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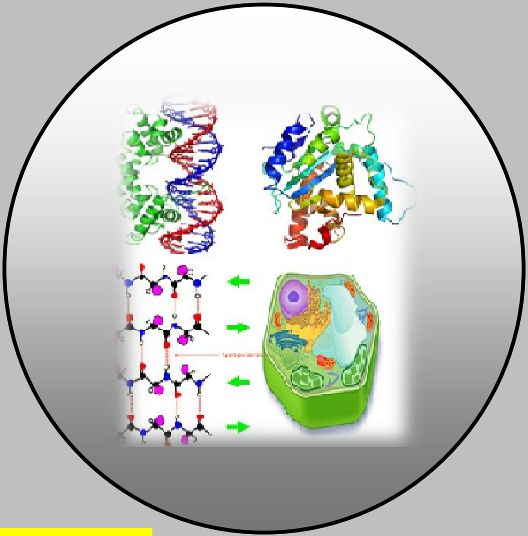

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RESEARCH PAPER

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Effects of pH on Sorption of Manganese, Cadmium and Lead from Aqueous Solution by Maize Cobs

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ABSTRACT

This investigation studies the use of a non-useful plant material as naturally occurring sorbent for the removal of cationic pollutants in waste water. The effect of pH on the sorption of Mn^{2+}, Cd^{2+}, and Pb^{2+} ion on maize cobs sorbent was studied. The contact time, ionic strength and the initial metal concentrations per unit mass of the sorbent on sorption of Mn^{2+}, Cd^{2+}, and Pb^{2+} ions were examined. The maximum pH (pH_{max}) was found to be 6.0, 5.0 and 4.0 with adsorption capacities of 9.02, 8.10 and 6.23 mg kg-^{1}for Mn^{2+}, $Cd^{2+}$and Pb^{2+} respectively at each equilibrium time, 200rpm, and 25^{0}C under10 to 50 mg kg^{-1} initial metal concentration. Sorption equilibrium isotherm was determined and correlated with Langmuir and Freundlich model. It was found that the Freundlich adsorption model of heterolayer best fitted the isotherm data. Surface characterization of maize cobs sorption of Mn^{2+}, Cd^{2+}, and Pb^{2+} ions indicates a physisorptionas the predominant mechanism for the sorption process. It is concluded that maize cobs can be use as an effective adsorbent for removal of heavy metals from aqueous solution.

Key words: *pH_{max}, Cadmium, Manganese, Lead, Maize cob and Sorption.*

INTRODUCTION

Heavy metals released by a human of anthropogenic emission in the environment are some of the major pollutants of soil and water resources (Loubna et al., 2007). Some metals such as copper, zinc and iron are considered bio-essential while others such as cadmium, lead, mercury, manganese and chromium are highly toxic. However, even bi-essential metals may cause physiological and ecological problems if present at significant concentration.

From an environmental protection point of view, heavy metals ions should be removed at the source in order to avoid pollution of natural water and subsequent metal accumulation in the food chain. Various physical and chemical techniques for removing metals ions from the wastewater include chemical precipitation, adsorption, ion exchange, extraction and membranes processes. Chemical precipitation is most common utilized conventional technique. However, the application of these methods is often limited due to their inefficiency, high capital investment or operational costs. Consequently, there is a growing requirement for novel, efficient and cost effective techniques for the remediation of metal bearing waste water before their discharge into the environment. Adsorption has been shown to be an economically feasible alternative method for removing heavy metals from waste water and water supply (Peterlene et al., 1999, Dakiky et al., 2002). Biosorption technology, utilizing natural metals or industrial and agricultural wastes to remove metal form aqueous media, often an efficient and cost-affordable alternative compound to traditional chemical, physical remediation and decontamination techniques. The uses of agricultural residue or industrial by product have been studied. These includes the use of sago waste (Quek et al., 1998), maize-starch, hazelnut shell (Bulut and Zeki, 2007), waste tea leaves, etc. Despite the relative simplicity and potential cost effectiveness of biosorption, metal removal using low-cost bio-sorbents is relatively improve and need further development before it may be applied routinely in practice and thus considered an alternative to the use of expensive ion-exchange resins or activated carbons. Maize cob is an abundant agricultural waste product with millions of tons being generated annual polluting the environment in Nigeria. The maize cobs have been recognized to have significant potential as a biosorbent for metal removal after simple pre-treatment. In this work, we investigated the potential of maize-cobs to act as a biosorbent under different pH for Mn^{2+}, Cd^{2+}, and Pb^{2+} removal.

