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Effect of Temperature Changes on Critical Micelle Concentration for Tween Series Surfactant

By May Essa Mahmood & Dhafer A. F. Al-Koofee

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Abstract - The critical micelle concentration (CMC) for polyoxyethylene sorbitan fatty acid esters (tween) series surfactant was determined by the fluorescence intensity technique. It has been measured against concentration of micelle at temperature range (298-348) °k . at 298°k the CMC for tween (20, 21, 40, 60 and 80) were (0.0499, 0.063, 0.0333, 0.0167 and 0.015) mM respectively. The critical micelle concentration (CMC) for all tween series decreased with increasing carbon atoms number for alkyl group, but increased with increasing the number of oxyethylene group. The CMC for all tween series decreased with increasing temperature, it slightly increased at higher temperature. Thermodynamic parameters (ΔG_m° , ΔH_m° , ΔS_m°) of the micelle formation were calculated from the temperature dependence on the CMC, ΔG_m° decreased when increasing temperature above the whole temperature range . It is found that (ΔG_m° , ΔH_m° , ΔS_m°) decreased with increasing carbon number for alkyl group, but increased with increasing the number of oxyethylene group.

Keywords : CMC, micelle Micellization thermodynamic, nonionic surfactant, Pyrene-3-carboxaldehyde, Tween.

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May Essa Mahmood ^α & Dhafer A. F. Al-Koofee ^σ

Abstract - The critical micelle concentration (CMC) for polyoxyethylene sorbitan fatty acid esters (tween) series surfactant was determined by the fluorescence intensity technique. It has been measured against concentration of micelle at temperature range (298-348) °k . at 298°k the CMC for tween (20, 21, 40, 60 and 80) were (0.0499, 0.063, 0.0333, 0.0167 and 0.015) mM respectively. The critical micelle concentration (CMC) for all tween series decreased with increasing carbon atoms number for alkyl group, but increased with increasing the number of oxyethylene group. The CMC for all tween series decreased with increasing temperature, it slightly increased at higher temperature. Thermodynamic parameters (ΔG_m° , ΔH_m° , ΔS_m°) of the micelle formation were calculated from the temperature dependence on the CMC, ΔG_m° decreased when increasing temperature above the whole temperature range . It is found that (ΔG_m° , ΔH_m° , ΔS_m°) decreased with increasing carbon number for alkyl group , but increased with increasing the number of oxyethylene group.

Keywords : CMC, micelle Micellization thermodynamic, nonionic surfactant, Pyrene-3-carboxaldehyde, Tween.

1. INTRODUCTION

Surfactants sometimes called surface active agents, which contain both hydrophobic group (hydrocarbon chain) and hydrophilic group (polar head) in the same surfactant molecule^[1-3].

In aqueous solutions, surfactant molecule starts to aggregate and form micelle in concentration called as

critical micelle concentration, and it is one of the most important physical parameters of surfactants. The properties of a surfactant (like conductivity, viscosity, osmotic pressure, density, polarity, specific heat, refractive index and solubilization power etc.) vary markedly when its concentration is higher or lower than its CMC, and the studies and industrial applications of a 2 surfactant are always based on the value of its CMC. Also, micelle formation enables emulsification, solubilization and dispersion [4-8].

In this study, polyoxyethylene sorbitan fatty acid esters (polysorbate or known as tween), it is a nonionic surfactants that use as a detergent and an emulsifier in a number of domestic, scientific and industrial applications, however the tween surfactant also have found use in cell lysis, nucleic acid isolation and cell fractionation. These surfactants are non-toxic and possess an extremely compatible set of physical properties that allow for widespread use along with other surfactants, for example, used tween surfactants with proteins to stabilize food foams [9-14].

The chemical name and the chemical formula of the tween series surfactants used in this study are presented in table (1), and their structures are shown in figure (1) [15-18].

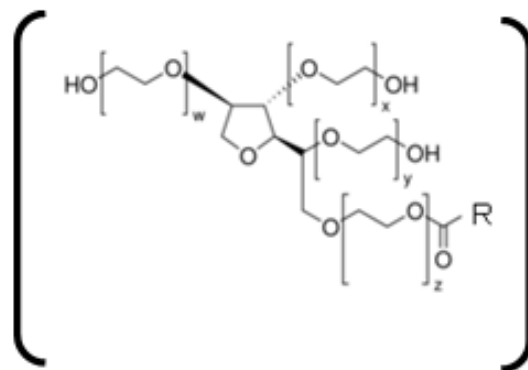


Figure (1) : Structure of Tween series surfactant

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Table (1) : structures of tween series surfactant

Table (1) : structures of tween series surfactant				
Surfactant	Chemical name	Chemical formula (R)	n	w+x+y+z
Tween20	Polyoxyethylen (20) Sorbitanmono-laurate	C_nH_{2n+1}	11	20
Tween21	Polyoxyethylen (4) Sorbitanmono-laurate	C_nH_{2n+1}	11	4
Tween40	Polyoxyethylen(20) Sorbitanmonopalmitate	C_nH_{2n+1}	15	20
Tween60	Polyoxyethylen(20) Sorbitanmono-stearate	C_nH_{2n+1}	17	20
Tween80	Polyoxyethylen(20) Sorbitanmonooleate	C_nH_{2n-1}	17	20

The fluorescence probe technique is becoming increasingly popular in the study of surfactant micellization due to its excellent sensitivity towards the environment surrounding the fluorophore which exhibits different fluorescence characteristics depending upon the properties of the solubilizing medium^[18-22].

For example, fluorescence probes such as pyrene-3-carboxaldehyde which are sensitive to the polarity of the solubilizing medium will exhibit different fluorescence behavior in micellar and nonmicellar solutions. Such changes of behavior as a function of surfactant concentration have been used to determine the critical micelle concentration (CMC) and other micelle characteristics of certain surfactants. However, from necessary in such applications to ensure the absence of any influence of the probe molecule itself on the specific property in question^[23-25].

II. EXPERIMENTAL

a) Materials and Methods

Tween with 99% purity 20, 21, 40 and 60 were purchased from SigmaAldrich, while tween 80 was purchased from Merck Corporation, pyrene-3-carboxaldehyde was purchased from Sigma-Aldrich and purified by two crystallization method from ethanol^[22].

All fluorescence spectra were recorded on RF-1501 spectrofluoro-photometer (Shimadzu) in a 1cm cell

emission spectra of pyrene-3-carboxaldehyde were obtained by exciting the samples at 360 nm, the maximum λ emission has been shown to involved as indicator correlated with solvent polarity^[22].

All surfactant stock solutions were prepared fresh in the range with deionized water and then allowed to equilibrate for 15 - 20 minutes^[15-16].

Stock pyrene-3-carboxaldehyde solution was prepared by dissolving 5mg in 10 ml of distilled water. Working mixtures for fluorescence measurements ($\leq 10^{-6}$ kmol/m³), a small aliquot (50 μ L) of the latter solution was transferred with an automatic pipette to a quartz fluorescence cell and mixed with the surfactant solution and appropriate volumes of distilled water to give a total final volume of 3ml, and to obtain the final surfactant concentrations range [(0.1-0.0001)mM]. The critical micelle concentration (CMC) values of the investigated surfactants were also determined from the measurements of the fluorescence emission spectrum of pyrene-3-carboxaldehyde around of 435 nm as a function of the surfactant concentration^[22, 26].

III. RESULTS AND DISCUSSION

a) Determination of Critical micelle concentration

Fluorescence studies were carried out in the presence of tween series surfactants, with varying alkyl chain lengths, from C11 - C17 and varying of number of

oxyethylene group (4, 20). In all cases, a similar enhancement in the emission intensity with a slight blue-shift in the emission maxima around of 435nm is observed. Figure (2) shown the fluorescence intensity as a function of wave length for tween 80.

The dependence of fluorescence of pyrene-3-carboxaldehyde on the concentration of tween series is illustrated in Figure (3). It is clear that an initial slowly decreased up to a certain surfactant concentration and decrease sharply above it. A lowering of the value of λ_{max} is an indication of the solubilization of the probes in a more hydrophobic environment than water-in this case surfactant micelles. Therefore the concentration at which the first break occurs should correspond to the critical micelle concentration (CMC).

The CMCs of tween (20, 21, 40, 60 and 80) which determined by this procedure were (0.0499, 0.063, 0.0333, 0.0167 and 0.015) mM respectively. These values agree well with the CMCs report ed in the literature [4, 7, 10, 18].

b) Effect of length chain and oxy ethylene group

In the same homologous series, increase in the length of the hydrocarbon chain usually leads to a reduction in the CMC, because formation of micelle becomes easier with increase in hydrophobicity. Therefore, the CMCs of tween 20, 40 and 60 formation are expected. The lower CMC of tween 80 may be due to un-saturation in the aliphatic chain which restricts the conformation of the chain figure (4). However, decreased in the CMC with increasing the number of oxyethylene group as illustrated in figure (5), because increasing the hydration of the hydrophilic polyoxyethylene group, that not favor the micellization. In other words, they reflect that polyoxyethylene group acts as solvophilic group, while hydrocarbon chain acts as solvophobic group.

c) Effect of temperature

The system temperature increases, the CMC initially decreases and then slightly increases, as shown in Figure (6). Owing to the smaller probability of hydrogen bond formation at higher temperatures, the initial decrease of the CMC with temperature is a consequence of the decreased hydrophilicity of the surfactant molecules. In other words, the increase in temperature causes the reduction in hydration of the hydrophilic oxyethylene group, which favour micellization. Consequently, as increase in temperature the micellization onset occurs at lower concentrations. On the other hand, dissolving the surfactant molecules in distilled water makes the hydrophobic group distorts the water structure. Additionally increase in temperature also causes an increase in the breakdown of the structured water surrounding the hydrophobic groups, which disfavors micellization. In addition to, the onset of micellization tends to occur at higher concentrations

when increase the temperature. The longer fatty acid chain length, (tween60, tween 80) due to an increase of the rupture of hydrogen bonds, that give no significant change in CMC.

d) Determination of thermodynamic parameters

For nonionic surfactants, the standard free energy of micelle formation, ΔG°_m , associated with the process that micelles are formed from monomeric surfactant molecules in aqueous solution, which related to the CMC by the following equation [27-31]:

$$\Delta G^{\circ}_m = R \cdot T \cdot \ln X_{cmc} \quad (1)$$

Where:

R is the gas constant,

T is the temperature

X_{cmc} stands for the CMC in the mole fraction unit

From the temperature dependence of ΔG°_m , the entropy of micelle formation, ΔS°_m was estimated on the basis of the following thermodynamic relation [32-34]:

$$\Delta S^{\circ}_m = -(\partial \Delta G^{\circ}_m / \partial T) \quad (2)$$

Then, the enthalpy of micelle formation, ΔH°_m , was calculated according to the relation as below :

$$\Delta H^{\circ}_m = \Delta G^{\circ}_m + T \Delta S^{\circ}_m \quad (3)$$

Thus thermodynamic parameters obtained for micelle formation are illustrated in table (2) for tween series.

