



Maize cob as an adsorbent for the removal of Pb^{2+} and Cr^{2+} from aqueous solution

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Abstract This study was carried out to investigate the adsorption efficiency of maize cob for the removal of Pb^{2+} and Cr^{2+} from aqueous solution using batch process. The experiment utilized maize waste, as an approach to address some levels of resource recovery. The results obtained indicated that maize cob is an effective adsorbent for the removal of Pb^{2+} and Cr^{2+} from aqueous solution because it has some useful functional groups (including C=N stretch, N-H O-H and C-H stretches), in addition to other adsorptive properties. The adsorption of Pb^{2+} and Cr^{2+} from aqueous solution is consistent with the mechanism of physical adsorption; it is time, concentration, adsorbent dose and pH dependent. Its adsorption characteristics best 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. Also the adsorption kinetic of the adsorbates agrees excellently with the pseudo first and second order kinetic models.

Keywords Heavy metal pollution, water, Pb^{2+} and Cd^{2+} , adsorption, maize waste

Introduction

Lead and chromium ions are one of the most commonly found heavy metals in industrial and some domestic wastes [1-2]. For example, lead is an essential component of wet cell batteries used in automobile and stationary engines. Mining has contributed significant output to the concentration of lead and chromium ions in the environment. Although the background concentrations of these metals in the environment may be relatively low, their potential activity can be easily enhanced when they are present in aqueous media such as industrial effluence (including waste water, used water, etc.). Most industries discharge their wastes into the surrounding water bodies or to the land which will eventually be released to the water bodies through surface runoff or the underground water system through seepage [3]. The discharge of such wastes, if enriched by heavy metal ions (such as lead and cadmium ions) will ultimately lead to aquatic pollution and through the food chain; man may be subjected to contamination.

Several countries have prescribed guidelines containing or expressing the maximum background concentrations of some heavy metals on the produced effluence. However, where industrial discharge is occurring background concentrations of heavy metals are usually higher than the permissible limits. Therefore, there is absolute need to adopt measures that can be used to reduce the concentration of heavy metals in industrial effluence, especially at the point of discharge. Adsorption is one of the best, cheaper and eco-friendly methods that have been successfully used in reducing the concentration of heavy metals in industrial waste [4-12]. Therefore, the present study is aimed at examining the adsorption potentials of maize waste for the removal of lead and chromium ion from aqueous solution.



Maize cobs are the waste product from the maize plant, which consist of the fibrous female inflorescence. Literature is relatively scanty on the use of maize cob as an adsorbent for the removal of lead and chromium ions from aqueous solution. However, Igwe *et al.*, (2005) [13] used maize cob and husk to removed Zn^{2+} , Cd^{2+} and Pb^{2+} from aqueous solution using batch adsorption process. The maize wastes were found to be efficient adsorbent for these heavy metal ions in aqueous solution. The adsorption efficiency of the maize wastes was influenced by the present of other ions, concentration of metal ions in the solutions and modification of the samples with carboxyl methyl cellulose.

Materials and methods

Materials

The samples (maize cobs) were collected from some local farmers within Ikot Ekpene metropolis, in Akwa Ibom State of Nigeria. The samples were thoroughly washed with distilled water, dried under the sun and were crushed to fine particulate size using a mill. The sample was modified by phosphoric acid, heated to a temperature of 120 °C, washed with distilled water repeatedly to a pH of 6.0. Lead and chromium standards were prepared and serially diluted solutions of the respective salts (20, 40, 60, 80 and 100 ppm) were obtained through dilution.

Adsorption experiment

Adsorption studies was carried out using batch method as reported elsewhere [14]. The respective concentrations of the studied heavy metals before and after adsorption were determined using atomic absorption spectrophotometer (Model no AA-6800-SHIMADZU). From the measured concentrations, the amount of the metal ion adsorbed in mg was calculated using the following equation,

$$q_e = \frac{MV(C_0 - C_s)}{1000} \quad 1$$

where q_e is the concentration of the adsorbate in mg/g of the adsorbent, C_0 and C_s are the initial concentration (before adsorption) and equilibrium concentration (after adsorption) of the metal ion, M is the mass of the adsorbate (in gm) and V is the volume of solution (in ml)

FTIR analysis

FTIR analysis was carried out using Shimadzu FTIR-8400S Fourier Transformed Infra red Spectrophotometer. The scanning range was within the wave number, 400 to 4000 cm^{-1} . Samples were prepared with KBr and with the aid of nujol oil, the sample were smeared on the sample holder and placed in the sample compartment of the machine. The resulting spectrum was printed directly from the attached computer and printer.

