EVALUATION OF ACTIVATED CARBON FROM MAIZE COBS AS LOW-COST ADSORBENT FOR ADSORPTION OF CR (VI) IONS FROM AQUEOUS SOLUTION OF THE SALT

Nale, Biki Y[1]*, Simon Saidu[1], Mubarak Liman[2] and Siaka, Stephen M[3].

[1, 3]Department of General Studies, School of Agricultural Technology Samaru Kataf, Nuhu Bamalli Polytechnic, Zaria.
[2]Department of Science Laboratory Technology, Nuhu Bamalli Polytechnic, Zaria.
*Corresponding author's e-mail: yusufnale@yahoo.com

ABSTRACT

A carbonaceous adsorbent prepared from maize cobs by acid treatment was tested for its efficiency in removing chromium (VI). The parameters studied include contact time, initial chromium concentration and pH. The experimental equilibrium data were tested using Langmuir and Freundlich isotherm equations. Adsorption Kinetics data were modelled using Pseudo first order and Pseudo second orders Kinetic equations and intraparticle diffusion model. Result indicates that the maximum monolayer adsorption capacity was found to be 5.77mg/g. Pseudo second order model best describe adsorption Kinetic data. Adsorption of chromium (VI) attained equilibrium within 120 min for the whole range of initial chromium concentrations (5 – 20 mg/L). A long contact time necessary to attain equilibrium indicates that the predominant mechanism is physical adsorption (physisorption). The optimum pH required for the maximum adsorption was found to be 2.

Key words: Adsorption, Isotherms, Kinetics, Physisorption and Equilibrium.

INTRODUCTION

The water pollution is mainly due to organics, inorganics, sediments, radioactive materials and heavy metals. Among these pollutants, the contribution of heavy metals to the environment is a major concern because of its toxicity, bioaccumulation, persistence and non-biodegradable nature. Industrial effluent containing chromium plays important role in polluting water bodies. Additional potential sources of chromium bearing waste include: Paints, photo engraving, tattooing, textile manufacturing, wood preservatives and welding of alloys or steel. Chromium (VI) is the most dangerous form of chromium and may cause health problems including; allergic reactions, skin rash, nose irritations and nose bleeding, ulcers, weakened immune system, genetic material alteration, kidney and liver damage and even as far as death of the individual (Eastmond *et al*., 2008). The world economy today is focusing on better waste management policies; hence the need to reduce wastes is to protect environment (EU, 2010).

There are several methods to treat metal contaminated effluent such as precipitation, ion exchange and adsorption etc, but the selection of the treatment methods is based on the concentration of waste and the cost of treatment (Cheung *et al*., 2001, Dezuane, 1990 and Ajmal *et al*., 2003). In the last few years, adsorption has been shown to be economically feasible alternative method for removing trace metal from waste water and water supplies (Allen & Brown, 1995).

Activated Carbon has been the most used adsorbent; nevertheless, it is relatively expensive (Khalid *et al.*, 2000). Cost is an important parameter for comparing the adsorbent materials. However, cost information is seldom reported and the expense of individual adsorbent varies depending on the degree of processing required and local availability (Bailey et al., 1999). Activated Carbon from cheap and readily available sources such as coal, coke, peat, wood, rice husk may be successfully employed for the removal chromium and other toxic heavy metals from aqueous solution (Sharma, 2001). The present study entails the use of activated carbon prepared from maize cob as an adsorbent for the removal of Cr (VI) from aqueous solution. The main aim of this work was to evaluate the feasibility of using the maize cob carbon for Cr (VI) removal.

MATERIALS AND METHOD

Preparation of Adsorbent

In the present study, maize cobs were used for the preparation of activated carbon. The maize cobs collected from the Kaduna Agricultural Development Projection (KADP) Samaru Kataf Farm were cleaned to remove loose flakes. The raw material was washed several times using tap water and finally distilled water. It was subsequently air-dried to remove excess water content. The dried samples were crushed using pestle and mortar into fine particles sizes. The samples were then stored in a clean polythene bag until analysis.

The maize cobs was carbonized at 500ºC for 40 mins according to method as described by Gimba and Bahago (2004) briefly a portion (2g) of the maize cob was weighed into crucible and mixed thoroughly with $2cm^3$ each of 0.10M H_3PO_4 at optimum conditions of temperature and time in a muffle furnace model GLM 3+ DL/IND for activation. The activated carbon was then washed with deionised water and soaked in 1% $NaHCO_3$ solution to remove any remaining acid. The samples were further washed with deionised water until no acidity and then dried at 105ºC for 5 hours (Dermibas *et al*., 2004). The dried material was ground and sieved to obtain the particle sizes of 300 - 850µm (Kagbu, 2001; Pattabhi *et al*., 2008) and stored in airtight container for further experiments.

Fourier Transform Infrared Spectrophotometer (FT – IR) Analysis

The activated carbon product was characterized for its functional group using FTIR spectrometer (Nicolet Magna-IR Model 550) analysis. For this, the activated carbon samples were brought to the constant weight in a drying oven at 50ºC for 24h and kept in the desiccators. Exactly 1mg dried activated carbon was mixed with 100mg KBr, which was initially dried at 110ºC in the sample disk. The FT – IR spectra was in the range of 450 – 400cm^{-1}. The absorption spectra were collected and analysed (Patnukao *et al*., 2008).

Preparation of Adsorbate

Cr (VI) stock solution (1000mg/L) was prepared in deionised water using analytical grade potassium dichromate ($K_2Cr_2O_7$). The working solution was obtained by diluting the stock solution in deionised water.

