JASEM ISSN 1119-8362
All rights reserved

Full-text Available Online at www.ajol.info and www.bioline.org.r/ja

J. Appl. Sci. Environ. Manage. *Dec.*, 2015
Vol. 19 (4) 737 - 748

Adsorption of Mn(II) and Co(II) ions from aqueous solution using Maize cob activated carbon: Kinetics and Thermodynamics Studies

[*1]ADEBAYO, GB; [2]ADEGOKE, HI; [1]JAMIU, W; [1]BALOGUN, BB; [3]JIMOH AA

1Department of Industrial Chemistry, University of Ilorin, P.M.B 1515, Ilorin, Nigeria.
2Department of Chemistry, University of Ilorin, P.M.B 1515, Ilorin, Nigeria.
3Department of Chemistry, Kwara State University, Malete, Nigeria
Corresponding Author: waschem06@gmail.com.
Telephone: +2348063029504

ABSTRACT: The adsorption of Mn(II) and Co(II) ions from aqueous solution was investigated using batch adsorption experiment at room temperature. The effect of pH, contact time, metal ion concentration and temperature were evaluated. The residual concentrations of the metal ions were determined by atomic absorption spectrophotometer. The results showed that maximum removal of Mn(II) and Co(II) ions occurred at pH 9. Some physico-chemical and spectroscopic characterization of the adsorbents were done such as moisture content, ash content, bulk density, volatile matter, iodine number, point of zero charge (PZC), XRF, and FTIR. The moisture and ash content of MCAC adsorbent were found to be 9.85±0.06 and 5.5±0.1% respectively. The bulk density was found to be 0.37±0.01g/m^3, iodine number of 367.66±30 mg/g and PZC of 6.8. The SEM micrograph shows particle grains and jelly like rough surfaces, FTIR analysis results show different functional group in the MCAB adsorbent such as O-H, C=O, and C=C stretching. Kinetic study shows that the pseudo-second order kinetic model best described the adsorption of metal ions. The equilibrium data fitted Langmuir, Freundlich and Temkin adsorption isotherms, in each case, the Langmuir model appears to have better regression coefficients than the Freundlich and Temkin. Thermodynamics investigation showed that Gibb's free energy change (ΔG) was negative indicating that the adsorption of Mn(II) and Co(II) ions by maize cob activated carbon were feasible and spontaneous. The positive value of enthalpy change (ΔH) implies that the reaction was endothermic while positive value of entropy change (ΔS) implies an irregular increase in the randomness at the solid/solution interface of the adsorbent during the adsorption process. © JASEM

http://dx.doi.org/10.4314/jasem.v19i4.22

***KEY WORD*:** Adsorption, Heavy metals, Kinetics, Thermodynamics

Introduction

The increase in use of potentially toxic elements over the past few decades has unavoidably resulted in the flux of metallic substances in the aquatic and terrestrial environment (Jimoh *et al*., 2012). These metals once released through anthropogenic activities cannot be destroyed or degraded and thus persist indefinitely in the environment, accumulate in living tissues throughout the food chain and pose a serious menace to human and public health (Renuga *et al.*, 2010).

Numerous concerted efforts have been made to remedy this occurrence, which includes the use of conventional methods such as ion exchange, membrane processing, electrolytic methods, chemical oxidation or chemical reduction, filtration, chemical precipitation and electrochemical treatment (Selvaraj *et al.*, 2003). However, most of these methods are not economically feasible for small and medium size industries; they also suffered from high operational and maintenance costs, generation of toxic sludge and elaborated procedure involved in the wastewater treatment. Commercial activated carbon is unequivocally accepted as universal adsorbent for wastewater treatment, but due to its cost, developing country like Nigeria cannot avoid this treatment technique as consequence of low income per capital (Bhatnagar and Sillanp, 2010).

In addition, adsorption technique was considered better in wastewater treatment because of simplicity of design, convenience and ease of operation (Wasewar *et al*., 2009). In the past two decades, biosorption process has emerged as a cost effective and efficient alternative method for wastewater treatment utilizing naturally occurring agricultural waste materials as biosorbents. A large variety of agricultural wastes and by-products have been examined for their capability to remove pollutants from wastewater (Cay *et al.*, 2011; Jimoh *et al*., 2012). Agricultural wastes are widely available, affordable and the presence of large amount of surface functional groups make agricultural wastes good alternatives to expensive synthetic adsorbents (Amarasinghe and Williams, 2007).

Maize (*Z. Mays*) is the most widely grown grain crop throughout the West Africa and America. However, the cob is unutilized, thereby becoming an environmental nuisance. It is found to contain abundant functional groups, such as hydroxyl, amino and carbonyl groups which contain lone pairs of electrons needed for adsorption of cationic pollutants in solution (Babarinde *et al*., 2012a).
The main objective of this work is to convert waste to wealth by using maize cob, a readily agricultural waste for the removal of Mn(II) and Co(II) from aqueous solution.

MATERIAS AND METHOD

Sample preparation: The maize cob was obtained from Ipata market in Ilorin metropolis, Kwara state. The sample was sun dried for some days, it was later dried in an oven at 105°C overnight (Fan *et al*., 2003 and, Itodo *et al*., 2009) after which it was crushed using laboratory mortar and pestle, followed by sieving using smallest sieve size of 0.09mm. Five grams of the sieved sample was weighed into 10 different pre-weighed crucibles and it was introduced into the furnace at the temperature of 500°C for 20 minutes, the pyrolysed sample was cooled and ground into a granulated size and then activated with H_3PO_4 (Viboon *et al.,* 2007). The char sample was mixed with 75% concentrated orthophosphoric acid in a beaker with the weight ratio of H_3PO_4/ char to be 0.1. The slurry was evaporated at 60°C for 24 hours, and a dried mixture consisting of activated char and H_3PO_4 were obtained (Lillo- Rodenas *et al*., 2003). This was followed by washing to neutral pH of 7 (Viboon et al., 2007). The sample was then poured in a beaker containing 250ml of 0.1M HCl for purification and stirred for 1hour. Finally the sample was rinsed to a pH 6-7 (Strinivasan *et al.,* 1999). The resulting activated carbon was kept in tightly closed container for application (Viboon *et al.,* 2007).

Sample characterization: Fourier transform infrared spectroscopy (FTIR) spectra of maize cob activated carbon sample was obtained using a FTIR spectrophotometer (Model shimadzu 8400S) in wave number range of 3500-400cm^{-1}. The activated carbon sample was placed on a silicon substrate transparent to infrared, and the spectra were measured according to the transmittance method. The micrographs of prepared activated carbon were obtained using a JSM-7001F scanning electron microscopy.

