Journal of Chemical and Pharmaceutical Research



J. Chem. Pharm. Res., 2010, 2(3):673-683

ISSN No: 0975-7384 CODEN(USA): JCPRC5

Surface Coverage and Adsorption Study of Dye Uptake by Derived Acid and Base Treated Mango Seed Shells

Itodo, H.U. and Itodo A.U. *

Department of Chemistry, Benue State University, Makurdi, Nigeria *Department of Applied Chemistry, Kebbi State University of Science and Technology, Aliero, Nigeria

ABSTRACT

Sulfuric acid (H_2SO_4) and Sodium hydroxide (NaOH) treated mango seed shells, subjected to a one way activation scheme was employed to study the adsorption capacities, intensities and mode of coverage of synthetic (commercial) dye uptake. Adsorption data obtained in this study indicate that the sorption of dye increases linearly with initial dye concentration. The adsorption data fitted well into both the Freundlich and Langmuir isotherms as indicated by high correlation of determination ($R^2 > 0.9$) in both cases. Mode of surface coverage however was best predicted by the Freundlich isotherm (heterogeneity) for the home base activated carbon as does the Langmuir model (homogeneous coverage) for the reference commercial carbon. According to this study, percent dye removal (>64%) was reportedly estimated for derived biosorbent as against a fairly higher value (> 86) for the reference carbon. Proximity of generated data to those reviewed in literatures, is an indication that mango seed shells could compare, to a good extent with commercial activated carbon for organic dye removal from waste dyestuff.

Key words: Surface Coverage, Adsorption, Methylene blue, Mango Shells

INTRODUCTION

The first evidence of polluted water is its colour and this is as a result of dissolved organic compound or highly coloured industrial waste. The appearance of colour in water is caused by the absorption of certain wavelength of normal light by the presence of coloured substance and light scattering caused by suspended matter. Millennium target is to achieve a way in which waste water can be recycled and reused and the best absorbent that can be used to absorb this colour as the activated carbon.

Activated carbons are high porosity, high surface area material manufactured by carbonization and activation of carbonaceous materials which find extensive use in the adsorption of pollutants from gaseous and liquid streams [1]. Activated carbon is a carbonaceous material which is amorphous in nature and in which a high degree of porosity is developed by the process of manufacturing and treatment [2]. Its high degree of porosity and surface area makes it the most versatile absorbent to be used for effective removal of organic solid that has extraordinarily large internal surface and pore volumes. The intrinsic properties of activated carbon are dependent on the raw material source [4]. Activated carbon with high specific surface area and pore volumes can be prepared from a variety of carbonaceous material such as coal, coconut shell, wood, agricultural wastes and industrial wastes. In industrial practices, coal and coconut shell are the two main sources for the production of activated carbon [4]. Other materials like lignite, petroleum, coke, saw dust, peat, fruit pits and nut shell may be to manufacture activated carbon but the properties of the finished material are governed not only by the raw material used but also the method of activation used. The source of this raw material was based on the need for developing low cost absorbent for pollution control as well as reducing the effect of environmental degradation poised by agricultural waste.

In early days of activated carbon, the source materials were mainly bone char and animal blood. Coke, coal bitumen and wood are some other raw materials for the production of activated carbon which later took the centre stage for reason of their availability [2]. Investigation showed that the source materials used to prepare activated carbon have significance effect on its pore structure, surface texture, resistance to fragmentation, and adsorption capacity. It is also necessary to use source materials which are economical and readily available for the manufacture of activated carbon. This is the reason why a wide variety of activated carbon has been prepared from agricultural waste. These agricultural wastes which are potential hazard in the environment and have little or no economic values are sourced cheaply and converted into activated carbon. Some of the waste that has been converted successfully into activated carbon is rice husk and rubber seed shell [5], coconut and groundnut shells [6], coconut tree, sawdust and coconut husk [7] among others.

Activated carbon from these materials has been used effectively to remove metal ions such as Cr^{3+} [10], Cd^{2+} , Ni^{2+} , Pb^{2+} , dye from textile effluent and other organics [8] to mention but a few. In selection of these materials, several factors which include: Industrially inexpensive material with high carbon and low inorganic (i.e low ash) content is preferred [9] and high density of precursor and sufficient volatile content are of considerable importance. This high density contributes to enhanced structural strength of the carbon, essential to withstand excessive particle crumble during use [9] are considered.

