REMOVAL OF CADMIUM (II), COBALT (II) AND NICKEL (II) IONS FROM AQUEOUS SOLUTION USING CORNCOB WASTE

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ABSTRACT

The rapid spate of development of many industries has led to wastes containing heavy metals being directly or indirectly discharged into the environment. This study employed the use of corncob an agricultural waste for adsorption of cadmium (II), cobalt (II), and nickel (II) in batch mode at room temperature. The residual metal was determined with flame atomic absorption spectrophotometer. The study investigated the influences of adsorbent dosage, solution pH, contact time, and initial metal concentration on the removal of metal ions. The Langmuir and Freundlich isotherm models were used to fit the equilibrium adsorption data. The reaction kinetics of the cadmium (II), cobalt (II) and nickel (II) removal from the aqueous solution were identified and correlated to the pseudo first and second order kinetic models. The results showed an increase in adsorption by metal ions studied with an increase in adsorbent dosage. Metal uptake showed a pH-dependent profile with optimum at pH values 4.0 for Cd (II) as well as Ni (II), and 8.0 for Co (II) ions. The Freundlich adsorption isotherms model fitted the experimental data best with the regression coefficient ranging between 0.837 and 0.989 for the metal ions. A kinetic study of the adsorption process showed that adsorption of cadmium (II), cobalt (II), and nickel (II) on corncob was observed to follow closely to the pseudo-second–order. It was concluded that corncob exhibited rapid adsorption capabilities and high efficiency in removal of cadmium (II), cobalt (II) and nickel (II) ions from aqueous solution.

Keywords: adsorption, aqueous solution, agricultural waste, corncob, industries, isotherms

INTRODUCTION

Environmental pollution by heavy metals has become an ecotoxicological hazard of prime interest and increasing significance (Pehlivan *et al*., 2012). Toxic metal contamination of industrial wastewater is an important environmental problem.

Many industries, such as automotive industries, metal finishing, electroplating, battery manufacturing, mining, electric cable manufacturing, tannery, steel and textile industries, release various concentrations of heavy metals like cadmium, zinc, cobalt, nickel, into the environment. Conventional methods for removing heavy metals from aqueous solutions include chemical precipitation, ion exchange, membrane processes and biosorption technologies. Among these different physicochemical processes, the sorption method shows the best prospects owing to its economic feasibility and environmentally friendly behaviour (Tan *et al*.,2010).In recent years much attention has been paid to sorption techniques and the design and synthesis of new sorbents for toxic metal ions. Biosorption is an emergent and low cost option to treat heavy metal pollutants that would otherwise create a serious environmental hazard (Pehlivan *et al*.,2012). Biosorption is assumed to arise from two basic mechanisms: an initial rapid metal ion uptake due to physical sorption and a subsequent slow uptake due to chemisorptions. Indeed, it has been reported that most metal biosorption of divalent metals occurs in a short time interval (about 15 min) after solid–liquid contact (Volesky,2001). Biosorption is a fast and reversible reaction of the heavy metals with the biomass matrix. The widespread industrial use of low-cost adsorbents for wastewater treatment is strongly recommended presently, due to their local availability, technical feasibility, engineering applicability and cost effectiveness. In recent years, a vast number of publications have been dedicated to the removal of heavy metals from wastewater by using sorption techniques with different low cost materials (Gupta *et al*., 2009 and Sdiri, 2012). Agricultural wastes are widely used for the purification of wastewater and vary greatly in their ability to remove metals from solution. Various agricultural by-products have been used for metal removal from wastewater, such as banana peels, coconut shell, cotton seed hulls , peat, peanut,, pine bark, hazelnut shell, orange peel, rice husk, sawdust, shells, soybean ,sugarcane bagasse, wood, wool (Hasar, 2003; Nasim*et al*., 2004 and Olayinka *et al*., 2005).The abundant natural occurrence and the presence of large amounts of surface functional groups make agricultural waste a good alternative to expensive synthetic adsorbents (Hasar, 2003 and Olayinka *et al*., 2007).Maize known as corn is an important cereal crop in sub-Saharan Africa and substantial staple food for more than 1.2 billion people in sub-Saharan Africa and Latin America(IITA, 2009). Annual production of maize is more compared to other cereals. Production of maize worldwide is 785 million tons, with the largest producer, the United States, producing 42%. Africa produces 6.5% and the largest African producer being Nigeria with nearly 8 million tons, followed by South Africa (IITA, 2009; Ogunjobi and Lajide, 2013). When harvested, corn wastes namely corncobs are either left to dry on the farm after which they are burnt off or found littering the streets of market places. This practice does not help in building an eco-friendly economy. A better approach to this is to convert them to more useful materials. Corncob is a heterogeneous material consisting of particles of irregular shapes having noticeable layers with pores of varying size which provides a possibility for the metal ions to be adsorbed. Corncob is basically composed of cellulose along with lignin, and all these components contribute as active sites for the adsorption of metal ions. Some studies have shown corncob as a good adsorbent for metal ions removal. Arunkumar *et al*., (2014) reported Ni ions removal from aqueous solution with the aid corncob, also (Muthusamy and Murugan, 2016) study shown that 95% Pb ions were successful adsorbed on the corncob biopolymer. Norozi and Haghdoost, (2016) reported that Mn (VII) was removed through adsorption at pH4 for 60 min duration in equilibrium-batch mode system. The modified corncob with polyacrylamine studied by (Lin *et al*., 2015) gave a better adsorption of Cd (II) ion.