It is found that ΔG°_m decreases monotonically as the temperature increases over the whole temperature range from (298 – 348)°K. ΔS°_m appear to be increase monotonically with an increase in temperature, the negative value of ΔG°_m of micellization is mainly due to the large positive value of entropy.

The increase in entropy of micellization in an aqueous medium can be explained from two aspects: First the iceberg formation of the water molecules surrounding the surfactant molecules would increase the system order, here the micellization process by removing the surfactant molecules from the aqueous medium to the micelle would certainly increase the entropy of the system simply due to the rupture of iceberg; second the degree of rotational freedom of the hydrophobic chain of surfactant molecules in the non-polar interior of the micelle is much larger than that in the aqueous medium; in other words, the configurationally entropy of hydrophobic chain of surfactant molecules is increased when the surfactant molecules are removed from the aqueous medium to the micelle.

The small enthalpy change means that in the micellization the attractive interaction among hydrophobic chains is opposed by the strong interaction of the oxyethylene chains of tween series with water molecules. Figure (7) shows the thermodynamic parameters as a function of temperature for tween 80.

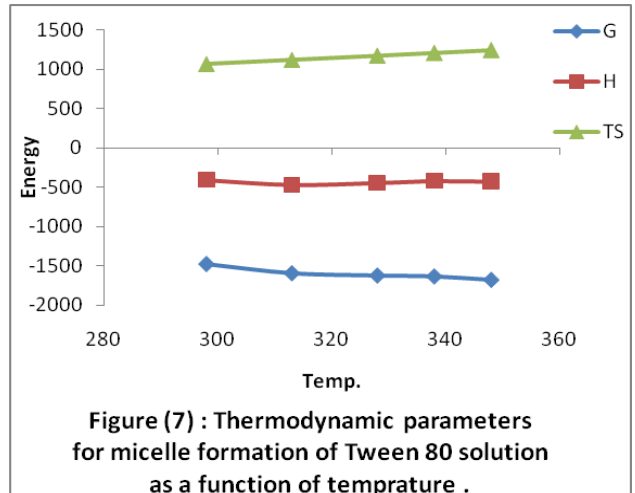
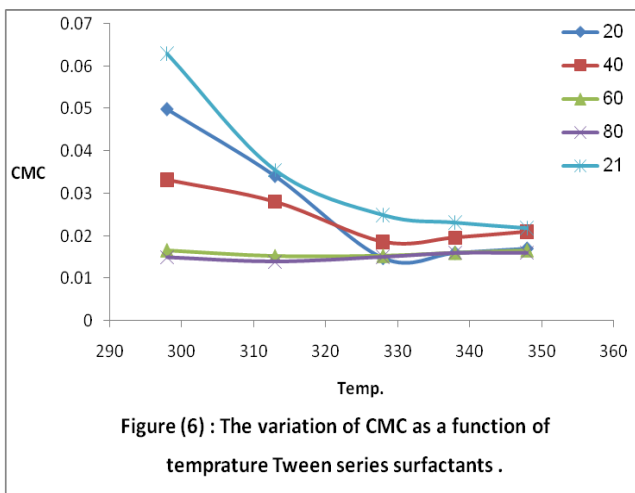
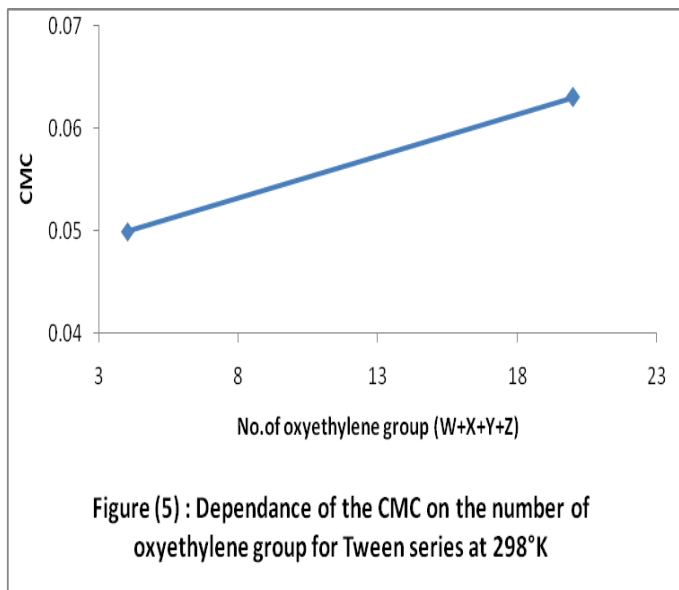
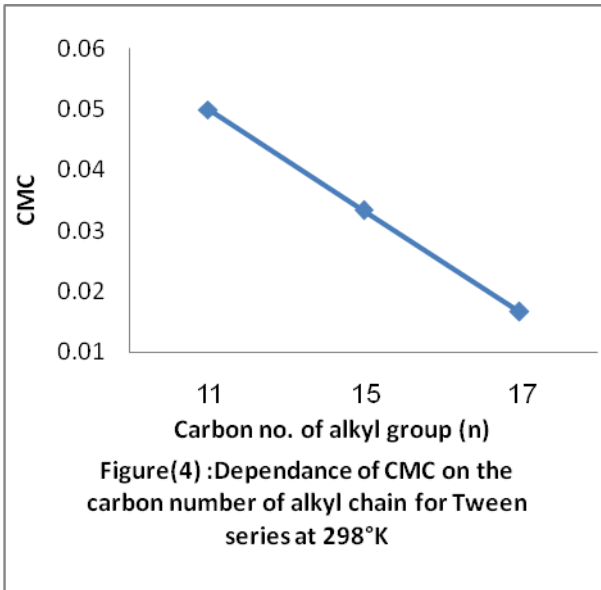
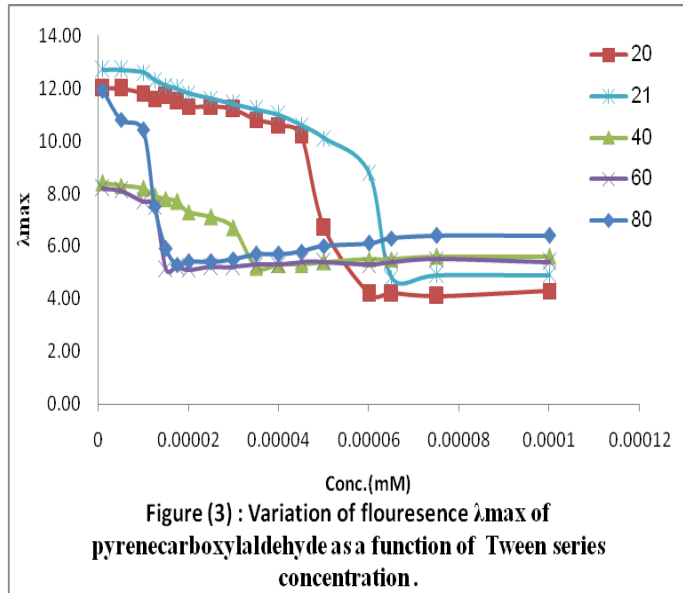
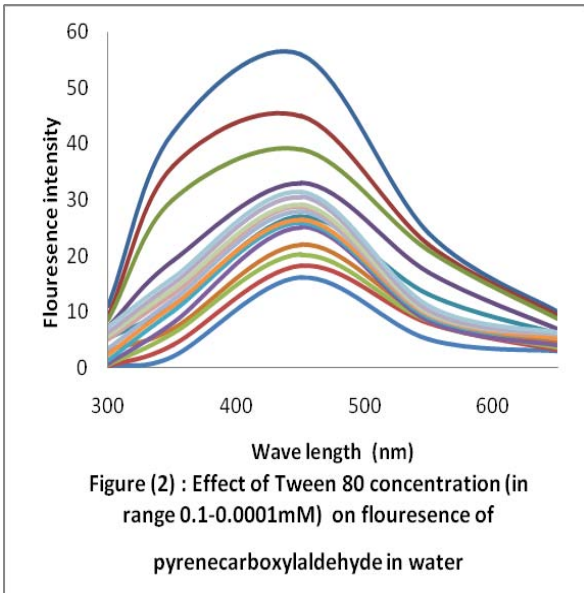
The thermodynamic parameters for micelle formation as a function of chain length for tween series surfactant, as shown in figure (8), it is found that $\Delta G^{\circ m}$, $\Delta H^{\circ m}$, and $\Delta S^{\circ m}$ are decreased with increasing the

chain length, the enthalpy ($\Delta H^{\circ m}$) is converted from endothermic for shorter chain length to exothermic for longer chain length.

The thermodynamic parameters for micelle formation as a function of number of oxyethylene group for tween series surfactant, as shown in figure (9), it is found that $\Delta G^{\circ m}$ is decreased with increasing the number of oxyethylene group, but $\Delta H^{\circ m}$, and $\Delta S^{\circ m}$ are increased.

Table (2) : CMC values, mole fraction and thermodynamic parameters for tween series surfactant in the range temperatures 298 -348°K

Table (2) : CMC values ,mole fraction and thermodynamic parameters for tween series surfactant in the range temperatures 298 -348°K						
Tween	Temp.(°K)	CMC(mM)	X _{CMC}	$\Delta G(\text{cal/mole})$	$\Delta H(\text{cal/mole})$	$\Delta S(\text{cal/mole})$
20	298	0.0499	0.23	-870.2	4245.234	14.24575
	313	0.0342	0.17	-1102.1	4270.822	13.6448
	328	0.0149	0.082	-1630.1	4000.311	12.19607
	338	0.0161	0.088	-1632.2	4169.869	12.33689
	348	0.0171	0.093	-1640.6	4333.128	12.45152
21	298	0.063	0.274	-766.8	3567.271	11.97071
	313	0.0356	0.176	-1080.2	3472.028	11.09274
	328	0.025	0.13	-1330.7	3439.686	10.48685
	338	0.0232	0.122	-1410.2	3505.625	10.37167
	348	0.0219	0.116	-1492.2	3569.064	10.25593
40	298	0.0333	0.166	-1062.4	1950.399	6.544963
	313	0.0281	0.144	-1204.2	1960.25	6.262779
	328	0.0186	0.1002	-1499.3	1816.801	5.539027
	338	0.0196	0.1054	-1511.1	1906.101	5.639353
	348	0.021	0.111	-1520.3	1998.002	5.741385
60	298	0.0167	0.091	-1419.9	-26.2219	-0.08799
	313	0.0153	0.084	-1540.3	-76.4703	-0.24431
	328	0.0154	0.0845	-1610.8	-76.8187	-0.2342
	338	0.0161	0.088	-1630.6	-49.851	-0.14749
	348	0.0167	0.091	-1660	-32.4833	-0.09334
80	298	0.015	0.082	-1477.9	-410.966	-1.37908
	313	0.0139	0.077	-1593.2	-472.561	-1.50978
	328	0.0151	0.083	-1622.4	-448.056	-1.36603
	338	0.0161	0.088	-1633.7	-423.553	-1.25312
	348	0.0161	0.088	-1677.1	-431.15	-1.23894