Batch Mode Adsorption Studies

Adsorption studies were performed in 100ml flasks where solutions of chromium ion (25ml) of different initial concentrations (5 – 20mg/L). Equal mass of 0.2g of maize cob of approximate particle size of 355µm was added to each metal ion solution and each was kept in shaker for 180min at room temperature of 30ºC (Ahmed and Kumar, 2008) to reach equilibrium. The flasks were

then removed from shaker and final concentration of chromium ion in the solution was analysed by using UNICAM 968 Atomic Absorption Spectrophotometer at 540nm. The adsorption capacity at equilibrium qe (mg/g) was calculated by;

$$qe = (Ci - Ce)V/M \quad \text{..... (1)}$$

where Ci and Ce (mg/L) are the liquid phase concentrations of chromium ion at initial and equilibrium concentrations respectively. V is the volume of the solution (L) and M is the mass dry adsorbent used (g). The effect of initial contact time and pH were studied. Adsorption Kinetic and Adsorption isotherm were applied to equilibrium data.

RESULT AND DISCUSSION

FTIR Spectrum

The Table 1 demonstrates that, after the adsorption the shifting occurs both to higher and lower wave numbers. This shift indicated that there were binding processes taking place on the surface of activated carbon (Pevasant *et al.*, 2003). The functional groups involved in the adsorption were as follows: Broad band 3750.26 – 3455.76cm^{-1} representing bonded OH groups and NH groups (Stuart, 2004) 2921.37 – 1952.67cm^{-1}, the aliphatic C-H groups, 1952.67-1561.07cm^{-1} , the C = O stretching group and 1037.01cm^{-1}, P-O-C stretching in a chain. These functional groups could act as chemical binding agents where carboxyl, hydroxyl and amine groups could dissociate negatively charged active surface. This means that these functional groups could attract the positively charge objects such as heavy metal ions (Volesky, 1990).

Table 1: Fourier Transform Infrared Spectrophotometer (FT-IR) Analysis of Activated Carbon prepared from Maize Cobs

FTIR Peak	Original Adsorption	Cr(VI) Loaded Ac	Diff	Assignment
1.	3750.26	3735.19	+15.07	Bonded-OH
2.	3455.76	3405.31	+50.45	
3.	2921.37	2921.68	-0.31	
4.	1952.67	1945.80	+6.87	Bonded-NH
5.	1561.07	1561.07	+0.00	
6.	1037.01	1036.21	+0.80	Aliphatic C-H group Aliphatic C-H group for anhydride C=O stretching C=O stretching P-O-C stretching

Adsorption Kinetic

Table 2 was deduced by plotting log (qe – qt) against time (t) as shown in Figure 1 for Cr (VI) ions adsorption on MCA with Ci = 5, 10, 15 and 20mg/1 at 30ºC. The qe exp

and qe cal values were found to be far from each other. Experimental results did not follow first order kinetics given by equation (1) as there was difference in two important aspects: (i) K_f (qe - qt) does not represent the number of available sites, and (ii) log qe was not equal to the intercept of the plot of log (qe – qt) Vs t

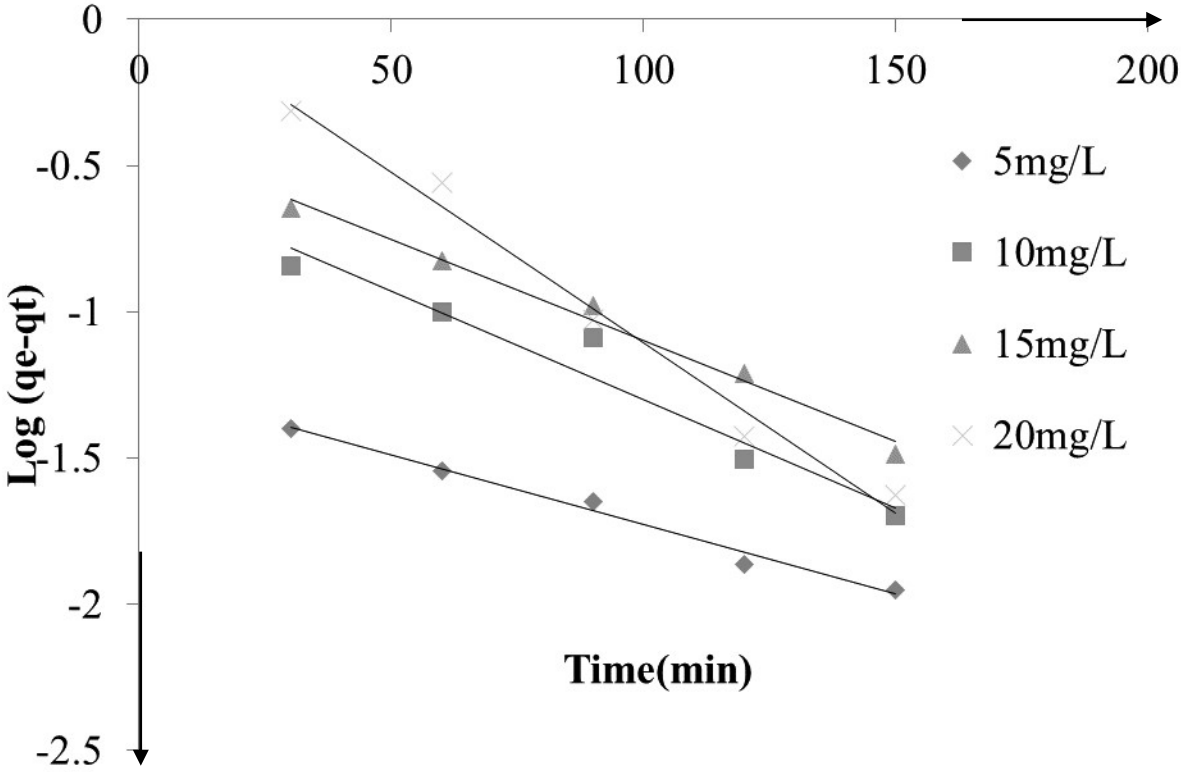

Figure 1: Lagergren plots for Cr (VI) ions Adsorption in Aqueous Solutions.