The objective of this study is to evaluate the efficiency of the agricultural waste materials otherwise known as biopolymer (corn cob) to remove cadmium (II), cobalt (II), and nickel (II) from different aqueous solutions. Batch adsorption process will been used to evaluate the maximum adsorption capacity of the corncob biopolymer. The main parameters to be investigated are pH, contact time, initial metal ions concentration and biosorbent dosage. Biopolymer characterization will also be determined with Fourier transform infra red(FT-IR) analysis and elemental analysis will be done.

MATERIAL AND METHODS

Material preparation (Adsorbent)

Corncobs were obtained from a local supplier, cut into small pieces and blended. They were sieved to pass through a 2 mm stainless steel sieve and the adsorbent was stored in clean polyethylene containers prior to analysis.

Physical Characteristics of the Corncob

The elemental analysis of the corncob was determined with VarioElementar EL 111 series model while the surface morphology of the adsorbents was investigated by Scanning electron microscope (SEM) with model (JOEL JSM 840 scanning electron microscope). Infrared (IR) spectra of the corncob were recorded on a Perkin-Elmer Fourier transform-IR (100 FT-IR) spectrophotometer with wavenumbers between 4000cm^{-1} to 650cm^{-1}

Batch Adsorption Studies

In this study, all chemical reagents used were analytical grade and deionized water was used to prepare all the solutions. The 1000 mg/L solutions of Co(II), Cd(II) and Ni(II) metal ions were prepared from analytical grade $Co(NO_3)_2 \cdot 6H_20$, Cd metal and $NiSO_4.7H_2O$ respectively. The preparation of the solutions of each of Co (II), Cd (II) and Ni(II)were achieved by dissolving 3.717 g, 1.000 g and 4.477 g respectively in deionized water and made up to 1000 mL in standard flasks. The prepared aqueous solutions (1000 mg/L) (stock solutions) were diluted with de-ionized water to obtain the working standard solutions.

Sorption capacity of corncob was determined by contacting 0.2-1.0 g of corncob with 50 mL of Cd, Co, and Ni solutions of known concentration (50 mgL^{-1}) in 250 mL Erlenmeyer flasks, shaken on a orbital shaker respectively for 2 hrs. The suspensions were agitated at 200 rpm, filtered out at the end of pre-determined time intervals, and finally analyzed for its metal ion concentrations using Atomic Absorption Spectrophotometric analysis (Analyst 200 AA, Perkin Elmer, USA). The effect of pH on the metal sorption by corncob was evaluated using varying pHs from 2 -8at the optimum dosage obtained from the dosage variation. The initial pH of the metal solution was adjusted to the desired pH value using 0.1 M HCl or 0.1 M NaOH. Numerous initial metal concentrations (20, 40, 60, 80, and 100 mgL^{-1}) were also been determined throughout the study after the optimum dosage and pH. The rate of metal sorption by corncob was determined by analysing the residual metal in the supernatant after contact durations of 10, 40, 50, 70, 90, and 120 min. Corn cob-free blank was used as the experimental control. The experiments were performed in duplicate and the average values were used in data analysis.