MATERIAL AND METHODS

Sorbent Preparation

The maize cobs collected from a local maize mill were cut into small pieces; air dried, powdered in a grinder and sieved through 450 µm and 300 µm mesh screens. The portion of the maize cob meal retained on the 300 µm mesh was steeped in dilute nitric acid solution for 8 hours rinsed with de ionized water and air dried.

Sorbate Preparation

1000 mg kg^{-1} of each of each metal stock was prepared by dissolving calculated amount equivalent of 1.00g of each metal in a specific compound ($MnSO_4.H_2O$, $CdCl_2$ and Pb $(NO_3)_2$) in 1litre distilled water (1000mg/l). Standard Mn^{2+}, Cd^{2+}, and Pb^{2+} solutions of 10, 20, 40 and 50 mg kg^{-1} were prepared serially by diluting the stock solutions respectively.

Contact Time Study

Equilibration time for the sorption model of Mn^{2+}, Cd^{2+}, and Pb^{2+} on maize cob was carried out on the metals ions. 30 ml of each selected concentration of salt solutions of heavy metals in distilled water were added each into 1g of maize cob meal weighed into shaking bottles at room temperature (25°C) under neutral pH each to determine the time required for each of the metal ion to reach adsorption equilibrium. Two drops of toluene was added to each solution in the bottles to inhibit microbial growth. The cob suspensions were shaken on a mechanical shaker at a speed of 200 rpm for 30, 60, 90, 120, 150 and 180mins. After the specified shaking time, the solution phase was filtered by using filter paper (whatman 110mm and 11mm pore size) for removing the suspended cob particles. A 10 ml of aliquot of supernant were analyzed for residual Mn^{2+}, Cd^{2+}, and Pb^{2+} respectively by Flame Atomic Absorption Spectrophotometer. The adsorbed heavy metal concentration in maize cob was taken as the difference between metal added in initial solution and the remaining metal in supernatant solution after equilibration. The time for metal adsorption to reach equilibrium was determined graphically from the plot of adsorption values against time of equilibrium. The adsorbed metal ions individually on maize cob per unit adsorbent mass was calculated as follows:

$Qe = (Co - Ce)\, V / m$……………………………………………. (1)

Co is the initial heavy metal concentrations (mg/l); Ce is the concentration of heavy metal at equilibrium (mg/l), m is the maize cob mass (m), V is the solution volume (l).

Calculations were made by using these data and adsorption curves were obtained.

pH Study

One gram of maize cob was weighed into different shaking bottles and 30 ml each of 10 mg kg^{-1} of salt solution of Mn^{2+}, Cd^{2+}, and Pb^{2+} was added. The pH of each solution was adjusted to the required pH value (2.0, 3.0, 4.0, .5.0 and 6.0) using 0.1N HCl and 0.1NNaOH solution from the stock solution. Then, the mixture was stirred in a shaker with speed of 200 r p m at 25°C for each of the equilibration time for Mn^{2+}, Cd^{2+}, and Pb^{2+}. After, the solution phase was filtered by using filter paper (whatman 110mm and 11mm pore size) for removing the suspended particles. A 10 ml of aliquot of supernant were analyzed for residual Mn^{2+}, Cd^{2+}, and Pb^{2+} respectively by Flame Atomic Absorption Spectrophotometer. The adsorbed heavy metal (Mn^{2+}, Cd^{2+}, and Pb^{2+}) on maize cob was taken as the difference between metal added in initial solution and the remaining metal in supernatant solution after equilibration. The optimum pH for metal adsorption was determined graphically from the plot of adsorption values against the design pH values.

