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Chemistry

Highlights

- Properties of Jute Fiber
- Impact of Chemical Treatments
- Metabolic Effects of Sulphur
- Non-Relativistic Wave Equations

Discovering Thoughts, Inventing Future

VOLUME 18 ISSUE 2 VERSION 1.0

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Chemistry

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Solutions of the Relativistic and Non-Relativistic Wave Equations with $l \neq 0$ for Modified Hylleraas Plus Attractive Radial Molecular Potential using Nikiforov-Uvarov Method

By Magu Thomas Odey, Benedict Iserom Ita, Pigweh Isa Amos, Akakuru Ozioma Udochukwu, Alexander I. Ikeuba & Louis Hitler
University of Calabar

Abstract- It is well known that the exact solutions play an important role in quantum mechanics since they contain all the necessary information regarding the quantum model under study. However, the exact analytic solutions of nonrelativistic and relativistic wave equations are only possible for certain potentials of physical interest. In this paper, bound state solutions of the Schrodinger and Klein-Gordon equations with Modified Hylleraas plus attractive radial potentials (MHARP), have been obtained using the parametric Nikiforov-Uvarov (NU) method which is based on the solutions of general second-order linear differential equations with special functions. The bound state eigen energy solutions for both wave equations were obtained. Also special cases of the potential have been considered and their energy eigen values obtained.

Keywords: schrodinger, klein-gordon, hylleraas, attractive radial, nikiforov-uvarov.

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Solutions of the Relativistic and Non-Relativistic Wave Equations with $l \neq 0$ for Modified Hylleraas Plus Attractive Radial Molecular Potential using Nikiforov-Uvarov Method

Magu Thomas Odey [α], Benedict Iserom Ita [σ], Pigweh Isa Amos[ρ], Akakuru Ozioma Udochukwu [ω],
Alexander I. Ikeuba [¥] & Louis Hitler [§]

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Keywords: schrodinger, klein-gordon, hylleraas, attractive radial, nikiforov-uvarov.

I. INTRODUCTION

It is now well known and widely understood that the exact solutions of the Schrodinger, Klein-Gordon and Dirac wave equations are only possible only for a handful of potentials of physical interest in a few cases such as the harmonic oscillator, Coulomb, pseudoharmonic potentials and others [1-4]. The total wave function of any quantum mechanical system basically provides implicitly the important information about the physical behavior of the system. Bound state solutions in most cases provides negative energies because usually, the energy of the particle is less than the maximum potential energy therefore, causing the particle to be trapped within the potential well [5]. The search of analytical bound state solutions of the Schrodinger equation for Hylleraas and as well as attractive radial potentials, have been of great interest as shown by many cases of specific potentials studied by means of different approaches to the centrifugal term and by using various methods such as the Nikiforov-Uvarov [4], asymptotic iteration [5], supersymmetric quantum mechanics [6], the path integral approach [7], numerical calculations [8] and many others.

We attempt to find the analytical approximate bound state solutions of Schrodinger and Klein-Gordon equations with modified Hylleraas plus attractive radial molecular potentials including the energy spectrum. Ever since Hylleraas proposed this potential [9] no much work has been reported on the bound state solution. The purpose of this paper is to use the Pekeris-like approximation [2, 3]to the centrifugal term to study the Schrodinger and Klein-Gordon equations for modified Hyllerras plus attractive potentials. The attractive radial potential which has been studied by many researchers [10,11] is one of the most important exponential-type potential in physics and chemical physics whereas Hylleraas potential can be used to study diatomic molecules [12,13].

II. SECTION 2: THEORETICAL APPROACH

a) *Review of parametric Nikiforov-Uvarov Method*

The NU method is based on the solutions of a generalized second order linear differential equation with special orthogonal functions. The Nikiforov-Uvarov method has been successfully applied to relativistic, nonrelativistic quantum mechanical problems and other fields of study as well [3, 14].The hypergeometric NU method has shown its power in calculating the exact energy levels of all bound states for some solvable quantum systems.

$$\Psi''_{\mathrm{n}}(\mathrm{s}) + \frac{\tilde{\tau}(s)}{\sigma(s)}\Psi'_{\mathrm{n}}(\mathrm{s}) + \frac{\bar{\sigma}(s)}{\sigma^2(s)}\Psi_{\mathrm{n}}(\mathrm{s}) = 0 \qquad (1)$$

Where σ(s) and $\bar{\sigma}$(s) are polynomials at most second degree and $\tilde{\tau}$(s) is first degree polynomials.The parametric generalization of the N-U method is given by the generalized hypergeometric-type equation.

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$$\Psi''(s) + \frac{c_1 - c_2 s}{s(1-c_3 s)}\Psi'(s) + \frac{1}{s^2(1-c_3 s)^2}[-\epsilon_1 s^2 + \epsilon_2 s - \epsilon_3]\Psi(s) = 0 \tag{2}$$

Thus eqn. (1) can be solved by comparing it with equation (2) and the following polynomials are obtained

$$\tilde{\tau}(s) = (c_1 - c_2 s),\ \sigma(s) = s(1-c_3 s),\ \overline{\sigma}(s) = -\epsilon_1 s^2 + \epsilon_2 s - \epsilon_3 \tag{3}$$

The parameters obtainable from equation (3) serve as important tools for finding the energy eigen value and eigen functions. They satisfy the following sets of equation respectively.

$$c_2 n - (2n+1)c_5 + (2n+1)(\sqrt{c_9} + c_3\sqrt{c_8}) + n(n-1)c_3 + c_7 + 2c_3 c_8 + 2\sqrt{c_8 c_9} = 0 \tag{4}$$

$$(c_2 - c_3)n + c_3 n^2 - (2n+1)c_5 + (2n+1)(\sqrt{c_9} + c_3\sqrt{c_8}) + c_7 + 2c_3 c_8 + 2\sqrt{c_8 c_9} = 0 \tag{5}$$

While the wave function is given as

$$\Psi_n(s) = N_{n,l} S^{c_{12}}(1-c_3 s)^{-c_{12}-\frac{c_{13}}{c_3}} P_n^{\left(c_{10}-1,\frac{c_{11}}{c_3}-c_{10}-1\right)}(1-2c_3 s) \tag{6}$$

Where

$$c_4 = \frac{1}{2}(1-c_1),\ c_5 = \frac{1}{2}(c_2 - 2c_3),\ c_6 = c_5{}^2 + \epsilon_1,\ c_7 = 2c_4 c_5 - \epsilon_2,\ c_8 = c_4{}^2 + \epsilon_3,$$

$$c_9 = c_3 c_7 + c_3{}^2 c_8 + c_6,\ c_{10} = c_1 + 2c_4 + 2\sqrt{c_8},\ c_{11} = c_2 - 2c_5 + 2\left(\sqrt{c_9} + c3\sqrt{c_8}\right)$$

$$c_{12} = c_4 + \sqrt{c_8}\ ,\ c_{13} = c_5 - \left(\sqrt{c_9} + c3\sqrt{c_8}\right) \tag{7}$$

and P_n are the orthogonal polynomials.

Given that
$$P_n{}^{(\alpha,\beta)} = \sum_{r=0}^{n} \frac{\Gamma(n+\alpha+1)\Gamma(n+\beta+1)}{\Gamma(\alpha+r+1)\Gamma(n+\beta-r+1)(n-r)!r!}\left(\frac{x-1}{2}\right)^r \left(\frac{x+1}{2}\right)^{n-r} \tag{8}$$

This can also be expressed in terms of the Rodriguez's formula

$$P_n{}^{(\alpha,\beta)}(x) = \frac{1}{2^n n!}(x-1)^{-\alpha}(x+1)^{-\beta}\left(\frac{d}{dx}\right)^n\left((x-1)^{n+\alpha}(x+1)^{n+\beta}\right)$$

III. Section 3: Bound State Solutions

a) Schrodinger Equation with Modified Hylleraas Plus Attractive Radial Molecular Potential

The l-State Schrodinger Equation with vector V(r), potential is given as [15]

$$\frac{d^2 R(r)}{dr^2} + \frac{2\mu}{\hbar^2}\left[(E - V(r)) + \frac{l(l+1)\hbar^2}{2\mu r^2}\right]R(r) = 0 \tag{9}$$

Where E is the eigen energy value, l is the angular momentum quantum number

The Modified Hylleras Potential is given as [9]

$$V(s) = \frac{V_o}{b}\left(\frac{a-s}{1-s}\right) \tag{10}$$

Where $S = e^{-2\alpha r}$, α is the screening parameter and determines the range of the potential, and V_o, b, a are the coupling parameters describing the depth of the potential well.

The Attractive Radial Potential [14]

$$V(s) = \frac{V_1 s^2}{(1-s)^2} + \frac{V_2 s}{(1-s)^2} + \frac{V_3}{(1-s)^2} \tag{11}$$

Where, screening parameter αdetermines the range of the potential, and $V_1, V_2, V_3$are the coupling parameters describing the depth of the potential well Making the transformation $s = e^{-2\alpha r}$ the sum of the potentials (MHARMP) in equations (2) and (3) becomes

$$V(s) = \left(\frac{V_1 s^2}{(1-s)^2} + \frac{V_2 s}{(1-s)^2} + \frac{V_3}{(1-s)^2} + \frac{V_o}{b}\left(\frac{a-s}{1-s}\right)\right) \tag{12}$$

The Pekeris-like approximation [15-17] is applied to the inverse square term, $\frac{1}{r^2} = \frac{4\alpha^2}{(1-s)^2}$ in eq. (12) to enable us to completely solve eq. (9).

Again, applying the transformation $s = e^{-2\alpha r}$ to get the form that parametric Nikiforov-Uvarov (NU) method is applicable, equation (9) gives a generalized hypergeometric-type equation as.

$$\frac{d^2R(s)}{ds^2}+\frac{(1-s)}{(1-s)s}\frac{dR(s)}{ds}+\frac{1}{(1-s)^2s^2}[(2\beta^2-J-P)s^2+(J+R-H-4\beta^2)s+(2\beta^2-R-B+\lambda)]R(s)=0 \tag{13}$$

Where

$$-\beta^2=\left(\frac{\mu E}{4\alpha^2\hbar^2}\right),\ B=\left(\frac{\mu}{2\alpha^2\hbar^2}\right)V_3,\ \lambda=l(l+1),\ P=\left(\frac{\mu}{2\alpha^2\hbar^2}\right)V_1,\ H=\left(\frac{\mu}{2\alpha^2\hbar^2}\right)V_2,\ J=\left(\frac{\mu}{2\alpha^2\hbar^2}\right)V_o, R=\left(\frac{\mu}{2\alpha^2\hbar^2}\right)V_o a \tag{14}$$

$$c_1=c_2=c_3=1, c_4=0, c_5=-\frac{1}{2}, c_6=\frac{1}{4}+2\beta^2-J-P, c_7=-4\beta^2-H+J+R,$$

$$c_8=2\beta^2-R-B+\lambda,$$

$$c_9=\frac{1}{4}+\lambda-H-B-P,$$

$$c_{10}=1+2\sqrt{2\beta^2-R-B+\lambda},$$

$$c_{11}=2+2\left(\sqrt{\frac{1}{4}+\lambda-H-B-P}+\sqrt{2\beta^2-R-B+\lambda}\right),$$

$$c_{12}=\sqrt{2\beta^2+P},$$

$$c_{13}=-\frac{1}{2}-\left(\sqrt{\frac{1}{4}+\lambda-H-B-P}+\sqrt{2\beta^2-R-B+\lambda}\right),$$

$$\varepsilon_1=2\beta^2-J-P,$$

$$\varepsilon_2=4\beta^2+H-J-R, \varepsilon_3=2\beta^2-R-B+\lambda \tag{15}$$

Now using equations (6), (14) and (15) we obtain the energy eigen spectrum of the MHARMP as

$$\beta^2=\left[\frac{(P+H+2B)-(J+2\lambda)-\left(n^2+n-\frac{1}{2}\right)-(2n+1)\sqrt{\frac{1}{4}+\lambda-H-B-P}}{\left(n+\frac{1}{2}\right)+2\sqrt{\frac{1}{4}+\lambda-H-B-P}}\right]^2-(R+B-\lambda) \tag{16}$$

The above equation can be solved explicitly and the energy eigen spectrum of MHARMP becomes

$$E=\frac{4\alpha^2\hbar^2}{\mu}\left\{\left[\frac{\Bigg(\bigg(\Big(\left(\frac{\mu}{2\alpha^2\hbar^2}\right)V_1+\left(\frac{\mu}{2\alpha^2\hbar^2}\right)V_2\Big)+\left(\frac{\mu}{\alpha^2\hbar^2}\right)V_2\bigg)-\bigg(\left(\frac{\mu}{2\alpha^2\hbar^2}\right)V_o+2l(l+1)\bigg)-\left(n^2+n-\frac{1}{2}\right)-(2n+1)\sqrt{\frac{1}{4}+l(l+1)-\left(\frac{\mu}{2\alpha^2\hbar^2}\right)V_2}-\left(\frac{\mu}{2\alpha^2\hbar^2}\right)V_3-\left(\frac{\mu}{2\alpha^2\hbar^2}\right)V_1}{(2n+1)+2\sqrt{\frac{1}{4}+l(l+1)-\left(\frac{\mu}{2\alpha^2\hbar^2}\right)V_2}-\left(\frac{\mu}{2\alpha^2\hbar^2}\right)V_3-\left(\frac{\mu}{2\alpha^2\hbar^2}\right)V_1}\right]\right\}-$$

$$\left(\left(\frac{\mu}{2\alpha^2\hbar^2}\right)V_o a+\left(\frac{\mu}{2\alpha^2\hbar^2}\right)V_3-l(l+1)\right) \tag{17}$$

b) Klein-Gordon Edquation with Modified Hylleraas Plus Attractive Radial Molecular Potential

The Klein-Gordon Equation with vector V(r), potential in atomic units ($\hbar = c = 1$) is given as [3]

$$\frac{d^2R(r)}{dr^2}+\left[(E^2-M^2)-2(E+M)V(r)+\frac{l(l+1)}{r^2}\right]R(r)=0 \tag{18}$$

Where $E, M, V(r), l$ are the relativistic energy, reduced mass, potential and angular momentum respectively. From eq. (12) we have the expression of the superposed or mixed potentials, MHARMP given as

$$V(s)=\left(\frac{V_1 s^2}{(1-s)^2}+\frac{V_2 s}{(1-s)^2}+\frac{V_3}{(1-s)^2}+\frac{V_o}{b}\left(\frac{a-s}{1-s}\right)\right) \tag{12}$$

Similarly, the Pekeris-like approximation [15-17] is applied to the inverse square term, $\frac{1}{r^2}=\frac{4\alpha^2}{(1-s)^2}$ in eq. (12) to enable us to completely solve eq. (18).

Again, applying the transformation $s=e^{-2\alpha r}$ to get the form that parametric Nikiforov-Uvarov (NU) method is applicable, equation (18) gives a generalized hypergeometric-type equation as

$$\frac{d^2R(s)}{ds^2}+\frac{(1-s)}{(1-s)s}\frac{dR(s)}{ds}+\frac{1}{(1-s)^2s^2}\left[(\beta^2-P-J)s^2+(-2\beta^2+J+R-B)s+(\beta^2-H-R+\lambda)\right]R(s)=0 \tag{19}$$

Where

$$\beta^2=\left(\frac{E^2+M_o^2}{4\alpha^2}\right),\ B=\left(\frac{E+M_o}{2\alpha^2}\right)V_2,\ \lambda=l(l+1),H=\left(\frac{E+M_o}{2\alpha^2}\right)V_3,R=\left(\frac{E+M_o}{2b\alpha^2}\right)V_o a,J=\left(\frac{E+M_o}{2b\alpha^2}\right)V_o,\ P=\left(\frac{E+M_o}{2\alpha^2}\right)V_1 \tag{20}$$

$$c_1=c_2=c_3=1,c_4=0,c_5=-\frac{1}{2},c_6=\frac{1}{4}+\beta^2-J-P,c_7=-2\beta^2-B+J+R,$$

$$c_8=\beta^2-H-R+\lambda,c_9=\frac{1}{4}-B-H-P+\lambda,c_{10}=1+2\sqrt{\beta^2-H-R+\lambda},$$

$$c_{11}=2+2\left(\sqrt{\frac{1}{4}-B-H-P+\lambda}+\sqrt{\beta^2-H-R+\lambda}\right),$$

$$c_{12}=\sqrt{\beta^2-H-R+\lambda},c_{13}=-\frac{1}{2}-\left(\sqrt{\frac{1}{4}-B-H-P+\lambda}+\sqrt{\beta^2-H-R+\lambda}\right),$$

$$\varepsilon_1=\beta^2-P-J,\varepsilon_2=2\beta^2+B-J-R,\varepsilon_3=\beta^2-H-R+\lambda \tag{21}$$

Now using equations (6), (20) and (21) we obtain the energy eigen spectrum of the MHARMP as

$$\beta^2=\left[\frac{(R-2\lambda-J)+(2H+B)-\left(n^2+n-\frac{1}{2}\right)-(2n+1)\sqrt{\frac{1}{4}-B-H-P+\lambda}}{(2n+1)+2\sqrt{\frac{1}{4}-B-H-P+\lambda}}\right]^2-(H+R-\lambda) \tag{22}$$

The above equation can be solved explicitly and the energy eigen spectrum of MHARMP becomes

$$E^2-M^2=-4\alpha^2\left\{\left[\frac{\left(\left(\frac{E+M_o}{2b\alpha^2}\right)V_o a-2l(l+1)-\left(\frac{E+M_o}{2b\alpha^2}\right)V_o\right)+\left(\left(\frac{E+M_o}{\alpha^2}\right)V_3+\left(\frac{E+M_o}{2\alpha^2}\right)V_2\right)-\left(n^2+n-\frac{1}{2}\right)-(2n+1)\sqrt{\frac{1}{4}-\left(\frac{E+M_o}{2\alpha^2}\right)V_3-\left(\frac{E+M_o}{2\alpha^2}\right)V_2-\left(\frac{E+M_o}{2\alpha^2}\right)V_1}}{(2n+1)+\sqrt{\frac{1}{4}+(l(l+1))-\left(\frac{E+M_o}{2\alpha^2}\right)V_1-\left(\frac{E+M_o}{2\alpha^2}\right)V_3-\left(\frac{E+M_o}{2\alpha^2}\right)V_2}}\right]\right\}-$$

$$\left(\left(\frac{E+M_o}{2b\alpha^2}\right)V_o a+\left(\frac{E+M_o}{2\alpha^2}\right)V_3-l(l+1)\right) \tag{23}$$

IV. SECTION 4: DISCUSSION

In this section, special case of potential considerations to the obtained bound state eigenenergy for Schrodinger and Klein-Gordon equations are considered.

a) Schrodinger Equation

Case I: From eq. (12) $when\ V_o=0$, eq. (17) is reduced to Schrodinger equation with Attractive radial potential given as:

$$E = \frac{4\alpha^2\hbar^2}{\mu}\left\{\left[\frac{\left(\left(\left(\frac{\mu}{2\alpha^2\hbar^2}\right)V_1+\left(\frac{\mu}{2\alpha^2\hbar^2}\right)V_2\right)+\left(\frac{\mu}{\alpha^2\hbar^2}\right)V_2\right)-(2l(l+1))-\left(n^2+n-\frac{1}{2}\right)-(2n+1)\sqrt{\frac{1}{4}+l(l+1)-\left(\frac{\mu}{2\alpha^2\hbar^2}\right)V_2}-\left(\frac{\mu}{2\alpha^2\hbar^2}\right)V_3-\left(\frac{\mu}{2\alpha^2\hbar^2}\right)V_1}{(2n+1)+2\sqrt{\frac{1}{4}+l(l+1)-\left(\frac{\mu}{2\alpha^2\hbar^2}\right)V_2}-\left(\frac{\mu}{2\alpha^2\hbar^2}\right)V_3-\left(\frac{\mu}{2\alpha^2\hbar^2}\right)V_1}\right]\right\}-$$

$$\left(+\left(\frac{\mu}{2\alpha^2\hbar^2}\right)V_3-l(l+1)\right) \tag{24}$$

Eq. (24) is similar to the bound state solution obtained in ref. [14]

Case II: From eq. (12) $\boldsymbol{when}\ V_1 = V_2 = V_3 = \mathbf{0}$, eq. (17) is reduced to Schrodinger equation with Modified Hylleraas potential given as:

$$E = \frac{4\alpha^2\hbar^2}{\mu}\left\{\left[\frac{-\left(\left(\frac{\mu}{2\alpha^2\hbar^2}\right)V_o+2l(l+1)\right)-\left(n^2+n-\frac{1}{2}\right)-(2n+1)\sqrt{\frac{1}{4}+l(l+1)}}{(2n+1)+2\sqrt{\frac{1}{4}+l(l+1)}}\right]\right\}-\left(\left(\frac{\mu}{2\alpha^2\hbar^2}\right)V_o a-l(l+1)\right) \tag{25}$$

b) Klein-Gordon Equation

Case I: From eq. (12) $\boldsymbol{when}\ V_o = \mathbf{0}$, eq. (23) is reduced to Schrodinger equation with Attractive radial potential given as:

$$E^2-M^2=-4\alpha^2\left\{\left[\frac{(2l(l+1))+\left(\left(\frac{E+M_o}{\alpha^2}\right)V_3+\left(\frac{E+M_o}{2\alpha^2}\right)V_2\right)-\left(n^2+n-\frac{1}{2}\right)-(2n+1)\sqrt{\frac{1}{4}-\left(\frac{E+M_o}{2\alpha^2}\right)V_3-\left(\frac{E+M_o}{2\alpha^2}\right)V_2-\left(\frac{E+M_o}{2\alpha^2}\right)V_1}}{(2n+1)+\sqrt{\frac{1}{4}+(l(l+1))}-\left(\frac{E+M_o}{2\alpha^2}\right)V_1-\left(\frac{E+M_o}{2\alpha^2}\right)V_3-\left(\frac{E+M_o}{2\alpha^2}\right)V_2}\right]\right\}-\left(\left(\frac{E+M_o}{2\alpha^2}\right)V_3-l(l+1)\right) \tag{26}$$

Case II: From eq. (12) $\boldsymbol{when}\ V_1 = V_2 = V_3 = \mathbf{0}$, eq. (23) is reduced to Schrodinger equation with Modified Hylleraas potential given as:

$$E^2-M^2=-4\alpha^2\left\{\left[\frac{\left(\left(\frac{E+M_o}{2b\alpha^2}\right)V_o a-2l(l+1)-\left(\frac{E+M_o}{2b\alpha^2}\right)V_o\right)-\left(n^2+n-\frac{1}{2}\right)-(2n+1)\sqrt{\frac{1}{4}+(l(l+1)}}{(2n+1)+\sqrt{\frac{1}{4}+(l(l+1))}}\right]\right\}-\left(\left(\frac{E+M_o}{2b\alpha^2}\right)V_o a-l(l+1)\right) \tag{27}$$

V. CONCLUSION

In this work, using the parametric generalization of the NU method, we have obtained approximately energy eigenvalues of the Schrodinger and Klein-Gordon equations for Modified Hylleraas and attractive radial molecular potential. Interestingly, the Dirac equation with the arbitrary angular momentum values for this potential can be solved by this method. The resulting eigen energy equations can be used to study the spectroscopy of some selected diatomic atoms and molecules.

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Electrochemical Determination of Propiconazole Residues in Grain Samples by Voltammetry at Carbon Nanotubes Paste Electrodes

By K. Sivasankar & T. Raveendranath Babu
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Abstract- In this study the residues of propiconazole in grains samples determined on the basis of its reduction behavior at carbon nanotubes paste electrodes. The reduction product is identified by using cyclic voltammetry and the universal buffer with pH range 2.0-6.0 is used as supporting electrolyte. The best curve and highest peak current are obtained in universal buffer at pH 4.0. Accumulation potential, Accumulation time and Scan rate were optimized. Calculations made of by standard addition method. The peak heights are in linear trend over the concentration range of 1.02 x 10^{-9} to 1.05 x 10^{-10} M. The relative standard deviation and correlation coefficient for propinacazole is 0.97% and 0.998 respectively.

Keywords: propiconazole, carbon nano tubes paste electrodes, DP-ASV, cyclic voltammetry, universal buffer, grains samples.

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Keywords: propiconazole, carbon nano tubes paste electrodes, DP-ASV, cyclic voltammetry, universal buffer, grains samples.

I. INTRODUCTION

Pest is any species that competes with human being for food, invades lawns and gardens, destroys wood in houses, and spreads disease or simply a nuisance. Worldwide about 100 species of plants, (which one calls weeds); animals (mostly insects), fungi and microbes (which can infect crop plants and livestock animals) cause about 90% of the damage to the crops. Insects cause much of the damage to the crops. Pesticides are designed to target specific pests, such as weeds, fungi, insects and parasites, but they can kill other species if they enter the wider environment. The manufacture, sale and use of pesticides are highly regulated, but, even so, pesticides can be detected widely at low levels in many parts of the environment.