Table 2: Kinetic Parameter for The Removal of Cr (VI) ions by MCA (T = 303K), M = 0.2g/L

Pseudo First – Order Model

Ci(mg/L)	qe, exp(mg/g)	qe, cal(mg/g)	K_f (min^{-1})	R^2
5	0.6125	0.0559	0.0111	0.9858
10	1.2063	0.2743	0.0170	0.9495
15	1.7813	0.3893	0.0159	0.9859
20	2.2500	1.1405	0.0267	0.9840

Table 3 was deduced by plotting t/qt against t (Fig 2), and h is obtained from intercept. Since qe is known from the slope,
Ks can be determined from the value of h. In Table 3, the qe exp and the qe cal values from the pseudo – second – order kinetic model are very close to each other. The calculated correlation coefficients are also closer to unity for the pseudo – second – order kinetic than for the pseudo – first order kinetic model. Therefore, the adsorption can be approximated more appropriately by the pseudo – second – order kinetic model for the adsorption of Pb (II) onto MCA. Mathialagan and Viraraghavan (2002) and Taly – Costodes *et al* (2003) have reported Ks values of 0.061 and 0.305 g/mg/min for Cd (II) adsorption on perlite and saw dust of PinusSylerstris, respectively. Ks values in the range of 0.0083 – 0.0215 g/mg min have been reported by Padmavathy *et al* (2003) for the adsorption of Ni (II) onto baker's yeast.

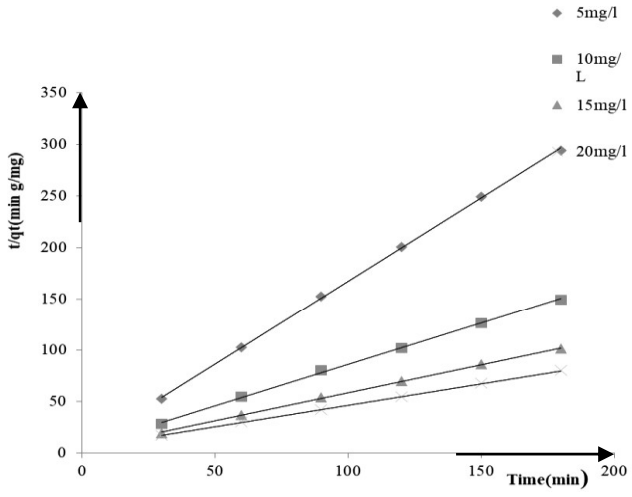

Figure 2: Pseudo-Second order kinetic plot for the removal of Cr (VI) ions by MCA

Table 3: Pseudo Second – Order Model for Cr (VI) ions

Ci	qe, exp (mg/g)	qe, cal (mg/g)	h (mg/g min)	Ks (g/mg min)	R^2
5	0.6125	0.6194	0.1748	0.4556	0.9996
10	1.2063	1.2446	0.1765	0.1137	0.9992
15	1.7813	1.8358	0.2588	0.0768	0.9994
20	2.2500	2.3952	0.2162	0.0377	0.9996

Table 4 was deduced by plotting qt against $t^{0.5}$. The extrapolation of the linear portions of the plots back to the y – axis gives intercept which provide the boundary of layer thickness. The slope of the Weber and Morris plots is defined as the parameter, characteristic of the rate values of kid is found higher in Pb(II). This shows that Weber and Morris model shows better representation than pseudo – first order kinetic model.

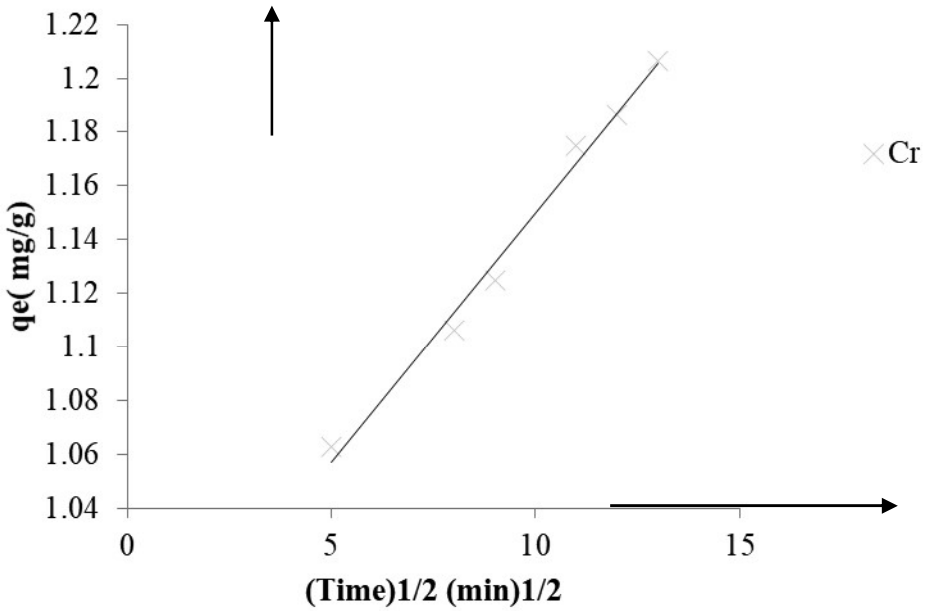

Fig. 3: Weber and Morris intraparticle diffusion plot for the removal of Cr (VI) ions by MCA (T=303K, Ci=20mg/L ,m=0.2mg/L).

