RESEARCH ARTICLE

ADSORPTION OF LEAD AND CHROMIUM IONS FROM AQUEOUS SOLUTION USING SORGHUM WASTE

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ABSTRACT

Adsorption of lead and chromium ions from aqueous solution by sorghum waste was studied using the batch process. The results obtained from the study, indicated that sorghum waste is an excellent adsorbent for the removal of Pb2+ and Cr6+ from aqueous solution. Their removal efficiency was found to increase with increase in the adsorbent dose but decreased with increase in the period of contact. Functional groups in the adsorbents that were involved in the adsorption of the metal ions under investigation were identified using FTIR spectroscopy. Adsorption characteristics of sorghum waste for Pb^{2+} and Cr^{6+} fitted the Freundlich, Temkin and Dubinin-Radushkevich adsorption models. From the Freundlich and Temkin models, the extent of interaction was established through the values of their respective adsorption constant. The fitness of the adsorption data to the Dubinin-Radushkevich isotherm confirmed the mechanism of physical adsorption characterized with adsorption energies that were less than 8 kJ/mol at all concentrations. Kinetic modelling revealed that the adsorption of Pb(II) and Cr(VI) ions by sorghum waste is consistent with the pseudo second order kinetic model,

Key Words: Pollution, Heavy metals, Pb^{2+} and Cd^{2+}, remediation.

INTRODUCTION

Heavy metals possess density greater than 5 g/cm^3 and are well known for their toxicity, especially at higher concentration (Banfalvi, 2011). Unfortunately, numerous industries are engaged in the production of heavy metal rich effluence into the environment (Livingstone, 2001; Vandert *et al.*, 2003). In Nigeria and most developing countries, the most prevalent environment for discharging most industrial wastes is the water body or some isolated terrestrial environments, which will ultimately lead to aquatic pollution, either directly or through surface runoff (Abaly *et al.*, 2006). Man is greatly dependent on various forms of water bodies for transportation, drinking water, food, recreation and other activities. This implies that any activity that affects aquatic environment will ultimately drop a serious impact on man.

In attempt to reduce the quantity of heavy metals that is discharged into the water bodies, certain environmental guidelines are in operation but the basic requirement is that the concentration of heavy metal ions in an effluence must be within a certain permissible limit. Options available for removing heavy metals from aqueous solution include filtration, ion exchange and others (Mehmet

et al., 2007;Chi *et al.*, 2009). However, once of the most effective method is the adsorption of the metal ions unto an adsorbent Kannan and Rengasamy, 2005).

In view of the above, several adsorbents have been developed and utilized for heavy metal removal but some of them are not environmentally friendly in that they remove heavy metal from aqueous system and end up contaminating the aqueous system through other route (Sharma *et al.*, 2010). Green approach has given better hope in targeting this problem through the use of plant materials, nano particle, micro organism including *Eichhornia crassipes*, *Commelina communis*, *Lettuce plant*, *Maize cob*, *Banana peels*, *Elsholtza Haichowensis*, Lime, maize waste, banana and organe peel waste etc (Amadurai *et al.*, 2003; Ekmekyapar and Kaykrogh, 2007; Igwe *et al.*, 2007; Gray *et al.*, 2006; Mehdizadeh *et al.*, 2014; Shiron *et al.*, 2001). The present study is aimed at using sorghum waste as an adsorbent for the removal of lead and chromium ions from aqueous solution.

Sorghum is one of the major raw materials in most breweries. Most often, the waste are difficult to manage, therefore in this study, attempt is made to re-use soghum waste as an adsorbent for heavy metals.

MATERIALS AND METHODS

All reagents used for the study were of analar grade while the sorghum waste sample was supplied by the Champion Breweries Limited, Uyo, Akwa Ibom State, Nigeria. The sample was sundried to a constant weight. The dried sample was crush to powder form using laboratory mortar and pestle. 400 g of the sample was treated with phosphoric acid, heated to a temperature of 120 ˚C. The activated sample was repeatedly washed with ionised water until the pH of the filtrate falls between 6.0-6.5.

Standard solutions of Pb and Cr ions were prepared from lead nitrate and chromium heptaoxodichromate and from there, serially diluted concentrations of their respective solutions (20, 40, 60, 80, and 100 ppm) were prepared.