Propiconazole ($C_{15}H_{17}Cl_2N_3O_2$) is broad spectrum fungicide (conazole fungicides). Defferent methods are employed for determination of propiconazole residues in environmental samples Lopez et al. [1] determined fungicides carbendazim, metalaxyl, folpet, and propiconazole in must and wine by using HPLC method. Karina et al. [2] determined Propiconazole Residue in Boronia Extract by using gass chromatography/mass spectroscopy.But there is no literature fond for the determination of propiconazole residues in environmental samples by using electro chemical methods such as polarography, voltammetry. Rasekhar reddy et al. [3-7] employed voltametry for the determination of oxabetrinil residues in environ mental samples. In this work deferential pulse adsorptive stripping voltammetry employed [8-12]. for the determination of propiconazole residues in vegetables.

II. INSTRUMENTS AND REAGENTS

This investigation performed by using a model meterohm Auto Lab 101 PG stat (Netherlands). CNTPE was used as working electrode for differential pulse adsorptive stripping voltammetry and cyclic voltammetry. pH measurements were carried out with an Eutech PC_510 cyber scan. Meltzer Toledo (Japan) Xp26 delta range micro balancer were used to weigh the samples during the preparation of standard solutions. All the experiments were performed at 250C.

All reagents used are analytical reagent grade. Double distilled water was used throughout the analysis. In the present investigation universal buffers of pH 4.0 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.

III. RESULT AND DISCUSSION

Propiconazole exhibits a single well-defined peak in the pH range 2.0 to 6.0(table 2.0) when potential was scanned from -1.05 V and so on at CNTPE (Fig.1.0) which is due to the reduction of the azomethine groups by taking 4 electrons. The experimental parameters that affect the AdSV signal carried out by considering stripping peak in order to establish the optimum conditions. Both standard addition and calibration methods are employed for the determination of propiconazole in grains.

The best curve and highest peak current was obtained in universal buffer at pH 4.0.An enhanced adsorption peak obtained at potential -0.60V .The accumulation time of 70 sec. is used for further studies.. The reduction peak current increased linearly with the scan rate over the range from 25 mVs^{-1} to 75 $mVs.^{-1}$ Better sensitivity was observed at $50mVs.^{-1}$

Electrode mechanism: Based on the results obtained from all the techniques, the electro-chemical reduction mechanism is as follows.

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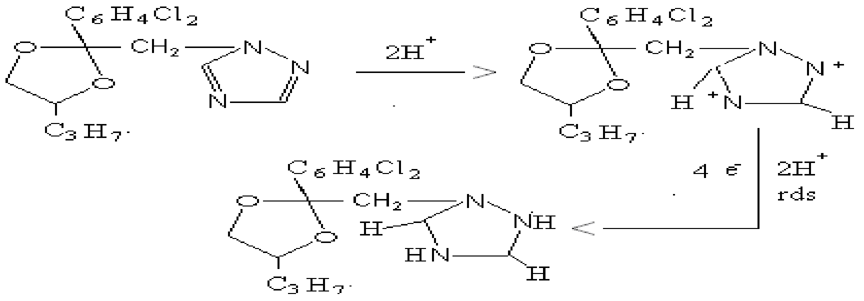

Figure

IV. RECOVERY EXPERMENTS

a) Analysis

Adsorptive stripping voltammetry is a suitable technique for the analysis of propiconazole due to its high sensitivity and resolution. The well resolved stripping voltammetric peak for the analytical purpose was obtained at pH 2.0 to 6.0.The peak heights are in linear trend over the concentration 1.02 x 10^{-9} to 1.05 x 10^{-10} M. The relative standard deviation and correlation coefficient for propinacazole is 0.97% and 0.998 respectively.

b) Determination of propiconazole in spiked grain samples

The developed analytical procedure has been applied to the quantitative estimation of propiconazole in grain samples. Grain (wheat, rice) samples sprayed with known amounts of propiconazole and left for 1-2 hours. Then the samples are weighed, crushed and homogenized. The extracts were prepared by treatment of the above sample with two 50 mL portions of acetone and evaporated to dryness. The residue of dissolved in methanol and transferred to a 100 mL volumetric flask. 1.0 mL of standard solution is transferred in to cell and made up with 9 mL of supporting electrolyte and then purged with oxygen free N_2 gas for 10 min. prior to each run. After obtaining the voltammogram, small addition of standard solutions are added and voltammogram recorded after each addition under similar experimental parameters Results obtained for the determination of propiconazole. The results are summarized in Table.2.0

V. CONCLUSIONS

In this approach for the determination of pesticide residues carbon nano tubes paste electrode is satisfactory applied to interpret the instrumental out puts without considerable errors and during the estimations pollution arises due to heavy metal electrodes such as mercury electrodes is avoided by using carbon electrodes.

Table 1.0: Typical cyclic voltammetric data of propiconazole, concentration: 1.0x10^{-5}M, scan rate: 50 mVs^{-1}

pH of the supporting electrolyte	$\frac{-E_p}{V}$	$\frac{i_p}{\mu A}$	$\alpha\, n_a$	$\frac{D \times 10^6}{cm^2\, s^{-1}}$	$\frac{k^0_{f,h}}{cm\, s^{-1}}$
2.0	0.95	8.2	0.45	1.50	4.10 x 10^{-9}
4.0	0.99	8.8	0.36	1.48	8.92 x 10^{-10}
6.0	0.94	8.1	0.28	1.28	6.23 x 10^{-12}

Table 2.0: Recoveries of propiconazole in spiked grain samples

Sample	Amount added (µg/mL)	Amount found (µg/mL)	Recovery (%)	Standard deviation
wheat	2.0 6.0	1.98 5.99	99.00 99.83	0.0512 0.0952
rice	3.0 5.0	2.98 4.97	99.33 99.40	0.004 0.071

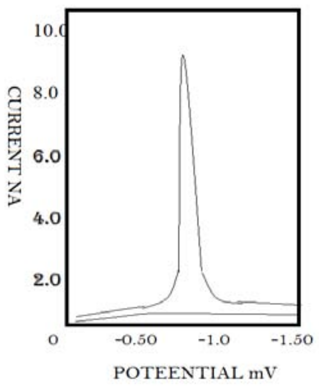

Fig. 1.0: Typical differential pulse adsorptive stripping voltammogram of propiconazole at CNTPE at pH 4.0.

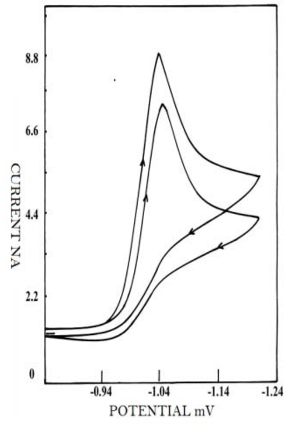

Fig. 2.0: Typical cyclic voltammogram of propiconazole at CNTPE at pH 4.0 concentration: 1.0×10^{-5} mM; scan rate: 50 mVs^{-1}

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Impact of Chemical Treatments and Coupling Agents on the Properties of Jute Fiber Reinforced by Polybutylene Composite

By Md. Mohsin Uddin Azad & Md. Islamul Haque
Northern University

Abstract- Jute and polybutylene have different characters in their properties. When they are blended, their blended composition shows various purposes. The goal of the research is to enhance the properties of jute fiber (JF) reinforced polybutylene (PB) composite. It was made by sample ho press molding method according to the weight percentage of 25 wt% filler (JF), 2wt% coupling agent (compatibilizer) degraded PB (DgPB) and maleated PB (MAPB) and 70 wt% matrix (PB). To improve the interfacial interactions between the fiber and PB, the fiber was chemically modified with 10w/v% NaOH, 6w/v% dicumyl peroxide (DCPO), 0.05 w/v% $K_2Cr_2O_7$ and 5 w/v% H_2O_2 solution. The water absorption, tensile and thermal properties of raw and surface treated fibers composites were compared in particular coupling agent. It has found that the fiber treatments and the addition of coupling agents, composites showed better properties. Among the composites, 10 wt/v% NaOH treated jute reinforced PB composite by using MAPB compatibilizer was presented better water absorption and mechanical properties.

Keywords: jute fiber (filler); polybutylene (matrix); composites; coupling agents and it's properties.

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IMPACTOFCHEMICALTREATMENTSANDCOUPLINGAGENTSONTHEPROPERTIESOFJUTEFIBERREINFORCEDBYPOLYBUTYLENECOMPOSITE

Strictly as per the compliance and regulations of:

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Keywords: jute fiber (filler); polybutylene (matrix); composites; coupling agents and it's properties.

I. INTRODUCTION

The development of composites furnished by lignocellulosic fibers as reinforcing materials of thermoplastic resin become popular since the lignocellulosic fibers are inexpensive; possess sufficient mechanical properties and environmentally friendly due to their biodegradation properties. In tropical countries, plenty of abundance lignocellulosic fibers like jute, hemp, ramie, sisal, okra fibers, plumb Oil fiber, etc. are grown and most of them have been employed for reinforcements in polymer matrices (Albano et al. 1999; Suardana et al. 2011; Khan et al. 2015b; Khan et al. 2016, Ramez A. Al-Mansob et al. 2013, Islam & Ani 2000). Among the lignocellulosic fibers, jute fiber is promising on account of availability, low densities, nonabrasive nature, high specific properties, high modulus and renewable nature. Jute (Corchorus capsularis) is one of the most common agricultural fibers is cultivated almost exclusively in Bangladesh. Therefore, due to their availability and suitable properties, jute fiber has the right potential for usage in composites.

Polybutylene (PB) is extensively used in engineering plastic materials for tremendous mechanical properties. It also has advantages like the economy (price), ecological (recycling behaviors) and higher thermal stability and the effectiveness of filler reinforced composite. However, during impregnation of PB by lignocelluloses fiber, the interface shows incompatibility i.e. hydrophilic lignocellulose fiber cannot mix properly with hydrophobic PB. Therefore, afford need to reduce incompatibility on the interfacial adhesion between filler and matrix polymers for manufacturing high-value composite materials.

A lot of conventional methods have practiced improving the interfacial adhesion of composites such as modifying the fiber surface before composite fabrication, using compatibilizer during moulding or matrix modification. The use of silane coupling agents, grafting by bifunctional monomers and the plasma treatment of the fiber surfaces are the most common techniques of interface modification of composites (Pothan et al. 2002; Khan et al. 2009; Khan et al. 2013a; El-Sabbagh 2014; Khan et al. 2015a; Khan et al. 2015b). In the present investigation, to improve the fiber matrix interaction, jute fiber surface has been modified by NaOH, dicumyl peroxide, potassium dichromate, and hydrogen peroxide. MAPB and DgPB have also used to improve interfacial properties which are well-known compatibilizers for filler and matrix. It has been reported methane protons of Isotactic PB is often caused oxidative degradation. The degradation reaction proceeds by a free radical chain reactive mechanism and formed carbonyl group (C=O) as well as hydroperoxide group (ROOH) (Alam et al. 2002). Another study used oxidative degraded PB (DgPB) as a compatibilizer of cellulose/PB composite (Miyazaki et al. 2008).

II. EXPERIMENTAL DESIGN

a) Materials

The water retted jute fiber (Corchorus capsularis) was collected from Kushtia district, Bangladesh. The polybutylene (PB) was obtained from

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Polyolefin Company (Singapore) Pvt. Ltd. in the form of pellets. Maleated polybutylene (MAPB) was purchased from Sigma-Aldrich in the granule form and degraded polybutylene (DgPB) was prepared in a crucible allowed by heating at 1300C for 20 h in the presence of air. All analytical reagent (AR) grade chemicals were used in the investigation.

b) *Fiber Processing*

Fibers were cut into 25-30 cm and then scoured by (6.5 g/L soap and 3.5 g/L of Na2CO3) solution at 70-75°C during 30 min. The fiber to solution weight ratio was maintained at 1:50. After scouring the fiber was several times with distilled water and dried in the open air (Mondal and Khan 2008). The dried fibers were chemically treated with four different chemicals, namely NaOH, dicumyl peroxide (DCP), K2Cr2O7 and H2O2.

The dried jute fibers were immersed in 10w/v% NaOH solution at 30ºC maintained the fiber to liquor ratio at 1:20 for 2 h. Then the fibers were washed repeatedly by distilled water and finally washed by dilute acetic acid to remove NaOH sticking to the fiber surface. The neutralize fibers were dried in air and finally stored in desiccator (Khan et al. 2015b).

6w/v% dicumyl peroxide (DCP) solution was prepared with acetone. The NaOH treated fiber was socked in the DCP solution for 30 min at 30°C maintained the fiber to liquor ratio at 1:11. The treated fiber was washed by distilled water and dried at room temperature. The NaOH treated fiber was treated by 0.055w/v% K2Cr2O7 solution maintained the fiber to liquor ratio 1: 15 for 30 min at 60ºC with occasionally added few drops of H2SO4. Then the fiber was washed by distilled water and dried in air (Khan et al. 2015b).

The jute fibers were treated by 5w/v% H2O2 solution maintained the fiber to liquor ratio 1: 80 for 2 h at 90°C. During the treatment the pH of adjusted by adding 7-8 drops of 0.2 M CH3COOH solution. The fiber was filtered and washed by distilled water. Then the fibers were immersed in 0.2 % Na2S2O6 solution maintained the fiber to liquor ratio 1:20 for 15 min at 30ºC. Finally the fiber was washed and dried in air and finally stored in the desiccator (Li and Wang 2013).

Table 1: Various types of composite sample prepared in different parameters

Sample	Fiber chemical treatments	Fiber wt%	Matrix	Coupling agent	Composite
A	No chemical treatment	30%	PB (70 wt%)	-	Raw JF+PB
B	No chemical treatment	30%	PB	DgPB (2wt%)	Raw JF+PB+DgPB
C	No chemical treatment	30%	PB	MAPB (2wt%)	Raw JF+PB+MAPB
D	10 w/v % NaOH	30%	PB (70 wt%)	-	10% NaOH JF+PB
E	10 w/v % NaOH	30%	PB (68 wt%)	DgPB (2wt%)	10% NaOHJF+PB+DgPB
F	10 w/v % NaOH	30%	PB (68 wt%)	MAPB (2wt%)	10% NaOH JF+PB+MAPB
G	6 w/v % DCP	30%	PB (70 wt%)	-	6% DCP JF+PB
H	6 w/v % DCP	30%	PB (68 wt%)	DgPB (2wt%)	6% DCP JF+PB+DgPB
I	6 w/v % DCP	30%	PB (68 wt%)	MAPB (2wt%)	6% DCP JF+PB+MAPB
J	0.055 w/v % $K_2Cr_2O_7$	30%	PB (70 wt%)	-	0.055% $K_2Cr_2O_7$ JF+PB
K	0.055 w/v % $K_2Cr_2O_7$	30%	PB (68 wt%)	DgPB (2wt%)	0.055% $K_2Cr_2O_7$JF+PB+DgPB
L	0.055 w/v % $K_2Cr_2O_7$	30%	PB (68 wt%)	MAPB (2wt%)	0.055 $K_2Cr_2O_7$ JF+PB+MAPB
M	5 w/v % H_2O_2	30%	PB (70 wt%)	-	5%H_2O_2 JF+PB
N	5 w/v % H_2O_2	30%	PB (68 wt%)	DgPB (2wt%)	5%H_2O_2JF+PB+DgPB
O	5 w/v % H_2O_2	30%	PB (68 wt%)	MAPB (2wt%)	5%H_2O_2 JF+PB+MAPB

c) *Composite Preparation*

The fiber bundles were cut into approx. 10cm length, and then placed in an air oven for a week to remove the fiber surface moisture. Virgin PB sheet was prepared in an open S-S mold. The mold was electrically heated by thermostat at 180°C for 115 min. Then it was placed in hydraulic press and pressure was set to 50 kN. It was then cooled by cold tap water flow and transparent PB sheet was obtained. The sheet was cut into 10×10 cm2 size and placed in a closed mold with the same dimension. The predetermined amount fibers were unidirectionally sprayed on the PB sheet (Table 1). The fixed amount of MAPB or DgPB was added as a compatibilizer. The fibers were then covered with PB sheets. The mold was put in between two hot plates of compression molding machine. Pressure and temperature were fixed at 50 kN and 180°C respectively. The heating was gradually increased up to 180°C. After 30 min, heating was stopped and, mold was cooled by tap water. Finally, the composite sample was taken out from the mold and cut for the mechanical testing.

d) *Measurements*

Tensile properties were measured using Universal Testing Machine (Hounsfield UTM 10KN) by standard ASTM D638 methods. The crosshead speed was 50 mm/min and gage length was 50 mm. The results are taken from the average of 10 measurements. The water absorption property was measured by ASTM D570 method. The specimens were dried in an oven at 80°C for 24h before testing. Then those samples were soaked into the water at room temperature.

The composites were taken out from the water after every 24h and all surface moisture was removed with tissue paper. The weight gain was calculated using Equation 1:

$$\text{Water absorption \%} = \frac{(w_t - w_0)\times 100}{w_0} \text{..........} \qquad (1)$$

Where, Wo and Wt are the initial weight and weight after water absorption, respectively. The data reported are an average value obtained from ten separate samples of each composite. The thermal properties of composites were assessed by thermo-gravimetric analyzer supplied by TA Instrument (EXTAR 6000 STATION, Seiko Instrument, Inc. JaPBn).

About 20 mg of composite sample was taken for each analysis. The heating was increased by the rate of 20°C/min from 25°C to 600°C in nitrogen environment (gas flow rate 50 ml/min).

III. Result and Discussion

The surface of jute fiber has been chemically modified through different chemical process. The performance of DgPB and MAPB coupling agents at interface modification of composites were investigated regarding their water absorption, mechanical and thermal properties.

a) *Water Absorption Properties*

Figure 1 shows the effect of immersion time on water absorption of raw and treated jute fiber PB composites. Raw JF+PB composite (Sample A) is taken as control for comparison. It shows that the lowest water absorption is found in case of 10% NaOH JF+PB+MAPB composite and water absorption is increased with the increase of immersion time. It is also observed that the addition of coupling agents MAPB and DgPB in composites give lower water absorption than JF+PB composite. With the addition of MAPB and DgPB coupling agents in composites, the percentage of water absorption is decreased. It may be due to the enhancement of surface adhesion of fibers and PB matrix that reduced the water consumption in the interfacial voids. Probably the coupling agents took part in the esterification reaction with the -OH group in jute fiber (Khan et al. 2013a).

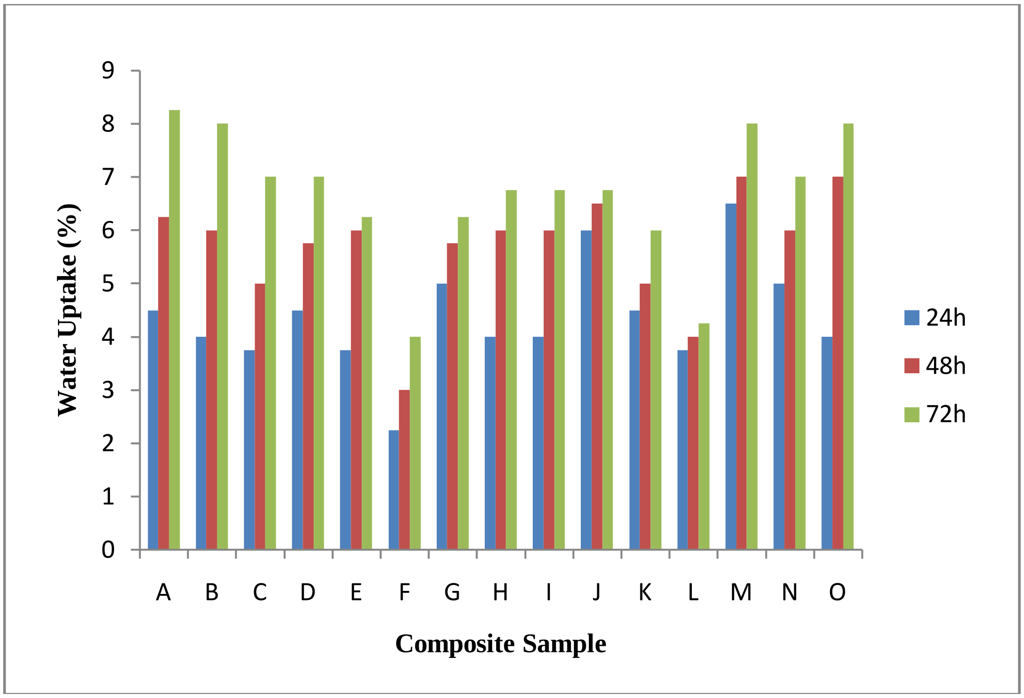

Fig. 1: Effect of immersion time on water absorption of raw and treated jute fibers PB composite

b) *Mechanical Properties*

The tensile properties of unidirectional jute fiber reinforced PB composites were investigated by means of the effect of coupling agents (DgPB, MAPB) and chemical treatments of fiber. The tensile strength, Young's modulus and elongations were obtained from tensile stress-strain data.

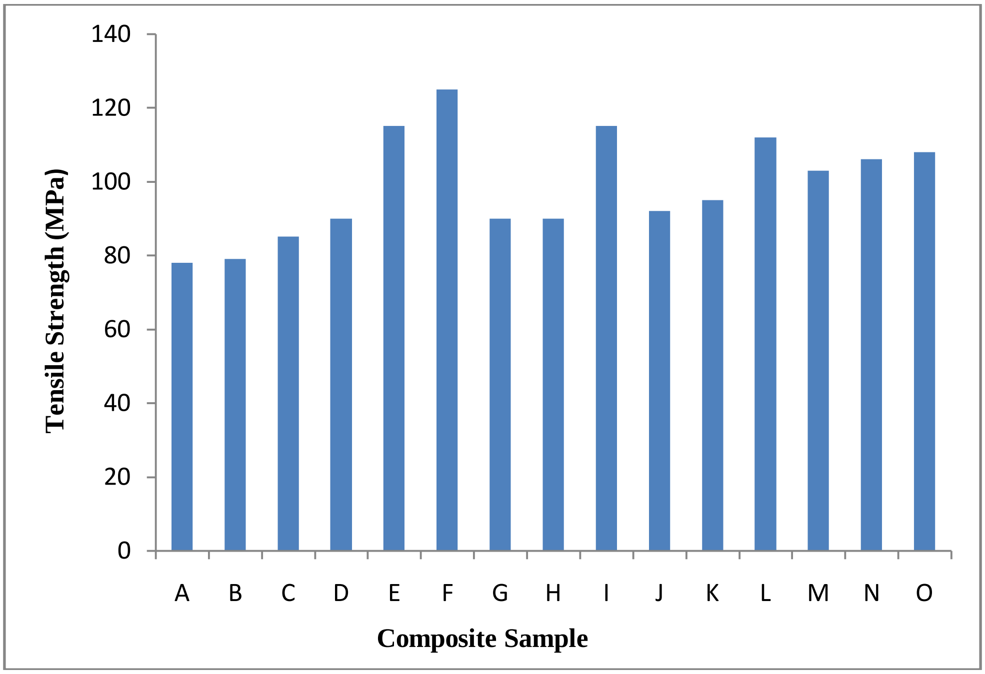

Fig. 2: The effect of chemical treatments and coupling agents on the tensile strength of raw and treated jute fiber PB composites

Fig. 2 shows the effect of chemical treatments and coupling agents (DgPB and MAPB) on tensile strength (TS) of raw and treated jute fibers PB composites. It is observed that the coupling agents added in both raw and treated jute fibers - PB composites yield higher TS than without coupling agents. Among the composites, the highest value of TS is found for 10% NaOH JF+PB+MAPB composite and the lowest value is obtained for raw JF+PB composite. The chemical treatments are employed in this investigation such as NaOH, DCPO, $K_2Cr_2O_7$, H_2O_2 are all oxidative treatments process. These treatments can make the fiber surface 'clean' due to the removal of impurities, pectin, waxes, hemicellulose and part of lignin. The removal of these substances enhances the surface roughness. Therefore, the jute fiber easily wetted by PB matrix. Also, interlocking between fiber and matrix is increased. The result shows, the presence of coupling agents caused better adhesion of jute fibers and polybutylene matrix and formed a strong interfacial bond between them. The coupling agents MAPB and DgPB have a similar molecular arrangement with extra functional groups which forms a chemical bond with hydrophilic jute fiber. The main PB chain of the coupling agents entangle the mutual chains of PB and therefore builds stronger interfacial adhesion between the PB matrix and jute fiber (Khan et al. 2013a; Miyazaki et al.2008, Khan et al. 2015a). Both coupling agents have a similar mechanism of bond formation via esterification between the -OH group in jute fiber and the reactive γ-lactone groups in the coupling agents (Khan et al. 2013a).