RESULTS AND DISCUSSION

Effect of Contact Time

The time taken to attain equilibrium for Mn^{2+}, Cd^{2+}, and Pb^{2+} at neutral pH, temperature of 25°C and centrifugation speed of 200 r p m using 1g of maize cob is shown in fig 1, 2, 3. It was observed that the amount of Mn^{2+}, Cd^{2+}, and Pb^{2+} adsorbed per unit mass of maize cob increased significantly with increase in initial concentration.

The adsorbed rate was very rapid in the first few minutes after which the rate decreased sharply and eventually reached a constant peak after at 120 minutes of the adsorption irrespective of concentrations (10 mg kg^{-1} to 50 mg kg^{-1}). Two hours was therefore indicated as the time for Mn^{2+}, Cd^{2+}, and Pb^{2+} adsorption to reach equilibrium. The necessary contact time to reach the equilibrium depends on the initial metal ion concentration. The uptake rate is controlled by the rate at which the metals (Mn^{2+}, Cd^{2+}, and Pb^{2+}) were transported from the exterior to the interior sites of the adsorbent. The adsorption capacity was observed to increase with the initial metal concentration for the series (10, 20, 40 and 50 mg kg^{-1}) for the selected heavy metals .This is due to larger surface area of the cob at the beginning of adsorption reaction. The amount of the metal ion each in their different series shows the same magnitude in their removal but varies in the adsorption capacity. However, the differential sorption of Mn^{2+}, Cd^{2+}, and Pb^{2+} ions may be ascribed to the difference in their ionic sizes. The ionic sizes of Mn^{2+}, Cd^{2+}, and Pb^{2+} are 0.67, 0.97, and 1.20 respectively.

The smaller the ionic size the greater its affinity to reactive sites. The adsorption capacity increased in the substrate with stronger bond for smaller size metal ion indicative that the competition of manganese with ionic radius of 0.67A has higher binding site than cadmium with ionic radius of 0.97A on maize cob. The lowest adsorption capacity of lead with weak bond on maize cob could be attributed to its highest ionic radius 1.20A.Mn^{2+}, $Cd^{2+}$and Pb^{2+} adsorbed by complexation reaction. This general trend of the sorption is due to the fact that metal ion with smaller ionic radius diffuse faster in aqueous systems and compete better for exchange site than for those with larger sizes. This trend in smaller ionic size was also observed for Cu^{2+},Cd^{2+} and Zn^{2+} using other biological adsorbents (Gardea-Torresde y*et al.*1996; Ho and Mckay*, 2000*; Horsfall *et al.* 2006).According to Cho *et al*. (2005) metal with smaller hydrolysis constant (Pk_H) has the increasing tendency to hydrolyse because of their larger charge-size function (z^2/r). The Pk_H for manganese to cadmium shows that cadmium will be hydrolyze to a greater extent than manganese indicating a higher binding for manganese > cadmium and lead has the least adsorption. So the adsorption capacities increases from $Mn^{2+} > Cd^{2+} > Pb^{2+}$.The long contact time of 2 hours observed to reach equilibrium for all the metal ions indicated that the predominant mechanism was physisorptions which encourage easy removal of the adsorbed heavy metals or regeneration of the spent adsorbent.

Effect of Initial Rate Concentration

The initial concentration provides a driving force to overcome all mass transfer resistances of the metals ion in the aqueous and solid phase. This led to higher probability of collision between the metal and active sites of the maize cob. The surface adsorption sites become exhausted at some point in time, it reached a constant value in which no more metal is removed from solution. At this point, the adsorbed amount of heavy metals on maize cob was in a state of dynamic equilibrium (Demibas, 2004).