Adsorption is the collection of a substance onto the surface of adsorbent solids. It is a removal process where certain particles are bound to an adsorbent surface by either physical or chemical attraction [10]. It is also the formation of layer of gas, liquid or solid to the surface of a solid or less frequently a liquid [11]. Adsorption occurs at solid-solid, gas-solid, liquid-liquid and liquid-gas interfaces [12]. It is often confused with absorption, where the substance being collected or removed actually penetrate into the solid. The reason why activated carbon is such an effective adsorbent material is due to its large number of pores. These provide a large surface area, relative to the size of the actual carbon particle

Adsorption isotherm is a functional expression for the variation of adsorption relative to the concentration of adsorbate in the bulk solution at constant temperature [13]. It describes the relation of between the adsorbate retained by the activated carbon and the adsorbate equilibrium concentration [13]. It was defined as a graphical representation showing the relationship between the amounts adsorbed by a unit weight of adsorbent for example activated carbon and the amount of adsorbate remaining in a test medium of equilibrium. It maps the distribution of adsorb able solute between the liquid and solid phases at various equilibrium concentration [15].

The adsorption isotherm is based on data that are specific for each system and the isotherm must be determined for every application. An adsorption isotherm besides providing a panorama of the course taken by the system under study in a concise form, it indicates how efficiently a carbon will allow an estimate of the economic feasibility of the carbons commercial application for the specific solute [15]. The major factors in determining the shape of an isotherm are:The number of compound in the solution, relative adsorb abilities of the compound, initial concentration of the solution, degree of competition among solutes for adsorption sites and characteristics of the generated carbon.

Adsorption isotherm can be generated based on numerous theoretical explanations and the two (2) main and well known isotherm models for surface coverage studies include; Langmuir isotherm and Freundlich isotherm models.

The theoretical conception behind the Langmuir isotherm is summarized below:

- i. The adsorption is an equilibrium process
- ii. The adsorption can not proceed beyond monolayer coverage
- iii. All sites are equivalent and the surface is uniform, i.e. the surface is perfectly flat on a microscopic scale.

The ability of a molecule to adsorb at a given site is independent of the occupation of the neighbouring sites. The relation between equilibrium surface coverage and gas pressure is thus, obtained by equating the expression below which holds for the Langmuir isotherm

Two convenient linear forms of the Langmuir equation are;

c/ $q_e = 1/bQ^0 + c/Q^0$ ------(1) 1/ $q_e = 1/Q^0 + [b/bQ^0] [1/c]$ -----(2)

A plot of $1/q_e$ against 1/c gives a straight line with a slop of $1/bQ^0$ and intercept of $1/Q^0$.

The Freundlich isotherm equation is a special case for heterogeneous surface and it is usually used to measure adsorption from solution in environmental engineering and specifically drinking water treatment application, the Freundlich isotherm is used and is therefore the most popular model for a single solute system. The equation is adequate to describe non-linear adsorption in a narrow range of adsorbate concentration and its mathematical simplicity enables it to be used easily. It also described adsorption processes on surface sites that are energetically heterogeneous. However, theoretically, the amount of adsorbed solute may become infinite as bulk solute concentration increases and this is a disadvantage (Freundlich, 1982 in [14, 15]). The logarithm form of the Freundlich isotherm is given as:

a plot of this equation gives a straight line curve when log qe is plotted against logc with slope as 1/n and intercept as logkf. The kf value increases with the total adsorption capacity of the adsorbent to bind the adsorbate. It is roughly an indicator of adsorption capacity and the 1/n is the adsorption intensity. The numerical value of n is a useful index of adsorption efficiency and is related to the energy of adsorption.

The amount of Dye at equilibrium, q_e is calculated from the mass balance equation given as equation 4 [1]

$$q_e = (C_O - C_e) V/W \dots (4)$$

where C_o and C_e are the initial and final Dye concentrations (mg/L) respectively. V is the volume of dye solution and M is the mass of the acid catalyzed Poultry waste sorbent (g). while t is the equilibrium contact time, when $q_e = qt$, equation 1 will be expressed as equation 5 below[1]

where $q_e = q_t$ and C_t is the concentration at time t. The calculations and graphical representation were performed in the Microsoft Excel package. The percent dye removal (RE %) was calculated for each equilibration by the expression presented as equation 6

 $R E(\%) = (C_0 - C_e)/Co \times 100, \qquad \dots \qquad (6)$

where R (%) is the percent of dye adsorbed or removed. The % removal and adsorption capacities were used to optimize the activation condition.(Maryam *et al.*, 2008). The test were done at a constant temperature of 25 ± 2^{0} C.

