iodine was titrated against $K_2S_2O_3$.

Total alkalinity (mg $CaCO_3$/L) was determined according to the method described by Strickland and Parsons.

Total Dissolved Salts (TDS) of the water samples were determined by weighing the residue left after complete drying of 100 cm^3 of the water sample at 120 °C for 2 hrs.

The reactivity of the produced material (CSH) towards heavy metals removal from aqueous solutions was also assessed. This was accomplished as follows: 100 mg of CSH was added to 100 ml of the tested water sample and the pH value was again controlled. The sample was stirred for 30 min. and filtered off. The filtrate was subjected to atomic absorption spectroscopy and determining the concentrations of Fe^{3+} and Mn^{2+} ions .

II. RESULTS AND DISCUSSION

The main water quality properties was examined before treatment with CSH and the results were TDS (3.090 g dm^3), (0.106 g dm^{-3}), DO (4.49 mg O_2 dm^{-3}), and total alkalinity determined (153.5 mg $CaCO_3$ dm^{-3}) respectively. This reveals that treatment with CSH has no appreciable effect upon the main water properties. The allowed concentrations of iron, and manganese are 200 and 50 µg/l respectively, according to health related guide level (HRGL) [20].

CSH was used for the treatment of waste water and underground water to remove Mn^{2+} and Fe^{3+} as examples for divalent and trivalent metal ions. The results for this treatment are shown in tables (1. 2 and 3).Tables (1and 2) give the removal of Fe^{3+} ions from water by using rice straw ash, CSH prepared from silica gel, and CSH from RSA. From these tables we could observe that the removal of Fe^{3+} ions from water by the prepared CSH was very efficient as almost 99.8 % from the initial amount of the metal ion in the solutions were removed.

Table 1. Removal of Fe^{3+} ions by CSH

Time hr	pH	Meas. conc.	Abs. conc.	%abs.
0	1.9	43.55	-	-
0.5	11.25	0.25	43.3	99.46
1.0	11.24	0.26	43.29	99.4
1.5	11.15	0.21	43.34	99.5
2.0	11.24	0.21	43.34	99.5
3.0	11.23	0.23	43.32	99.47
4.0	10.8	0.07	43.48	99.84
		For underground water		
4.0	11.72	Nil	5	100 %

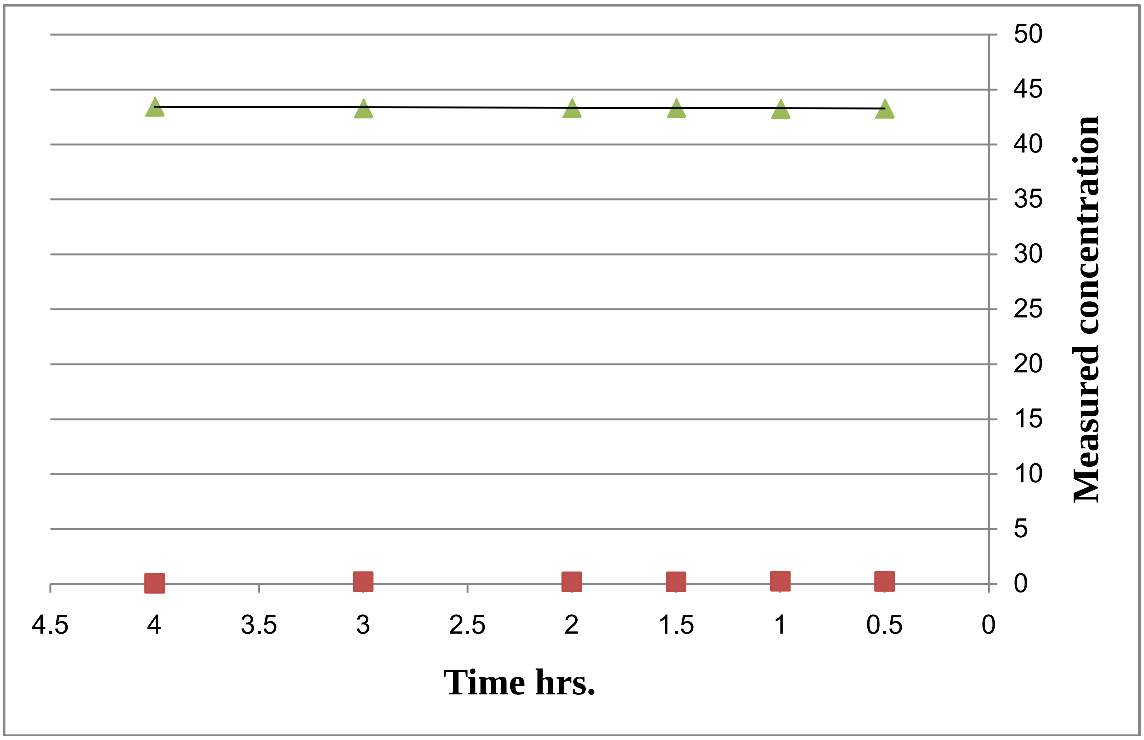


Fig. 1. The relation between time (hrs.) and the removed concentration of Fe^{+3} ions

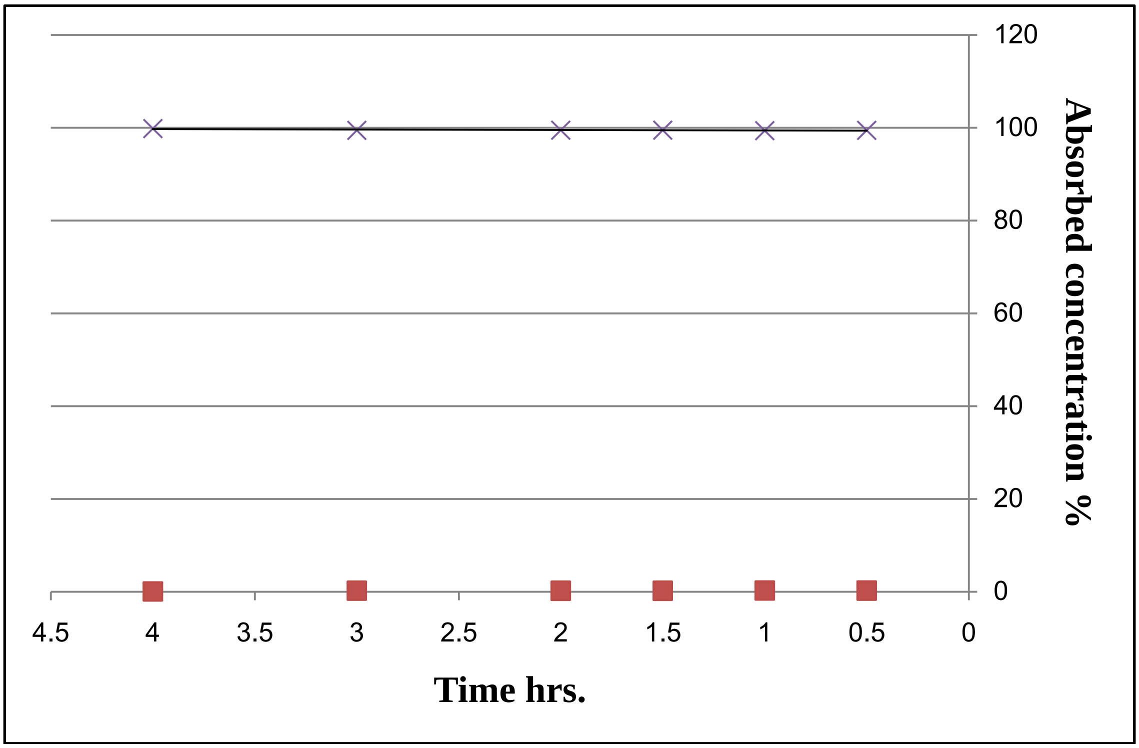


Fig. 2. The relation between time (hrs.) and the percent of the removed concentration of Fe^{+3} ions

Table 2. Removal of Fe $^{3+}$ ions by ash and CSH from silica gel

		Ash		
Time hr	pH	Meas. Conc.	Abs. conc.	%abs.
0	1.9	50.0	-	-
0.5	2.33	16.17	27.38	62.87
4.0	2.15	0.40	43.15	99.08
		CSH from silica gel		
4.0	11.25	0.19	43.36	99.56

Table 3. includes the data for the removal of Mn^{2+} ions from water using rice straw ash, CSH prepared from silica gel, and CSH from RSA. The results show that the removal of Mn^{2+} ions from water by the prepared CSH is very efficient as almost 99.85 % of the initial amount of the metal ion in the solutions were removed.

Table 3. Removal of Mn^{2+} ions by CSH .

Time hr	pH	Meas. Conc.	Abs. conc.	% abs.
0	8.52	9.958	-	-
1.0	11.74	0.021	9.937	99.79
2.0	11.62	0.029	9.929	99.71
2.5	11.44	7.21	21.11	74.5
3.0	11.61	0.017	9.941	99.83
4.0	10.8	0.07	43.48	99.84
		For underground water		
4.0	11.72	0.017	0.033	99

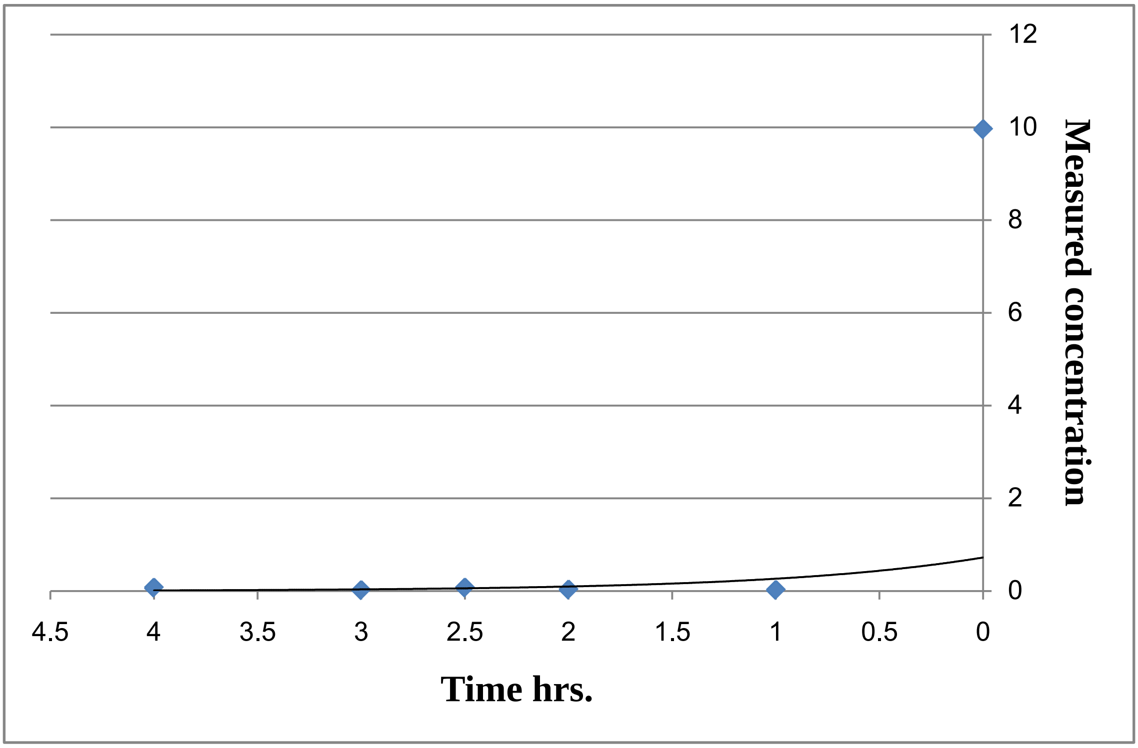


Fig. 3. The relation between time (hrs.) and the removed concentration of Mn^{+2} ions

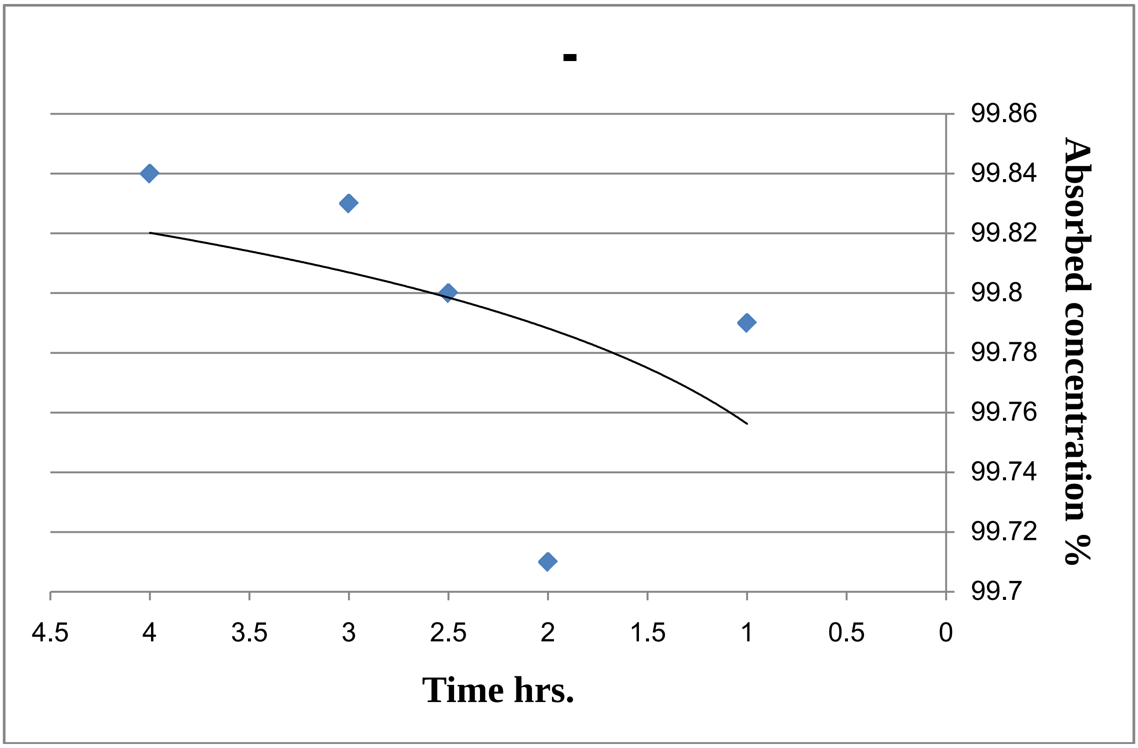


Fig. 4. The relation between time (hrs.) and the percent of the removed concentration of Mn^{+2}ions

a) Results Illustrated by the last tables and figures:

1. Using calcium silicate to overcome the acidity of the waste water since adding calcium silicate acidic pH jumped from 1.9 to 11.8.
2. Calcium silicate removed both Fe^{+3} and Mn^{+2} ions and that is obvious when the treatment time 0.5 hr and in spite of we continued to four hours of treatment to determine whether the adsorption process is a reversible.
3. A comparison between the raw material (ash remaining after burning) and materials prepared (calcium silicate) to determine the effectiveness of each of them in water treatment has been shown that the effectiveness of calcium silicate in the removal of both Fe^{+3} and Mn^{+2} ions are very high (99.8) and that could be explained as follows:

Two mechanisms of the removal of the ions from water using calcium silicate.

1. The very clear and known one is the adsorption on the surface of the used materials.
2. The second one the effect of the used calcium silicate on the PH of the medium which assist the ions to be hydrolyzed and found surrounded with OH^- ions.

b) X-Ray Diffraction analysis (XRD)

The XRD measurements for three samples of (CSH) prepared from heap fired RSA and obtained under different conditions were carried out in order to investigate the changes occurring due to their formation reactions.

Figure (I) shows the result of these measurements. There are two forms of CSH, these two forms have chemical composition as CSH (I) (0.8-1.5 CaO. SiO_2. 0.5-2.5 H_2O) and CSH (II) (1.5-2.0 CaO. SiO_2. 1-4 H_2O) [21]. natural plombieriteis are closely similar but gives no basal X-ray diffraction.

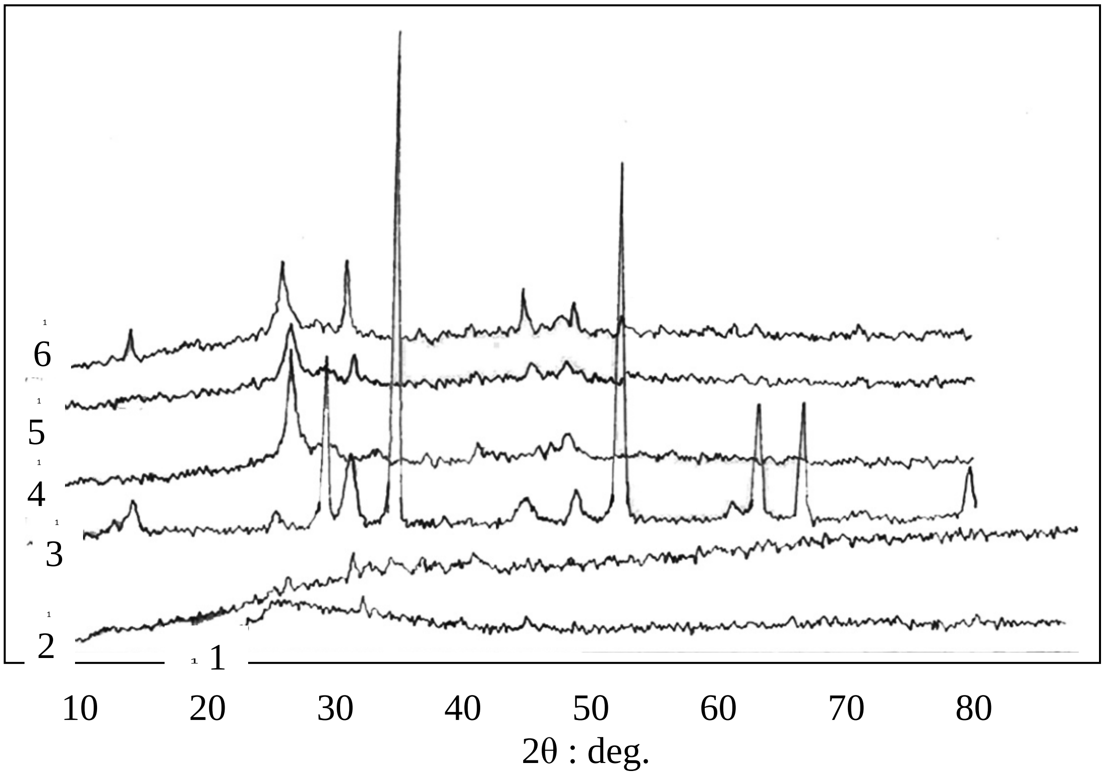


Fig. 5. XRD patterns for CSH samples; 1, 2 ash samples, 3 CaO sample, 4, 5 CSH samples and 6 CSH with Fe^{3+}.

The crystal form Crumpled foils (semi-crystalline) and basal spacing of CSH (I) varies with both water content and Ca / Si ratio hence several varieties exist. Powder data relate to fibber bundles. Some other varieties give powder patterns close to that of CSH (1) . The basal spacing, if it occurs , is always about 10 Å [22]. From fig.(1) and CSH (II) were formed and also the two forms are convertible. This is due to two main factors, the water content, and Ca / Si ratio.

III. Conclusion

Removal of divalent (Mn^{+2}) as well as trivalent (Fe^{+3}) ions on the surface of calcium silicate was found to be very efficient; the percent of uptake reached 99.84 % of Fe^{3+} from waste water and most of that present in underground water. The amount from Mn^{2+} ions removed from waste water samples reached about 99.85 %, and most of that present in underground water.

In this research there was a comparative study between four types of materials to be used in water treatment; Pure calcium silicate (CSH free from carbon and other insoluble matters in NaOH solution), Calcium silicate in presence of carbon and other insoluble matters in NaOH solution), Pure calcium silicate (CS prepared from silica jel) and Ash remained after burning of rice straw (active carbon and amorphous silicon oxide). It was clear through the results in the previous tables and graphs indicated that the samples from all four materials were effective in this field, as was expected.

Calcium silicate in presence of carbon and other insoluble matters in NaOH solution) gave the best results and appeared the most efficiency, as a result of this paper the use of residue for the manufacture of paper in the preparation and detail the material used for water treatment, gave this high efficiency.

References Références Referencias

1. Ropek, D. and Para, A. *"The Effect of Heavy Metal Ions and Their Complexions upon Growth, Sporulation and Pathogenicity of the Entomopathogenic Fungus Paecilomyces farinosus"*, Polish Journal of Environmental Studies, 12 (2) (2003), 227-230
2. Omid Tavakoli and Hiroyuki Yoshida *"Effective Recovery of Harmful Metal Ions from Squid Wastes Using Subcritical and Supercritical Water Treatments" Environ. Sci. Technol.*, 39 (7), (2005) 2357–2363
3. Medhat A. Shaker *"Thermodynamic profile of some heavy metal ions adsorption onto biomaterial surfaces"* American Journal of Applied Sciences, August, 2007
4. Tewari, P. K. and Singh, A. K. *"Amberlite XAD-7 impregnated with Xylenol Orange: a chelating*

collector for preconcentration of Cd(II), Co(II), Cu(II), Ni(II), Zn(II) and Fe(III) ions prior to their determination by flame AAS" Fresenius J Anal Chem, 367 (6) (2000) 562-567

5. Enghag, P., Encyclopedia of the Elements – Technical Data, History, Processing, Applications. Weinheim, WILEY-VCH Verlag GmbH & Co. KgaA. 2004.
6. Emsley, J., *"Nature's Building Blocks – An A-Z guide to the elements. Reprinted with corrections",* Oxford, Oxford University Press, 2003.
7. Issa R. M., Abou-Sekkina M. M., Bastawisy A. E. and El-helece W. A.; *"Calcium silicate hydrate (CSH) from Egyptian heap fired rice straw ash (RSA). Preparation, characterization & some application".* Environmental Science J. (ESAIJ), 5(2), (2010) 168-172.
8. Issa R. M., Abou-Sekkina M. M., Khedr A. M. Bastawisy A. E., and El-helece W. A.; *"Exploration on industrial production and thermo-chemical properties of Egyptian rice straw cellulose pulps and xanthates"* 2nd Conference on Chemical Engineering and Advanced Materials (CEAM), VIRTUAL FORUM , Naples, (2010).
9. Abou-Sekkina M. M., Issa R. M., Bastawisy A. E. and El-helece W. A.; *"Characterization and Evaluation of Thermodynamic Parameters for Egyptian Heap Fired Rice Straw Ash (RSA)". International Journal of Chemistry* (IJC), 2(1), (2010) 81-88.
10. Issa R. M., Abou-Sekkina M. M., Bastawisy A. E., Khedr A. M. and El-helece W. A.; *"Egyptian Rice Straw application for Useful Products Throughout Chemical Treatments":* Environmental Science J. (ESAIJ), 4(6), (2009) 530-536.
11. Eysenback , E. *"Pretreatment of industrial Waste",* as Manual of Practice No. FD-3, PP. 153, Water Environmental Federation, Alexandria, Virginia, 223114 – 1994, USA, (1992) .
12. Seeling, B.:, E. Derikson, E, and Bergsrud, F. *"Treatment Systems for Household Water supplies – Iron and Manganese Removal"* , Feb. 1992, Ae – 1030, Water Quality NDSU Extension Service, North Dakota University, (1992) .
13. IPCS *"Environmental Health Criteria 17- Manganese",* WHO, Geneva (1981)
14. Saric, M. "In Handbook on the toxicology of Metals", (ed.1. Friberg, GF, Nordberg, and V. B. Vouk) 2nd edn. Vol. – 11, Elsevier, Amsterdam, 354 (1986) .
15. Mozzi, R. and Warren, B., Apply. Cryst. J., 3, (1970) 251-257 .
16. Jose James and Subba, M., Rav. Ceme. And Concr. Res., 16, (1986) 296-301.
17. Khalil, E. and Aouf, M., Bull. NRC, Egypt, 23, (1998) 269-274.
18. Ying, J. and Benziger, J. Am. Ceram. Soc. J., 79, (1993) 2561-2567.
19. Issa, R. M., Abou-Sekkina, M. M., Khedr, A.M., Bastawisy, A.E-D . and El-Helece, W.A., *"Trace the exploitation of Egyptian rice straw through thermal measurements",* Arabian Journal of Chemistry (2011).
20. Bellamy, L. J., "the infrared spectra of complex molecules", 2nd Ed., 126.
21. Nakamoto, k. "infrared spectra of inorganic and coordination compound" (1963) .
22. Hartani, K., Alsousy, K. and Aila, H. *"Studies of the Adsorptive Decoloration of Aqueous Solutions by MDFSD",* Arabian Journal of Chemistry (2011).

This page is intentionally left blank

Global Journal of Science Frontier Research
Chemistry
Volume 12 Issue 1 Version 1.0 January 2012
Type : Double Blind Peer Reviewed International Research Journal
Publisher: Global Journals Inc. (USA)
Online ISSN: 2249-4626 & Print ISSN: 0975-5896

Environmental Pollution Induced By an Aluminium Smelting Plant in Nigeria

By A. R. Ipeaiyeda, N. S. Umo, G. E. Okojevoh
University of Ibadan, Ibadan, Nigeria

Abstract - The extent of pollution of Imo, Utaewa Rivers and Essene Creek being sources of drinking water were assessed due to the smelting activities of the Aluminium Smelter at Ikot Abasi City, Nigeria. Soil and plants samples in the field near the water bodies were equally assessed. The physicochemical parameters investigated on all sampled water bodies were within the WHO and USEPA limits for drinking water with the exception of salinity, turbidity, TDS and few heavy metals (Mn, Fe, Al, Pb). The overall average levels of these parameters were 7.6±2.8 % (salinity), 16±12 FTU (Turbidity), 793±250 mg/L (TDS), 2.59±0.48 mg/L (Mn), 0.49±0.27 mg/L (Al) and 0.85±0.43 mg/L (Pb). Principal component biplot revealed strong and positive metal loadings whose ranges were (1.284−1.687), (0.499−0.515) and (0.959−1.630) for Essene Creek, Imo River and Utaewa River respectively. Similarly, clauster analysis showed that elemental compositions of soil and plants in the vicinity of aluminium smelter were traceable to the smelting activities. Also, accumulation of airborne particle by vegetation and surface soil was resulted from the activities in the smelting site. Al (1830−2170 μg/g) and Zn (141−147 μg/g) were more abundant at 0-5 cm soil depth than other metals (Cd, Mn, Ni, Fe, Pb, Co). Bioccumulation results revealed increased metal uptake by Vernonia amygdalia (Bitter leaves), Manihot esculenta (Cassava) and Carica papaya (Paw-paw) at the sites closest to the industry, hence can be used as good biomarkers for soil pollution.

Keywords : Pollution, Heavy metal, Bioaccumulation, Multivariate analysis.

GJRE Classification : FOR Code: 070105, 030201

Environmental Pollution Induced By an Aluminium Smelting Plant in Nigeria

A. R. Ipeaiyeda[α], N. S. Umo[Ω], G. E. Okojevoh[β]

Abstract - The extent of pollution of Imo, Utaewa Rivers and Essene Creek being sources of drinking water were assessed due to the smelting activities of the Aluminium Smelter at Ikot Abasi City, Nigeria. Soil and plants samples in the field near the water bodies were equally assessed. The physicochemical parameters investigated on all sampled water bodies were within the WHO and USEPA limits for drinking water with the exception of salinity, turbidity, TDS and few heavy metals (Mn, Fe, Al, Pb). The overall average levels of these parameters were 7.6±2.8 % (salinity), 16±12 FTU (Turbidity), 793±250 mg/L (TDS), 2.59±0.48 mg/L (Mn), 0.49±0.27 mg/L (Al) and 0.85±0.43 mg/L (Pb). Principal component biplot revealed strong and positive metal loadings whose ranges were (1.284−1.687), (0.499−0.515) and (0.959−1.630) for Essene Creek, Imo River and Utaewa River respectively. Similarly, clauster analysis showed that elemental compositions of soil and plants in the vicinity of aluminium smelter were traceable to the smelting activities. Also, accumulation of airborne particle by vegetation and surface soil was resulted from the activities in the smelting site. Al (1830−2170 μg/g) and Zn (141−147 μg/g) were more abundant at 0-5 cm soil depth than other metals (Cd, Mn, Ni, Fe, Pb, Co). Bioccumulation results revealed increased metal uptake by *Vernonia amygdalia* (Bitter leaves), *Manihot esculenta* (Cassava) and *Carica papaya* (Paw-paw) at the sites closest to the industry, hence can be used as good biomarkers for soil pollution.