The percentage of metal adsorption by the adsorbents was calculated using this equation:

$$\%\text{Adsorption efficiency of the metal ions} = \frac{C_o - C_e}{C_o} \text{x100 Eq. (1)}$$

C_o and Ce were initial and residual concentrations (mg/L) of ions studied, respectively.

Adsorption capacity was computed by using the mass balance equation for the adsorbent:

Adsorption capacity (mg/g) $q = \frac{(C_o - C_e)V}{W}$ Eq. (2)

Where Co and Ce (mgL^{-1}) are the concentration of ions at initial and equilibrium time t, respectively, V is the volume of ions solution (L) and W is the mass of corncob (g).

Equilibrium Modeling

Isotherm studies give information on the capacity of biosorbent. Sorption isotherms are characterised by certain constants and describe the mathematical relationship between the quantity of adsorbate and concentration of adsorbate remaining in the solution at equilibrium. The sorption data of the ions have been correlated with the Langmuir and Freundlich models Eq.(3)and(4). These isotherms relate metal uptake per unit weight of biosorbent (qe) to the equilibrium metal ion concentration in the bulk fluid phase (Ce).

Langmuir model:

$$q_e = \frac{Q_x K_L . C_e}{1 + K_L . C_e} \qquad \text{Eq. (3)}$$

where q_e (mg./g) is the maximum metal uptake capacity under the given conditions per unit weight of corncob to from a complete monolayer on the surface and K_L is the equilibrium adsorption constant which is related to the affinity of the binding site, Ce is the equilibrium metal ion concentration in the bulk fluid phase.

The Freundlich model:

$$q_e = K_f C^{1/n} \qquad \text{Eq.(4)}$$

where

K_f and n are Freundlich constants which features the system, indicating the adsorption intensity. The equation can be linearised in logarithmic form and the Freundlich constants can be determined.

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \qquad \text{Eq.(5)}$$

Kinetic modeling

The mechanism of adsorption of ions was tested using the pseudo first order Lagergren

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \qquad \text{Eq.(6)}$$

where *q*e and *qt* are the amounts of the metal ions adsorbed (mg/g) at equilibrium and at time *t* (min), respectively, and K_1 is the adsorption rate constant (1/min). The integrated rate law becomes:

$$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303t} \qquad \text{Eq.(7)}$$

The applicability of the second order expression which has been applied for analysing chemisorptions kinetics rate is expressed as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad \text{Eq.(8)}$$

Where $q_e$andq_t are the sorption capacity at equilibrium and at time t, respectively (mg/g) and k_2 is the second order rate constant (g/mg.min). For the boundary conditions to q_t=0 to q_t= $q_t$at t=0 to t=t; the integrated rate law becomes:

$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} - kt$ and this can be written as:

$$\frac{t}{q_e} = \frac{1}{k_2 q_e^{\,2}} + \frac{1}{q_e} t \qquad \text{Eq.(9)}$$

The plot t/q_t versus t of equation gives a linear relationship from which qt and k_2 can be determined from the slope and intercept of the plot (Gupta and Babu 2009)

RESULTS AND DISCUSSION

Characterisation of the Corncob

Table 1 gives a detailed elemental composition of the corncob. The corncob consist mainly high percentage of carbon (43.8%). The SEM micrograph of corn cob is shown Figure 1. It is clear from this image that the surface is rough, porous and irregular shapes. Figure 2 displays the FT-IR spectra of corncob in its natural form. The spectra displayed several peaks representing that corn cob is composed of various functional groups which possibly help in binding of the metal ions. The appearance of a peak in natural corn cob at 3325 cm^{-1} represents –OH stretching and N-H stretch of amines. The peak at 2916 cm^{-1} and 2160 cm^{-1}correspond to the presence of – CH_3 , –CH_2 –CH stretching of aliphatic groups and of C=C stretching respectively. The peaks at 1633 cm^{-1} indicates the presence of C=O stretching / N-H bending of amides. The peaks at 1244 cm^{-1} and 1017 cm^{-1} stretching of C–N the amine group and C-O of alcohol respectively.