Table 4: Weber And Morris Intra-Particle Diffusion for The Removal of Cr (VI) ions by MCA (T = 303K, Ci = 10mg/L, M = 0.2mg/L)

	Cr(VI)ions
Kid(mg/g min	Kid(mg/g min	0.0180
I (mg/g)	I (mg/g)	0.9643
R^2	R^2	0.9897

Table 5 was deduced by plotting log R against log t. The correlations of the values of log R (% removal) and log (time) (Fig. 3) also resulted in linear relationship, as evidenced by R^2 – values close to unity (Table 4). This also indicates that the process of intra-particle diffusion is taking place in these adsorption systems. The divergence in the value of slope from 0.5 indicates the presence of intra-particle diffusion process as one of the rates limiting steps (McKay *et al.*,1980)

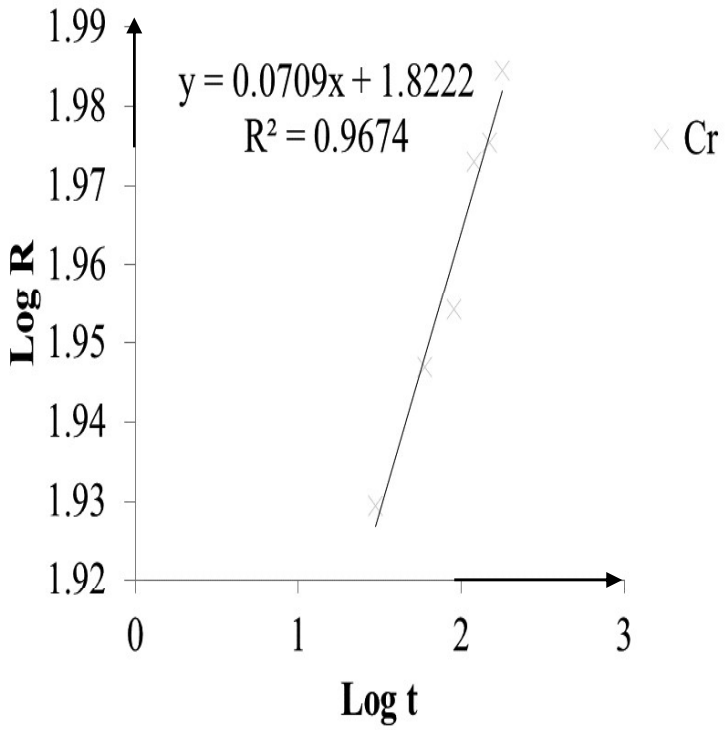

Fig. 4: The correlation of the values of Log(R%) and Log(time) for the Cr (VI) ions.

Table 5: The Correlation of the Values of Log (% Removal) and Log (Time) for the Various metal ions;

Slope	0.0709
Intercept	0.2606
R^2	0.9674

Adsorption Isotherms

Table 6 was deduced by plotting Ce/qe against Ce. The values of Langmuir and Freundlich constants were obtained.

Fig. 5 indicates that the adsorption of adsorbate on activated carbon follows the Langmuir isotherm. The Langmuir constant value is given in Table 6. The maximum adsorption capacity Qo, showed that the maize cob had a mass capacity for Cr^{6+} (5.77mg/g). The b is related to the apparent energy of adsorption for Cr^{6+} (0.068L/mg). This showed that the energy of adsorption is favourable to Cr^{6+} probably due to its small ionic radius; hence all binding sites may be available to Cr^{6+}. This preferential adsorption could be explained in terms of ionic radius of the metal ion. Adsorption of the metal was tested using separation factor R_L.

The separation parameter for the metal is less than unity indicating that maize cob biomass is an excellent adsorbent