In Northern Nigeria, researched on the preparation and adsorption of activated carbon from coconut shell. He reported that coconut shell can be used for both laboratory and industrial purpose depending on their method of preparation. In a joint work, He later studied the adsorption of methylene blue by activated carbon from coconut shell it was also shown from a comparative studied on the adsorption of Azodyes using activated carbon from Arachis Hypogea and Cocus nucifera shells. The result showed that both precursors can be used for the removal of dyes in aqueous solution [5]. work on the preparation and evaluation of activated carbon from the preparation of activated carbon [5]. Widely published research on the generation, adsorption and evaluation of activated carbon from selected animal and agricultural wastes in Northern Nigeria is on the laboratory run [1,11,17,20].

The present study is aimed at generating activated carbon from Mango seed, a locally available agricultural by products, thereby adding value to the waste and reducing solid wastes from the environment, to investigate the adsorptive properties of the prepared activated carbon, to test for type of surface coverage using isotherms, to evaluate and compare the generated data with that of reference commercial carbon. This work is limited to the use of mango seed shells as precursors for the production of activated carbon and its characterization which includes: iodine number, bulk density, pH, conductivity measurement, ash content and others.

EXPERIMENTAL SECTION

A large number of semi dried mango seeds were randomly obtained from waste baskets, waste depots and sites within wuruku market, Makurdi. The collected samples were deseeded. The hard epicarps (shells) were properly washed, using sponge and plenty water to remove all surface impurities and were then sundried. The samples were dried over night in an over at a temperature of 100°c after which they were pounded using a local mortar and pistil followed by sieving. The obtained powdered sample were stored in an air tight container. The method adopted for the sampling was described elsewhere [18]. The reagents employed in this study includes: Mehtylene blue $C_{16}H_{18}CIN_3S$, Concentrated hydrochloric acid and Potassium hydroxide procured from prolabo Chemicals and were of analytical grades.

1200 ppm Methylene Blue Stock Solution was prepared. 0.12g of methylene blue was dissolved in 10cm^3 of distilled water. It was transferred into a 100cm^3 volumetric flask shaken and made to make with distilled water from which a working concentration of between 10 - 50mg/l was prepared. A 1 M solution of each activant;H₂SO₄ and NaOH was prepared. Blank solution was used to monitor possible contamination or remove interference. It was prepared to contain the same volume of reagent used with the exception of methylene blue. Equilibrium data (before and after interaction) was generated from absorbance reading using a spectrophotometer set at a predetermined wavelength of 630nm.

PROXIMATE ANALYSIS

The moisture content, ash content, bulk density, pH measurement, conductivity measurement % yield and % burn off of the were estimated.

Carbonization: This was done using 3g of the pretreated mango shells (sample). It was introduced into six difference preweighed and clean crucibles. The crucible and the pretreated sample were placed in the furnace at a temperature of 500° c for 5 minutes after which the samples were poured down from the crucible into an ice bath. The excess water was drained and the wet sample was sun dried. The process was repeated until a substantial amount of the carbonized sample was obtained. The obtained carbonized sample was washed using 0.1m HCL to remove surface ash which was followed using hot water and finally with distilled water to remove residual acid. The solid obtained was first sun dried and then dried in the oven at a temperature of 100° c for one hour [6]. The percentage yield of the sample on heating was calculated as:-

% yield = weight of sample after carbonization $X \ 100$ - - (7) weight of sample before carbonization Activation process: Here the one step process was used and in this process, 3g of the raw sample was mixed with the activating agent (prepared chemicals) the mixture was left standing for 24 hrs after which it was placed in the furnace at a temperature of $800^{\circ}c$ for five minutes. The sample was removed, poured out into an ice bath, the excess water was drained and the sample was allowed to dry at room temperature. The procedure was repeated for different residual time (5 min and 10 min) using the activating agent [6].

The washed sample was rinsed using distilled water to remove residual acid. The sample was oven dried at temperature of 110°c over night. Washing of the sample was completed when a pH of 6 to 8 was ascertained [16].

Batch Adsorption Test: The batch absorption techniques was used for the experimentation. Here the adsorption test was carried out in batches such that 0.1g of the obtained activated carbon was interacted with 10ml of methylene blue solution using a 20ml Erlenmeyer flask. The mouth of the flask was closed very tight to avoid evaporation of the mixture and was left standing for 24 hrs, the process was followed by filtration using the Whattman filter paper. 10ml of distilled water used as control was also interacted with 0.1g of the activated carbon and was left standing for each of the test. All the test was carried out at a constant temperature of $25\pm 2^{\circ}c$ [6].