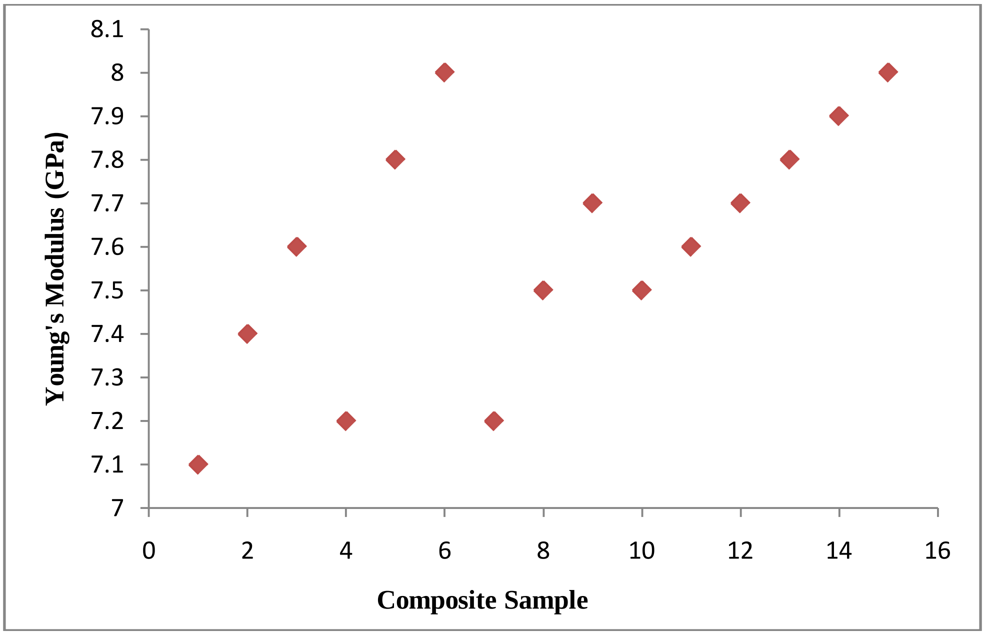

Fig. 3: The effect of chemical treatments and coupling agents on Young's modulus of raw and treated jute fiber PB composites

Fig. 3 shows the comparison of the effect of chemical treatments and coupling agents on YM of raw and treated jute fibers PB composites. It shows that the addition of coupling agents increases YM of raw and treated jute fibers PB composites. The highest and lowest values of YM are obtained for 10% NaOH JF+PB+MAPB and raw JF+PB composites, respectively.

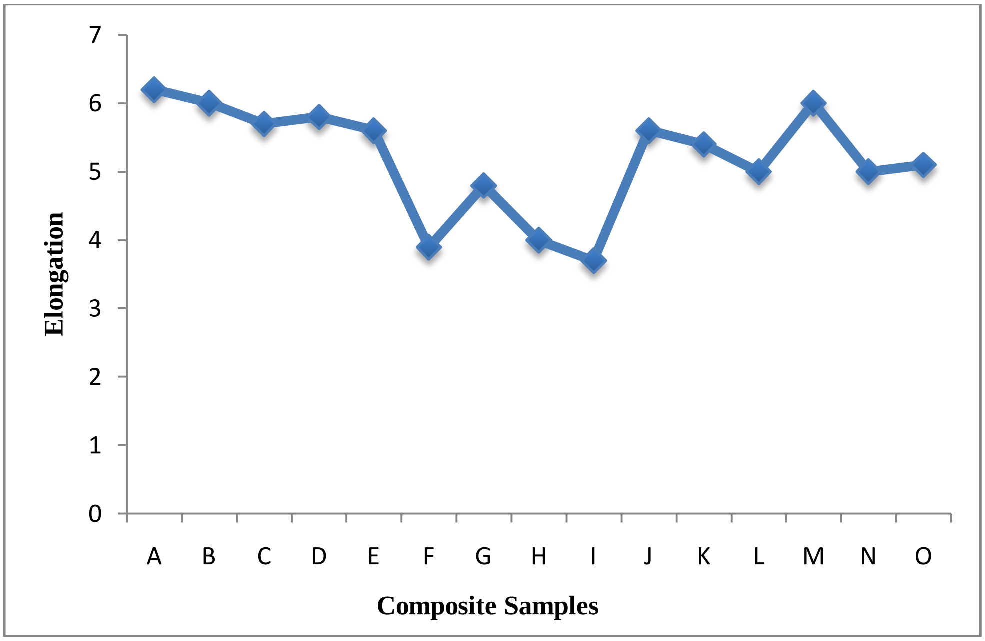

Fig. 4: The effect of chemical treatments and coupling agents on elongation at break of raw and treated jute fiber PB composites

Fig. 4 shows the effect of chemical treatments and coupling agents on elongation properties (PE) of raw and treated jute fibers PB composites. From the Figure 4, it is observed that the highest PE value was found for raw JF+PB composite, then 10%NaOH JF+PB+MAPB and the lowest for 0.05% K2Cr2O7 JF+PB+MAPB composites. The lower values of elongation for composites which were made by using chemical treated fiber and coupling agents may be due to the increase of brittleness of the composite.

Table 2 shows the properties of sawdust reinforced polybutylene composites of some previous research. Since the properties of composites mostly depend on the properties of matrix use on it. The improvement of mechanical properties of our composites is much higher than others. On the other hand, a great extent of water uptake was also found in this study.

Table 2: Comparative Result from Some Previous Study

Amount of Sawdust	Chemical treatments	Compatibilizer	Method of Molding	Tensile strength(MPB)	Tensile Modulus (GPB)	Water absorption (%)	Ref.
15 wt%	Diazonium salt		Injection	28.4	1.2	0.2	Rahman et. al 2010
40 wt%		DCP or BPO peroxide/maleic anhydride(MAH)	Compression	24.8	-	-	Santos et al. 2016
50 wt%	3- Aminopropyl tri ethoxy silane	MAH	Injection	49	-	-	Kim et al. 2010
	3-Methacryloxy p ropyl trimethoxy silane (MPS)	MAH	Injection	49	-	-	
	Vinyl trimethoxy silane	MAH	Injection	49.2	-	-	
30 wt%	NaOH	MAPP	compression	127	8.1	2.1	
	NaOH	DgPP	compression	118	7.9	3.9	

IV. CONCLUSION

The study illustrates the properties of composites fabricated by hot press molding method using polybutylene (PB) as matrix and jute fibers. The 2wt% DgPB and MAPB are used as a compatibilizer to improve the surface adhesion between the hydrophilic jute fibers and hydrophobic PB matrix. As a result, composites showed higher mechanical properties than that of composites prepared by without coupling agent. In case of, the raw JF+PB composite have higher ability to absorb water and 10%NaOH JF+PB+MAPB composite has lower ability to absorb water.

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Determination of Pesticides in Environmental Samples

By Puchakayala Sujana & Thommandru Raveendranath Babu
Rayalaseema University

Abstract- This is an approach to determine the residual amounts of pesticides with various activities present in environmental samples by applying electro chemical technique adsorptive stripping voltammetry. Average amounts for ten replicates founded by using carbon nano tubes paste electrodes as working electrodes. statistical concepts such as standard deviation and correlation coefficient and in all the findings in this approach all the possible errors are minimised and accuracy is maximised. Water samples of various areas are collected and investigated for pesticide residues before and after the application of pesticides.

Keywords: pesticides, adsorptive stripping voltammetry, carbon nano tubes paste electrodes, water samples.

GJSFR-B Classification: FOR Code: 259999

DETERMINATIONOFPESTICIDESINENVIRONMENTALSAMPLES

Strictly as per the compliance and regulations of:

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Puchakayala Sujana [α] & Thommandru Raveendranath Babu [σ]

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I. Introduction

Despite the fact that pesticides are useful for the control of various pests, many of them are hazardous chemicals. They are perilous because they can poison the land, the water and the air. Some pesticides do not break down for a long time. These types of pesticides are often used when something must be protected from pest attack for a long period of time, for example, protecting houses from termite attack. Pesticides which remain in the soil or on the treated surface are also often called residual chemicals[1-7].

When residual pesticides get into the environment they can remain poisonous and active for many years. If applied incorrectly or used in the wrong place, these chemicals may spread to other land areas and possibly to the water supply.

There are good reasons (advantagespesticides are very effective. This means that nearly all the target pests which come in contact with these pesticides are killed Results are quick. This means the pests are killed within a very short time.

Using pesticides can be an economical (cheap) way of controlling pests. Pesticides can be applied quickly and there is not the high labour cost which might apply to other methods of control, such as removing weeds by hand.

If pesticides are not used correctly, they can affect human health or cause serious injury or death to the pesticide operator, other people or household pets. Pesticides can also directly affect other non-target animals. For example, a gardener spraying his garden to kill caterpillars will probably also kill harmless lady bird beetles and praying mantises. If pesticides are used incorrectly or applied wrongly, they may find their way into places where they are not wanted, for example, they might be washed into rivers or into the soil. In this article an elstroanalytical method voltammetry supported by statistical findings was applied.

a) *Instruments and reagents*

Electro analytical determinations conducted using a model meterohm Auto Lab 101 PG stat (Netherlands). CNTPE was used as working electrode for differential pulse adsorptive stripping voltammetry and cyclic voltammetry. pH measurements were carried out with an Eutech PC_510 cyber scan. Meltzer Toledo (Japan) Xp26 delta range micro balancer were used to weigh the samples during the preparation of standard solutions. All the experiments were performed at 250C.

All reagents used are analytical reagent grade. Double distilled water was used throughout the analysis. In the present investigation universal buffers of pH 4.0 was used as supporting electrolytes and are prepared by using 0.2 M boric acid, 0.05M citric acid and 0.1M trisodium orthophosphate solutions.

b) *Measurements and calculations*

In this standard addition method, the voltammogram of the unknown is first recorded after which a known volume of standard solution of the same electro active species is added to the cell and second voltammogram is taken. From the magnitude of the peak height, the unknown concentration of species may be calculated using the following equations.

$$\text{C (un known)} = \frac{C_s \, x V}{V_t \, x i_2} \, x \, i_1$$

II. Result and Discussions

Well resolvable and reproducible peak obtained for each sample is useful for the analysis of water samples. The optimum pH to get well defined peak for the detection is found to be 4.0. The peak current is found to vary linearly with the concentration of the pesticide over the range 1.0 x 10^{-5}M to 1.0 x 10^{-9}M. The lower detection was limit found to be 1.02 x 10^{-9}M. The correlation coefficient and relative standard deviation

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(for 10 replicates) obtained using the above procedure [8-15].

a) Recovery experlments

A stock solution (1.0 x 10^{-3} M) of each sample is prepared in dimethyl formamide. In voltammetric cell, 1 mL of standard solution is taken and 9 mL of the supporting electrolyte (pH 4.0) is added to it. Then the solution is de aerated with nitrogen gas for 10 min. after obtaining the voltammogram, small additions of standard solution are added and the voltammograms are recorded under similar experimental conditions. The optimum conditions for analytical estimation at pH 4.0 are found to be pulse amplitude of 25 mV, applied potential of -0.35V and scan rate 40 $mVs.^{-1}$.

Water samples are collected from paddy fields which sprayed by the pesticides under investigation 48 hours after spraying the pesticides. These samples were filtered through a Whatman No.41 filter paper and Aliquots of water samples were taken in a 25mL graduated tube, to it buffer solution was added and analyzed as described above. The recoveries of samples obtained in water samples ranged from 51.00 to 57.00% and the results are summarized in Table 1.0.

Table 1.0: Recoveries of pesticides in water samples

Name of the pesticide	Amount added (mg/L)	Amount found (mg/L)	*Recovery (%)	Standard deviation
1. Aldicarb	4.0	2.15	53.75	0.07
2. Thiodicarb	4.0	2.36	59.00	0.05
3.Chlorpropham	4.0	2.31	57.75	0.16
4. Fenclorim	4.0	2.25	56.25	0.06
5. Isoxidefen	4.0	2.10	52.50	0.17
6. Fenclorazole	4.0	2.18	54.50	0.07
7. Phenothrin	4.0	2.22	55.00	0.15
8. Bynapycril	4.0	2.26	59.45	0.03

**Average of 10 replicates*

III. Conclusions

In this approach statistical parameters for the determination of pesticide residues satisfactory applied to interpret the instrumental out puts without considerable errors. And during the estimations pollution arises due to heavy metal electrodes such as mercury electrodes is avoided by using carbon electrodes.

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Development of Porosity of Low Cost Activated Carbon from Post-Consumer Plastics and Lignocellulosic Waste Materials using Physico-Chemical Activation

By Abdoul Ntieche Rahman, Hambate Gomdje Valery, Dayirou Njoya, Abdoul Wahabou, Abdelaziz Bacaoui & Abdelrani Yaacoubi

University of Maroua

Abstract- Low-cost adsorbents (from Oil Palm Shell (OPS) and polyethyleneterephtalate (PET)) were prepared by physical activation with steam and Physico-chemical activation using both KOH and steam in the way to study the modification of porosity, pores size distribution and surface functional group. The activated samples obtained by physical activation are microporous with a surface area between 1000and 1500 m2/g, while the other obtained by physicochemical activation contain a well-developedporosity which consists of micropores, mesopores and likely macropores with a surface area between 991 and 1413 m2/g. The adsorption of methylene blue (MB) and iodine (I2) show that physicochemical activation produced a strongly developed internal surface, which is open at the surface by, mesopores and possibly macropores. FTIR spectrum of ACs prepared shows many peaks belonging to different functional groups.

Keywords: *physicochemical activation; porosity; functional group; low-cost adsorbent; activated carbon.*

GJSFR-B Classification: *FOR Code: 030699*

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Keywords: physicochemical activation; porosity; functional group; low-cost adsorbent; activated carbon.

I. INTRODUCTION

The increasing demand for porous materials for environmental remediation has focused the efforts to the development of new methods of preparation of activated carbon. Activated carbons are widely used adsorbents; this is attributed to their well-developed internal porosity, large surface area and multiples functions at the surface which are active sites [1, 2]. Activated carbons can be produced from any carbon-containing organic materials, but the structure of the obtained carbon is closely linked to the structure of the raw material. However, the best raw materials for the preparation of the good activated carbon are materials having a high content of carbon and inexpensive [3,4]. As a result, wastes of lignocellulosic origin [5-9] and plastics wastes [10-14] are used, to obtain the low-cost active carbon.

The porous texture and functional groups on the surface of the AC also depend on the preparation process. There are many studies on the preparation of AC which are grouped in two: (i) Chemical activation, which consists of impregnation of the raw material with a strong dehydrating agent (KOH, H_3PO_4, ZnCl ...) before carbonization. (ii)The physical activation, in this process the precursor is first carbonized at a temperature between 500 to 700°C under inert atmosphere (N_2 gas) and then activated in a stream of steam or carbon dioxide or air [15-17]. Whatever the method used is varied some parameters such as the final heating temperature, the temperature rise rate, the residence time at the final temperature, the thermal conductivity of the precursor [2].

Research on the preparation of activated carbons frequently uses the two methods mentioned above, by varying the precursor and/or the preparation parameters. It is therefore important to explore new preparation methods by combining these two classical methods of preparation and to study its impact on the quality of the adsorbent material obtained.The economic advantage of the use of activated carbons in water treatments based on adsorption processes can be enhanced by exploring new synthetic routes or using nonvaluable by-products, residues or post-consumer waste materials as precursors for their preparation [10].

In the present investigation, different types of activated carbon were prepared using lignocellulosic waste and post-consumer plastics. The objective is to increase the porosity of the obtained adsorbent during

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the preparation process. Two methods of preparation will be used, physical activation with water vapour, which is a very well-known method for generating micropores into AC [1-5], on the other hand a new method will be experimented by combining the method of physical activation with the method of chemical activation that we designate in this work by physicochemical activation method.

II. Experimental Methods

a) Preparation of activated carbon

The precursors of ACs prepared are both Post-consumer plastic in polyethyleneterephtalate(PET) and Oil Palm Shell (OPS). The OPS samples grinned into small particle sizes ranging between 0.5 to 1.5 mm in diameter, dried at 110°C for 24hrs in the oven to remove all the moisture content weight and PET samples were cut down to desirable particle sizes and dried in sunlight for 5hrs. OPS and PET were mixed in the weight ratios 1:1 and 2:1 and were then subjected to carbonization using a cylindrical furnace. The heating started at room temperature with a temperature increment rate of 10°C/min up to a final temperature of 600 °C. The heating process was stabilized with nitrogen at a flow rate of about 100 mL/min. The residence time of the samples at the final stabilized temperature of 600°C was 3hrs. After heat treatment, the nitrogen flow was stopped, and the charcoals were cooled down to room temperature. Four carbonized compounds were obtained; one from OPS, one from PET, two from the mixture of the two in the ratio 1/1 and ½.

i. Physical activation

In the activation process, 5–6 g of the char were suggested to physical activation with steam (0,13 mL/min) in a furnace by heating the reactor from room temperature to 850 °C at a heating rate of 10 °C/min, with a residence time of 2 hrs.

ii. Physico-chemical activation

Before the physical activation step, 5–6g of the carbonized samples were mixed with Potassium hydroxyl in the ratio 1:2 (char/KOH) and dried in the oven overnight at 110ºC. The mixtures were activated with steam (0,13mL/min) in a furnace by heating the reactor from room temperature to 850ºC at a heating rate of 10ºC/min, with a residence time of 2hrs. After the activation, the steam flow was stopped, and the obtained ACs were cooled down to room temperature and washed with distilled water to a pH of 7.

b) Characterization of Activated Carbon

Textural characterization was performed by adsorption–desorption N_2 isotherms at – 195, 8 °C. The adsorption isotherms experiments were performed by MICROMERITICS TRISTAR 3000. Corresponding surface area S_{total} and Sext, micropore area S_{micro} and volume v_{micro}, total pore volume and pore diameters were obtained by Brunauer–Emmet–Teller (BET), Harkins–Jura (HJ), t-plot method and *Barrett-Joyner-Halenda (BJH)* methods, respectively. For BET analysis, experimental points measured at a relative pressure of nitrogen gas p/p^0 below 0.3 on the adsorption branch were used. Fourier-transform infrared spectroscopy (FTIR), Raman spectra, transmission of electron microscopy (TEM), and X-ray diffraction (XRD) were also performed to characterize the samples.

c) Adsorptions tests

The iodine number (I_2) of activated carbon was obtained by the Standard Test Method by titration with sodium thiosulphate. By batch experiment, methylene blue (MB) solution was mixed with activated carbon and shaken at the rate of 200 rpm at room temperature. After the completed reaction, the solutions were filtered, and the residual concentrations of methylene blue solutions were then determined by using a spectrophotometer at 660 nm. The equilibrium adsorption capacities (Qe) of the AC were determined based on the adsorbate mass balance using Equation 2:

$$Qe = \frac{(Co - Ce)V}{m} \quad (1)$$

Where *Co* and *Ce* are the initial and equilibrium concentrations of the dye (mg/L) respectively, *V* is the volume of the aqueous solution (L), and *m* (g) is the mass of activated carbon used.

III. Results and Discussion

Eight samples of activated carbon were obtained in this work: four samples prepared by physical activation from lignocellulosic material and post-consumer plastic named OPSAC and PETAC and from their mixture the ratios 1:1 and 2:1 respectively named COM1 and COM2; equally four sample with the same precursor prepared by physicochemical activation named OSPIAC, PETIAC, COM1I, and COM2I.

a) Adsorption-desorption isotherms

Figure 1 and figure 2 show respectively the adsorption isotherms of nitrogen obtained from AC prepared from the pure raw material and their mixture.

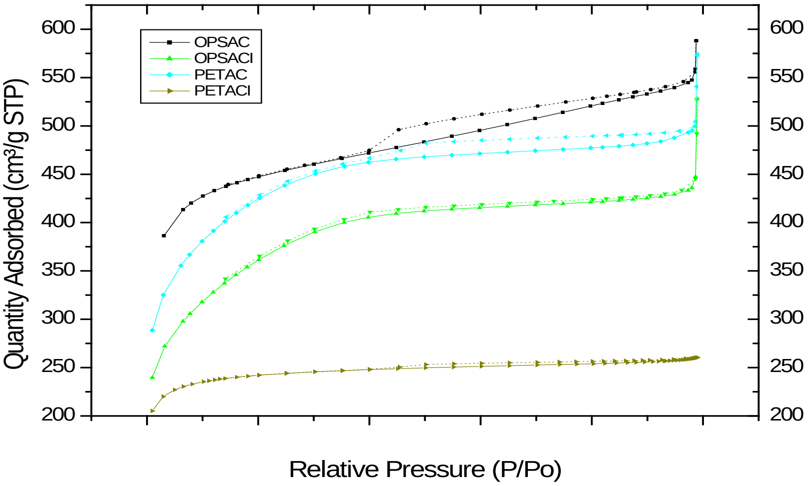


Figure 1: N_2 adsorption–desorption isotherms of ACs obtained from oil palm shell and PET by both physical activation and physicochemical activation method with steam and KOH

Adsorption-desorption of nitrogen is an important tool to analyze the structure of the prepared carbon. The adsorption in the gas phase shows clearly that the two samples prepared by physical activation adsorb better than those obtained by physicochemical activation (Figure1). Indeed the adsorption isotherms of the samples OPSAC and PETAC indicate the higher nitrogen volume adsorbed at low relative pressure. The knee shape at relative pressures close to unity shows a more rapid increase in adsorption due to the phenomenon of capillary condensation in mesopores. This can be explained by the formation of hysteresis (Figure.1), the pronounced intensity of hysteresis imply the presence of mesopores or macropores at the surface. On the other hand for the two samples obtained by physicochemical activation from the same raw materials, they adsorb less than the others, and the hysteresis is almost not visible. This shows that these two samples are essentially microporous, the mesopores if they exist serve as the gateway to the micropores, this shows the existence of a highly developed network of porosity[18-20].

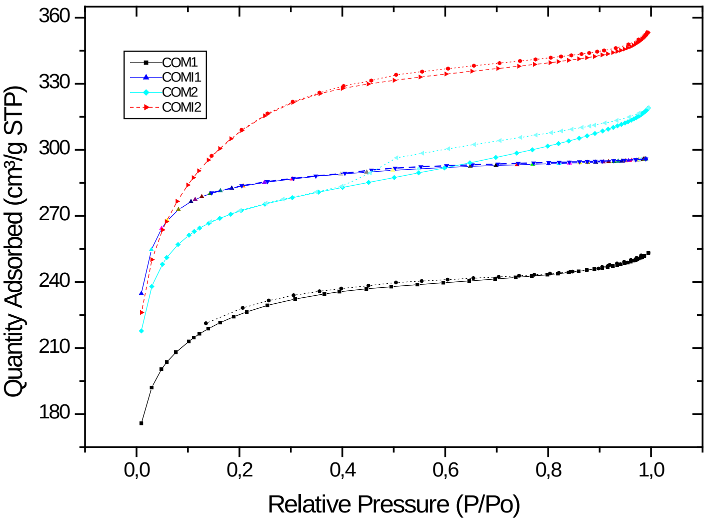


Figure 2: N_2 adsorption–desorption isotherms of ACs obtained from the mixture of oil palm shell and PET in the ration 1/1 and ½ by both physical activation and physicochemical activation method with steam

The composite samples behave differently from those prepared from pure raw materials; figure 2 shows that the samples obtained by physicochemical activation adsorb better than those prepared by physical activation. It is difficult to explain this phenomenon. However, we can assume that during the carbonization process, gaseous and volatiles compounds evolved from the solid, followed by a restructuring of the carbonaceous structure between the two constituents of the mixture, during this process, the formation of soot can appear. The char is constituted of a group of disordered short graphitic crystals containing micropores, which are often not accessible from the external surface because the mesopore network is blocked by soot deposition.The impregnation of the char bye KOH before the activation allow to remove soot and free carbon at the external surface and render micropore accessible. As we have seen for the carbons prepared from the pure precursors, the physicochemical activation generates materials possessing essentially the micropores.

Surface area and porosity values of the activated carbons are presented in Table 2. It shows that the activated carbons had remarkable BET surface area, due to the high micropore content [18-20].

Porosimetry parameters such as micropore area, micropore volume, cumulate volume and pore diameter were also compiled in Tables 2. It can be seen that the ACs had remarkable BET surface area in agreement with micropores content. The micropore area contribution is around 70% for AC prepared by physical activation, these quantities of micropores reduce (25.59 for OPSACI and (36.6) for PETACI) when the same raw material is submitted to the physicochemical activation. This can be explaining the fact that the activation process using both steam and KOH enhances the volume and enlarges the diameters of the pores. We can also suggest that impregnation with KOH widen existing micropores and the formation of large pores by burnout of the walls between the adjacent pores and leads to the formation of pores wider (mesopores and macropores).