Keywords : Pollution, Heavy metal, Bioaccumulation, Multivariate analysis.

I. INTRODUCTION

Smelting of aluminium does not come without its environmental problems. There have been a number of recent studies investigating the emissions of various pollutants during the aluminum smelting process. Some of the studies were laboratory-scale investigations which quantitatively determined the species present in flue gases (Wei, 1996). Other investigation concentrated on the emissions from aluminium smelters. The pollutants identified in the studies were chlorinated organic compounds (Laue et al., 1994; Westberg and Selden, 1997), organic compounds containing chlorine and sulphur (Sinkkonen et al., 1994), polycyclic aromatic hydrocarbons (PAHs) (Aittola et al., 1993; Westberg and Selden, 1997; Healy et al., 2001), heavy metals (Kozanoglou and Catsiki, 1997). PAHs in general are mutagenic and/or carcinogenic in nature. Also, heavy metal load from smelting activities near water bodies has been proved to result in contamination of river and has various implications on the ecosystem (Ellis, 1987, Vucadin and Odzak, 1991, Malea and Haritonidis, 1995; Kozanoglou and Catsiki, 1997). These toxic pollutants may eventually reach human bodies through the food chains and inhalation of polluted air. In addition, the dumping of smelting by-products in aluminium smelter inhabited areas brings up crucial questions about the degree of metal contamination and the effects on human life. Regions near such activities need to be under investigation in order to avoid gross pollution.

It was for this reason that this investigation was conducted on the aluminium smelter in Ikot Abasi city, Nigeria. The surrounding vegetation has turned yellowish and some of the agricultural plants around the vicinity of the factory have been observed for poor growth and yield. Consequent upon this, there is possibility that the vicinity of the company is susceptible to pollution arising from the smelting activities. The parameters mentioned in this study were metals, salinity, dissolved cations and anions. The aims of the study were to investigate the surface water quality of water bodies in the vicinity of aluminium smelter, and distribution of heavy metals in soil and plants. This study provides background information on the environmental status of the vicinity of aluminium smelter in the tropical area of south-south region of Nigeria.

II. MATERIALS AND METHODS

a) Sampling area

The Aluminium smelter at Ikot Abasi city is in the southern part of Nigeria where aluminium smelting activities have been on-going for more than a decade. It is the second largest producer of primary aluminium in the world (BNW News, 2004; World Bank, 2009). The smelting site is located at latitude 4°34´N and longitude 7°54´E and bordered by water bodies namely Imo River that opens-up to Atlantic Ocean, Utaewa River and Essene Creek. The area belongs to the southern rain forest climate and is relatively populated. A control site was located at about 3km upstream of Essene Creek. Figure 1 shows the Aluminium smelter company and the sampling locations. The description of locations, sample codes and the type of samples collected are highlighted in Table 1.

Author [α] : Department of Chemistry, University of Ibadan, Ibadan, Nigeria
Author [Ω] : School of Earth and Environment, Institute for Climate and Atmospheric Science, United Kingdom. Tel.: + 234(0) 833 -394-8469, E-mail : ayosade2003@yahoo.com, ar.ipeaiyeda@mail.ui.edu.

b) *Sample Collection and preservation*

Water samples were collected monthly between September 2009 and December 2009 from Imo River (IR), Utaewa River (UT) and Essene Creek (EC) at eight locations each. Eight water samples were equally collected from Jaja Creek (JC) situated at the control site with thoroughly cleaned polyethylene bottles without disturbing the water. Water samples collected for metal analyses were acidified with HNO_3.

Soil and plant samples were collected from three locations [Pot Room (PR), Jetty (J), and Cast House (CH)] on the fields near the company as well as from the field near Jaja Creek situated at the control site. Leaves of Cassava (*Manihot esculenta*), Paw-paw (*Carica papaya*) and Bitter leaves (*Vernonia amygdalia*) were collected and thoroughly washed with distilled water. The vegetation samples were dried in an oven at 60 °C, and ground with agate mortal and pestle. The samples were then sieved with 0.5mm mesh size and kept in polythene bags. The air-dried soil samples were pulverized with agate mortar and pestle to a fine powder and then sieved through a 100 - mesh screen sieve to obtain homogenous particles.

c) *Sample preparation and analysis*

Five grams of soil samples was digested with 50mL of aqua regia (HCl and HNO_3 - 3:1 v/v) in a beaker placed on hot plate in a fume hood for 1 hour. The filtered extract was used for metal analysis. The vegetation samples were equally weighed into vitreosil crucibles and nitric acid was added as an ashing aid just before the commencement of ashing. The vegetation samples were dry-ashed in a muffle furnace at 500 °C. The ash was dissolved with hot 2M HNO_3 and was filtered where necessary. Extract of the soil and vegetation samples were analysed for cadmium, manganese, zinc, nickel, iron, aluminium, lead and cobalt using atomic absorption spectrophotometer (UNICAM 939/59). Quality control of metal measurements in soil, vegetation and water was verified by including blanks and carrying out recovery study by spiking. All recoveries were within the range of 92.3-98.7 %. A blank sample was incorporated for every ten soil and vegetation extracts analysed. The acid solutions used for extraction were made from Analar grade stock acids, while the distilled water was doubled deionised. Standards for the atomic absorption analysis were obtained as the commercial BDH stock metal standards from which working standards were prepared by appropriate dilution. For other water quality parameters, the analytical data quality was ensured through careful standardization, procedural blank measurements and duplicate samples.

Conductivity and salinity were recorded with a HACH conductivity/salinity meter model CO150, dissolved oxygen was determined by the alkali-azide modification of Winkler's technique, alkalinity was determined titrimetrically while nitrate was determined colorimetrically using phenoldisulphonic acid method. Phosphate and sulphate were determined colorimetrically using ascorbic acid and turbidimetric methods respectively according to the standard method (APHA –AWWA,1998).

d) *Data treatment and multivariate statistical methods*

Duncan multiple range test of variable at $p < 0.05$ was used to ascertain statistical significance in the soil quality data. Multivariate analysis of the data was performed through Cluster Analysis (CA) and Principal Component Analysis (PCA). The distributions of metals within soil profile were represented by means of Box and Whisker Plots (Winderlin et al., 2001). All mathematical and statistical computations were made using Excel 2003 (Microsoft, 2003) and STATISTICA 6.0 (StatSoft, Inc., USA, 2001).

III. RESULTS AND DISCUSSION

The results of the physicochemical parameters conducted on the water samples from the Imo, Utaewa Rivers, Essene Creek and Jaja Creek are summarized in Tables 2 and 3. Table 4 specifically gives the averages and ranges for parameters used to assess the suitability of these water bodies (Imo , Utaewa Rivers and Essene creek) around the smelting company for beneficial purposes such as drinking and industrial use. In all the sampled water bodies, the physicochemical parameters as shown in Table 4 were generally within the WHO and USEPA guidelines for drinking water with the exception of salinity, turbidity, TDS and few heavy metals (Mn, Fe, Al, and Pb).

The pH values of water from the Imo River, Utaewa River, Essene and Jaja Creeks were within the range of 6.1 and 7.2. Water from the rivers and creeks could be considered acidic since their average pH values were below 7.0. Water pH of 6.3±0.2 and 6.5±1.1 for Essene and Utaewa were the least and highest averages values (Table 2) and were significantly different from the average water pH of Jaja Creek at the control site. Acidification of water samples could have led to the release of loosely bonded ions present on the surface of suspended particle matter; thereby increasing the metal concentration in water samples. Essene Creek and Utaewa River revealed turbidity levels of 25.3±2.1 FTU and 25.0±2.5 FTU respectively, which were significantly higher than the WHO limit of 5 FTU (Table 2). The TDS constituent of Imo River, when compared to the same constituent of Essene Creek and Utaewa Rivers, was indeed higher by factors 3.99 and 3.19 respectively. Correspondingly, sulphate was higher by factors of 0.34 and 0.52 respectively. The average levels of TDS and sulphate for the Imo River water were 1370±21mg/L and 547±71 mg/L respectively (Table 2). High level of TDS is traceable to the impact of navigation on the river.

The average salinity for the Imo River was 13.0±1.1% while 3.2±0.4% and 4.8±0.7% were obtained for the Essene Creek and Utaewa River. These salinity levels were observed to exceed the limit of 0.5%, thus making the water toxic to sensitive freshwater life and not portable for human consumption. High salinity level indicates an increase in the concentration of total dissolved solids in water and can often be detected by an increase in the chloride, an important anion of many dissolved salts. A positive correlation coefficient (0.526) between TDS and salinity was observed. Increases in salinity up to 0.1 % (1,000mg/L) can have lethal and sub lethal effects on aquatic plants and invertebrates (Hart *et al*., 1991). The observed salinity levels for the Essene Creek, Imo and Utaewa Rivers are high enough to induce a variety of other effects within both aquatic and terrestrial ecosystems. These effects include acidification of the water bodies (Lofgren, 2001), mobilization of toxic metals through non-exchange (Norrstron and Bergstedt, 2001), changes in mortality and reproduction of aquatic plants and animals (Strayer and Smith, 1992; James *et al*., 2003; Eaton *et al*., 1999), altered community composition of plants (Eaton *et al*., 1999; Richburg *et al*, 2001; Elshahed *et al*., 2004). At relatively low concentration of salinity, salt has been shown to inhibit denitrification (Cunningham, et al., 2009, 2010; Kaushal, et al., 2005) a process critical for removing nitrate and maintaining water quality in surface waters. Increased salinity is an important ecological variable in explaining the extremely low abundance and diversity of freshwater life observed in the Imo and Utaewa Rivers.

The water quality monitoring data (Table 2) found its application in the classification of rivers into utility classes based on quality indices. Some water quality indices have been reported in different part of the world (Pesce and Wunderlin, 2000; Simeonov et al., 2000). There is no water classification index established for Nigerian rivers and streams yet. However, the well utilized water index of Prati *et al.* (1971) was applied to the data of this study using the parameters pH, turbidity, suspended solids, DO, BOD, and COD. The categories of classification ranged from Utility Class I to V which corresponds to excellent for drinking, irrigation and industrial use without treatment (Class I), suitable for drinking (Class II), slightly polluted (Class III), polluted (Class IV) and heavily polluted water which is not fit for any of these beneficial purposes (Class V). Based on the Prati scale, Imo River, Essene Creek and Utaewa River are categorized under Class III (Table 3) which is indicative of water not suitable for beneficial purposes such as drinking, irrigation and industrial use, but may be rigorously treated for use by private consumers. The classification showed that Jaja creek at the control site fell into Class II reflecting that its water sample is suitable as sources of municipal water supply.

The overall average concentrations of Mn, Fe, Al and Pb (Table 4) in surface waters studied were higher than the WHO and USEPA limits and hence the waters portability are impaired for drinking. The only exception was the zinc with concentration lower than the USEPA limit of 5.0 mg/L. The Imo River contained Mn, Fe and Al levels of 2.52±0.71 mg/L, 0.37±0.10 mg/L and 0.77±0.13 mg/L respectively. The respective corresponding concentrations in Essene Creek were 2.62±0.42 mg/L, 0.59±0.41mg/L and 0.52±0.08 mg/L while Utaewa River contained 2.70±0.30 mg/L, 0.49±0.05 mg/L and 0.15±0.03 mg/L respectively. These metal concentrations that were above the limits may be attributed to deposits resulting from the company's smelting activity. The Imo River (IR) and Essene Creek (EC) serve as water channels to ships bringing the raw materials for the company and other commercial activities. The discharge from exhausts of ships and speed boats using leaded fuels explains the high lead levels of 0.90±0.17mg/L and 0.84±0.50 mg/L in waters from the Imo River and Essene Creek. The high concentrations of aluminium with ranges of 0.67–0.91 mg/L and 0.50–0.60 mg/L for Imo River and Essene Creek (Table 3) are not unexpected as alumina (Al_2O_3) being the major raw material used in the company splits into water bodies occasionally during off-loading to the conveyor belt.

Principal Components (PC) analysis was performed on the standardized data matrix (Table 5) of metal concentrations in surface water samples. This is necessary to explain the structure of the underlying data set. The experimental data was standardized in order to avoid mis-calculation due to wide differences in data dimensionality (Liu *et al*., 2003). Standardization tends to increase the influence of small variance and reduce of large ones. Furthermore, the standardization procedure eliminates the influence of different units of measurement and renders the data dimensionless (Benza-Deano *et al*., 2008). Liu *et al*.(2003) classified the factor loading as "strong", "moderate", and "weak" corresponding to absolute loading values of >0.75, 0.75-0.50 and 0.50-0.30 respectively. The first component (PC1) explained 62.2% of total variance (Table 5) and has strong and moderate positive metal loadings for water from Essene Creek (1.284- 1.687) and Imo River (0.499-0.515). Principal component biplot in Figure 2 indicates that Al, Pb, Co and Fe are associated with the strong and metal loadings in PC1.Essene Creek (EC) and Imo River (IR) sampling points that lie to the right of the origin on the first component axis and closer to the metal (Al, Pb, Co, and Fe) vectors have the highest metal concentrations. The control sampling points (Jaja creek) that lie to the left of the origin and far from the metal vectors have the lowest metal concentrations. It was revealed in Figure 2 that Zn and Mn accounted for 18.1 % (as indicated by PC2) of total metal load of Utaewa River. The metal loading was strong with a range of 0.959- 1.630 (Table 5) and was an indication of water pollution arising from the fall out of scrap iron and aluminium bars during navigation.

Table 6 shows that pH, total organic carbon (TOC),total organic matter (TOM), sand, silt and clay compositions of soil samples from Jetty, Cast House and Pot Room sampling points are not significantly different from the corresponding compositions of soil from the control site. Soil sample from the cast house where the smelted aluminium is processed into bars contains the highest aluminium level of 24500±3300 μg/g. The highest concentrations of Cd (2.17±0.55 μg/g), Zn (132±160 μg/g), Pb (144±48 μg/g) in the soil were above the corresponding levels of 0.125 μg/g (Cd), 59.8 μg/g (Zn), 8.62 μg/g (Pb) in smelting waste contaminated soil from Sierra Almagrera in Spain (Navarro *et al.*, 2008). On the other hand, the highest concentrations of Ni(15.2±3.7 μg/g) and Co (3.5±3.4 μg/g) were far below levels of 119 μg/g (Ni) and 16.8 μg/g (Co) reported by Navarro *et al.*(2008).

Box and Whisker plots in Figures 3 and 4 shows the distribution of Fe, Pb, Al, Co, Cd, Mn, Zn and Ni at various depths. The results indicate that Al and Zn are more abundant at 0-5cm soil depth than other metals suggesting that Al and Zn will be more readily available in soil for uptake by crops. The values for Cd, Mn, Fe and Co are highest at 10-15cm soil depth while Pb concentrations are nearly constant. The soil quality data was further subjected to cluster analysis to explore their temporal trend. A dendogram shown in Figure 5 grouped all the sampling points for soil samples into two main clusters (A and B). Cluster A includes majorly soil samples with the highest average aluminium concentration obtained from the Cast house, where bars are being packaged for export. The second cluster B includes the rest of the analyzed soil (samples from Jaja Creek, Pot Room and Jetty sites). The cluster was further divided into two sub-clusters (b_1 and b_2). Sub-cluster b_1 includes the samples from Jaja Creek (control site) while sub-cluster b_2 includes samples from the Pot room and Jetty sites. The sites in sub-cluster b_2 have similar characteristics and natural sources types. This implies that the elemental composition of soil from the control site differs significantly from what obtained for Cast House, Pot Room and Jetty soil samples. Therefore, elevated metals concentrations in soil from Cast House, Pot Room and Jetty sites indicate soil contamination resulting from smelting activity around the sites.

Concentrations of metals investigated in crops and leaf samples are shown in Table 7. Crop samples contained lower metal concentrations than soil samples. Bitter leaf, a vegetable for common people, had the highest acumulation factors of 11.4 (Cd), 3.59 (Zn), 4.71 (Mn), 12.6 (Ni), 8.82 (Fe), 52.7 (Al). The highest accumlation factor of 14.3 for Pb was observed in cassava leaves. These accumulation factors reflect the generally high levels of metals and their degrees of contamination in the crops. Also, it is intresting to infer that bitter and cassava leaves can be used successfully as biomarkers for heavy metal pollution in soil. High aluminium concentration on the leaves is attributed to the atmospheric particulate deposition occurring around the smelting area. Cluster analysis as shown in Figure 6 was able to distinguish between metal concentrations in crops from the contaminated sites and that from the control site. The classification indicates the aluminium smelter as the anthropogenic source of metal contamination for crops.

IV. Conclusion

These findings revealed that smelting activities were the dominant source of contamination of Essene Creek, Imo and Utaewa Rivers which are major sources of drinking water for the community at a far distance downstream. There was an increasing evidence of metal pollution in Ikot Abasi soil and edible crops planted on it. Further research on air quality assessment of the area is necessary in drawing a better conclusion on the overall effect of the aluminium smelting on environments of Ikot Abasi.

ACKNOWLEDGEMENTS

The authors would like to acknowledge Ikot Abasi Local Government Area for giving permission to collect samples in the area and the technical assistance given by Mrs. Iniobong Ogbonna.

References Références Referencias

1. Aittola, J-P, Paasivirta J, Vattulainen A. (1993), “Measurements of organochloro compounds at a metal reclamation plant”, *Chemosphere,* Vol. 27, pp 65–72.
2. APHA .1998. Standard methods for the examination of water and wastewater. 20th ed. Washington D.C.: American Water Works Association/Water Environment Federation.
3. Biafra Nigeria World News (BNW News). 2004. Who takes over the Aluminium Smelter Company of Nigeria? http://news.biafranigeriaworld.com/archive/2004/aug/09/201.html., (retrieved January, 2011)
4. Bouza-Deaño, R., Ternero-Rodriguez, M. and Fernandez-Espinosa, A. J. (2008), “Trend study and assessment of surface water quality in the Ebro River (Spain)”, *Journal of Hydrology,* Vol. 361, pp 227-239.
5. Cunningham M. A., Menking, K. M., David P. Gillikin, D. P., Smith, K. C., Freimuth, C. P., Belli, S. L., Pregnall, A. M., Schlessman, M. A., and Batur, P. (2010), “Influence of open space on water quality in an urban stream”, *Physical Geography,* Vol. 31, No. 4, pp 336-356.
6. Cunningham, M. A., O'Reilly, C. M., Menking, K. M., Gillikin, D. P., Smith, K. C., Foley, C. M., Belli, S. L., Pregnall, A. M., Schlessman, M. A. and Batur, P. (2009), “The suburban stream syndrome: evaluating land use and stream impairments in the suburbs”, *Physical Geography,* Vol. 30, No. 3, pp 269-284.
7. Eaton, L. J., Hoyle, J. and King, A. (1999), “Effects

of deicing salt on lowbush blueberry flowering and yield", *Canadian Journal of Plant Science,* Vol. 79, No. 1, pp 125-128.

8. Ellis, D. V. (1987), "A decade of environmental impact assessment of marine and coastal mines" *Marine mining,* Vol. 6, pp 355-417.
9. Elshahed, M. S., Najar, F. Z., Roe, B. A., Oren, A., Dewers, T. A. and Krumholz, L. R. (2004), "Survey of archaeal diversity reveals an abundance of halophilic archaea in a low-salt, sulfide- and sulfur-rich spring", *Applied and Environmental Microbiology,* Vol. 70, pp 2230-2239
10. Hart, B. T., Bailey, P., Edwards, R., Hortle, K., James, K., McMahon, A., Meredith, C and Swadling, K. (1991), "A review of the salt sensitivity of the Astralian freshwater biota", *Hydrobiologia,* Vol. 210, pp 105-144.
11. Healy, J., Bradley, S. D., Northage, C. and Scobbie, E. (2001), "Inhalation exposure in secondary aluminium smelting", Annals of Occupational Hygiene, Vol.45, No. 3, pp 217−225
12. James, K., Cant, B. and Ryan, T. (2003), "Responses of freshwater biota to rising salinity levels and implications for saline water management", *Australian Journal of Botany,* Vol. 51, pp 703-713.
13. Kaushal, S. S., Groffman, P. M., Likens, G. E., Belt, K. T., Stack, W. P., Kelly, V. R., Band, L. E., and Fisher, G. T. (2005). "Increased salinization of fresh water in the northeastern United States", Proceedings of the National Academy of Sciences of the United States of America, Vol. 102, No. 38, pp 13517-13520
14. Kozanoglou, C. and Catsiki, V. A. (1997), " Impact of products of a ferronickel smelting plant to the marine benthic life", *Chemoshere,* Vol. 34, No.12, pp 2673−2682
15. Laue, G., Herrmann D, Mo¨der M, Herzschuh R. (1994), "Analysis of slags and filter dusts from aluminium recycling processes", *Chemosphere,* Vol. 29, pp 1947–56.
16. Liu, C. W., Lin, K. H. and Kuo, Y. M. (2003), "Application of factor analysis in the assessment of groundwater quality in a blackfoot disease area in Taiwan", *Science Total Environmental,* Vol. 313, pp 77-89
17. Lofgren, S. (2001), "The chemical effects of deicing salt on soil and stream water of five catchments in southeast Sweden", *Water, Air, and Soil Pollution,* Vol. 130, pp 863-868.
18. Malea, P. and Haritonidis, S. (1995), "Local distribution and seasonal variation of Fe, Pb, Zn, Cu, Cd, Na, K, Ca and Mg concentrations in the seagrass Cymodocea nodosa (Ucria) Asehers in the Antikyra Gulf, Greece", *Marine Ecology,* Vol. 16, No. 1 pp 41-56.
19. Navarro, A., Cardellach, E., Mendoza, J.L., Corbella, M. and Domènech, L. M. (2008), "Metal mobilization from base-metal smelting slag dumps in Sierra Almagrera (Almería, Spain)", *Applied Geochemistry,* Vol. 23, No. 4 pp 895–913.
20. Norrstrom, A.-C. and E. Bergstedt. (2001), "The impact of road de-icing salts (NaCl) on colloid dispersion and base cation pools in roadside soils", *Water, Air, and Soil Pollution,* Vol. 127, No. 1-4 pp 281-299.
21. Pesce, S. F. and Wunderlin, D. A. (2000), "Use of water indices to verify the impact of Cordoba City (Argentina) on Suquia River", *Water Research,* Vol. 34, No. 11 pp 2915-2926.
22. Prati, L., Pavanello, R. and Pesarin, F. (1971), " Assessment of surface water quality by a single index of pollution", *Water Resources,* Vol. 5, p 741.
23. Proceeding of the National Academy of Sciences of the United States of America U S A. (2005), September 20; Vol. 102, No. 38, pp 13517–13520.
24. Richburg, J.A., Patterson III, W.A. and Lowenstein, F. (2001), "Effects of road salt and *Phragmites australis* invasion on the vegetation of a western Massachusetts calcareous lake-basin fen", *Wetlands* Vol. 21, No. 2, pp 247-255
25. Simeonov, V., Stefanov, S. and Tsakovki, S. (2000), "Environmentrical treatment of water quality survey data from Yantra River, Bulgaria", *Mikrochima Acta,* Vol. 134, No. 1-2, pp 15-21.
26. Sinkkonen, S., Vattulainen, A., Aittola, J-P., Paasivirta, J., Tarhanen J and Lahtipera, M. (1994), "Metal reclamation produces sulphur analogues of toxic dioxins and furans", *Chemosphere,* Vol. 28, pp 1279–88.
27. Sokal, R. R. and Rolf, F. J. (1981), "Biometry: The Principle and Practice of Statistics in Biological Research", 2nd ed. New York: W. H. Freeman Company.
28. Strayer, D. L., and L. C. Smith. (1993), "Distribution of the zebra mussel (Dreissena polymorpha) in estuaries and brackish waters", In: Nalepa, T. F. and Schloesser, D. W. (eds.). "Zebra Mussels: Biology, Impacts, and Control", Lewis Publishers, Boca Raton, Florida. pp. 715-727.
29. The International Aluminium Institute (IAI). (2000), http://www.worldaluminium.org/production/smelting/index.html.,(retrieved December, 2010).
30. United State Environmental Protection (USEPA) (1999), National recommended water quality criteria-correction: EPA 822/Z-99-001. Washington, DC.
31. Vukadin, I. and Odzak, N. (1991), " Fate and distribution of chromium in waters, sediment and mussels of the Kastela Bay", UNEP, 1991. MAP Technical Reports Series No. 59.
32. Wei Y-L. (1996), "Distribution study of priority pollutant PAHs from a laboratory aluminium-can chip smelting furnace", *Journal of Hazardous Materials,* Vol. 49, pp267–80.
33. Westberg H, Selden A. (1997), "Emissions of some

organochlorine compounds in experimental aluminium degassing with hexachloroethane", *Applied Occupational and Environmental Hygiene,* Vol. 12, pp 178–83.

34. WHO. (2006), Guidelines for drinking-water quality, 3rd ed. Retrieved Nov. 12th, 2008, from http://www.who.int/water_sanitation_health/dwq/gdwq3rev/en/index.html.
35. Winderlin, D. A., Diaz, M. P., Ame, M. V., Pesce, S. F., Hued, A. C. and Bistoni, M. A. (2001), "Pattern recognition techniques for the evaluation of spatial and temporal variations in water quality. A case study: Suquia river basin (Cordoba-Argentina)", *Water Research,* Vol. 35, pp 2881-2894.
36. World Bank. (2009). The aluminum industry in West and Central Africa. Extractive industries and development series No. 13. http://siteresources.worldbank.org/EXTOGMC/Resources/3369291266963339030/eifd13_wa_aluminum.pdf.,(retrieved January, 2011)

Table 1 : Description of sampling locations, sample code and type of sample collected

Sampling location	Sample code	Location description	Sample collected
Pot Room	PR	Located North-East (NE) of the company with respect to the main gate. It covers a wide expanse of land up to 6 hectares. The location (PR) shares the same fence with the facility where the alumina is smelted in pots. Hence the name 'pot room'.	Soil and plant
Jetty	J	This is the North of the company with respect to the gate. It is mid-point far from the PR and Cast House.	Soil and plants
Cast House	CH	Located North-West of the company with respect to the main gate. The cast house is where the smelted aluminium is cast into ingots (bars) ready for export. The sampling site shares the same fence with the Cast House.	Soil and plants
Imo River	IR	This is located south of the company with respect to the gate. It is the water that host the harbour where raw material arrives and finished product leaves.	Water
Essene Creek	EC	It is a major tributary of IR that borders the company at the far south-west. It is closer to the CH than any other facility of the company.	Water
Utaewa River	UT	The river borders the company at the far South-east (SE). It is closer to the PR and the power plant of the company than any other facility of the company.	Water
Jaja Creek (Control site)	JC	It was the reference site situated at 1 km upstream of Essene Creek. It is a drainage stream located North of the company	Water, soil and plants

Table 2 : Average values and ranges of physicochemical characteristics of the water from Imo river (IR), Essene creek(EC), Utaewa river (UR) and Jaja creek (JC)

Sampling location	pH	Temp. (^oC)	Cond. (µS/cm)	Turbidity FTU	TS (mgL^{-1})	TDS (mgL^{-1})	TSS (mgL^{-1})	Hardness (mgL^{-1})	SO_4^{2-} (mgL^{-1})	PO_4^{3-} (mgL^{-1})	NO_3^- (mgL^{-1})	DO (mgL^{-1})	COD (mgL^{-1})	Salinity (%)	Utility class
IR	6.4±0.1 6.2-6.7	24.0±0.2 23.9-24.2	21.9±0.2 21.7-22.0	3.3±0.6 3.0-4.0	1380±25 1360-1410	1370±21 1350-1390	18.7±1.5 17-20	170±2 168-172	549±71 480-622	1.14±0.11 1.03-1.21	11.1±0.2 9.8-12.8	4.8±0.2 4.0-6.2	38.7±0.6 35.0-40.2	13.0±1.1 12.0-14-2	III
EC	6.3±0.2 6.1-6.5	25.0±1.1 24.0-26.1	5.9±0.2 5.8-6.1	25.3±2.1 23.0-27.0	355±15 342-372	343±17 327-360	12.3±2.5 10-15	161±2 160-162	113±11 101-121	3.4±0.2 3.25-3.61	10.3±0.1 8.91-10.5	4.4±0.1 3.9-5.5	39.8±1.1 36.6-41.0	3.2±0.4 2.8-3.6	III
UR	6.5±1.1 6.2-7.2	26.0±0.4 24.1-26.5	6.3±0.1 5.5-6.2	25.0±2.5 22.5-27.3	452±17 412-473	430±14 401-495	22.7±1.2 19.6-23.8	165±5 153-180	120±8 101-146	2.19±0.2 1.82-2.40	11.8±0.1 10.5-12.5	4.5±0.2 4.1-5.2	44.4±0.6 40.1-49.4	4.8±0.7 4.32-5.01	III
JC	7.1±0.1 7.0-7.2	25.0±0.2 24.0-25.6	5.3±0.1 4.8-5.7	1.54±0.27 1.10-1.93	186±11 152-195	178±9 162-201	8.42±0.73 7.56-10.4	70.6±5.3 521-84.3	4.2±1.1 3.62-5.71	0.08±0.01 0.05-0.09	0.74±0.1 0.52-1.01	6.8±0.2 6.01-7.21	17.2±3.0 15.1-22.6	0.93±0.21 0.75-1.14	II

Table 3 : Average values and ranges of metal concentrations (mgL^{-1}) in water from Imo River (IR), Essene Creek(EC), Utaewa River (UR) and Jaja Creek (JC)

		Cd	Zn	Mn	Ni	Fe	Al	Pb	Co
IR	Mean±SD	< 0.001	0.08±0.03	2.52±0.71	< 0.001	0.37±0.10	0.77±0.13	0.9±0.17	0.05±0.01
	Range		0.07-0.12	1.82-3.23		0.28-0.48	0.67-0.91	0.71-1.02	0.05-0.06
EC	Mean±SD	< 0.001	0.12±0.02	2.62±0.42	< 0.001	0.59±0.41	0.52±0.08	0.84±0.50	0.03±0.01
	Range		0.11-0.14	2.14-2.92		0.46-1.05	0.50-0.60	0.80-1.90	0.01-0.06
UR	Mean±SD	< 0.001	0.15±0.02	2.70±0.30	< 0.001	0.49±0.05	0.15±0.03	0.81±0.05	0.04±0.01
	Range		0.13-0.17	2.41-3.01		0.51-0.53	0.12-0.18	0.75-0.99	0.03-0.04
JC	Mean±SD	< 0.001	0.02±0.01	0.42±0.10	< 0.001	0.10±0.03	0.04±0.01	0.49±0.03	0.02±0.01
	Range		0.01-0.04	0.32-0.52		0.07-0.13	0.04-0.05	0.39-0.59	0.01-0.03

Table 4 : Water quality standards compared with the overall water quality of rivers and creeks in the vicinity of aluminium smelting company.