Adsorption experiment

The adsorption experiments were performed using batch method as described elsewhere (Baysal *et al.*, 2009). The experiments were conducted separately using various concentrations of the heavy metal ions, various sizes of the adsorbent and at various period of contact respectively. In each case, the concentration of the metal ion adsorbed were determined using AAS (model no AA-6800-SHIMADZU) and the equilibrium amount of metal adsorbed was calculated using the following equation (Yahaya *et al.*, 2009).

$$q_e = \frac{MV(C_0 - C_e)}{1000} \qquad 1$$

where q_e is the amount of adsorbate ion adsorbed in milligram per gram of the adsorbent, C_0 is the initial concentration of the metal ion before adsorption process, C_e is the equilibrium concentration of the metal ion in the filtrate after adsorption process and M is the mass in gram of the adsorbent, V is the volume of the solution in ml.

FTIR analysis

FTIR analysis of the sample before and after adsorption of the respective heavy metal ion was carried out using Scimadzu FTIR-8400S Fourier transform infra-red spectrophotometer. Each sample was prepared in KBr and the analysis was carried out by scanning the sample through a wave number range of 400 to 4000 cm^{-1}.

RESULTS AND DISCUSSIONS

Fig, 1 shows the variation of the amount of lead and chromium ions adsorbed with time at 303 K. The plots revealed that the amount of lead ion adsorbed increases with increase in the period of contact of the adsorbent with the aqueous solution. However, the amount of chromium ions adsorbed was found to increase with time between 20 and 40 minutes but decreases between 40 and 60 minutes and finally increases with increase in the period of contact. Generally, it has been established that within a few minutes, several changes may occur within the adsorbate-adsorbent equilibra. According to Ji, *et al.* (2009), metal ion adsorption reaches equilibrium, within 5–15 min. From Fig.1 it can be seen that Pb (II)-sorghum, Cr (VI)-sorghum, equilibra were attained within 20 minutes. It is also

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evident from the plots that the amount of Pb ions adsorbed is higher than the amount of Cr ions adsorbed.

Adsorption kinetics is significant in predicting the rate of removal of heavy metal ions from aqueous solution. In order to investigate the mechanism of adsorption (of the studied heavy metals) at various initial concentrations and temperatures, characteristic adsorption rate constants were calculated, using a pseudo first-order equation of Lagergren, (which is based on solid capacity) and pseudo second-order equation (which is based on solid phase adsorption).

Adsorption of heavy metals unto a non-living cell is generally considered as a rapid process The Lagergren equation for pseudo first order kinetics can be written as follows (Eddy and Ekop, 2005)

$$\log(q_e - q_t) = \log(q_e) - \left(\frac{k_1}{2.303}\right)t \qquad 2$$

where q_e and q_t are the amount of metal ion adsorbed (mgg^{-1}) at equilibrium and at any time, t (minutes) respectively. $k_1(min^{-1})$ is the equilibrium rate constant of pseudo first-order sorption. From equation 2, a plot of $\log(q_e - q_t)$ versus t is expected to be a linear (provided the Lagergren model is obeyed) with slope and intercept equal to $k_1/2.303$ and $\log(q_e)$ respectively. Calculated values of , k_1, q_e, and R^2, deduced from a pseudo first order plots (Figure, not presented) are presented in Table 1. The correlation coefficient for a Pseudo first order kinetic model were found to be very low hence the adsorption of Pb(II) and Cr(VI)ions onto sorghum waste do not obey Lager-green Pseudo first order kinetic equation. Therefore, a Psedo second order kinetics was considered.

A differential form of Pseudo second order kinetic model can be written according to equation 3 (Odoemelam and Eddy, 2009)

$$\frac{t}{q_e} = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{1}{q_e}\right)t \qquad 3$$

The implication of equation 3 is that a plot of $\frac{t}{q_e}$ versus t should be a straight line with slope and intercept equal to $\frac{1}{q_e}$ and $\frac{1}{k_2 q_e^2}$ respectively. Figs. 2 shows a Pseudo second order plot for the adsorption of lead and chromium ions unto sorghum

waste. Kinetic constants deduced from the slope and intercept of the plots are also shown in Table 1 From the results obtained, it can be seen that values of R^2 for a Pseudo second order model are closer to unity (unlike those for the Pseudo first order model) indicating that the adsorption of Pb(II) and Cr(VI) ions by sorghum waste is consistent with a Pseudo second order kinetic.