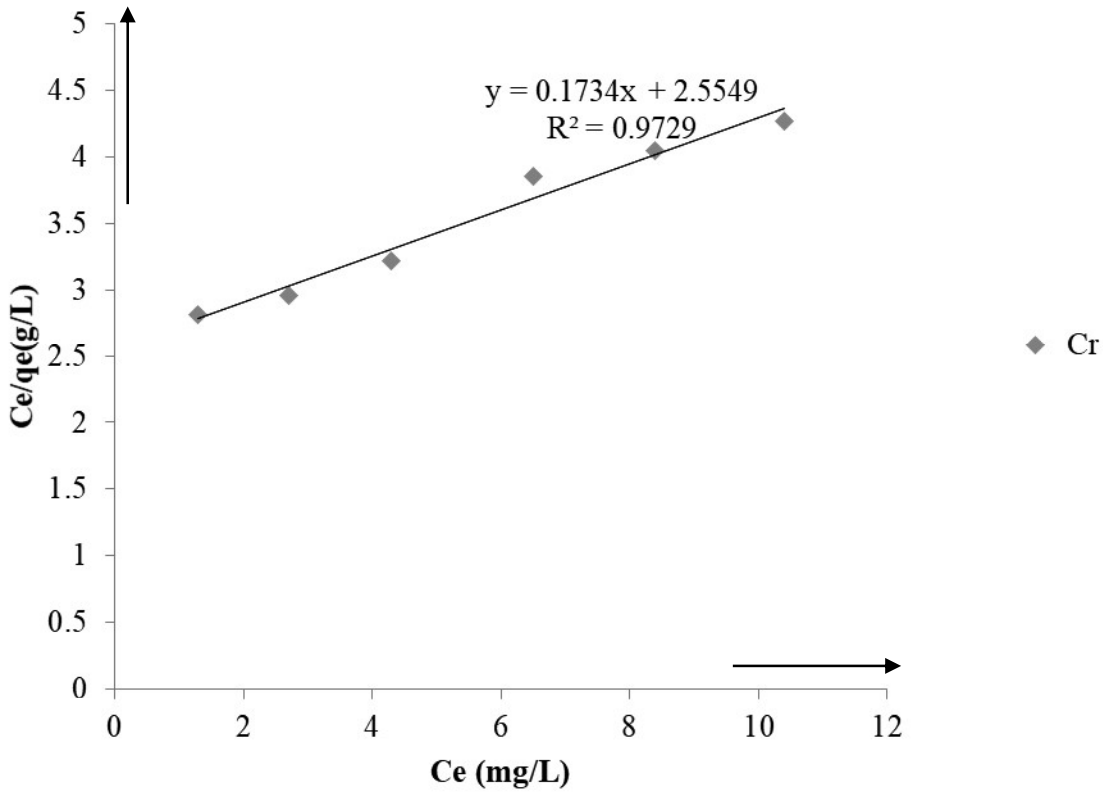

Figure 5: Langmuir isotherm plot for Cr (VI) ions adsorption in aqueous solutions

Table 6: Sorption Isotherm Constants Coefficients of Activated Carbon prepared from Maize Cobs.

Adsorbate	**Langmuir Constant**				**Freundlich Constant**		
	Q max (mg/g)	**b(L/mg)**	**R^2**	**R_L**	**K_F(mg/g)**	**N**	**R^2**
Chromium	5.7670	0.0677	0.9729	0.3299	0.3982	1.2757	0.9938

Fig. 6 reveals log qe against log Ce .The linear logarithmic plots show that the adsorption followed Freundlich model. It also indicates that the average energy of adsorption decreases with increasing adsorption capacity values of K_F and n were calculated from the intercept and slope and is given in Table 5 along with the Langmuir constant. The value of n between 1 and 10 represent good adsorption of the adsorbate onto the adsorbent (McKay et al., 1982). Values of Qe predicted by both models, as wells as the experimental values, is in Fig.6 for Chromium

ions. This also show that the Langmuir model fitted the results slightly better than Freundlich model

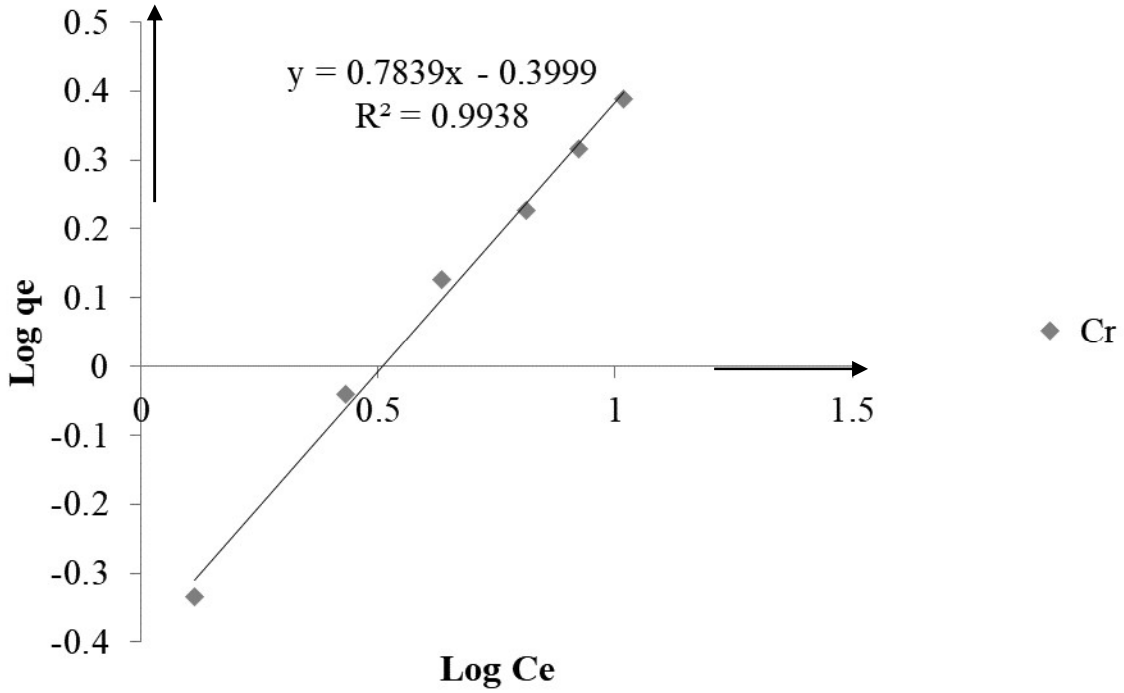

Fig. 6: Freundlich isotherm plot for Cr (VI) ions adsorption in aqueous solutions

Effect of Contact

Fig.7 reveals that the uptake of adsorbate species is fast at the initial stages of the contact period, and thereafter, it becomes slower near the equilibrium. In between these two stages of the uptake, the rate of adsorption is found to be constant. This is obvious from the fact that a large number of vacant surface sites are available for adsorption during the initial stage, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases. The adsorption capacity of this metal increased rapidly in the beginning of the reaction and reached equilibrium at different time. The Chromium reached equilibrium at 120min. A long contact time necessary to reach equilibrium indicates that the predominant mechanism is physical adsorption. The contact time obtained in this study indicates that physisorption may be involved (Ho *et al*., 1996).