Preparations of aqueous solutions : All chemicals (BDH, England) used in this study were of analytical reagent grade and were used without further purification. Standard solutions of Mn (II) and Co (II) used for the study were prepared from $MnCl_2.4H_2O$ and $CoCl_2.6H_2O$ respectively. The working solution with different concentrations of the metal ions was prepared by appropriate dilution of the stock solution immediately prior to their use with de-ionized water.

Adsorption procedure: Effect of initial metal ion concentration; Different concentrations of the adsorbate were prepared (5, 10, 15, 20, 25, and 30 mg/l) by serial dilution of the stock solution and then contacted with a fixed dosage of the adsorbent of 0.2g and 25ml of the adsorbate in 100ml conical flask. It was then agitated for 2hrs. At the end of time the mixture were filtered and analyzed using Atomic Absorption Spectrophotometer (210VGP model) (Jimoh *et al*., 2012).

Effect of Contact Time: The effect of contact time on metal adsorption was studied using metal ion concentration that gave optimal adsorption at different time intervals (30, 60, 90, 120, 150 and 180min). A 25 ml of metal concentration (equilibrium concentration) of the adsorbate were contacted with 0.2 g dosage of the adsorbent, the mixture was well corked and were shaken using multi-purpose flask shaker for 2hr. After completion of the reaction, conical flasks were taken out and resulting solution with adsorbent were filtered and analyzed using Atomic Absorption spectrophotometer (210VGP model) (Abdus-Salam and Itiola, 2012).

Effect of Adsorbent Dose: The metal ion concentration that gave optimal adsorption per 0.2g was used. A 25 ml of the adsorbate was contacted with varying amounts of the adsorbent doses (0.1, 0.2, 0.3, 0.4, and 0.5) grams at the equilibrium concentration (concentration of maximum adsorption). The mixture was agitated with an orbital mechanical shaker for 2hr. The resultant solution with the adsorbent in the flask was filtered and the filtrates were analyzed using Atomic Absorption Spectrophotometer (AAS). This will enable us to see the exact adsorbent dose which will be sufficient for optimal removal of the metals (210VGP model) (Abdus-salam and Itiola, 2012).

Effect of pH: A 25 ml of the optimum (equilibrium) concentration for Co(II) were contacted with 0.2g of the adsorbent in a 100ml conical flask and the pH of the solution matrix was varied with 0.1M HCl and 0.1M NaOH to obtained pH of 3, 5, 7, 9 and 11.The solution were equilibrated for 2 hr, filtered and the residual metal ion concentrations were analyzed using Atomic Absorption Spectrophotometer (210VGP model) (Elaigwu *et al., 2009*).

Effect of Temperature: The Temperature was varied between 30 and 70° C i.e. (30, 40, 50, 60 and 70) ^{o}C. A 25 ml of the optimum concentration for Co (II) were contacted with 0.2 g of the adsorbent in a 100ml conical flask. The mixtures were equilibrated for 2 hr at stated temperatures. The flask were then brought out and filtered. The filtrates were analyzed using

Atomic Absorption Spectrophotometer (210VGP model) (Abdus-Salam and Itiola, 2012). The amount of metal ion adsorbed by the acid modified and activated carbon was calculated by using the following equation $Q_e = \frac{V(C_0 - C_e)}{M}$ (1) Where q_e is the quantity adsorbed (mg/L), C_o and C_e are the initial and final concentration of metal ion in solution at any time, t (mg/L), *V is* the total volume of the metal standard solution in the flask (L), M is the mass of adsorbent used (g) (Ajmal *et al.*, 2000)

RESULTS AND DISCUSSION

Physico-chemical and spectroscopic characterization of the activated carbon sample

Table 1: Physico-chemical properties of adsorbent prepared from maize cob

Properties	Activated carbon
Moisture content (%)	9.85±0.06
Ash content (%)	5.5±0.1
Bulk density (g/m^3)	0.37±0.01
Yield (%)	72.50±0.01
Volatile matter (%)	22.21±1.0
Point of zero charge	6.8
Iodine number (mg/g)	367.66±30

Moisture content is the amount of water retained by the sample and suggests extensive porosity in the structure of all adsorbents. Although, moisture content of the activated carbon has no effect on its adsorptive power, it has been observed that if the moisture content of adsorbent is high its adsorptive capacity will be reduced and it would necessitate utilizing an additional weight of the carbon during treatment process. (Sugunadevi *et al*., 2002). The moisture content of the activated carbon was 9.85±0.06%, higher than the value reported elsewhere Mane et al., 2005, (9.7%), and Salman *et al*., 2011, (4.5%)

The ash content shows the amount of inorganic constituents associated with carbon. Ash content of adsorbents usually increases with increase in carbonization temperature. This was believed to be due to lowered volatile matter (Gan *et al*., 2004). The percentage ash contents for the adsorbent obtained was 5.5±0.1%, lower than the value of adsorbents reported by Salman *et al.*, 2011, (10.5%), Aloko and Adebayo, 2008, (29.24) and close to the value reported elsewhere, Mane *et al*., 2005, (5.6%) and Elnasri *et al.*, 2013, (5.9%). The ash content of adsorbents increased with decreased percentage of volatile matter which indicates that ash is non-volatile as reported (Gan *et al., 2004).*

Bulk density indicates the fiber content of the precursor. It is an important parameter when carbon is removed by filtration, because it determines the quantity of carbons that is contained in a filter of a given solid capacity and how much treated liquid is retained by the filter cake. Carbons with adequate density also help to improve the filtration rate by forming an even cake on the filter surface. Activated carbon adsorbent density is 0.37±0.01, which was lower than the value reported by Itodo *et al.,* 2011, (0.53g/m^3), Onundi *et al.*, 2011, (0.864g/m^3), the value was moderate when compared with literature values. Generally, an adsorbent with high bulk density need not be regenerated frequently because it can hold more adsorbate per unit weight (Yang and Lua., 2003).

The percentage yield obtained for the activated carbon adsorbent is 72.50±0.01%. This is an indication of high percentage yield compared to the reported percentage yield of 51% by Faust and Aly, (1983); Sahu *et al*., 2010, (46.08%). The activated carbon adsorbent obtained have good percentage yield, Ash content and volatile matter than the acid modified adsorbent as reported elsewhere, Raffiea *et al.*, 2012.