Effect of adsorbent dose

The effect of adsorbent dose on the amount of Pb(II) and Cr(VI) ions removed was studied by the application of different doses ranging from 0.2 to 1.0 g of the adsorbent at heavy metal concentration of 600 mg/l and at a room temperature (as shown in Fig.3). The removal of Pb(II) and Cr(VI) ions was observed to be dependent on the amount of sorghum wastes used. That is, the more the biomass, the higher the removal efficiency. This increase in the efficiency of removal with increasing adsorbent dosage may be attributed to the increase in the number of adsorption sites (El Nemr *et al.*, 2009).

Effect of concentration of heavy metal in solution.

Fig. 4 show plots for the variation of amount of Pb (II) and Cr (VI) ions adsorbed (%) (per unit mass of the adsorbent) with their respective concentrations . From the Figures, it is evident that the amount of heavy metal ions adsorbed per unit mass of sorghum waste increases with increase in the concentration of their respective heavy metal ions in the aqueous solution. This may be due to an increase in the rate of diffusion of the heavy metal ions to the sorghum surface. Such increase in rate will certainly increase the sticking probability of the heavy metal as a result of the increase in the amount of adsorbate approaching the surface of the adsorbent.

Adsorption isotherm analysis

The equation for the Freundlich adsorption model can be written in the form given by equation 4.(Ji *et al.*, 2009)

$$q_e = kC_e^{\frac{1}{n}} \qquad 4$$

where *k* and *n* are the Freundlich's constants related to the adsorption capacity and adsorption intensity of the adsorbent and they characterized the system.

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From the logarithm of both sides of equation 4. equations 5 was obtained upon simplification,

$$log(q_e) \ = \ logk \ + \ \frac{1}{n}logC_e \quad 5$$

K and *n* can be determined from the linear plot of log q_e versus log C_e (Fig.5) while 1/*n* can be estimated from the slope of the plot. 1/n is an index for the adsorption intensity of the heavy metal ion onto the sorbent or surface heterogeneity and its becomes more heterogeneous as its value gets closer to zero. 1/n value less than unity points implies adsorption behavior, similar to the Langmuir isotherm (which assumes that the surface is homogenous) while 1/*n* above 1 is indicative of cooperative adsorption. The Freundlich adsorption constants evaluated from the isotherms for Pb(II) and Cr(VI) ions are presented in Table 2. Values of R^2 calculated from the plots, reveal that the Freundlich model fitted the experimental data better than the Langmuir model indicating that there is no homogeneous distribution of active sites onto adsorbent surface (Wambu *et al.*, 2011). It is significant to note that Freundlich isotherms for the studied heavy metals have excellent correlation coefficient and that the isotherms are parallel to each other suggesting that the adsorption of Pb(II) and Cr(VI) ions onto sorghum waste follows similar mechanism. Calculated values of 1/n were relatively higher than unity, suggesting the existence of cooperative adsorption (Hamadi et al., 2001).

The adsorption of Pb(II) and Cr(VI) ions by sorghum waste was also found to obey the Temkin adsorption isotherm, which can be written according to equation 6 (Wambu *et al.*, 2011),

$$q_e \ = \ A \ + \ BlnC_e \qquad 6$$

where *A* is the Temkin adsorption potential, and *B* is the Temkin constant related to the heat of sorption while q_e (mg/g) and C_e (mg/l) are equilibrium adsorbate concentrations in the solid and aqueous phases respectively. The plots of q_e versus lnC_e (Fig. 6) for the studied heavy metals, were linear (R^2 values were very close to unity as shown in Table 2) indicating the application of the Temkin model to the adsorption of the studied heavy metals.

Adsorption parameters deduced from the plots are recorded in Table 2. The results obtained indicated that values of Temkin constants were relatively high, which implies that the strong interaction between the adsorbate and adsorbent is consistent with ion-exchange mechanism or chemical interface between the metal ions and sorghum surfaces (Okwunodulu and Eddy, 2014).