Table 1: Porous parameters of the activated carbons (impregnated carbons)

	S_{BET} (m^2/g)	S_{mi} (m^2/g)	S_e (m^2/g)	% Smi	Pores volumes(cm^3/g)		Pores sizes (nm)		
					V_{micro}	V_{cum}	BET $_{ads}$	BJH_{des}	BJH_{ads}
OPSAC	1442.49	1000.37	442.12	69.35	0.498	0.352	2.3967	4.7779	4.4546
PETAC	1063.46	753.88	309.60	70.89	0.335	0.5950	2.2380	4.1903	3.8736
OPACI	1221.7	312.6	909.1	25.59	0.1602	0.4909	2.2655	3.7693	3.7441
PETACI	1412.9	516.7	896.1	36,52	0.2634	0.4553	2.2085	3.7252	3.6253

Table 2: Porous parameters of the activated carbons (impregnated carbons)

	S_{BET} (m^2/g)	S_L (m^2/g)	S_{mi} (m^2/g)	S_e (m^2/g)	Pores volumes(cm^3/g)			Pores sizes (nm)		
						V_{micro}	V_{cum}	BET $_{ads}$	BJH_{des}	BJH_{ads}
COM1	774.7		632.21	168.58	81,61	0.251	0.3892	1.9838	3.0756	2.9440
COM2	955.89		714.41	241.47	74.74	0.315	0.4553	2.0551	3.8893	3.7054
COM1I	991.45	1227.8	829.93	161.52	83.71	0.3674	0.4574	1.8453	2.8920	2.8846
COM2I	1084.9	1274.5	570.26	514.7	52.56	0.2507	0.5439	2.0053	2.8875	2.9176

b) *Adsorption in aqueous solution*

The methylene blue (MB) test was used to estimate the adsorption capacity of carbon to organic compounds from aqueous solution. The samples obtained showed good adsorption capacity for MB (Table 3). This indicated that all the samples were effective adsorbents and also accentuating the use of ACs in the elimination of large molecules in aqueous media particularly certain colorants [21]. For adsorption of I_2, important values were also obtained, which showed high micropores contained in the ACs samples (Table1). The adsorption in liquid phase shows consistency with the results found by the analysis bet. The adsorption values for I_2 for all the samples prepared by physical activation were between 930 and 1237 $mol.g^{-1}$ expressing the high adsorption capacities of the samples to smaller molecules indicating the presence of micropores.

However the adsorption of the BM is higher for the samples prepared by physicochemical activation than those obtained by physical activation, this shows the presence external pores (mesopores and macropores for instance).

The adsorption in liquid phase shows that physico-chemical activation produced a strongly developed internal surface, which is open at the surface by, mesopores and possibly macropores. This is important for the higher removal of both micropollutants and organic compounds due to the accessibility of internal pores sites [9, 22].

Table 3: Value of quantities of methylene blue and iodine adsorbed

Activated carbon	OPSAC	OPSACI	PETAC	OPSACI	COM1	COM1I	COM2	COM2I
IBM (mg/g)	317,26	472,42	288,37	460,03	455,58	493,02	215,92	334,88
II_2(mg/g)	930,23	827,91	1110,41	567,44	1237,31	348,99	1221,45	380,26

c) *Analysis of Fourier Transform Infrared Spectroscopy (FTIR)*

To see the effects of KOH on the impregnation of carbonized material, we need to compare the spectrum of a sample obtained by physical activation in Figure 4 to that obtained by physicochemical activation in Figure 5. The frequency range studied is between 400 and 4000 cm^{-1}, it can provide valuable information about the functional groups on the surface of the materials. These spectra show three main absorption peaks at about 1097 cm^{-1}, 1660 cm^{-1}, 3391 cm^{-1}. From this comparison, it is clear that the bands of samples obtained by physicochemical activation are more intense than those prepared by physical activation, this simply demonstrates that the impregnation of the samples with KOH during physicochemical enhance the surface functions. The intense vibration found at 3391 is due to the existence of hydroxyl groups on the surface, and of the adsorbed water, the absorption peak around 1120 cm^{-1} indicated the existence of C=O bond stretch. The absorption peak around 1600 cm^{-1} can be attributed to both C=C aromatics cycles and carbonyl C=O stretching vibration; this zone justifies the fact that there is not graphitization during the carbonization process of all samples which is favorable for the formation of porosity into the structure of the carbon structure [20].

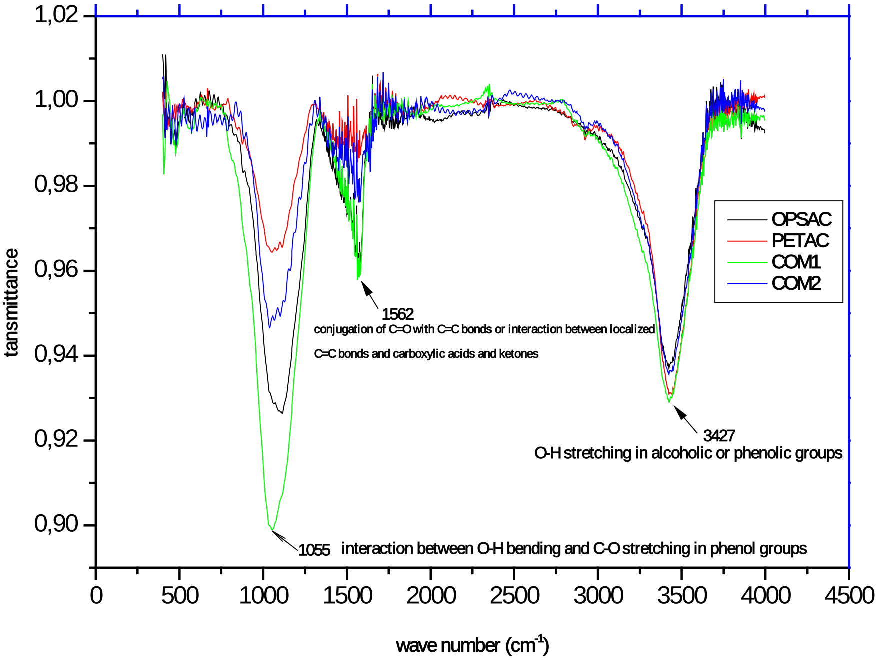


Figure 3: FTIR spectra of four activated Carbons obtained from both oil palm shell and post-consumer plastics using physical activation method with steam

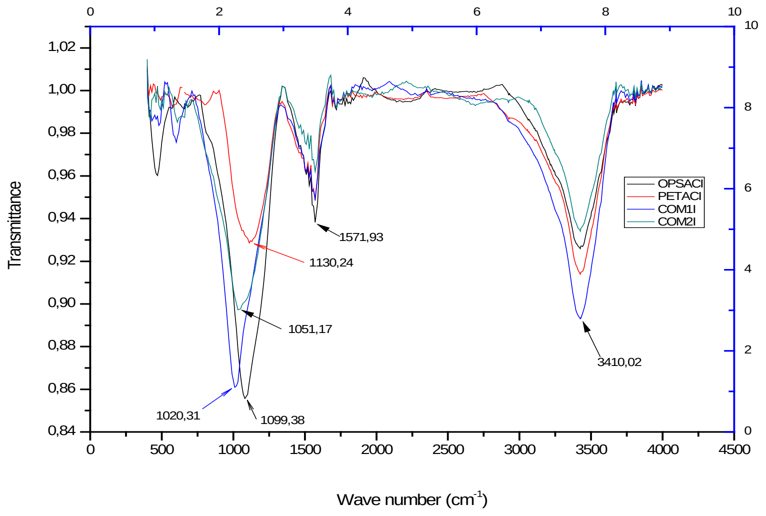


Figure 4: FTIR spectra of four activated Carbons obtained from both oil palm shell and post-consumer plastics using physicochemical activation method with steam and KOH

d) Raman spectroscopy

Raman spectroscopy has been an important tool in such investigations because it allows to a better understanding of the microstructure of the carbon (Yan Wang). The Raman spectrum reveals disordered graphitic materials suggested by the two Raman modes the peaks at 1590 cm^{-1} (G-band) corresponds to and E_{2g} mode of hexagonal graphite and is related to the vibration of sp^2 hybridized carbon atoms in a graphite layer which means that materials are composed of graphitic carbon.

The D band at about 1360 cm^{-1}result from large defects within a carbon network, it is the vibration of carbon atoms with dangling bonds in the plane termination of disordered graphite. The relative Raman intensity of the D and G bands is, therefore, a measure of the degree of order in amorphous carbon samples (Yan Wang). We observed that the intensity of the G and D bands enhance when the carbonaceous material is impregnated with KOH. This confirms that impregnation of carbon increase lattices into carbon material and then developed the internal network of AC obtained [22,23].

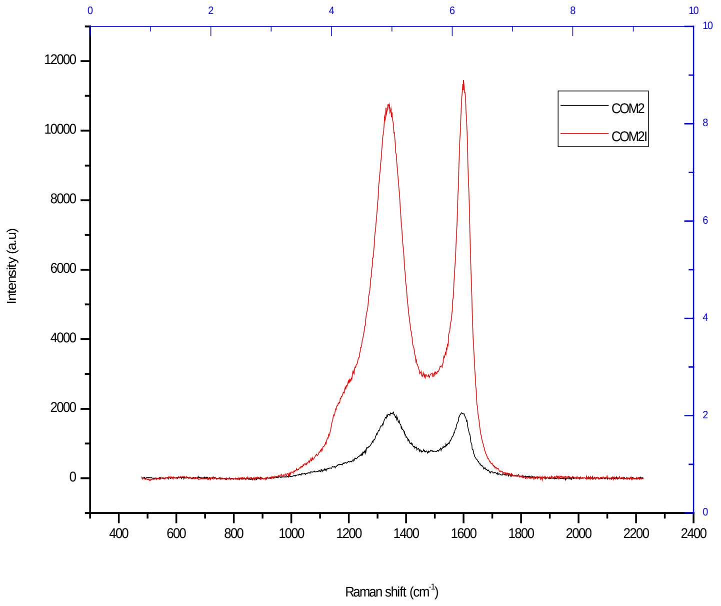


Figure 5: The Raman spectra of ACs obtained by mixing lignocellulosic material and post-consumer plasticsin the ratio 1:2, COM2 is prepared by physical activation with steam, COM2I is prepared by physicochemical activation, char is impregnated by KOH before activation under steam at 800°C

e) X-ray diffraction

The X-ray diffraction (XRD) patterns of ACs obtained from the same precursor by physical activation and physico-chemical activation COM2, and COM2I are shown in figure X. The sharp diffraction peak in the COM2I sample appearing at 2θ = 20, 98°; 2θ = 50,44°; 2θ = 67,5°, 2θ = 73,9° may be attributed to the presence of ash due to the impregnation of char by KOH before activation process with steam. However, these peaks disappeared from the sample prepared by physical activation COM2. The XRD patterns of COM2 and COM2I exhibit in Figure X respectively peaks at 2θ=36,06°, 2θ=41,3° attributed to the turbostratic structure of carbon materials, the peak intensity increased significantly for the sample obtained by physical activation, which indicated an increase graphitization in the structure of carbon material [11,22].

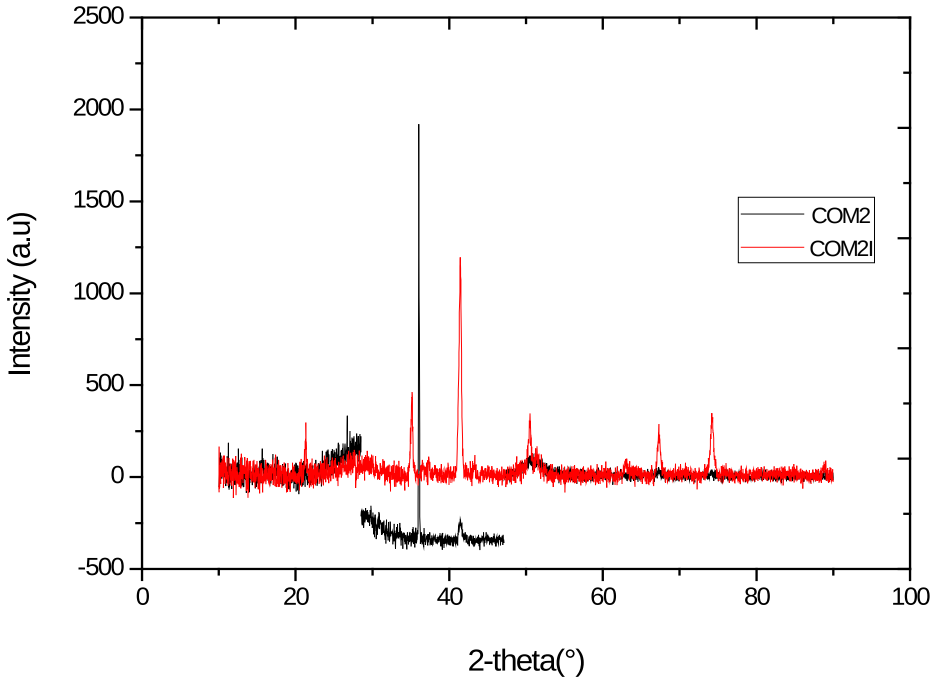
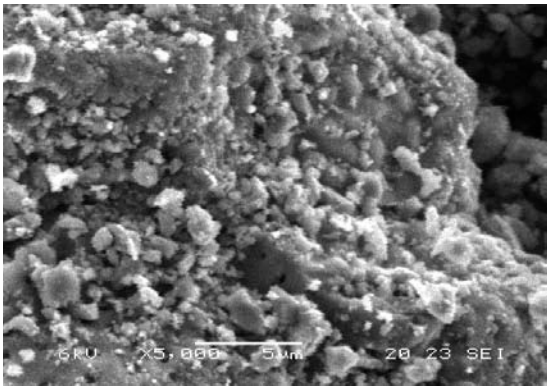


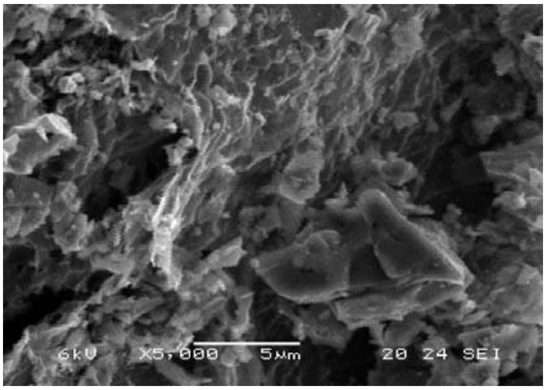
Figure 6: XRD patterns of ACs obtained by mixing lignocellulosic material and post-consumer plastics, COM2 is prepared by physical activation with steam, COM2I is prepared by physicochemical activation char is impregnated by KOH before activation under steam

f) Scanning electron microscopy of activated carbon

Scanning electron microscopy (SEM) is used to observe better the microstructure of the activated carbons prepared. The micrographs obtained are shown in FIGS.



(a)



(b)

Figure 7: SEM images of a) COM2 is prepared by physical activation with steam, b) COM2I is prepared by physic-chemical activation, and char is impregnated by KOH before activation under steam at 800°C

Examination of these images reveals that independently of the composition of raw material the entire sample studied are characterized by aggregates of different sizes and irregular shapes. For sample prepared by physical activation, small pores are observed over the entire surface of the samples, the for samples prepared by physicochemical activation we can observed pores diameter ranging from 0 to 5 µm which give to a higher developed network porosity inside the carbon samples [11, 22].

IV. Conclusion

Activated carbons were prepared from lignocellulosic material and post-consumer plastic by combining physical and chemical activation named physicochemical activation, the same precursor was subjected to physical activation for comparison. The results showed that samples obtained by physical activation are essentially microporous with a surface area between 1000 and 1500 m^2/g. Physicochemical activation leads to the higher development of porosity of ACs by transforming micropores at the surface to mesopores. The adsorption test in aqueous solution shows an affinity of four samples prepared by physicochemical activation to methylene blue, which show external mesopores which connected external surface to the internal pores. FTIR spectrum of ACs prepared shows many peaks belonging different functional groups, samples obtained by physico-chemical activation give peaks more intense than those obtained by physical activation showing that they are more functional group at the surface of ACs obtained by physicochemical activation. Raman and DRX spectrum show that impregnation of char increase lattice into carbon material and then developed the internal network of AC obtained, It was found in this study that physicochemical activation allows obtaining ACs with higher developed porosity constituted of micropores, mesopores, and likely macropores.

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Metabolic Effects of Sulphur Derivative Pesticides in Fish Samples of Fresh Water in Bangladesh

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Northern University

Abstract- In Bangladesh, there are lots of fishes in abundance. Fifteen fresh water fish samples namely *Puntius sarana* (Shawrputi), *Channa punctatus* (Taki), *Wallogonia attu* (Boal), *Macrognathus aculiatus* (Baim), *Ailia coila* (Kajoli), *Mystus cavasisus* (Gulsa), *Ompok pabda* (Pabda),*Corica soborna* (Kachki), *Mystu svittatus* (Tengra), *Glossogobius giuris* (Baila), *Macrobrachium malcolmsli* (Chingri), *Amblypharyngodon microlepis* (Mola), *Anabas testudineus* (Koi), *Channa striatus* (Shol), *Heteropnueste fossilis* (Shing). These fish samples were collected from two rivers and a cultured fish pond. The samples were extracted by QuEChERS method, cleaned up with conc. H_2SO_4 and cleaned extracts were analyzed by GC-ECD. Small size cultured Koi fish sample which did show detectable amount of sulphur containing pesticides and its metabolites was used for the recovery experiments.

Keywords: OSPs, biomagnification, gas chromatography, fresh water fish and food chain.

GJSFR-B Classification: FOR Code: 039999

METABOLICEFFECTSOFSULPHURDERIVATIVEPESTICIDESINFISHSAMPLESOFFRESHWATERINBANGLADESH

Strictly as per the compliance and regulations of:

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Keywords: OSPs, biomagnification, gas chromatography, fresh water fish and food chain.

I. Introduction

Organosulpher Pesticides (OSPs) which are highly stable and bio-accumulative compounds identified as hazardous environmental contaminants for decades [1, 2]. As Bangladesh is an agricultural country, these compounds are used in the country from the middle of the twenty first century in agriculture to increase crop production and other purposes including controlling vector diseases [3]. It is long persistence in the environment and transport long distances via air, water and sediment. The major exposure of the persistent OSPs to humans is via contaminated food, drinking water, inhalation and dermal uptake [2, 4]. OSPs including Fenitrothion, Endosulfan, Thiobencarb, Thiocyclam have been banned in Bangladesh after signing Stockholm Convention [4, 5]. Aquatic ecosystems in Bangladesh are very much susceptible for being contaminated with pesticides and other pollutants. Pesticides enter into the aquatic systems either by direct discharge or transported by evaporation and/or run-off processes [4]. OSPs and its metabolites are not soluble in water but can be present as suspended materials associated with the phytoplankton, algae or through adsorption on soil or sediment [2, 3]. Fish and other aquatic organism can easily be contaminated by taking these suspended materials as their food [1]. Fish is one of the important bio-indicator of bioaccumulation of organic pollutants in fatty tissues and it is one of the sources for accumulation of OSPs to human blood through food chain. Presence of OSPs and its metabolites were reported by our research group in fresh & dry fish, chicken meat and human blood samples [7-11]. In continuation of our work on chemical contaminants in food and environment, we are now reporting the presence of OSPs in fifteen fresh water fish samples from two different rivers and cultured water pond.

II. Materials and Methods

a) Sample Collection

Fifteen live fish samples were collected from Madaripur (Padma river) and Barishal (Arial Kha river and cultured fish pond). The collected fish samples were kept in jip-locked plastic bag with label in chill-box then transported to the laboratory and stored in the freezer at -20°C until extraction carried out. Name sizes, place of collection are given Table 1.

b) Chemicals, Reagents and Solvents

The certified standards; Fenitrothion, Endosulfan, Thiobencarb, Thiocyclam (99% purity) were purchased from Merck, Germany. Analytical grade anhydrous magnesium sulfate and sodium sulfate were purchased from Scharlau, Spain. Analytical grade solvent such as hexane and acetone were purchased from Sigma Aldrich. Sulfuric acid (98%) and sodium chloride were purchase from Merck, Germany.

c) Apparatus and Equipment

All evaporations were carried out by rotary vacuum evaporator at water bath temperature not exceeding 50°C. The residual solvent of the dried mass

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was removed by a freeze dryer (Adward, RV12). Anhydrous sodium and magnesium sulphate were heated at 300°C in a furnace (Carbolite, GSM 11/8 Hope valley, S336 RB, England). For 4 hours and dried materials were kept in a vacuum desiccators.

Calibrated balance, volumetric flasks and pipettes (calibrated by BSTI) were used for the analysis. Gas Chromatography (Shimadzu 2010) coupled with Electron Captured Detector (GC-ECD) used for analysis was calibrated by local agent of the company (AQC).

Table 1: Fish samples collected from Madaripur and Barishal

Fish samples from Padma river

Serial No.	Scientific Name	Local Name	Size (cm)
01	*Channa punctatus*	Taki	27.0-28.0
02	*Wallogonia attu*	Boal	46.0
03	*Macrognathus aculiatus*	Baim	16.0-17.7
04	*Ailia coila*	Kajoli	11.0-12.0
05	*Mystus cavasisus*	Gulsa	12.0-13.2
06	*Ompok pabda*	Pabda	12.0-12.5
07	*Corica soborna*	Kachki	2.9

Fish sample of Arial Kha river

Serial No.	Scientific Name	Local Name	Size (cm)
01	*Mystus vittatus*	Tengra	8.0-8.4
02	*Channa punctatus*	Taki	17.0-17.8
03	*Glossogobius giuris*	Baila	11.0-12.5
04	*Macrobrachium malcolmsli*	Chingri	3.9
05	*Amblypharyngodon microlepis*	Mola	3.7
06	*Anabas testudineus*	Koi	11.0-11.5
07	*Macrognathus aculiatus*	Baim	11.0-12.5
08	*Channa striatus*	Shol	34.0
09	*Heteropnueste fossilis*	Shing	14.4-15.0

Fish sample from cultured pond in Barishal

Serial No.	Scientific Name	Local Name	Size (cm)
01	*Puntius sarana*	Shawrputi	21.2-22.0

Gas Chromatograph (GC-2010 Shimadzu) coupled with Electron Capture detector, (GC-ECD) was used for analysis. Separations were performed on HP-5 quartz capillary column (30 m long 250 μm i.d: 0.25 μm film thickness), nitrogen was used as carrier (column flow 1.92 mL/min.) as well as make up gas. The injector and detector temperatures were set 300°C and 350°C, respectively and the oven temperature was programmed as 100°C (2 min hold) to 200°C (4 min hold) and 20°C rise per min. All the injections (1 μL) were done in split less/spit mode. Identifications of the analyte samples were done by comparing retention time of corresponding certified standard samples and quantification by using external calibration curves of the corresponding reference samples.

d) Extractions and Clean-up

Large fish samples were divided into head, abdominal and dorsal parts and small fish whole samples were taken for analysis. Each of the fish sample was homogenized by a kitchen blender 50-60 g in each jip lock bag was kept in a freezer until analysis carried out. Freeze dried fish samples (10g) were refluxed with n-hexane (60 mL 3; 30 min each time). The combined n-hexane extract was evaporated to dryness and percent fat content was determined and expressed on fresh weight basis (Tables 2 and 3).

Fish sample (10 g 3 for replicate study was taken out from the freezer, thawed and extracted by QuEChERS (Quick, Easy, C0heap, Effective, Rugged and Safe) method [12]. The extract was cleaned with sulphuric acid treatment [13]. The cleaned extract was analysed by GC-ECD. Standard deviations were calculated from three replicate analyses (Tables 2 and 3).