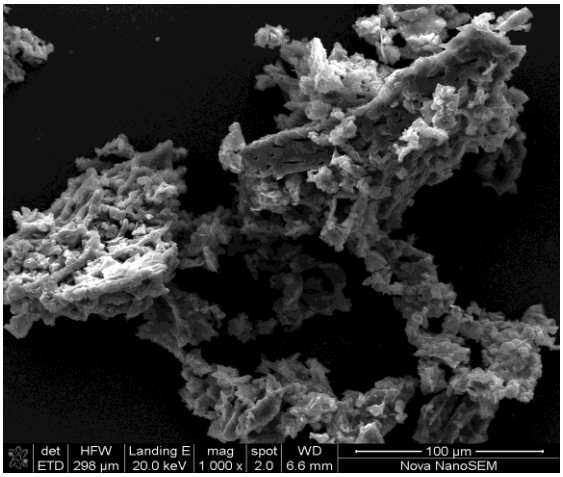
Volatile matter is due to the presence of organic compounds present in the raw material. It was evident that at longer carbonization period, more volatiles are released from the char, thereby resulting to a higher burn off and a corresponding lower yield (Itodo *et al.*, 2011). The volatile matter obtained for the activated carbon adsorbent was 22.21±1.0%, which is higher than the value reported by Raffiea *et al*., 2012 (20.9%).

The Point of Zero Charge (PZC) is a phenomenon of adsorption, and it describes the condition when the electronic charge density on a surface is zero (Kirby 2010). The PZC is located at the point of interception of the curves when traced to the pH axis. The PZC is (usually) the pH value at which a solid submerged in an electrolyte exhibit zero net electronic charge on the surface. The pHpzc of the adsorbent is 6.8 which are lower than the value reported elsewhere by Elnasri *et al.*, 2013 (7.3).

The Iodine number is the most fundamental parameter used to characterize activated carbon performance. It is measure of activity level of the adsorbent, the higher the iodine number, the higher the degree of activation and the development of the microporous structure (Raffiea *et al*., 2012). It is often reported in mg/g. The iodine number of the activated carbon adsorbent is 367.66±30mg/g, which is lower than the one reported by Raffiea *et al*., 2012, (798 mg/g).

The surface morphology of the activated carbon was analyzed by scanning electron microscopy (SEM), the corresponding SEM micrographs being obtained at 1000 and 10000 magnifications as shown in

Figures 1 and 2. The micrographs revealed particle grains and jelly like rough surface area which generally believe to be a good requirement for the adsorptive properties. It can be clearly seen that chemical activation resulted in a porous structure and the opening of pores on the surface of activated carbon as reported elsewhere (Deng *et al*., 2010). It is generally observed that pore structure development is influenced by many factors, such as inorganic impurities and the initial structure of the carbon precursor (Deng *et al*., 2010).



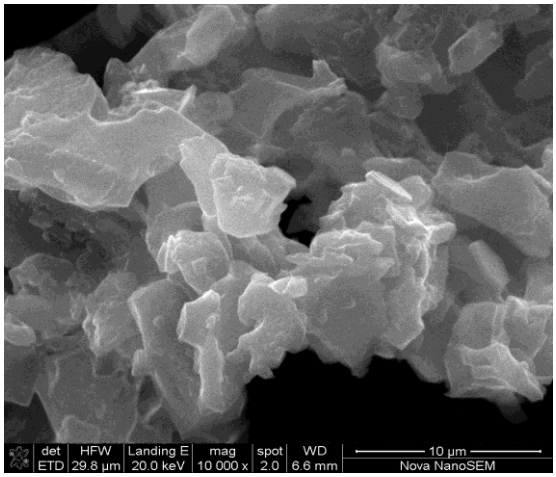


Fig. 1 (SEM micrograph for activated carbon at 1kx) **Fig. 2 (SEM Micrograph for activated carbon at 10kx)**

The chemical structure of the adsorbent is of vital importance in understanding the adsorption process. The FTIR technique is an important tool to identify the characteristic functional groups, which are instrumental in adsorption process (Das and Mondal, 2011). The FTIR spectrum of the maize cob activated carbon was used to determine the vibrational frequency changes in the functional groups in the adsorbent. As seen in Fig.3, the adsorption peak around 3410.26 cm^{-1} indicates the existence of free hydroxyl groups, the C-H stretching vibration around 2906.82 cm^{-1} indicate the presence of alkanes. The peaks around 1693.56cm^{-1} corresponds to the C=O stretching that may be attributed to the hemicelluloses and lignin aromatic groups (Deng *et al*., 2010).The C=C stretching vibrations around 1593.25cm-1 indicative of alkenes and aromatic functional groups. The peaks in the 1141.90 cm^{-1} corresponds to vibration of CO group in lactones. Some week bands were also observed in the range of 600-700 cm^{-1}, indicating the presence of C-C stretching

.

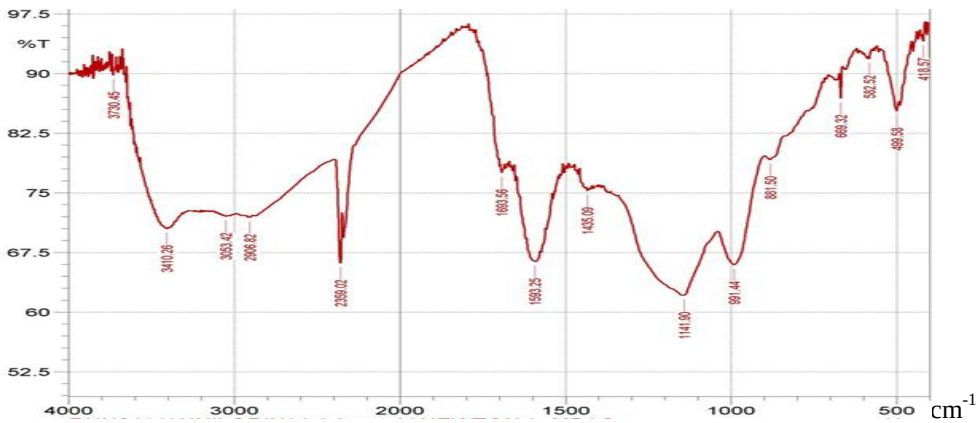


Fig. 3. FTIR spectrum for the activated carbon

Adsorption experiment results: Effect of Initial Concentration: The adsorption of metal ions by an adsorbent is strongly dependent on the initial concentration of metal ions in solution. It can be seen that as initial concentration of metal ions were increased from 5 ppm to 30 ppm, corresponding increase in the adsorption capacities also occurred until the maximum adsorption attained at initial concentration of 20ppm after which the adsorption decreases. The actual amount of Mn (II) and Co (II)

ions adsorbed per unit mass of activated carbon increased with increase in metal ion concentration. It has been reported that as the metal ion concentration is increasing, more ions are available for adsorption on the adsorbent (Adegoke *et al*., 2014). The rapid increase in the rate of adsorption have also been attributed to the sufficient surface area to accommodate more metal available in the solution due to the effect of concentration gradient which is the main driving force for the adsorption process (Mishra *et al*., 2009). The results obtained corroborated the findings of Okeimen and Onyenkpa (2000) and Elaigwu *et al*. (2009) that as the concentration of the adsorbate increase, the metal ions removed also increase.