Results and Discussions

Effect of period of contact and adsorption kinetics

The variation of concentration of lead (II) and chromium (II) ions adsorbed by maize cob with time is shown in Fig. 1. The Figure reveals that the amount of chromium ions adsorbed first increases with time (between the first 20 to 40 minutes) before decreasing (between 40 and 60 minutes) and finally increases with increase in the period of contact. On the other hand, the amount of lead ions adsorbed increases with the period of contact. According to Ji, *et al.* (2009) [15], metal ion adsorption reaches equilibrium, within 5–15 min. However, the approach of adsorption equilibria for the studied adsorbates was within the first 20 minutes. The adsorption of heavy metals onto the surface of the adsorbent depends on various factors, including the period of contact, concentration of metal ion in the solution, availability of vacant adsorption sites, temperature, etc. With respect to effect of contact time, most of these parameters were maintained constant (except time). However, it is significant to state that before adsorption, adsorption sites are free but when adsorption starts, the sites are gradually occupied as the period of contact increases. This explain why the amount of Cr (II) and Pb (II) ions adsorbed by maize cob increase with time. Also, as the adsorption continues, competitive processes such as desorption may set in, hence the amount of ions adsorbed may decreased, explaining the drop in adsorption capacity (especially for chromium ions). The pattern obtained for the variation of the amount of chromium and lead ions adsorbed with time is comparable to result obtained by other [16].



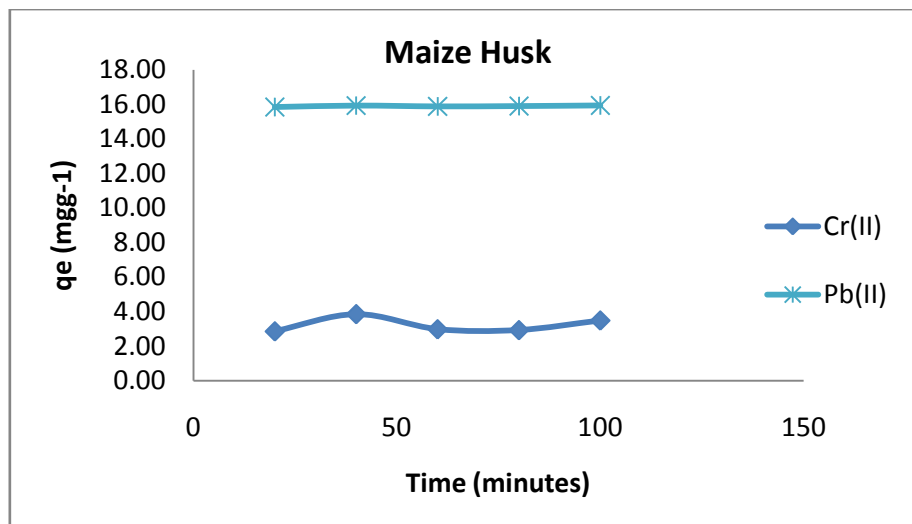


Figure 1: Variation of the amount of heavy metal ion adsorbed per unit mass of the adsorbent (Maize waste) with time

Adsorption kinetics for the prediction of the rate of removal of various concentrations of lead and chromium ions from aqueous solution were analyzed using solid capacity (a pseudo first-order equation of Lagergren) and solid phase adsorption (a pseudo second-order equation) models. The adsorption of heavy metals onto a non-living cell is generally considered to be a rapid process and according to Eddy and Ekop (2005) [17], the Lagergren equation for a pseudo first order kinetics can be written as

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

Where q_e and q_t are the amount of metal ion adsorbed (mgg^{-1}) at equilibrium and at any time, t (minutes) respectively. $k_1(\text{min}^{-1})$ is the equilibrium rate constant of pseudo first-order sorption. The implication of equation 2 is that plotting of $\log(q_e - q_t)$ versus t should be linear with slope and intercept equal to $k_1/2.303$ and $\log(q_e)$ respectively. The Lagergren pseudo first order plots for the adsorption of lead and chromium ions by maize waste are shown in Fig. 2. Values of k_1 , q_e , and R^2 , deduced from the plots are presented in Table 1. The high correlation coefficients (R^2) calculated from the plots confirmed that the adsorption of Pb(II) and Cr(VI) ions onto maize waste is consistent with the Lager-green Pseudo first order kinetic equation.