RESULTS AND DISCUSSION

Table 1: Bulk density of activated carbon from mango shell using 1M and 2M solution of salt and acid

Bulk density with	1M solution	Bulk density with 2M solution		
Samples	Density	Samples	Density	
MS/H ₂ SO ₄ /5	0.122	MS/H ₂ SO ₄ /5	0.109	
MS/H ₂ SO ₄ /10	0.142	MS/H ₂ SO ₄ /10	0.111	
MS/NaOH/5	0.169	MS/NaOH/5	0.115	
MS/NaOH/10	0.189	MS/NaOH/10	0.116	

Table 2. I ci centage bui il vii vi activateu cai bui fi vin mango snen using fivi anu 201 solution of salt anu av	Table 2: I	Percentage burn	off of activated	l carbon from 1	nango shell using	1M and 2M	solution of	salt and ad
--	------------	-----------------	------------------	-----------------	-------------------	-----------	-------------	-------------

Burn off with 1	M solution	Burn off with 2M solution		
Samples	% burn off	Samples	% burn off	
$MS/H_2SO_4/5$	67.78	MS/H ₂ SO ₄ /5	65.67	
MS/H ₂ SO ₄ /10	70.11	MS/H ₂ SO ₄ /10	69.00	
MS/NaOH/5	74.44	MS/NaOH/5	73.33	
MS/NaOH/10	77.78	MS/NaOH/10	77.78	

Table 3: pH measurement for the 1M and 2M treated acid and salt samples

Sample	pH(1M sample)	pH(2M sample)
Raw sample	5.12	5.12
Comm.	2.94	2.94
MS/H ₂ SO ₄ /5	5.21	5.82
MS/H ₂ SO ₄ /10	6.47	6.58
MS/NaOH/5	7.35	7.64
MS/NaOH/10	8.14	8.10

Samples	Conductivi	ty(µS/cm)
_	(1M sample	(2M sample)
Raw sample	228	228
Comm.	2850	2850
MS/H ₂ SO ₄ /5	250	565
MS/H ₂ SO ₄ /10	193	411
MS/NaOH/5	1820	1058
MS/NaOH/10	872	1047

Table 4: Conductivity measurement for the 1M and 2M treated acid and salt samples

Table 5: Percentage yield of activated carbon from mango shell using 1M and 2M solution of salt and acid at different residual time

% yield for 1M solution		% yield for 2M solution		
Samples	yield (%)	Samples	yield (%)	
$MS/H_2SO_4/5$	32.22	$MS/H_2SO_4/5$	34.33	
MS/H ₂ SO ₄ /10	29.89	MS/H ₂ SO ₄ /10	30.00	
MS/NaOH/5	25.56	MS/NaOH/5	26.67	
MS/NaOH/10	22.22	MS/NaOH/10	22.22	

Table 6a: Concentration of methylene blue treated with 1M of both acid and salt using 0.1g adsorbent per10ml adsorbate measured at 630nm

Samples	10mg/l	15mg/l	20mg/l	25mg/l	50mg/l
Untreated MB	1.524	1.559	1.567	1.569	1.598
Comm.	0.151	0.175	0.213	0.217	0.397
MS/H ₂ SO ₄ /5	0.328	0.301	0.396	0.464	0.564
MS/H ₂ SO ₄ /10	0.354	0.387	0.394	0.542	0.642
MS/NaOH/5	0.395	0.407	0.497	0.542	0.598
MS/NaOH/10	0.433	0.490	0.554	0.529	0.610

Table 6b: Concentration of methylene blue treated with 2M of both acid and salt using 0.1g adsorbent per 10ml adsorbate measured at 630nm

Samples	10mg/l	15mg/l	20mg/l	25mg/l	50mg/l
Untreated MB	1.524	1.559	1.567	1.569	1.598
Comm.	0.101	0.104	0.116	0.213	0.217
MS/H ₂ SO ₄ /5	0.142	0.156	0.211	0.228	0.310
MS/H ₂ SO ₄ /10	0.162	0.166	0.191	0.237	0.401
MS/NaOH/5	0.149	0.155	0.151	0.157	0.239
MS/NaOH/10	0.113	0.127	0.158	0.236	0.226

Table 6c: Freundlich and Langmuir isotherms parameters of Methylene Blue uptake by Mango shell Activated Carbon