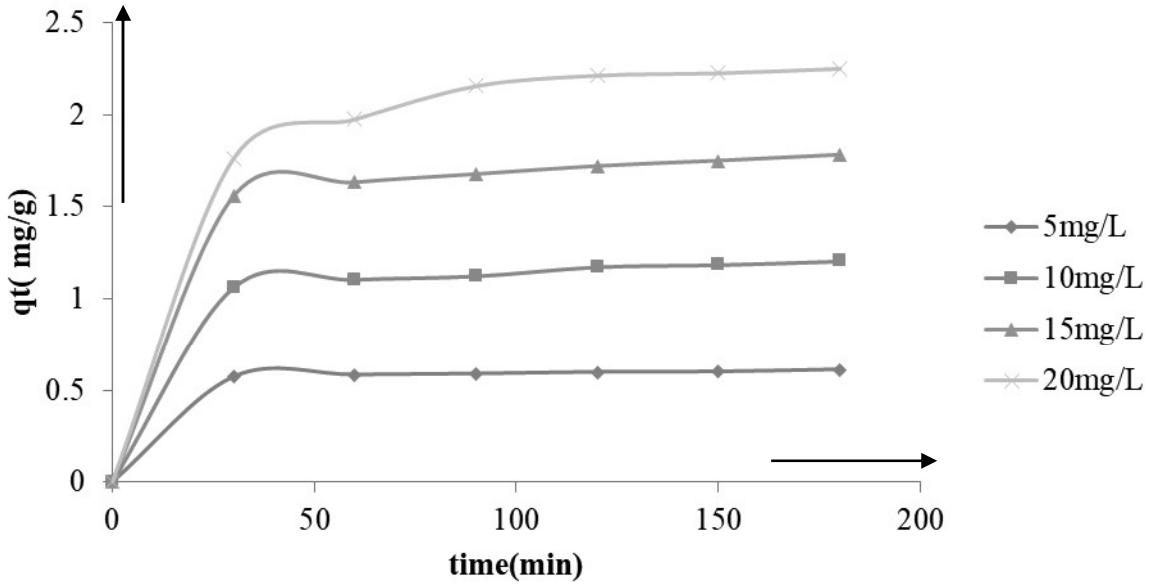

Fig. 7: Effect of contact time for Cr (VI) ions removal by MCA

Effect of Initial Concentration

The effect of initial concentration on the extent of adsorption of Cr (VI) metal ions onto MCA at m= 0.2g/L is shown in Fig.8. It was evident that metal ions removal decreased with an increase in initial concentration. This indicates that there exists a reduction in immediate solute (metal ion) adsorption, owing to the lack of available active sites required for the high initial concentration of metal ions (Kannan & Srinivasan, 1998). The actual amount of metal ions adsorbed per unit mass of MCA increased with an increase in Ci.