Table1: The % elemental analysis of corn cob

Element	Percentage present
Carbon	43.75
Hydrogen	6.21
Nitrogen	0.34
Sulphur	0.06

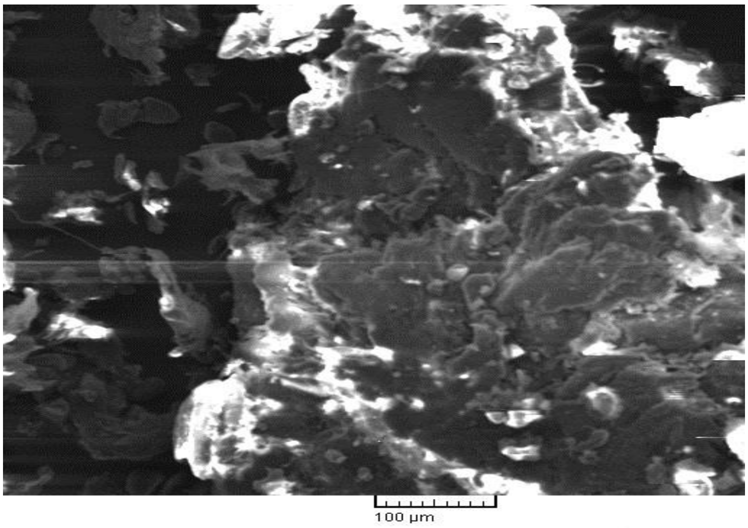

Fig. 1: SEM micrograph of Corn cob

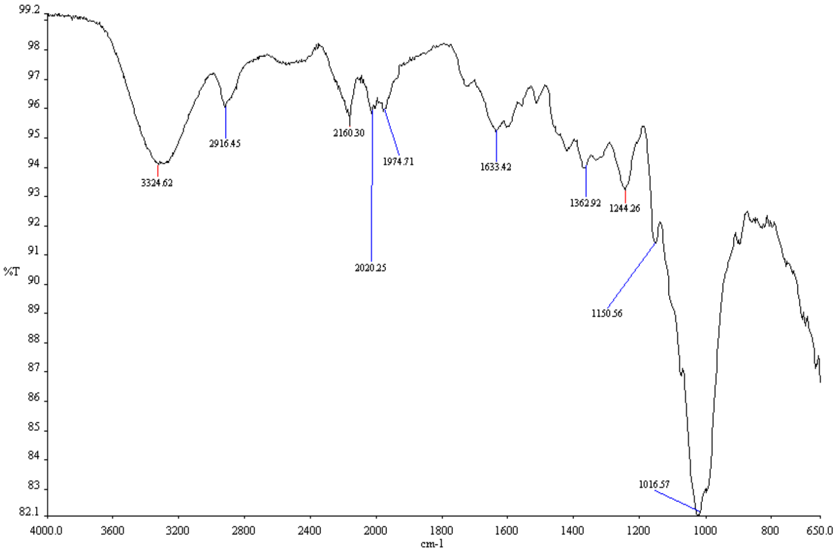

Fig. 2: FTIR spectra of corncob.

Effect of adsorbent dosage on the adsorption of metal ions

The effect of the dosage of corncob on adsorption of Cd^{2+}, Co^{2+}, and Ni^{2+}ions were monitored. Various adsorbent dosages varying between 0.2 and 1.0 g were used. The results obtained from Fig (3); show that the ion removal increased with increase in adsorbent dose, but it then decreased, however saturation of the adsorbent resulted in the decrease of the adsorption after certain dosage. Increasing removal of ions with adsorbent dosage can be linked to increased surface area and the availability of more adsorption sites. There was observed a rise in adsorption from 18.6 to 84.7% for Co and 26.2 to 78.5% for Ni as the dosage of adsorbent was varied from 0.2 to 0.8g while Cd gave a rise of 89.7 to 91.4% from 0.2 to 1.0g.