Parameter	*Mean±SD	Range	Water Quality Standard		
			^{a}WHO	^{b}USEPA	^{c}New Zealand
Temperature (^{o}C)	24.7±0.9	23.9-26.5	27 – 28	-	-
Conductivity (µS/cm)	12.8±2.5	5.5-22	1000	-	-
pH	6.4±0.3	6.1-7.2	6.5 - 9.2	6.5 – 8.5	-
Turbidity (NTU)	16±12	3.0 – 27.3	5	-	-
TDS (mg/L)	793±250	327-1390	1000	500	-
TSS (mg/L)	16.4±4.4	10 – 23.8	-	-	-
TS (mg/L)	809±540	342-1410	-	-	-
Total hardness (mg/L)	166±5	160-172	500	-	-
DO (mg/L)	4.67±0.3	3.9-6.2	6	-	-
Salinity (%)	7.6±2.8	2.8-14.2	0.5	-	-
COD (mg/L)	40.3±0.9	35.0-49.4	-	-	-
SO_4^{2-} (mg/L)	300±230	101-622	400	250	-
PO_4^{3-} (mg/L)	2.25±1.1	1.03-3.61	0.51 - 3.50	-	-
NO_3^- (mg/L)	9.11±0.6	8.91-12.8	50	10	50
Cd (mg/L)	-	<0.001	0.003	0.005	0.004
Zn (mg/L)	0.11±0.03	0.06-0.14	5	5.0	-
Mn (mg/L)	2.59±0.48	1.82-3.23	0.4	0.05	0.4
Ni (mg/L)	-	<0.001	0.07	-	0.08
Fe (mg/L)	0.49±0.27	0.28-1.05	0.05 - 0.36	0.3	-
Al (mg/L)	0.57±0.25	0.12-0.91	0.2	0.05 – 0.2	0.1
Pb (mg/L)	0.85±0.43	0.71-1.90	0.01	0.015	0.01
Co (mg/L)	0.04±0.02	0.01-0.06	-	-	-

WHO= WHO Drinking water guidelines, USEPA= US Environmental Protection Agency. ^{a}*Source*= WHO (2006), ^{b}*Source*= USEPA (1999), ^{c}*Source*= New Zealand (2005), *= Overall mean of water quality of Imo river, Essene creek and Utaewa river(This study)

Table 5 : Principal components analysis scores (loadings) of metal concentrations on the first six rotated principal components (PCs) for various sampling locations.

Sampling location	PC1	PC2	PC3	PC4	PC5	PC6
IR-1	0.499	-0.758	-0.976	-0.589	0.460	0.002
IR-2	0.515	-1.083	-1.095	0.181	-0.051	-0.002
IR-3	0.512	-0.039	-0.770	0.877	-0.431	0.002
EC-1	1.775	-0.203	0.503	-0.392	-0.330	-0.008
EC-2	1.284	-0.530	0.536	-0.848	-0.330	0.005
EC-3	1.687	-0.868	1.137	0.926	0.353	0.001
UR-1	0.509	0.959	0.210	-0.166	0.303	0.003
UR-2	0.287	1.297	-0.191	0.108	-0.086	-0.003
UR-3	0.882	1.630	-0.246	0.018	0.148	0.001
JC-1	-2.412	0.091	0.326	0.028	-0.304	0.005
JC-2	-2.502	-0.349	0.416	-0.117	0.060	0.00001
JC-3	-2.638	-0.147	0.152	-0.026	0.207	-0.007
% Variance	62.2	18.1	11.0	6.45	2.21	0.0004
%Total Variance	62.2	80.3	91.3	97.8	100	100
Eigenvalue	2.57	0.75	0.456	0.27	0.09	0.00002

Table 6 : Average levels and range of physicochemical properties of soil samples from sampling locations – Jetty, Cast House, Pot Room and Jaja Creek

	Jetty (J)		Cast House (CH)		Pot Room (PR)		Jaja Creek – Control site (JC)	
	Mean±SD	Range	Mean±SD	Range	Mean±SD	Range	Mean±SD	Range
pH	6.4±2.4^{a}	4.2-9.0	8.0±2.4^{a}	5.5-10.3	7.4±4.5^{a}	3.0-7-1	7.1±0.4^{a}	6.8-7.5
TOC (%)	0.88±0.70^{a}	0.09-1.39	0.66±0.04^{a}	0.61-0.68	0.49±0.33^{a}	0.29-0.87	0.78±0.15^{a}	0.62-0.91
TOM (%)	0.15±0.12^{a}	0.02-0.24	0.11±0.01^{a}	0.10-0.12	0.08±0.06^{a}	0.05-0.15	0.10±0.01^{a}	0.10-0.11
Sand (%)	59.2±2.4^{c}	56.4-60.8	42.5±2.0^{a}	40.4-44.4	51.1±2.3^{b}	48.4-52.4	60.9±3.0^{c}	58.2-64.2
Silt (%)	5.2±5.5^{a}	0.40-11.2	3.2±1.6^{b}	1.6-4.8	8.9±3.9^{a}	5.6-13.2	7.0±1.6^{a}	8.4-7.4
Clay (%)	35.7±3.4^{a}	32.4-39.2	54.3±0.5^{b}	54.0-54.8	40.0±5.8^{a}	34.4-46.0	32.1±4.6^{a}	27.4-36.5
Cd (mg/kg)	1.9±0.7^{b}	1.20-2.60	2.17±0.55^{b}	1.60-2.70	1.43±0.57^{b}	0.80-3.20	0.14±0.15^{a}	0.06-0.32
Zn (mg/kg)	39±42^{a}	8.50-87.7	127±170^{a}	18.7-319	132±160^{a}	29.6-41.8	14.0±5.8^{a}	9.65-20.5
Mn (mg/kg)	21.9±8.2^{a}	13.4-29.8	88±19^{ab}	76.6-109	164±130^{b}	104-311	11.0±2.1^{a}	8.94-13.2
Ni (mg/kg)	13.2±4.7^{ab}	8.5-17.8	15.2±3.7^{b}	12.9-19.5	12.6±1.3^{ab}	11.1-13.5	7.7±1.7^{a}	7.68-9.3
Fe (mg/kg)	1690±200^{b}	1490-1890	2250±23^{c}	2220-2260	2230±79^{c}	2140-2290	1240±210^{a}	1067-1478
Al (mg/kg)	9680±540^{a}	9320-10300	24500±3300^{bc}	21000-27500	17700±6600^{b}	12300-15800	5440±1200^{a}	4562-6780
Pb (mg/kg)	27.4±3.9^{a}	24.8-32.0	111±43^{b}	83.0-161	144±48^{b}	163-184	23.9±3.6^{a}	20.8-27.9
Co (mg/kg)	0.27±0.30^{a}	<0.001-0.6	1.60±0.45^{a}	1.1-2.0	3.5±3.4^{a}	1.9-7.5	0.02±0.01^{a}	0.01-0.03

Mean values with different superscripts in a row are significantly different at p=0.05; Total Organic Carbon (TOC), Total Organic Matter (TOM)

Table 7 : Average metal concentrations (μg/g) and the accumulation factors (AF) in plants from the vicinity of aluminium smelting company and control site.

Plant type	Sample code	Cd, μg/g (AF)	Zn, μg/g (AF)	Mn, μg/g (AF)	Ni, μg/g (AF)	Fe, μg/g (AF)	Al, μg/g (AF)	Pb, μg/g (AF)	Co, μg/g (AF)
*Bitter leave	BL	0.8(11.4)	141(3.59)	27.3(4.71)	4.8(12.6)	179(8.82)	1830(52.7)	18.3(5.34)	<0.001(NA)
*Cassava leave	CL	0.5(2.38)	142(2.53)	148(3.73)	5.7(2.71)	112(2.96)	2170(38.3)	38.7(14.3)	<0.001(NA)
*Paw-paw	PL	0.9(15.0)	147(1.94)	15.0(3.88)	8.3(2.87)	68.4(5.56)	1830(37.4)	16.4(6.83)	<0.001(NA)
**Bitter leave (from control site)	PLC	0.07	39.3	5.8	0.38	20.3	347	0.34	<0.001
**Cassava leave (from control site)	CLC	0.21	56.2	39.7	2.1	37.9	567	0.27	<0.001
**Paw-paw (from control site)	PLC	0.06	75.9	3.87	2.89	12.3	489	0.24	<0.001

(*) = Each value in the row is an overall average concentration of nine determinations and
(**) = Each value in the row is an overall average concentration of triplicate determinations
NA = Not applicable

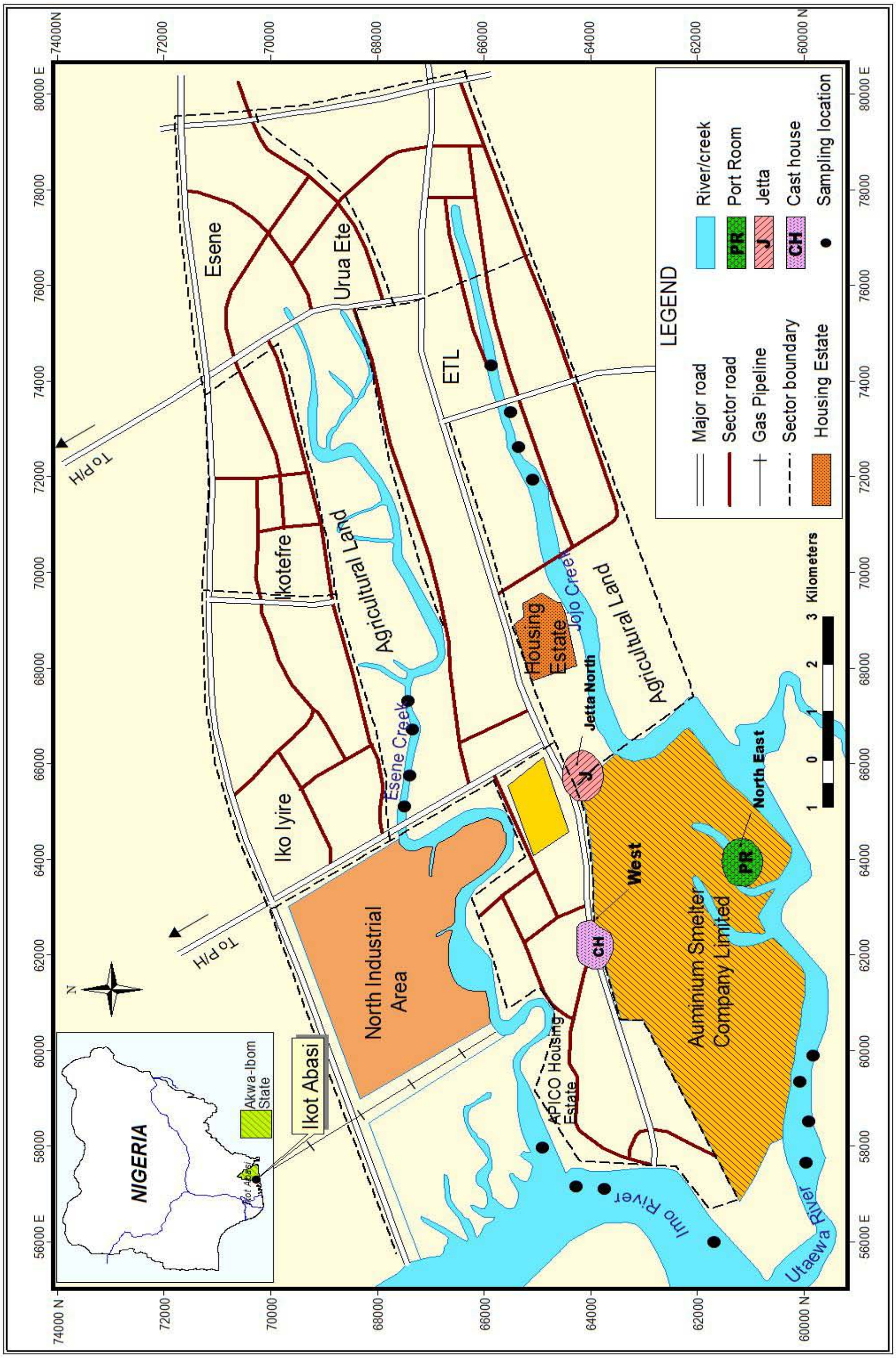


Figure 1 : Map of the study area showing the various sampling locations

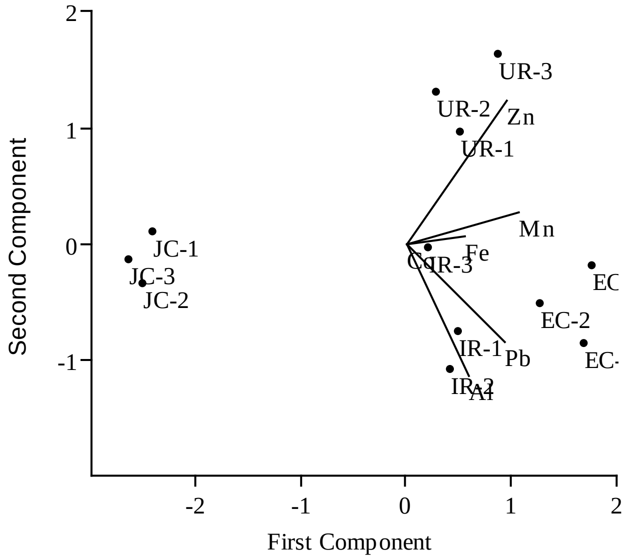


Figure 2 : Principal component biplot of heavy metal concentrations in Imo River (IR), Utaewa River (UR), Essene Creek(EC) and Jaja Creek (JC).

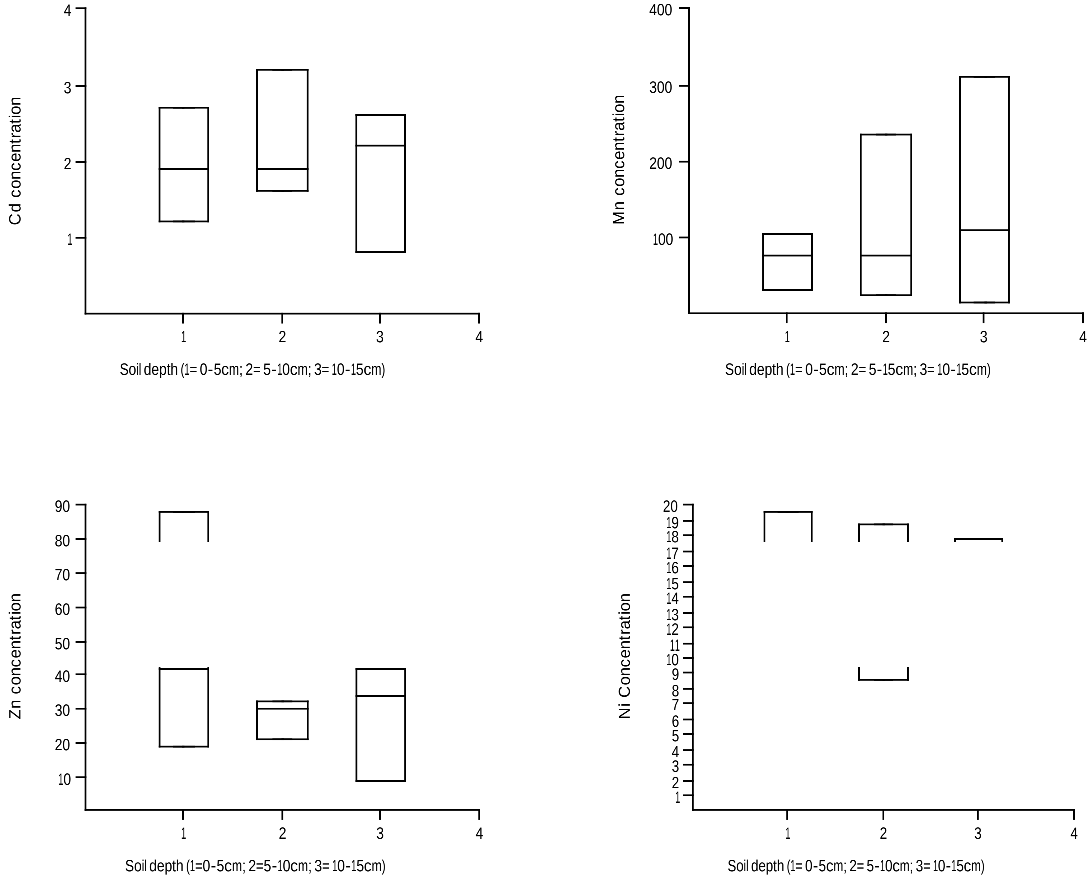


Figure 3 : Distribution of Cd, Mn, Zn and Ni concentrations (μg/g) within the soil profile.

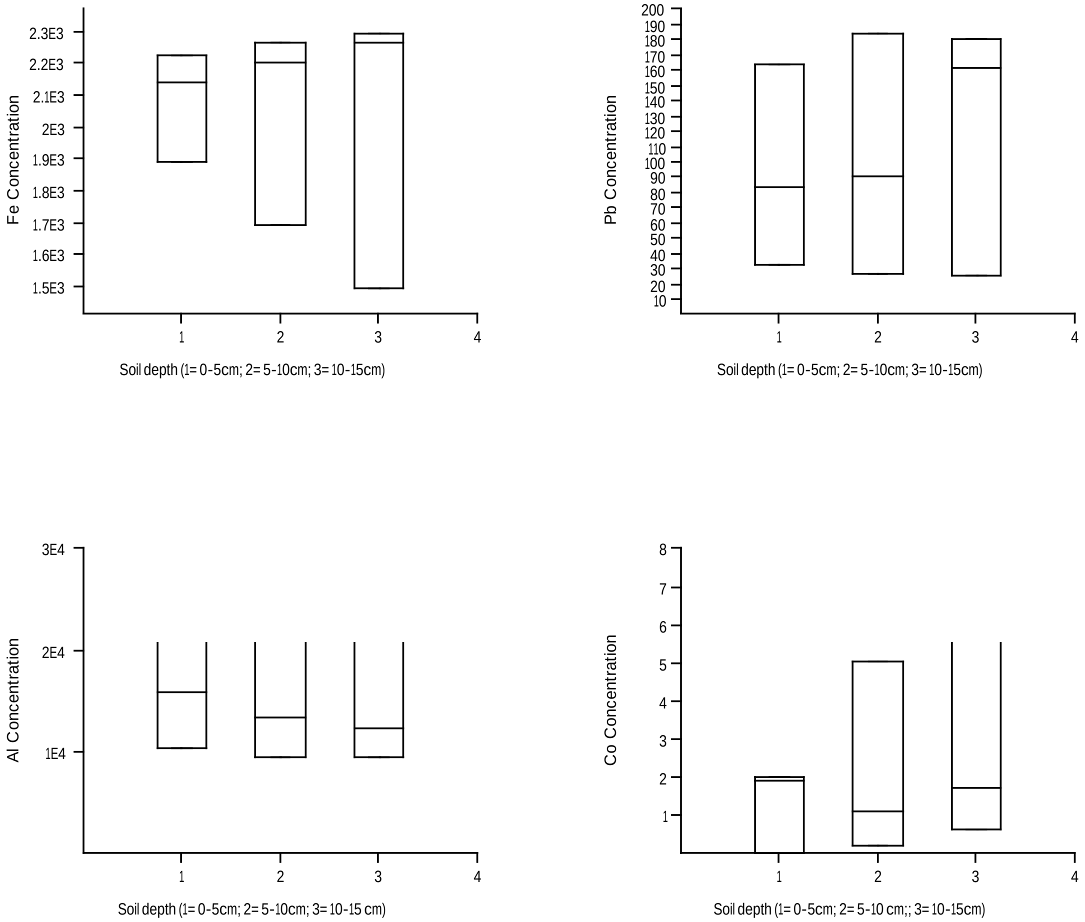


Figure 4 : Distribution of Fe, Pb, Al and Co concentrations (μg/g) within the soil profile.

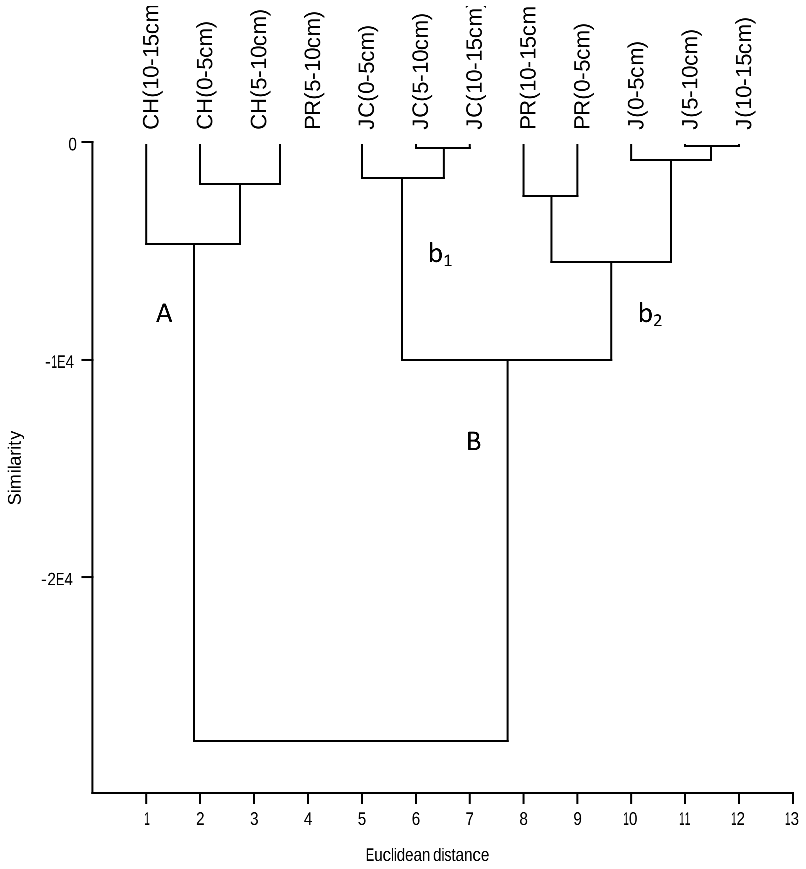


Figure 5 : Dendogram showing clustering of sampling on soil from various locations (Pot room=PR; Jetty= J; Cast House= CH, Jaja Creek= JC).

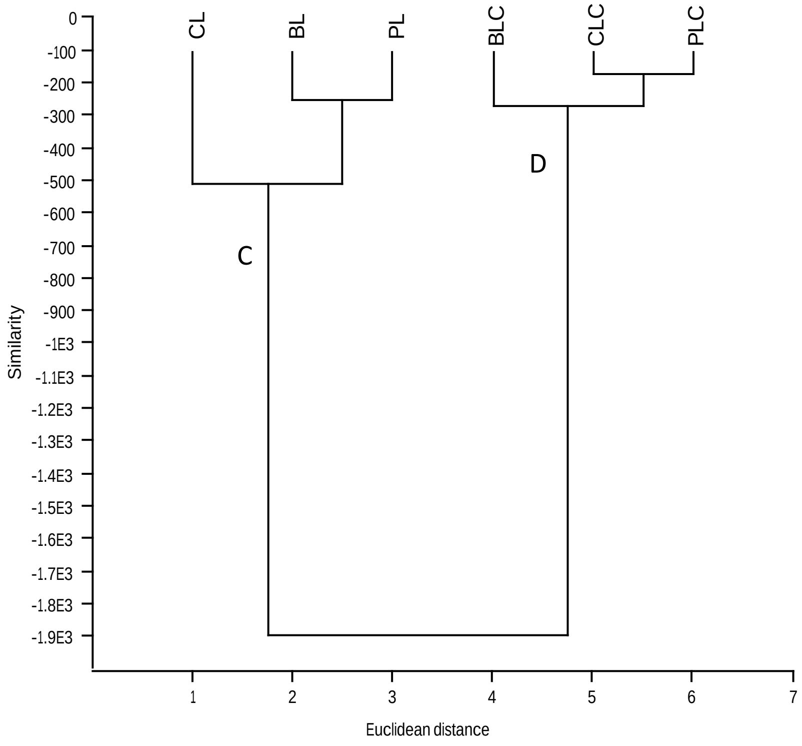


Figure 6 : Dendogram showing classification of metals concentrations in plants (Cassava leave= CL; Bitter leave=BL; Paw-paw=PL) from sampling sites and control site (Cassava leave= CLC; Bitter leave=BLC; Paw-paw=PLC).

This page is intentionally left blank

GLOBAL JOURNAL OF SCIENCE FRONTIER RESEARCH
CHEMISTRY
Volume 12 Issue 1 Version 1.0 January 2012
Type : Double Blind Peer Reviewed International Research Journal
Publisher: Global Journals Inc. (USA)
Online ISSN: 2249-4626 & Print ISSN: 0975-5896

Inhibition of Mild Steel Corrosion Using Plectranthus Tenuiflorus (Shara) Plant as Safe and Green Inhibitor in Acidic Solutions

By Aisha M. Al-Turkustani, Nabeeh M. Al-Marhabi
King Abdulaziz University, Jeddah KSA

Abstract - Plectranthus tenuiflorus (Shara) plant was investigated as safe (green) inhibitor on the corrosion of mild steel in 2.0 M H_2SO_4 solution using weight loss and hydrogen gas evolution technique. The results showed that Shara plant aqueous extract is good inhibitor for mild steel in this medium. The inhibition efficiency increases with the inhibitor concentration and decreases with rising temperature. The inhibition is attributed to adsorption of the inhibitor molecules on mild steel surface. Adsorption characteristics of the aqueous extract of Shara plant were approximated by Langmuir adsorption isotherm. Effect of temperature is studied in the range (30-70) ^{o} C and determination of activation parameters is also discussed.

Keywords : Mild steel; corrosion; plectranthus tenuiflorus (Shara); acidic solutions.