Table 2: Residual amounts of OSPs in the fish samples collected from Padma river

Fish sample	Amount of OSPs and its metabolites (ng/g) in fresh weight basis				Fat (%)
	Fenitrothion	Endosulfan	Thiobencarb	Thiocyclam	
Taki abdominal	4.36 ± 0.17	4.32 ± 0.24	2.99 ± 0.48	3.36 ± 0.46	15.03
Taki dorsal	4.91 ± 0.64	4.47 ± 0.73	1.30 ± 0.09	1.88 ± 0.14	12.56
Taki head	2.86 ± 0.14	3.01 ± 0.09	0.85 ± 0.03	1.81 ± 0.04	8.53
Gulsha	7.01 ± 0.91	9.13 ± 0.79	14.15 ± 1.17	24.03 ± 1.30	54.32
Kachki	4.05 ± 0.26	4.15 ± 0.30	8.55 ± 0.59	9.56 ± 0.37	26.31
Pabdha	9.71 ± 0.69	5.69 ± 0.35	16.33 ± 4.68	17.08 ± 0.60	48.81
Boal abdominal	6.18 ± 0.30	1.76 ± 0.03	0.86 ± 0.04	1.21 ± 0.02	11.01
Boal dorsal	9.71 ± 0.69	1.21 ± 0.03	0.66 ± 0.04	0.64 ± 0.09	10.22
Boal head	4.69 ± 0.07	2.82 ± 0.21	1.05 ± 0.05	1.80 ± 0.25	12.36
Kajoli	2.26 ± 0.32	20.53 ± 0.83	2.51 ± 0.11	6.71 ± 0.21	32.01
Baila	9.75 ± 0.48	14.38 ± 0.66	12.61 ± 0.42	25.35 ± 0.56	62.09

Table 3: Residual amounts of OSPs in the fish samples collected from Arial Kha river

Fish sample	Amount of OSPs and its metabolites (ng/g) in fresh weight basis				Fat (%)
	Fenitrothion	Endosulfan	Thiobencarb	Thiocyclam	
Taki	6.26 ± 0.31	8.79 ± 0.19	0.18 ± 0.00	10.09 ± 0.46	25.32
Baila	4.70 ± 0.11	4.82 ± 0.35	0.31 ± 0.00	0.55 ± 0.05	10.38
Chingri	4.63 ± 0.47	4.18 ± 0.24	1.92 ± 0.04	2.23 ± 0.06	12.96
Mola	12.06 ± 0.75	6.20 ± 0.29	0.65 ± 0.03	1.19 ± 0.04	20.10
Koi	1.55 ± 0.04	1.71 ± 0.04	0.2 ± 40.03	1.21 ± 0.05	4.710
Baim	33.92 ± 1.37	37.25 ± 3.35	4.73 ± 0.33	2.91 ± 0.04	78.81
Shol	3.57 ± 0.41	3.98 ± 0.41	0.17 ± 0.04	5.06 ± 0.49	12.78
Tenra	19.93 ± 1.40	22.16 ± 1.40	0.49 ± 0.03	4.41 ± 0.33	46.99
Shing	7.81 ± 0.48	7.84 ± 0.48	0.31 ± 0.00	1.69 ± 0,07	17.65
Swarputi	2.82 ± 0.23	2.73 ± 0.06	1.42 ± 0.05	1.61 ± 0.05	8.58

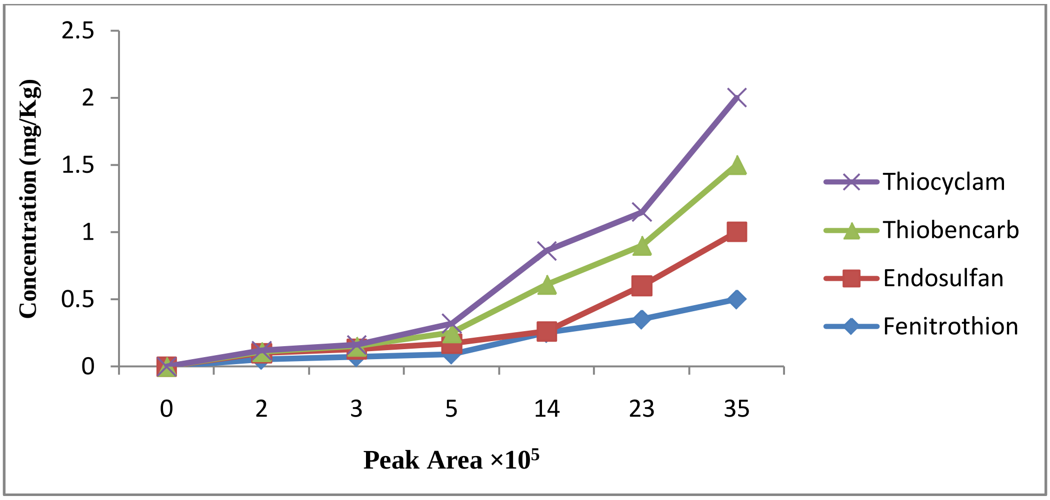

Figure: Calibration curves for standard OSP solutions

To get recovery experiments, we have collected two Rui fish *(Labeo rohita)* from local market as a blank fish matrix. We blended bone free fish and took 5gm for use. We spiked OSPs solution to the fish tissue and allowed stand for 2 hr to let the pesticides to be absorbed into the samples. The samples were extracted freed and cleaned-up by following the same procedure as described above and made final volume 1.0mL. The recovery of the each analyte was calculated according to the following formula:

$$R = \frac{A_m \times C_{st} \times 100}{A_{st} \times C_m \times M_{st}}$$

Where R is the recovery (%), A_m is the peak area of the analyte in the matrix, A_{st} is the peak area of the analyte in the standard, C_m is the concentration of the analyte in the matrix, C_{st} is the concentration of the analyte in the standard, and M_{st} is the spiking level (mg/kg). The percentage recoveries for fish samples were found to be 90%-98%, 101%-123%, 80%-104% and

75%-95% for Fenitrothion, Endosulfan, Thiobencarb and Thiocyclam, respectively.

III. Results and Discussion

Fourteen fish samples from two rivers Padma (Madaripur) and Arial Kha (Barishal) were selected to find out overview of environmental contaminants in two different areas. One fish sample cultured in fish pond was taken to evaluate contaminants which get fish feed and grow faster than naturally live fishes. Most of the small indigenous fishes were adult in their size and size of two large fish samples, boal and shol were also adult size.

Boneless flesh part of large fish and cultured fish samples were studied for sulphur derivatives and metabolites whereas in case of small indigenous fish samples total edible parts including head were taken.

By Calibrating all the apparatus, balance and the GC-ECD were used during the experiments. Three replicate analyses were done for each of the analysis and standard deviation was calculated are satisfactory level. Regression coefficient, r^2 were 0.996 for Fenitrothion, Endosulfan, Thiobencarband 0.999 for Thiocyclam. Percent recovery of the standards were 80% - 123%, which were in the range 75% - 130% and acceptable for fish samples according to standard methodology.

Sulphur derivatives and its metabolites varied from sample to sample. Small fish adult samples showed the presence of higher amount OSPs than other fish samples. The OSPs accumulation depends on mainly on fat content as they deposit in fatty tissue of fishes. Other factors like food habit, lipid content, digestion metabolism rate, excretion rate and habitat etc. also contribute to OSPs accumulation in fish species [6]. In the herbivorous mola fishes, higher amount of fat content is responsible for higher amount of OSPs. Furthermore, the mola fish was found extensively in rivers, canals, beels and ponds throughout the country [7]. The baila is a carnivorous [6]. As we know that OSPs are biomagnified sometimes 7,000 times greater in the top consumer to first consumer. This fish is on the top position in the food chain and contained the higher value. The lowest value of OSPs is found in shole, taki and boal, these three are highly carnivorous. As we mentioned previous OSPs accumulation depends on not only food habit but also on metabolism rate, excretion rate and fat content. In these three fishes their metabolism and excretion rate is higher [6] and fat content also too low. Therefore, although these are carnivorous, they have lower amount of OSPs. The swarputi is a cultured fish and it contains comparatively lower amount of OSPs (Table 3) although it is omnivorous and contained higher amount of fat. Thus in cultured fishes OSPs residue is comparatively low than that of marine and river fishes. The amounts of OSPs content were varied in different part of the same fish. In taki and boal fish samples, the abdominal part contained higher amount of OSPs than their dorsal and head parts (Table 2).Thus in cultured fishes OSPs residue is comparatively low than that of marine and river fishes. However, the residual OSPs in all the fish samples were below maximum residue limit (MRL) of OSPs in fish, but continuous consumption of such fishes may cause a threat to human health as a result of biomagnifications. As OSPs are a long persistent and bioaccumulative substance in the environment, intake of significant amount of this slow poison with our diet is a matter of health concern.

IV. Conclusions

From the present study, the residual amount of OSPs and its metabolites were found in cultured fishes lower than river fish samples. Furthermore, the overall results of OSPs are lower than previous studies. Thus, extensive and indiscriminate uses of organosulphur pesticides especially Fenitrothion, Endosulfan, Thiobencarb and Thiocyclam are decreasing day by day. This study was area-specific giving a holistic picture of the floodplains of our country. The further work is required to determine the overall picture of the pollutants in aquatic environment of Bangladesh.

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Adsorption Equilibrium of Nitrates Ions onto Oil Palm Shells-based Activated Carbons

By Kouotou Daouda, Abdoul Ntieche Rahman, Hambate Gomdje Valery, Ndi Julius Nsami, Abdoul Wahabou & Ketcha Joseph Mbadcam

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Abstract- In this study, two oil palm shells-based activated carbon adsorbents were prepared by physicochemical activation and were evaluated for their ability to remove nitrate ions from an aqueous solution in a batch process. Steam was used as physical activation agent in combination with H_3PO_4 and KOH as chemical activating agents, respectively. The H_3PO_4-carbon (ACOPS-H_3PO_4) and the KOH-carbon (ACOPS-KOH) oil palm shell activated carbons had a BET surface area of 564 and 838 m^2/g, respectively, and were essentially microporous. The effects of various parameters such as contact time, initial solution pH and adsorbent dosage on nitrate ions uptake were investigated. The experimental results obtained showed that the adsorption equilibrium was reached within 70 mn. The amount of nitrate intake was observed to gradually increase when the amount of adsorbent used was varied from 0.2 to 1.2 g reaching a maximum value as from 1 g of adsorbent.

Keywords: *activated carbons; isotherms; nitrates; oil-palm shells; physicochemical activation.*

GJSFR-B Classification: *FOR Code: 259999*

ADSORPTIONEQUILIBRIUMOFNITRATESIONSONTOOILPALMSHELLSBASEDACTIVATEDCARBONS

Strictly as per the compliance and regulations of:

Adsorption Equilibrium of Nitrates Ions onto Oil Palm Shells-based Activated Carbons

Kouotou Daouda [α], Abdoul Ntieche Rahman [σ], Hambate Gomdje Valery [ρ], Ndi Julius Nsami [ѡ],
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Keywords: activated carbons; isotherms; nitrates; oil-palm shells; physicochemical activation.

I. INTRODUCTION

Nitrate ions in the water are of various origins and are toxic even at very low concentrations. Nitrate salts such as potassium nitrate, sodium nitrate, calcium nitrates or ammonium nitrate are used in the manufacture of nitrogen-based fertilizers. Nitrates are also used in the formulation of special cement, as food additives and dyes, for the coagulation of latex, in nuclear industries and for the control of odors and corrosion in hydraulic systems. Thus, due to their high solubility in water nitrate ions are found in groundwater and are disastrous for aquatic ecosystems through eutrophication process. The main risk for human health associated with intake of nitrate is related to the capacity of the human organism to transform nitrates to nitrites. No studies seem to exist that report chronically toxic effects of nitrates without relating them to nitrites effects. These nitrites attach to hemoglobin and cause the disease known as methemoglobinemia which is more frequently encountered with infants. Nitrates can also be converted in the gastrointestinal tract to nitrosamines whose presence seems to favor the development of prostate, pharynx, esophagus or colon cancers.

Elimination of these substances is achieved through processes resorting to several techniques: biological treatment for biodegradable ones, coagulation, oxidation, precipitation, filtration, ions exchange, ultra filtration, reversible osmosis, electrochemical deposition and adsorption [1-3]. Many of these methods are not economically feasible in small- and medium-size and even in large industries since they are very costly. Besides, their use may sometimes expose to different forms of pollution, hence the necessity to choose simple, economical, and efficient and above all nonpolluting techniques such as adsorption onto a microporous solid like an activated carbon [3].

In short, activated carbon is a solid heat-resistant material with an adsorption capacity defined by its pore volume and functional groups, typically oxygenated functional groups present at the surface. Activated carbon main applications are, among others, in discoloring, deodorization, detoxifying of potable waters as well as purification of air, chemicals, food products, etc. It is also used as a catalyst or catalyst support.

The main objective of the present study is to prepare oil palm shells-based activated carbons and evaluate their ability to remove nitrates from an aqueous solution. To this effect, activated carbons are prepared from oil palm shells by carbonization and physicochemical activation using steam for physical activation in combination with H_3PO_4 and KOH as chemical activating agents, respectively.

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Textural characterization of the adsorbents as well as investigation of some effects such as contact time, initial solution pH and adsorbent dosage on nitrates uptake are conducted. The equilibrium adsorption data are analyzed with Langmuir and Freundlich isotherm models to establish the most appropriate correlation for the adsorption system. Kinetics studies are performed to investigate the compliance of nitrate ions adsorption onto the prepared adsorbents with three commonly used kinetic models: pseudo-fist-order, pseudo-second-order, and intra particle diffusion models.

II. Materials and Methods

a) Preparation of activated carbons

i. *Carbonization*

The method adopted in this study was physicochemical activation. It consisted in carbonizing the oil palm shells first, followed by impregnation using a series of chemical agents and finally by steam activation.

A mass of 60 g of the oil palm shells sample with particles mesh size within 1–2 mm, was fed in the furnace reactor. The furnace was brought to the carbonization temperature (800°C)and maintained at this temperature for a residence time of 60 min under nitrogen atmosphere supplied at a flow rate of 100 mL/min during the temperature rise as well as the furnace cooling stages. The char produced was then recovered and weighed. The carbonization apparatus was a large electrical automatic regulator-fitted furnace (CARBOLITE 1200C Tube Furnaces, KEISON Products).

ii. *Impregnation*

a. *Impregnation of the oil palm shell char with KOH*

A quantity of the char obtained was weighed and introduced in an Erlenmeyer containing saturated potassium hydroxide(KOH) solution to achieve the desired impregnation ratio. The mixture was agitated for two hours at 60°C. The product was then dried at 120°C for 24 h to allow for complete water evaporation.

b. *Impregnation of the oil palm shell char with H_3PO_4*

A quantity of the char obtained was weighed and introduced in an Erlenmeyer containing phosphoric acid (H_3PO_4) solution to achieve the desired impregnation ratio. The mixture was agitated for two hours at 60°C.The product was then dried at 120°C for 24 h to allow for complete water evaporation.

iii. *Activation*

Preparation of adsorbent: The reactor was filled with a mass of 10g of impregnated char and then placed in the furnace. The furnace was brought to the activation temperature between 600and 799°C and maintained at this temperature for three hours under steam activation with a supply flow rate of 0.1 mL/min. The sample was withdrawn following the cooling down of the furnace to ambient temperature. Two samples, H_3PO_4-impregnated (ACOPS-H_3PO_4) and KOH-impregnated (ACOPS-KOH), were prepared in this work. After the activation process, both samples were thoroughly washed with distilled water several times until pH 6–7 was achieved, the KOH-impregnated sample being washed with a 0.1 N hydrochloric acid solution before the use of distilled water. The washing process is continued until complete elimination of chloride and phosphate ions from the residual water [4]. The samples washed were dried in an oven at 110°C for 24 h. The extent of activation was obtained by calculating the ratio of the masses obtained after activation to the masses before activation. The samples were ground in a porcelain mortar, sifted with a sieve of mesh size less than 0.1mm and kept for subsequent tests. The activation process was carried out in an electrical THERMOLYNE Type 21100 furnace. The temperature was controlled by a thermocouple type K, and the activation reactor was made of stainless steel and equipped with a degassing system at the inlet. Figure 1 describes the time and energy aspects of the carbonization-activation procedure used in this study.

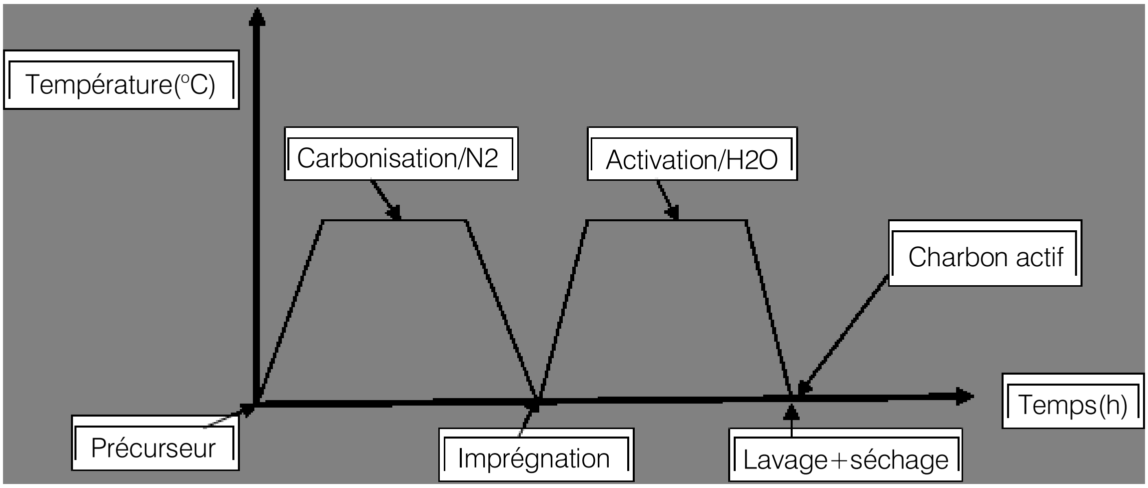


Figure 1: Main scheme of the activated carbons preparation from oil-palm shells

b) Characterization of the activated carbons

Adsorption of N_2 is a standard procedure used for the determination of the specific surface area of the activated carbons prepared. Before adsorption process, all the molecules susceptible to be present in the porous structure of the sample are eliminated by degassing under vacuum at an appropriate temperature during a definite period. In this work, the degassing was carried out for six hours at 200°C. The adsorption-desorption isotherms are obtained from liquid nitrogen at 77 K and under atmospheric pressure using Micro meritics TriStar 3000 V6.08 instrument.

c) Batch adsorption equilibrium studies

Batch adsorption was carried out at room temperature. For each experiment, 20 mL of nitrate ions solution of known concentration was mixed with a known mass of adsorbent. The pH of the solution was adjusted either with 0.1 N HCl or 0.1 N NaOH. The concentration of nitrate in the solution was determined by using the colorimetric method as described by Namasivayam et *al.*[5,6]. The concentration was determined at the wavelength of 410 nm using a UV-Visible spectrophotometer TECHMEL S23A with the maximum absorption wavelength of 1000 nm.

Batch adsorption tests were carried out by adding a fixed amount of adsorbent (0.1 g) into some 250 mL conical flasks containing a definite volume (20 mL in each case) of different initial concentrations (20-100mg/L) of nitrate solution without changing pH (2) at room temperature. The flasks were placed on a shaker and suspension was agitated for 45 minutes with S-BEL and 50 minutes with S-TIK by using a magnetic stirrer.

The amount of nitrate adsorbed onto the adsorbent at equilibrium, q_e (mg/g), was calculated by the following expression:

$$q_e = (C_0 - C_e)*V/W \qquad (1)$$

where C_0 and C_e(mg/L) are the initial and equilibrium nitrate concentration, respectively, V (L)is the volume of solution, and W (g) is the mass of the ACOPS adsorbent.

d) Kinetics adsorption experiments

The procedure of kinetic tests was identical to those of equilibrium tests. The aqueous samples were taken at preset time intervals, and the concentrations of nitrate were similarly measured.

The amount of adsorption at time t, q_t (mg/g) was calculated by:

$$q_t = (C_0 - C_t)*V/W \qquad (2)$$

where C_0 and C_t (mg/L) are the liquid phase concentrations of the nitrate at initial and any time t, respectively. V (L) is the volume of solution and W (g) is the mass of the ACOPS adsorbent.

III. RESULTS AND DISCUSSION

a) Textural and surface characteristics of prepared activated carbons

Two activated carbons prepared from oil palm shells by physicochemical activation under inert atmosphere were obtained. ACOPS-H_3PO_4 and ACOPS-KOH were the activated carbons obtained after impregnation of the char by phosphoric acid (H_3PO_4) and potassium hydroxide (KOH), respectively.

Nitrogen adsorption-desorption curve provides qualitative information on the adsorption mechanism and porous structure of the carbonaceous materials [7-10]. The adsorption-desorption isotherms of N_2 for the activated carbons are presented in Figure 2. It could be seen that both samples exhibited type I isotherms corresponding to micro pores by the International Union of Pure and Applied Chemistry (IUPAC) classification since neither displayed a hysteresis loop. The pore texture parameters obtained from the N_2 adsorption isotherms were summarized in Table 1.The BET surface areas of the prepared activated carbons were found to be 564.03 m^2/g and 838.03 m^2/g, with the total pore volume of 0.23 cm^3/g and 0.39 cm^3/g for ACOPS-H_3PO_4 and ACOPS-KOH, respectively. From the data, it was inferred that the BET surface area and total pore volume of ACOPS-H_3PO_4 and ACOPS-KOH were greatly improved, implying pore development during the H_3PO_4- and KOH-activation stage[10]. The impregnation of the two samples by KOH and H_3PO_4 during the preparation contributed strongly to the development of a micro porous structure. Additionally, the sample ACOPS-KOH presented greater adsorption volume of N_2 compared with ACOPS-H_3PO_4.The extent of porosity governs the sorption kinetics of adsorbates depending upon the nature of both adsorbate and adsorbent. [11]. This showed that H_3PO_4 and KOH were effective in creating well-developed pores on the surface of the char, leading to activated carbons with the large surface area and porous structure. The structural heterogeneity is characterized regarding pore size distribution. According to the classification of IUPAC-pore dimensions, the pores of adsorbents are grouped into micropore($d < 2$ nm), mesopore ($d = 2$-50 nm) and macropore ($d > 50$ nm).The pore size distributions of the prepared activated carbons are shown in Figure 3 with a sharp peak detected at pore diameter between 1 and 2 nm. Moreover, as can be seen from Figure 3, the majority of pores were of size within the interval of the diameter corresponding to micropores since 72% of pores had a diameter less than 2 nm with however the presence of super-micropores which are pores whose diameters are in the range 2-4 nm. This revealed that the activated carbons derived from oil palm shells were predominantly microporous.

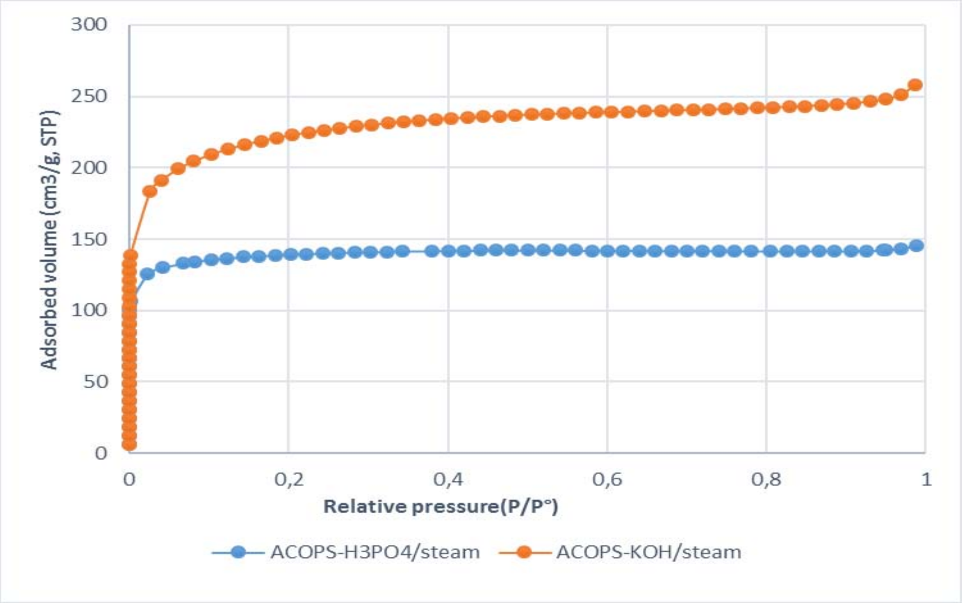


Figure 2: Isotherms for the adsorption-desorption of N$_2$onto the activated carbons (ACOPS-H$_3$PO$_4$) and (ACOPS-KOH) prepared from oil-palm shells

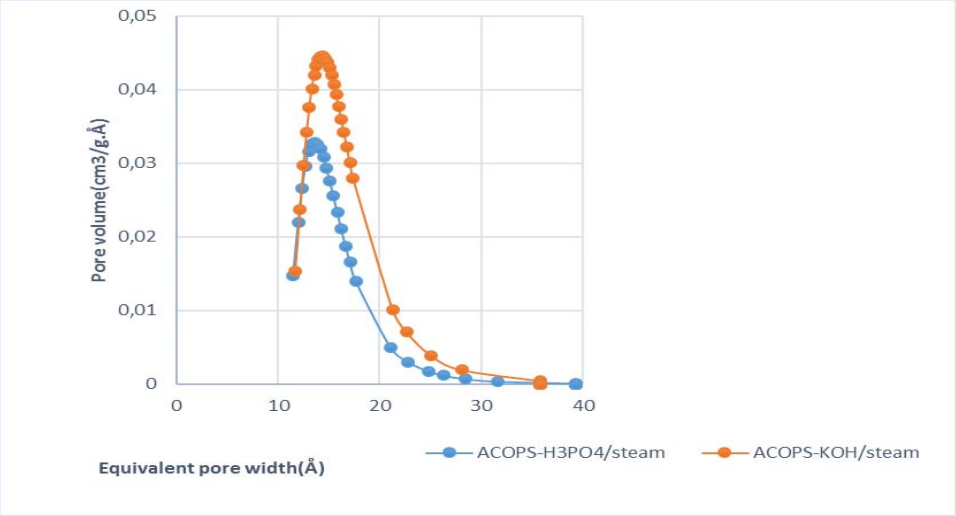


Figure 3: Pore size distribution ofthe activated carbons (ACOPS-H$_3$PO$_4$) and (ACOPS-KOH) prepared from oil-palm shells

Table 1: Pore structure parameters of the oil palm shells-derived activated carbon adsorbents

Type	S_{BET} (m^2/g)	S_{mic} (m^2/g)	V_{tot} (cm^3/g)	V_{mic} (cm^3/g)	V_{mes} (cm^3/g)	Pore structure
ACOPS-H$_3$PO$_4$	564.03	538.89	0.23	0.21	0.02	Microporous
ACOPS-KOH	838.03	813.46	0.39	0.33	0.06	Microporous

S_{BET}, BET surface area; S_{mic}, micropore surface area; V_{tot}, total pore volume; V_{mic}, micropore volume;V_{mes}, micropore volume.

b) *Fourier Transform Infrared (FTIR) spectra*

Oxygen-containing surface functional groups which can be formed during activation process or introduced by oxidation after preparation of activated carbon play important role in influencing the surface properties and adsorption behavior of activated carbons [12]. The FTIR spectroscopy has been performed on the prepared activated carbons to reveal such surface functional groups.