In order to predict the mechanism of adsorption of Pb(II) and Cr(VI) ions, the characteristic porosity of the adsorbent and the apparent energy of adsorption, the adsorption data were fitted into the Dubinin-Radushkevich (D-R) adsorption equation which can be expressed according to equation 7 (Hamadi *et al.*, 2001)

$$lnq_e \ = \ lnX_m \ - \ \beta\left(RTln\left(1+\frac{1}{C_e}\right)\right)^2 \quad 7$$

where q_e(mgl/g) is the concentration of the adsorbate adsorbed in the adsorbent, X_m(mg/g) is the maximum sorption capacity, β (mg^2/kJ^2) is a constant related to the mean adsorption energy, R (kJ/mol/K) is the gas constant and T (K) is the temperature. The bracketed terms in equation 7 represent the polanyl potential while the constant, β is related to the mean adsorption energy (E) according to the following equation,

$$E \ = \ \frac{1}{(2\beta)^{\frac{1}{2}}} \qquad 8$$

From equation 7, a plot of lnq_e versus $\left(RTln\left(1+\frac{1}{C_e}\right)\right)^2$ should give a straight line with slope and intercept equal to β and lnX_m respectively.

Fig 8 shows the D-R isotherms for the adsorption of Pb(II) and Cr(VI) ions by sorghum wastes. Adsorption parameters deduced from the isotherm are shown in Table 3. From the results obtained, the adsorption energy for the studied heavy metal ions are less than the threshold value of 8 kJ/mol/ therefore, the adsorption of Pb(II) and Cr(IV) ions onto sorghum waste is consistent with the mechanism of physical adsorption.

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Table 1: Pseudo first and second order rate constants for the adsorption of lead (II) and Cr (VI) ions by sorghum wastes

Cation	q_e (mg/g)	k_1 (min^{-1})	R^2	q_e (mg/g)	k_2 (gmg^{-1}min^{-1})	R^2
Pb(II)	1.6494	4.61 x 10^{-5}	0.0534	59.88024	5.74	1.0000
Cr(II)	0.7302	552.72 x 10^{-5}	0.4876	14.74926	253.13	0.9733

Table 2: Freundlich and Temkin parameters for the adsorption of some heavy metals by sorghum wastes.

Metal ion	Freundlich parameters			Temkin parameters		
	n	logk	R^2	B	A	R^2
Pb(II)	0.9975	-0.6073	1.0000	27.898	32.92	0.9471
Cr(II)	0.9943	-0.6134	1.0000	27.909	32.95	0.9478

Table 3.: Peaks and frequencies of IR absorption by sorghum waste

Peak (cm^{-1})	Intensity	Assignment
692	68.26	C-Cl stretch due to alkyl halide
1052	49.48	C-O stretch due to alcohol or carboxylic acid
1158	50.10	C-N stretch due to amine
1268	49.13	C-O stretch due to carboxylic acid
1655	33.49	C=O stretch due to carboxylic acid
2925	24.04	C-H stretch due to alkane
3306	22.30	N-H stretch due to amine
3451	22.17	OH stretch due to alcohol
3528	23.46	OH stretch due to alcohol

Table 4: Peaks and frequencies of IR absorption by sorghum waste due to adsorption of Pb (II) ions

Peak (cm^{-1})	Intensity	Assignment
1044	9.16	C-O stretch due to alcohol or carboxylic acid
1254	9.51	C-O stretch due to carboxylic acid
1630	9.09	C=O stretch due to carboxylic acid
2930	7.74	C-H stretch due to alkane
3425	6.84	OH stretch due to alcohol

Table 5: Peaks and frequencies of IR absorption by sorghum waste due to adsorption of Cr(VI) ions

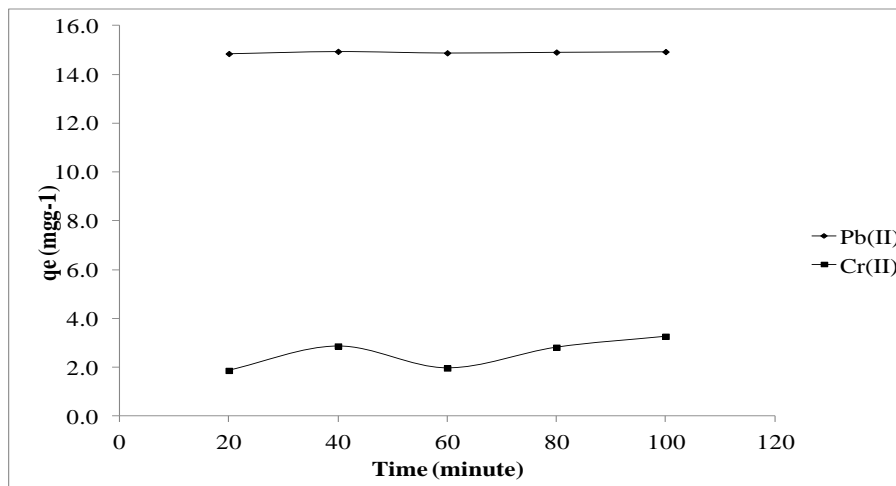| Peak (cm^{-1})	intensity	Assignment
629	10.92	C-Cl stretch due to alkyl halide
1646	7.59	C=O stretch due to carboxylic acid
2928	4.93	C-H stretch due to alkane
3420	3.94	OH stretch due to alcohol