GJRE Classification : FOR Code: 070105, 030201

INHIBITION OF MILD STEEL CORROSION USING PLECTRANTHUS TENUIFLORUS SHARA PLANT AS SAFE AND GREEN INHIBITOR IN ACIDIC SOLUTIONS

Inhibition of Mild Steel Corrosion Using *Plectranthus Tenuiflorus (Shara)* Plant as Safe and Green Inhibitor in Acidic Solutions

Aisha M. Al-Turkustani [α], Nabeeh M. Al-Marhabi [Ω]

Abstract - Plectranthus tenuiflorus (Shara) plant was investigated as safe (green) inhibitor on the corrosion of mild steel in 2.0 M H_2SO_4 solution using weight loss and hydrogen gas evolution technique. The results showed that *Shara* plant aqueous extract is good inhibitor for mild steel in this medium. The inhibition efficiency increases with the inhibitor concentration and decreases with rising temperature. The inhibition is attributed to adsorption of the inhibitor molecules on mild steel surface. Adsorption characteristics of the aqueous extract of *Shara* plant were approximated by Langmuir adsorption isotherm. Effect of temperature is studied in the range (30-70) ° C and determination of activation parameters is also discussed.

Keywords : Mild steel; corrosion; plectranthus tenuiflorus (Shara); acidic solutions.

I. INTRODUCTION

The meaning of the word corrosion is the substance usually a metal or its alloys which change in its properties because of a reaction with its environment. Normally it specifically applies to metals. Corrosion causes enormous losses which rise yearly with the increased using of metals industrial development. The accepted concept of the corrosion is that it is a result of an electrochemical reaction taking place on the surface of the metal where the metal is converted in to metal oxides or other corrosion products with some metals.

Corrosion affects most of industrial sector and may cost billions of dollars each year for preventing and replacement of maintenance [1]. Thus, modern world today made an investigation to overcome this problem by doing enrichment study of corrosion inhibitors. Mild steel (MS) is a material of choice and it is finds application in many industries, due to low cost and easy availability and good tensile strength besides various other desirable properties, ease to fabricate Various reaction vessels, pipes, tanks etc., in most of the chemical industries but it suffers from severe corrosion in aggressive environments [2]. Acids are used to remove oxides, shop - soil and other contaminants from metal surfaces. Acids are also used for derusting and pickling, the cleaning of refinery equipment oil well acidizing and acid descaling and the removal of calcareous deposits from boilers. Radiators of vehicles, pipelines carrying water or petroleum products heat exchangers, etc. [3].Although there are numerous options for controlling the corrosion of metals, the use of inhibitors is one of the best methods of protecting metals against corrosion.

Corrosion inhibitors are widely used in industry to reduce the corrosion rate of metals and alloys in contact with aggressive environments. Most of the corrosion inhibitors are synthetic chemicals, expensive and very hazardous to environments. Therefore, it is desirable to source for environmentally safe and green inhibitors [4,5].Natural products can be considered as a good source for this purpose. The possible replacement of some expensive chemicals as corrosion inhibitors for metals in acid cleaning process by naturally occurring substances of plant origin has been studied [6-13].

The aim of this study was to investigate the inhibition effect of *Plectranthus tenuiflorus (Shara)* plant as a cheap, safe, green, raw and non- toxic corrosion inhibitor on mild steel corrosion in sulphuric acid solution.

II. EXPERIMENTAL

a) Material

i. *Inhibitor*

Plant peraparation: *Shara* plant leaves were collected from Jeddah region; Saudi Arabia (Figure 1).

Plectlranthus tenuiflorus (Euphorbiaceae family), is the generic name for *Shara*, a perennial succulent herb; having a pleasantly aromatic juice. *Shara* her it is a large genus of the Lamiaceae family widely distributed in tropical regions of Africa, Asia and Australia [14-16] that natively grows in western and southern region of Saudi Arabia [17,18]. Several *Plectranthus* species are cultivated as ornamentals or as sources of essential oils, whereas other are used as edible tubers, or as food flavorings [15,19]. In folk medicine, they are employed for headaches, sores, burns, dermatitis, acute edematous otitis acuta, stomachache, against nausea, scorpion stings and as purgative [20-24]. In Western region, it is used as eardrop for earache and inflammation of middle ear

---

About [α]: King Abdulaziz University, Girls College, Chemistry Department, Jeddah KSA. E-mail : (a.m.turkustani@hotmail.com)
About [Ω]: King Abd El- Aziz University, Girls College, Chemistry Department, Jeddah, KSA. E-mail : (ao-ao-55@hotmail.com)

[23], whereas it is prescribed in Asia for a remedy sore throat [18].

Stock solution of aqueous extract of *Shara* plant were prepared by weighing 120 g of chopped leaves mixing (blending) in a blender with 200 ml de-ionized water for 15 minuts, heating until 90° C (before boiling). The mixture is cooled for 24 hours. The aqueous extract was separated by filtration and then kept the filtrate solution in a flask at low temperatures in a refrigerator. From the stock solution of aqueous extract of *Shara* plant, the inhibitor test solutions were prepared in a concentration range (1.0%v/v – 30%v/v).

ii. *Specimen*

The metal used for the study was mild steel electrode of the chemical composition was (wt%) P (0.035), Si (0.03), Mn (0.5), Cr (0.9), C (0.38) and Fe (97.64), it was a rod with the length is 4.0 cm and diameter is 1.0 cm. The specimen surface was polished with different grade of emery papers (60, 120, 220, 400, 600, 800 and 1200), washed with de-ionized water, degreased with acetone and dried with a stream of air and weighed.

iii. *Solution*

All chemicals used were of analytic grade. The blank corroding solution was H_2SO_4 (PAI-Panreac). Appropriate concentration (2.0 M) of acid solution was prepared using de-ionized water in the absence and presence of various concentrations of aqueous extract of *Shara* Plant.

b) *Methods*

i. *Hydrogen gas evolution (Gasometric) method*

The gasometric assembly used for the measurement of hydrogen gas evolution from the reaction was as originally described [12,25]. A reaction vessel was connected to a burette through a delivery tube. The 2.0 M H_2SO_4 solution was introduced into a two-necked flask, and the initial volume of air in the burette was recorded. Thereafter, mild steel sample was dropped into the H_2SO_4 solution, and the flask quickly closed. The volume of H_2 gas evolved from the corrosion reaction was monitored by the volume change in the level of the paraffin oil. The change in volume was recorded every 5 min. for 60 min. The same experiment was repeated in the presence of the inhibitor.

Hydrogen gas evolution measurements were carried out at 30, 40, 50, 60 and 70° C. From the volume of hydrogen gas evolved per minute, corrosion rate (R), inhibition efficiency (%I) and degree of surface coverage (θ), were calculated using equations 1, 2 and 3, respectively.

$$R\ (\mathrm{ml\ cm^{-2}}) = (V^0_{Ht} - V^1_{Ht}{}') / t \qquad (1)$$

$$\%I = [1 - V^1_{Ht} / V^0_{Ht}] \times 100 \qquad (2)$$

$$\theta = \%I / 100 \qquad (3)$$

Where V^1_{Ht} is the volume of hydrogen gas at time t for inhibited solution and V^0_{Ht} is the volume of hydrogen gas evolved at time t for uninhibited solution.

ii. *Weight loss (Gravimetric) method*

After complete of each test mild steel sample is separated from the test solution, washed with de-ionized water and with acetone, dried with stream of air and then re-weighting. From the weight loss results, the corrosion rate (R`), inhibition efficiency (%I) of the inhibitor and degree of surface coverage (θ), were calculated using equations 4, 6 and 7, respectively,

$$R`\ (\mathrm{g\ h^{-1}\ cm^{-2}}) = W/At \qquad (4)$$

$$\%I = (1 - W_1 / W_2{}^{\circ}) \times 10 \qquad (5)$$

$$\theta = 1 - W_1/W_2$$

Where W_1 and W_2 are the weight losses (g/dm^3) for mild steel in the absence and presence of the inhibitor in H_2SO_4 solution, respectively, and θ is the degree of surface coverage of the inhibition.

III. RESULTS AND DISCUSSION

a) *Effect of inhibitor concentration*

Figure (2) shows the relation of hydrogen gas with time for mild steel corrosion in 2.0 M H_2SO_4 solution in the absence and presence of different concentrations of aqueous extract of *Shara* plant at 30° C. It is clear that, at low concentration (1.0%v/v) for the aqueous extract of *Shara* plant acceleration of the corrosion occurs (increase in the slope of the curve), and the corrosion rate decrease by increasing the concentration of the extract of *Shara* plant. Similar results were obtained from weight loss measurements. Table (1) illustrate the corrosion rates (R' and R) and inhibition efficiency (I%) obtained from WL and HE, respectively.

From Table (1), it can be seen that the values of corrosion rate for mild steel in 2.0 M H_2SO_4 solution containing aqueous extract of *Shara* plant decreased as concentration of inhibitor increased from the two methods, and the inhibition efficiency increase. This results are due to that the adsorption amount and coverage of inhibitor on mild steel surface increases by increasing the inhibitor concentration, except at low concentration (1.0%v/v) of the inhibitor which give an increase in corrosion rate (acceleration) from the two methods.

b) *Adsorption isotherm*

The nature of inhibitor interaction on the corroding surface during corrosion inhibition of metals has been deduced in terms of adsorption characteristics of the inhibitor. The decrease in the corrosion rate by the addition of aqueous extract of *Shara* plant is attributed to either adsorption of the plant components on the metal surface or, the formation of a barrier film separating the metal surface from the corrosive medium [26, 27].

Figure (3) shows the relation between I% and $\log C_{inh}$ for the investigated extract from hydrogen evolution (Gasometric) and weight loss (Gravimetric) methods. As can be readily seen, the plots have the form of *S*-shaped adsorption. This indicates that the aqueous extract of *Shara* plant inhibit the acid dissolution for mild steel by adsorption the molecules of the *Shara* plant at metal acid solution interface, also the obtained figure indicated one step of adsorption .

Basic information on the interaction between the inhibitor and the mild steel surface can be provided by the adsorption isotherm. For this purpose, the values of surface coverage (θ) at different concentrations of *Shara* plant in 2.0 M H_2SO_4 have been evaluated from weight loss and hydrogen evolution measurements using the equations (7) and (8) to explain the best isotherm to determine the adsorption process from the experimental data obtained.Attempts were made to fit these θ values to various isotherms including Frumkin, Langmuir, Temkin and Freundlich. An excellent fit was obtained for aqueous extract of *Shara* plant, using the following Langmuir adsorption isotherm equation [28].

$$\Theta = KC_{EX} / 1 + KC_{EX} \qquad (7)$$

$$C / \Theta = 1/K + C \qquad (8)$$

Where C_{EX} is the concentration of aqueous extract of *Shara* plant, K is adsorption constant and θ is degree of coverage. It can be seen from Figure (4) using equation (8) that straight lines of a slope less than unit is found. The slopes of the C/Θ versus C plots show deviation from unity, which can be attributed to the molecular interaction between the adsorbed inhibitor species on mild steel surface [29, 30].

The values of adsorption constant ($K_{ads.}$) and the standard free energy of adsorption ($\Delta G^\circ_{ads.}$) were calculated using the equation:

$$\ln K = \ln 1/55.5 - \Delta G^\circ_{ads} / RT \qquad (9)$$

Where one molecule of water is replaced by one molecule of inhibitor [31, 32]. The numerical value (1/55.5) in equation (9) stands for the molarity of water. The values of $K_{ads.}$ and $\Delta G^\circ_{ads.}$ for aqueous extract of *Shara plant* were recorded in Table (2). The negative ΔG°_{ads}. values are consistent with the spontaneity of the adsorption process and the stability of the adsorbed layer on the mild steel surface [33]. It generally accepted that the values of ΔG°_{ads}. up to -20 kJ mol^{-1} the types of adsorption were regarded as physisorption, the inhibition acts due to the electrostatic interaction between the charged molecules and the charged metal, while the values around -40 kJ mol^{-1} or smaller, were seen as chemisorptions, which is due to the charge sharing or a transfer from the inhibitor molecules to the metal surface to form covalent bond [34, 35]. The ΔG°_{ads}. values obtained in this study equal to -46.31 to -52.89 kJ mol^{-1}. It was suggested that the adsorption mechanism of investigated inhibitor on mild steel in 2.0 M H_2SO_4 solution was typical of chemisorptions.

c) *Effect of temperature on the performance of Shara inhibitor*

To gain insight into the nature of inhibitor adsorption, the effect of temperature (30, 40, 50, 60, and 70° C) on the corrosion behavior of mild steel in the absence and presence of 5%v/v of aqueous extract of *Shara* plant was studied by weight loss and hydrogen evolution measurements. Figures (5 and 6) show the results of HE for mild steel corrosion in 2.0 M H_2SO_4 in the absence and presence of fixed concentration (5%v/v) of aqueous extract of *Shara* plant at different temperatures from 30 to 70° C. The obtained results (R' and R) and I% are given in Tables (3 and 4) and Figures (7 and 8). It is clear that, the corrosion rate of mild steel in the absence and presence of *Shara* extract increased with rising temperature, this is due to an increase in temperature usually accelerates corrosive processes, particularly in media in which H_2 gas evolution accompanies corrosion, giving rise to higher dissolution rates of the metal.The plots in Figure (8) show that the inhibition efficiency generally decreased with rising temperature apart from the observed increase in 40° C. The increase in inhibition efficiency with rising temperature can be explained may be to the synergistic effect between the molecules of the compounds occurs in *Shara* plant extract. The decrease in inhibition efficiency with increasing temperature may be attributed to a possible shift of the adsorption-desorption equilibrium towards desorption of some adsorbed inhibitor molecules from the mild steel surface due to increased solution agitation resulting from higher rates of H_2 gas evolution at higher temperatures. This shows a weak adsorption interaction between mild steel surface and the inhibitor [11, 36-39].

The apparent activation energy (E_a), enthalpy and entropy (ΔH^o and ΔS^o) for the corrosion process in the absence and presence of *Shara* extract were calculated from Arrhenius equation [40].

$$\log R = -E_a / 2.303\, RT + A \qquad (10)$$

Where A is the pre-exponential factor and *R* is universal gas constant and T is absolute temperature, and from (b) the transition-state equation

$$\log R / T = (\log R / Nh + \Delta S^o / R) - \Delta H^o / 2.303\, R \qquad (11)$$

Where *h* is plank's constant and N is Avogadro's number.

A plot of logR from ML and HE methods against1/T gives a straight lines with slope of $-E_a/2.303R$, as shown in Figure (9), E_a values for the corrosion were estimated and recorded in Table (5).

It was found that E_a value for mild steel corrosion obtained in free acid solution are of the same order of magnitude as those observed by other authors [41-43] for mild steel corrosion in some acid media. It is also of the order of activation energies encountered for the hydrogen evolution reaction. This is in accordance with the fact that the hydrogen evolution reaction in the absence of inhibitor is the rate-determining step for the overall corrosion reaction. However, the average value for the inhibited solutions is higher than that for the uninhibited solution (Table 5), indicating a strong adsorption of the inhibitor at the metal surface which leads to increase the energy barrier for the corrosion process. On the other hand, it is in the order of activation energies of diffusion processes [9, 13, 44, 45].

A plot of logR/T against 1/T (Equation 11) also gives a straight lines, as shown in Figure (10). The slopes of these lines are $-\Delta H^{\circ}/2.303R$ and the intercept is $\log R/Nh+\Delta S^{*}/R$, from which the values of ΔH° and ΔS° were deduced (Table 5). It is clear for the inhibited solution, according to Antropov and Grigoryev [46] the presence of inhibitor leads the corrosion system to pass from less random to more orderly arrangements, and hence a less negative value of entropy is observed. Values of the entropy of activation ΔS° in the absence and in presence of the studied inhibitor are negative. This implies that the activated complex in the rate determining step represents an association rather than a dissociation step [43]. This means that the activated molecules were in higher order state than that at the initial stage [47, 48].

d) Mechanism of inhibition

The obtained results indicated that aqueous extract of *Shara* plant performs a good inhibition for the corrosion of mild steel in H_2SO_4 acidic solution.

Shara plant comprises of two substances: essential oil, in which Thymol (85.3%) is the principle component. And, the whole substance leaues juice containing oxygenated trypenoids, mono terpinoid substances, seven amino acids (Ala, leu, Glu, Asp, Asn, phe and His) and several minerals including Ca, Mg and Zn [49].

The main components of *Shara* plant are hydroxyl aromatic compounds, phynolic compounds such Thymol, Tannius, Amino and Triple terbens. Such compounds facilitates the formation of a complex with the dissolved iron ions. The formation of insoluble complex on the metal surface isolates the metal from the aggressive solution and therefore inhibits the corrosion process.

IV. CONCLUSION

Results obtained from the two methods employed revealed that:

1. The aqueous extract of Shara plant is an effective inhibitor for mild steel corrosion in 2.0 M H2SO4.
2. The inhibition efficiency of the extract increases by increasing the extract concentration and decrease when rising temperature.
3. The inhibition efficiencies obtained by weight loss and hydrogen evolution methods are in reasonably good agreement.
4. The adsorption of the extract on mild steel surface in an acidic medium follows Langmuir adsorption isotherm.
5. The inhibition mechanism was further corroborated by the values of activation parameters obtained from the experimental data.

REFERENCES REFERENCES REFERENCIAS

1. P. R. Roberge*, Mc Graw Hill* (2008) 19.
2. M. J. Sanghvi; S. K. Shukla ; A. N. Misra; M. R. Padh and G. N. Meiita, *Bull of Electrochemistry,* 13 (8-9) August –September: (1997) 358.
3. Kumkum Srivastava and Poonam Srivastava, *Corrosion preventlon & control* (1980) 1.
4. H. Ashassi-Sorkhabi; M. R. Majidi and K. Seyyedi, *Applied Surface Science,* 225 (2004) 176.
5. A.Y. El-Etre, *Corros. Sci.,* 40 (1998) 1845.
6. A. M. Al-Turkustani; S. T. Arab and L. S. S. Al-Qarni, *J. Saudi Chem. Soc.,* 15 (2011) 73.
7. M. Benabdellah; M. Benkaddour; B. Hammouti; M. Bendahhou and A. Aouniti, *Elsevier,* 1(2006).
8. A.Chetouani; B. Hammouti and M. Benkaddour, *Emeraid.,* 33 (1) (2004) 26.
9. E. A. Noor, *Egypt. J. Chem.* 47 (3) (2004) 305.
10. N. C. Oforka and E. E. Ebenso, *J. Corrs. Eng.,*1(2004).
11. E. E. Oguzie, *Mater. Chem. & Phys.* 99 (2006) 441.
12. K.O. Orubite and N. C. Oforka, *Elsevie ,* (2004) 1.
13. R. Subha and R. Saratha, *J. Corrs. Sci. Eng.,* 10 (2006) 1.
14. I. E. Codd, lamiaceae. In: Flora of southern Africa, leistner, O.A.(Ed). Vol.27, BRI, Department of Agriculture and water supply, *Pretoria, South Africa,* (1985) 137.
15. I. Ascensao; I. Mota and M. M. De Castro, *Ann. Bot.,* 84 (1999) 434.
16. M. H. A. Abdel Mogib; Albar H. and S.M. BaHerjee, *Chemislry of the genus Plectran thus. Molecules,* 7 (2002) 271.

17. S. Collenette, "Wild Flowers of Saudi Arabia" Ist Edn, *Internahoual Asclepiad society publisher ltd, London* (1998).
18. M. A. Rahmm; T. S. Mossa; M. S. Al-said and M. A. Al-yahya, *Fitoterapia,* 75 (2004) 149.
19. E. Perro, *Matieres Premieres Usuellesdu Regne Vegetal Masson, Paris,* (1994) 1689.
20. V.B. Dash and V. L. K. Shyap, *Concept publishing Co., New Delhi,* (1987) 711.
21. S., C. Cosentino; T. G. Tuberose; B. Pisano; M. Satta; V. Mascia and F. Palmas, *Lett. Applied Microbiol.,* 29 (1999) 130.
22. F. Cateni; G. Falsone and J. Zilic, *Mini Rev Med Chem.,* 5 (2003) 425.
23. M. Chandrasekaran and V. Venkatesalu, *S. ,J. Ethnopharmacol.,* 91(2004) 105.
24. K. J. Kim; H. H. Yu; S. I. Jeong; T. D. Cha; S. M. Kim and Y. O. You, *J. E. Thnopharmacol,* 91 (2004) 81.
25. A. I. Onuchukwu, "The kinetics and mechanism of hydrogen evolution on corroding aluminum in alkaline medium" *Mater. Chem.& Phys.,* 25 (1998) 227.
26. A.S. Fouda and M. El-Semongym, *J. India Chem. Soc., LIX,* 89 (1982).
27. S.T. Arab; A. M. Al-Turkustani and S.Y. Al-Nami, *J. Kor. Chem. Soc.,* 52 (3) (2008) 281.
28. A.El-Awady; B. A. Abd El-Nabey; S. Aziz; M. Khalifa; H. Al-Ghanedy, *Int.J.chem.,* 1 (1990) 169.
29. A. Azim; L. A. Shalaby and H. Abbas, *Corros. Sci.,* 14 (1974) 21.
30. M. A. Migahed; H. M. Mahammed and A. M. Al-Sabagh, *Mater. Chem.& Phys.* 80 (2003) 169.
31. I'O. Bockris; D. A. Swinkls, *J. Electrochem. Soc.,* 111 (1964) 736.
32. A.Y. El-Etre, *App. Surf. Sci.,* 252 (2006) 8521.
33. A. Popova; E. Sokolova; S. Raicheva and M. Chritov, *Corros. Sci.,* 45 (2003) 33.
34. Z. Szlarska-Smialowska and J. Mankovwski, *Corros. Sci.,* 18 (1978) 953.
35. A. Yurt; S. Ulutas and H. Dal, *Appl. Surf. Sci.,* 253 (2006) 919.
36. A. Aytac; U. Ozmen; M. Kabsakaloglu, *Mater. Chem. Phys.,* 89 (2005) 176.
37. O. K. Okorosaye and N.C. Oforka, *J. Appl. Sci. Environ. Manage.,* 8 (1) (2004) 56.
38. V. S. Sastri, "Corrosion Inhibition, Principles and Applications" *John Wiley & Sons, New York* (1998).
39. E. E. Oguzie, *Plgment and Resia Technology,* 34 (6) (2005) 321.
40. I. Putilova; S. Balezin and V. Barannik, "Metallic Corrosion Inhibitors" *Pergamon, Oxford* (1960).
41. O. L. Riggs, *J. Corrosion,* 24 (1968) 125.
42. S.T. Arab and E.A. Noor, Corrosion, 49(2) (1993) 122.
43. S. S. Abd-El- Rehim; S. A. M. Refaey; F. Taha; M.B. Saleh and R. A. Ahmed, J.Appl. Electrochem., 31 (2001) 429.
44. J. Heyrovsky and J. Kuta, " Principles of Polarogrophy " *Czochoslovak Academy of Sience, Prague,* 228 (1965).
45. S. T. Arab and K. M. Emran, *Inter. J. Appl. Chem.,* 3 (2007) 69.
46. L.A. Antropov and Y. A. Suvgira, Protection of Metals , 3 (1967) 597.
47. M. Abdallah, *Corros. Sci.,* 45 (2003) 2705.
48. A. S. Fouda; A. A. Al-Sarawy and E. E. El-Katori, *Desalination,* 201 (2006) 1.
49. T. Alsofyani, "Elemenlary studies on leaves Components of Cluytia myricoides , Euryops arabicus and Plactranthus tenuiflorus and defining their effects on growth of microorganismi and tissnes cells" *Master Thesis, King Abdul Aziz University, Jeddah* (2006).

Table 1 : Corrosion rates and inhibition efficiencies for mild steel in 2.0 M H_2SO_4 in the presence of different concentrations of aqueous extract of *Plectranthus tenuiflorus (Shara*) plant at 30° C.

C_{inh}(%V/V)	Corrosion Rate		Inhibition Efficiency	
	$R'_{MLM}\times10^4$ ($g. cm.^{-2} min.^{-1}$)	$R_{HEM}\times10^2$ ($ml. cm.^{-2} min.^{-1}$)	I_{MLM}%	I_{HEM}%
0.0	1.7734	7.1101	-	-
1.0	2.0091	8.9901	-13.29	-26.44
2.0	1.3553	6.0227	23.58	15.29
3.0	1.2236	5.0810	31.00	28.54
5.0	0.7785	3.2101	56.10	54.85
10.0	0.6674	2.8011	62.37	60.60
20.0	0.3955	1.6833	77.70	76.33
30.0	0.0381	0.1848	97.85	97.40

Table 2 : Adsorption isotherm parameters and correlation coefficients for *Shara* plant onto mild steel in 2.0 M H_2SO_4 at 30° C.

Methods	slope	Correlation Coefficients	$K_{ads.}$(M^{-1})	ΔG_{ads}(kJ mol^{-1})
MLM	0.9443	97.46	0.1485	- 52.89
HEM	0.9055	93.63	0.1144	- 46.31

Table 3 : Corrosion rates for mild steel in 2.0 M H_2SO_4 at different temperatures.

Temperature	30	40	50	60	70
$R'_{MLM}\times10^4$ ($g. cm.^{-2} min.^{-1}$)	1.7734	6.8532	9.9715	12.5273	23.9880
$R_{HEM}\times10^2$ ($ml. cm.^{-2} min.^{-1}$)	7.1101	35.5804	42.9553	68.2364	107.3421

Table 4 : Corrosion rates for mild steel in 2.0 M H_2SO_4 + 5%v/v of aqueous extract of *Shara* plant at different temperatures.

Temperature	30	40	50	60	70
$R'_{MLM}\times 10^4$ (g. cm.$^{-2}$ min.$^{-1}$)	0.7785	2.1023	5.0057	7.2212	20.2551
$R_{HEM}\times 10^2$ (ml. cm.$^{-2}$ min.$^{-1}$)	3.2079	11.3274	19.0520	35.8479	90.1684
I_{MLM}%	56.10	69.31	49.80	42.36	15.56
I_{HEM}%	54.88	68.16	55.65	47.47	16.00

Table 5 : Activation parameters for corrosion reaction of mild steel in 2.0 M H_2SO_4 in the absence and presence of various concentration of aqueous extract of *Shara* plant.

Method	$C_{inh.}$ (%v/v)	E_a (kJ. mol.$^{-1}$)	ΔH^* (kJ. mol.$^{-1}$)	ΔS^* (J. mol.$^{-1}$ k^{-1})
ML	0.0	50.63	47.94	-156
	5%v/v	67.07	64.39	-110
HE	0.0	53.07	50.40	-97
	5%v/v	87.74	65.06	-57

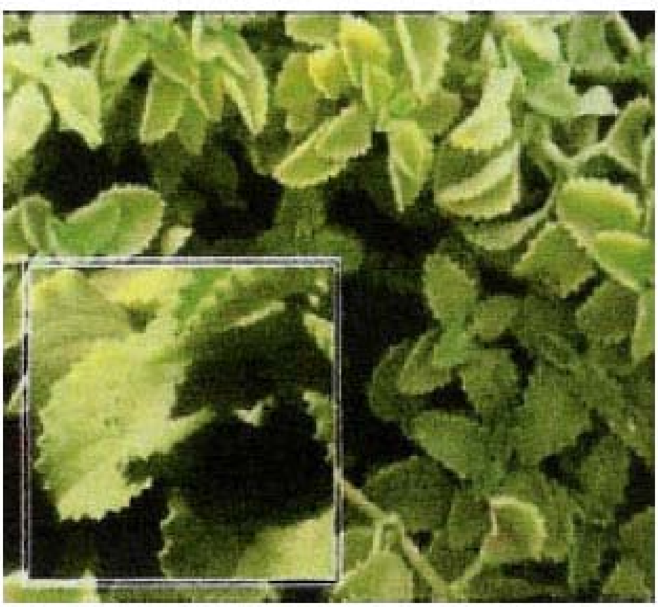


Fig.1 : Plectranthus tenuiflorus (Shara) plant leaves that collected from Jeddah region; Saudi Arabia.

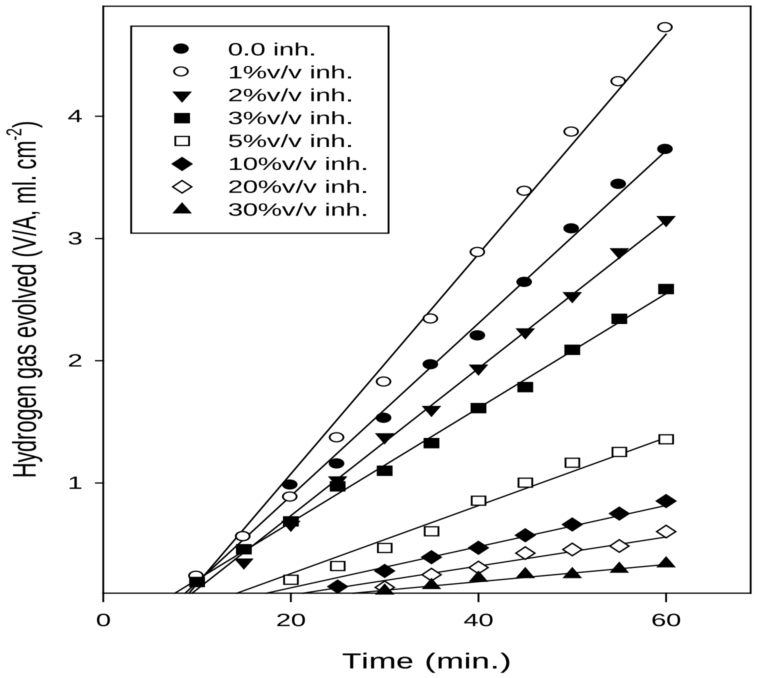


Fig.2 : Volume of hydrogen / time curves for mild steel corrosio in 2.0 M H_2SO_4 in the absence and presence of different concentratic of aqueous extract of *Shara* plant at 30 C.