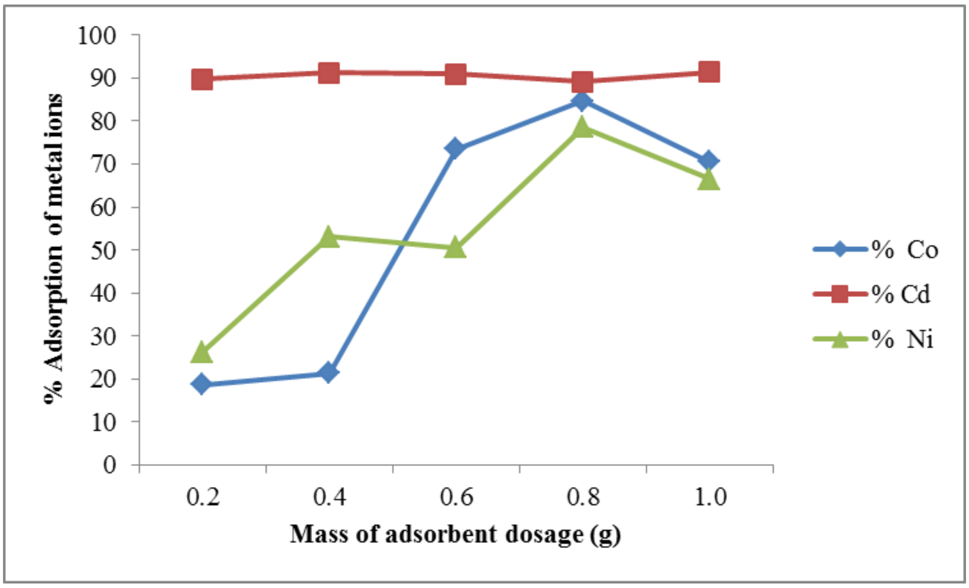

Fig. 3: Effect of adsorbent dosage on the ions

Effect of pH on the adsorption of metal ions

The pH is an important parameter controlling adsorption capacity of the adsorbent. The adsorption experiments were carried out at the pH range of 2.0–8.0. The removal of Cd^{2+}, Co^{2+}, and Ni^{2+} ions was pH dependent. The % adsorption capacity by the corncob is shown in Fig. 4. It is observed that a gradual rise in the adsorption of the metal ions took place with increase in pH from 2.0 to 8.0 for Co^{2+}, 2.0-4.0 for $Cd^{2+}$and Ni^{2+}. The low biomass-metal binding capacity in lower pH is due to the competition of metal ions with protons for active sites, as the functional groups on corncob biomass surface are protonated. It is also because of the electrostatic repulsion between the protonated surface and the metal ions. The rapid increase in the removal of Co^{2+} from this pH can be attributed to the formation of metal hydroxide thereby removal was mostly due to precipitation and not by sorption. The rate of adsorption increased from 26.0% to 95.7% for Cd^{2+}, 18.3% to 86.6% for $Co^{2+}$and 72.0% to 98.2% for Ni^{2+}, as the higher pH weakens the competition between the metal ions and H^+ions bond to the biomass, and H^+ions got replaced by the metal ions Azouaou *et al.* (2010). The maximum adsorption was found at pH 4.0 for both $Cd^{2+}$and $Ni^{2+}$and 8.0 for Co^{2+}.