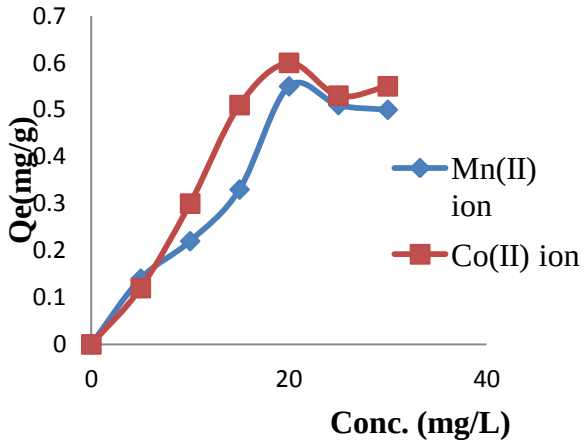


Fig 4. Effect of initial metal ions concentration on the adsorption of Mn(II) and Co(II) ion by Maize cob activated carbon

Effect of Contact Time: The adsorption of metal ions from aqueous solution is controlled by the rate of reaction which determines the equilibrium time. It is one of the important characteristics defining the efficiency of an adsorbent (Krishnan and Anirudhan, 2003). The time of the adsorbent-adsorbate is of great importance in adsorption, because it depends on the nature of the system used. The effects of agitation time for the adsorption of Mn(II) and Co(II) ions were studied between 30 and 180minutes. Maize cob activated carbon sample had maximum adsorption capacity within 120 minutes of the experiment; further increase in contact time had no significant effect on the adsorption capacity. The maximum adsorption capacity observed at 120 minutes of contact time may be due to large number of vacant sites available, which later slowed down and may be attributed to exhaustion of remaining surface sites and repulsive force between the adsorbent and metal ions

.

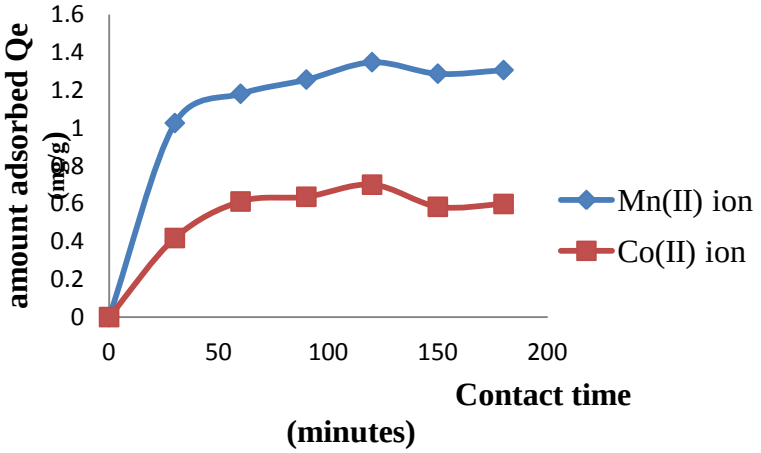


Fig 5. Effect of contact time on the adsorption of Mn(II) and Co(II) onto maize cob activated carbon

Effect of pH: The initial pH of a solution is a very important factor to be considered in adsorption studies as it has been observed to play a major role in the adsorption of metal ions by various adsorbents, because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction (Badmus *et al*., 2007; Sheng *et al*., 2004). The effect of pH on the Mn(II) and Co(II) ions adsorption capacities of maize cob

adsorbent was conducted at various pH ranging 3-11 with 20 mg/L fixed initial metal ion concentrations and contact time of 2hours. The result shows that the maximum adsorption was observed at pH 9 for both metal ions, it can be seen that the amount adsorbed increases with increases in pH. Similar trend were reported in literature elsewhere (Kobya *et al.*, 2005).

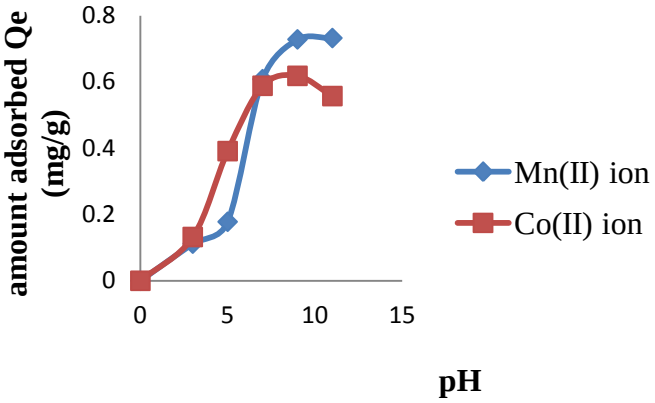


Fig. 6. Effect of pH on the sorption of Mn(II) and Co(II) onto maize cob adsorbent

Effect of Adsorbent dose: The influence of different amounts of adsorbents dose 0.1-0.5g on Mn(II) and Co(II) ions adsorption at constant initial metal ion concentration of 20 mg/L, contact time of 2hours and the temperature of 298K, showed decrease in the quantity adsorbed with increase in adsorbent dosage rate as the number of sorbate ions concentration decreases per active site available for sorption on the surface (Yu *et al.*, 2000). The effect of adsorbent dose on adsorption of Mn(II) and Co(II) ions on maize cob adsorbent, and maximum adsorption was observed at 0.1g for maize cob adsorbents. The observation shows that small amount of adsorbent gave maximum adsorption; this may be due to the high surface area and micropore volume of the sample (Babarinde *et al.*, 2012a).

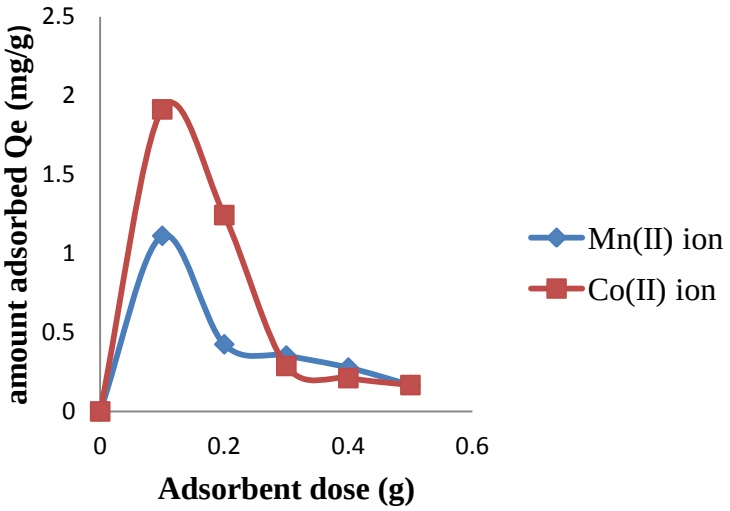


Fig 7. Effect of adsorbent dose on the adsorption of Mn(II) and Co(II) onto maize cob activated carbon

Effect of Temperature: The study showed that there was gradual increase in the removal efficiency for all the metal ions as temperature increases from 303 to 343K. The increase in the amount of metal ions adsorbed as temperature increases might be attributed to the fact that the adsorption by maize cob adsorbent may involve not only physical but also chemical adsorption, and sometimes may also involve bond rupture (Jimoh *et al.*, 2013). From the result obtained, it can be seen that the number of adsorption sites tend to increase with increase in temperature which may be an indication of possible chemical interactions between the adsorbate and the adsorbent (Ekop and Eddy, 2010).