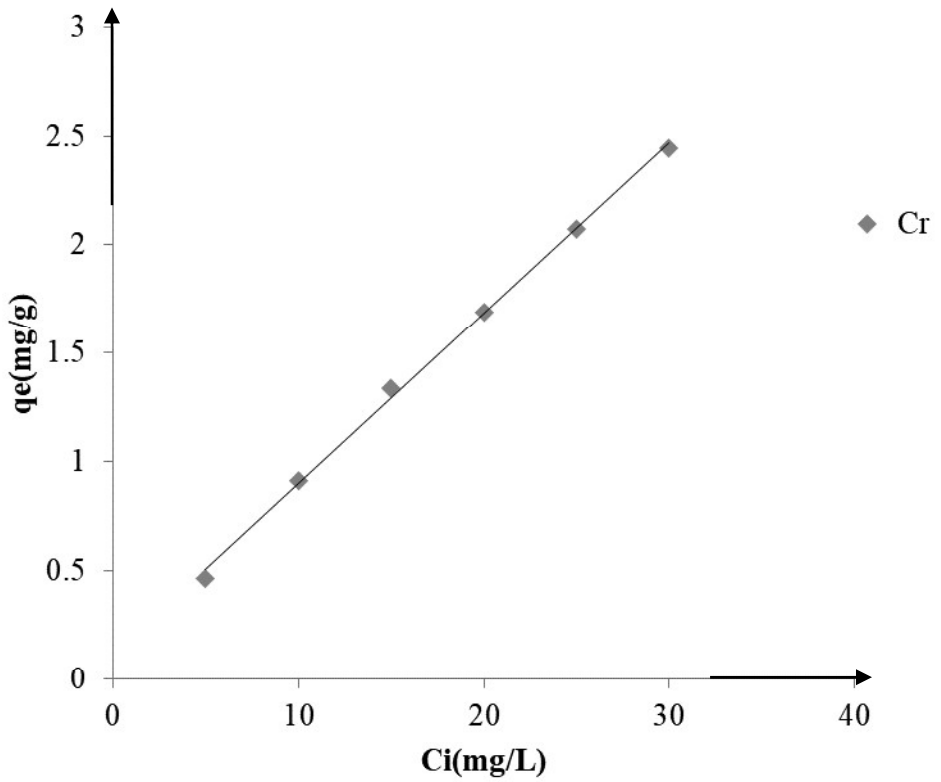

Fig. 8: Effect of initial ion concentration on Cr (VI) ions removal by MCA

Effect of pH

Fig.9 showed that for metal ion Cr^{6+}, the removal by MCA decreased as the pH of the solution decreased. The critical pH value for Chromium is 2. According to Low *et al* (1995) at low pH values the surface of the adsorbent would be closely associated with hydronium ions (H_3O^+) which will access of metal ion Cr^{6+} by attractive forces to the surface functional groups, consequently increasing the percentage of the metal removal by enhancing the removal of Cr^{6+}. At pH 1-2, the predominant Cr (VI) was $HCrO_4^-$ (Dakiky *et al.*, 2002; Hadi *et al.*, 2001), and therefore electrostatic attraction occurred between the positively charged adsorbent and negatively charged $HCrO_4^-$. However, the decrease in Cr (VI) removal at higher pH values was apparently due to the competiveness of another Cr (VI) species (CrO_4^-) and OH^- ions in the bulk (Sekar *et al*.,2004).

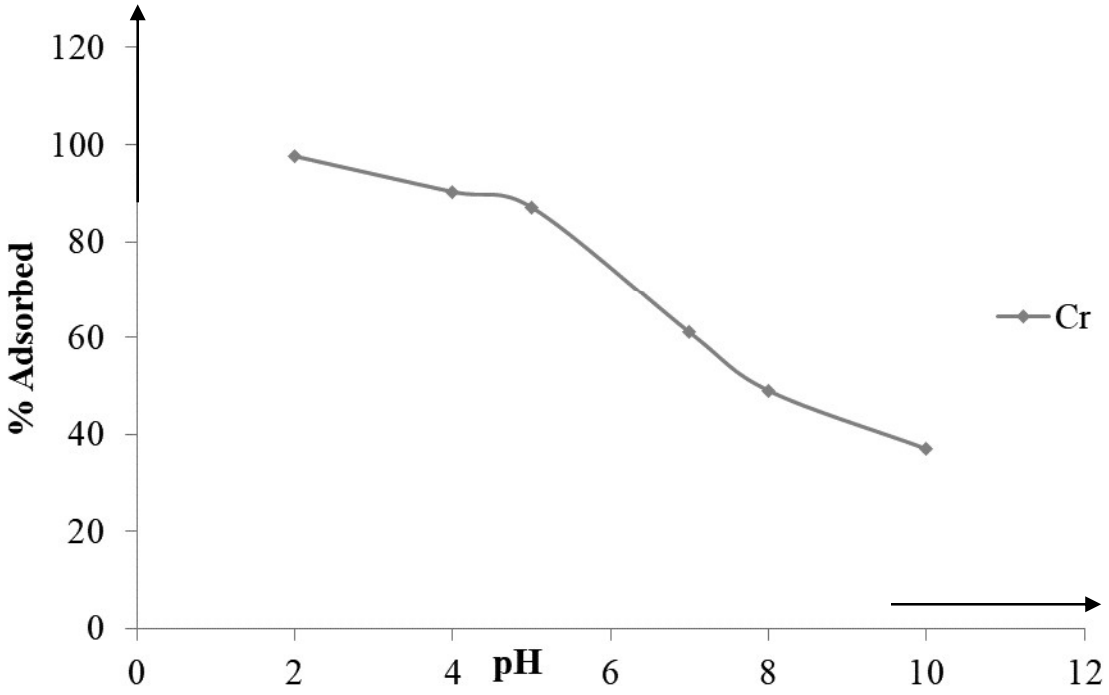

Fig. 9: Effect of pH on Cr (VI) ions removal by MCA

CONCLUSION

The kinetics of Cr (VI) ion adsorption onto maize cob biomass was found to be based on the assumption of intraparticle diffusion-controlled pseudo second order mechanism with physisorption being the predominant mechanism.

The contact time obtained in this study indicates that physisorption is involved in the adsorption process. The adsorption of the metal ion is pH dependent. It was noted that ionic radius has an influence in the magnitude of metal loading on the adsorbent. The adsorption capacity increases with increase in smaller ionic radius metal ion.

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REFERENCES

Ahmad R. and Kumar, R. (2008). Adsorption study of patent blue VF using Ginger waste material. *Iran chemical Resource,* 1, 85-94

Ahmedna, M. (1998). Granular-activated carbon from agricultural by products: *Carbon properties* and their relationship, to sugar decolorization potential. *PhD Dissertation,* Louisiana state University, Baton Rouge, L. A.

Ajmal, M., Rao, R. A., Anwar, S. Ahmed, J. and Ahmed, R (2003). Adsorption Studies on rice husk. Removal and Recovery of Cd (II) from Wastewater, *Bioresource Technol*., 86, 147 – 149.

Akporhonor, E. E. and Egwaikhide, P.A. (2007). Removal of selected metal ions from aqueous solution by adsorption onto chemically modified maize cobs. *International Journal of*

Applied Environmental Sciences, 2(2), 93-94

Allen, S. J. and Brown, P. A (1995). Isotherm analyses for single component and multi component metal sorption on to lignite. *J. Chem. Technol. Biotechnol*., 62, 7 – 14.