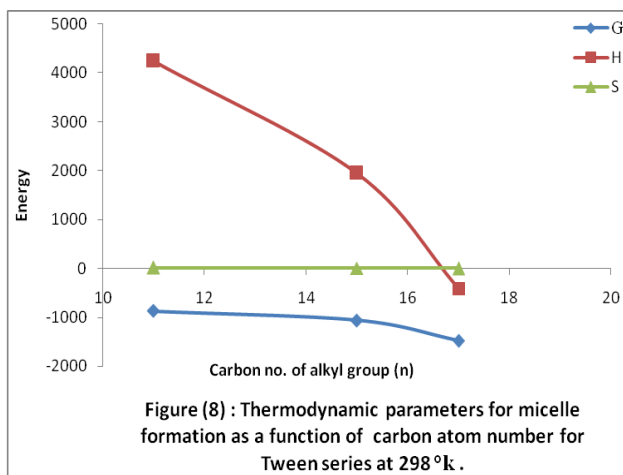
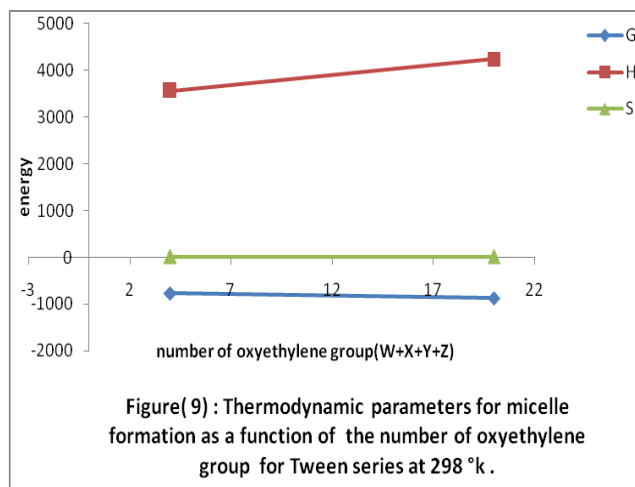


Figure (8) : Thermodynamic parameters for micelle formation as a function of carbon atom number for Tween series at 298 °k .



Figure(9) : Thermodynamic parameters for micelle formation as a function of the number of oxyethylene group for Tween series at 298 °k .

IV. CONCLUSION

The fluorescence technique is very good and easy for determination the critical micelle concentration for nonionic surfactant, the incensement in fluorescence intensity is accompanied by a concomitant blue-shift in the emission maximum, and often by the evolution of a shoulder in the blue region.

The changes in the nature of the surfactant (such as changes in chain length and polar head group) have a severe effect on the subsequent self-assembly in aqueous medium. The increase in hydrophobic character of the surfactant decreases the CMC, induces sphere-to-rod transition at lower concentration and increases the solubilizing, but the increase in hydrophilic character of the surfactant increase the CMC.

The temperature is affected on the tween series surfactant that shorter chain than longer one, which shows no significant change in CMC. The increase in temperature causes the reduction in hydration of the hydrophilic oxyethylene group, which favors micellization, which has a severe effect on the CMC.

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Kitchen Resources, Reasoning Ability Levels and Academic Performance and Retention of SS2 Chemistry Students in Calabar, Nigeria

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Kitchen Resources, Reasoning Ability Levels and Academic Performance and Retention of SS2 Chemistry Students in Calabar, Nigeria

NJA, Cecilia Obi^α & Iroha Kalu^σ

Abstract - This study examined kitchen resource, reasoning ability level, academic performance and retention of SS2 Chemistry students in Thermo-chemistry. Thermochemical activities in the kitchen such as, fermentation of samples of five different juices (mango, orange, pineapple, grape and paw-paw), heating capacities of five samples of wood (mango, orange, guava, almond and rubber), induced thermal decomposition of five samples of shellfish shells powder (mangrove snail shell, fresh water periwinkle shell, freshwater snail shell, clam shell and mangrove periwinkle shell) and dissolution of five samples of glucose (2g, 4g 6g, 8g and 10g) were used for the study. The sample comprised 240 drawn from four secondary schools in Calabar Education Zone of Cross River State of Nigeria. Quasi experimental factorial research design was used for this study. Chemistry Achievement Test (Cat), Chemistry Retention Test (Cat), and Reasoning Ability Test (Rat) were used for data collection. Analysis of covariance (ANCOVA) was used in the analysis of data. From the findings, the use of kitchen resources enhanced the performance and retention level of high and low reasoning ability level of students exposed to kitchen resources during the teaching of Thermochemistry. It was recommended that teachers should be encouraged to adopt kitchen resources in science teaching.

1. BACKGROUND TO THE STUDY

Humans live in a world of science and throughout their entire lives they encounter issues and problems that have their foundation in science. Science is the bedrock of scientific and technological careers and development (Uche & Umoren, 1998). An ultimate purpose of science is to discern the order that exists between and among the various facts (Gottlieb, 2011). Science can also be said to be the concerted human efforts to understand, or to understand better, the history of the natural world and how this world works, with observable physical evidence as the basis of that understanding. It is done through observation of natural phenomena and/or through experimentation that tries to stimulate natural process under controlled conditions (Science, 2011).

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Chemistry occupies an enviable position in the senior Science national curriculum. Chemistry as a subject of study combines with other natural science subjects of Physics, and Biology to qualify students for admission into tertiary institutions to read such courses as Medicine/Surgery, Pharmacy, Engineering, Science Education, Science, Agriculture etcetera (JAMB, 2010/2011 UME/D).

Science education at all levels of education in Nigeria is in a deplorable state from the primary, secondary and to the tertiary institutions. There is a problem of dearth in science resources and this contributes to students' poor academic performance in Chemistry at the secondary school level (Nkanu, 2009, 2008; Opera, 2008; Oriade, 2008; Udo, 2006; Uche & Umoren; 1998).

Science being an activity has been designed such that it be taught through a series of activities in schools (Afemikhe, 1992). The National Policy on Education (2004) has demanded a complete integration of both theory and practical in Science teaching at school. Studies carried out by Ivowi (1999) in Biology, Chemistry and Physics; reveal that teachers do not completely comply with the provisions for teaching these subjects. The most commonly cited reason is the lack of Science equipments in schools. Although efforts appear to be made in building science laboratories and supplying science equipments, these have not matched demands of schools in any satisfactory manner (Oriade, 2008).

Since the problem above is enormous and the absence of these facilities appears to adversely affect the teaching and learning of science, some measures need to be taken. It was based on this that this study attempts to look inward at the resources in the kitchen and how they can be used to teach Thermochemistry. The modern kitchen is stocked with quality materials, and is probably the safest chemical laboratory in the world (Hayward 1992). Many activities and materials

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abound in the kitchen. The early days of a learner's development are centered round the home, and the kitchen. The kitchen is a unit of the home and special consideration of the home as a resource in teaching science can be seen in the light of the modern kitchen being regarded as a workshop of various practices, which expose the learner to in experiences, in the various aspects of the subject of Chemistry (Eshiet, 1996).

Reasoning encompasses all thinking activities that involve making or testing inferences. This includes inductive reasoning and deductive reasoning. Reasoning is also closely related to problem solving and creativity. The ability to reason has a fundamental impact on one's ability to learn from new information and experiences because reasoning skills determine how people comprehend, evaluate, and accept claims and arguments.

It has been discovered that people generally perform better with relations that can be visualized leading to a spatial representation theory for reasoning and eventually, a semantic theory (Johnson-Laird 2006). The work of Guilford & Sternberg (2011) suggests that there are many different kinds of reasoning abilities and that reasoning skills are task specific. It is on the basis of this premise that the study designed reasoning ability questions in order to place students into different ability group and to find out how reasoning ability affects students academic performance and retention in Thermochemistry.

Ausubel in his book "Educational Psychology: A Cognitive View" (1968) said that if I had to reduce all educational psychology in just one principle, I would say that, the most important single factor influencing learning is what the learner already knows, ascertain this and teach him.

Concepts are meaningful only when the learner can visualize them and subsume them within a cognitive-structure. This means that the learners already understand more generic concepts that incorporate or include the concept one is trying to teach. This can be achieved when a Chemistry teacher uses resources form the environment (e.g kitchen) as learners can visualize the materials they already know as advance organizer in teaching and learning process.

It has been discovered that people generally perform better with relations that can be visualized leading to a spatial representation theory for reasoning and eventually, a semantic theory (Johnson-Laird 2006). The work of Guilford & Sternberg (2011) suggests that there are many different kinds of reasoning abilities and that reasoning skills are task specific.

II. RESEARCH METHODOLOGY

A quasi experimental factorial research design was used for this study. The design is a modification of

the pretest posttest retention test control group design with one treatment variable and one moderator variable. The 2x2 factorial designs were used. The study was carried out in Calabar Educational Zone also known as Southern Education/Zone of Cross River State.

The population for this study comprised all the Senior Secondary (SS2) Chemistry Students in public secondary schools in Calabar Educational Zone of Cross River State. For the purpose of this study, two instruments were used. They were: Chemistry Achievement Test (Cat) and Reasoning Ability Test (Rat).

The Chemistry achievement test (Cat) was an instrument developed by the researcher for data collection. Cat was a 60 item five response option objective test. Reasoning ability test (RAT) was an instrument used to monitor the reasoning mode of students.

This instrument provided both the correct response option and matching reason in order to identify students who merely guessed answers since they will not be able to choose the correct reason. Rat consisted of 24 – items, 12 questions that were followed with 12 reasons why such an option was chosen

a) Sampling Technique

A multi-stage, involving the use of stratified random sampling and purposive sampling was used for the study. The sample was made up of (240) Senior Secondary School Chemistry students from four schools in four Local Government Areas in Calabar Education Zone, made up the sample for the study. A break- down of this figure showed 120 students each in the experimental and control groups respectively.

b) Data Collection and Analysis

Two hypotheses were used for this study:

Hypothesis one: There is no significant difference between the academic performance of students with different reasoning ability levels when taught with and without kitchen resources. Analysis of Covariance using pretest as covariate was used for data analysis.