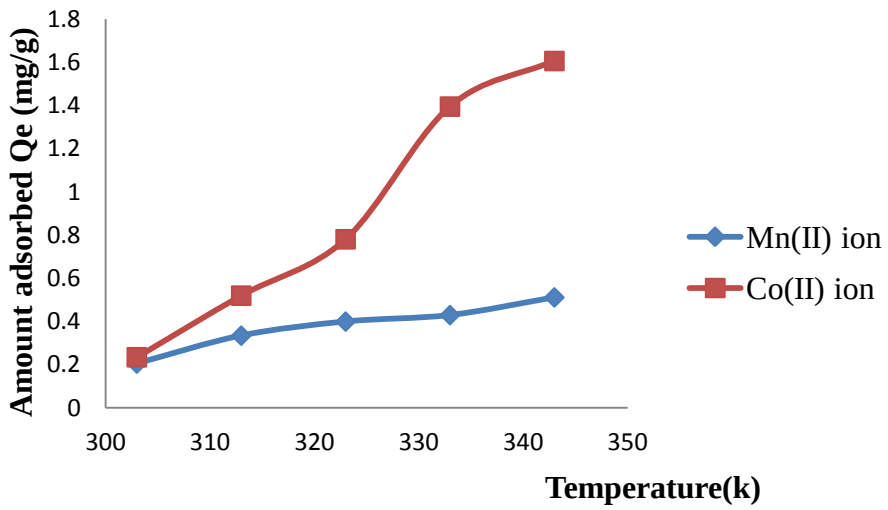


Fig 8. Effect of temperature on the sorption of Mn(II) and Co(II) ions onto maize cob adsorbent.

Adsorption isotherms: Three adsorption isotherms were employed on the experimental data obtained in this research work and their respective formula are given below. (i) Langmuir adsorption isotherm, Langmuir adsorption isotherm equation is given below:

$\frac{Ce}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}}$ (2) where Ce is the equilibrium concentration (mg/L), q_e is the amount adsorbed at equilibrium (mg/g), q_{max} is the maximum amount of adsorption with complete monolayer coverage on the adsorbent surface (mg/g) and K_L is the Langmuir constant (L/mg) (Langmuir, 1918). (ii) Freundlich adsorption isotherm

Freundlich isotherm is the earliest known relationship describing the adsorption equation and is often expressed as $log\ q_e = log\ k_f + \frac{1}{n} log\ C_e$ (3)
Where Qe is the quantity of solute adsorbed at equilibrium (adsorption density: mg of adsorbate per g of adsorbent). C_e is the concentration of adsorbate at equilibrium, K_f and n are the empirical constants dependent on several factors and n is greater than one. (Najua *et al.*, 2008)
(iii) Temkim isotherm Temkim isotherm is given by the following equation: $Q_e = \frac{RT}{b} ln\ K_T\ C_e$ (4)
Equation above can be linearized into the following:: $Q_e = B\ ln\ K_T + B\ ln\ C_e$ (5) $where\ B = \frac{RT}{b}$
Regression of q_e against lnC_e enables the determination of isotherm constant K_T and B. The K_T is the equilibrium binding constant (L/mg) corresponding to maximum binding energy and constant is related to the heat of adsorption.

The Langmuir isotherm plots are presented in Figure 9 & 10. The various parameters are shown in Tables 2. From Table 2, the adsorption of Mn(II) and Co(II) ions onto maize cob activated carbon can best be described by Langmuir isotherm based on the correlation coefficient values and other constant parameters obtained. This means that the adsorption of the metal ions onto maize cob activated carbon was physical, heterogenous and multilayer in nature (Najua *et al.*, 2008). The parameters of the Langmuir isotherms show that Langmuir isotherm model is a better isotherm than the Freundlich and Temkin model as represented in Table 2. The order of fitness was Langmuir> Freundlich > Temkin. This is similar to the obtained results by (Jimoh *et al.* 2011 and Wasewar *et al.* 2009).

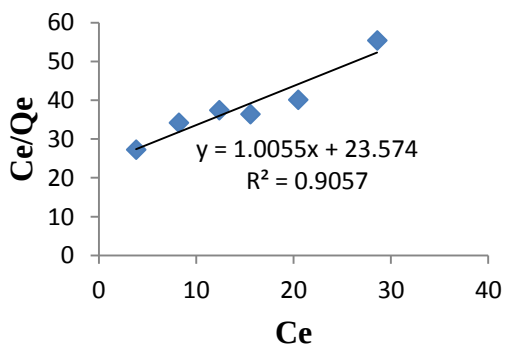


Fig 9. Langmuir plot for Mn(II) onto Maize cob adsorbent

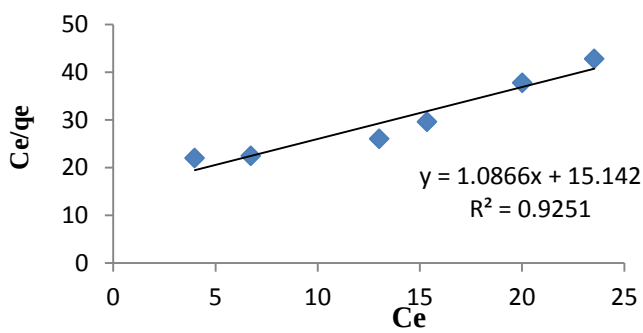


Fig 10: Langmuir plot of Co(II) onto Maize cob adsorbent

Table2. Langmuir, Freundlich and Temkin isotherm parameters for the adsorption of Mn(II) and Co(II) ions by maize cob activated carbon.

Metal ion	Langmuir parameters			Freundlich parameters			Temkin parameters		
	q_{max} (mg/g)	K_L (L/mg)	R^2	K_f (mg/g)	1/n	R^2	B (Kj/mol)	K_T (L/mg)	R^2
Mn(II)	0.930	0.045	0.915	0.054	0.726	0.887	0.179	1.094	0.679
Co(II)	0.920	0.071	0.925	0.048	0.843	0.864	0.256	0.463	0.256

Adsorption kinetics: In analysis of the kinetics profile of this sorbent material, pseudo-first, pseudo-second order and Elovich kinetics model were employed and the equations are stated as follows.