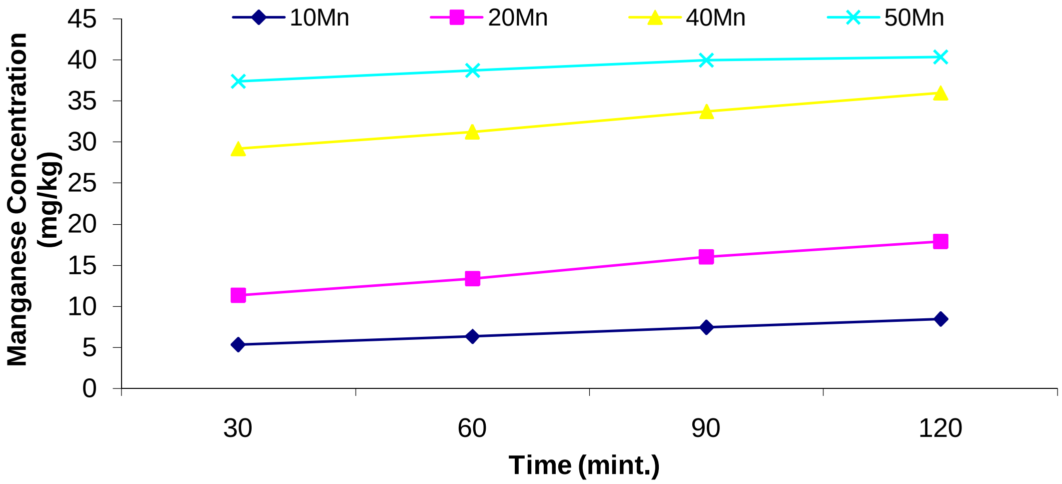

Figure 1. Time of attainment of manganese adsorption equilibrium at pH of 7.0, 10mg kg^{-1} and temperature of 25^{o}C and centrifugation speed of 200 rpm.

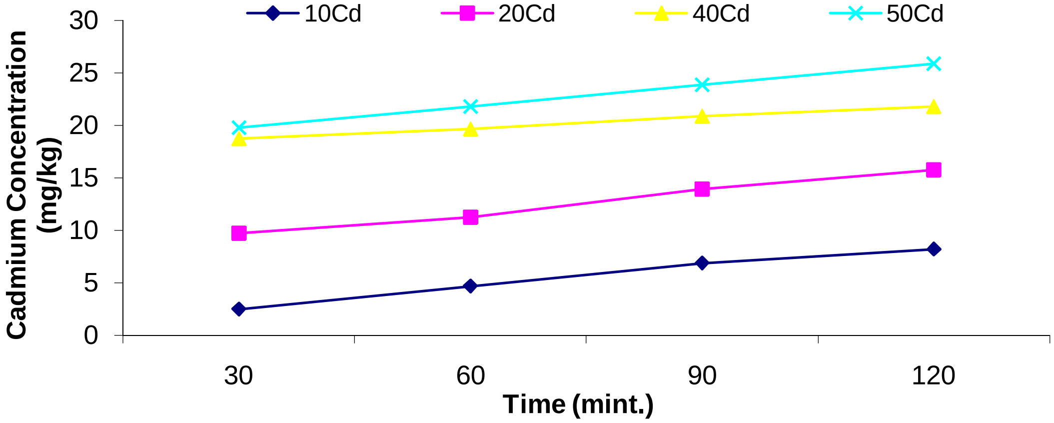

Figure 2. Time of attainment of Cadmium adsorption equilibrium at pH of 7.0, 10mg kg^{-1} and temperature of 25^{o}C and centrifugation speed of 200 rpm.