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Fig. 1: Variation of the amount of heavy metal ion adsorbed per unit mass of the adsorbent (Sorghum waste) with time

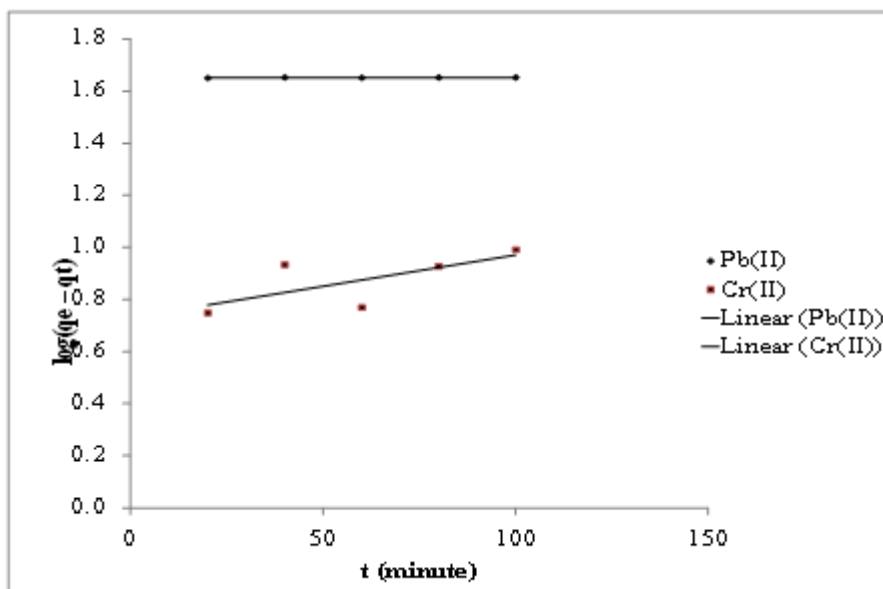**Fig. 2: Variation of log (q_e – q_t) with t for the adsorption of lead and chromium (VI) ions by sorghum waste.**

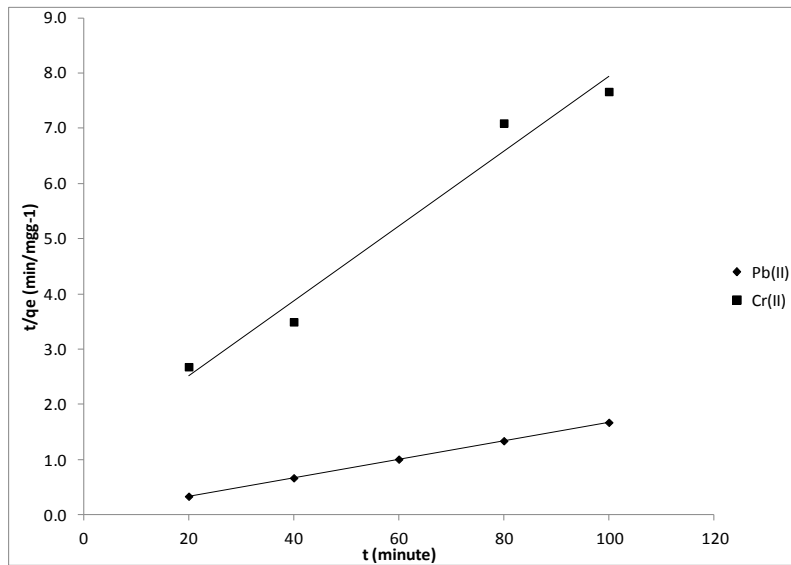**NSIKAK BASSEY ESSIEN, NNABUK OKON EDDY**