Hypothesis two: There is no significant difference in the retention of students of different reasoning ability levels when taught with and without kitchen resources analysis of covariance was also used for analysis.

i. Test for hypothesis one

Table 1

Mean standard deviation and summary of 2x2 analysis of covariance of effect of treatment and reasoning ability level on SS 2 Chemistry students' performance in Thermochemistry

Treatment		Reasoning ability		Mean	Std. Deviation	N
Experimental		High		47.61	9.74	64
		Low		47.73	8.60	56
		Total		47.67	9.19	120
Control		High		18.84	6.37	45
		Low		15.63	6.14	75
		Total		16.83	4.40	120
Total		High		35.73	16.56	109
		Low		29.35	17.52	131
		Total		32.25	17.35	240
Source of variation	Sum of squares	Df	Mean squares	F	Sig level	Partial Eta square
Corrected Model	59504.631	4	14876.158	280.877	.000*	.827
Intercept	29020.555	1	29020.555	547.937	.000*	.700
PRE	2171.305	1	2171.305	40.996	.000*	.149
TRT	52814.424	1	52814.424	997.190	.000*	.809
Reasoning Ability	122.051	1	122.051	2.304	.130	.010
Treatment x Reasoning ability	62.484	1	62.484	1.180	.279	.005
Error	12446.369	235	52.963			
Total	321566.000	240				
Corrected total	71951.000	239				

R squared = .827 (adjusted R squared = .824) F-critical = 3.86 *p>.05.

A glance at the descriptive statistics, in Table 1 indicates that there is a slight difference in the mean between high ability groups; and low ability 47.61 and 47.73 respectively. Examination of Table 1 further shows that the high reasoning ability students in the experimental group, had an almost equivalent mean (x=47.61). Thermochemistry posttest scores to low reasoning ability level students with a mean of x = 47.73. On the other hand, the high reasoning ability level students in the control groups had a higher mean (x=18.84) Thermochemistry past test scores than their low reasoning ability level counterparts (x = 15.63).

However, the results also showed that students who were taught with kitchen resources had higher post

test achievement scores in Thermochemistry (x=47.67) were compared with the control groups, (taught without kitchen resources) x = 32.25. The result of the 2x2 analysis of variance presented in Table 15, showed that, treatment main effect was significant (F=997.190; P<.05); reasoning ability was not significant (F=2.304, P>.05). The interaction of treatment with reasoning ability was not significant (F=1.180; p>.05). The null hypothesis was rejected for treatment.

Further observation of Table 1 shows that 80.9% (.809) variance was accounted for by treatment, 1% (.010) by reasoning ability and 0.5% (.005) by interaction between treatment and reasoning ability.

ii. Test for hypothesis two

Table 2

Means, standard deviations and summary of 2x2 analysis of ANCOVA of effect of treatment and reasoning ability level on SS 2 Chemistry students' retention in Thermochemistry

Treatment	Reasoning Ability	Mean	Std. deviation	N
Experimental	High	47.44	9.74	64
	Low	47.39	8.79	56
	Total	47.42	9.28	120
control	High	13.84	4.84	45
	Low	11.00	4.76	75
	Total	12.07	4.97	120
Total	High	33.57	18.47	109

		Low	26.56	19.29	131	
		Total	29.74	19.21	240	
Source of variation	Sum of squares	Df	Mean squares	F	Sig level	Partial Eta square
Corrected Model	76398.990	4	19099.748	381.573	.000*	.867
Intercept	27105.461	1	27105.461	541.510	.000*	.697
Pretest	1194.025	1	1194.025	23.854	.000*	.092
Treatment	70183.914	1	70183.914	1402.128	.000*	.856
Reasoning ability	109.260	1	109.260	2.183	.141	.009
Treatment x Reasoning Ability	50.171	1	50.171	1.002	.318	.004
Error	11762.993	235	50.055			
Total	300458.000	240				
Corrected total	88161.983	239				

R squared = .867 (Adjusted R squared = .864) F-critical = 3.86 * P> .05.

Generally the mean retention scores of the high reasoning ability level group ($\bar{x}=33.57$) was higher than the low reasoning ability level group ($\bar{x}=26.56$) in both experimental and control. The result of the 2x2 Analysis of Variance in respect to retention presented in Table 16, showed that, treatment effect was significant ($F_{1402.128}, P < .05$); reasoning ability was not significant ($F=2.183; P > .05$). The interaction effect between reasoning ability level and treatment was not significant ($F=1.002; P > .05$).

The Table also indicates that treatment accounted for 85.6% (.856) variance, reasoning ability was 0.9% (.009) and interaction effect was 0.4% (.004). With respect to reasoning ability the null hypothesis was retained. Thus, the contribution of reasoning ability is minimal taken individually (0.9%) and in combination with treatment (0.4%).

c) Discussion of Findings

The first hypothesis sought to find out if there was significant influence of reasoning ability on SS2 Chemistry students' academic performance in Thermochemistry when taught with and without kitchen resources. The finding of this study revealed as shown in Table 1 earlier that there was no significant difference in the interaction of treatment and reasoning ability level on students' performance in Thermochemistry. The critical F-value of 3.86 was higher than the calculated F-value of 1.180. The explanation of this result is that reasoning ability level of students does not affect their performance level when taught with and without kitchen resources. This therefore means that both low and high reasoning ability level students can benefit when taught using kitchen resources.

This finding in respect to treatment main effect and the interaction of treatment and reasoning ability is consistent with the findings of Nkanu (2009) who reported no significant difference in the performance of high and low reasoning ability levels students exposed to the same learning situation. In a similar vein, Adeboye (2008) reported no significant difference in achievement gains between subjects in each reasoning ability level

who used different methods. Ejilo (2002) found that both high and low reasoning ability level students could do well in science if exposed to similar learning conditions.

The result of the second hypothesis in Table 2, showed that, the two way interaction between reasoning ability level and treatment when retention level of students were considered showed that, the critical F value of 3.86 was higher than the table F-value of 1.002.. It therefore means that reasoning ability level of students does not interact with treatment as far as retention level of Chemistry students is concerned. The finding therefore shows that both high and low ability level students can retain Thermochemical concepts when taught using kitchen resources. Kitchen resources are good for all categories of reasoning ability level students when retention level is sought. This finding in respect to treatment main effect and the interaction of treatment and reasoning ability is consistent with the findings of Ya-Wen and Hsia (2009) study of the influence of reasoning ability on the performance/retention of students in secondary schools.

III. CONCLUSION

The study showed the importance and significant role played by instructional materials (Kitchen resources) on students' achievement, especially in Chemistry. They have positive influence in achievement in Chemistry. This explains why a subject like Chemistry will require real objects and activities/experiment that can convert topics that seem imaginary to concrete for students' understanding. It made students to use their intellectual ability during the learning and teaching process. It encouraged creativity, bringing learning homewards and often improved and enhanced students' achievement.

IV. RECOMMENDATIONS

- 1) There is the need for the development of positive attitudes by teachers towards the use of kitchen resources for their students. This will encourage the development of their proficiency.

- 2) Teachers should bring their teaching to the level of the students' aptitude by using familiar instructional resources (kitchen) and make classroom interactions more interesting so as to arouse the interest of the students and academic excellence.

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Assessment of Water Quality in and Around Jamkhandi City, Bagalkot District, Karnataka State, India

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Abstract - The assessment of water quality and suitability for drinking and domestic (cooking) purposes was carried out from Jamkhandi city of Bagalkot District. The Bore water (Ground water), Surface water (Open well water) and Municipal water were assessed by examining various physico-chemical parameters such as pH, EC, TDS, TA, TH, DO, COD, BOD, Calcium, Magnesium, Chloride, Sulphate, Sodium and Trace element concentration like Iron, Manganese Cobalt and Copper called dissolved metals have been analyzed. The analyzed results were compared with WHO and ISI drinking water standards. On the basis of pH, EC and Hardness out of 62 Bore wells, 08 Open wells and 09 Municipal water samples, 57 Bore wells, 06 Open wells and all 09 municipal water samples were within the permissible limit and useful (safe) for drinking and cooking purposes.

Keywords : jamkhandi city, ground water, open wells, municipal water, physico-chemical parameters.

I. INTRODUCTION

Assessment of water quality is an important issue, especially the studies of ground water, open water and municipal water. Assessment is a function of Physico-chemical parameter which is highly influence by geological formations and anthropogenic activities. Among the various sources of water, ground water is said to be safest water for drinking and domestic purpose.

Jamkhandi is one of the important Taluk place of Bagalkot District, located at latitude 16°19'48" N (16.504672° N) and 75°18'24"E (75.291401°E). This Taluk is comprises 48 villages with the population of 4, 08,441. Area of the Jamkhandi city is about 12.6 km² (4.9 miles), population residing in this city is found to be 1, 51,747. And daily public floating is 15,765. The people residing in this city are depended on Bore wells, Municipal water and very few were depended on Open wells for drinking and domestic purpose. River Krishna is the life-line for Bagalkot and Bijapur districts. The Almatti (Dam) reservoir situated in Bagalkot district of Karnataka State. The irrigation potential of 87490 hectares and hydropower generation having an installed

capacity of 290 mw¹. The water spread area is 487.87 sq. kms. with a fetch of 124 kms. The storage capacity at the Dam site has been 3486 m cum (123.08 TMC). The maximum flood discharges of 31.007 cum (10, 95,000 cusecs/min.) had been designed to be discharge through the 26 vents of the spill ways, having radial crest gate of size 15 m x 15.25 m with crest level at RL 50.016 mtrs out of 519.60 mtrs. Total catchment of Almatti reservoir is 359.25 sq. kms. (138.71 sq. miles). Rain fall 635 cms. In Bagalkot District and it is recorded 50 cms in Dam site during September 2009^{1,2}.

River Krishna divides Jamkhandi taluk in to two equal parts, and the city is interior of 10 kms from Krishna river belt, where the municipal pipe lines connected and Krishna river water act as life-line for the public for their domestic needs and drinking purpose. The river Krishna flow gradually began to rise in June, pick up in July and over flow in August and September, the flood lift reached maximum height and gradually falling through, October to January and by February found to be almost dry or lean flow. Hence, due to irregular water supply of water by municipality in summer season, the public residing in and around the city depended upon Bore well water for drinking and cooking purpose. In the view of the above the present investigation is under taken to study the water health conditions (Physico-Chemical parameters) of Bore wells, open well and municipal waters from the different Colonies and different locations of the Jamkhandi city.

II. EXPERIMENTAL

An investigation was conducted to know the Physico-Chemical parameters and the effect of conjunctive use of Ground (Bore) water. Bore water samples and others were collected from various colonies of Jamkhandi city in March 2013 and April 2013. Samples were collected in plastic bottles and brought to the research laboratory for further analysis and for quality assessment the standard methods were followed^{3,4}. Temperature, pH, EC, and TDS were analyzed on the sampling site. The water samples brought to the laboratory for DO, COD, BOD measurements. The samples for DO were fixed in BOD bottles at the site and analyzed the parameter by Winkler method. All the parameters were analyzed within

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a day; the observed results were compared with WHO⁵, ISI⁶ drinking water standards.