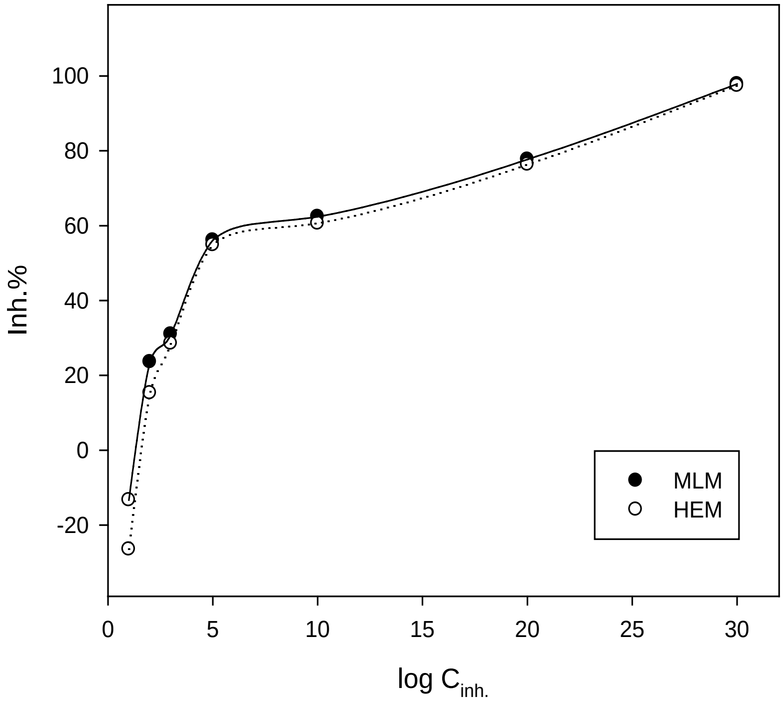


Fig.3 : The variation of inhibition efficiency (Inh.%) against log C for steel in 2.0M H_2SO_4 in the absence and presence of *Shara* extract at 30° C.

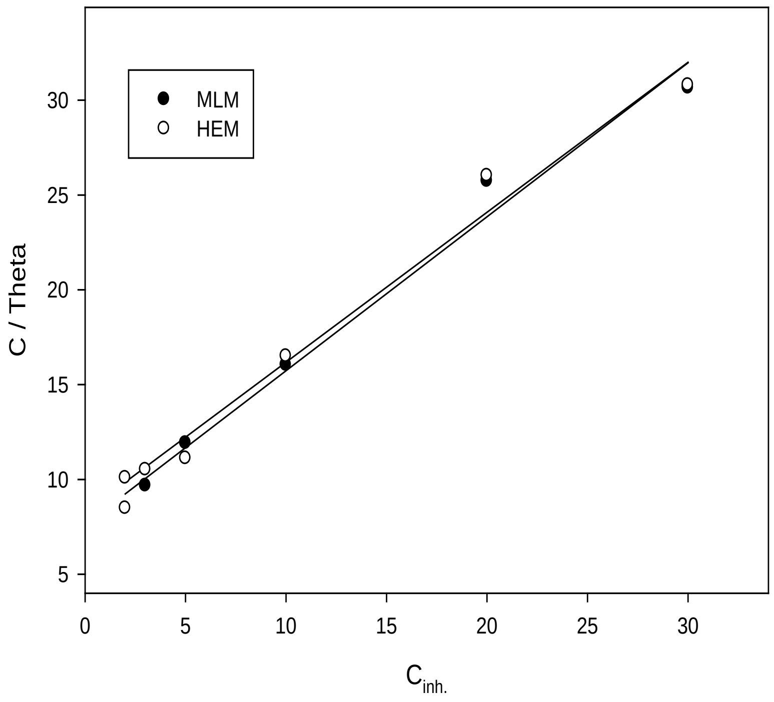


Fig.4 : The relation between C/θ against $C_{inh.}$ of aqueous extract of *Shara* for steel corrosion in 2.0 M H_2SO_4 at 30° C (Langmiur isotherm).

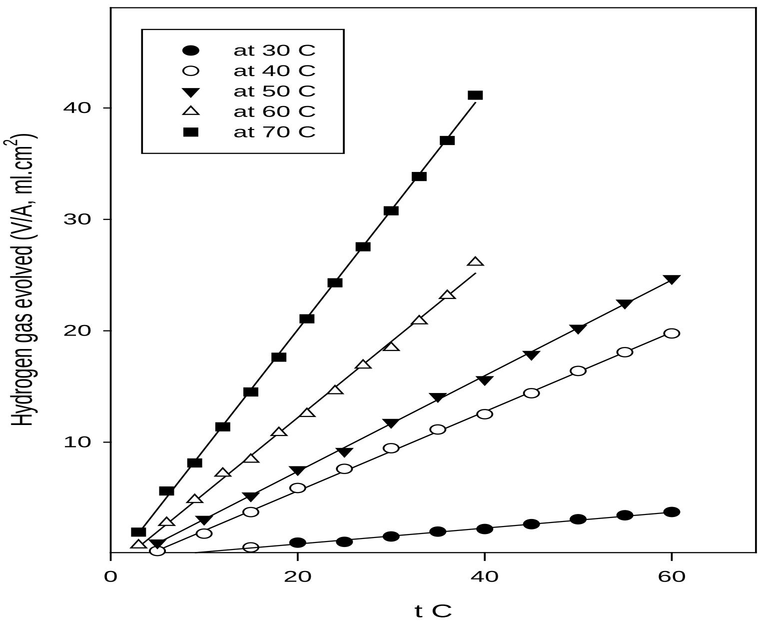


Fig .5 : volume of hydrogen/time curves for mild steel corrosion in 2.0 M H_2SO_4 at different temperatures.

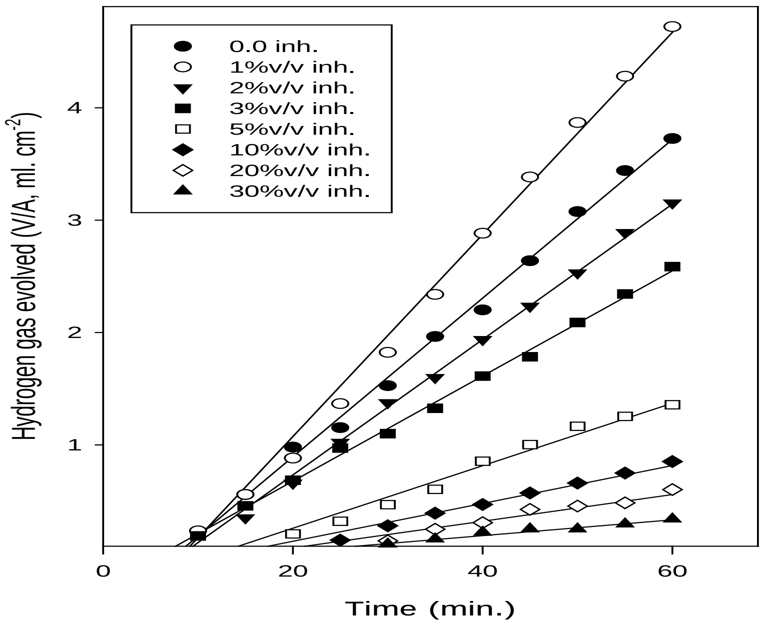


Fig. 6 : volume of hydrogen/time curves for mild steel corrosion in 2.0 M H_2SO_4 in the absence and presence of 5%v/v of aqueous extract of *Shara* plant at different temperatures.

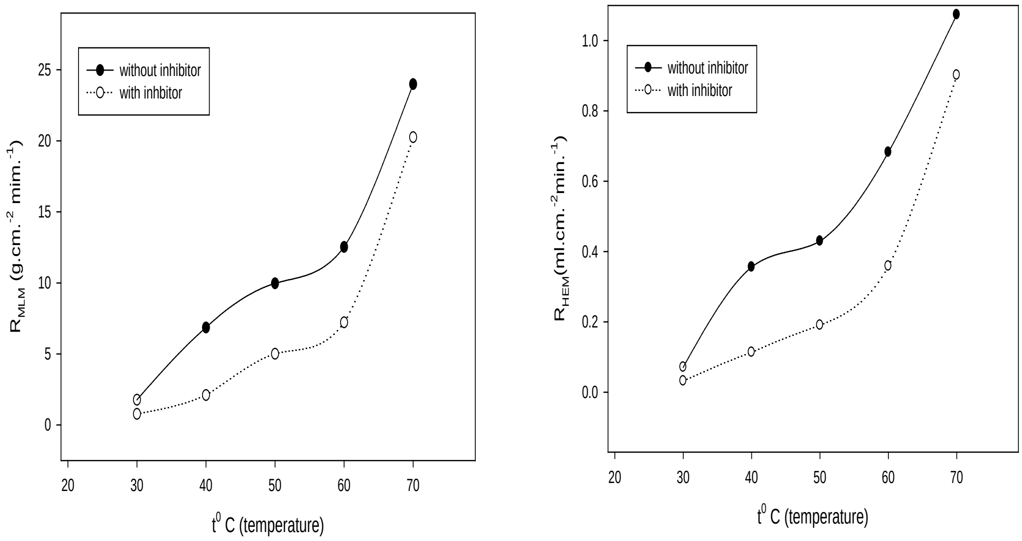


Fig.7 : The relation between corrosion rate (R_{ML} and R_{HE}) of equeous extract of *Shara* plant and temperature in H_2SO_4 solution.

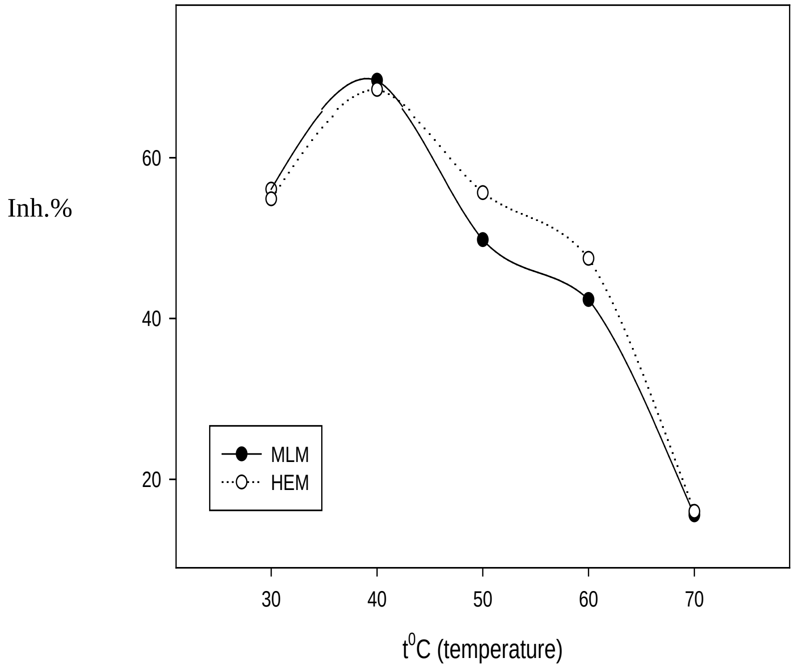


Fig.8 : The relation between inhibition efficiency (Inh.) of aqueous extract of *Shara* plant and temperature in H_2SO_4 solution.

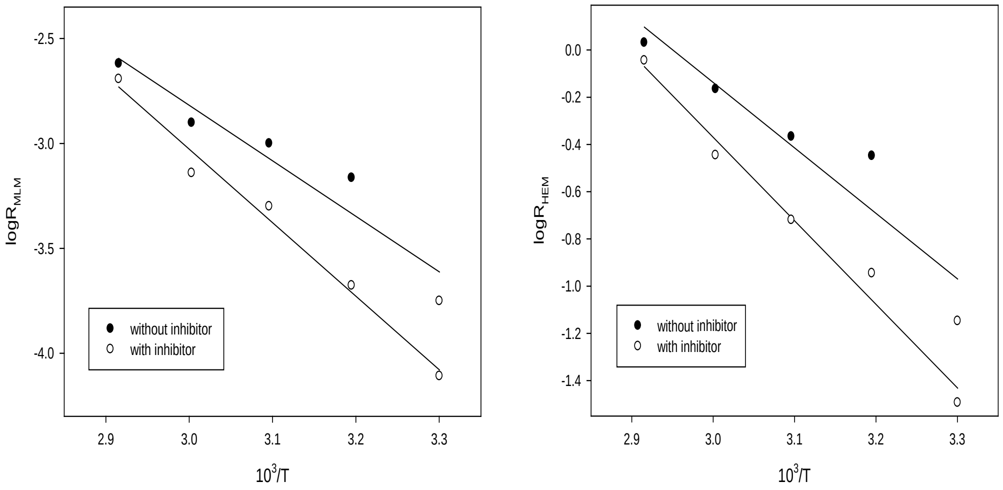


Fig.9 : Arrhenius plots for the dissolution of mild steel in 2.0M H_2SO_4 in the absence and presence of 5.0%v/v of aqueous extract of *Shara* plant.

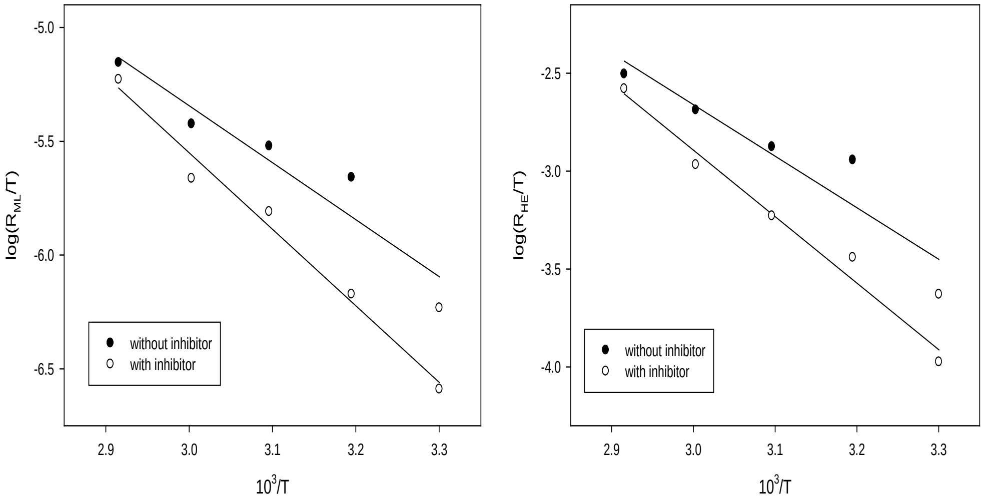


Fig.10 : The relation between log(R/T) vs. 1/T for the corrosion of mild steel in 2.0 M H_2SO_4 in the absence and presence of 5.0%v/v of aqueous extract of *Shara* plant.

GLOBAL JOURNAL OF SCIENCE FRONTIER RESEARCH
CHEMISTRY
Volume 12 Issue 1 Version 1.0 January 2012
Type : Double Blind Peer Reviewed International Research Journal
Publisher: Global Journals Inc. (USA)
Online ISSN: 2249-4626 & Print ISSN: 0975-5896

Interaction between Cryptand 222 and Tetracyanoethylene in Di and Trichlorom Ethane Solutions

By Abolfazl Semnani, Ali Reza Firooz, Leila Kashefi Kheyrabadi, Hamid Shakoori Langeroodi , Safieh Heidarizadeh Rizi
University of Isfahan, Isfahan, 81746-73441, I.R. Iran

Abstract - A spectrophotometric study concerning the interaction between cryptand 222 as n-donor and TCNE as π - acceptor has been performed in di and tri chloromethane solutions at temperatures 5, 10, 15, and 20°c. The results of continuous variation and mole ratio methods indicate the formation of 1:1 complexes in both solvents and at all temperatures. The stability constants and the molar absorption coefficients at different temperatures have been calculated from the computer fitting of absorbance- mole ratio data in **MATLAB** soft ware. The results indicate that Kf values in $\mathbf{CHCl_3}$ are more than the corresponding amounts in $\mathbf{CH_2Cl_2}$. In the case of **€**, the reverse trend is observed. The $\Delta H°$and $\Delta S°$ values were obtained by Vant Hoff method. The obtained data show that the enthalpy of complex formation in two solvents is favorable. While entropy is favorable in the case of $\mathbf{CHCl_3}$ and unfavorable in the case, of $\mathbf{CH_2Cl_2}$. The possible reasons for such observation are discussed. The kinetic results confirm an overall second order reaction which is first order with regard to each reactant. The formation of free ions is rejected by the conductometric measurments.

Keywords : Halomethanes, C222, TCNE, Spectrophotometry, Charge transfer, Thermodynamic, Kinetics.

GJRE Classification : FOR Code: 030503

INTERACTION BETWEEN CRYPTAND 222 AND TETRACYANOETHYLENE IN DI AND TRICHLOROM ETHANE SOLUTIONS

Interaction between Cryptand 222 and Tetracyanoethylene in Di and Trichlorom Ethane Solutions

Abolfazl Semnani[α], Ali Reza Firooz[Ω], Leila Kashefi Kheyrabadi[β], Hamid Shakoori Langeroodi[ψ], Safieh Heidarizadeh Rizi[¥]

Abstract - A spectrophotometric study concerning the interaction between cryptand 222 as n-donor and TCNE as π-acceptor has been performed in di and tri chloromethane solutions at temperatures 5, 10, 15, and 20°c. The results of continuous variation and mole ratio methods indicate the formation of 1:1 complexes in both solvents and at all temperatures. The stability constants and the molar absorption coefficients at different temperatures have been calculated from the computer fitting of absorbance- mole ratio data in MATLAB soft ware. The results indicate that K_f values in $CHCL_3$ are more than the corresponding amounts in CH_2CL_2. In the case of ϵ, the reverse trend is observed. The ΔH° and ΔS° values were obtained by Vant Hoff method. The obtained data show that the enthalpy of complex formation in two solvents is favorable. While entropy is favorable in the case of $CHCL_3$ and unfavorable in the case, of CH_2CL_2. The possible reasons for such observation are discussed. The kinetic results confirm an overall second order reaction which is first order with regard to each reactant. The formation of free ions is rejected by the conductometric measurments

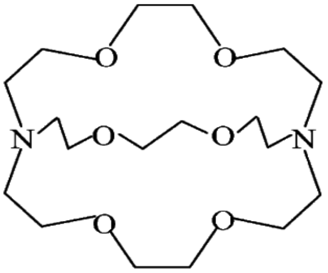
Keywords : Halomethanes, C222, TCNE, Spectrophotometry, Charge transfer, Thermodynamic, Kinetics

I. INTRODUCTION

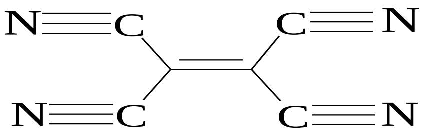
Since the first synthesis of crown ethers [1] and cryptands [2], there has been an intensive amount of research work on the thermodynamic and kinetics of complexation of these ligands with various cations in a wide variety of solvent systems [3]. Moreover, the molecular complexes of crowns and cryptands have been followed [4]. Interest in molecular complexes is strongly stimulated by their possible applications in different areas such as separation processes, biomimetric receptors, catalytic reactions and conversion of chemical energy to optical or electronic signals. In continue of our interest to molecular complexes of crowns and cryptands [5-10], here we report the results of complexation of cryptand 222 with TCNE in di and trichlolromethane solutions.

II. EXPERIMENTAL

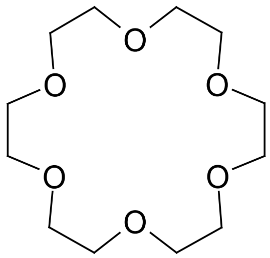
The macrocycle C222 and TCNE (both from Merck) were recrystallized from reagent gradre n-hexane and dried over P2O5. Reagent grades of di and trichlorometahne (both from Merck) were used without any further purification.



Cryptand 222 (C222)



Tetracyanoethylene (TCNE)



18-Crown-6

All UV-Vis spectra and absorbance measurements were made with a UV-Vis-NIR spectrophotometer Cary 500 at different temperatures.

Author [α] [¥] : Department of Chemistry, Faculty of Science, University of Isfahan, Isfahan, 81746-73441, I.R. Iran.
Author [Ω] [β] : Department of Chemistry, Faculty of Science, University of Shahrekord, Shahrekord, 115, I.R. Iran.
Author [ψ] : Petrokimia Sepahan Company, Mobarekeh Industrial City, Isfahan, Iran.

Conductance measurements were carried out with a conductivity meter 180 from Orion research Company.

III. RESULTS AND DISCUSSION

Absorption spectra of 1.0× 10-4 M solution of C222 in trichloromethane in the precence of varying concenteations of TCNE are shown in Fig. 1. Because of similarity, the corresponding spectra due to dichloromethane are not shown. Each spectrum was recorded 20 minutes after preparing the fresh solution. As it can be seen upon addition of C222 to the solution of TCNE, a new band is appeared in 350-450 nm region. As, none of the reactants, do not have any absorption in this spectral region. The new band can be attributed to the formation of charge transfer complex between C222 as n-donor and TCNE as π - acceptor [11].

In order to determine the effective site of complexation, the spectrum of 1:1 mixture of 18C6 (i.e. a compound without nitrogen atom) and TCNE was recorded. As, new band was not observed, it can be concluded that the oxygen atoms of C222 do not play an important role and the complexation mainly occur through nitrogen atoms.

The needed time for reaction completeness was determined by monitoring the absorbance of 1:1 mixture of 1.0×10-4 M solution of C222 and TCNE at 400 nm and at different temperatures (Fig. 2). As it can be seen, after 15 minutes, reaction will be terminated. Therefore, in the next experiments, absorbances were measures 20 minutes after mixinof reagents.

The stoichiometry of the complexes at different temperatures was obtained by the absorbance vs. mole ratio [12] and Job methods [13]. Sample plots are shown in Figs. 3 and 4, respectively. Both series of plots clearly confirm 1:1 stoichiometry. Moreover, in both cases upon temperature rising, the curvature of plots is decreased.

Based on spectral, mole ratio and Job evidences it can be concluded that through the reaction between C222 and TCNE, 1:1 charge transfer complex is formed.

$$\text{TCNE} + \text{C222} \leftrightarrows \text{TCNE: C222} \qquad (1)$$

For the evaluation of the formation constants from absorbance-mole ratio data, a none-linear least squares curve fitting program (curve fitting toolbox in MATLAB) was used [14,15]. The program is based on the iteration adjustment of calculated absorbances to the observed values.

The observed absorbance of complex at its λmax is given by equation (2). The mass balance equations can be written as (3) and (4), and the formation constant of the complex as in (5). Substitution of (3) and (4) in (5) and rearrangement yield (6).

$$\text{Abs.} = \epsilon b[DA] \qquad (2)$$

$$C_D = [D] + [DA] \qquad (3)$$

$$C_A = [A] + [DA] \qquad (4)$$

$$K_f = [DA]/[D][A] \qquad (5)$$

$$K_f\,[DA]^2 - (C_A\,K_f + C_D\,K_f + 1)\,[DA] + K_f\,C_D\,C_A \qquad (6)$$

With use an approximation value for K_f, the free DA concentration, [DA], were calculated by solution of second order equation. Then, with using from data of DA concentration as x data and data of observed absorbance as y data, the least squares fit technique is used for fitting the data. The output of this fitting is the coefficient of line fit. The coefficient of x values is ϵ (molar absorption coefficient). The obtained coefficient were used for calculation of data of absorbance with using of parabolic fit. To find the least squares error, the sum of squares of differences between the parabolic fit and the actually data must be evaluated. Refinement of parameters (K_f value) was continued until the sum of squares of the residuals between calculated and observed values of the absorbance for all experimental points was minimized.

Sample curve fittings are shown in Fig. 5. The good agreement between the experimental and calculated data confirm the accuracy of the results. The final logKf and ϵ values obtained by MATLAB are given in Table 1. The data indicate that at all temperatures logKf values due to trichloromethane are higher than the corresponding values in dichloromethane. In the case of ϵ, the reverse trend is observed. Greater $\log K_f$ in trichloromethane means that in this media, the contribution of solvent in entropy, enthalpy or both of them is more favorable than dichloromethane. On the other hand, despite both TCNE and C222 are nonpolar. Their resulting complex is polar and will show diplole-diploe interactions with polar species. Clearly, such interactions will be higher with more polar species. So, it is anticipated that dicholoromethane with dipole moment of 1.5 [16], do have more solute–solvent interactions (with polar charge transfer complex) than that of trichloromethane with dipole moment of 1.15 [16]. Greater dipole-dipole interactions cause that in CH_2Cl_2 orientation of complex particles to be more than of $CHCl_3$. This results in higher absorption cross section [17]. The net effect is the enhancement of ϵ. Therefore, the observation of higher ϵ in CH_2Cl_2 is not unexpected.

The thermodynamic parameters were obtained by the plot of $\log K_f$ vs. $1/T$ (sample plot is shown in Fig. 6) [18]. The obtained values for $\Delta H°$ are -26.3 kJ/mol and -25.4 kJ/mol in di and trichloromethane, respectively. Also, the $\Delta S°$ values were obtained as -16.3 J/mol.°K in dichloromethane and +25.13 J/mol.°K in trichloromethane.

It is well known that the final stability of complex depends on the sum of entropy and enthalpy changes through the complexation process [18]. On the other hand, the salvation, affects both $\Delta S°$ and $\Delta H°$ values. The effect on $\Delta S°$, relates to positive entropy changes due to desolvation of reactants and negative entropy changes due to solvation of complex. The effect on $\Delta H°$, relates to enthalpy changes during desolvation of reactants and solvation of complex.

The enhanced enthalpy changes in both solvents indicate that the amount of realized energy through complex formation and complex solvation is higher than consumed energy for desolvation of reactants. In addition, positive $\Delta S°$ in dichloromethane indicates that absolute entropy increase through desolvation of reactants is more than absolute entropy decrease through complex formation and complex solvation. Negative $\Delta S°$ in trichloromethane proves that entropy changes through desolvation of reactants or solvation of complex in recent solvent differs from corresponding values of dichloromethane.

The existence of nitrogen atoms on C222 and TCNE beside the location of three electron-withdrawing groups on carbon atom of trichloromethane, enhances the hydrogen bond formation between solvent and reactants. These bonds are broken through complex formation and some solvent molecules are realized in solvent. The net result is the positive $\Delta S°$. In the case of dichloromethane, the hydrogen bonds are considerably weaker. So, positive effect (through solvent realization) on overall $\Delta S°$ is considerably less than trichloromethane, which causes the observation of overall negative $\Delta S°$ in this solvent.

With the aim of determination of reaction order relative to each of reactants, the absorbance of the various solutions with different TCNE/C222 mole ratios were measured. The measurements were made two minutes after mixing the reactatns. Sample data due to trichloromethane are given in Tables 2 and 3, respectively. As it can be seen, at all temperatures and in both cases, the variation of absorbance is proportional to the variation of TCNE/C222 mole ratio or vice versa. Similar trend was observed in dichloroemethane. Based on the recent data it can be concluded that in both solvents a second order reaction in which the order of TCNE and C222 are 1 is followed.

The conductances as a function of C222/TCNE or TCNE/C222 in both solvents were measured. Considerable change was not observed. So it can be concluded that the adducts of TCNE and C222 in both solvents are nonionic.

IV. CONCLUSIONS

Based on the obtained results it can be concluded that:

1. In both solvents 1:1 complexes are formed.
2. The stability of complexes in $CHCl_3$ are higher than CH_2Cl_2.
3. The ϵ of complexes in CH_2Cl_2 are greater than $CHCl_3$.
4. In both solvents, the $\Delta H°$ of complex formation are negative.
5. Because of hydrogen bonding between the solvent and reactants, the $\Delta S°$ $CHCl_3$ is positive.
6. At all temperatures, the reaction order relative to both of reactants is 1:1
7. The resulting adducts are nonionic.