Textural characteristics and surface functional groups of raw palm shell as well as of H_3PO_4-pre-impregnated activated carbons were previously investigated. The main surface functional groups present in the palm shell were reportedly found to be carbonyl groups (such as ketone and quinine), ethers and phenols [13].

The spectra of analysis by Fourier Transform Infrared spectroscopy (FTIR) of the various activated carbon samples prepared in this study are presented in Figure 4. The spectra show that the surface functional groups of the activated carbons do not exhibit significant differences, independently of the activating agent used. Only slight differences on the intensity and broadness of the bands could be observed. Both activated carbon samples absorb nearly at the same bands, the peaks relating to the KOH-activated sample being broader than those about H_3PO_4-activated sample. For the H_3PO_4-activated sample the main surface functional groups present were presumed to be phenols, carboxylic acids (or carboxylic anhydrides if they are close together) and carbonyl groups (either isolated or arranged in quinine-like fashion), all of which are typical acidic functional groups [14-15].

The various spectra display the following bands:

- Two broad overlapping bands at 3010-2800 characteristic of H—C—H asymmetric and symmetric stretch of alkanes and 3010-3600 cm^{-1}characteristic of O—H bond refer to the O—H stretching in hydroxyl functional groups and adsorbed water.
- A band at around 1750 cm^{-1} which is assigned to the stretching vibration of the C═O bond in carboxylic acids, anhydrides, aldehydes, ketones, and lactones or isolated carbonyl groups.
- A broad band in the range 1480 to 1650 cm^{-1} which can be due to C═C stretching in aromatic rings.
- A broad band of 1250-650 cm^{-1} which is ascribed to C—O bending in carboxylic acids and derivatives and also possibly to C—OH stretching in phenols and C—O—C stretching in ethers.
- A peak between 450-510 cm^{-1} attributed to C—H out-of-plane bending in benzene derivatives.

The spectra reveal that for the KOH-activated carbon, the greater extent of oxidation by KOH enhances absorption bands at 500 cm^{-1}, 1000 cm^{-1}, and 3000 cm^{-1} and broaden the one around 3400 cm^{-1}. Moreover, it is to be noted that the various samples absorb with different intensities which indicates that the treatment of the activated carbon by the various activating agents has led to important modifications of surface functional groups.

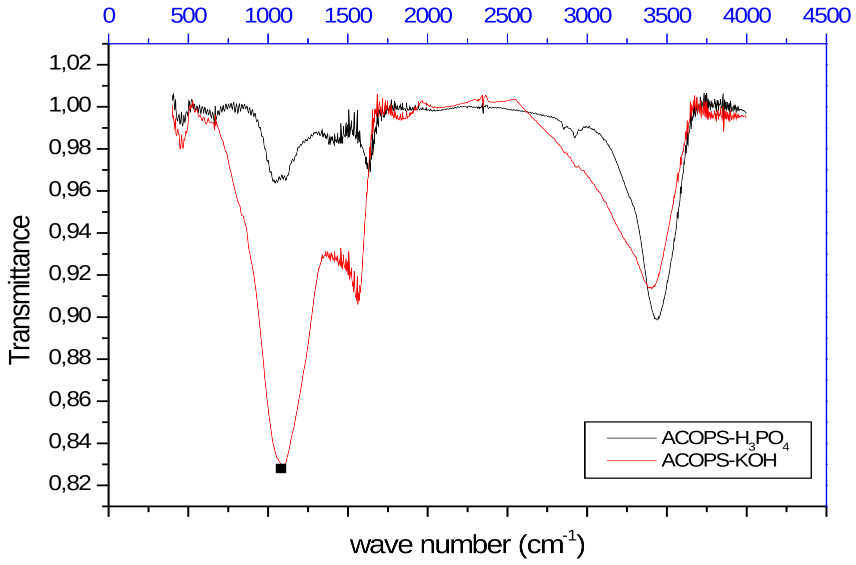
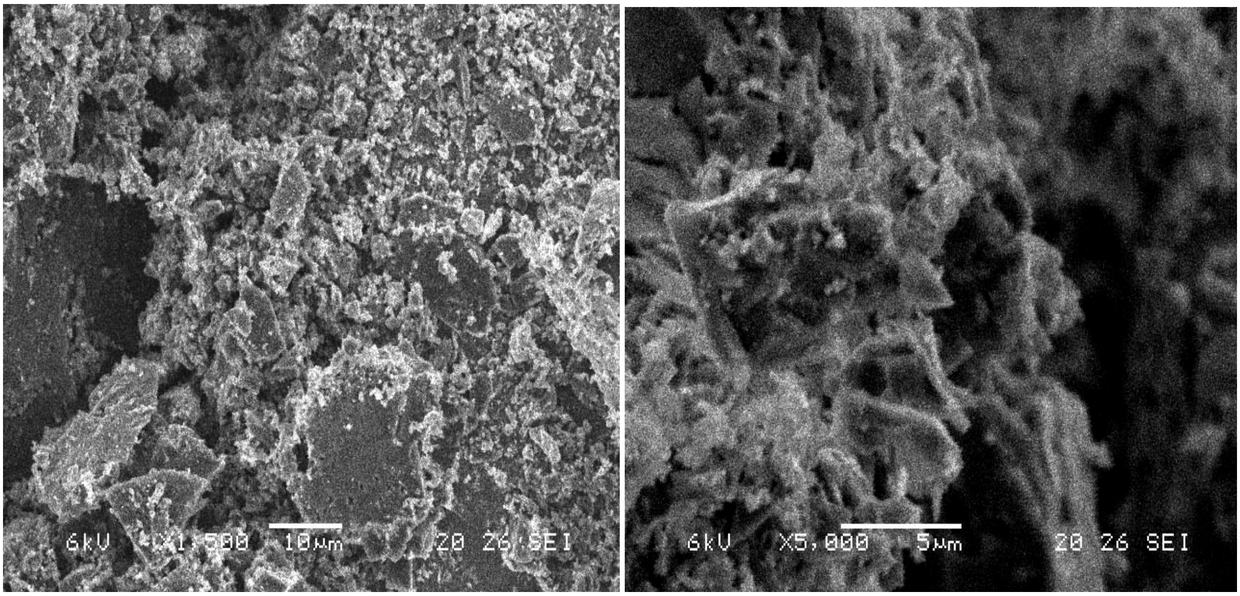


Figure 4: FTIR spectra of the oil-palm-shell activated carbon prepared by H_3PO_4 and KOH activation

c) *Surface characterization by SEM*

Scanning electron microscopy (SEM) was used to observe the surface physical morphology of the activated carbons prepared. The surface physical morphology of the activated carbon samplesACOPS-H_3PO_4 and ACOPS-KOH prepared was examined using the scanning electron micrographs as depicted in Figure 5 (a and b). The surface texture of the precursor oil palm shell carbon was previously described as being dense, compact, constricted and covered by deposited tarry substances. Conversely, it can be seen (Figure 5 (a) and (b)) that SEM images of the H_3PO_4- and KOH-activated carbons display a series of pores and irregular cavities of different sizes and different shapes on the external surface of carbons as compared to the precursor. These pores and cavities were the results from the release of volatile components and the evaporation of the H_3PO_4 and KOH impregnating agents from the H_3PO_4- and KOH-impregnated derived compounds leaving the space previously occupied by the reagent. [16]. This shows that H_3PO_4 and KOH were effective in creating well-developed pores on the surface of the precursor, hence leading to the activated carbon with the large surface area and porous structure.[17].



(a) (b)

Figure 5: Scanning electron microscope (SEM) images of the activated carbon (a) ACOPS-$H_3PO_4$and (b) ACOPS-KOH

d) Effect of contact time on the adsorption of nitrate ions

Adsorption kinetic is an important characteristic for evaluating the efficiency of adsorption. The amount of nitrate adsorbed, q_t versus times is depicted in Figure 6.As can be seen from Figure 6, the amount of nitrate adsorbed on the activated carbons increases as the contact time increases; at some point in time, it reaches a constant value beyond which no more nitrate is further removed from the solution. At this point, the amount of nitrate desorbing from the activated carbons is in a state of dynamic equilibrium with the amount of nitrate being adsorbed on the activated carbons. The amount of nitrate adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under those operating conditions. It is apparent from Figure 6 that the kinetic of nitrate adsorption consists of two phases, an initial stage when the adsorption process increased sharply and a second gradually slower phase when it approached equilibrium. During the rapid adsorption period, whose duration time was approximately 50minutes in the present study, the tendency of adsorbent to adsorption was high and therefore, the slope of adsorption curve was steep. The initial high rate of nitrate adsorption was attributed to the greater availability of binding sites on the surface of the adsorbents at the early stages of the adsorption process. Slow adsorption period was between 50 and 80 minutes in the present study. During this period, the slope of adsorption curve was gradually flattened, and the nitrate adsorption was gradually decreased until reaching zero. This phenomenon is attributed to the reduction of immediate solute adsorption due to the lack of available open sites for nitrate adsorption. This usually occurs as the external surface of adsorbent is rapidly saturated by nitrate anion, and therefore the adsorption rate reduces [18].

Moreover, the time profiles of nitrate adsorption as can be seen in Figure 6 are single, smooth and continuous curves leading to saturation, suggesting possible monolayer coverage of nitrate onto the surface of the activated carbons. The equilibrium time was around 70 min for both ACOPS-H_3PO_4 and ACOPS-KOH and the adsorption capacities at equilibrium (q_e) were found to be 48 and 55 mg/L for ACOPS-H_3PO_4 and ACOPS-KOH, respectively. The present findings are consistent with the results obtained by other researchers who investigated the adsorption of nitrate onto various adsorbents [19].

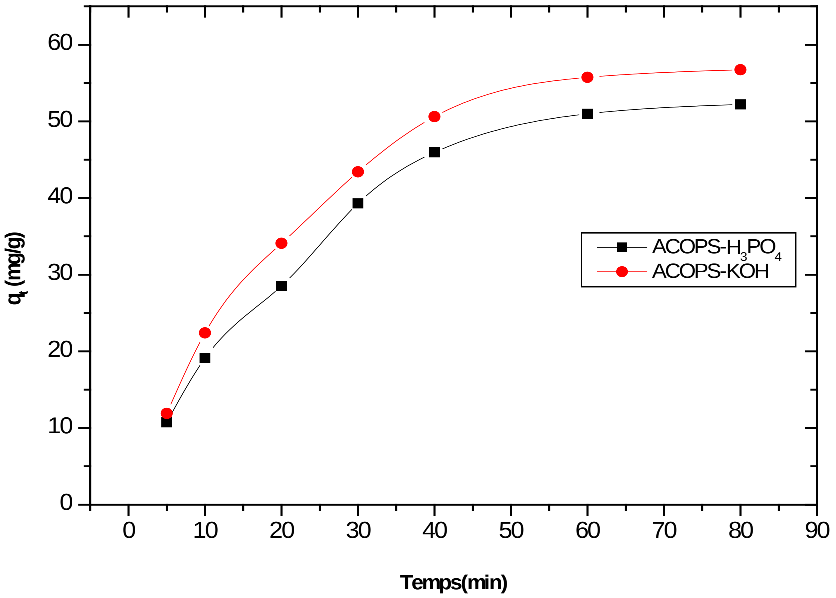


Figure 6: Effect of contact time on the adsorption of nitrate ions onto the activated carbons (ACOPS-H_3PO_4) and (ACOPS-KOH) prepared from oil-palm shells

e) Effect of adsorbent dosage on nitrate adsorption

To assess the optimum amount of the activated carbon prepared to be used for the adsorption of nitrate ions from aqueous solution, adsorption experiments were performed in which different amounts of the activated carbons samples were used with 10 mg/L nitrate solutions. The amount of adsorbent was varied from 0.2 g to 1.2 g. Figure 7 shows the removal of nitrate as a function of adsorbent dosage. It is apparent from the figure that by increasing the adsorbent dose the amount of adsorbed nitrate increases from 20 mg/g to 48 and 55 mg/g for ACOPS-H_3PO_4 and ACOPS-KOH, respectively which is due to the increase in the adsorbent surface area of the adsorbents. In general, increasing the amount of solid adsorbent in the system causes an increase in adsorption area, and thus more sites are available. It is readily understood that the number of sites available for adsorption increases by increasing the adsorbent dose and it, therefore, results in an increase of the amount of nitrate adsorbed. This study showed that the adsorption capacity of the activated carbons increased with increase in adsorbent dose up to a particular region and then reaches an equilibrium level at higher doses. It is observed that after a dosage of about 1g, the amount of nitrate adsorbed remained essentially constant at 48 and 55 mg/g for the activated carbon samples of ACOPS-H_3PO_4 and ACOPS-KOH, respectively; there was no significant change in the amount of nitrate removed by either adsorbent. Therefore the results indicate that the removal efficiency increases up to optimum dosage beyond which the removal efficiency is negligible. This may be due to the difficulty for the nitrate particles to come closer to the adsorption sites either because of the accumulation of these particles around active sites or because of the agglomeration of adsorbent particles which reduces the total adsorption surface[20].

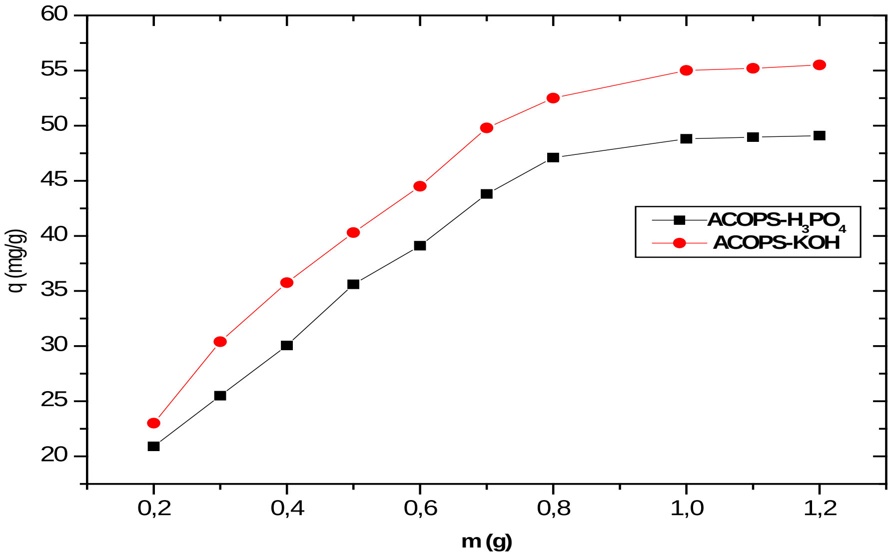


Figure 7: Effect of adsorbent dose on the adsorption of nitrate ions on to the activated carbons (ACOPS-H_3PO_4) and (ACOPS-KOH) prepared from oil-palm shells

f) Effect of initial solution pH on nitrate adsorption

The pH of an aqueous solution exerts a profound influence on the extent of adsorption of adsorbate molecule by regulating the charge of the surface functional groups of the adsorbent as well as the ionization of the adsorbate molecules. The effect of pH on nitrate removal from aqueous solution by ACOPS-H_3PO_4 and ACOPS-KOH samples was investigated in the pH range 3.5 – 6.5. The initial pH of the nitrate solution was adjusted by addition of 0.10 M HCl or NaOH. The experimental result of the adsorption of nitrate on ACOPS-H_3PO_4 and ACOPS-KOH as a function of pH is shown in Figure 8. Figure 8 shows a clear decrease of the number of nitrate ions adsorbed by the adsorbent as the solution pH increased. Nitrate uptake was higher at lower pH, and as the pH of the solution increased, the extent of nitrate adsorption decreased significantly. This decrease in the adsorption capacity observed for both adsorbents as the pH increased could be attributed to the depletion of the positive hydrogen ions thereby promoting activities of electrostatic repulsion between the negative charge of nitrate anions and the adsorbents surface. Competition between OH^- (at high pH) and nitrate anions for positively charged adsorption sites could also be suspected of being responsible for the decrease in nitrate uptake [21]. The reason for good removal of nitrate at the lower acidic pH is that due to the excess of protons in solutions, the functional groups of activated carbon become protonated and thereby reducing the negative charges on the surface. This enhances nitrate adsorption through electrostatic attraction. [22]. In the present study, nitrate adsorption is highest at pH 3.5. It could be suggested that the surface of ACOPS-H_3PO_4 and ACOPS-KOH adsorbents becomes more positively charged. Positively charged surface sites on the adsorbents favor the adsorption of the nitrate anions due to electrostatic attraction. Similar trends in connection with the influence of the pH of the medium on the extent of adsorption of various solutes onto different adsorbents were reported in the literature [23, 24].

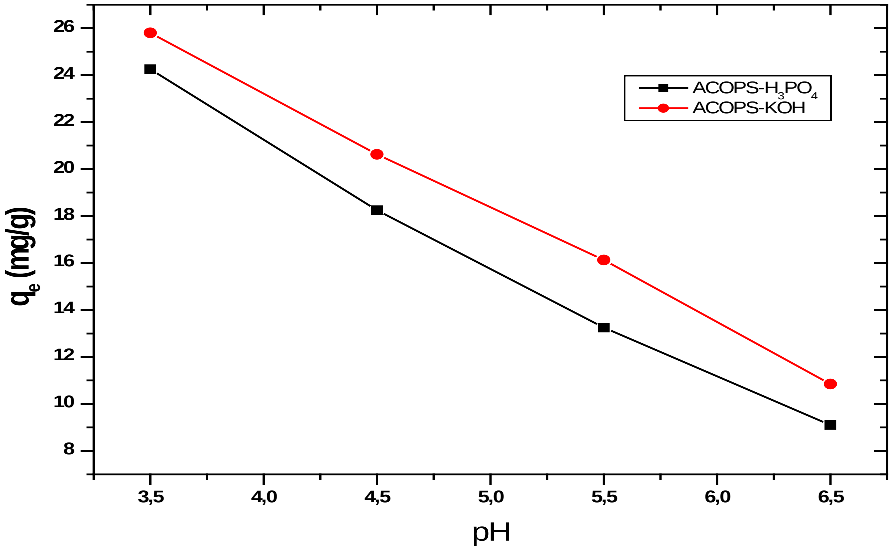


Figure 8: Influence of pH on the adsorption of nitrate ions onto the activated carbons (ACOPS-H_3PO_4) and (ACOPS-KOH) prepared from oil-palm shells

g) *Equilibrium adsorption isotherms*

The equilibrium adsorption isotherm model is fundamental in describing the interactive behavior between adsorbate and adsorbent and is very important to understand the adsorption behavior of solid-liquid adsorption system. It indicates the distribution of adsorbate between solution and adsorbent at equilibrium state of the adsorption process. It is expressed by relating the amount of adsorbate taken up per gram of adsorbent, q_e (mg/g), to the equilibrium solution concentration, C_e (mg/L), and at different concentrations of adsorbate solutions [25, 26]. Analysis of isotherm data is important for predicting the adsorption capacity of the adsorbent, which is one of the main parameters required to ascertain the adsorption effectiveness of an adsorbent. Several isotherm models are used for this purpose. In the present study, two commonly used isotherm models, the Langmuir and the Freundlich models [27] are selected to analyze the experimental equilibrium datato establish the most appropriate correlation for the adsorption of nitrate onto the prepared activated carbons.

h) *The Langmuir isotherm*

The Langmuir isotherm is based on the assumptions that adsorption takes place on the surface of the adsorbent at a finite number of localized active sites that are identical and equivalent with a homogeneous distribution of adsorption energies, without significant lateral interaction and steric hindrance among adsorbed species, even on the adjacent sites. The model does not consider the surface heterogeneity of the adsorbent and assumes monolayer coverage of adsorbate, that is, the adsorbent is saturated after the formation of one layer of adsorbate on the surface of adsorbent [28].

The mathematical expression of Langmuir isotherm is given as:

$$q_e = q_{max}K_LC_e/(1 + K_LC_e) \tag{3}$$

The linearized form of the Langmuir model is given as:

$$C_e/q_e = 1/K_Lq_{max} + C_e/q_{max} \tag{4}$$

Where C_e (mg/L) is the equilibrium concentration of the remaining solute in the solution, q_e (mg/g) is the amount of the solute adsorbed per unit mass of adsorbent at equilibrium, q_{max} (mg/g) is the amount of adsorbate per unit mass of adsorbent at complete monolayer coverage, related to adsorption capacity, and K_L (L/mg) is the Langmuir constant related to adsorption energy and rate of adsorption. In this work, the experimental data are plotted in (Figure 9) asC_e/q_e versus C_e in the nitrate concentration range of 10 to 30 mg/L for both samples of the activated carbons prepared bythe linear form of Langmuir isotherm equation (4). Two straight lines were obtained. The Langmuir isotherms parameters q_{max} and K_L values were calculated from the slopes ($1/q_{max}$), and intercepts ($1/K_Lq_{max}$) of linear plots of C_e/q_e versus C_e (Figure 9) are given in Table 2.It can be seen from Table 2 that for the Langmuir model, the values of the monolayer adsorption capacity (q_{max}) of the adsorbents are 65.488 mg/g and 68.166 mg/g for ACOPS-H_3PO_4 and ACOPS-KOH, respectively indicating that ACOPS-KOH had a greater total adsorption capacity than ACOPS-H_3PO_4.The values of maximum adsorption capacity (q_{max}) of the adsorbents were 65.488 mg/g and 68.166 mg/g for ACOPS-H_3PO_4 and ACOPS-KOH, respectively indicating that ACOPS-KOH had a greater total adsorption capacity than ACOPS-H_3PO_4.It appears(Table 2) that the correlation coefficients (R^2) of Langmuir model are 0.969

and 0.995 for ACOPS-H_3PO_4 and ACOPS-KOH samples, respectively. The linearity of the plots (Figure 9), as confirmed by the correlation coefficients being close to 1 for both adsorbents, together with a good agreement observed between the theoretical monolayer adsorption capacity $q_{max,cal}$ and the experimental value $q_{max,exp}$ (Table 2)indicate the compliance of the adsorption data with Langmuir model and illustrate the homogeneous character of the surface of the adsorbents.

The value of Langmuir constant K_L indicates the favorability of the process as well as the affinity between solute and adsorbent. Thus, the higher the value of K_L, the greater the driving force for adsorption. K_L values obtained, 0.3201 L/mg and 0.3056 L/mg for ACOPS-H_3PO_4 and ACOPS-KOH, respectively were large enough to lead to the conclusion that the adsorption of nitrates onto these activated carbons was favored in the concentration range considered[29].

In general, the K_L value for the adsorption of nitrate is less than 1 L/mg [30]. The values of K_l as obtained by several authors and reported in the literature for the adsorption of NO_3^- on different types of adsorbents together with the ones determined in work are presented in(Table 3). In comparison with the values shown herein, the K_L values obtained in the present study (0.3201 and 0.3056 L/mg for ACOPS-H_3PO_4 and ACOPS-KOH, respectively) were within the suggested interval and indicated good affinity and a high-energy adsorption process.

One of the essential characteristics of the Langmuir model can be expressed by a dimensionless constant called separation factor, R_L, which is determined as follows [31]:

$$R_L = 1/(1 + K_L C_0) \qquad (5)$$

Where C_0 is the initial adsorbate concentration (mg/L). The value of R_L indicates the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$). In the present study, R_L values calculated by equation (5) for nitrate adsorption onto the activated carbons prepared ACOPS-H_3PO_4 and ACOPS-KOH for the initial nitrate concentration interval considered ($10 \leq C_0 \leq 30$ mg/L) are shown in Table 2. The R_L values obtained for ACOPS-H_3PO_4 ($0.0943 \leq R_L \leq 0.238$) and ACOPS-KOH($0.0983 \leq R_L \leq 0.246$) lie well within the range $0 < R_L < 1$ indicating that the adsorption process onto both ACOPS-H_3PO_4 and ACOPS-KOH sample is favorable [32,33].