III. RESULTS AND DISCUSSION

For the Assessment of water quality in and around Jamkhandi city, the city is equally divided into five suitable residential zones (regions), each zone contains eight Colonies. The water quality assessment results obtained from 62 water samples of 40 colonies of Jamkhandi city. The zone wise analysis reports are given in Tables 1 to Table 5 for Bore wells, Table 6 for Open wells; Table 7 showed the water quality assessment report of Municipal water and Table 8 indicates the water quality standards for references. A comparison of the physico-chemical data of ground (Bore) water samples, open well water and municipal water samples have been made with drinking water standards^{7,9}.

All the samples were collected during the months of March 2013 and April 2013. All the drinking water samples were clear, colorless and odorless except one ground water sample located at Govt. Primary School near Jumma Masjid (Mudhol Road) of Jamkhandi city.

a) Temperature

Temperature is an important biologically significant factor, which plays an important role in the metabolic activities of the organisms¹⁷. The water Temperature ranged from 24°C to 29°C in all the samples.

b) pH Values

pH is considered as an important ecological factor and provides an important piece factor and piece of information in many types of geochemical equilibrium or solubility calculation¹⁸. pH is a term used universally to express the intensity of the acid and alkaline condition of water samples. Most of the waters of open wells were slightly alkaline due to the presence of Carbonates (CO_3^{2-}) and Bicarbonates (HCO_3^-). The pH values of Bore wells water samples ranged from 6.34 to 8.0, all the samples pH values were within the permissible limit except two colonies such as Kubar galli and Gouwali galli bore wells, where as the pH values were recorded to be 6.2 and 6.4 respectively which are acidic in nature. The pH values of few bore wells were exceptional and may reflect contamination by strong bases such as sodium hydroxide and calcium hydroxide¹⁰.

c) Electrical Conductivity (EC)

It is an indicator of the degree of mineralization of water. The EC is correlated with total dissolved solids¹⁹. It is a measure of water capacity to convey electric current. It signifies the amount of total dissolved salts. Presence of high EC values in water indicates the presence of high amount of dissolved inorganic substances in ionized form. Electrical Conductivity

values ranged from 0.428 to 2.094 m mhos and indicate the presence of some ionic matter such as Calcium, Magnesium, Chloride, Sulphate, carbonate bicarbonate and some trace elements. All the EC- values of water samples were within the legal limit, most of ground (Bore) water content substantial amounts of dissolved CO_2 , HCO_3^- and Hydroxides, these constituents are the results of dissolution of minerals in the soil and atmosphere¹¹.

d) Total Dissolved Solids (TDS)

TDS indicates the salinity behavior of ground water. Water containing more than 500 ppm of Total Dissolved solids is not considered desirable for drinking water supplies, but in unavoidable case 1500 ppm is also allowed¹⁴ for domestic use. In the present investigation the TDS values of water samples of all bore wells except few colonies bore waters found more than 500 ppm. The TDS values of bore located at Professor Colony (213 ppm), Rameshwar colony (401 ppm) Saradha colony (447 ppm), Siddarameshwar colony (285 ppm). In general the TDS values of collected water samples ranged in between 213 ppm to 1164 ppm.

e) Total Alkalinity (TA)

Alkalinity of water is its capacity to neutralize a strong acid and it is normally due to the presence of CO_3^{2-} , HCO_3^- and hydroxides and the presence of cations such as Calcium, Sodium and Potassium content in the water samples. In the present study the Total Alkalinity and the Total Hardness of water samples were ranged from 5.6 ppm to 34 ppm and 47.5 ppm to 153.03 ppm were found to be within the permissible limit respectively. In 5 colonies the TH values found around 180.0 ppm to 182.5 ppm also found within the prescribed limit. High alkalinity in water bodies leads to sour taste and salinity.

f) Total Hardness (TH)

Hardness is the property of water which prevents the lather formation with soap and increases the boiling points of water¹⁵. The total hardness may be due to the presence of divalent cations like Calcium, Magnesium found abundant in ground water. In the present investigation the TH of water samples ranged in between 47.5 ppm to 153.03 ppm this indicates that out of 62 samples (40 colonies) 05 samples were fall under very hard category above 180 ppm. (Locations: Arali katti Bore well near Kadasiddeshwar mangal Karyalaya, Bore well at Govt. Primary School near Jumma Masjid Awati Galli (Mudhol Road), Bore well at Kosti galli in front of Hittinmath swamiji house, and Bore well at Gauwalli galli near Banashankari Govt. School, and Bore well located at Kubar Galli).

g) Calcium and Magnesium Hardness

Calcium hardness ranged from 4.3 ppm to 51.60 ppm these values were close resembling and were within the permissible limit. Magnesium hardness

values ranged from 3.1 ppm to 22.8 ppm and were within the permissible limit of 30 to 150 ppm (WHO). Jain et al¹² and others reported that high concentration of hardness (150 to 300 ppm) may cause heart diseases and kidney problems.

h) Chloride content

The Chloride concentration serves as an indicator of pollution by sewage. Chloride occurs in all Ground waters widely in varying concentration. Excessive chloride in potable water is not particularly harmful. Chloride in excess (more than 250 ppm) impart a salty taste to water, People accustomed to higher Chloride in water are subjected to Laxative effects¹⁶. In the present investigation the chloride values ranged from 6.4 ppm to 65.32 ppm all the samples were within the permissible legal range.

i) Dissolved Oxygen (DO)

It is very important parameter, The DO values indicate the degree of pollution in water bodies. The low values of DO in water indicate the heavy contamination of organic matter and such water sample possesses bad smell, this is due to anaerobic decomposition of organic waste¹³. In the present study DO values of water samples ranged in between 4.8 ppm to 7.0 ppm, out of 62 samples 57 samples were within the permissible limit by WHO and ISI standards while 05 samples were < 3.5 ppm which exceeds the permissible limit.

j) Sulphate

Sulphate of water samples were recorded and ranged in between 17.8 ppm to 52.5 ppm in ground water, 14.85 ppm to 61.82 ppm in open well water and 28.92 ppm to 68.42 ppm all the values found within permissible limits. Sulphate concentration in water samples around 1000 ppm; it has Laxative effect and causes gastro intestinal irritation²⁰.

In general Open well waters are not safest for drinking purpose, this is because the contamination of organic matter, the development of algae, fungi and microorganism. The organic waste and unknowingly dumping E-waste in water body, the water constituency may change as result the development of Bacteria like Mico-colifurom (M-Coli), Escherichia-Coli (E-Coli) and

pseudomonas aeruginosa. Hence, the development of ammonia in the water body due to the decomposition of organic matter and leads to bad odour of the water. In the present investigation the pH and EC found in between 7.02 – 7.74 and 0.2 – 1.32 respectively. The TDS found more than legal limit ranging in between 679 ppm 1121 ppm, the total alkalinity ranged in between 26 ppm – 75 ppm. The total hardness found in between 61.8 ppm 306.12 ppm the total hardness of open well located at Jambukeshwar temple were found to be 306.12 ppm, which is more than legal limit.

Calcium and Magnesium hardness in open wells ranged in between 13.06 ppm – 121.31 ppm and 11.65 ppm to 81.32 ppm, the open well water located at Jambukeshwar temple were found very hard and not fit for drinking and cooking purposes. The DO values of open well ranged in between 4.4 ppm – 6.5 ppm. Chloride and Sulphate ions found in between 42.60 ppm to 174.32 ppm and 14.85 to 61.82 ppm respectively and such ions concentration found within the prescribed limit.

The municipal waters pH and EC values are within the range of standards. TDS found slightly more than the legal limit. DO found in between 4.1 to 6.1 ppm, Chloride, Sulphide ions also found within the legal limit. Calcium hardness and Magnesium hardness were also found within the permissible limit.

COD determines the organic load where present in the water samples. The COD values found within the 6.1 ppm to 6.8 ppm within the permissible limit. The BOD determination indicates the amount of oxygen utilized by micro organisms. In the present investigation the BOD values ganged in between 1.5 ppm to 1.8 ppm, within the legal limit. The presence of trace elements in water samples of three sources, all the values were found within the permissible range. The data of COD, BOD and Trace elements were not shown in the Tables.

Figure 1 and Figure 2 indicate the Comparison between the Physical parameters of Ground water (GW), Surface water (SW) and Municipal water (MW) and the Chemical parameter, Hardness of Ground water (GW), Surface water (SW) and Municipal water (MW) respectively.

Table 1 : Physico-Chemical parameters of Bore well water of Jamkhandi city at various locations. (Zone: South region of the city)

Location	pH	EC	TDS	TA	TH	DO	Ca ⁺⁺	Mg ⁺⁺	Cl ⁻	SO ₄ ⁻
Zum Zum Colony	7.0	1.510	790	18.00	93.0	5.3	16.84	10.31	48.2	48.12
Awati galli	6.7	1.683	786	11.15	182.5	3.2	42.74	30.26	34.6	41.2
Azad nagar	6.6	1.570	723	28.00	75.4	5.1	16.46	13.70	28.5	38.2
Momin Galli	7.1	1.360	634	20.00	83.4	5.4	20.05	13.32	32.2	28.2

Ullagaddi oni	6.7	1.710	778	10.11	100.7	4.9	24.06	16.22	41.8	35.9
Metri Galli	6.9	1.510	821	12.01	88.3	4.2	16.80	18.53	38.9	46.3
Kosti Galli	7.0	1.950	900	20.02	181.3	3.2	46.38	26.14	37.5	28.2
Baghash Galli	6.5	1.820	839	12.10	59.5	5.1	15.80	18.00	27.3	21.3

Table 2: Physico-Chemical parameters of Bore well water of Jamkhandi city at various locations.
(Zone: West region of the city)

Location	pH	EC	TDS	TA	TH	DO	Ca ⁺⁺	Mg ⁺⁺	Cl ⁻	SO ₄ ⁻
Siddamuthy oni	7.6	1.46	820	26	80.3	5.3	14.40	17.72	29.9	17.8
Ramadev Galli	7.0	2.08	942	24	52.6	6.1	14.43	16.61	31.3	33.4
Gadad Galli	6.7	1.72	790	20	136.3	6.0	40.01	6.61	32.8	52.5
Mallappana Oni	6.7	1.61	835	20	104.9	5.7	25.24	16.70	29.8	41.8
Kumbar oni	6.2	2.09	956	11	181.5	3.3	23.90	22.8	29.2	19.9
Market Galli	6.5	1.58	891	28	91.2	5.8	29.80	6.69	33.4	21.3
Nyamagoudar Oni	7.1	1.87	869	34	92.9	5.2	17.72	19.42	38.8	28.3
Arali katti oni	7.5	1.83	956	14	180.0	3.4	48.76	23.64	23.6	24.8