Isotherms	Eqn $(y =)$	\mathbb{R}^2	Parameters	Values.
Enough dligh Comm	0.594 ± 0.112	0.020	1/n	0.584
Fleundhein Comm.	$0.364x \pm 0.112$	0.939	\mathbf{k}_{f}	1.294
Langmuir Comm.	0.557x+0.199	0.958	q _m (mg/g)	5.029
Enoundlich MAC	0.601×0.249	0.075	1/n	0.601
Freundlich MAC.	0.001X-0.248	0.975	k _f	0.564
Langmuir MAC.	1.966x+0.241	0.958	$q_m(mg/g)$	4.149

 $MAC - 1M H_2SO_4$ treated Mango shell activated carbon. Comm.- Commercial activated carbon K_F (units in mgg⁻¹ ($1mg^{-n(n)}$)

Proximate Analysis : Estimation of certain physicochemical parameters is critical in characterizing the adsorbents. The optimum temperature for activation was experimentally determined elsewhere to range between 600- 800°c above which high level of residual ash sets in [32,33].

(i) Comparison on tables 1 revealed that the bulk density of the carbon reduced considerably for high (2M) activated samples and could be linked to corrosive effect of the chemical on the biomass during pore formation (Table 1)

(ii) Activation burn off is high with a resultant low % yield at a longer activation dwell time (Table 2).

(iii) The commercial carbon was designed to function as acidic carbon (pH <3) and could be prescribed for specific applications (Table 3).

(iv) Adsorption by Commercial and NaOH carbon could be through ion exchange with ionic sorbate order than physisorption alone. This could be predicted from their conductivity result (Table 4)

(v) The % yield is least for the 10 minutes scheme as a result of a more thermal decomposition with more ash deposition or volatilization, resulting from an initial pyrolysis followed by activation. (Table 5)

Effect of activating agent and activant concentration

Screening test based on absorbance reading was first conducted to obtain the run and series that could compete well with the commercial carbon upon which further analysis in this research will rely. It is believe that there is an inverse relationship between absorbance and adsorption as earlier predicted by the Beer Lambert relationship. Hence, Table 6b showed that absorbance reading by $1M H_2SO_4$ modified adsorbent is least (high adsorption) and this is next to data presented for the commercial carbon. Thus Mango shells upon activation with 1M activants was promising for this studies and critical for consideration. A close observation unveil the fact that performance by 2M activated samples may be retarded by steric hindrances by more matrix while that of NaOH could be linked to poor pore size development [16, 20].

Effect of initial dye concentration

Figure 1a showed that the extent of adsorption or dye uptake decreases as the initial dye concentration increases form 10ppm to 50ppm. The possible reason for this is the competition for sorption site as the number of contesting adsorbate increases. The extent of decrease is more pronounced for the derived than it does for the commercial activated carbon. It could imply that the carbon dose and sorbate concentration selected in this work is more favourable to the commercial carbon.



Applicability of sorption isotherm (Surface Coverage Study)

The data in the Table 6c were constants generated from figures of type 2 and 3 on appendix which are characterized with good positive correlation coefficient. The Table shows that the modeling of data generated using Freundlich isotherm gave a better linearity and applicability ($R^2>0.975$) for sorbent prepared by adsorbents, 1M H₂SO₄. On the contrary, the Langmuir isotherm gave the best fit for the commercial carbon ($R^2>0.958$).It thus implies that adsorption of methylene blue dye onto the derived activated carbon was onto a heterogeneous surface [1].



Evaluation of adsorption intensities and capacities

The degree of heterogeneity of adsorption surface was also measured from the 1/n values. According to previous findings [1,16], Freundlich equation slope (1/n), ranging between 0 and 1 is a measure of surface heterogeneity. Surface become more heterogeneous as 1/n values get closer to zero. Based on this, Sorbents, with least 1/n value, 0.584 presented a more heterogeneous surface as made evidence by the commercial carbon. This finding could be linked to the particle size and the nature of activating agent [1,16]. It should not be unknown that 1/n ranging between 0 and 1 is a measure of adsorption Intensity. Hence, 1/n < 1 and > 1 are indication of normal and cooperative adsorption respectively. It thus implies that the adsorption

of dye onto mango shell biosorbent is a normal type of adsorption which could be linked to the possible suitability of biomass [20].