Fig. 3: Variation of $\dfrac{t}{q_e}$ with t for the adsorption of chromium and lead ions by sorghum waste
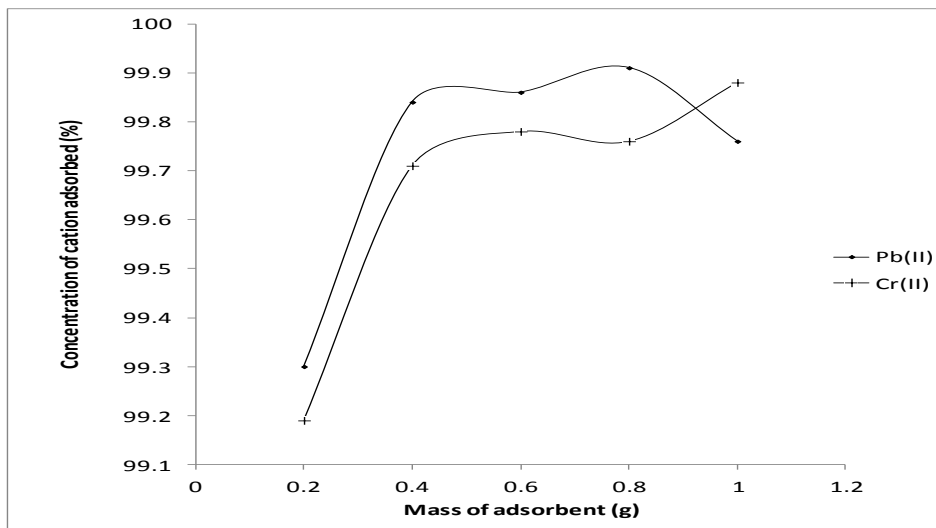
Fig. 4: Variation of the concentration of adsorbed heavy metal ions with mass of the adsorbent for the adsorption of some heavy metal ions by sorghum waste.
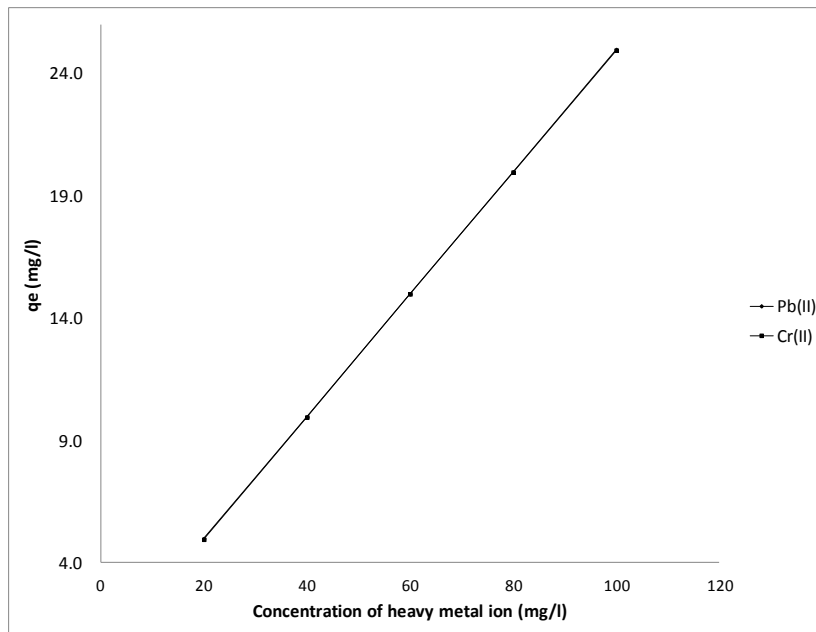
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Fig. 5: Variation of amount of heavy metal ion adsorbed (by sorghum waste) with concentration of the metal ion in solution