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

Cation	q_e (mg/g)	k_1 (min^{-1})	R^2	q_e (mg/g)	k_2 ($\text{gmg}^{-1}\text{min}^{-1}$)	R^2
Pb(II)	1.0055	0.0055	0.9278	78.1250	0.0002	0.9644
Cr(II)	1.0051	0.0051	0.8904	25.0000	0.0013	0.9172

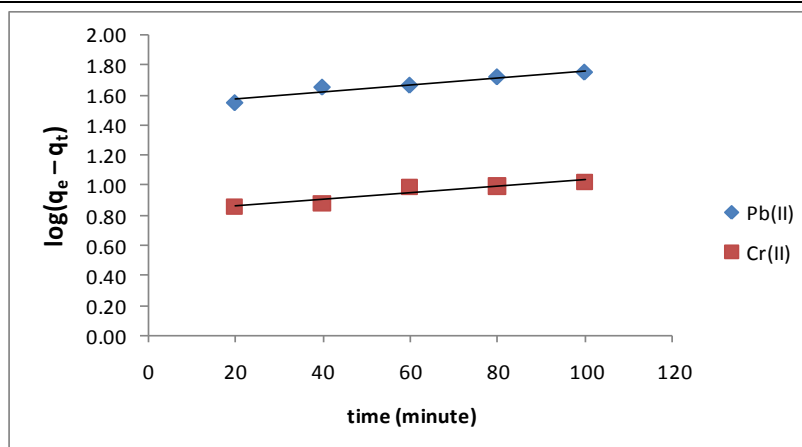


Figure 2: Variation of $\log(q_e - q_t)$ with t for the adsorption of some heavy metal ions by maizewaste

On the other hand, the differential form of Pseudo second order kinetic model can be written as [18]

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

According to equation 3, a plot of $\frac{t}{q_e}$ versus t should be linear with slope and intercept equal to $\frac{1}{q_e}$ and $\frac{1}{k_2 q_e^2}$ respectively, if this model is obeyed. Figs. 3 presents a Pseudo second order plot for the adsorption of lead (II) and chromium (II) ions unto maize waste. Kinetic parameters deduced from the slope and intercept of the plots are also recorded in Table 1. R^2 values obtained for the Pseudo second order model pointed towards excellent degree of linearity, hence the adsorption of Pb(II) and Cr(VI) ions by maize waste supports the Pseudo first and second order kinetics.

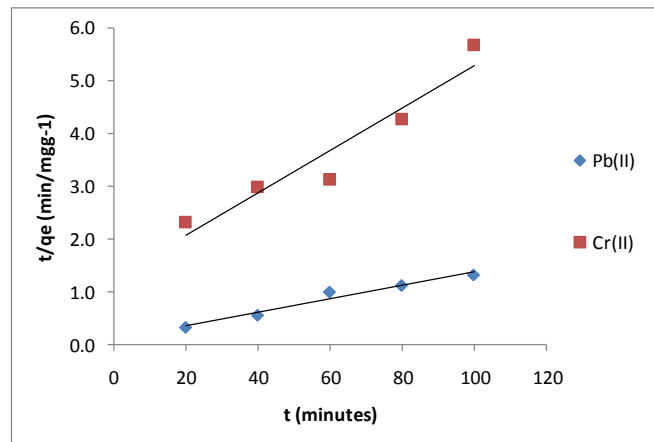


Figure 3: Variation of $\frac{t}{q_e}$ with t for the adsorption of some heavy metal ions by maize waste