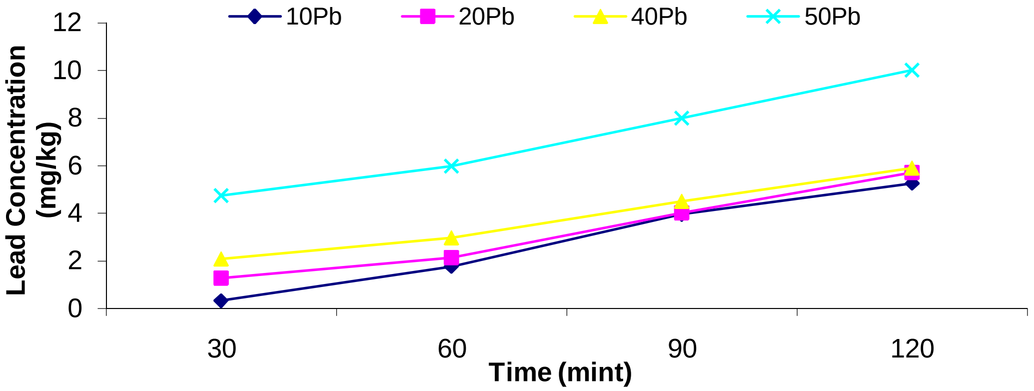

Figure 3. Time of attainment of lead adsorption equilibrium at pH of 7.0, 10mgkg^{-1}, temperature of 25^{o}C and centrifugation speed of 200 rpm.

The equilibrium uptake increased with the increasing of initial metal ions at the range of experimental concentration. Initial rate of the sorption capacity was greater for higher initial heavy metals concentrations, because the resistance to each of the metal uptake decreased as the mass transfer driving force increased so the initial rate of adsorption in metals was greater for higher initial adsorbate concentrations (50 mg kg^{-1}) than for the lowest concentration (10 mg kg^{-1}) of metals ions (manganese, cadmium, and lead) on maize cob. This agrees with the work of Okiemen et al (1987) work on the adsorption on cellulosic material.

Effect of pH

The acidity of solution (pH) is one of the most parameters controlling uptake of heavy metals from wastewater and aqueous solutions. Heavy metals adsorption on maize cob with varying range of pH of 2.0, 3.0, 4.0, 5.0 and 6.0, 1g adsorbent, 2 hours contact time and 10 mg kg^{-1} of adsorbate concentration were kept constant. This pH range was chosen in order to avoid metal solid hydroxide precipitation (8-14). Results showed in Fig 4 that, the initial pH on the adsorption dynamics for manganese, cadmium and lead ions on maize cob were significantly affects the extent of sorption of the metals by maize cob and the adsorption capacities increases for the metals when the pH increases from 2.0 to 6.0.

The variation in the removal of the metal ions by maize cob with respect to pH can be elucidated by considering the surface charge of the sorbent materials and speciation of each of the metals ion. The -COO- ligands attract the positively charged Mn^{2+}, $Cd^{2+}$and Pb^{2+} and binding occurs, indicating that the binding process is an ion exchange mechanism that involves an electrostatic interaction between the negatively charged groups in the cell walls and the metallic cations.

The minimal adsorption capacity obtained for all the metals ions at low pH is partly due H^+ ion that competes with Mn^{2+}, $Cd^{2+}$and Pb^{2+} for the surface of the adsorbent. This could be due to the excess of H^+ ion surrounding the binding sites making sorption unfavorable. The solution pH affects the sorbent surface charge and makes the active site reactive for Mn^{2+}, $Cd^{2+}$and Pb^{2+} removal. The pH_{max} was found to be 6.0, 5.0 and 4.0 for Mn^{2+}, $Cd^{2+}$and Pb^{2+}respectively. The pH_{max} for lead and cadmium ion were 5.2 and 4.3 respectively as deduced by Dermirbas (2004).