Allen, S.E., Grimsham, H.M., Parkinson, J.A., and Quarmby, C. (1974). Chemical analysis of Ecological materials. *Blackwell Scientific Publications, Oxford*, 80-81.

Bailey, S. E., Olin, T. J, Bricka, R. M and Adrian, D. D (1999). A review of potentially low – cost sorbents for heavy metals, *Water Resource*, 33, 469 – 2479.

Cheung. C. W., Porter, J. E. And McKay, G., (2001). Sorption Kinetic analysis for the removal of cadmium ions from effluents using bone char. *Water Resource*, 35, 605 – 621.

Dakiky, M., Khamis, M., Manassara, A., and Mereb, M. (2002). Selective Adsorption of Chromium (VI) in industrial Wastewater using low-cost abundantly available adsorbents. *Advance Environmental Research*, 6, 533-540.

Dermibas, E., Kobya, M., Sentrurk, E, Ozkan, T. (2004). Adsorption for the removal of Chromium (VI) from aqueous solution on the Activated Carbon prepared agricultural waste, *Water SA,* 30, 533

Eastmond, D. A; MacGrecor J. J. and Slesinskin, R S (2008). Trivalent Chromium Assessing the Genotoxic Risk of an Essential Trace Element and widely used Human and Animal Nutritional Supplement. (*Critical Reviews in Toxicology,* 38(3), 173 – 190.

European Union (2010). Waste and the Environment, *Luxembourg publications office (htpp://europa.eu*)

Gimba, C. E. and Bahago N. A. (2004). Adsorption of Copper, Cadmium and Chromium using activated carbon derived from *Arachishypogaea shells*. *Chem Class Journal,* 208-213

Ho, Y.S., Wase, D.A.J and Forster, C.F (1996). Removal of lead ions from aqueous solution using sphagnum moss peat as adsorbent. *Water SA* 22, 219-224.

Huang, C.Y., Kent, R.S and Marshall, S.A. (1973). Temperature dependence of Hyperfine- structure splitting of divalent Manganese in single crystal magnesium oxide. *Physics Rev. Lett*. B7, 552—553

Kagbu, J.A. (2001). A search for local options in textile effluent treatment materials, *PhD Thesis,* Ahmadu Bello University, Zaria, Nigeria, 124-145

Kannan, K.S and Srinivasan, T. (1998). Studies on the adsorption of copper by low-cost carbonaceous adsorbents. *Indian Journal of Environmental protection*. 18(3), 194-200.

Khalid, N., Ahmad, S., Toheed, A and Ahmad, J (2000). Potential of rice husk for antimony removal. *Applied Radiat isot*., 47, 467.

Leimkuehler, P.E (2010). Production, Characterization and Applications of Activated Carbon, *A thesis* presented to the Faculty of the Graduate School University of Missouri In Partial Fulfillment of the Requirement for the *degree Master of Science*.

Mathialagan, T. and Viraraghavan, T. (2002). Adsorption of cadmium from aqueous solutions by perlite. *Journal of Hazard Mater*, B94, 291-303.

McKay, G., Blair, H.S and Gardener, J.R. (1982). Adsorption of dyes on chitin I. Equilibrium studies, *Journal of applied polymer science*, 27, 3043-3057.

McKay, G., Otterburn, M.S and Sweeny, A.G. (1980). The removal of colour from effluent using various adsorbents: III- Silica: rate process. *Water Resource*, 14,10-20.

Padmavathy, V., Vasudevan, P. and Dhingra, S.C. (2003). Biosorption of nickel (II) ions on baker's yeast. *Process Biochemistry,* 38, 1389-1395.

Patnukao, P., Kongsuwan, A. and Pavasant, P. (2008). Batch adsorption of copper and lead on activated carbon from *Eucalyptus camaldulensis Dehn*. bark. *Journal of Environmental sciences,* 20, 1028-1034

Pattabhi, S., Madhavakrishnan, S., Manickavasagam, K., Rasappan, K. S., Shabudeen, P. S. and Venkatesh, R. (2008). RicinusCommunis Pericarp Activated carbon used as an adsorbent for the removal of Ni^{2+} from aqueous solution. *E - Journal of chemistry.* **5**(4), 761-769.

Pevasant P., Apiratikul R., Sungkhum V., Suthiparinyanont P., Wattanachira S. and Marhaba T. (2003). Biosorption of Cu^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+} using dried marine green *macroalga caulerpalentillifera*, *Bioresources Technology,* 97, 2321-2329.

Sekar, M., Sakthi, V., and Rengaraj, S. (2004). Kinetics and Equilibrium Adsorption study of Lead (II) onto Activated Carbon prepared from coconut shell. *J. Colloid Interface Sci*. 279, 307-313.

Sharma, V. C (2001). Adsorption of Cr (VI) onto Wollastonite: Effect of pH, *India Journal of chemical Technology*, 8, 186.

Stuart, B. (2004). *Infrared Spectroscopy Fundamentals and Applications. Analytical Techniques in the Sciences*. John Wisley and Sons Ltd. 76-80.

Taly-Costodes, V.C., Fauduet, H. and Porte, A. (2003). Delacroix, Removal of Cd(II) and Pb(II) ions from aqueous solutions, by adsorption onto saw dust of *pinussylvestris*. *Journal of Hazard Mater,* B105,121-142.

Volesky, B (1990). *Biosorption of heavy metal*. Boston: CRC Press. 240-25