Effect of adsorbent dose

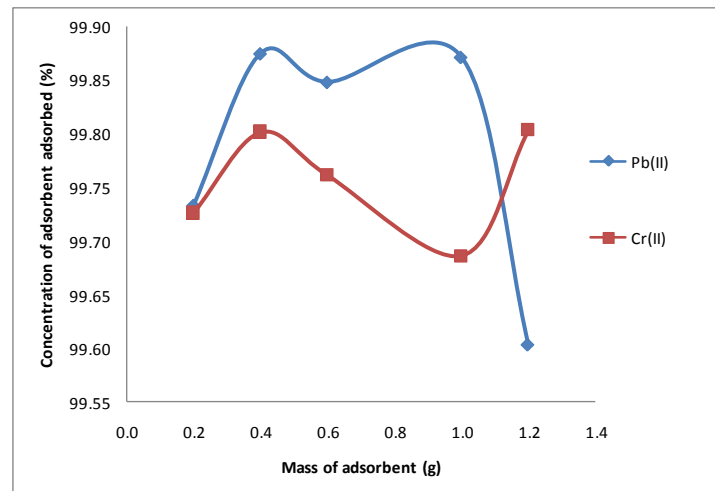


Figure 4: Variation of the concentration of adsorbed heavy metal ions with mass of the adsorbent for the adsorption of some heavy metal ions by maize waste

The adsorption capacity of plant materials may vary with the concentration of the adsorbent. Therefore, the effect of different concentrations of the adsorbent on the removal of lead and chromium ions from aqueous solution was investigated by varying the concentration of the maize waste (between 0.2 to 1.0 g) in the adsorption experiments while pH, time and adsorbate's concentration were held constant. Fig. 4 shows plots for the variation of the amount of lead and chromium ions adsorbed by various masses of the adsorbent. The plots evidently reveal that lead and chromium ions removal first increases as the adsorbent mass increases but after some time, the concentration of heavy metal removed decreases. However, after the threshold level, the amount of chromium ions removed was found to increase with increase in the mass of the adsorbent. This increase in the efficiency of removal with increasing adsorbent dosage may be attributed to the increase in the number of



adsorption sites [19]. The observed trend suggest that for a given adsorbent and for a given metal ion, there may be a maximum mass of adsorbent that is needed for effective removal of heavy metal and that beyond the limit, the adsorption may increase or decreases appreciably.

Effect of concentration of lead and chromium ions in solution

Fig. 4 shows plots for the variation of amount of Pb (II) and Cr (VI) ions adsorbed with concentration. The Figure reveals that the amount of lead and chromium ions adsorbed per unit mass of the adsorbent increases with increasing concentration. Prior to adsorption, transport process such as diffusion may be a driving force, in bringing the ions close to the adsorbent's surface. Increase in concentration can increase the rate of diffusion of the heavy metals to the adsorbent until adsorption equilibrium is established. This explains why the adsorption of lead and chromium ions increases with increase in the concentration of the heavy metals in the solution. In addition, increase in the rate of diffusion can lead to increase in the sticking probability of the heavy metal ions.

Adsorption isotherm

Adsorption characteristics of the adsorbates (lead and chromium ions) were investigated by fitting data into different adsorption models. The test indicated that the data best fitted Freundlich and Temkin adsorption models, The assumption sustaining the Freundlich adsorption model can be expressed according to equation 4 [15].

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

Where k and n are the Freundlich's constants that characterized the system. They are related to the adsorption capacity and adsorption intensity of the adsorbent and they characterized the system. Simplification of equation 4 to a linear model through logarithm expression yielded equation 5

$$\log(q_e) = \log k + \frac{1}{n} \log C_e \quad 5$$

The expression of equation 5 indicates that K and n can be determined from the linear plot of $\log q_e$ against $\log C_e$ (Fig.6) 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. It is related to surface heterogeneity. The surface becomes more heterogeneous as the ratio ($1/n$), gets closer to zero. $1/n$ values less than unity suggest adsorption behavior that is similar to the Langmuir isotherm (which assumes that the surface is homogenous) while values of $1/n$ above unity is indicative of cooperative adsorption. The Freundlich adsorption constants evaluated from the isotherms (Fig. 6) for Pb(II) and Cr(VI) ions are presented in Table 2. The closeness of R^2 values to unity confirms that the Freundlich model fitted the experimental data. Since values of $1/n$ are greater than unity, cooperative adsorption is ascertained in the adsorption behavior of lead and chromium ions unto maize cob [20-21]. The observed isotherms for lead and chromium ions are parallel to each other suggesting that their adsorption follows similar mechanism.