 K_f , is the Freundlich constant which denote or depicts the adsorption capacity, unit in mgg⁻¹ $(1mg^{-1})^n$ of adsorbent. It is defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto the sorbent for the a unit equilibrium concentration. Biomass, activated with 1M acid presented a higher value compared to that of the commercial carbon. The higher the value of K_f (intercept),the higher the absorption capacity [20] . K_F (units in mgg⁻¹ $(1mg^{-n(n)})$ is defined as the distribution coefficient and represents the quantity of dye, adsorbed onto the activated carbon for a unit equilibrium concentration. This high adsorption capacity by derived sorbent could be accepted based on Freundlich interpretation for a non uniform surface coverage.

Langmuir constant, q_m is a measure of the maximum adsorption capacity [19]. Table 6c revealed further that q_m value for commercial carbon(5.029) is fairly higher than that of the derived carbon. This is in good agreement with earlier work conducted by a research team for the adsorption of methylene blue onto sheanut shell [1]. This was however based on a monolayer coverage.

CONCLUSION

Highlights of results presented in this works shows that Mango shell is a potentially low cost precursor for generation of activated biosorbent, giving up to 60% dye removal. The isotherm evaluation gave isotherm experimental data that agrees with those of researches reviewed earlier. To this regards, adsorption falls within favorable limits as confirmed from the Freundlich constants (1/n < 1) and Applicability of the two models for the sorted adsorbent is not the same with that of the commercial carbon due to different surface coverage. A critical comparative study showed that for all the series of the adsorption study, the values of the maximum saturation capacity (q_m) and normal adsorption capacity (k_f) falls within range for concentration dependent physisorption. The same trend is applicable to the other biosorbent series.

REFERENCES

[1] Itodo A.U. and Itodo H. U. 2010. Academia Arena 2(3): 41-50

[2] Abram, J. (**1973**).. Paper and Proceedings of Water Research Association Conference held at the University of Readings. 3-5 April, 1973.

[3] Bansode, R., Losso, J., Marshall, E., Rao M. and Portier, J. (**2003** *Bioresource Tech.* **90**. (2):175-184.

[4] Tsai, W; Chang, C; Wang, Y; Chang, C., Chien, F. and Sun, H. (2001). Bioresource Technology. 78 (2): 203-208.

[5] Okiemen, F.E; Ojokoh, F.I; Okiemen, C.O and Wuana, R.A. (2004). *Chemelass Journal*. :191-196.

[6] Gimba, C; Ocholi, O. and Nok, A. (2004). *Nig Journal of Scientific Research*. 4 (2): 106-110.

[7] Babaninde A.A.N., (2002). Pure and Appl. Sci. 5 (i), 81 – 85

[8] Otero, M., Razade, F, Calvo, L.F, Garcia, A.I, Martin-Villacorta I., (2003). *Bioresource technology*, 87 : 221 – 230.

[9] Manocha, S. M. (2003). Porous Carbon. Sadhana. 23: (1&2): 335-348.

[10]. Steve , K. and Erika, T. (**1998**). Activated carbon M reynold, T., Paul, A.. Environmental Engineering 2^{nd} Edn. PWS Publishing Co. p 25, 350, 749.

[11]. Itodo A.U. and Itodo H.U. (2010). Academia Arena. 2(3): 51-60

[12] Cheremisinoff, P.N and Ellerbusch F. *Carbon Adsorption Handbook*. An Arbor Science Publisher Inc, Michigan. pp 241 – 279.

[13] Weber, W.J (**1972**). Physiochemical Processes for Water Quality Control. Wiley Interscience, London. Pp 199 – 245.

[14] Hartman J.R (1947). Colloid Chemistry, Houghton Mifflin Company, Cambridge. Pp 47-51

[15] Chilton, N; Jack, N; Losso, N; Wayne, E. and Marshall, R. (2002). *Bioresoruce Technology* 85 (2): 131-135

[16] Ahmedna M., Marshal, W. and Rao, M. (**2000**). *Bioresource and Technology*. 71(2): 113 – 123.

[17] Itodo, A.U. (**2008**). Ph.D Research proposal submitted to Dept of pure and Applied Chemistry, Usmanu Danfodiyo Univ. Sokoto.

[18] Itodo, A.U; Abdulrahman, F.W; Hassan, L.G; Maigandi, S. A and Happiness, U.O (**2009a**). *Nigerian Journal of Basic and Applied Science*.17(1):38-43.

[19] Abechi S. E., (2006). MSc thesis, Ahmadu Bello Universisty, Zaria, Nigeria

[20] Itodo, A.U; Abdurrahman F.W; Hassan L.G; Maigandi S.A; U.O. Happiness; Dogonyaro, A.I; and Sadiq I.S (**2009**). *African journal of physical science*, 2(2): 70-75