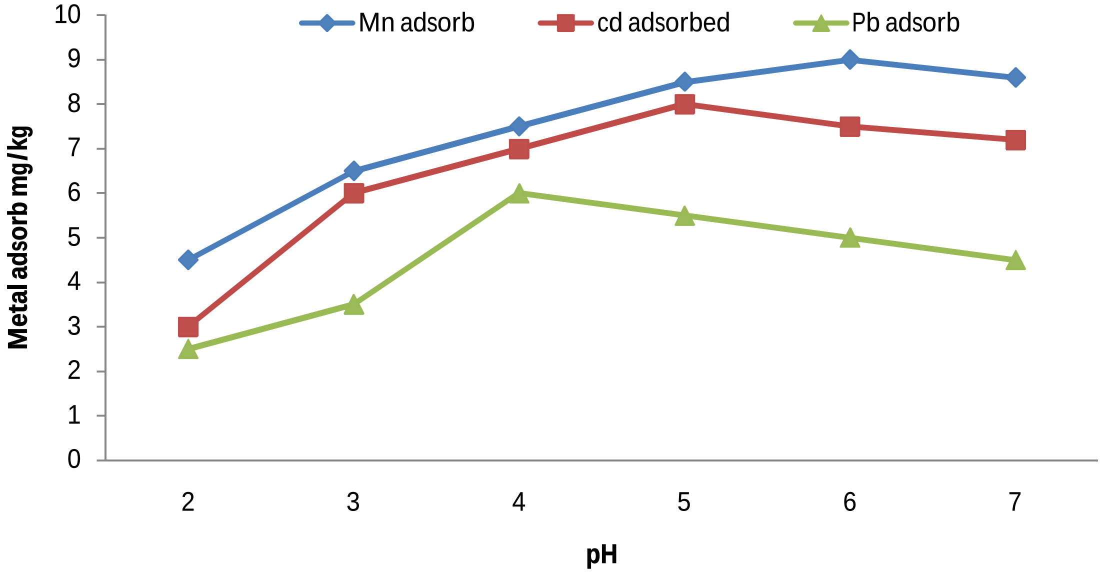

Figure 4. Fitted Curve showing the effect of maize cob pH on manganese, cadmium, and lead adsorption by maize cob.

Adsorption Isotherms

The adsorption characteristics of manganese, cadmium and lead was determined by fitting the adsorption data into both Freundlich, (1926) and Langmuir (1918) equations respectively.

Freundlich Isotherm: This is use for modeling the adsorption on heterogenous surfaces. This can be explained by the equation:

The linear form of equation (4) can be written as:

$Qe = K_fCe^{1/n}$ .... (2)

$\text{Log } Qe = 1/n \log Ce + \log k_f$.. (3)

Qe = the quantity of ions absorbed per unit weight of absorbent.
Ce = the equilibrium concentration of the adsorbate after adsorption has taken place.
"K_f" = Freundlich constant; and "1/n" = adsorption intensity.

Mn^{2+}, $Cd^{2+}$and Pb^{2+} adsorption isotherm using Freundlich approach in the study is presented as a function of the equilibrium concentration of metal ions in the aqueous medium at neutral pH, 25°C and contact time of 120 minutes is shown in Figure 5, 6 and 7. These adsorptions gave a linear fit form of the model with the coefficient of determination (R^2) of 0.96, 0.96 and 0.81 for Mn^{2+}, $Cd^{2+}$and Pb^{2+} which are strong correlation. The order of the distribution of coefficient (R^2) decreased from $Mn^{2+} > Cd^{2+} > Pb^{2+}$, it showed that the maize cobs surface had maximum capacity for $Mn^{2+} > Cd^{2+} > Pb^{2+}$.

The Freundlich adsorption co-efficients (k_f and 1/n) were numerical values that characterized the maize cob surface for its affinity for the metals. All the metals exhibited a slope (1/n) defined as adsorption intensity which is less than unity thereby exhibiting a favorable condition for the maize cob surface which agrees with Horsfall and Abia (2003). The 1/n that was less than unity implies that the surface site heterogeneity was predominant for the adsorption of the metals on maize cob that is, there was broad distribution of adsorption of the ions on the maize cob surface. The adsorption capacity (k_f) for Mn^{2+}, $Cd^{2+}$and $Pb^{2+}$by maize cob were positive value which predicted that the quantity adsorbed on maize cob corresponds to complete heterogeneous layer coverage.