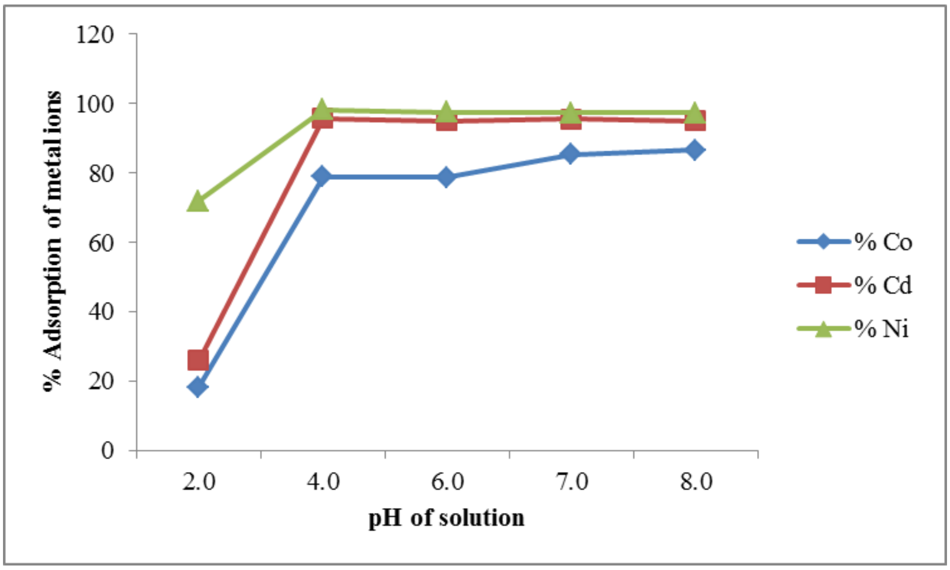

Fig. 4: Effect of pH on the metal ions

Effect of concentration on the adsorption of metal ions

The initial concentration is an important factor to be considered for effective adsorption of the metal ions. The adsorption experiments with varying initial concentrations of 20–100 mg L^{-1}, with fixed adsorbent dosage at optimum pH for each metal ion were carried out. The adsorption capacity of the biomass increased with increasing concentration of the metal ions, however, the optimum concentration for$Co^{2+}$and $Cd^{2+}$was observed to be 40 mg/L and Ni^{2+} was 30 mg/L after which there was a decrease in the percentage removal as the concentration increased as shown in Fig (5). The phenomenon showed that corn cob biomass has fixed number of active sites that become saturated at a certain concentration of the metal ions. In addition, the results obtained showed that the adsorbent can be efficiently used for removal of metal ions from wastewater with low metal ion concentrations.