REFERENCES REFERENCES REFERENCIAS

1. C. J. Pedersen, J. Am. Chem. Soc., 89, 7017 (1967).
2. B. Dietrich, I. M. Lehn, and J. P. Sauvage, Tetrahedron Lett., 2885 (1969).
3. R. M. Izatt, J. S. Braclshaw, S. A. Nielson, J. D. Lamb, J. J. Christensen, and D. Sen, Chem. Rev. 85, 271 (1985).
4. R. M. Izatt, J. S. Bradshaw, K. Pawlak, R. L. Bruening & B. J. Tarbet, Chem. Rev. 92, 1261 (1992).
5. A. Semnani & M. Shamsipur, Spectrochim. Acta, 49A, 411 (1993).
6. A. Semnani & M. Shamsipur, J. Chem. Soc., Dalton Trans, 22, 15 (1996).
7. A. Semnani, H. R. Pouretedal, M. H. Keshavarz & A. R. Firooz, Polish J. Chem. 80, 2055 (2006).
8. Semnani, A. R. Firooz, H. R. Pouretedal, and M. H. Keshavarz, Chemistry, Vol. 19, No. 4, 1 (2009)
9. M. Javsadian, A. R. Firooz, A. Semnani, H. R. Pouretedal, and M. H. Keshavarz, Bull. Chem. Soc. Ethiop., Vol. 22, 2, 287 (2008).
10. A. Semnani, A. R. Firooz, M. H. Keshavarz and M. Oftadeh, Chemistry, Vol. 19, No. 3, 80 (2010)
11. R. Foster, "Organic Charge Transfer Complexes", Academic Press, London nd New York (1969).
12. M. T. Beck, I. Nagypal, "Chemistry of Complex Equilibria", John Wiley & Sons; NewYork (1990).
13. P. Job, Ann Chim. 9, 113 (1928).
14. P. Gans, "Data Fitting in the Chemical Sciences by the Method of Least Squares", Sohn Wiley & Sons; England (1992).
15. M. Quhn, J. Guckenheimer, B. R. Land, R. Harrs, A. S. Warrick, Nurophysiology, 94, 2883 (2005).
16. CRC hand book
17. R. S. Mulliken, "Molecular Complexes ", Wiley-Interssciece, NewYork (1990).
18. C. E. Mortimer, "Chemistry", 7th ed., Wadsworth Publishing Company: NewYork (1986).

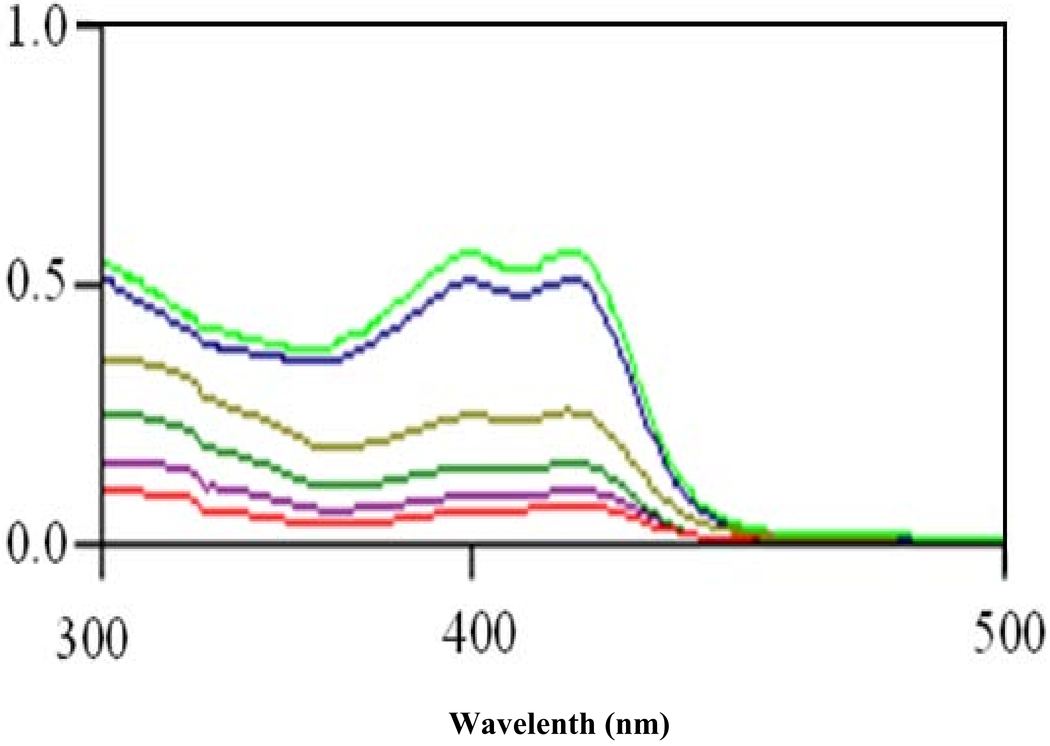


Fig.1 : Absorption spectra of 1.0×10-4 M C222 in the presence of varying concentration of TCNE at 20 0C. The ratio of TCNE to C222 from bottom to top are: 0.15, 0.25, 0.50, 1.00, 1.50, 2.5.

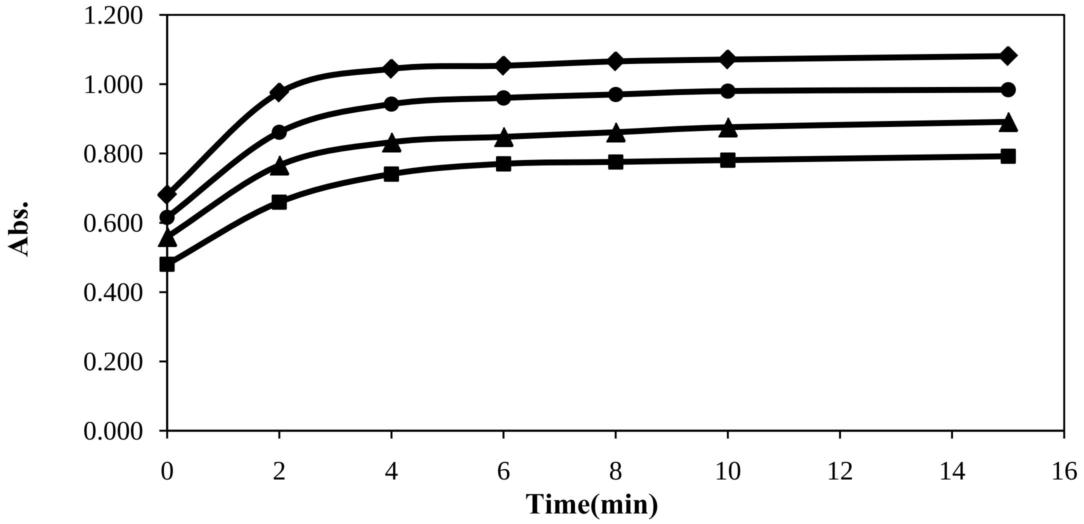


Fig. 2 : Plots of absorbance vs. time for 1.0× 10-4 M C222 in trichloromethane in different temperatures. From bottom to top: 5, 10, 15, and 20°c.

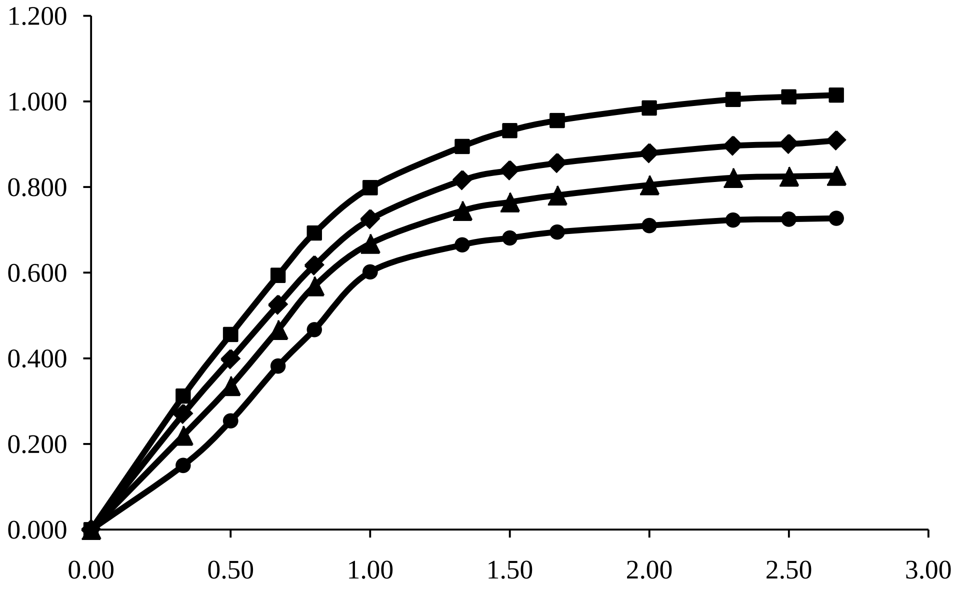


Fig.3 : Absorbance vs. mole ratio plots for 2.0×10-4 M C222 in dichloromethane solution at different temperatures. (■) 5 0C, (▲) 10 0C, (●) 150C and (♦) 20 0C.

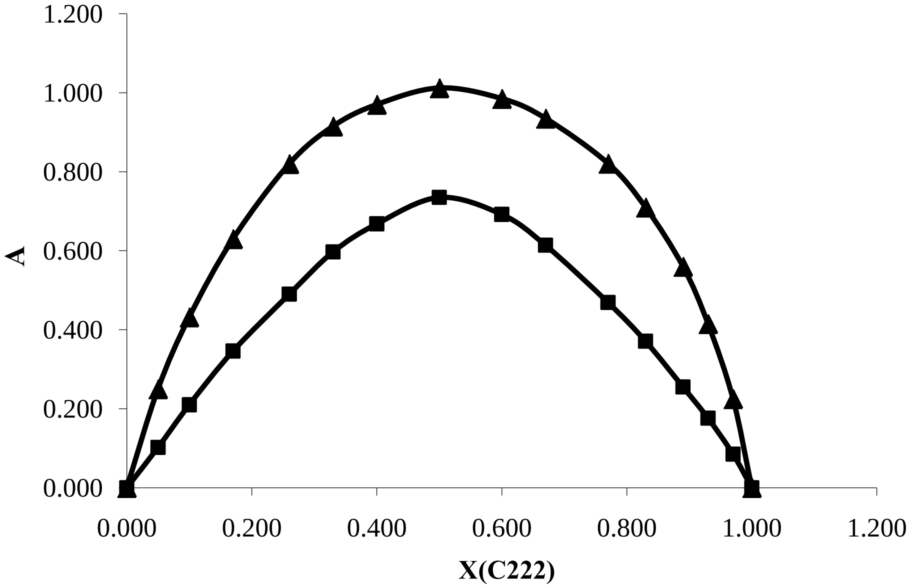


Fig.4 : Job plots at different temperatures in dichloromethane. The concentration of stock solutions and the final volume of each solution are 2.5×10-4 M and 3ml, respectively. (■) 5 0C, and (●) 20 0C.

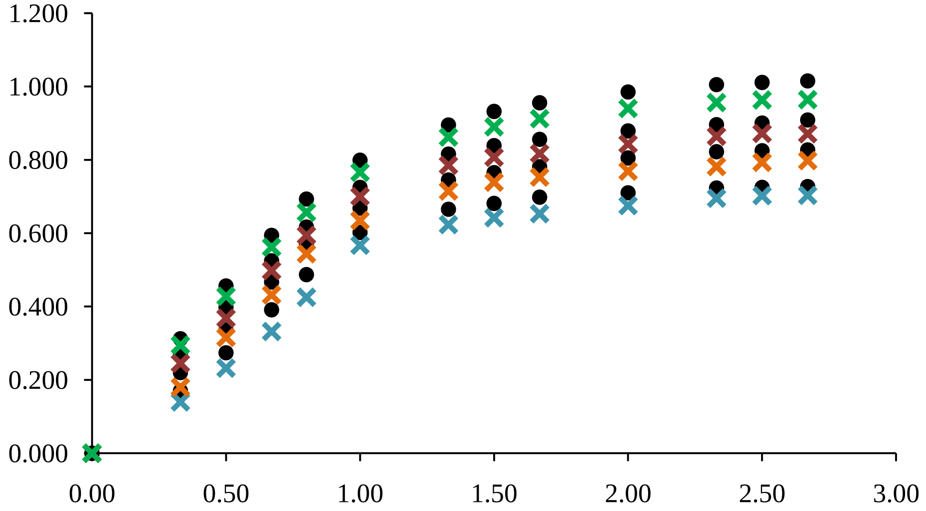


Fig.5 : Computer fitting of absorbance vs. mole ratio data indichloromethane at different temperatures; (●) experimental points and (×) calculated points.

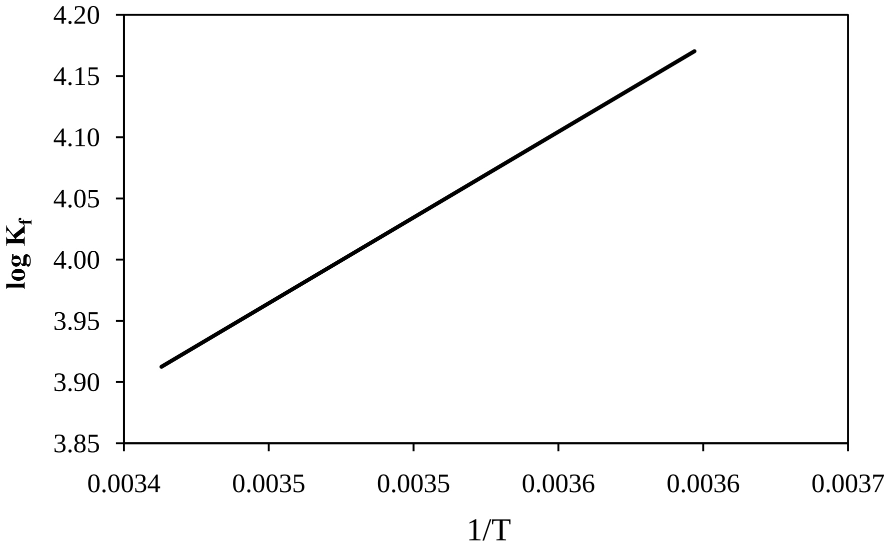


Fig.6 : The plot of $\log K_f$ vs. $1/T$ in dichloromethane solution.

Table 1 : Final log K_f and € values at different temperatures in CH_2Cl_2

T	278	283	288	293
Log K_f in CH_2Cl_2	4.17±0.02	4.08±0.02	4.01±0.01	3.91±0.01
Log K_f in $CHCl_3$	6.08±0.04	5.99±0.01	5.91±0.02	5.84±0.01
€ in CH_2Cl_2	7947±238	8549±256	9088±273	1186±336
€ in CHCl3	3552±107	3927±117	4576±138	4912±147

Table 2 : Data due to determination of reaction order relative to TCNE in trichloromethane solution

TCNE/C222	**◌́Absorbance at 5°c**	**◌́◌́Absorbance at 10°c**	**Absorbance at 15°c**	**Absorbance at 20°c**
0.33	0.095	0.143	0.211	0.287
0.67	0.191	0.228	0.422	0.577
1.00	0.290	0.432	0.639	0.867
1.33	0.383	0.575	0.850	1.142

Table 3 : Data due to determination of reaction order relative to C222 in trichloromethane solution

C222/TCNE	**Absorbance at 5°c**	**Absorbance at 10°c**	**Absorbance at 15°c**	**Absorbance at 20°c**
0.33	0.098	0.151	0.211	0.295
0.67	0.195	0.302	0.442	0.640
1.00	0.293	0.461	0.668	0.878
1.33	0.391	0.611	0.892	1.181

Global Journal of Science Frontier Research
Chemistry
Volume 12 Issue 1 Version 1.0 January 2012
Type : Double Blind Peer Reviewed International Research Journal
Publisher: Global Journals Inc. (USA)
Online ISSN: 2249-4626 & Print ISSN: 0975-5896

Ionic liquid assisted Synthesis and Characterization of metallic Molybdenum and Molybdenum oxide nanoparticles

By Madu, A. N, Ayi, A. Ayi, Njoku, M I, Iwuoha, G. N.

Crawford University, Ogun State. Nigeria

Abstract - Nanostructured **Mo** and **MoO_3** colloidal dispersions have been obtained reproducibly through reduction of ammonium molybdate by sodium borohydride in ionic liquids. When **$(NH_4)_6Mo_7O_{24}.4H_2O$** is reduced by **$NaBH_4$** in both 1-ethyl-3-methyl imidazolium dicyanamide and 1-butyl-3-methylimidazoliumdicyanamide at **180ºC**, nanostructured **MoO_3** formed as the major phase. The XRD pattern confirmed the crystalline nature of the material. The most representative reflections of **MoO3** (JCPDS: 47-1081) were indexed in monoclinic crystal system (space group P2 1/c (14) Y-unique) . The average mean diameter of 53.8nm was calculated using Debye-Scherrer equation from full width at half-maximum (FWHM) of (111), (-311), (160), (-421), (330) and (413) planes for material in IL **EmimN(CN)2**. But in **$BmimN(CN)_2$** the diameter was estimated to be 40.8nm. When the reduction was carried out in EmimOTf and BmimOTf, the products consists of metallic molybdenum and **MoO3**. The crystalline phase of MoO3 is rodlike and is determined to be orthorhombic, space group Pbnm(62) with the cell dimensions **[a=3.963, b=13.856, c=3.696 Ǻ.; Vol.=203. Ǻ3, Z=4, ρ=4.7096gcm^{-1}]** corresponding to **MoO_3** **(JCPDS: (35-0609)**. The average diameter of 51.0 and 48.9nm was calculated respectively for particles in IL EmimOTf. UV-Visible absorption spectra of the fraction in ionic liquid dispersed in ethanol .shows that the predominant feature in the spectra is the spin-allowed ligand-to-metal charge transfer **(LMCT)** from **O^{2-} ion** t_{iu} orbital to **a d^0 e_g** orbital, which is observed in the range 200-300nm centred at 212nm in the UV region. This strongly indicates the presence of metallic Molybdenum with particle size less than 100nm.

Keywords : Molybdenum, nanostructured, aggregates, crystalline, Ionic liquid.

GJSFR-A Classification : FOR Code: 030302, 030204

IONIC LIQUID ASSISTED SYNTHESIS AND CHARACTERIZATION OF METALLIC MOLYBDENUM AND MOLYBDENUM OXIDE NANOPARTICLES

Strictly as per the compliance and regulations of :

Ionic liquid assisted Synthesis and Characterization of metallic Molybdenum and Molybdenum oxide nanoparticles

Madu, A. N[α], Ayi, A. Ayi[Ω], Njoku, M I[β], Iwuoha, G. N.[ψ]

Abstract - Nanostructured **Mo** and **MoO_3** colloidal dispersions have been obtained reproducibly through reduction of ammonium molybdate by sodium borohydride in ionic liquids. When **$(NH_4)_6Mo_7O_{24}.4H_2O$** is reduced by **$NaBH_4$** in both 1-ethyl-3-methyl imidazolium dicyanamide and 1-butyl-3-methylimidazoliumdicyanamide at **180°C**, nanostructured **MoO_3** formed as the major phase. The XRD pattern confirmed the crystalline nature of the material. The most representative reflections of **MoO_3** (JCPDS: 47-1081) were indexed in monoclinic crystal system (space group P2 1/c (14) Y-unique) . The average mean diameter of 53.8nm was calculated using Debye-Scherrer equation from full width at half-maximum (FWHM) of (111), (-311), (160), (-421), (330) and (413) planes for material in IL **EmimN(CN)$_2$**. But in **BmimN(CN)$_2$** the diameter was estimated to be 40.8nm. When the reduction was carried out in EmimOTf and BmimOTf, the products consists of metallic molybdenum and **MoO_3**. The crystalline phase of MoO_3 is rodlike and is determined to be orthorhombic, space group Pbnm(62) with the cell dimensions **[a=3.963, b =13.856, c =3.696 Å, Vol.=203. Å^3, Z =4, ρ=4.7096gcm^{-1}]** corresponding to **MoO_3 (JCPDS: (3 5-0609)**. The average diameter of 51.0 and 48.9nm was calculated respectively for particles in IL EmimOTf. UV-Visible absorption spectra of the fraction in ionic liquid dispersed in ethanol .shows that the predominant feature in the spectra is the spin-allowed ligand-to-metal charge transfer **(LMCT)** from **O^{2-} ion t_{iu}** orbital to **a d^0 e_g** orbital, which is observed in the range 200-300nm centred at 212nm in the UV region. This strongly indicates the presence of metallic Molybdenum with particle size less than 100nm. A shift to longer wavelength with a decreasing intensity of absorption signals larger particles and aggregates of molybdenum oxide phase.

Keywords : Molybdenum, nanostructured, aggregates, crystalline, Ionic liquid.

I. INTRODUCTION

Transition metal nanoparticles exhibits very interesting size-dependent physical and chemical properties which makes them useful in diverse areas of applications (Lu,Salabas and Schuth, 2007; Thathagar, Beckers and Rothenberg,2002). Metallic Mo and molybdenum oxide nanoparticles in particular have been used as chemical sensor materials and as catalysts for olefin metathesis reactions (Braun, Eichen, Sivan and Ben-Yoseph,1998; Redel, Krämer, Thomann and Janiak, 2009). The performance of nanomaterials in many of these applications requires the control over the size, the morphology and the surface structure, which is based on the appropriate control of the parameters that influence nucleation and growth. Such a control over the growth and morphology of nanomaterials can be achieved by the use of ionic liquids with high degree of self-organization and templating effect.

The use of ionic liquids in the synthesis of inorganic materials has received a great deal of attention (Brennecke and Maginn, .2001; Welton, 1999; Fadeev and Meagher, 2001; Wilkes, 2004; Holbrey and Seddon, 1999; Seddon, 1997) not only because it is environmentally friendly deriving from its negligible vapour pressure,(Rebelo, Canongia Lopes, Esperancüa and Filipe, 2005; Paulechka, Zaitsau, Kabo and Strechan, 2005; Earle, Esperancüa, Gilea, Canongia-Lopes, Rebelo, Magee, Seddon and Widegren, 2006) but also because very large number of possible combinations of cations and anions allows one to fine-tune the properties of the synthesized product for specific applications. Syntheses of metal nanoparticles in ionic liquids have been vigorously pursued by different research groups. Majority of such syntheses are carried out either by chemical reduction of the metal salts in the presence of reducing agents (Kim, Demberelnyamba, Lee, 2004; Li, Friedrich and Taubert, 2008) (such as glycerol, cellulose, sodium citrate, sodium borohydride etc.) or by thermal and photochemical decomposition of metal carbonyls

E. Redel, J. Krämer, R. Thomann and C. Janiak 2008). The studied the formation of Mo NPs via step-wise reductioin of ammonium molybdate salt in imidazolium-based ionic liquids. Herein we report the synthesis of stable metallic Molybdenum and molybdenum oxide nanoparticles using 1-alkyl-3-methylimidazolium-based (AMIM) ionic liquids.

II. EXPERIMENTAL

By dispersing $(NH_4)_6Mo_7O_{24}.4H_2O$ salt in ionic liquids: RmimN(CN)$_2$), RmimOTf, EmimES and RmimNTf$_2$ (Where R = 1-Ethyl-3-methylimidazolium, or 1-Butyl-3-methylimidazolium ions, N(CN)$_2$) = dicyanamide, OTf = Triflate, ES = Ethylsulfate, NTf$_2$ =

Author [α] [ψ] : Crawford University, Faith-City Igbesa. Ogun State. Nigeria
E-mail : josalex67@yahoo.com
Author [Ω] : Department of Pure and Applied Chemistry University of Calabar, Calabar
Author [β] : University of Port Harcourt, Port Harcourt. River State. Nigeria

bis(trifluorosulfonylimide) and heating under reflux in the presence of $NaBH_4$ for 24h at a temperature of 180°C, air stable molybdenum and / or molybdenum oxide nanoparticles have been reproducibly obtained in the ionic media. In a typical synthesis, $(NH_4)_6Mo_7O_{24}.4H_2O$ (30.896mg; 0.025mmol) was dispersed in IL $EmimN(CN)_2$ (1031.3mg; 5mmol) and sonicated for 10mins before introducing $NaBH_4$(3.78mg; 1mmol). The resultant colourless solution with molar composition 10IL :5$(NH_4)_6Mo_7O_{24}.4H_2O$: 2$NaBH_4$ was heated at 180°C under reflux for 24h.The product, a dark red colloidal dispersion of the particles were gathered by centrifugation for analyses and the ionic liquids recycled.

III. INSTRUMENTS AND CHARACTERIZATION

WAXS and SAXS: Wide angle X-ray diffraction (XRD) was done on an ENRAF Nonius FR 590 diffractometer with a Cu K□ X-ray tube fitted with an Inel CPS 120 hemispherical detector ranging from 1 to 120 degrees 2□ SAXS curves were recorded at room temperature with a Nonius rotating anode instrument (4 kW, Cu K□) with pinhole collimation and a MARCCD detector (pixel size: 79). The distance between sample and detector was 74 cm, covering a range of the scattering vector s = 2/□ sin □ = 0.04 - 0.7 nm^{-1} (□ = scattering angle, □ = 0.154 nm). 2D diffraction patterns were transformed into a 1D radial average of the scattering intensity.

The UV spectrophotometric measurements were performed on Agilent 8453 spectrometer using 10mm quartz cuvettes. The UV absorption spectral data of the fraction of the nanoparticles in ionic liquid (as well as the solid gathered by centrifugation) dispersed in ethanol were collected at room temperature. Dynamic light scattering experiments were performed on Zeta sizer Nano instrument: Nano ZS Zen 3500 fitted with a 532nm green laser. TEM images were acquired on a Zeiss EM 912 at an acceleration voltage of 120 kV. One droplet of the suspension was applied to a 400 mesh carbon-coated copper grid and left to dry in air. SEM was done on a LEO1550 Gemini operated at 20kV.

IV. RESULTS AND DISCUSSION

Nanostructured Mo and MoO_3 colloidal dispersions (Dark red in IL ($EmimN(CN)_2$, EmimES, $BmimN(CN)_2$), Brown (in BmimOTf, $EmimNTf_2$, $BmimNTf_2$), olive green in (EmimOTf) have been obtained reproducibly through reduction of ammonium molybdate by sodium borohydride in ionic liquids. When $(NH_4)_6Mo_7O_{24}.4H_2O$ is reduced by $NaBH_4$ in both 1-ethyl-3-methyl imidazolium dicyanamide and 1-butyl-3-methyl imidazoliumdicyanamide at 180°C, nanostructured MoO_3 nanoparticles formed as the major phase and shown in Table1.

In Figure 1 we present the XRD pattern of the products obtained in IL $EmimN(CN)_2$ and $BmimN(CN)_2$. The pattern confirmed the crystalline nature of the material. The most representative reflections of MoO_3 (JCPDS: 47 -1081) were indexed in monoclinic crystal system (space group P2 1/c (14) Y-unique) with the following cell parameters a=7.118, b= 5.366, c=5.568 Å , β=91.99°, Vol=212.5 $Å^3$, Z =4, density =4.4991gcm^{-3} . The average mean diameter of 53.8nm was calculated with the help of Debye-Scherrer equation from full width at half-maximum (FWHM) of (111), (-311), (160), (-421), (330) and (413) planes for material in IL $EmimN(CN)_2$. But in $BmimN(CN)_2$ the diameter was estimated to be 40.8nm.

In Figure 2 we show the SEM image of this material in $EmimN(CN)_2$ and in Figure 3 we show the TEM micrograph in $EmimN(CN)_2$. These data indicate that the MoO_3 nanoparticles consist of rectangular plates and are mono-dispersed.