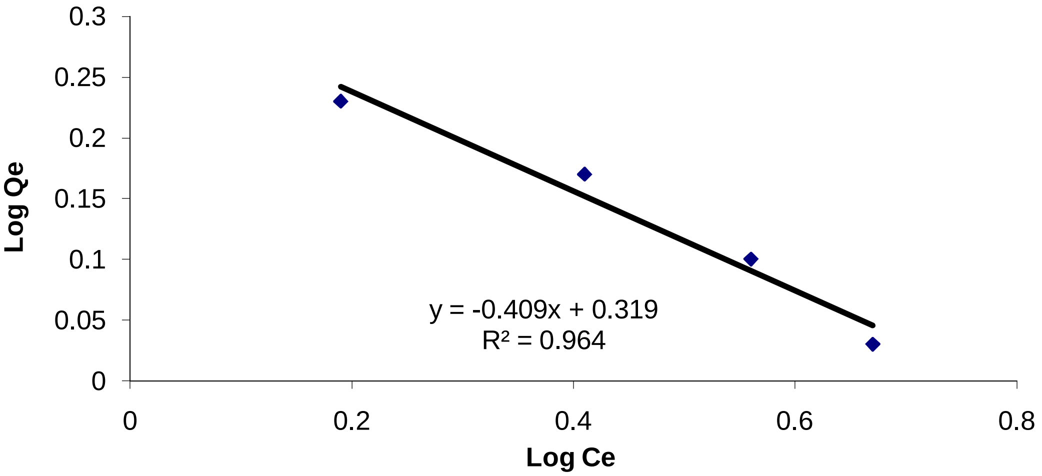

Figure 5. Freundlich adsorption isotherm for manganese at neutral pH, 10mg kg^{-1}initial concentration and 25°C.

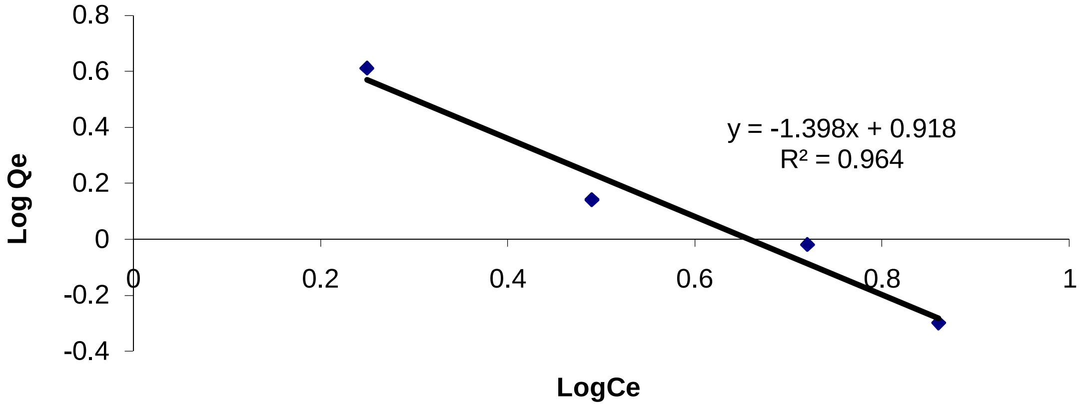

Figure. 6. Freundlich adsorption isotherm for cadmium at neutral pH, initial concentration of 10 mg kg^{-1} and 25^{o}C.