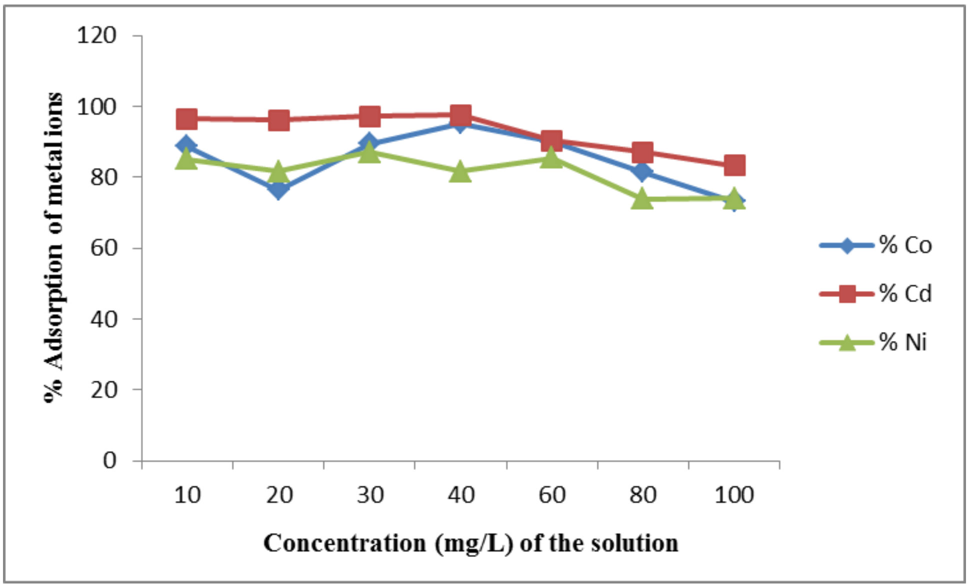

Fig. 5: Effect of initial concentration on the metal ions

Effect of contact time on the adsorption of metal ions

The results for the effect of contact time on adsorption of metal ions are shown in Fig (6). A pH of 4.0 was used for $Cd^{2+}$and Ni^{2+} solutions while a pH of 8.0 was used for Co^{2+} solution. The results showed the increase of adsorption efficiency with initial contact of 20–50 min. The process became slower with no further significant adsorption beyond 120 min. It was observed that the corn cob biomass had a constant percentage of 78.5% for Ni^{2+} all through the contact time used which meant equilibrium was rapidly reached and as quickly as 40 mins, the adsorption sites where already saturated to maximum uptake capacity. Co^{2+} and Cd^{2+} had an initial increase on percentage adsorption but after 50 min contact time the percentage adsorption remained constant at 54.4% and 94.6% respectively. This might be due to saturation of the adsorption site after 50 min after which little or no increase in percentage adsorption was observed as contact time increased. The fast initial uptake of the metal ions occurred through physical adsorption to the corn cob surface, since the adsorption phenomenon tend to attain instantaneous equilibrium (Acheampong *et al*. 2012). Being that the biomass has fixed active sites adsorbing only a metal ion forming a monolayer; the uptake at initial stages was rapid and then decreases with time. The metal removal rate seems significant for developing adsorbent based water technology in the future (Hegazy *et al.* 2011).

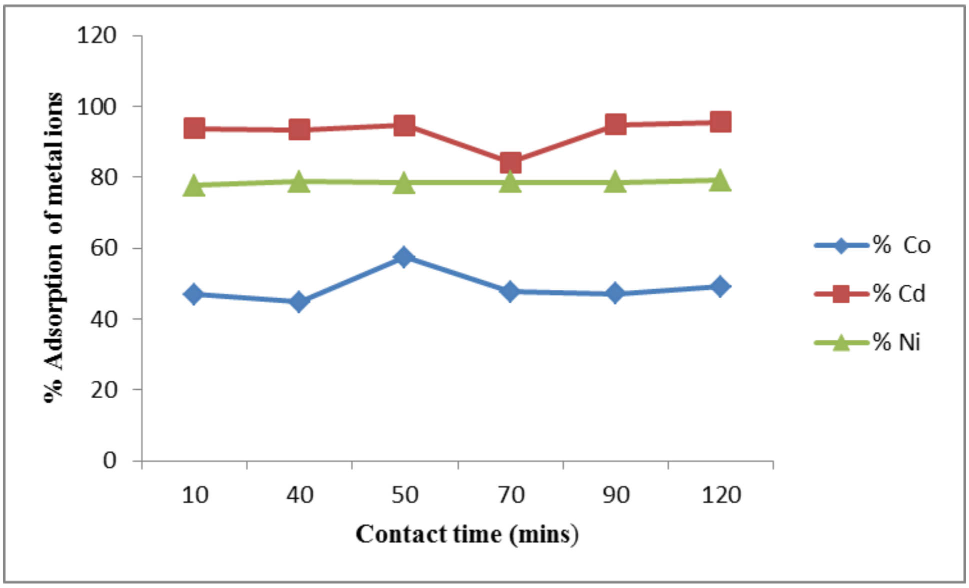

Fig. 6: Effect of contact time on the metal ions

Adsorption isotherms

The equilibrium relationship between adsorbent and metal ions in the solution was explained using two isotherm models, Freundlich and Langmuir similar to (Pehlivan *et al.*,2006). The Freundlich isotherm assumes a monolayer sorption with a heterogenous energetic distribution of active sites accompanied by interaction between adsorbed molecules (Liu and Liu, 2007).The linear form of the equation is described by plotting log q_e against log C_e as described in Eq (5) where qe(mg g^{-1}) is the amount of metal ion adsorbed at equilibrium by the adsorbent, Ce (mgL^{-1}) is the equilibrium concentration, K_f (mgg^{-1}) and n are constants representing the adsorption capacity and intensity of adsorption. The graphs plotted gave straight lines with correlation coefficients (R^2) of 0.989, 0.929 and 0.837 for Cd^{2+}, Co^{2+}, and Ni^{2+} ions adsorption respectively given in Table (2). The slopes and intercepts obtained were used to calculate n and K_f values in Table (2). The n value indicates the degree of non linearity between solution concentration and adsorption as follows: if n=1, then adsorption is linear; if n<1, then adsorption is a chemical process; if n>1, then adsorption is a physical process. The n values for Cd and Ni are 1.46 and 1.81 respectively; this indicated a physical process whereas the n value of Co was 0.90 which indicated chemical process. This can be related to the effect of pH on the adsorption process for Co.