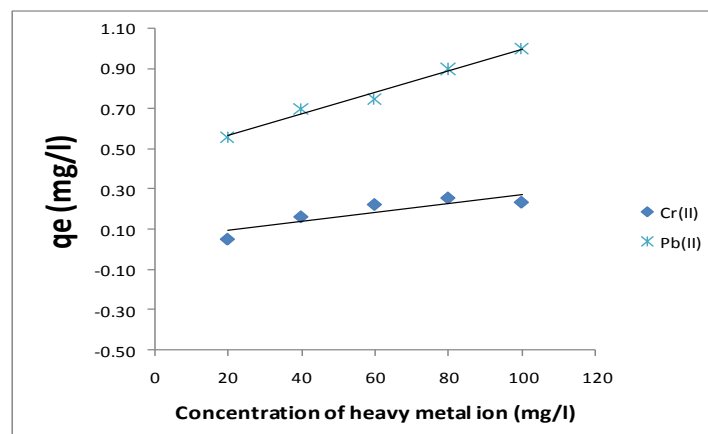


Figure 5: Variation of amount of heavy metal ion adsorbed (by maize waste) with concentration of the metal ion in solution



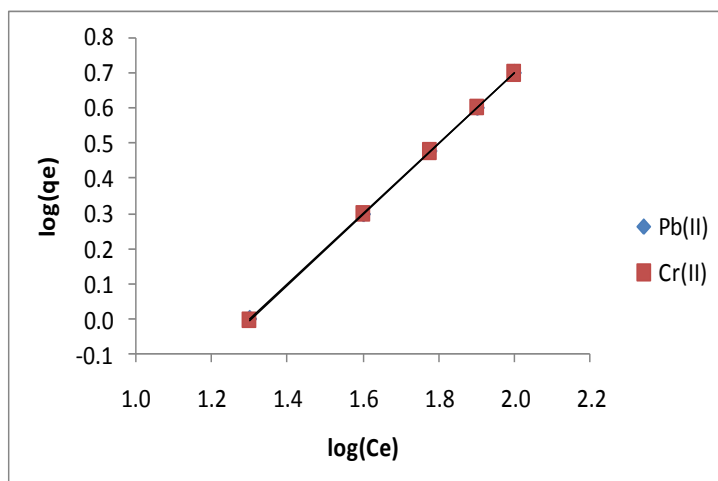


Figure 6: Variation of $\log(q_e)$ with $\log(C_e)$ for the adsorption of some heavy metals by maize waste

Table 2: Freundlich and Temkin parameters for the adsorption of Lead (II) and Chromium(II) ions by maize wastes

Metal ion	Freundlich parameters			Temkin parameters		
	n	logk	R ²	B	A	R ²
Pb(II)	0.1793	-6.5819	0.9472	1.3402	1.018	1.0000
Cr(II)	0.1792	-6.5904	0.9576	1.3127	1.0057	1.0000

The adsorption of Pb(II) and Cr(VI) ions unto maize waste was also found to obey the Temkin adsorption isotherm, expressed in equation 6 [21],

$$q_e = A + B \ln C_e \tag{6}$$

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. Equation 6 implies that a plots of q_e versus $\ln C_e$ should be linear with slope and intercept equal to B and A respectively. Fig. 7 shows the Temkin isotherms for the adsorption of lead and chromium ions unto the surface of maize cob. Also, the closeness of R^2 values to unity confirms the application of the Temkin model to the adsorption of the studied heavy metals. Adsorption parameters deduced from the plots are also presented in Table 2. The results obtained indicated that values of Temkin constants were relatively high, suggesting the existent of strong interactions between the adsorbates and the adsorbent. These interactions may be consistent with ion-exchange mechanism or chemical interface between the metal ions and maize cob surfaces [22].