(i) Pseudo-first order kinetics: The rate law is given below: $\frac{dq_t}{dt} = k_1(q_e - q_t)$ (6) Where, q_e and q_t are the amount of Co(II) adsorbed at equilibrium and time t, respectively. K_1 is the rate constant for the pseudo first order adsorption. The integrated law is given as follows: $log(q_e - q_t) = logq_e - \frac{K}{2.303}$ (7)

A plot of $log(q_e - q_t)$ against t was made and the values of k_1 and q_e were obtained from the slope and intercept, respectively (Ho and Mckay, 2000). (ii) Pseudo-second order kinetics: The linear form of pseudo-second order kinetics model is given as: $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t$ (8) Where, q_e and q_t are the amount of metal ion adsorbed per unit mass of the adsorbent (in mg g^{-1}) at equilibrium and time *t*, respectively, and k_2 is the pseudo second order rate constant. A linear plot of t/q_t against t confirms the fitness of data to this model (Ho and Mckay, 2000)

(iii) The Elovich Model

The Elovich model equation is generally expressed as: $q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t)$ (9)

Where α is the initial adsorption rate (mg.g $^{-1}$ min $^{-1}$). β is the desorption constant (g.mg $^{-1}$) during any experiment. If the adsorption process fits the Elovich model, a plot of q_t against ln(t) should yield a linear relationship with a slope of $(\frac{1}{\beta})$ and an intercept of $(\frac{1}{\beta})\ln(\alpha\beta)$. The conformity between experimented data and the model- predicted values was expressed by the correlation coefficients (R^2, value close or equal to 1). A relatively high R^2 value indicates that the model successfully describes the adsorption kinetics (Chien and Clayton, 1980; Sparks,1986).

The kinetics of an adsorption is probably the most important factor in predicting the rate at which adsorption takes place for a given system. Three kinetic models were employed. These are the pseudo-first order, the pseudo-second order and the Elovich equations. The models were examined for suitability using their correlation coefficient, R^2 as reported elsewhere (Jimoh *et al*., 2013). Our result revealed that the adsorption of the metal ions could be best explained using the pseudo-second order. This was due to the higher correlation regression coefficient R^2 value. This trend was the same as reported elsewhere (Idris *et al.*, 2012). The pseudo second order plots were presented in figure 11, and the parameters are shown in Table 3.

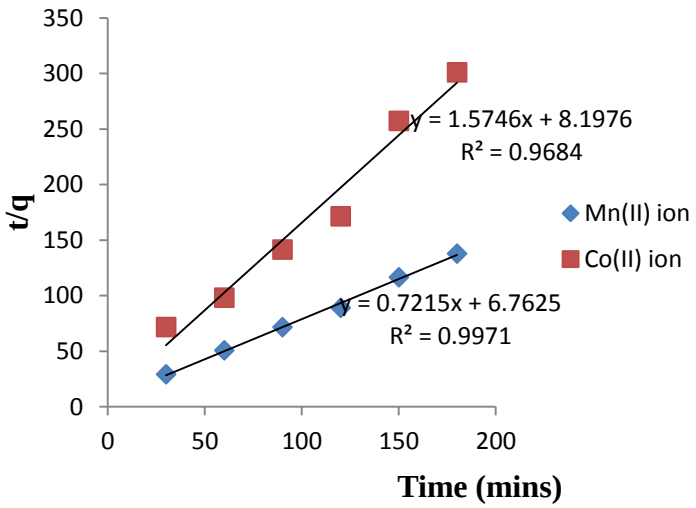


Fig 11. Pseudo-second order plot for adsorption of Mn(II) and Co(II) onto maize cob activated carbon.

Table 3. Parameters of the Pseudo-second order kinetic model for the adsorption of Mn(II) and Co(II) ions by maize cob activated carbon.

Metal ion	pseudo second-order	parameters	
K_2 ($gmg^{-1}min^{-1}$)	q_e (mgg^{-1})		R^2
Mn(II)	0.076	1.386	0.997
Co(II)	0.302	0.635	0.968

Adsorption thermodynamics: The thermodynamics parameters such as Gibbs free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were also studied in order to understand better the effect of temperature on the adsorption of Co(II) ions. The Gibb's free energy change (ΔG) is related to the thermodynamics equilibrium constant by the following equation:

$$K_c = \frac{C_{Ae}}{C_e} \qquad (10)\ \Delta G^0 = -RT \ln K_c$$

$$(11)\ \log K_c = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \qquad (12)$$

Where, K_c is the equilibrium constant, C_e is the equilibrium concentration in solution (mg/L) and C_{Ae} is the solid-phase concentration at equilibrium (mg/L)., ΔG, ΔH and ΔS are changes in Gibbs free energy (kJ/mol), enthalpy (kJ/mol) and entropy (J/mol/K), respectively. R is the gas constant (8.314 J/mol/K) and T is the temperature (K). The values of ΔH and ΔS was determined from the slope and the intercept of Van't Hoff plots of log K_c versus 1/T (Mohan and Singh, 2002).

From Table 4, it could be observed that enthalpy change (ΔH) and entropy change (ΔS) was positive for all the metals ions while Gibb's free energy change (ΔG) were negative in the same way. The negative values of Gibb's free energy change (ΔG) at all temperatures examined indicates that the adsorption of Mn(II) and Co(II) ions by maize cob was feasible and correspond to a spontaneous physical adsorption of the metal ions, which indicate that this adsorption process does not gain external energy (Vimonses et al., 2009). The positive values of enthalpy change (ΔH) revealed that the adsorption process was endothermic and non-physical in nature. Furthermore, positive values of entropy change (ΔS) was an indication of an irregular increase in the degree of the randomness at the adsorbent-adsorbate interface during the adsorption. The order of spontaneity of the biosorption process was found to be Mn(II) < Co(II) which was contrary to the findings reported for the biosorption of these metal ions with banana leaf by Babarinde et al. (2012b).

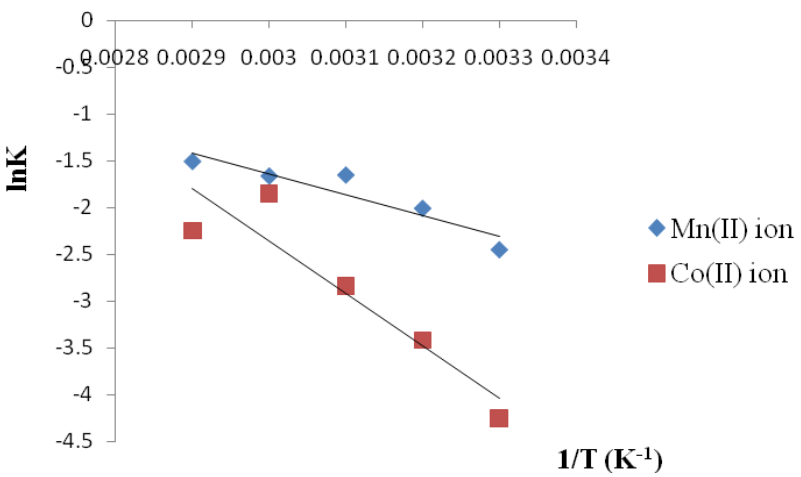


Fig 12. Thermodynamic plots for the adsorption of Mn(II) and Co(II) by maize cob activated carbon.