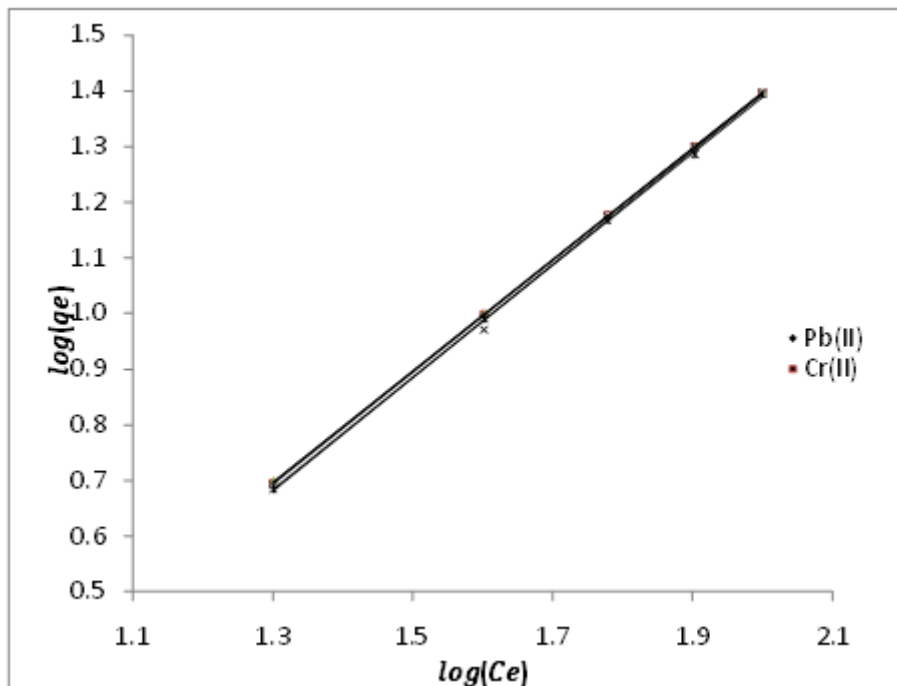**Fig. 6: Variation of log(q$_e$) with log(C$_e$) for the adsorption of some heavy metals by sorghum waste.**

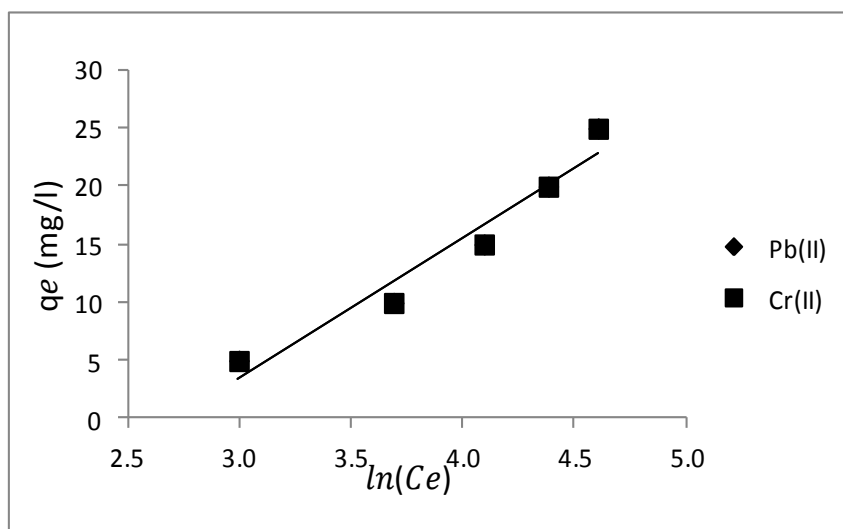**NSIKAK BASSEY ESSIEN, NNABUK OKON EDDY**