When the reduction was carried out in EmimOTf and BmimOTf, the products consists of metallic molybdenum and MoO_3. The XRD pattern is shown in Fig.4. The crystalline phase of MoO_3 is rodlike and is determined to be orthorhombic, space group Pbnm(62) with the cell dimensions [a=3.963, b=13.856, c=3.696 Å.; Vol.=203. $Å^3$, Z=4, ρ=4.7096gcm^{-1}] corresponding to MoO_3 (JCPDS: (35-0609). Additional peak at 2θ = 38.9689°, with d-spacing 2.30933Å corresponding to MoO_3 (060) reflection is observed in the material prepared in IL BmimOTf. The average diameter of 51.0 and 48.9nm was calculated respectively for particles in IL EmimOTf and BmimOTf. The SEM and TEM images of the material in EmimOTF are presented in Figure 5 and Figure 6 respectively. These data clearly indicate that there are two crystalline phases in the product: the rod-like nanocrystals are the MoO_3 phase while the cuboid is the metallic molybdenum. From the intensity data of the XRD peaks, the fraction of metallic molybdenum (f_{Mo}) was calculated using the equation:

$$f_{Mo} = \frac{I_{(110)}}{I_{Mo(110)} + I_{MoO_3(200)}}$$

Where $I_{(110)}$ is the intensity of (110) metallic molybdenum reflection and $I_{(200)}$ is the intensity of (200) MoO_3 . The calculation shows that the material consists of 59% Mo and 41% MoO_3. Thus at the beginning of the reaction, the ammonium molybdates is converted into the oxide phase Mo_7O_{24} $(MoO_{3.42})_7$ which undergoes reduction to MoO_3 phase. The MoO_3 phase is then reduced step-wisely to metallic Mo. When this reduction is carried out in IL EmimES, metallic Mo constitutes the major crystalline phase. In Figure 7 we show the XRD pattern of this material in EmimES, In Figure 8 we present the XRD pattern of reduction products in IL EmimNTf2 and in Figure 9 and 10, we present the SEM and TEM images of the synthesized nanoparticles in

EmimNTf$_2$. It should be noted that all the XRD peaks of the material obtained in EmimMS are identified as Mo_4O_{11} peaks from JCPDS card 65-2473, while those in IL EmimNTf$_2$ are MoO_3 peaks from JCPDS card 65-2421. It is worthy of note that the XRD peaks for the oxide phases in all the ionic liquids used in this study are of orthorhombic crystals. The oxides nanostructures are quite faceted and monodisperse.

The UV-Visible absorption spectra of the fraction in ionic liquid dispersed in ethanol is presented in Figure11. The predominant feature in the spectra is the spin-allowed ligand-to-metal charge transfer (LMCT) from O^{2-} ion t_{iu} orbital to a d^0 e_g orbital, which is observed in the range 200-300nm centred at 212nm in the UV region. This is a strong indication of the presence of metallic Molybdenum with particle size less than 100nm. A shift to longer wavelength with a decreasing intensity of absorption signals larger particles and aggregates of molybdenumoxide phase.

Table 1 : Colour and Crystal system of Metallic Mo and oxides nanostructures in different ionic liquids.

Ionic liquids	Colour	Products	Crystal system
BmimBF$_4^-$	Light yellow	Mo_4O_{11}(JCPDS: 65-2473)	Orthorhombic
BmimCN)$_2$N$^-$ Emim(CN)$_2$N	Dark red	MoO_3 (JCPDS:47-1081)	Monoclinic
BmimTfO$^-$ EmimTfO	Brown Olive green	Mo MoO_3 (JCPDS: 65-2421)	Cubic Orthorhombic
BmimNTf$_2$ EmimNTf$_2$	Brown Brown	MoO_3 (JCPDS: 65-2421)	Orthorhombic
EmimMS	Brown	Mo_4O_{11}(JCPDS: 65-2473)	Orthorhombic
EmimES	Dark red	Mo	Cubic

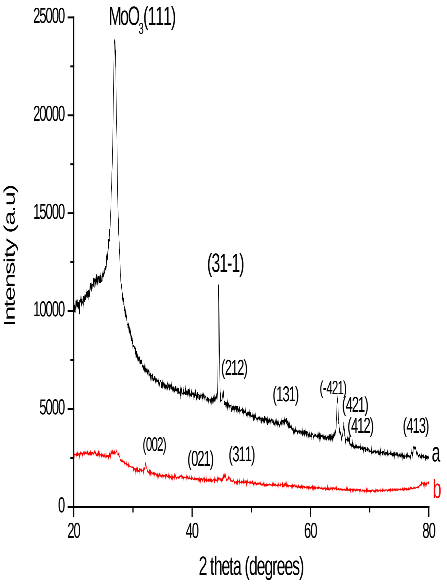


Fig.1 : XRD pattern of sample in EmimN(CN)$_2$ and BmimN(CN)$_2$

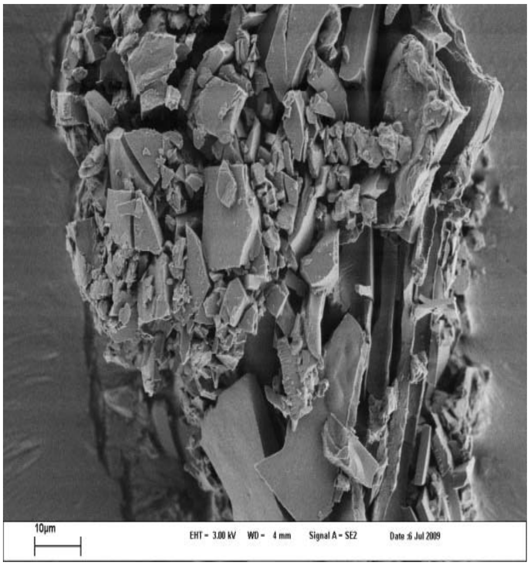


Fig.2 : SEM image of sample in EmimN(CN)$_2$

Fig.3 : TEM image of Material in EmimN(CN)$_2$

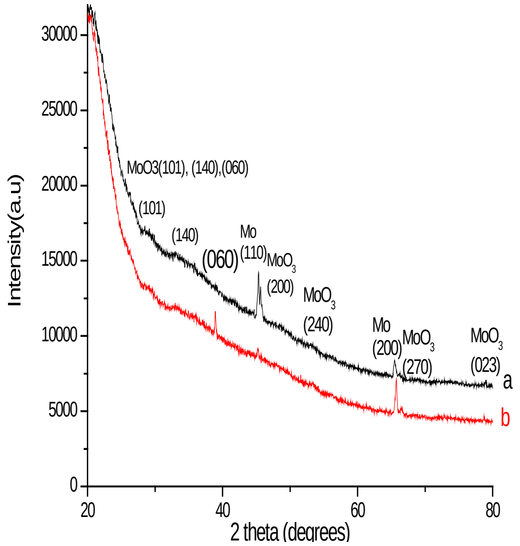


Fig.4 : XRD pattern of in EmimOTf and BmimOTf

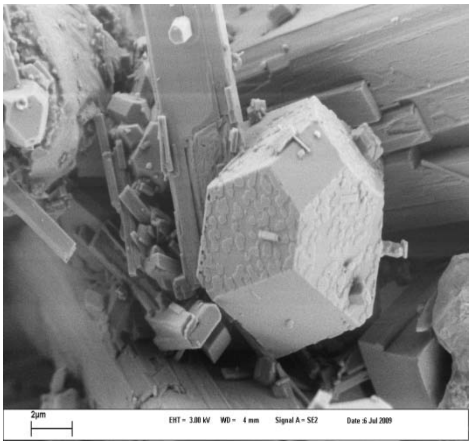


Fig.5 : SEM images of sample in EmimOTf

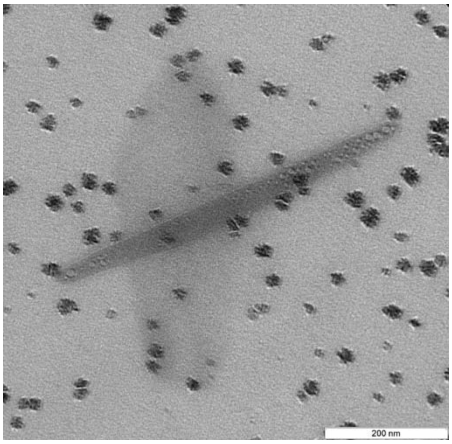


Fig.6 : TEM images of sample in EmimOTf

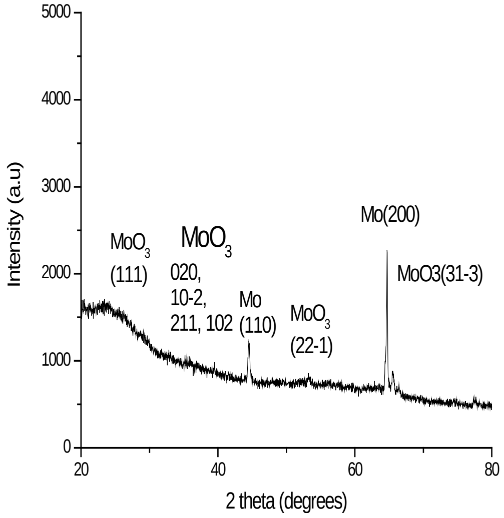


Fig. 7 : XRD pattern of sample in EmimES

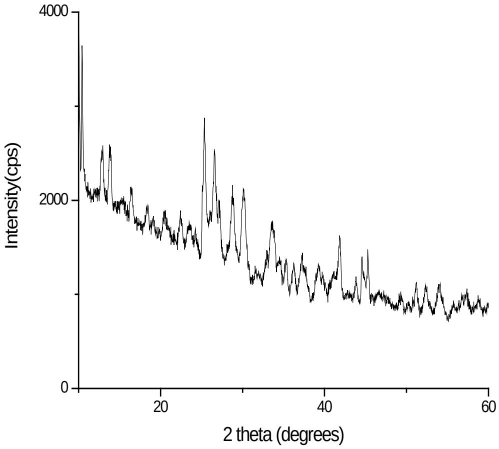


Fig.8 : XRD pattern of sample in EmimNTf$_2$

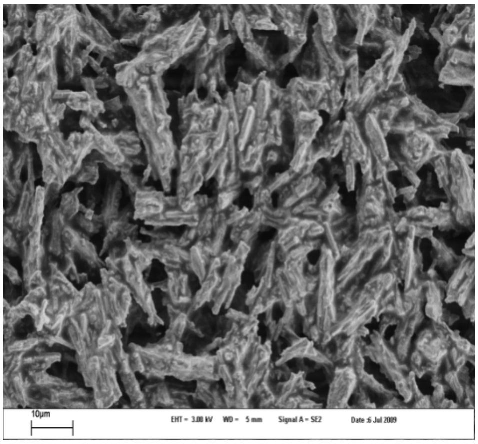


Fig. 9 : SEM image of material in NTf_2

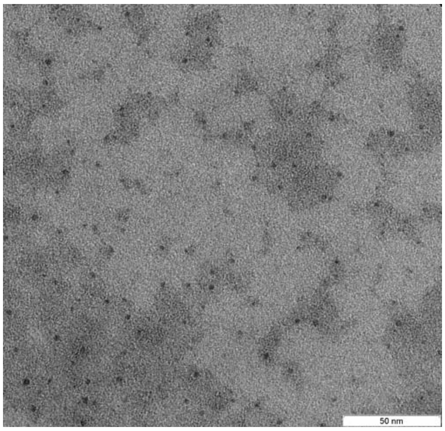


Fig. 10 : TEM image of material in NTf_2

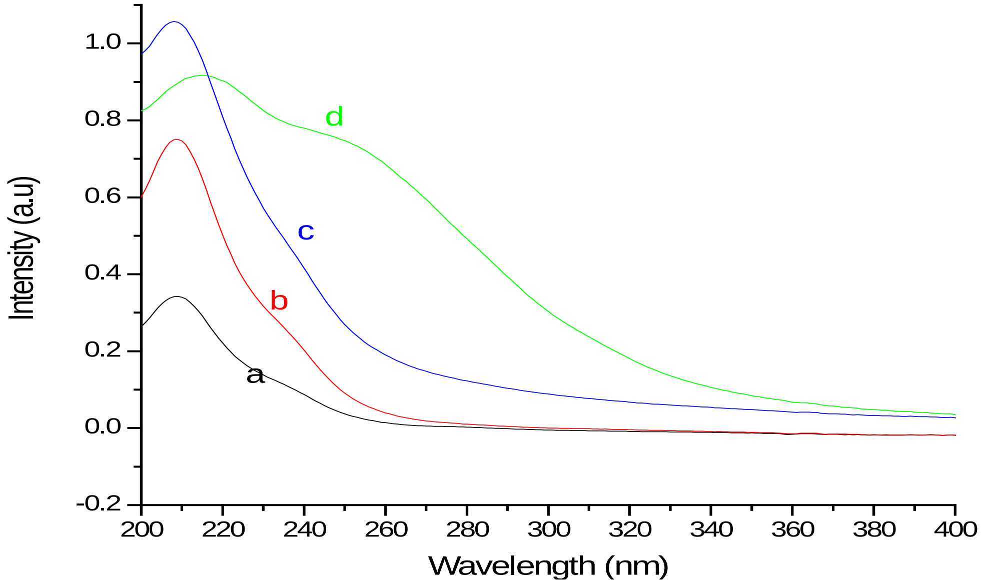


Fig. 11 : The UV-Visible absorption spectra of the fraction in ionic liquid dispersed in ethanol

V. CONCLUSION

Nanostructured Mo and MoO_3 colloidal dispersions have been successfully obtained via the reduction of ammonium molybdate by sodium borohydride in ionic liquids. UV-Visible absorption spectra shows that the predominant feature in the spectra is the spin-allowed ligand-to-metal charge transfer (LMCT) from O^{2-} ion t_{iu} orbital to a d^0 e_g orbital, which is observed in the range 200-300nm centred at 212nm in the UV region. This strongly indicates the presence of metallic Molybdenum with particle size less than 100nm. A shift to longer wavelength with a decreasing intensity of absorption is indicative of larger particles and aggregates of molybdenum oxide phase.

REFERENCES REFERENCES REFERENCIAS

1. Lu, AL, Salabas, EIF. Schuth F (2007). Ionic liquids as a source of positive and negative standards. Angewandte Chemie Int. Ed. 46 1222.
2. Thathagar MB, Beckers J and Rothenberg G (2002).Copper-catalyzed Suzuki-Miyaura cross coupling reaction. *Journal of American Chemical Society124*, 11858.
3. Braun E, Eichen Y, Sivan U and Ben-Yoseph G (1998). DNA-templated assembly and electrode attachment of a conducting silver wire. *Nature.391*, 775.
4. Redel E, Krämer J, Thomann R and Janiak C (2009). Stable cobalt, rhodium and iridium nanoparticles in ionic liquids. *Journal of Organometallic Chemistry. 694, 1069-1075.*

5. Brennecke JF and Maginn EJ (2001). Ionic liquids: innovative fluids for chemical processing. *AIChE J. 47*, 2384-2389.
6. Welton T (1999). Room-temperature ionic liquids. Solvents for synthesis and catalysis. *Chem, Rev. 99*, 2071-2083.
7. Fadeev AG and Meagher MM (2001). Opportunities for ionic liquids in recovery of biofuels. *Chem. Commun*, 295.
8. Wilkes JS (2004). Properties of ionic liquids solvents for catalysis. *J. Mol.Catal. A*: *Chem. 214*, 11-17.
9. Holbrey JD.and Seddon KR.(1999). Ionic liquids. *Clean Prod. Processes. 1*, 223-236.
10. Seddon KR (1997). Ionic liquids for clean technology. *J. Chem. Technol. Biotechnol.* 68, 351-356.
11. Rebelo LPN, Canongia Lopes JN, Esperancüa JMSS and Filipe E (2005). On the critical temperature, normal boiling point, and vapor pressure of ionic liquids. *J. Phys. Chem.B 109*, 6040-6043.
12. Paulechka YU, Zaitsau DzH, Kabo GJ and Strechan AA (2005). Vapor pressure and thermal stability of ionic liquid 1-butyl-3 methylimidazolium bis (trifluoromethylsulfonyl) amide. *Thermochim. Acta, 439*, 158-160.
13. Earle MJ, Esperancüa JMSS, Gilea MA, Canongia Lopes JN, Rebelo LPN, Magee J W, Seddon KR and Widegren JA (2006). The distillation and volatility of ionic liquids. *Nature. 439*, 831-834.
14. Kim KS, Demberelnyamba D and Lee H (2004). Ionic liquids in synthesis. *Langmuir.* 20, 556.
15. Li Z, Friedrich A and Taubert A (2008). Synthesis of ZnO particles on zinc foils in ionic liquids precursors. *Mater. Chem.* 18, 1008.
16. Redel E, Krämer J, Thomann R and Janiak C (2008). Stability and growth behavior of transition metal nanoparticles in ionic liquids. *Organometallics.* 27, 1976.

Global Journals Inc. (US) Guidelines Handbook 2011

www.GlobalJournals.org

FELLOW OF ASSOCIATION OF RESEARCH SOCIETY IN SCIENCE (FARSS)

- 'FARSS' title will be awarded to the person after approval of Editor-in-Chief and Editorial Board. The title 'FARSS" can be added to name in the following manner. eg. Dr. John E. Hall, Ph.D., FARSS or William Walldroff Ph. D., M.S., FARSS
- Being FARSS is a respectful honor. It authenticates your research activities. After becoming FARSS, you can use 'FARSS' title as you use your degree in suffix of your name. This will definitely will enhance and add up your name. You can use it on your Career Counseling Materials/CV/Resume/Visiting Card/Name Plate etc.
- 60% Discount will be provided to FARSS members for publishing research papers in Global Journals Inc., if our Editorial Board and Peer Reviewers accept the paper. For the life time, if you are author/co-author of any paper bill sent to you will automatically be discounted one by 60%
- FARSS will be given a renowned, secure, free professional email address with 100 GB of space eg.johnhall@globaljournals.org. You will be facilitated with Webmail, SpamAssassin, Email Forwarders, Auto-Responders, Email Delivery Route tracing, etc.
- FARSS member is eligible to become paid peer reviewer at Global Journals Inc. to earn up to 15% of realized author charges taken from author of respective paper. After reviewing 5 or more papers you can request to transfer the amount to your bank account or to your PayPal account.
- Eg. If we had taken 420 USD from author, we can send 63 USD to your account.
- FARSS member can apply for free approval, grading and certification of some of their Educational and Institutional Degrees from Global Journals Inc. (US) and Open Association of Research,Society U.S.A.
- After you are FARSS. You can send us scanned copy of all of your documents. We will verify, grade and certify them within a month. It will be based on your academic records, quality of research papers published by you, and 50 more criteria. This is beneficial for your job interviews as recruiting organization need not just rely on you for authenticity and your unknown qualities, you would have authentic ranks of all of your documents. Our scale is unique worldwide.
- FARSS member can proceed to get benefits of free research podcasting in Global Research Radio with their research documents, slides and online movies.
- After your publication anywhere in the world, you can upload you research paper with your recorded voice or you can use our professional RJs to record your paper their voice. We can also stream your conference videos and display your slides online.
- FARSS will be eligible for free application of Standardization of their Researches by Open Scientific Standards. Standardization is next step and level after publishing in a journal. A team of research and professional will work with you to take your research to its next level, which is worldwide open standardization.

- FARSS is eligible to earn from their researches: While publishing his paper with Global Journals Inc. (US), FARSS can decide whether he/she would like to publish his/her research in closed manner. When readers will buy that individual research paper for reading, 80% of its earning by Global Journals Inc. (US) will be transferred to FARSS member's bank account after certain threshold balance. There is no time limit for collection. FARSS member can decide its price and we can help in decision.

MEMBER OF ASSOCIATION OF RESEARCH SOCIETY IN SCIENCE (MARSS)

- 'MARSS' title will be awarded to the person after approval of Editor-in-Chief and Editorial Board. The title 'MARSS" can be added to name in the following manner. eg. Dr. John E. Hall, Ph.D., MARSS or William Walldroff Ph. D., M.S., MARSS
- Being MARSS is a respectful honor. It authenticates your research activities. After becoming MARSS, you can use 'MARSS' title as you use your degree in suffix of your name. This will definitely will enhance and add up your name. You can use it on your Career Counseling Materials/CV/Resume/Visiting Card/Name Plate etc.
- 40% Discount will be provided to MARSS members for publishing research papers in Global Journals Inc., if our Editorial Board and Peer Reviewers accept the paper. For the life time, if you are author/co-author of any paper bill sent to you will automatically be discounted one by 60%
- MARSS will be given a renowned, secure, free professional email address with 30 GB of space eg.johnhall@globaljournals.org. You will be facilitated with Webmail, SpamAssassin, Email Forwarders, Auto-Responders, Email Delivery Route tracing, etc.
- MARSS member is eligible to become paid peer reviewer at Global Journals Inc. to earn up to 10% of realized author charges taken from author of respective paper. After reviewing 5 or more papers you can request to transfer the amount to your bank account or to your PayPal account.
- MARSS member can apply for free approval, grading and certification of some of their Educational and Institutional Degrees from Global Journals Inc. (US) and Open Association of Research,Society U.S.A.
- MARSS is eligible to earn from their researches: While publishing his paper with Global Journals Inc. (US), MARSS can decide whether he/she would like to publish his/her research in closed manner. When readers will buy that individual research paper for reading, 40% of its earning by Global Journals Inc. (US) will be transferred to MARSS member's bank account after certain threshold balance. There is no time limit for collection. MARSS member can decide its price and we can help in decision.

AUXILIARY MEMBERSHIPS

ANNUAL MEMBER

- Annual Member will be authorized to receive e-Journal GJSFR for one year (subscription for one year).
- The member will be allotted free 1 GB Web-space along with subDomain to contribute and participate in our activities.
- A professional email address will be allotted free 500 MB email space.

PAPER PUBLICATION

- The members can publish paper once. The paper will be sent to two-peer reviewer. The paper will be published after the acceptance of peer reviewers and Editorial Board.

PROCESS OF SUBMISSION OF RESEARCH PAPER

The Area or field of specialization may or may not be of any category as mentioned in 'Scope of Journal' menu of the GlobalJournals.org website. There are 37 Research Journal categorized with Six parental Journals GJCST, GJMR, GJRE, GJMBR, GJSFR, GJHSS. For Authors should prefer the mentioned categories. There are three widely used systems UDC, DDC and LCC. The details are available as 'Knowledge Abstract' at Home page. The major advantage of this coding is that, the research work will be exposed to and shared with all over the world as we are being abstracted and indexed worldwide.

The paper should be in proper format. The format can be downloaded from first page of 'Author Guideline' Menu. The Author is expected to follow the general rules as mentioned in this menu. The paper should be written in MS-Word Format (*.DOC,*.DOCX).

The Author can submit the paper either online or offline. The authors should prefer online submission.Online Submission: There are three ways to submit your paper:

(A) (I) First, register yourself using top right corner of Home page then Login. If you are already registered, then login using your username and password.

(II) Choose corresponding Journal.

(III) Click 'Submit Manuscript'. Fill required information and Upload the paper.

(B) If you are using Internet Explorer, then Direct Submission through Homepage is also available.

(C) If these two are not conveninet , and then email the paper directly to dean@globaljournals.org.

Offline Submission: Author can send the typed form of paper by Post. However, online submission should be preferred.

PREFERRED AUTHOR GUIDELINES

MANUSCRIPT STYLE INSTRUCTION **(Must be strictly followed)**

Page Size: 8.27" X 11'"

- Left Margin: 0.65
- Right Margin: 0.65
- Top Margin: 0.75
- Bottom Margin: 0.75
- Font type of all text should be Swis 721 Lt BT.
- Paper Title should be of Font Size 24 with one Column section.
- Author Name in Font Size of 11 with one column as of Title.
- Abstract Font size of 9 Bold, “Abstract” word in Italic Bold.
- Main Text: Font size 10 with justified two columns section
- Two Column with Equal Column with of 3.38 and Gaping of .2
- First Character must be three lines Drop capped.
- Paragraph before Spacing of 1 pt and After of 0 pt.
- Line Spacing of 1 pt
- Large Images must be in One Column
- Numbering of First Main Headings (Heading 1) must be in Roman Letters, Capital Letter, and Font Size of 10.
- Numbering of Second Main Headings (Heading 2) must be in Alphabets, Italic, and Font Size of 10.

You can use your own standard format also.
Author Guidelines:

1. General,

2. Ethical Guidelines,

3. Submission of Manuscripts,

4. Manuscript’s Category,

5. Structure and Format of Manuscript,

6. After Acceptance.

1. GENERAL

Before submitting your research paper, one is advised to go through the details as mentioned in following heads. It will be beneficial, while peer reviewer justify your paper for publication.

Scope

The Global Journals Inc. (US) welcome the submission of original paper, review paper, survey article relevant to the all the streams of Philosophy and knowledge. The Global Journals Inc. (US) is parental platform for Global Journal of Computer Science and Technology, Researches in Engineering, Medical Research, Science Frontier Research, Human Social Science, Management, and Business organization. The choice of specific field can be done otherwise as following in Abstracting and Indexing Page on this Website. As the all Global

Journals Inc. (US) are being abstracted and indexed (in process) by most of the reputed organizations. Topics of only narrow interest will not be accepted unless they have wider potential or consequences.

2. ETHICAL GUIDELINES

Authors should follow the ethical guidelines as mentioned below for publication of research paper and research activities.

Papers are accepted on strict understanding that the material in whole or in part has not been, nor is being, considered for publication elsewhere. If the paper once accepted by Global Journals Inc. (US) and Editorial Board, will become the copyright of the Global Journals Inc. (US).

Authorship: The authors and coauthors should have active contribution to conception design, analysis and interpretation of findings. They should critically review the contents and drafting of the paper. All should approve the final version of the paper before submission

The Global Journals Inc. (US) follows the definition of authorship set up by the Global Academy of Research and Development. According to the Global Academy of R&D authorship, criteria must be based on:

1) Substantial contributions to conception and acquisition of data, analysis and interpretation of the findings.

2) Drafting the paper and revising it critically regarding important academic content.

3) Final approval of the version of the paper to be published.

All authors should have been credited according to their appropriate contribution in research activity and preparing paper. Contributors who do not match the criteria as authors may be mentioned under Acknowledgement.

Acknowledgements: Contributors to the research other than authors credited should be mentioned under acknowledgement. The specifications of the source of funding for the research if appropriate can be included. Suppliers of resources may be mentioned along with address.

Appeal of Decision: The Editorial Board's decision on publication of the paper is final and cannot be appealed elsewhere.

Permissions: It is the author's responsibility to have prior permission if all or parts of earlier published illustrations are used in this paper.

Please mention proper reference and appropriate acknowledgements wherever expected.

If all or parts of previously published illustrations are used, permission must be taken from the copyright holder concerned. It is the author's responsibility to take these in writing.

Approval for reproduction/modification of any information (including figures and tables) published elsewhere must be obtained by the authors/copyright holders before submission of the manuscript. Contributors (Authors) are responsible for any copyright fee involved.

3. SUBMISSION OF MANUSCRIPTS

Manuscripts should be uploaded via this online submission page. The online submission is most efficient method for submission of papers, as it enables rapid distribution of manuscripts and consequently speeds up the review procedure. It also enables authors to know the status of their own manuscripts by emailing us. Complete instructions for submitting a paper is available below.

Manuscript submission is a systematic procedure and little preparation is required beyond having all parts of your manuscript in a given format and a computer with an Internet connection and a Web browser. Full help and instructions are provided on-screen. As an author, you will be prompted for login and manuscript details as Field of Paper and then to upload your manuscript file(s) according to the instructions.

To avoid postal delays, all transaction is preferred by e-mail. A finished manuscript submission is confirmed by e-mail immediately and your paper enters the editorial process with no postal delays. When a conclusion is made about the publication of your paper by our Editorial Board, revisions can be submitted online with the same procedure, with an occasion to view and respond to all comments.

Complete support for both authors and co-author is provided.

4. MANUSCRIPT'S CATEGORY

Based on potential and nature, the manuscript can be categorized under the following heads:

Original research paper: Such papers are reports of high-level significant original research work.

Review papers: These are concise, significant but helpful and decisive topics for young researchers.

Research articles: These are handled with small investigation and applications

Research letters: The letters are small and concise comments on previously published matters.

5.STRUCTURE AND FORMAT OF MANUSCRIPT

The recommended size of original research paper is less than seven thousand words, review papers fewer than seven thousands words also.Preparation of research paper or how to write research paper, are major hurdle, while writing manuscript. The research articles and research letters should be fewer than three thousand words, the structure original research paper; sometime review paper should be as follows:

Papers: These are reports of significant research (typically less than 7000 words equivalent, including tables, figures, references), and comprise:

(a)Title should be relevant and commensurate with the theme of the paper.

(b) A brief Summary, “Abstract” (less than 150 words) containing the major results and conclusions.

(c) Up to ten keywords, that precisely identifies the paper's subject, purpose, and focus.

(d) An Introduction, giving necessary background excluding subheadings; objectives must be clearly declared.

(e) Resources and techniques with sufficient complete experimental details (wherever possible by reference) to permit repetition; sources of information must be given and numerical methods must be specified by reference, unless non-standard.