Table 4. Thermodynamic parameters for the adsorption of Mn(II) and Co(II) by maize cob activated carbon

Metal ion	**ΔH**	**ΔS**	**ΔG** (KJ/mol)				
	KJ/ mol	J/mol/K	303K	313K	323K	333K	343K
Mn(II)	+16.803	+20.502	- 6.195	--6.400	- 6.605	6.810	7.015
Co(II)	+46.475	+119.805	36.254	-37.452	38.650	39.848	41.046

Conclusion: Based on the above study the following conclusions were drawn: (i) pH, contact time, metal ions concentration and temperature had a remarkable effect on the metal uptake level by the substrate. (ii) The biosorption process of the metal ions was best described by a pseudo-second order. (iii) The

equilibrium data could be best explained by Langmuir than Freundlich and Temkin isotherm. (iv) Thermodynamics investigation showed that Gibb's free energy change (ΔG) was negative indicating that the adsorption of Mn(II) and Co(II) ions by maize cob activated carbon were feasible and spontaneous. The positive value of enthalpy change (ΔH) implies that the reaction was endothermic while positive value of entropy change (Δ*S*) implies an irregular increase in the randomness at the solid/solution interface of the adsorbent during the adsorption process.

REFERENCES

Abdus-salam, N. and Itiola, A.D.: Potential Application of Termite Mound for Adsorption and Removal of Pb(II) from aqueous Solutions. J. Iran chem. Soc. 9, 373-382 (2012).

Adegoke H. I., Adekola F. O., Fatoki O. S., and Ximba B.J.: Adsorption of Cr (VI) on synthetic Hematite nanoparticles of different morphologies. Korean journal of chemical engineering. 2(1): 142-154 (2014).

Ajmal, M., Rao, B., Ahmad, R. A., Ahmad, J.: Adsorption studies on Citrus reticulate (fruit peel of orange): Removal and recovery of Ni(II) from electroplating wastewater. J. Hazard. Mater. 79: 117-131 (2000).

Aloko, D. F., and Adebayo G. A.: Production and Characterization of Activated carbons from Agricultural waste. J. Eng. Applied Sci. 2(2), 440-444 (2008).

Amarasinghe, B. M., Williams, A. R.: Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater. Chem. Eng. J. 132: 299-309 (2007).

Babarinde, N. A. A., Babalola, J. O., Adegoke, J., Muraizu, U., Ogunbanwo, T., Ogunjinrin, F.: Kinetic, equilibrium and thermodynamics studies of the biosorption of Ni(II), Cr(III) and Co(II) from aqueous solutions using banana (Musa acuminata) leaf. Int. J. Phy. Sci. 7: 1376-1385 (2012b).

Babarinde, N. A. A.; Babalola, J. O.; Adegoke, J.; Osundeko A. O, .; Ibidapo, T.; Nwabugwu, C. A.; Ogundimu, O. F.: Kinetic, equilibrium and thermodynamics studies of the biosorption of Ni(II), Cr(III) and Co(II) from aqueous solutions using cocoyam (colocasia esculenta) leaf. pacific. J.of Sci.and tech. 13(2): 272-282 (2012a).

Badmus M. A. O, Audu, T. O. K, and Anyata B. U.: Removal of Lead ion from Industrial Waste waters by Activated carbon from Periwinkle shells. Turkish J. Env. Sci. 31: 251-263 (2007).

Bhatnagar, A.; Sillanp, M.: Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment-a review. Chem. Eng. J. 24: 277-296 (2010).

Cay, S.; Uyanik, A.; Ozasik, A.: Single and binary component adsorption on copper(II) and cadmium(II) from aqueous solution using tea industry waste. Sep. Purif. Technol. 38: 273-280 (2004).

Chien, S.H., Clayton, W.R.: Application of Elovich equation to the kinetics of phosphate release and sorption on soils. Soil Sci. Am. J. 44, 265-268 (1980).

Das B. and Mondal N. K.: Calcareous soil as new adsorbent to remove Lead from aqueous solution: Equilibrium, Kinetics and Thermodynamic Study. Universal J. Environs. Res. Tech, 1(4), 515-518 (2011).

Deng H. Li G., Yang H., Tang J., and Tang J.: Preparation of Activated carbons from cottonstalk by microwave assisted KOH and K_2C0_3 activation. Chem. Eng. Journal, 163, 373-381 (2010).

Ekop A. S and Eddy, N. O.: Thermodynamic Study on the Adsorption of Pb^{2+} and Zn^{2+} from aqueous solution by human hair. E- journal of chemistry. 7(4), 1296- 1303 (2010).

Elaigwu S.E, Usman L.A, Awolola G.V, Adebayo G.B. and Ajayi R.M.K.: Adsorption of Pb (II) from aqueous solution by activated carbon prepared from cow dung Adv. In. Net. Applied Sci. 3(3), 442-446 (2009).

Elnasri N. A, Mutaz A. E, and Mohammed A. E.: Physico-chemical Characterization and Freundlich isotherms of Adsorption of Fe(II) from aqueous solution by using Activated carbon prepared from Doum fruit waste. Arch. Appl. Sci. Res, 5(5): 149- 158 (2013).

Fan M., Marshall W., Daugaard D., Brown C.: Steam activation of chars produced From oat hulls. Bioresource Technology. 93 (1):103-107 (2003).

Faust, S. D and Aly O. M.: *Chemistry of water treatment*; Butterworths Publishers: Boston, London Wellington, pp211 (1983).

Gan, Q., Allen, S., and Matthews, R.: Activation of waste MDF sawdust charcoal and its

reactivedye adsorption characteristics. Waste Management, 24(2): 84-85 (2004).

Ho, Y. S.; McKay, G.: Pseudo-second order model for sorption process. Process Biochem. 34: 451-465 (2000).

Idris, S., Iyaka Y. A., Dauda B. E. N., Ndamitso M. M and Umar M. T.: Kinetic Study of Utilizing Groundnut Shell as an Adsorbent in Removing Chromium and Nickel from dye effluent. American chemical science journal. 2(1): 12-24 (2012)

.

Itodo, A.U., Abdulrahman, F.W., Hassan L.G., Maigandi, S.A., Happiness U.O.:Thermodynamic, equilibrium, kinetics and adsorption mechanism of industrial dye removal by chemically modified poultry droppings activated carbon. Nigerian Journal of Basic and Applied Science; 17(1):38-43 (2009).