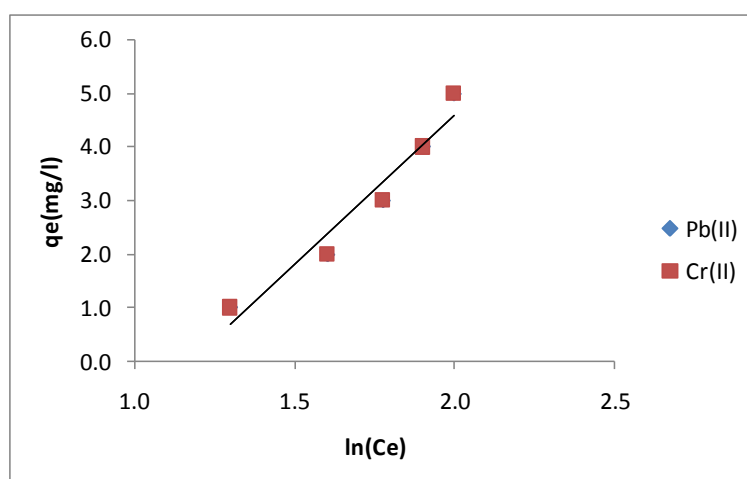


Figure 7: Variation of q_e with $\ln(C_e)$ for the adsorption of some heavy metal ions by maize waste

Dubinin-Radushkevich (D-R) adsorption model is unique in predicting the mechanism of adsorption of Pb(II) and Cr(VI) ions, the characteristic porosity of the adsorbent and the apparent energy of adsorption. The model conforming to the Dubinin-Radushkevich (D-R) adsorption can be expressed according to equation 7 [23].

$$\ln q_e = \ln X_m - \beta \left(RT \ln \left(1 + \frac{1}{c_e} \right) \right)^2 \quad 7$$

Where q_e (mg/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 represents the polanyi potential while the constant, β is related to the mean adsorption energy (E) according to the following equation,

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

Application of equation 7 to the adsorption of lead and chromium ions onto maize cob surface reveals that plotting of $\ln q_e$ versus $\left(RT \ln \left(1 + \frac{1}{c_e} \right) \right)^2$ were linear with slope and intercept equal to β and $\ln X_m$ respectively. This is shown in Fig. 8. Dubinin-Radushkevich adsorption parameters calculated from the slopes and intercepts of the plots are presented in Table 3. From the obtained results, the adsorption energy for lead and chromium ions are less than the threshold value of 8 kJ/mol/ therefore, the adsorption of Pb(II) and Cr(IV) ions onto maize cob is consistent with the mechanism of physical adsorption.

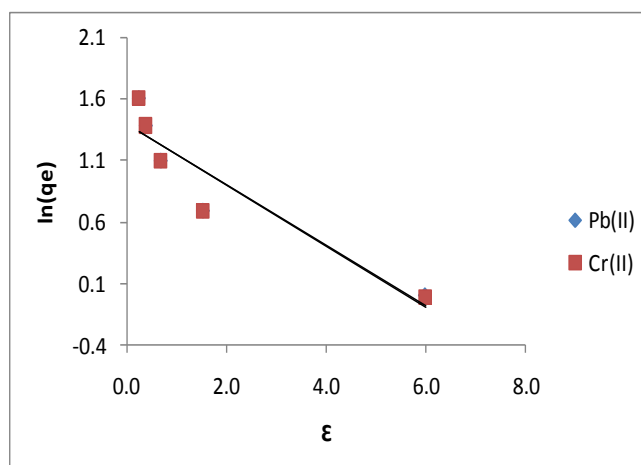


Figure 8: Variation of $\log(q_e)$ with ε for the adsorption of some heavy metal ion by maize waste

Table 3: D-R parameters for the adsorption of Pb(II) and Cr(II) ions by maize waste

Metal ion	$\beta(\text{mg}^2/\text{kJ}^2)$	$\ln(X_m)$	E (kJ/mol)	R^2
Pb(II)	0.2458	1.3914	1.4262	0.8688
Cr(II)	0.2470	1.389	1.4228	0.8703