Table 3: Physico-Chemical parameters of Bore well water of Jamkhandi city at various locations.
(Zone: East region of the city)

Location	pH	EC	TDS	TA	TH	DO	Ca ⁺⁺	Mg ⁺⁺	Cl ⁻	SO ₄ ⁻
Gouli Galli	6.4	2.49	1164	18.2	182.0	3.2	49.63	23.17	31.2	32.4
Jolad Bazar	6.6	1.22	981	19.8	142.7	5.6	39.36	17.72	42.6	36.1
Barapet Galli	6.7	1.72	790	21.2	64.0	6.1	19.42	6.16	42.6	45.2
Maratha Galli	6.8	1.13	872	24.0	85.9	6.2	19.81	14.56	34.6	38.9
Bara Imam Galli	7.2	1.15	786	28.0	151.0	5.4	43.71	16.70	34.8	28.9
Korawa Galli	6.6	1.20	584	18.0	145.7	5.3	51.60	6.69	28.4	25.4
Halyalkar GalliS	6.8	1.25	912	32.0	153.1	4.8	41.79	19.42	36.1	26.5
Sabade Galli	6.8	1.81	833	30.0	115.1	4.6	26.23	19.81	39.76	31.2

Table 4: Physico-Chemical parameters of Bore well water of Jamkhandi city at various locations.
(Zone: Central region of the city)

Location	pH	EC	TDS	TA	TH	DO	Ca ⁺⁺	Mg ⁺⁺	Cl ⁻	SO ₄ ⁻
Ganapati Galli	6.7	1.943	9.4	26	98.6	5.1	29.64	9.81	36.92	41.8
Hokkala Bhavi	6.8	1.130	892	30	116.9	5.2	33.03	13.72	56.08	44.5

Jambakeshwar Galli	6.7	1.721	790	20	121.1	6.2	26.84	21.60	65.32	39.1
Paga Galli	6.5	1.251	798	32	150.5	4.9	14.40	19.81	61.32	32.5
Mali Galli	6.6	1.223	725	34	98.1	5.3	21.52	17.72	58.32	41.8
Prabhath Nagar	8.0	1.228	640	19	56.2	5.5	16.30	6.16	16.32	25.5
Teacher Colony	6.3	1.422	849	6.4	81.0	4.9	27.8	4.6	17.60	34.8
LIC Colony	6.8	1.323	912	12.1	100.6	5.8	25.6	14.56	21.50	28.9

Table 5: Physico-Chemical parameters of Bore well water of Jamkhandi city at various locations. (Zone: North region of the city)

Location	pH	EC	TDS	TA	TH	DO	Ca ⁺⁺	Mg ⁺⁺	Cl ⁻	SO ₄ ⁻
Rudra Math Oni	7.9	1.170	718	12.5	134.0	6.1	36.90	16.7	23.4	32.5
Professor Colony	7.0	0.428	213	6.7	19.8	6.2	14.80	3.1	6.4	19.2
Rameshwar Colony	6.6	0.915	401	6.8	116.5	6.3	28.61	18.0	13.6	16.8
Sarada Colony	6.4	0.855	447	7.4	47.5	6.4	10.71	8.3	13.8	26.6
GLBC Colony	7.1	1.126	612	11.2	93.5	6.5	25.82	11.6	15.6	27.8
Siddarameshwar Colony	6.3	0.535	285	5.61	19.8	7.0	14.32	3.6	8.2	35.5
Post Colony	7.0	1.310	761	9.8	98.7	6.1	32.80	6.7	21.5	48.2
APMC Yard	7.2	1.780	912	11.4	62.0	5.9	16.54	8.3	20.2	18.9

Table 6: Water quality parameters of Open wells in Different parts of Jamkhandi City

Location	pH	EC	TDS	TA	TH	DO	Ca ⁺⁺	Mg ⁺⁺	Cl ⁻	SO ₄ ⁻
Girish Nagar	7.74	0.48	864	26	145.1	4.8	32.80	25.22	46.80	14.85
APMC Yard	7.41	0.64	746	31	61.8	5.0	13.06	11.65	56.82	24.69
Kadapatti Temple	7.30	0.20	679	28	98.9	5.2	19.46	20.10	42.66	48.15
Mendigeri Bhavi	7.16	0.29	912	62	112.6	4.6	25.60	19.45	59.81	38.69
Jambakeshwar Temple	7.02	1.32	1121	45	506.6	4.4	121.31	81.32	174.32	61.82
Vittal Mandir	7.12	0.51	923	53	188.1	5.8	49.61	25.61	76.03	54.96
AkkaTangi Bhavi	7.58	0.62	825	75	241.5	6.2	64.12	32.49	126.52	63.18
P & T Dept.	7.36	0.92	764	36	156.3	6.5	36.31	26.21	56.82	51.98

Table 7: Municipal water quality report at few locations in the Jamkhandi City

Location	pH	EC	TDS	TA	TH	DO	Ca ⁺⁺	Mg ⁺⁺	Cl ⁻	SO ₄ ⁻
Hanuman Temple	6.72	1.10	713	28	137.7	4.8	26.48	28.58	38.28	44.21
Sajji Hanuman Temple	6.92	1.08	816	35	188.9	5.0	40.10	35.47	29.76	38.64
AmbaBhavani Temple	6.58	1.23	769	42	69.4	5.2	14.43	13.34	15.56	28.92
Jagadayallamma Temple	7.01	0.93	964	20	84.8	4.9	15.23	18.69	29.76	58.86

Yallaling Math	6.59	0.98	1124	45	65.9	4.1	10.401	15.99	26.92	61.14
Rameshwar Colony	7.14	1.01	1021	62	139.5	4.5	21.65	34.14	72.36	68.42
B.L.D.E. A'S College	7.30	1.05	992	58	99.9	5.3	20.02	19.95	29.76	49.92
Nandikeshwar Temple	6.89	0.99	1002	46	154.0	5.8	27.26	34.32	38.28	39.38
Kadapatti Basavanna temple	6.92	0.86	981	25	221.9	6.1	9.65	78.79	81.94	45.46

Table 7: Municipal water quality report at few locations in the Jamkhandi City

Parameters	Unit	WHO (1961)	ISI (1991)
pH	6.5 – 8.5	6.5 – 8.5
EC	ds/m μS/cm	1.4 1400	1.4 1400
TDS	Ppm	< 500	< 500
TA	Ppm	75 – 120	75 – 120
TH	Ppm	500	300
DO	Ppm	4 – 6	7
Ca ⁺⁺	Ppm	75	75 -100
Mg ⁺⁺	Ppm	50	30 -150
Cl ⁻	Ppm	200	250
SO ₄ ⁻	ppm	150	150 -250

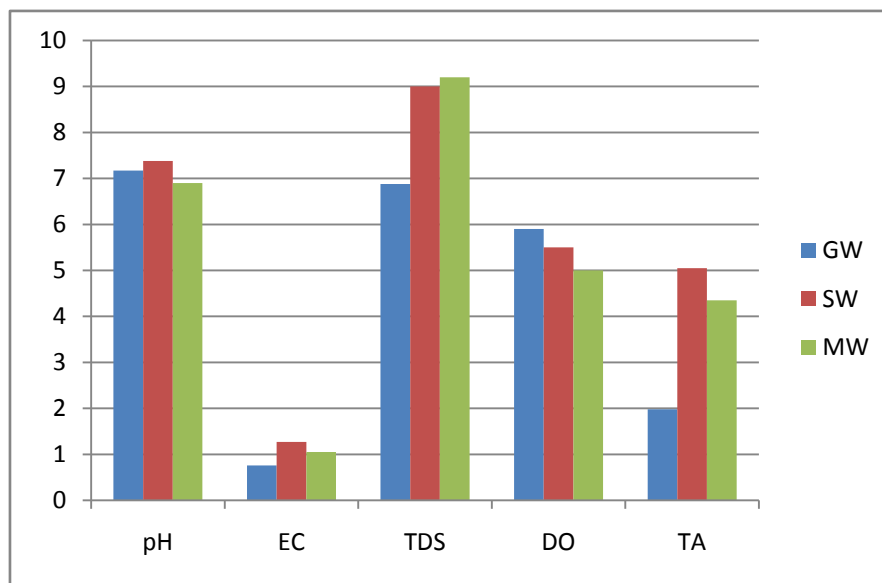


Figure 1: Comparison between the Physico-Chemical parameters of Ground water (GW), Surface water (SW) and Municipal water (MW)

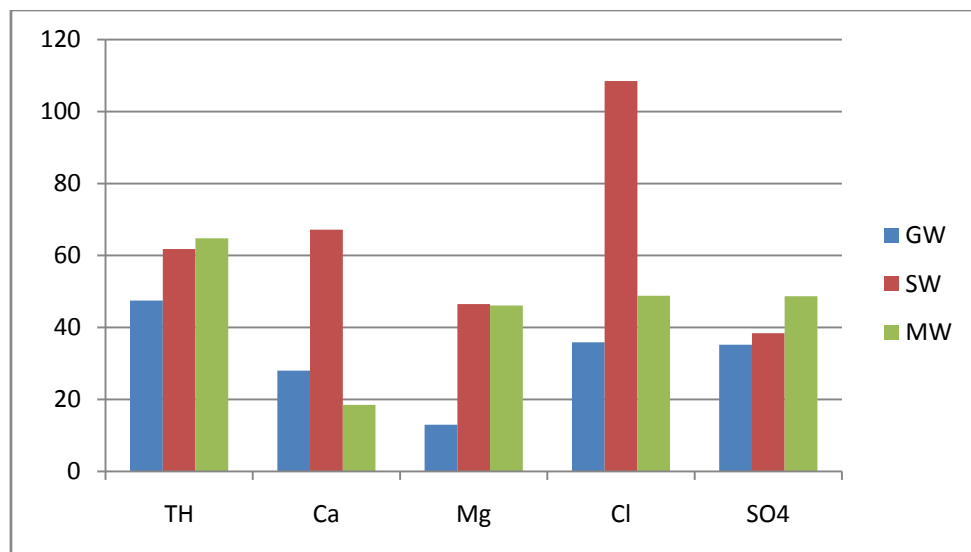


Figure 2 : Comparison between the Chemical parameter and Hardness of Ground water (GW), Surface water (SW) and Municipal water (MW)

IV. CONCLUSION

Due to the absence of Chemical Industries in the nearby place of this city, no toxic ions were identified even in trace amounts, the Fluoride ion concentrations of these samples were very low (<0.04 ppm to <0.06 ppm) and all these facts showed a good sign for the uses of water for drinking and cooking purpose.