Table 2: Constants for equilibrium isotherm models with error analysis values

Adsorbent	q_{max} (mg/g)	K_L (L/mg)	R_L	Error analysis R^2
Langmuir isotherm model				
ACOPS-H_3PO_4	65.488	0.3201	$0.0943 \leq R_L \leq 0.238$	0.969
ACOPS-KOH	68.166	0.3056	$0.0983 \leq R_L \leq 0.246$	0.995

Adsorbent	K_F	1/n	Error analysis R^2
Freundlich isotherm model			
ACOPS-H_3PO_4	19.935	0.543	0.967
ACOPS-KOH	10.007	0.800	0.961

Table 3: q_{max} and K_L values for the adsorption of nitrate on different types of coals

Adsorbent	q_{max} mg/g	K_L L/mg	Ref.
Sugar beet bagasse charcoal	9.14	0.070	Reference 34
Cationic polymer-modified GAC	27.56	0.048	Reference 35
Activated carbon	14.5	0.027	Reference 4
$ZnCl_2$ activated coir pith carbon	10.30	0.096	Reference 29
Activated carbon modified with $CaCl_2$	1.83	0.140	Reference 30
$ZnCl_2$ modified lignite granular activated carbon (LGAC5)	12.06	0.156	Reference 36
Mineral Clay (New Clay)	250	0.307	Reference 37
NaOH activated rice husk carbon	86.2	0.017	Reference 38
H_3PO_4 activated oil-palm shell carbon	65.49	0.320	This study
KOH activated oil-palm shell carbon	68.17	0.306	This study

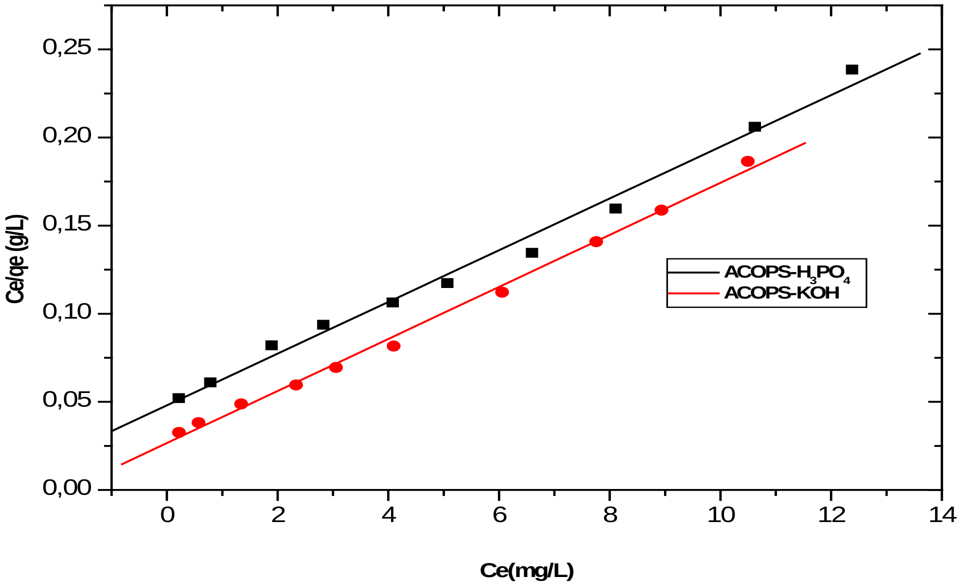


Figure 9: Langmuir isotherm linear plots for the adsorption of nitrate ions onto the activated carbons (ACOPS-H_3PO_4) and (ACOPS-KOH) prepared from oil-palm shells

i) The Freundlich adsorption isotherm

Freundlich isotherm [39] model is an empirical equation proposed for the description of surface heterogeneity of the adsorbent and multilayer adsorption. This model states that interactions take place in several active adsorption sites accompanied by interactions between adsorbed molecules with a non-uniform distribution of adsorption heat and affinities over the heterogeneous surface. It assumes that as the amount of solute adsorbed rises, the binding surface energy decreases exponentially which is characteristic of multilayer adsorption[40].

The Freundlich isotherm model mathematically expresses the surface heterogeneity and exponential distribution of the active sites and their energies; it is defined as:

$$Q_e = K_F C_e^{1/n} \quad (6)$$

The linearized logarithmic form of Freundlich isotherm model is given as follows:

$$\ln Q_e = \ln K_F + (1/n)\ln C_e \quad (7)$$

Where C_e (mg/L) is the equilibrium concentration of the adsorbate, Q_e (mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbentat equilibrium, K_F [(mg/g)(L/mg)$^{1/n}$] and n are the Freundlich adsorption constants. K_F relating to the extent of adsorption indicates the adsorption capacity of the adsorbent, and 1/n is a dimensionless quantity related to the adsorption intensity and the surface heterogeneity of the adsorbent material (the surface becoming more heterogeneous as 1/n value approaches zero)[42]. The value of 1/n indicates how favorable the adsorption process is. A value 1/n between 0 and 1 indicates high adsorption capacity and favorable adsorption. When $1/n > 1$, the adsorption is not favorable, the adsorption interactions become weak, and the adsorption capacity decreases. [43-46]. This model was shown to give good results for low adsorbate concentrations. The adsorption data obtained from the samples studied were plotted according to the linearized Freundlich adsorption isotherm and are shown as a plot of ln Q_e versus ln C_e in Figure 10.The values of the parameters of Freundlich equation, K_F, and 1/n, were determined from the intercept and slope of the plot of ln Q_e versus ln C_e and are listed in Table 2. The values of the adsorption constants K_F and the exponent *1/n* in the Freundlich equation(Table 2) inferred from the curves of Figure 10 allow assessing whether the adsorption of nitrate ion on the samples of the activated carbons studied is favorable or not. The smaller the value of *1/n* (that is $0 < 1/n < 1$) and the greater the value of K_F, the stronger are the interactions between the nitrate ions and the adsorbent signifying greater affinity between the nitrate ions and the activated carbon. [47]. The constant K_F may be used to compare the adsorption process of the same solute for different adsorbents. These comparisons help establish the system with the most efficient adsorption. The Freundlich adsorption constants K_F obtained from Figure 10were (19.935 and 10.007) for ACOPS-H_3PO_4 and ACOPS-KOH, respectively. As can be seen from Table 2, the values of 1/n in the present study were in the range 0-1 (0.543 and 0.800 for ACOPS-H_3PO_4 and ACOPS-KOH, respectively) revealing favorable adsorption conditions of nitrate by both activated carbons[48]. Moreover, the correlation coefficients of the linearized Freundlich isotherm model for nitrate adsorption onto the samples ACOPS-H_3PO_4 ($r^2 = 0.967$) and ACOPS-KOH($r^2 = 0.961$) were both close to 0.96, which implied that in the range of concentrations considered in this study, Freundlich adsorption model was appropriate for explaining the adsorption of nitrate ions on the samples investigated.

In summary, both of Langmuir and Freundlich isotherms were greatly suitable to explain experimental data due to r^2 greater than 0.96.

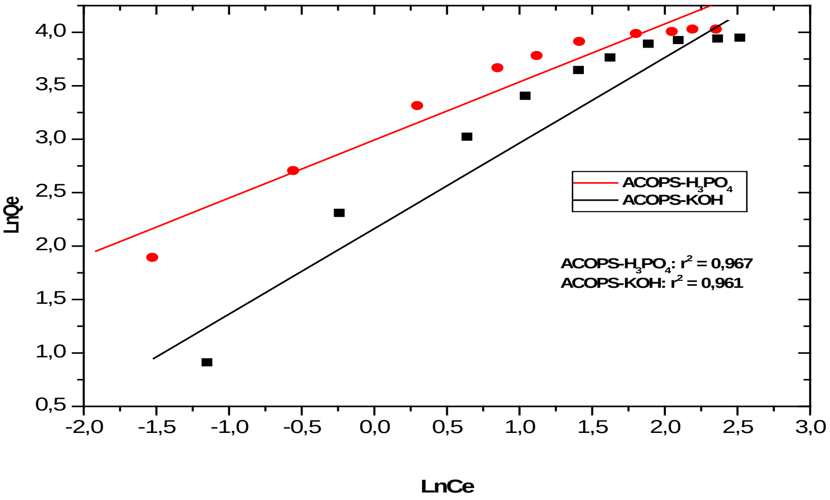


Figure 10: Freundlich isotherm linear plots for the adsorption of nitrate ions onto the activated carbons (ACOPS-H_3PO_4) and (ACOPS-KOH) prepared from oil-palm shells

j) *Adsorption kinetics*

The application of the pseudo-second-order kinetic model to the data by plotting t/q_t concerning to time t is shown in Figure 11.The values of the equilibrium adsorption capacity, (q_e), the pseudo-second order rate constant, (k_2), the initial adsorption rate, (h), calculated from the slope and the intercepts of the straight lines of the t/q_t versus t plots shown in Figure 11 together with the correlation coefficients, (r^2), are listed in Table 4.The correlation coefficient (r^2) values for pseudo-second-order equation are 0.995 and 0.994 for ACOPS-H_3PO_4 and ACOPS-KOH, respectively indicating a good fit of pseudo-second-order rate model to experimental kinetic data. It suggests that this model is capable of describing the kinetic behavior for the adsorption of nitrates onto the activated carbons prepared. Furthermore, the equilibrium adsorption capacities calculated from the pseudo-second-order model (q_{ecal}) are similar to the experimental values (q_{eexp}) for both activated carbons. The pseudo-second-order rate constants (k_2) are 5.433 g/mg min for ACOPS-H_3PO_4 and 5.014 g/mg min for ACOPS-KOH. The h value calculated from pseudo-second-order equation is higher for ACOPS-H_3PO_4 than for ACOPS-KOH, indicating a higher mass transfer rate for ACOPS-H_3PO_4, indicating a higher mass transfer rate for ACOPS-H_3PO_4[49].

The intra particle diffusion plots for the adsorption of nitrate onto ACOPS are presented in Figure 12.k_p (mg/g $min^{0.5}$), the intra particle diffusion rate constant can be obtained from the slope of the q_t versus $t^{0.5}$ plot and is listed in Table 4. The plot of q_t versus $t^{0.5}$ using kinetic data up to 80 min gives correlation coefficients (r^2) values of 0.961 for ACOPS-H_3PO_4 and 0.966 for ACOPS-KOH adsorbents. The linearity of the plots indicates that intra particle diffusion might play a significant role in the initial stage of adsorption of nitrate onto ACOPS adsorbents because the intra particle diffusion equation is valid only for initial kinetic data [50].

The adsorption kinetics of nitrate onto ACOPS-H_3PO_4 and ACOPS-KOH using both pseudo-second-order and intra particle diffusion models show a good fit to experimental kinetic data, but the pseudo-second-order rate model is a better fit than the intraparticle model. This second-order kinetic behavior suggests that the adsorption mechanism is the rate-controlling step [51].

Table 4: Constants of different kinetic and intra particle diffusion models

Adsorbent	C_0 (m^2/g)	q_e (exp) (mg/g)	Pseudo-second-order equation				Intraparticle diffusion	
			q_e (cal) (mg/g)	k_2 (g/mg min)	h (mg/g min)	r^2	k_p (mg/g $min^{0.5}$)	r^2
ACOPS-H_3PO_4	🟩	52.200	76.336	5.433	31659.1	0.995	7.519	0.961
ACOPS-KOH		56.738	72.516	5.014	26366.5	0.994	6.918	0.966

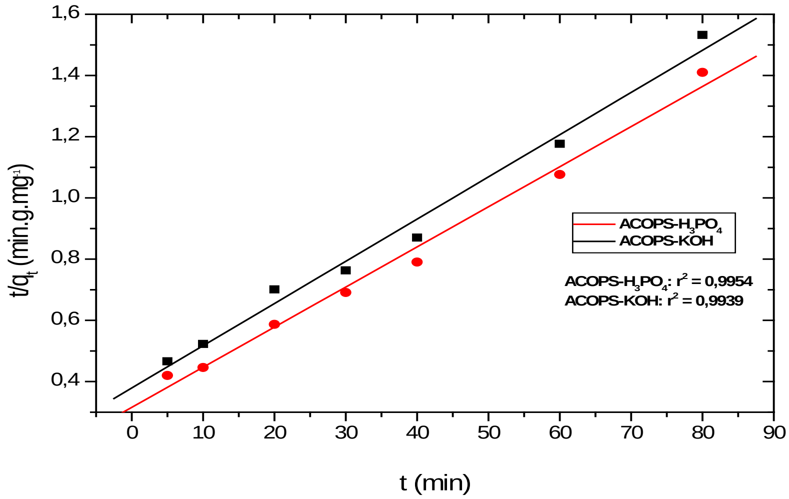


Figure 11: Pseudo-second-order kinetic plots for the adsorption of nitrate ions onto the activated carbons (ACOPS-H_3PO_4) and (ACOPS-KOH) prepared from oil-palm shells

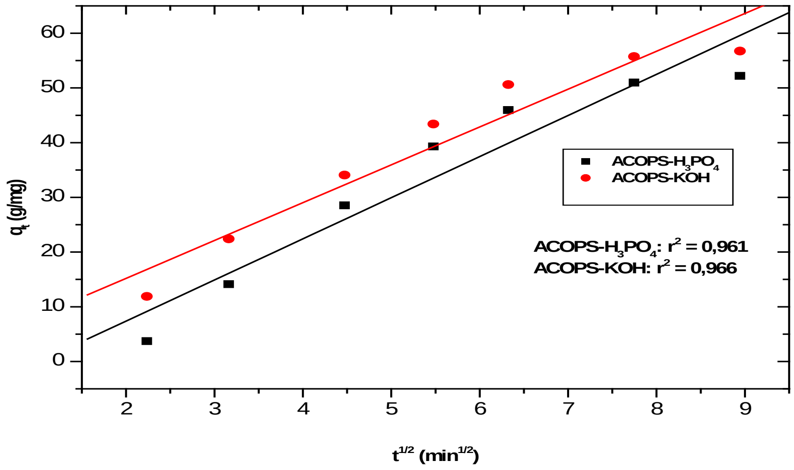


Figure 12: The intra particle diffusion model for the adsorption of nitrate ions onto the activated carbons (ACOPS-H_3PO_4) and (ACOPS-KOH) prepared from oil-palm shells

IV. CONCLUSION

Activated carbons were prepared from oil palm shells by physicochemical activation using H_3PO_4 and KOH as the chemical activating agents on the one hand and steam as the physical activating agent on the other. The ability of the H_3PO_4 and KOH activated carbons, labeled ACOPS-H_3PO_4 and ACOPS-KOH respectively, to remove nitrate ions from aqueous solutions was investigated. The N_2 adsorption showed that the adsorbents were essentially of micro porous nature and mesopores if present were situated at the surface and served as gateways to micropores. Experimental data indicated that the adsorption process was influenced by the solution pH as well as by the adsorbent dosage. The more acidic the solution pH the greater the number of nitrate ions adsorbed by both adsorbents. The adsorption capacities of both adsorbents were higher at higher adsorbent dosage values. Kinetics studies of the adsorption of nitrate ions onto the sample adsorbents showed that the adsorption process was rapid with 90% of the nitrate ions uptake being achieved within the first forty minutes of the process and that the adsorption mechanism could be described by pseudo-second-order kinetics. The adsorption isotherms of nitrate ions onto the activated carbons prepared were adequately described by Langmuir and Freundlich models. The maximum adsorption capacities as determined from Langmuir isotherms were 65 and 68.166 mg/g for ACOPS-H_3PO_4 and ACOPS-KOH, respectively. These results revealed that high adsorption capacity of nitrate could be achieved from oil-palm-shell H_3PO_4 or KOH activated carbons. Furthermore, the higher adsorption capacity of nitrate onto ACOPS-KOH, 68.166 mg/g, compared with that of ACOPS-H_3PO_4, 65 mg/g, suggested ACOPS-KOH was a better adsorbent for removal of nitrate from aqueous solution.

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Seasonal Assessment of Heavy Metals in Water at Effluents Discharge Points into the New Calabar River, Port Harcourt, Southern Nigeria

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Abstract- Water samples were collected at three different effluents discharge points into the New Calabar River. The samples were digested using standard methods. The digests were subsequently examined for heavy metals concentrations using atomic absorption spectrophotometer (AAS). Heavy metals results in the samples showed Ni as the most concentrated metal with a mean value of 2.52±0.055, 1.42±0.01 and 1.275±0.045 mg/L at Iwofe, Jetty, Minipity and Police Post stations respectively, this was followed by the concentration values of Cr, which were 1.72±0.06, 2.17±0.02 and 1.355±0.015 mg/L at the Iwofe Jetty, Minipiti and Police Post sample stations respectively. The least concentrated metal observed in this study was Cd with amean range of 0.03- 0.28 mg/L in the stations. This was followed by the values of Cu from the station which ranged between 0.035 - 1.22 mg/L. The general order of the concentration of metals was Ni>Cr>Fe>Zn>Pb>Cu>Cd. All the metals examined in the water samples except Zn were higher than the WHO maximum standard for drinking water.

Keywords: effluents, discharge points, heavy metals, pollution, contamination.

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Abstract- Water samples were collected at three different effluents discharge points into the New Calabar River. The samples were digested using standard methods. The digests were subsequently examined for heavy metals concentrations using atomic absorption spectrophotometer (AAS). Heavy metals results in the samples showed Ni as the most concentrated metal with a mean value of 2.52±0.055, 1.42±0.01 and 1.275±0.045 mg/L at Iwofe, Jetty, Minipity and Police Post stations respectively, this was followed by the concentration values of Cr, which were 1.72±0.06, 2.17±0.02 and 1.355±0.015 mg/L at the Iwofe Jetty, Minipiti and Police Post sample stations respectively. The least concentrated metal observed in this study was Cd with amean range of 0.03 - 0.28 mg/L in the stations. This was followed by the values of Cu from the station which ranged between 0.035 - 1.22 mg/L. The general order of the concentration of metals was Ni>Cr>Fe>Zn>Pb>Cu>Cd. All the metals examined in the water samples except Zn were higher than the WHO maximum standard for drinking water. Contamination factor analysis showed that the samples were either severely or excessively polluted by most of the metals. However, Zn and Cu were within the range of contamination in the sampled stations. Pollution load index indicated that the stations ranged from severe pollution to excessive pollution. Contamination degree assessment indicated very high degree of contamination and the modified degree of contamination showed that all the stations were within ultra high degree of contamination. Generally, the result indicated a high degree of water pollution by heavy metals at the discharge point. Therefore caution should be taken to control the sources of these pollutants, which have put this aquatic environment under serious threat.

Keywords: effluents, discharge points, heavy metals, pollution, contamination.

I. Introduction

One of the ways through which water is polluted is by the discharge of effluents or wastewater from industries, homes, runoffs, drifts, precipitation, etc (Al-Zubaidi, 2012).The problem of pollution and waste discharge resulted from urban drift issues and industrial development. The concept and reality of waste production is divers in nature and as such, the wastes so generated can take the form of solids and fluids (liquids and gases). To adequately solve or manage pollution issues, the nature and origin of the pollutant must be ascertained. This will help in the general application of the type of treatment system to be put in place (Abedi and Najafi, 2001).

One of the most commonly found pollutants in effluent discharge are heavy metals. They are known to be toxic and have accumulative tendencies in living organisms. Heavy metals do not easily decompose or undergo biological reactions. They are known to produce negative effects on the environment and are subsequently become part of the food chain. When humans eventually consume these organisms, they become toxic and eventually cause different diseased conditions (Mansourri and Madani, 2016).

Heavy metals are implicated in different health problems such as dwarfism, developmental disorders, cancer, organs destruction and malfunction, nervous system impairment, and in extreme cases, mortality (Iyamaet al., 2014). Exposure or contact with some heavy metals, namely mercury and lead, it even low concentrations can result in self destruction or breakdown of the immune system. Lowered immune system leadsto a combination of diseases like rheumatoid arthritis, kidneys disease andbrain damage which is not reversible. At higher doses, heavy metals can cause irreversible brain damage (Barakat, 2010).

The introduction of high concentrations of heavy metals into aquatic environment leads to grave health and environmental consequences, such as illness, wastewater treatment cost and application of the water for irrigation purposes. In nature, heavy metals are present in trace quantities in most cases. They enter into water bodies through leakage from rocks, fly ash or dust, forest fires, volcanic eruption and foliage from vegetation (Ogoyi *et al*., 2011). The effluent arising from domestic and industrial activities are in most cases discharged into aquatic water bodies such as rivers, streams, estuaries, etc. This action results in the pollution load or burden on that aquatic environment receiving the discharged effluents. Therefore, this study was undertaken to examine the concentrations of some heavy metals at the discharge point along the New Calabar River.

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II. MATERIALS AND METHODS

Water samples were collected at the different effluent discharge points into the New Calabar at low tide with plastic bottles previously washed plastic bottles. The samples were collected twice each in the different seasons. The water samples were collected at a depth of 20 cm below the water surface. The samples were fixed on site by the addition of two drops of70% concentrated nitric acid and mixed thoroughly after corking it. The samples were transported to the laboratory in an ice pack container and then stored in at a temperature of 4°C.

In the laboratory, the samples were prepared for analysis, first by digesting them with amixture of mineral acids (Marcus and Edori, 2017) and heated in a steam bath to obtain a clear colour and the content filtered with size 1 Whatmann filter paper.

The filtrates or digest were subjected to metal analysis using atomic absorption spectrophotometer (AAS), model SE-71906 UK. The results obtained were validated by taking three different measurement and further validation by comparing with the values obtained from standard laboratory samples. Mean ± Standard deviations were used to represent the data obtained for the seasons.

The data obtained for the heavy metals were subjected to contamination factor (CF), pollution load index (PLI), degree of contamination (CD) and modified degree of contamination (mCD) analysis. The different formulae used were:

$CF = \frac{Concentration\ \ of\ metal\ in\ measured\ \ sample\ \ (Cm)}{Concentration\ \ of\ metal\ at\ backgroud\ \ level\ (Cb)}$ (Lacatusu, 2000),

$PLI = CFI\ \times CF2\ \times CF3\ \times CF4 \ldots \ldots \ldots \ldots \times CFn)1/n$ (Thomilson *et al*., 1980),

Where $CFI\ \times CF2\ \times CF3\ \times CF4 \ldots \ldots \ldots \ldots \times CFn$ are the individual contamination factors of the different elements to the nth number and 1/n is the nth root of the number of metals measured.

$CD = \sum_{I=1}^{N} CFI$ (Hakanson, 1980)

$\mathrm{mCd} = \frac{1}{N} \sum_{I=1}^{N} CFI$ (Hakanson, 1980)

Where, *N* is the number of elements determined, *CF* is the contamination factor, CD is the contamination degree and mCD is the modified contamination degree.

III. RESULTS AND DISCUSSION

The data for the both dry and rainy seasons and the mean values are given in Tables 1-3. It was observed that in both seasons that the concentrations of the heavy metals were more at the Iwofe station than the other station. Also, the results in both dry and rainy season were not statistically different.

The results obtained for copper (Cu) at Iwofe and Minipitistations were higher than the required value for drinking water by WHO, while the values obtained at the police Post station was lower than the WHO standard. The concentration values obtained for Cu in this work is similar to those observed by Marcus and Edori (2016) in two other rivers within the state. Cu, though an essential metal at low concentrations, is known to be toxic at reasonably higher concentrations. Health implications of Cu to humans after high level in take include liver and kidney injury, anaemia, stomach pain, vomiting, headache and vomiting in children (Salem *et al*., 2000).

The concentration values obtained for Pb in the various stations were all higher than the WHO maximum value for drinking water. The findings on Pb in this work corroborates the findings of other authors (Marcus and Eori, 2016; Stanley *et al*., 2017). However, the values obtained for Pb were higher than those observed in another study of effluents from the petrochemical industry discharged into Ekerekana River (Marcus and Edori, 2017) and oily waste water effluents (Wokoma and Edori, 2017) and those obtained by Jenyo-Oni and Oladele, (2016). Lead Pb as a metal is not required by both plants and animals at any concentration. It is considered as a poison or toxicant even at very low concentrations (Edori and Edori, 2012). Pb is associated with different diseased conditions such as blood poisoning and reduced acumen, lesserIQ, neurobehavioral disorder, hearing and speech deformations, growth retardation and irregular behavior in children (Hertz-Picciotto, 2000), while in adults, it causes low sperm count, and induces abortion in women (Flora *et al*., 2007). Other effects of Pb may include brain and kidney impairment, intestinal diseases and distortion in vitamin D production (Apostoliet *al*., 1998).