FTIR study

FTIR provides a means of detecting functional groups and their fundamental frequency of vibrations. Application of FTIR in adsorption study can aid in the identification of functional groups that are involved in adsorption or even the mechanism of adsorption. Peaks and frequencies of IR absorption obtained for maize waste are presented in Table 4. The spectrum revealed the presence of C-X stretch due to alkyl halide at 705 cm^{-1} , C=N stretch due to amide or amine at 2220 , N-H stretch due to amine at 3388 cm^{-1} , O-H and C-H stretches due to hydroxyl group and alkyl at 3900 and 1366 cm^{-1} respectively. When maize waste was used as an adsorbent for Pb, the resultant spectrum gave some adsorption frequencies and peaks, which are recorded in Table 5. Fig. 5 reveals that the C-X stretch due to alkyl group was shifted from 705 to 646.17 cm^{-1} , the C-N stretch due to amine and amides acid was shifted from 1034 to 1030.02 cm^{-1} , the $\text{C}\equiv\text{C}$ stretch due to triple bonded carbon was shifted from 2220 to 2353.23 cm^{-1} , the O-H stretch due to alcohol was shifted from 3900 to 3428.58 cm^{-1} while the C-H stretch due to ethane at 1366 was shifted to 2928.04 cm^{-1} . These shifts in frequencies of IR adsorption



imply that there is interaction between Pb and the maize waste surfaces. On the other hand, the C-H stretch due to Carbon-Carbon bond, the $\text{-C}\equiv\text{N}$ stretch due to Carbon-Amide triple bond were missing in the spectrum suggesting that these functional groups were used in the adsorption of Pb (II) ions [22].

Table 4: Peaks and intensity of IR absorption by maize waste

Peak (cm^{-1})	Intensity	Assignment
705	19.88	C-X stretch
845	19.45	C-H "oop"
1034	22.31	C-N stretch
1366	21.88	C-H rock
2220	20.76	$\text{-C}\equiv\text{N}$ stretch
2358	21.88	$\text{-C}\equiv\text{C-}$ stretch
3388	23.67	N-H stretch
3900	20.56	OH stretch

Table 5: Peaks and frequencies of IR absorption by maize waste due to adsorption of Pb (II) ions

Peak (cm^{-1})	Intensity	Assignment
646.17	20.529	C-X stretch
1030.02	19.502	C-N stretch
1428.34	19.842	C-C stretch
1641.48	19.989	$\text{-C}=\text{C}$ stretch
2353.23	18.787	$\text{-C}\equiv\text{C-}$ stretch
2928.04	18.377	C-H stretch
3428.58	16.259	OH stretch

Table 6 shows peaks and intensity of IR adsorption by maize in the presence of Cr(VI) ions as adsorbate while Table 6 presents similar data when maize waste was used for the adsorption of Cr(VI) ions. The spectrum of maize hob before and after Cr(II) ions adsorption revealed that the C-X stretch due to alkyl halide at 705 was shifted to 600.85 cm^{-1} , the C-H stretch due to ethane was shifted from 845 to 1430.26 cm^{-1} , the C-N stretch due to amine was shifted from 1034 to 1038.7 cm^{-1} , the OH stretch due to alcohol was shifted from 3900 to 2935.76 cm^{-1} , $\text{-C}\equiv\text{C}$ due to carbon-carbon triple bond was shifted from 2358 to 2353.23 and the N-H stretch due to amine/amide was shifted from 3388-3419.9 indicating that there is some interactions between the maize surface and the adsorbed Cr (II) ions. On the other hand, the $\text{-C}\equiv\text{N}$ stretch at 2220 was missing in the spectrum after the adsorption of Cr(II) ions indicating that this bond were used in the adsorption process [23].

Table 6: Peaks and intensity of IR absorption by maize waste after adsorption of Cr(II) ions

Peak (cm^{-1})	Intensity	Assignment
600.85	22.315	C-X stretch
1038.7	22.585	C-N stretch
1430.26	23.504	C-H rock
1640.51	23.458	$\text{-C}=\text{C-}$ stretch
2353.23	22.008	$\text{-C}\equiv\text{C-}$
2935.76	21.409	OH stretch
3419.9	18.566	N-H stretch

Conclusion

The present study reveals that maize cob is an excellent adsorbent for the removal of lead and chromium ions from aqueous solution. The adsorbent possess characteristics that fitted the Freundlich and Temkin adsorption models. Its adsorption potential is strongly attributed to the possession of suitable functional groups and the potential of rendering cooperative adsorption property. The mechanism of adsorption of lead and chromium ions by maize cobs is physical adsorption, characterized by low adsorption energies.



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