The assessment of water quality and Evaluated parameters reveals that among the three sources (ground, open and municipal waters), the safest water should be ground water, because of its quality and physico-chemical parameters found within the prescribed limit except few bore wells already discussed in detail. It is necessary to improve the water quality of open well (Surface) water by adapting Chlorination. Which helps to control the growth of microbial and should be avoided the decomposition of organic matter were present in the water body.

River Krishna is the main source for water supply to Jamkhandi city. Hence, municipal water quality found to better during full flow of the river (rainy season), the municipality authorities supplies the water to the public after filtration through filter bed. It is suggested that the municipal authorities should follow the technical methods like chlorination which helps to control the development of microbial and bring down the hardness of water. During the lean flow of river water has contamination of maximum percentage of organic matter and inorganic ions make the municipal water unfit for drinking and cooking purpose.

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Removal of Cationic Dye Methylene Blue onto Moroccan Clay

Ghizlane Mouchid ^α, Ibtissam Maghri ^σ, Mohamed Elkouali ^ρ, Abdelkbir Kenz ^ω, Mohamed Talbi[✉] & Aicha Amougay [§]

Abstract - This study reports the adsorption of Methylene Blue dye, a cationic dye used in dyeing cotton, wood and silk, on the crude and purified clay from Morocco. The adsorption experiments demonstrated that adsorption equilibrium is established after 20 minutes. Various experimental parameters were analyzed: adsorbent mass, initial dye concentration, adsorbent particle size. The experimental results showed that adsorption of Methylene Blue onto Moroccan Clay are related to the mass of the adsorbent and the initial dye concentration. The adsorption capacity was determined using the Langmuir and Freundlich isotherms. The adsorption kinetics of Methylene Blue was studied using the equations of the First-order and Second order reactions. The kinetics of adsorption of Methylene Blue dye onto Moroccan Clay can be described by a Second-order model. Results showed that the Moroccan clay can be considered as a good adsorbent for the removal of Methylene Blue and treatment of industrial wastewater.

Keywords : adsorption, moroccan clay, cationic dye, methylene blue, adsorption isotherms, kinetic models, industrial wastewater.

I. INTRODUCTION

Problems of water pollution that we know come from all human activities, domestic, industrial and agricultural. The national and international scientific research focuses its activities in the field of the environment, to the development of technical, economic and easy to implement. Among these techniques, there is adsorption on activated carbon. This treatment was effective but in most cases very costly. The researches are then directed to methods of treatment using natural materials because of their availability and their low cost. For this, several studies have been devoted to the search for new materials that can replace the activated carbon. Many kinds of adsorbents have been developed for various applications [1–9]. All these considerations led our research team to examine the last few years, the problem of development of techniques for removal of dyes and adsorption of new natural materials less expensive due to their abundance.

Clays with considerable economic interest, they can be one of the most important industrial materials,

they are important in geology, agriculture, construction and environmental applications, in addition to their interest in clarifying oils, currently, they are increasingly used in various fields: there are clays for liquid fertilizer suspension, nano composites and plastic clays for adsorption of waste [10].

II. METHODS

a) Clay origin

Our clay, the purpose of this study, denoted (AR), comes from the city Safi the region Douar Oued Brahim Ben Dehmane, located about 35 km from the region El yousofia in Morocco .

b) Preparation of Clay

The experimental protocol used for the preparation of samples is illustrated in the following chart: The crude sample in the form of blocks is crushed and ground, the homogeneous powder obtained was washed with distilled water. After filtration, the residue was dried in an oven for 48 hours at 70°C. Finally, it is ground and sieved to a particle size between 40 and 100 microns

c) Optimization of adsorption of methylene blue on Clay

In order to optimize the conditions of adsorption of methylene blue on clay, we studied the effect of a number of factors may be involved in the process of this phenomenon: Effect of adsorbent dose, Effect of concentration and Effect of particle size of Moroccan clay

d) Adsorption Isotherms Modeling

i. Langmuir model

The second most commonly used model [11] is that of Langmuir. Initial assumptions are that the solid adsorbent has a limited adsorption capacity (q_m), all the active sites are identical, they can only complexing solute molecule (monolayer adsorption) and that there is no interaction between the adsorbed molecules.

$$\frac{1}{q_e} = \left(\frac{1}{q_m} \right) + \left(\frac{1}{K_L \cdot C_e \cdot q_m} \right) \quad (\text{Langmuir I}) \quad (1)$$

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$$\frac{C_e}{q_e} = \left(\frac{1}{K_L \cdot q_m} \right) + \left(\frac{C_e}{q_m} \right) \quad (\text{Langmuir II}) \quad (2)$$

When q_e and q_m are expressed in mg.g^{-1} and C_e mg.L^{-1} , the constant K_L is expressed in L.mg^{-1} . Some authors define the ratio R_L as a unitless quantity indicating whether more favorable adsorption tends to zero as R_L ($R_L < 0$) and much worse than R_L tends towards a to 1 ($R_L = 1$) [12].

$$R_L = \frac{1}{1 + K_L \cdot C_0} \quad (3)$$

ii. *Freundlich model*

The simple model and empirical Freundlich is the most commonly used. We consider that it applies to many cases, especially in the case of multilayer adsorption with possible interactions between the adsorbed molecules [13,14].

$$q_e = K_F \cdot C_e^n \quad (4)$$

The most common form exploited is the plot in logarithmic scale variations q_e according to C_e :

$$\log q_e = \log K_F + n \log C_e \quad (5)$$

Another possible use of the results by the Freundlich isotherm plot is in logarithmic scale changes in the distribution coefficient K_d based q_e :

$$\log K_d = \left(\frac{1}{n} \right) \log k_F + \left[\frac{(n-1)}{n} \right] (\log q_e) \quad (6)$$

K_F is a constant which relates to the adsorption capacity. This is often expressed as mg.L^{-1} and q_e as mg.g^{-1} unit $K_F \text{ mg} (1-n) \cdot \text{Ln.g}^{-1}$. Consistent with the relationship between K_F and the maximum capacity of adsorption (q_m) is:

$$K_F = \frac{q_m}{C_0^n} \quad (7)$$

The constant n (dimensionless) gives an indication of the intensity of adsorption. It is generally accepted [15] that low values of n ($0.1 < n < 0.5$) are characteristics of a good adsorption, whereas higher values indicate a moderate adsorption ($0.5 < n < 1$) or low ($n > 1$).

e) *Adsorption Kinetics modeling*

i. *first order Model*

The first order model is usually expressed by [16]:

$$\frac{dq(t)}{dt} = k_1 (q_e - q(t)) \quad (8)$$

This equation (1) becomes after integration, as follows [17,18]:

$$\ln(q_e - q(t)) = \ln q_e - k_1 \cdot t \quad (9)$$

ii. *Second order model*

It is an equation that is often used in the representation of adsorption kinetics. It is in the form [19]:

$$\frac{dq(t)}{dt} = k_2 (q_e - q(t))^2 \quad (10)$$

This equation (3) becomes after integration, as follows [19]:

$$\frac{1}{q(t)} = \frac{1}{k_2 \cdot q_e^2 \cdot t} + \frac{1}{q_e} \quad (11)$$

III. RESULTS AND DISCUSSIONS

a) *Adsorbate Concentration Effect*

The figure 1 shows the adsorption kinetics of methylene blue onto clay at different initial concentrations. We notify a decrease in the residual concentration. After sixty minutes, it reaches a constant value whatever the initial concentration; this shows that the equilibrium time is independent of the initial concentration of the dye.

b) *Effect of Adsorbent Dose*

The adsorption kinetics of methylene blue with three different masses of adsorbents is shown in figure 2. From these results, the biosorption is important for a mass of 0.4g.L^{-1} of adsorbent.

c) *Adsorbent Particle Size Effect*

In this study we used different size fractions. The adsorption kinetics of methylene blue is shown in Figure 3. The adsorption capacity is better for a size range $< 40 \mu\text{m}$ for clay because the adsorption depends on the external surface of the adsorbent material increases with the fineness of its particles.

d) *Modeling Adsorption Isotherms*

i. *Langmuir and freundlich isotherms*

The experimental isotherms of adsorption equilibrium and maximum adsorption capacity have been validated in detail by the Langmuir model (Table 1) and Freundlich model (Table 2). The isotherms obtained were L-type according to the classification of Giles [20],

which promotes a monolayer adsorption and the interaction between the adsorbate and the adsorbent is important.

The results show that the maximum adsorption capacity (q_m) obtained from Langmuir model decreases with increasing the concentration value of the Methylene Blue (C_0). The adsorption of methylene blue onto clay is favorable (R_L tends to 0).

The low values of maximum adsorption capacities obtained from the Freundlich model, confirm that the molecule of Methylene Blue is not strongly adsorbed inside the pores because of its size. The adsorption of methylene blue onto clay is good ($0,1 < n < 0,5$).

ii. First and second order models

First and second order equation accounting both with theoretic and experimental point of view was used to describe the adsorption kinetics of Methylene Blue onto Clay

The calculated q_e values are lower than the experimental value. The values of k_1 , q_e and regression coefficients provided in Table 3, demonstrate that methylene blue adsorption by Clay are not first-order.

The correlation coefficients (R^2) for these plots are superior (in most cases > 0.9) (Figure 3). The experimental q_e values were compared to q_e values determined by second order rate kinetic models. The q_e values calculated from the pseudo second order kinetic model exhibit excellent agreement with the experimental q_e values (Figure 3). Thus, the sorption process is pseudo-second order. The pseudo-second order model is based on the assumption that the rate-limiting step is a chemical sorption between the adsorbate and adsorbent. This provides the best correlation of the data.