The values obtained for Zn in the various stations were below the WHO standard. Zn is an essential micronutrient required in both plants and animals at trace level for effective biochemical functions (Meshram *et al*., 2012). The low level of Zn in this work is in agreement with observations made by other authors in similar environments (Olufemi *et al*., 2011; Bhardwaj *et al*., 2017), but quite lower than those observed in surface water in Esi River, Western Niger Delta (Akporido and Onianwa, 2015).Low intake of zinc in pregnant women can result in birth defects.

The values obtained for Cd in the different sampled station were above the recommended WHO levels in drinking water. The values recorded for Cd in this work at the Iwofe Jetty are higher than those observed by Wokhe, (2015) in another Nigerian River, but fall within the range observed by Olufemi *et al*., (2011) in another river in Nigeria. However, the values obtained in the other two stations (Minipiti and Police Post) were within the range observed in other studies elsewhere and Nigeria (Manoj *et al*., 2012; Wokhe, 2015; Ibrahim *et al*., 2016). Cadmium (Cd) is an unwanted metal in both plants and animals. It has not been documented to activate any aspect of plant or animal life, rather it is considered as a pollutant and toxicant to the environment (Banerjee, 2003).Exposure to both short and long term is associated with different organ dysfunctions and diseased conditions such as hypertension, decrease in weight, anaemia, lymphocytosis, increased protein content in urine, emphysema and lung fibrosis (if inhaled), atherosclerosis, stomach and back pains, and marginal neuropathy. Others are cough, pneumonia and general body weakness(Tchounwou *et al*., 2014).

The concentrations of Fe in all the sample stations were higher than the maximum recommended value of 0.03 mg/L by WHO. Iron (Fe) is a very vital metal required by both animals and plants for metabolic functions (Xing and Liu, 2011). Fe is a component of blood, and it is the element that is responsible for the colour of blood. At concentrations greater than 0.03mg/L, it adds taste and colour to water (Iyama *et al*., 2014). The speciation of Fe in water bodies are either in the Fe (II) or Fe (III) states. Fe deficiency leads to anaemic conditions where resistance to diseases is reduced (Banjari *et al*., 2015).

The values observed for Ni in the various stations were all higher than the WHO standard value for drinking water. The values observed for Ni in this study were higher than those observed in Ubeji River (Olufemi *et al*., 2011), Ijana River, Warri (Owamah, 2013) and Lake Asejire (Jenyo-Oni, and Oladele, 2016).Ni as an important element play some role in body metabolism such as activation of enzymes. It is present in both plants and animals. However, at high concentrations, it becomes toxic to consumers (Divrikli *et al*., 2003).

The values obtained for Cr in the water samples from the various stations were higher than the acceptable limit in drinking water. Chromium (Cr) concentrations observed in this work were above the values observed in other work in similar environments (Owamah, 2013; Shakirat and Akinpelu, 2013; Jenyo-Oni, and Oladele, 2016). Chromium (Cr) exist in different oxidations states, of which the most stable are the +3 and +6 oxidation states. It has been found that its toxicity is manifested in humans or animals when consumed as Cr (III), thatis in the +3 oxidation state (Tchounwou *et al*., 2014).

Table 1: Heavy metals concentration at the different effluents discharge points into the New Calabar River in the dry season

Heavy metals (mg/L)	Location		
	Iwofe Jetty	Minipiti	Police Post
Copper (Cu)	1.23 ± 0.03	0.04 ± 0.00	0.27 ±0.01
Lead (Pb)	1.34 ± 0.00	0.64 ± 0.02	0.48 ±0.07
Zinc (Zn)	1.69 ± 0.12	1.33 ± 0.21	0.84 ± 0.10
Cadmium (Cd)	0.25 ± 0.00	0.06 ± 0.00	0.03 ± 0.00
Iron (Fe)	1.44 ± 0.02	1.19 ± 0.03	0.79 ± 0.21
Nickel (Ni)	2.57 ± 0.23	1.43 ± 0.11	1.23 ± 0.08
Chromium (Cr)	1.78 ± 0.13	2.19 ± 0.16	1.34 ± 0.41

Table 2: Heavy metals concentration at the different effluents discharge points into the New Calabar River in the rainy season

Heavy metals (mg/L)	Location		
	Iwofe Jetty	Minipiti	Police Post
Copper (Cu)	1.21± 0.16	0.03 ± 0.00	0.24 ± 0.01
Lead (Pb)	1.25 ± 0.02	0.70 ± 0.02	0.43 ± 0.11
Zinc (Zn)	1.31 ± 0.12	1.29 ± 0.34	0.91 ± 0.24
Cadmium (Cd)	0.31 ± 0.00	0.04 ± 0.01	0.03 ± 0.00
Iron (Fe)	1.32 ± 0.05	1.15 ± 0.25	0.68 ± 0.02
Nickel (Ni)	2.46 ± 0.12	1.41 ± 0.04	1.32 ± 0.21
Chromium (Cr)	1.66 ± 0.48	2.15 ± 0.35	1.37 ± 0.41

Table 3: Mean concentrations of heavy metals in the two seasons at the effluents discharge points into the New Calabar River

Heavy metals (mg/L)	Location			WHO Standard
	Iwofe Jetty	Minipiti	Police Post	
Copper (Cu)	1.22±0.01	0.035±0.005	0.255±0.015	1.00
Lead (Pb)	1.295±0.045	0.67±0.03	0.455±0.025	0.01
Zinc (Zn)	1.5±0.19	1.31±0.02	0.875±0.035	3.0
Cadmium (Cd)	0.28±0.03	0.05±0.01	0.03±0.00	0.003
Iron (Fe)	1.38±0.06	1.17±0.02	0.735±0.055	0.03
Nickel (Ni)	2.52±0.055	1.42±0.01	1.275±0.045	0.02
Chromium (Cr)	1.72±0.06	2.17±0.02	1.355±0.015	0.05

The result of the contamination index of the heavy metals is shown in Table 4. Based on the intervals of contamination proposed by Lacatusu, (2000), Cu was uncontaminated at the Minipiti sample station, slightly contaminated at the Police Post sample station and slightly polluted at the Iwofe Jetty sample station. Zinc (Zn) showed moderate contamination in all the sampled stations. Cadmium showed very severe pollution at the Police Post station and excessive pollution at Minipiti and Iwofe Jetty stations. The three stations examined showed that the water were excessively polluted with lead (Pb), iron (Fe), nickel (Ni) and chromium (Cr).

The observed values of contamination index in this work were higher than those observed by Marcus and Edori, (2017) at Ekerekana River due to refinery wastewater.

Table 4: Contamination index of heavy metals of water samples at the Effluents discharge points

Heavy metals (mg/L)	Location		
	Iwofe Jetty	Minipiti	Police Post
Copper (Cu)	1.22	0.035	0.255
Lead (Pb)	129.5	67	45.5
Zinc (Zn)	0.5	0.44	0.292
Cadmium (Cd)	93.33	16.67	10
Iron (Fe)	46.0	39.0	24.5
Nickel (Ni)	126.0	71.0	63.75
Chromium (Cr)	34.4	43.4	27.1

The result of pollution load index, degree of contamination and modified degree of contamination is given in Table 5.The results obtained for Pollution load indexproposed by (Thomilson et al., 1980)when analysed based on Lacatusu(2000), incidence of contamination or pollution chart indicated that Iwofe Jetty location was excessively polluted, Minipiti and Police Post stations were severely polluted. In all the sampled stations, using contamination degree assessment, there was a marked observation of very high degree of contamination when the result obtained in these locations were compared with Hakanson (1980) terminologies on contamination levels of water and sediment polluted or contaminated with heavy metals. The modified degree of contamination which was proposed by Hakanson (1980) result showed that all the sampled stations fall within the ultra high degree of contamination.

Table 5: Pollution load index (PLI) and degree of contamination (CD) and modified degree of contamination (mCD) of water samples at the Effluents discharge points

Pollution Description	Iwofe Jetty	Minipiti	Police Post
PLI	20.399	7.981	7.443
CD	430.95	237.565	171.397
mCD	61.429	33.938	24.485

IV. CONCLUSION

The result obtained from this work is an indication of anthropogenic pollution. The concentrations of the heavy metals in the various drainage outlets showed higher values than those of the standard. Therefore the water is not suitable for consumption. Efforts should be put in place to check all the input sources to make sure that they do not discharge beyond the allowable concentrations of these metals from their effluents, otherwise there is the likely hood of pollution explosion arising from heavy metals.

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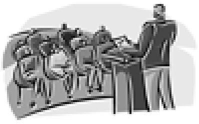

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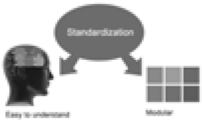

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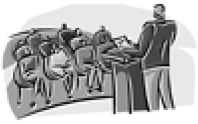

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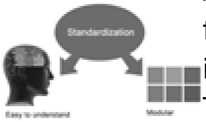

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f) Results which should be presented concisely by well-designed tables and figures.
g) Suitable statistical data should also be given.
h) All data must have been gathered with attention to numerical detail in the planning stage.

Design has been recognized to be essential to experiments for a considerable time, and the editor has decided that any paper that appears not to have adequate numerical treatments of the data will be returned unrefereed.

i) Discussion should cover implications and consequences and not just recapitulate the results; conclusions should also be summarized.
j) There should be brief acknowledgments.
k) There ought to be references in the conventional format. Global Journals recommends APA format.

Authors should carefully consider the preparation of papers to ensure that they communicate effectively. Papers are much more likely to be accepted if they are carefully designed and laid out, contain few or no errors, are summarizing, and follow instructions. They will also be published with much fewer delays than those that require much technical and editorial correction.

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

FORMAT STRUCTURE

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

All manuscripts submitted to Global Journals should include:

Title

The title page must carry an informative 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) where the work was carried out.

Author details

The full postal address of any related author(s) must be specified.

Abstract

The abstract is the foundation of the research paper. It should be clear and concise and must contain the objective of the paper and inferences drawn. It is advised to not include big mathematical equations or complicated jargon.

Many researchers searching for information online will use search engines such as Google, Yahoo or others. By optimizing your paper for search engines, you will amplify the chance of someone finding it. In turn, this will make it more likely to be viewed and cited in further works. Global Journals has compiled these guidelines to facilitate you to maximize the web-friendliness of the most public part of your paper.

Keywords

A major lynchpin of research work for the writing of research papers is the keyword search, which one will employ to find both library and internet resources. Up to eleven keywords or very brief phrases have to be given to help data retrieval, mining, and indexing.

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

Choice of the main keywords is the first tool of writing a research paper. Research paper writing is an art. Keyword search should be as strategic as possible.

One should start brainstorming lists of potential keywords before even beginning 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 a research paper?" Then consider synonyms for the important words.

It may take the discovery of only one important paper to steer in the right keyword direction because, in most databases, the keywords under which a research paper is abstracted are listed with the paper.

Numerical Methods

Numerical methods used should be transparent and, where appropriate, supported by references.

Abbreviations

Authors must list all the abbreviations used in the paper at the end of the paper or in a separate table before using them.

Formulas and equations

Authors are advised to submit any mathematical equation using either MathJax, KaTeX, or LaTeX, or in a very high-quality image.

Tables, Figures, and Figure Legends

Tables: Tables should be 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. Authors must submit tables in an editable format and not as images. References to these tables (if any) must be mentioned accurately.

Figures

Figures are supposed to be submitted as separate files. Always include a citation in the text for each figure using Arabic numbers, e.g., Fig. 4. Artwork must be submitted online in vector electronic form or by emailing it.

PREPARATION OF ELETRONIC FIGURES FOR PUBLICATION

Although low-quality images are sufficient for review purposes, print publication requires high-quality images to prevent the final product being blurred or fuzzy. Submit (possibly by e-mail) EPS (line art) or TIFF (halftone/ photographs) files only. MS PowerPoint and Word Graphics are unsuitable for printed pictures. Avoid using pixel-oriented software. Scans (TIFF only) should have a resolution of at least 350 dpi (halftone) or 700 to 1100 dpi (line drawings). 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: Authors are advised 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. Also, you can email your editor to remove the color fee after acceptance of the paper.

TIPS FOR WRITING A GOOD QUALITY SCIENCE FRONTIER RESEARCH PAPER

Techniques for writing a good quality Science Frontier Research paper:

1. Choosing the topic: In most cases, the topic is selected by the interests of the author, but it can also be suggested by the guides. You can have several topics, and then judge which you are most comfortable with. This may be done by asking several questions of yourself, like "Will I be able to carry out a search in this area? Will I find all necessary resources to accomplish the search? Will I be able to find all information in this field area?" If the answer to this type of question is "yes," then you ought to choose that topic. In most cases, you may have to conduct surveys and visit several places. Also, you might have to do a lot of work to find all the rises and falls of the various data on that subject. Sometimes, detailed information plays a vital role, instead of short information. Evaluators are human: The first thing to remember is that evaluators are also human beings. They are not only meant for rejecting a paper. They are here to evaluate your paper. So present your best aspect.

2. Think like evaluators: If you are in confusion or getting demotivated because your paper may not be accepted by the evaluators, then think, and try to evaluate your paper like an evaluator. Try to understand what an evaluator wants in your research paper, and you will automatically have your answer. 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.

3. Ask your guides: If you are having any difficulty with your research, then do not hesitate to share your difficulty with your guide (if you have one). They will surely help you out and resolve your doubts. If you can't clarify what exactly you require for your work, then ask your supervisor to help you with an alternative. He or she might also provide you with a list of essential readings.

4. Use of computer is recommended: As you are doing research in the field of science frontier then this point is quite obvious. Use right software: Always use good quality software packages. If you are not capable of judging good software, then you can lose the quality of your paper unknowingly. There are various programs available to help you which you can get through the internet.

5. Use the internet for help: An excellent start for your paper is using Google. It is a wondrous search engine, where you can have your doubts resolved. You may also read some answers for the frequent question of how to write your research paper or find a model research paper. You can download books from the internet. If you have all the required books, place importance on reading, selecting, and analyzing the specified information. Then sketch out your research paper. Use big pictures: You may use encyclopedias like Wikipedia to get pictures with the best resolution. At Global Journals, you should strictly follow here.

6. Bookmarks are useful: When you read any book or magazine, you generally use bookmarks, right? It is a good habit which helps to not lose your continuity. You should always use bookmarks while searching on the internet also, which will make your search easier.

7. Revise what you wrote: When you write anything, always read it, summarize it, and then finalize it.

8. Make every effort: Make every effort to mention what you are going to write in your paper. That means always have a good start. Try to mention everything in the introduction—what is the need for a particular research paper. Polish your work with good writing skills and always give an evaluator what he wants. Make backups: When you are going to do any important thing like making a research paper, you should always have backup copies of it either on your computer or on paper. This protects you from losing any portion of your important data.

9. Produce good diagrams of your own: Always try to include good charts or diagrams in your paper to improve quality. Using several unnecessary diagrams will degrade the quality of your paper by creating a hodgepodge. So always try to include diagrams which were made by you to improve the readability of your paper. Use of direct quotes: When you do research relevant to literature, history, or current affairs, then use of quotes becomes essential, but if the study is relevant to science, use of quotes is not preferable.

10. Use proper verb tense: Use proper verb tenses in your paper. Use past tense to present those events that have happened. Use present tense to indicate events that are going on. Use future tense to indicate events that will happen in the future. Use of wrong tenses will confuse the evaluator. Avoid sentences that are incomplete.

11. Pick a good study spot: Always try to pick a spot for your research which is quiet. Not every spot is good for studying.

12. Know what you know: Always try to know what you know by making objectives, otherwise you will be confused and unable to achieve your target.

13. Use good grammar: Always use good grammar and words that will have a positive impact on the evaluator; use of good vocabulary does not mean using tough words which the evaluator has to find in a dictionary. Do not fragment sentences. Eliminate one-word sentences. Do not ever use a big word when a smaller one would suffice.

Verbs have to be in agreement with their subjects. In a research paper, do not start sentences with conjunctions or finish them with prepositions. When writing formally, it is advisable to never split an infinitive because someone will (wrongly) complain. Avoid clichés like a disease. Always shun irritating alliteration. Use language which is simple and straightforward. Put together a neat summary.

14. 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 for your topic. You may also maintain your arguments with records.

15. Never start at the last minute: Always allow enough time for research work. Leaving everything to the last minute will degrade your paper and spoil your work.

16. Multitasking in research is not good: Doing several things at the same time is a bad habit in the case of research activity. Research is an area where everything has a particular time slot. Divide your research work into parts, and do a particular part in a particular time slot.

17. Never copy others' work: Never copy others' work and give it your name because if the evaluator has seen it anywhere, you will be in trouble. Take proper rest and food: No matter how many hours you spend on your research activity, if you are not taking care of your health, then all your efforts will have been in vain. For quality research, take proper rest and food.

18. Go to seminars: Attend seminars if the topic is relevant to your research area. Utilize all your resources.

19. Refresh your mind after intervals: Try to give your mind a rest by listening to soft music or sleeping in intervals. This will also improve your memory. Acquire colleagues: Always try to acquire colleagues. No matter how sharp you are, if you acquire colleagues, they can give you ideas which will be helpful to your research.

20. Think technically: Always think technically. If anything happens, search for its reasons, benefits, and demerits. Think and then print: When you go to print your paper, check that tables are not split, headings are not detached from their descriptions, and page sequence is maintained.

21. Adding unnecessary information: Do not add unnecessary information like "I have used MS Excel to draw graphs." Irrelevant and inappropriate material is superfluous. Foreign terminology and phrases are not apropos. One should never take a broad view. Analogy is like feathers on a snake. Use words properly, regardless of how others use them. Remove quotations. Puns are for kids, not grunt readers. Never oversimplify: When adding material to your research paper, never go for oversimplification; this will definitely irritate the evaluator. Be specific. Never use rhythmic redundancies. Contractions shouldn't be used in a research paper. Comparisons are as terrible as clichés. Give up ampersands, abbreviations, and so on. Remove commas that are not necessary. Parenthetical words should be between brackets or commas. Understatement is always the best way to put forward earth-shaking thoughts. Give a detailed literary review.

22. Report concluded results: Use concluded results. From raw data, filter the results, and then conclude your studies based on measurements and observations taken. An appropriate number of decimal places should be used. Parenthetical remarks are prohibited here. Proofread carefully at the final stage. At the end, give an outline to your arguments. Spot perspectives of further study of the subject. Justify your conclusion at the bottom sufficiently, which will probably include examples.

23. Upon 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 for 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 of 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 criteria peer reviewers will use for grading the final paper.

Final points:

One purpose of organizing a research paper is to let people interpret your efforts selectively. The journal requires the following sections, submitted in the order listed, with each section starting on a new page:

The introduction: This will be compiled from reference matter and reflect the design processes or outline of basis that directed you to make a study. As you carry out the process of study, the method and process section will be constructed like that. The results segment will show related statistics in nearly sequential order and direct reviewers to similar intellectual paths throughout the data that you gathered to carry out your study.

The discussion section:

This will provide understanding of the data and projections as to the implications of the results. The use of good quality references throughout the paper will give the effort trustworthiness by representing an alertness to 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 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 avoid:

- Insertion of a title at the foot of a page with subsequent text on the next page.
- Separating a table, chart, or figure—confine each to a single page.
- Submitting a manuscript with pages out of sequence.
- In every section of your document, use standard writing style, including articles ("a" and "the").
- Keep paying attention to the topic of the paper.
- Use paragraphs to split each significant point (excluding the abstract).
- Align the primary line of each section.
- Present your points in sound order.
- Use present tense to report well-accepted matters.
- Use past tense to describe specific results.
- Do not use familiar wording; don't address the reviewer directly. Don't use slang or superlatives.
- Avoid use of extra pictures—include only those figures essential to presenting results.

Title page:

Choose a revealing title. It should be short and include the name(s) and address(es) of all authors. It should not have acronyms or abbreviations or exceed two printed lines.

Abstract: This summary should be two hundred words or less. It should clearly and briefly explain the key findings reported in the manuscript and must have precise statistics. It should not have acronyms or abbreviations. It should be logical in itself. Do not cite 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 approaches 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. Use comprehensive sentences, and do not sacrifice readability for brevity; you can maintain it succinctly by phrasing sentences so that they provide more than a 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 limit the initial two items to no more than one line each.

Reason for writing the article—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 for this; results of any numerical analysis should be reported. Significant conclusions or questions that emerge from the research.

Approach:

- o Single section and succinct.
- o An outline of the job done is always written in past tense.
- o Concentrate on shortening results—limit background information to a verdict or two.
- o Exact spelling, clarity 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 of comprehending and calculating the purpose of your study without having to refer to other works. The basis for the study should be offered. Give the most important references, but avoid making a comprehensive appraisal of the topic. Describe the problem visibly. If the problem is not acknowledged in a logical, reasonable way, the reviewer will give no attention to your results. Speak in common terms about techniques used to explain the problem, if needed, but do not present any particulars about the protocols here.

The following approach can create a valuable beginning:

- Explain the value (significance) of the study.
- Defend the model—why did you employ this particular system or method? What is its compensation? Remark upon its appropriateness from an abstract point of view as well as pointing out sensible reasons for using it.
- Present a justification. State your particular theory(-ies) or aim(s), and describe the logic that led you to choose them.
- Briefly explain the study's tentative purpose and how it meets 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 for every section. If you make the four points listed above, you will need at least four paragraphs. Present surrounding information only when it is necessary to support a situation. The reviewer does not desire to read everything you know about a topic. Shape the theory 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 soundly written procedures segment allows a capable scientist to replicate 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 to give the least amount of information that would permit another capable scientist to replicate 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 section, mention the specific item describing the way, but draw the basic principle while stating the situation. The purpose is to show 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:

Materials may be reported in part of a section or else they may be recognized along with your measures.

Methods:

- Report the method and not the 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—detail how procedures were completed, not how they were performed on a particular day.
- If well-known procedures were used, account for the procedure by name, possibly with a reference, and that's all.

Approach:

It is embarrassing to use vigorous voice when documenting methods without using first person, which would focus the reviewer's interest on the researcher rather than the job. As a result, when writing up the methods, most authors use third person passive voice.

Use standard style in this and 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 as 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. Use statistics and tables, if suitable, to present consequences most efficiently.

You must clearly differentiate material which would usually be incorporated in a study editorial from any unprocessed data or additional appendix matter that would not be available. In fact, such matters should not be submitted at all except if requested by the instructor.

Content:

- Sum up your conclusions in text and demonstrate them, if suitable, with figures and tables.
- In the manuscript, explain each of your consequences, and point the reader to remarks that are most appropriate.
- Present a background, such as by describing the question that was addressed by creation of an exacting study.
- Explain results of control experiments and give 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 manuscript.

What to stay away from:

- Do not discuss or infer your outcome, report surrounding information, or try to explain anything.
- Do not include raw data or intermediate calculations in a research manuscript.
- Do not present similar data more than once.
- A manuscript should complement any figures or tables, not duplicate information.
- Never confuse figures with tables—there is a difference.

Approach:

As always, use past tense when you submit 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 section.

Figures and tables:

If you put figures and tables at the end of some details, make certain that they are visibly distinguished from any attached appendix materials, such as raw facts. Whatever the position, each table must be titled, numbered one after the other, and include a heading. All figures and tables must be divided from the text.

Discussion:

The discussion is expected to be the trickiest segment to write. A lot of papers submitted to the journal are discarded based on problems with the discussion. There is no rule for how long an 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 implications of the study. The purpose here is to offer an understanding of your results and support all of your conclusions, using facts from your research and generally accepted information, if suitable. The implication of results should be fully 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 the prospect, and let it drop at that. Make a decision as to whether each premise is supported or 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 an experiment might be personalized to accomplish a new idea.
- Give details of all of your remarks as much as possible, focusing on mechanisms.
- Make a decision as to whether the tentative design sufficiently addressed the theory and whether or not it was correctly restricted. Try to present substitute explanations if they are sensible alternatives.
- One piece of 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 other available information. Present work done by specific persons (including you) in past tense.

Describe generally acknowledged facts and main beliefs in present tense.

The Administration Rules

Administration Rules to Be Strictly Followed before Submitting Your Research Paper to Global Journals Inc.

Please read the following rules and regulations carefully before submitting your research paper to Global Journals Inc. to avoid rejection.

Segment draft and final research paper: You have to strictly follow the template of a research paper, failing which your paper may get rejected. You are expected to write each part of the paper wholly on your own. The peer reviewers need to identify your own perspective of the concepts in your own terms. Please do not extract straight from any other source, and do not rephrase someone else's analysis. Do not allow anyone else to proofread your manuscript.

Written material: You may discuss this with your guides and key sources. Do not copy anyone else's paper, even if this is only imitation, otherwise it will be rejected on the grounds of plagiarism, which is illegal. Various methods to avoid plagiarism are strictly applied by us to every paper, and, if found guilty, you may be blacklisted, which could affect your career adversely. To guard yourself and others from possible illegal use, please do not permit anyone to use or even read your paper and file.

CRITERION FOR GRADING A RESEARCH PAPER (COMPILATION) BY GLOBAL JOURNALS

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.

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

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