(f) Results should be presented concisely, by well-designed tables and/or figures; the same data may not be used in both; suitable statistical data should be given. All data must be obtained with attention to numerical detail in the planning stage. As reproduced design has been recognized to be important to experiments for a considerable time, the Editor has decided that any paper that appears not to have adequate numerical treatments of the data will be returned un-refereed;

(g) Discussion should cover the implications and consequences, not just recapitulating the results; conclusions should be summarizing.

(h) Brief Acknowledgements.

(i) References in the proper form.

Authors should very cautiously consider the preparation of papers to ensure that they communicate efficiently. Papers are much more likely to be accepted, if they are cautiously designed and laid out, contain few or no errors, are summarizing, and be conventional to the approach and instructions. They will in addition, be published with much less delays than those that require much technical and editorial correction.

The Editorial Board reserves the right to make literary corrections and to make suggestions to improve briefness.

It is vital, that authors take care in submitting a manuscript that is written in simple language and adheres to published guidelines.

Format

Language: The language of publication is UK English. Authors, for whom English is a second language, must have their manuscript efficiently edited by an English-speaking person before submission to make sure that, the English is of high excellence. It is preferable, that manuscripts should be professionally edited.

Standard Usage, Abbreviations, and Units: Spelling and hyphenation should be conventional to The Concise Oxford English Dictionary. Statistics and measurements should at all times be given in figures, e.g. 16 min, except for when the number begins a sentence. When the number does not refer to a unit of measurement it should be spelt in full unless, it is 160 or greater.

Abbreviations supposed to be used carefully. The abbreviated name or expression is supposed to be cited in full at first usage, followed by the conventional abbreviation in parentheses.

Metric SI units are supposed to generally be used excluding where they conflict with current practice or are confusing. For illustration, 1.4 l rather than 1.4 × 10-3 m3, or 4 mm somewhat than 4 × 10-3 m. Chemical formula and solutions must identify the form used, e.g. anhydrous or hydrated, and the concentration must be in clearly defined units. Common species names should be followed by underlines at the first mention. For following use the generic name should be constricted to a single letter, if it is clear.

Structure

All manuscripts submitted to Global Journals Inc. (US), ought to include:

Title: The title page must carry an instructive title that reflects the content, a running title (less than 45 characters together with spaces), names of the authors and co-authors, and the place(s) wherever the work was carried out. The full postal address in addition with the e-mail address of related author must be given. Up to eleven keywords or very brief phrases have to be given to help data retrieval, mining and indexing.

Abstract, used in Original Papers and Reviews:

Optimizing Abstract for Search Engines

Many researchers searching for information online will use search engines such as Google, Yahoo or similar. By optimizing your paper for search engines, you will amplify the chance of someone finding it. This in turn will make it more likely to be viewed and/or cited in a further work. Global Journals Inc. (US) have compiled these guidelines to facilitate you to maximize the web-friendliness of the most public part of your paper.

Key Words

A major linchpin in research work for the writing research paper is the keyword search, which one will employ to find both library and Internet resources.

One must be persistent and creative in using keywords. An effective keyword search requires a strategy and planning a list of possible keywords and phrases to try.

Search engines for most searches, use Boolean searching, which is somewhat different from Internet searches. The Boolean search uses "operators," words (and, or, not, and near) that enable you to expand or narrow your affords. Tips for research paper while preparing research paper are very helpful guideline of research paper.

Choice of key words is first tool of tips to write research paper. Research paper writing is an art.A few tips for deciding as strategically as possible about keyword search:

- One should start brainstorming lists of possible keywords before even begin searching. Think about the most important concepts related to research work. Ask, "What words would a source have to include to be truly valuable in research paper?" Then consider synonyms for the important words.
- It may take the discovery of only one relevant paper to let steer in the right keyword direction because in most databases, the keywords under which a research paper is abstracted are listed with the paper.
- One should avoid outdated words.

Keywords are the key that opens a door to research work sources. Keyword searching is an art in which researcher's skills are bound to improve with experience and time.

Numerical Methods: Numerical methods used should be clear and, where appropriate, supported by references.

Acknowledgements: Please make these as concise as possible.

References

References follow the Harvard scheme of referencing. References in the text should cite the authors' names followed by the time of their publication, unless there are three or more authors when simply the first author's name is quoted followed by et al. unpublished work has to only be cited where necessary, and only in the text. Copies of references in press in other journals have to be supplied with submitted typescripts. It is necessary that all citations and references be carefully checked before submission, as mistakes or omissions will cause delays.

References to information on the World Wide Web can be given, but only if the information is available without charge to readers on an official site. Wikipedia and Similar websites are not allowed where anyone can change the information. Authors will be asked to make available electronic copies of the cited information for inclusion on the Global Journals Inc. (US) homepage at the judgment of the Editorial Board.

The Editorial Board and Global Journals Inc. (US) recommend that, citation of online-published papers and other material should be done via a DOI (digital object identifier). If an author cites anything, which does not have a DOI, they run the risk of the cited material not being noticeable.

The Editorial Board and Global Journals Inc. (US) recommend the use of a tool such as Reference Manager for reference management and formatting.

Tables, Figures and Figure Legends

Tables: Tables should be few in number, cautiously designed, uncrowned, and include only essential data. Each must have an Arabic number, e.g. Table 4, a self-explanatory caption and be on a separate sheet. Vertical lines should not be used.

Figures: Figures are supposed to be submitted as separate files. Always take in a citation in the text for each figure using Arabic numbers, e.g. Fig. 4. Artwork must be submitted online in electronic form by e-mailing them.

Preparation of Electronic Figures for Publication

Even though low quality images are sufficient for review purposes, print publication requires high quality images to prevent the final product being blurred or fuzzy. Submit (or e-mail) EPS (line art) or TIFF (halftone/photographs) files only. MS PowerPoint and Word Graphics are unsuitable for printed pictures. Do not use pixel-oriented software. Scans (TIFF only) should have a resolution of at least 350 dpi (halftone) or 700 to 1100 dpi (line drawings) in relation to the imitation size. Please give the data for figures in black and white or submit a Color Work Agreement Form. EPS files must be saved with fonts embedded (and with a TIFF preview, if possible).

For scanned images, the scanning resolution (at final image size) ought to be as follows to ensure good reproduction: line art: >650 dpi; halftones (including gel photographs) : >350 dpi; figures containing both halftone and line images: >650 dpi.

Color Charges: It is the rule of the Global Journals Inc. (US) for authors to pay the full cost for the reproduction of their color artwork. Hence, please note that, if there is color artwork in your manuscript when it is accepted for publication, we would require you to complete and return a color work agreement form before your paper can be published.

Figure Legends: Self-explanatory legends of all figures should be incorporated separately under the heading 'Legends to Figures'. In the full-text online edition of the journal, figure legends may possibly be truncated in abbreviated links to the full screen version. Therefore, the first 100 characters of any legend should notify the reader, about the key aspects of the figure.

6. AFTER ACCEPTANCE

Upon approval of a paper for publication, the manuscript will be forwarded to the dean, who is responsible for the publication of the Global Journals Inc. (US).

6.1 Proof Corrections

The corresponding author will receive an e-mail alert containing a link to a website or will be attached. A working e-mail address must therefore be provided for the related author.

Acrobat Reader will be required in order to read this file. This software can be downloaded

(Free of charge) from the following website:

www.adobe.com/products/acrobat/readstep2.html. This will facilitate the file to be opened, read on screen, and printed out in order for any corrections to be added. Further instructions will be sent with the proof.

Proofs must be returned to the dean at dean@globaljournals.org within three days of receipt.

As changes to proofs are costly, we inquire that you only correct typesetting errors. All illustrations are retained by the publisher. Please note that the authors are responsible for all statements made in their work, including changes made by the copy editor.

6.2 Early View of Global Journals Inc. (US) (Publication Prior to Print)

The Global Journals Inc. (US) are enclosed by our publishing's Early View service. Early View articles are complete full-text articles sent in advance of their publication. Early View articles are absolute and final. They have been completely reviewed, revised and edited for publication, and the authors' final corrections have been incorporated. Because they are in final form, no changes can be made after sending them. The nature of Early View articles means that they do not yet have volume, issue or page numbers, so Early View articles cannot be cited in the conventional way.

6.3 Author Services

Online production tracking is available for your article through Author Services. Author Services enables authors to track their article - once it has been accepted - through the production process to publication online and in print. Authors can check the status of their articles online and choose to receive automated e-mails at key stages of production. The authors will receive an e-mail with a unique link that enables them to register and have their article automatically added to the system. Please ensure that a complete e-mail address is provided when submitting the manuscript.

6.4 Author Material Archive Policy

Please note that if not specifically requested, publisher will dispose off hardcopy & electronic information submitted, after the two months of publication. If you require the return of any information submitted, please inform the Editorial Board or dean as soon as possible.

6.5 Offprint and Extra Copies

A PDF offprint of the online-published article will be provided free of charge to the related author, and may be distributed according to the Publisher's terms and conditions. Additional paper offprint may be ordered by emailing us at: editor@globaljournals.org .

the search? Will I be able to find all information in this field area? If the answer of these types of questions will be "Yes" then you can choose that topic. In most of the cases, you may have to conduct the surveys and have to visit several places because this field is related to Computer Science and Information Technology. Also, you may have to do a lot of work to find all rise and falls regarding the various data of that subject. Sometimes, detailed information plays a vital role, instead of short information.

2. Evaluators are human: First thing to remember that evaluators are also human being. They are not only meant for rejecting a paper. They are here to evaluate your paper. So, present your Best.

3. Think Like Evaluators: If you are in a confusion or getting demotivated that your paper will be accepted by evaluators or not, then think and try to evaluate your paper like an Evaluator. Try to understand that what an evaluator wants in your research paper and automatically you will have your answer.

4. Make blueprints of paper: The outline is the plan or framework that will help you to arrange your thoughts. It will make your paper logical. But remember that all points of your outline must be related to the topic you have chosen.

5. Ask your Guides: If you are having any difficulty in your research, then do not hesitate to share your difficulty to your guide (if you have any). They will surely help you out and resolve your doubts. If you can't clarify what exactly you require for your work then ask the supervisor to help you with the alternative. He might also provide you the list of essential readings.

6. Use of computer is recommended: As you are doing research in the field of Computer Science, then this point is quite obvious.

7. Use right software: Always use good quality software packages. If you are not capable to judge good software then you can lose quality of your paper unknowingly. There are various software programs available to help you, which you can get through Internet.

8. Use the Internet for help: An excellent start for your paper can be by using the Google. It is an excellent search engine, where you can have your doubts resolved. You may also read some answers for the frequent question how to write my research paper or find model research paper. From the internet library you can download books. If you have all required books make important reading selecting and analyzing the specified information. Then put together research paper sketch out.

9. Use and get big pictures: Always use encyclopedias, Wikipedia to get pictures so that you can go into the depth.

10. Bookmarks are useful: When you read any book or magazine, you generally use bookmarks, right! It is a good habit, which helps to not to lose your continuity. You should always use bookmarks while searching on Internet also, which will make your search easier.

11. Revise what you wrote: When you write anything, always read it, summarize it and then finalize it.

12. Make all efforts: Make all efforts to mention what you are going to write in your paper. That means always have a good start. Try to mention everything in introduction, that what is the need of a particular research paper. Polish your work by good skill of writing and always give an evaluator, what he wants.

13. Have backups: When you are going to do any important thing like making research paper, you should always have backup copies of it either in your computer or in paper. This will help you to not to lose any of your important.

14. Produce good diagrams of your own: Always try to include good charts or diagrams in your paper to improve quality. Using several and unnecessary diagrams will degrade the quality of your paper by creating "hotchpotch." So always, try to make and include those diagrams, which are made by your own to improve readability and understandability of your paper.

15. Use of direct quotes: When you do research relevant to literature, history or current affairs then use of quotes become essential but if study is relevant to science then use of quotes is not preferable.

16. Use proper verb tense: Use proper verb tenses in your paper. Use past tense, to present those events that happened. Use present tense to indicate events that are going on. Use future tense to indicate future happening events. Use of improper and wrong tenses will confuse the evaluator. Avoid the sentences that are incomplete.

17. Never use online paper: If you are getting any paper on Internet, then never use it as your research paper because it might be possible that evaluator has already seen it or maybe it is outdated version.

18. **Pick a good study spot:** To do your research studies always try to pick a spot, which is quiet. Every spot is not for studies. Spot that suits you choose it and proceed further.

19. Know what you know: Always try to know, what you know by making objectives. Else, you will be confused and cannot achieve your target.

20. Use good quality grammar: Always use a good quality grammar and use words that will throw positive impact on evaluator. Use of good quality grammar does not mean to use tough words, that for each word the evaluator has to go through dictionary. Do not start sentence with a conjunction. Do not fragment sentences. Eliminate one-word sentences. Ignore passive voice. Do not ever use a big word when a diminutive one would suffice. Verbs have to be in agreement with their subjects. Prepositions are not expressions to finish sentences with. It is incorrect to ever divide an infinitive. Avoid clichés like the disease. Also, always shun irritating alliteration. Use language that is simple and straight forward. put together a neat summary.

21. Arrangement of information: Each section of the main body should start with an opening sentence and there should be a changeover at the end of the section. Give only valid and powerful arguments to your topic. You may also maintain your arguments with records.

22. Never start in last minute: Always start at right time and give enough time to research work. Leaving everything to the last minute will degrade your paper and spoil your work.

23. Multitasking in research is not good: Doing several things at the same time proves bad habit in case of research activity. Research is an area, where everything has a particular time slot. Divide your research work in parts and do particular part in particular time slot.

24. Never copy others' work: Never copy others' work and give it your name because if evaluator has seen it anywhere you will be in trouble.

25. Take proper rest and food: No matter how many hours you spend for your research activity, if you are not taking care of your health then all your efforts will be in vain. For a quality research, study is must, and this can be done by taking proper rest and food.

26. Go for seminars: Attend seminars if the topic is relevant to your research area. Utilize all your resources.

27. Refresh your mind after intervals: Try to give rest to your mind by listening to soft music or by sleeping in intervals. This will also improve your memory.

28. Make colleagues: Always try to make colleagues. No matter how sharper or intelligent you are, if you make colleagues you can have several ideas, which will be helpful for your research.

29. **Think technically:** Always think technically. If anything happens, then search its reasons, its benefits, and demerits.

30. Think and then print: When you will go to print your paper, notice that tables are not be split, headings are not detached from their descriptions, and page sequence is maintained.

31. Adding unnecessary information: Do not add unnecessary information, like, I have used MS Excel to draw graph. Do not add irrelevant and inappropriate material. These all will create superfluous. Foreign terminology and phrases are not apropos. One should NEVER take a broad view. Analogy in script is like feathers on a snake. Not at all use a large word when a very small one would be sufficient. Use words properly, regardless of how others use them. Remove quotations. Puns are for kids, not grunt readers. Amplification is a billion times of inferior quality than sarcasm.

32. Never oversimplify everything: To add material in your research paper, never go for oversimplification. This will definitely irritate the evaluator. Be more or less specific. Also too, by no means, ever use rhythmic redundancies. Contractions aren't essential and shouldn't be there used. Comparisons are as terrible as clichés. Give up ampersands and abbreviations, and so on. Remove commas, that are, not necessary. Parenthetical words however should be together with this in commas. Understatement is all the time the complete best way to put onward earth-shaking thoughts. Give a detailed literary review.

33. Report concluded results: Use concluded results. From raw data, filter the results and then conclude your studies based on measurements and observations taken. Significant figures and appropriate number of decimal places should be used. Parenthetical remarks are prohibitive. Proofread carefully at final stage. In the end give outline to your arguments. Spot out perspectives of further study of this subject. Justify your conclusion by at the bottom of them with sufficient justifications and examples.

34. After conclusion: Once you have concluded your research, the next most important step is to present your findings. Presentation is extremely important as it is the definite medium though which your research is going to be in print to the rest of the crowd. Care should be taken to categorize your thoughts well and present them in a logical and neat manner. A good quality research paper format is essential because it serves to highlight your research paper and bring to light all necessary aspects in your research.

INFORMAL GUIDELINES OF RESEARCH PAPER WRITING

Key points to remember:

- Submit all work in its final form.
- Write your paper in the form, which is presented in the guidelines using the template.
- Please note the criterion for grading the final paper by peer-reviewers.

Final Points:

A purpose of organizing a research paper is to let people to interpret your effort selectively. The journal requires the following sections, submitted in the order listed, each section to start on a new page.

The introduction will be compiled from reference matter and will reflect the design processes or outline of basis that direct you to make study. As you will carry out the process of study, the method and process section will be constructed as like that. The result segment will show related statistics in nearly sequential order and will direct the reviewers next to the similar intellectual paths throughout the data that you took to carry out your study. The discussion section will provide understanding of the data and projections as to the implication of the results. The use of good quality references all through the paper will give the effort trustworthiness by representing an alertness of prior workings.

Writing a research paper is not an easy job no matter how trouble-free the actual research or concept. Practice, excellent preparation, and controlled record keeping are the only means to make straightforward the progression.

General style:

Specific editorial column necessities for compliance of a manuscript will always take over from directions in these general guidelines.

To make a paper clear

· Adhere to recommended page limits

Mistakes to evade

- Insertion a title at the foot of a page with the subsequent text on the next page

- Separating a table/chart or figure - impound each figure/table to a single page
- Submitting a manuscript with pages out of sequence

In every sections of your document

· Use standard writing style including articles ("a", "the," etc.)

· Keep on paying attention on the research topic of the paper

· Use paragraphs to split each significant point (excluding for the abstract)

· Align the primary line of each section

· Present your points in sound order

· Use present tense to report well accepted

· Use past tense to describe specific results

· Shun familiar wording, don't address the reviewer directly, and don't use slang, slang language, or superlatives

· Shun use of extra pictures - include only those figures essential to presenting results

Title Page:

Choose a revealing title. It should be short. It should not have non-standard acronyms or abbreviations. It should not exceed two printed lines. It should include the name(s) and address (es) of all authors.

Abstract:

The summary should be two hundred words or less. It should briefly and clearly explain the key findings reported in the manuscript--must have precise statistics. It should not have abnormal acronyms or abbreviations. It should be logical in itself. Shun citing references at this point.

An abstract is a brief distinct paragraph summary of finished work or work in development. In a minute or less a reviewer can be taught the foundation behind the study, common approach to the problem, relevant results, and significant conclusions or new questions.

Write your summary when your paper is completed because how can you write the summary of anything which is not yet written? Wealth of terminology is very essential in abstract. Yet, use comprehensive sentences and do not let go readability for briefness. You can maintain it succinct by phrasing sentences so that they provide more than lone rationale. The author can at this moment go straight to shortening the outcome. Sum up the study, with the subsequent elements in any summary. Try to maintain the initial two items to no more than one ruling each.

- Reason of the study - theory, overall issue, purpose
- Fundamental goal
- To the point depiction of the research
- Consequences, including definite statistics - if the consequences are quantitative in nature, account quantitative data; results of any numerical analysis should be reported
- Significant conclusions or questions that track from the research(es)

Approach:

- Single section, and succinct
- As a outline of job done, it is always written in past tense
- A conceptual should situate on its own, and not submit to any other part of the paper such as a form or table
- Center on shortening results - bound background information to a verdict or two, if completely necessary
- What you account in an conceptual must be regular with what you reported in the manuscript
- Exact spelling, clearness of sentences and phrases, and appropriate reporting of quantities (proper units, important statistics) are just as significant in an abstract as they are anywhere else

Introduction:

The **Introduction** should "introduce" the manuscript. The reviewer should be presented with sufficient background information to be capable to comprehend and calculate the purpose of your study without having to submit to other works. The basis for the study should be offered. Give most important references but shun difficult to make a comprehensive appraisal of the topic. In the introduction, describe the problem visibly. If the problem is not acknowledged in a logical, reasonable way, the reviewer will have no attention in your result. Speak in common terms about techniques used to explain the problem, if needed, but do not present any particulars about the protocols here. Following approach can create a valuable beginning:

- Explain the value (significance) of the study
- Shield the model - why did you employ this particular system or method? What is its compensation? You strength remark on its appropriateness from a abstract point of vision as well as point out sensible reasons for using it.
- Present a justification. Status your particular theory (es) or aim(s), and describe the logic that led you to choose them.
- Very for a short time explain the tentative propose and how it skilled the declared objectives.

Approach:

- Use past tense except for when referring to recognized facts. After all, the manuscript will be submitted after the entire job is done.
- Sort out your thoughts; manufacture one key point with every section. If you make the four points listed above, you will need a least of four paragraphs.
- Present surroundings information only as desirable in order hold up a situation. The reviewer does not desire to read the whole thing you know about a topic.
- Shape the theory/purpose specifically - do not take a broad view.
- As always, give awareness to spelling, simplicity and correctness of sentences and phrases.

Procedures (Methods and Materials):

This part is supposed to be the easiest to carve if you have good skills. A sound written Procedures segment allows a capable scientist to replacement your results. Present precise information about your supplies. The suppliers and clarity of reagents can be helpful bits of information. Present methods in sequential order but linked methodologies can be grouped as a segment. Be concise when relating the protocols. Attempt for the least amount of information that would permit another capable scientist to spare your outcome but be cautious that vital information is integrated. The use of subheadings is suggested and ought to be synchronized with the results section. When a technique is used that has been well described in another object, mention the specific item describing a way but draw the basic principle while stating the situation. The purpose is to text all particular resources and broad procedures, so that another person may use some or all of the methods in one more study or referee the scientific value of your work. It is not to be a step by step report of the whole thing you did, nor is a methods section a set of orders.

Materials:

- Explain materials individually only if the study is so complex that it saves liberty this way.
- Embrace particular materials, and any tools or provisions that are not frequently found in laboratories.
- Do not take in frequently found.
- If use of a definite type of tools.
- Materials may be reported in a part section or else they may be recognized along with your measures.

Methods:

- Report the method (not particulars of each process that engaged the same methodology)
- Describe the method entirely
- To be succinct, present methods under headings dedicated to specific dealings or groups of measures
- Simplify - details how procedures were completed not how they were exclusively performed on a particular day.
- If well known procedures were used, account the procedure by name, possibly with reference, and that's all.

Approach:

- It is embarrassed or not possible to use vigorous voice when documenting methods with no using first person, which would focus the reviewer's interest on the researcher rather than the job. As a result when script up the methods most authors use third person passive voice.
- Use standard style in this and in every other part of the paper - avoid familiar lists, and use full sentences.

What to keep away from

- Resources and methods are not a set of information.
- Skip all descriptive information and surroundings - save it for the argument.
- Leave out information that is immaterial to a third party.

Results:

The principle of a results segment is to present and demonstrate your conclusion. Create this part a entirely objective details of the outcome, and save all understanding for the discussion.

The page length of this segment is set by the sum and types of data to be reported. Carry on to be to the point, by means of statistics and tables, if suitable, to present consequences most efficiently.You must obviously differentiate material that would usually be incorporated in a study editorial from any unprocessed data or additional appendix matter that would not be available. In fact, such matter should not be submitted at all except requested by the instructor.

Content

- Sum up your conclusion in text and demonstrate them, if suitable, with figures and tables.
- In manuscript, explain each of your consequences, point the reader to remarks that are most appropriate.
- Present a background, such as by describing the question that was addressed by creation an exacting study.
- Explain results of control experiments and comprise remarks that are not accessible in a prescribed figure or table, if appropriate.
- Examine your data, then prepare the analyzed (transformed) data in the form of a figure (graph), table, or in manuscript form.

What to stay away from

- Do not discuss or infer your outcome, report surroundings information, or try to explain anything.
- Not at all, take in raw data or intermediate calculations in a research manuscript.

- Do not present the similar data more than once.
- Manuscript should complement any figures or tables, not duplicate the identical information.
- Never confuse figures with tables - there is a difference.

Approach

- As forever, use past tense when you submit to your results, and put the whole thing in a reasonable order.
- Put figures and tables, appropriately numbered, in order at the end of the report
- If you desire, you may place your figures and tables properly within the text of your results part.

Figures and tables

- If you put figures and tables at the end of the details, make certain that they are visibly distinguished from any attach appendix materials, such as raw facts
- Despite of position, each figure must be numbered one after the other and complete with subtitle
- In spite of position, each table must be titled, numbered one after the other and complete with heading
- All figure and table must be adequately complete that it could situate on its own, divide from text

Discussion:

The Discussion is expected the trickiest segment to write and describe. A lot of papers submitted for journal are discarded based on problems with the Discussion. There is no head of state for how long a argument should be. Position your understanding of the outcome visibly to lead the reviewer through your conclusions, and then finish the paper with a summing up of the implication of the study. The purpose here is to offer an understanding of your results and hold up for all of your conclusions, using facts from your research and generally accepted information, if suitable. The implication of result should be visibly described. Infer your data in the conversation in suitable depth. This means that when you clarify an observable fact you must explain mechanisms that may account for the observation. If your results vary from your prospect, make clear why that may have happened. If your results agree, then explain the theory that the proof supported. It is never suitable to just state that the data approved with prospect, and let it drop at that.

- Make a decision if each premise is supported, discarded, or if you cannot make a conclusion with assurance. Do not just dismiss a study or part of a study as "uncertain."
- Research papers are not acknowledged if the work is imperfect. Draw what conclusions you can based upon the results that you have, and take care of the study as a finished work
- You may propose future guidelines, such as how the experiment might be personalized to accomplish a new idea.
- Give details all of your remarks as much as possible, focus on mechanisms.
- Make a decision if the tentative design sufficiently addressed the theory, and whether or not it was correctly restricted.
- Try to present substitute explanations if sensible alternatives be present.
- One research will not counter an overall question, so maintain the large picture in mind, where do you go next? The best studies unlock new avenues of study. What questions remain?
- Recommendations for detailed papers will offer supplementary suggestions.

Approach:

- When you refer to information, differentiate data generated by your own studies from available information
- Submit to work done by specific persons (including you) in past tense.
- Submit to generally acknowledged facts and main beliefs in present tense.

ADMINISTRATION RULES LISTED BEFORE SUBMITTING YOUR RESEARCH PAPER TO GLOBAL JOURNALS INC. (US)

Please carefully note down following rules and regulation before submitting your Research Paper to Global Journals Inc. (US):

Segment Draft and Final Research Paper: You have to strictly follow the template of research paper. If it is not done your paper may get rejected.

- The **major constraint** is that you must independently make all content, tables, graphs, and facts that are offered in the paper. You must write each part of the paper wholly on your own. The Peer-reviewers need to identify your own perceptive of the concepts in your own terms. NEVER extract straight from any foundation, and never rephrase someone else's analysis.

- Do not give permission to anyone else to "PROOFREAD" your manuscript.

- Methods to avoid Plagiarism is applied by us on every paper, if found guilty, you will be blacklisted by all of our collaborated research groups, your institution will be informed for this and strict legal actions will be taken immediately.)
- To guard yourself and others from possible illegal use please do not permit anyone right to use to your paper and files.

CRITERION FOR GRADING A RESEARCH PAPER (COMPILATION) BY GLOBAL JOURNALS INC. (US)

Please note that following table is only a Grading of "Paper Compilation" and not on "Performed/Stated Research" whose grading solely depends on Individual Assigned Peer Reviewer and Editorial Board Member. These can be available only on request and after decision of Paper. This report will be the property of Global Journals Inc. (US).

Topics	Grades		
	A-B	**C-D**	**E-F**
Abstract	Clear and concise with appropriate content, Correct format. 200 words or below	Unclear summary and no specific data, Incorrect form Above 200 words	No specific data with ambiguous information Above 250 words
Introduction	Containing all background details with clear goal and appropriate details, flow specification, no grammar and spelling mistake, well organized sentence and paragraph, reference cited	Unclear and confusing data, appropriate format, grammar and spelling errors with unorganized matter	Out of place depth and content, hazy format
Methods and Procedures	Clear and to the point with well arranged paragraph, precision and accuracy of facts and figures, well organized subheads	Difficult to comprehend with embarrassed text, too much explanation but completed	Incorrect and unorganized structure with hazy meaning
Result	Well organized, Clear and specific, Correct units with precision, correct data, well structuring of paragraph, no grammar and spelling mistake	Complete and embarrassed text, difficult to comprehend	Irregular format with wrong facts and figures
Discussion	Well organized, meaningful specification, sound conclusion, logical and concise explanation, highly structured paragraph reference cited	Wordy, unclear conclusion, spurious	Conclusion is not cited, unorganized, difficult to comprehend
References	Complete and correct format, well organized	Beside the point, Incomplete	Wrong format and structuring

INDEX

save our planet

Global Journal of Science Frontier Research

Visit us on the Web at www.GlobalJournals.org | www.JournalofScience.org
or email us at helpdesk@globaljournals.org

ISSN 9755896