The Langmuir isotherm assumes the uptake of metal ions on ahomogenous surface by monolayer adsorption without any inter-action between adsorbed ions according to (Hoand McKay, 2000).The linear form of the equation in Eq.(3) indicated where Ce (mg L^{-1}) is the equilibrium concentration, q_e is the amount of metal ion adsorbed at equilibrium, q_{max} is the maximum adsorption capacity and K_L is the equilibrium Langmuir constant. The plots of Ce/qe versus Ce gave straight lines with correlation coefficients (R^2) as reported in Table 2. The values of R^2 for corncob adsorbent indicated the Langmuir isotherm not favourable for the adsorption.

Table 2: Comparison of Langmuir and Freundlich isotherm parameters for Cd^{2+}, Co^{2+} and Ni^{2+} ions adsorption to corn cob adsorbent

	Metal ion in solution		
Isotherm parameters	Cd^{2+}	Co^{2+}	Ni^{2+}
	Freundlich Isotherm		
Equation of graph	y= 0.551x-0.704	y= 1.114x-1.721	y= 0.686x – 0.959
K_f	0.1977	0.019	0.11
1/n	0.551	1.114	0.686
n	1.81	0.898	1.458
R^2	0.989	0.929	0.837
	Langmuir isotherm		
Equation of graph	y= 0.256x+ 14.92	y= 0.068x+17.49	y= 0.310x + 15.12
q_{max}	3.9	14.7	3.23
K_L	0.262	257	0.213
R^2	0.895	0.415	0.749

y is q_e (mg./g) (the maximum metal uptake capacity); x is Ce (the equilibrium metal ion concentration)

Adsorption Kinetics

The determination of the mechanism involved in the adsorption of Cd^{2+}, Co^{2+} and Ni^{2+} ions onto corn cob was done using two kinetic models (pseudo first and pseudo second order).The linear equations used are stated in Eqn. 6-9. The models were used on experimental data and the values obtained are shown in Table (3). The regression coefficients obtained from the pseudo first order kinetic graph were low. This suggested none applicability of the pseudo first order kinetic model to the experimental data of the adsorption of the metal ions studied. The pseudo second order kinetics gave high values of regression correlation coefficient in Table (3). This implies that the mechanism of adsorption of the metal ions studied on corn cob followed pseudo second order kinetics.

Table 3: Comparison of pseudo-first order and pseudo-second order kinetic for Cd^{2+}, Co^{2+} and Ni^{2+} ions adsorption to corn cob adsorbent

	Metal ion in solution		
	Cd^{2+}	Co^{2+}	Ni^{2+}
	pseudo-first order		
Equation of graph	y = 8E-05x + 1.115	y = 0.000x + 1.110	y = 5E-05x + 1.153
R^2	0.713	0.014	0.645
		pseudo-second order	
Equation of graph	y = 1.435x + 3.248	y =1.139x + 1.420	y = 1.105x + 0.354
R^2	0.997	0.975	1

y is ($q_e - q_t$) for pseudo-first order; y is t/q_x for pseudo-second order while x is time for both

CONCLUSION

The results from the study showed the ability of corn cob for cadmium (II), cobalt (II) and nickel (II) ions removal from aqueous solutions. The optimum pH required for maximum adsorption was found to be 4.0 for cadmium ion (II), nickel (II), and 8.0 for cobalt (II) ions. The Freundlich adsorption isotherms model fitted the experimental data best with the regression coefficient of 0.989 for cadmium, 0.929 for cobalt and 0.837 for Nickel. The adsorption mechanism in the adsorbent for cadmium and nickel is a physical process while Cobalt is a chemical process. Corncob exhibited rapid adsorption capabilities and high efficiency in removal of cadmium (II), cobalt (II) and nickel (II) ions from aqueous solution.

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