Fig. 7: Variation of q_e with $ln(C_e)$ for the adsorption of some heavy metal ions by sorghum
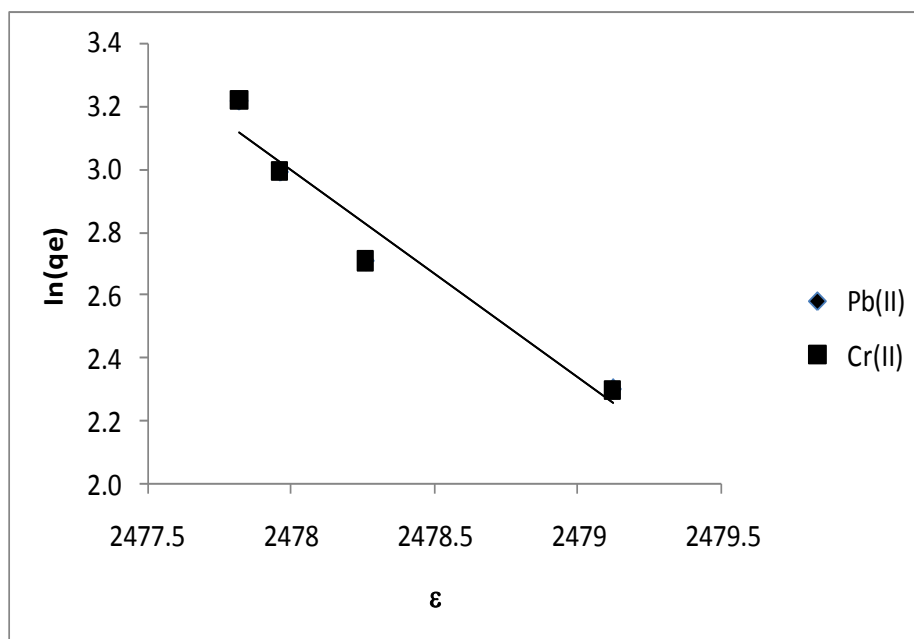

Fig. 8: Variation of $log(q_e)$ with ε for the adsorption of some heavy metal ion by sorghum

FTIR study

Peaks and frequencies of IR absorption obtained for sorghum are presented in Table 4. The spectrum revealed the presence of C –Cl stretch due to alkyl halide at 692 cm^{-1}, C=O stretch due to alcohol or carboxylic acid at 1052, C-N stretch due to amine at 1158 cm^{-1}, C-O and C=O stretches due to carboxylic acid at 1268 and 1655 cm^{-1} respectively, C-H stretch due to alkane at 2925 cm^{-1}, N-H stretch due to amine at 3306 cm^{-1} and OH stretches at 3451 and 3528 cm^{-1} due to alcohol.

When sorghum waste was used as an adsorbent for Pb, the resultant spectrum gave some adsorption frequencies and peaks, which are recorded in Table 5. A close comparison of the two set of results revealed that the C-O stretch due to

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alcohol/carboxylic acid was shifted from 1052 to 1044 cm^{-1}, the C-O stretch due to carboxylic acid was shifted from 1268 to 1254 cm^{-1}, the C=O stretch due to carboxylic acid was shifted from 1655 to 1630 cm^{-1}, the C-H stretch due to alkane was shifted from 2925 to 2930 cm^{-1} while the OH stretch due to alcohol at 3450.77 was shifted to 3425 cm^{-1}. These shifts in frequencies of IR adsorption imply that there is interaction between Pb and the sorghum surface. On the other hand, the C-Cl stretch due to alkyl halide, the C-N stretch due to amine, the N-H stretch due to amine and the OH stretch due to amine were missing in the spectrum suggesting that these functional groups were used in the adsorption of Pb (II) ions (Okwunodulu and Eddy, 2014).

Table .6 shows peaks and intensity of IR adsorption by sorghum in the presence of Cr(VI) ions as adsorbate while Table 7 present similar data when sorghum waste was used for the adsorption of Cr(VI) ions. . Examination of the spectrum of sorghum waste before and after Cr(II) ions adsorption revealed that the C-Cl stretch due to alkyl halide at 692 was shifted to 629 cm^{-1}, the C=O stretch due to carboxylic acid was shifted from 1655 to 1646 cm^{-1}, the C-H stretch due to alkane was shifted from 2925 to 2928 cm^{-1} and the OH stretch due to alcohol was shifted from 3451 to 3420 cm^{-1} indicating that there is some interactions between the sorghum surface and the adsorbed Cr (II) ions. On the other hand, the OH stretch at 3528 cm^{-1}, the N-H stretch at 3306 cm^{-1}, the C-O stretch at 1268 cm^{-1}, the C-N stretch at 1158 cm^{-1} and the C-O stretch at 1052 cm^{-1} were missing in the spectrum after the adsorption of Cr(II) ions indicating that these bonds were used in the adsorption process (Eddy, 2009).

CONCLUSION

The present study was aimed at investigating the adsorption properties of sorghum waste for lead and chromium ions. The results of the study revealed that sorghum waste is good adsorbents for lead and chromium ions. These adsorbents functions through the mechanism of physical adsorption and their adsorption properties is consistent with a pseudo second order kinetics while its characteristics is best described by Freundlich, Temkin and Dubinin-Radushkevich adsorption isotherms.

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