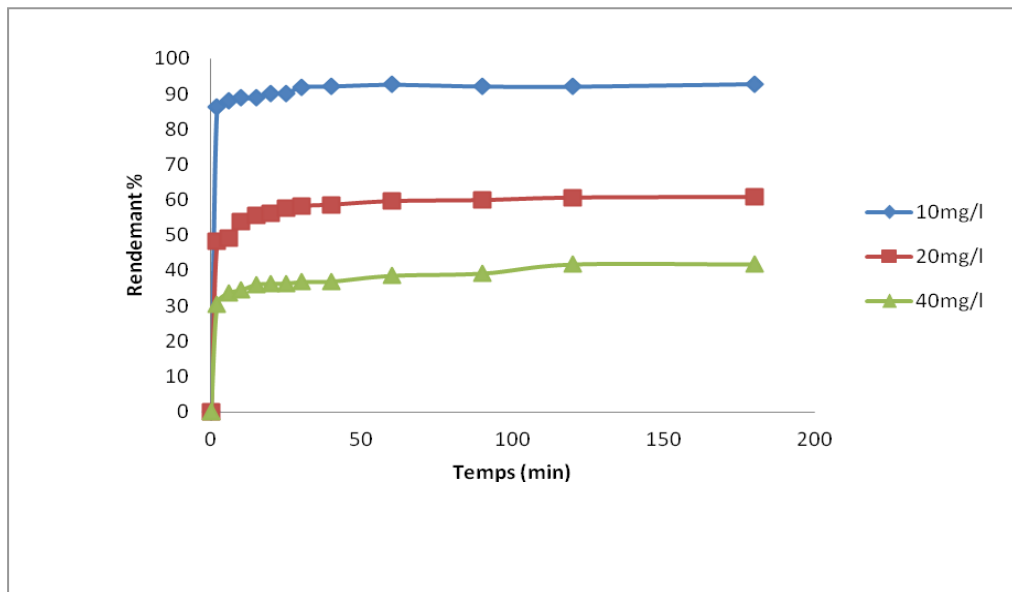


Figure 1 : Effect of Methylene Blue concentration, pH = 6,8; $g < 0,056$ mm; adsorbent dosage 4 g.L^{-1} ; ambient temperature

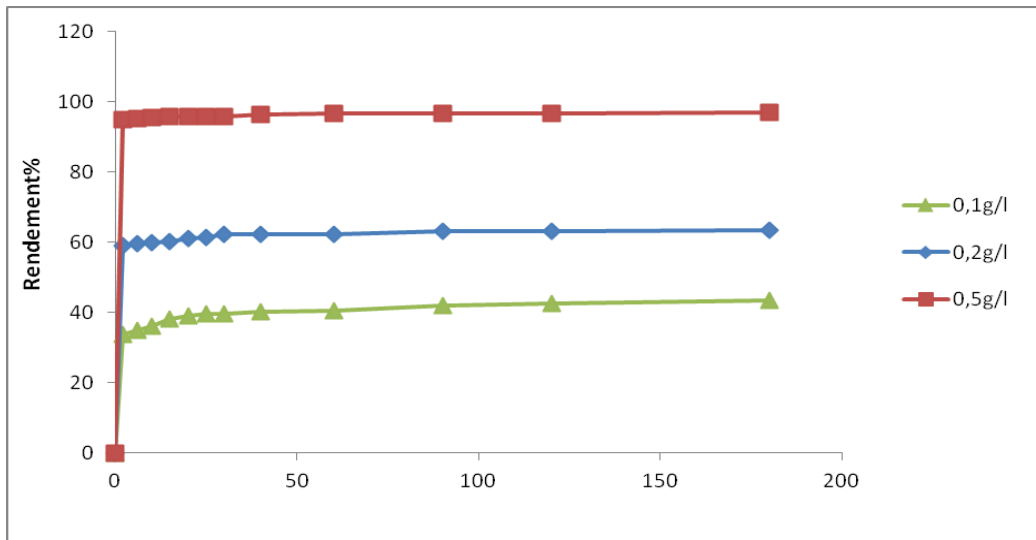


Figure 2 : Effect of adsorbent dose, pH = 6,8; initial concentration 10 mg.l⁻¹; G <0,056 mm; ambient temperature

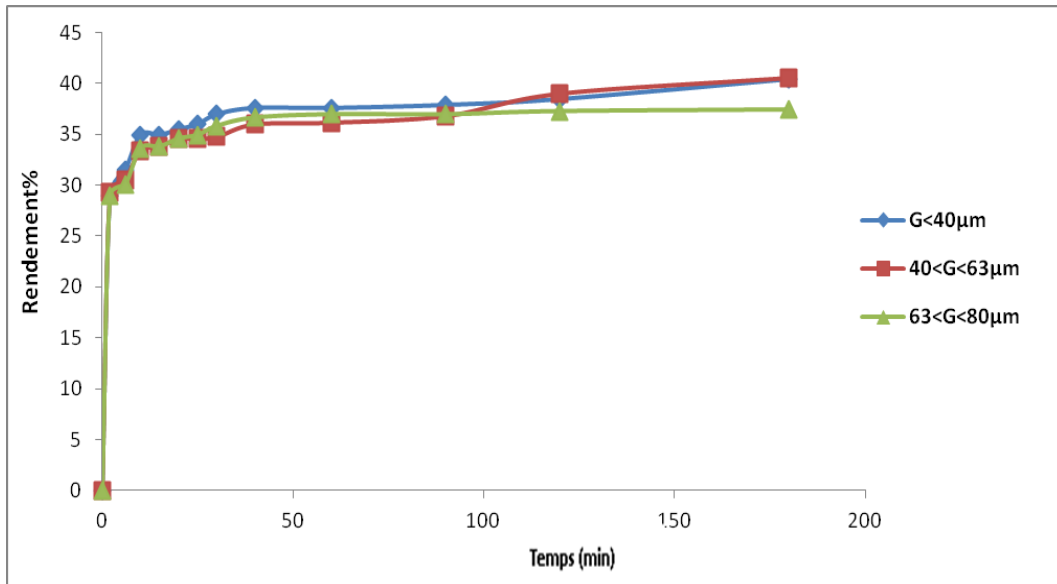


Figure 3 : Effect of adsorbent particle size, pH = 6,8; initial concentration 10 mg.L⁻¹; adsorbent dosage 4 g.L⁻¹; ambient temperature

Table 1 : Parameters of Langmuir adsorption of Methylene Blue onto Moroccan Clay

Langmuir 1 isotherm					
Experience	K _L (L.mg ⁻¹)	q _m (mg.g ⁻¹)	R ²	R _L	$\overline{R_{L_i}} = \sum_{j=1}^5 R_{L_{ij}}$
Exp1:10mg ⁻¹	1,1367	71,9425	0,9436	0,0285	0,034
				0,0215	
				0,0917	
				0,0145	
				0,0124	
Exp2: 20mg ⁻¹	0,6182	73,5294	0,9709	0,0512	0,034
				0,0389	

				0,0313	
				0,0273	
				0,0226	
Exp3: 40mg ⁻¹	0,8861	71,4286	0,9615	0,0363	0,024
				0,0274	
				0,0221	
				0,0185	
				0,0158	
Langmuir 2 isotherm					
Exp1: 10mg ⁻¹	1,433	71,9425	0,9973	0,0227	0,015
				0,0172	
				0,0138	
				0,0115	
				0,0099	
Exp2: 20mg ⁻¹	1,2752	71,9425	0,9969	0,0255	0,017
				0,0192	
				0,0154	
				0,0129	
				0,0111	
Exp3: 40mg ⁻¹	1,6023	70,922	0,9985	0,0204	0,014
				0,0154	
				0,0123	
				0,0103	
				0,0084	
Langmuir 3 isotherm					
Exp1: 10mg ⁻¹	0,8578	71,949	0,9142	0,0374	0,025
				0,0283	
				0,0227	
				0,0191	
				0,0164	
Exp2: 20mg ⁻¹	1,6526	73,566	0,9539	0,0197	0,013
				0,0149	
				0,0119	
				0,0098	
				0,0085	
Exp3: 40mg ⁻¹	1,1534	71,523	0,9457	0,0281	0,019
				0,0212	
				0,0171	
				0,0142	
				0,0122	
Langmuir 4 isotherm					
Exp1: 10mg ⁻¹	0,7842	72,6535	0,9142	0,0408	0,027
				0,0309	
				0,0249	
				0,0208	
				0,0179	
Exp2: 20mg ⁻¹	1,7325	73,566	0,9539	0,0189	0,015
				0,0142	
				0,0114	
				0,0095	
				0,0082	
Exp3: 40mg ⁻¹	1,2196	48,3642	0,9457	0,0266	0,019
				0,0201	
				0,0172	
				0,0135	
				0,0116	

Langmuir 5 isotherm					
Exp1: 10mg ⁻¹	0,8256	72,2226	0,9142	0,0388	0,026
				0,0294	
				0,0237	
				0,0198	
				0,017	
Exp2: 20mg ⁻¹	0,599	73,6527	0,9539	0,0527	0,035
				0,0401	
				0,0323	
				0,02701	
Exp3: 1:40mg ⁻¹	0,8472	71,6831	0,9457	0,0379	0,025
				0,0286	
				0,023	
				0,0193	
				0,0166	

Table 2 : Parameters of Freundlich adsorption of Methylene Blue onto Moroccan Clay

Freundlich isotherm				
Experience	K _F (mg ⁽¹⁻ⁿ⁾ L ⁿ g ⁻¹)	n	R ²	q _m (mg.g ⁻¹)
Exp1: 10mg ⁻¹	5,29	0,1251	0,9983	8,1
				8,4
				8,63
				8,83
				9
Exp2: 20mg ⁻¹	5,13	0,1475	0,9912	8,47
				8,84
				9,14
				9,38
				9,6
Exp3: 40mg ⁻¹	5,31	0,1205	0,9887	8
				8,28
				8,5
				8,7
				8,86

Table 3 : Parameters of First and Second order model of Methylene Blue adsorption onto Moroccan Clay

C ₀ (mg.l ⁻¹)	10	20	40	20	20	20
m _s (g)	0,02	0,02	0,02	0,01	0,02	0,05
Q _o (mg.g ⁻¹) Experimental 1 st Order	46,4195	60,852	83,5285	86,64	63,329	38,7706
Q _o (mg.g ⁻¹) theoretic 1 st Order	13,72	46,47	90,86	50	20,39	4,98
K ₁	0,387	0,3911	0,3722	0,2621	0,3494	0,3573
R ²	0,7686	0,9153	0,5459	0,8659	0,8134	0,6692
Q _o (mg.g ⁻¹) experimental 2 nd Order	42,01	46,23	60,98	67,02	162,17	37,65

Q_e (mg.g ⁻¹) theoretic 2 nd Order	43,29	48,78	62,11	67,11	162,28	37,88
K_2	-5,34	-1,05	-0,86	-0,74	-1,48	-13,94
R^2	0,8801	0,8316	0,8912	0,9283	0,9705	0,9605

IV. CONCLUSION

This work demonstrates that natural clay from Yousfia can be used as a metal ion adsorbent for treating water/wastewater contaminated with methylene blue.

The removal of methylene blue by adsorption onto clay was found to be rapid at the initial period of contact time and then slows down with increasing reaction time. The application of adsorption models allowed us to conclude that: The kinetic study of the phenomenon of adsorption follows the model of second order, because the correlation coefficient R^2 (2nd order) is higher than the correlation coefficient R^2 (1st Order). We can conclude that this is a Chemisorption. On average R_L is constant and close to 0. This shows that the adsorption is more favorable. We can say therefore that the clay can be considered as a good adsorbent for the removal of Methylene blue in aqueous solution. We have a good adsorption because for the different concentrations, we note that ($0.1 < n < 0.5$). This study showed that the clay could be used as an adsorbent to remove Methylene Blue dye from aqueous solution.

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- 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.
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- 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

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- 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
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- 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."
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- 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.



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<i>References</i>	Complete and correct format, well organized	Beside the point, Incomplete	Wrong format and structuring

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