Itodo, A.U, Itodo, H.U., Atiku, F.A., Kolo, R.A., and Kwaido A.A.: Dyes Uptake onto Processed Raw Mango Seed back. Asian J. of Plant Sci. Res., 1(1), 57-66 (2011).

Jimoh, T. O. , Yisa, J., Ajai, A. I., Musa, A.: Kinetics and Thermodynamics Studies of the Biosorption of Pb(II), Cd(II) and Zn(II) Ions from Aqueous Solution by Sweet Orange (Citrus sinensis) Seeds. International Journal of Modern Chemistry. 4(1): 19-37 (2013).

Jimoh, T. O., Buoro, A. T. and Muriana, M.: Utilization of Blighia sapida (Akee apple) pod in the removal of lead, cadmium and cobalt ions from aqueous solution. Journal of Environmental Chemistry and Ecotoxicology . 4(10), 178- 187 (2012).

Jimoh, T.; Egila, J. N.; Dauda, B. E. N.; Iyaka, Y. A.: Pre-concentration and removal of heavy metal ions from aqueous solution using modified charcoal. J. Environ.Chem.Ecotoxicol. 3(9): 238-243 (2011).

Kirby, B. J.: Micro and Nanoscale Fluid Mechanics: Transport in Microfluidic Devices. 3(2), 76-77 (2010).

Kobya, M. E. Demirbas, E. Senturk, M. I.: Adsorption of Heavy metal ions from aqueous solutions by activated carbon prepared from apricot stone. Bioresources Technology, 96: 1518-1521 (2005)

Krishnan, K. A.; Anirudhan, T. S.: Removal of cadmium(II) from aqueous solutions by steam-activated sulphurised carbon prepared from sugar cane bagasse pith: Kinetics and equilibrium studies. Water SA, 29(2):147-156 (2003).

Langmuir I.: The adsorption of gases in plane surfaces of glass, mica and Platinum. J. American Chem. Society. 40, 1361-1403 (1918).

Lillo-Rodenas M.A., Cazorla Amoros, D., Linares-Solono, A.: Behaviour of Activated carbons with different pore size distribution and surface oxygen groups for Benzene and Toluene Adsorption at low concentration carbon. Afr. J. Biotechnol. 43; 1758-1767 (2003).

Mane, S. W., Vanjara, A. K and Sawant, M. R.: Removal of Phenol from Wastewater using Date seed carbon. Journal of the Chinese Chemical Society. 52, 1117-1122 (2005).

Mishra, S. Prakash, D. J., and Ramakrishna, G.: Characterization and Utilization of Mahua oil cake- A new adsorbent for the removal of Congo red Dye from Aqueous phase. Elect. J. Env. Agric. Food chemistry. 8, 425-436 (2009).

Mohan, D., and Singh, K.P.: Single component and multicomponent Adsorption of cadmium and zinc using activated carbon derived from baesse: agricultural waste. Water Res. 36: 2304-2318 (2002).

Najua, D.T., Luqman, C.Z., Zawani, S.A.: Adsorption of copper from aqueous solution by Elais Guineensis Kernel activated carbon. Journal of Engineering Sci. & Tech. (5)180-189 (2008)..

Okeimen, F. E.; Onyenkpa, V. U.: Binding of cadmium, copper, lead and nickel ions with melon (Citrullus vulgaris) seed husk. Biol. Waste. 29: 11-16 (2000).

Onundi, Y. B., Mamun, A. A, Al-Khatib, M. F., Al-Saadi. M. A. and Suleyman, A. M. Heavy metals Removal from Synthetic Wastewater by a novel nano-size composite adsorbent. Int. J. Environ. Sci. Tech. 8(4): 799-806 (2011).

Raffiea, B. J., Palanisamy, P. N and Sivakumar, P.: Preparation and Characterization of Activated carbon from thevetia peruviana for the removal of dyes from textile waste water. Advances in Applied Science Research, 3(1), 377-383 (2012).

Renuga, D. N.; Manjusha, K.; Lalitha, P.: Removal of hexavalent chromium fromaqueous solution using an eco-friendly activated carbon adsorbent. Pelagia Library Adv. Appl. Sci. Res, 1: 247-254 (2010).

Sahu J. N., Achrya J. and Meikap, B. C.: Optimization of Production conditions for activated carbons from Tamarind wood by zinc chloride using response surface methodology. Bioresource Technology. 101: 1974-1982 (2010).

Salman, M., Athar, M. Shafique, U., Din, M. I., Rehman, R., Akram, A. and Ali, S. Z.: Adsorption Modelling of Alizarin Yellow on Untreated and Treated charcoal.Turkish J. Eng. Env. Sci. 35, 209-216 (2011).

Selvaraj, K.; Manonmani, S.; Pattabhi, S.: Removal of hexavalent chromium using distillery sludge. Bioresour. Technol. 89: 207-211 (2003).

Sheng, P.X., Ting Y-P, Chen J.P., Hong L.: Sorption of lead, copper, cadmium, zinc and nickel by marine algal biomass: characterization of biosorptive capacity and investigation of mechanisms. J. Colloid Interface Sci. 275 (1): 131-141 (2004).

Sparks, D.L.: Kinetic of reaction in pure and mixed systems, in soil physical chemistry. CRC Press, Boca Raton. pp34-66 (1986).

Strinivassan, S.K., Tyagi, R., and Pant, N.: Adsorption of heavy metal ions on carbonaceous material developed from the waste slurry generated in local fertilizer plant. J. Water Resources. (23) 111-161 (1999).

Sugunadevi, S.R., Sathishkumar, M., Shanthi, K., Kadiruvelu, K. and Pattabhi S.: The adsorption of Cd(II) ions on sulphuric acid treated wheat bran. J. Hazard. Mater. 137(2): 849-855 (2002).

Viboon, S., Chiravoot, P., Duangdao, A. and Duangduen, A.: Preparation and Characterization of activated carbon from the pyrolysis of physic nut (jatropha curcas L.) waste. J. American Chem. Society. 3(2): 133-137 (2007).

Vimonses, V., Lei, S., Jin, B., Chow, C. W. K., Saint, C.: Kinetic study and equilibrium analysis of Congo red adsorption by clay materials. Chem. Eng. J148: 354-364 (2009).

Wasewar, K. L., Mohammad, A., Prasad, B., Mishra, I. M.: Batch adsorption of Zn(II) ion using tea factory waste as an adsorbent. Desalination, 244: 66-71 (2009**)**.

Yang, T. and Lua A.: Characteristics of activated carbons prepared from pistachio-nut shells by physical activation. Journal of Colloid and Interface Science. 267, 408-417 (2003).