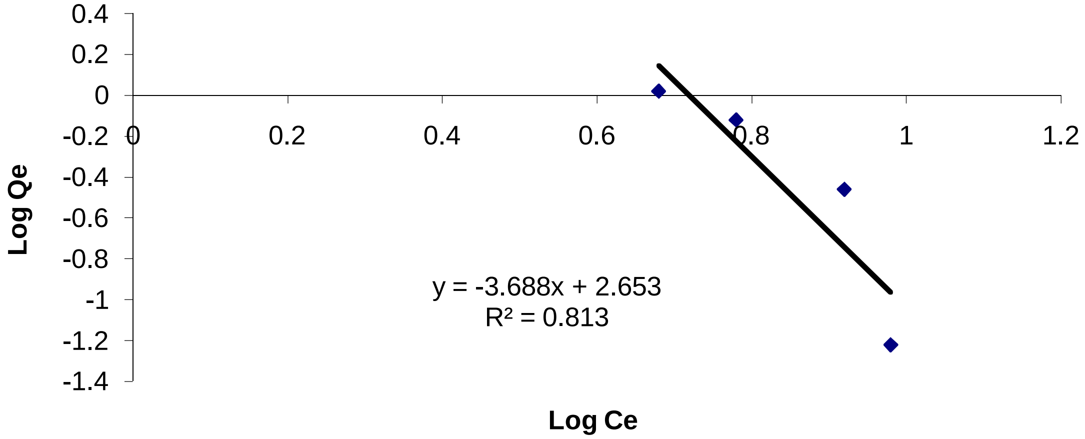

Figure 7. Freundlich adsorption isotherm for lead at neutral pH and initial concentration of 10 mg kg^{-1} and 25^{o}C.

Langmuir Adsorption Isotherm

This model suggests that the uptake occurs on homogenous surface by monolayer sorption without interaction between sorbed molecules. The model assumed uniform energies of adsorption onto the surface. Langmuir isotherm can be defined according to the following

$Qe== V_mkCe /1 +kCe$ ………………………………………………………… (4)

Qe = the quantity of ions absorbed per unit weight of absorbent.

Ce = the equilibrium concentration of the adsorbate after adsorption has taken place.

V_m is the monolayer capacity and “k” is the equilibrium constant.

The linear form of equation (6) can be written as follow:

$Ce/Qe = 1/kV_m + Ce/V_m$.. (5)

The sorption of the metals ions (Mn^{2+}, Cd^{2+} and Pb^{2+}) on maize cob showed a non linearity with Langmuir linear equation as shown in Fig 8, 9 and 10. This indicates that the adsorption in Mn^{2+}, Cd^{2+} and Pb^{2+}did not occur at the homogeneous surface molecules to each other in the plane of the active site maize cob.

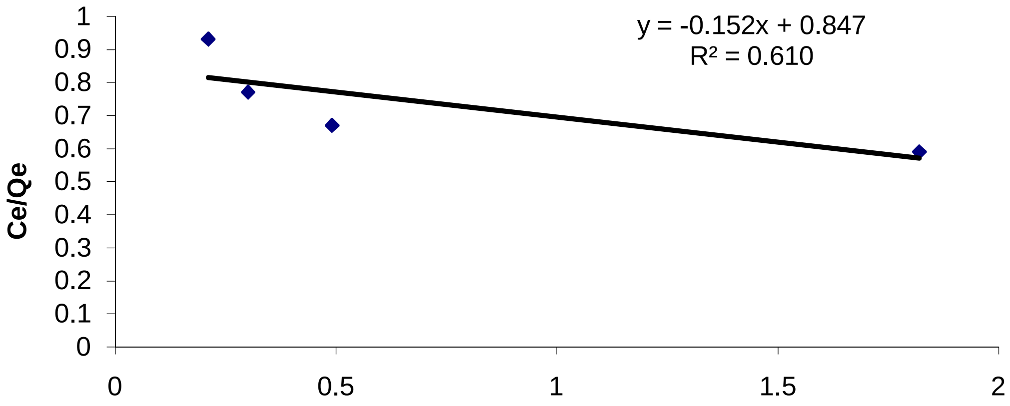

Figure 8. Langmuir adsorption isotherm for manganese at neutral pH and initial concentration of 10 mg kg^{-1} and 25^{o}C.

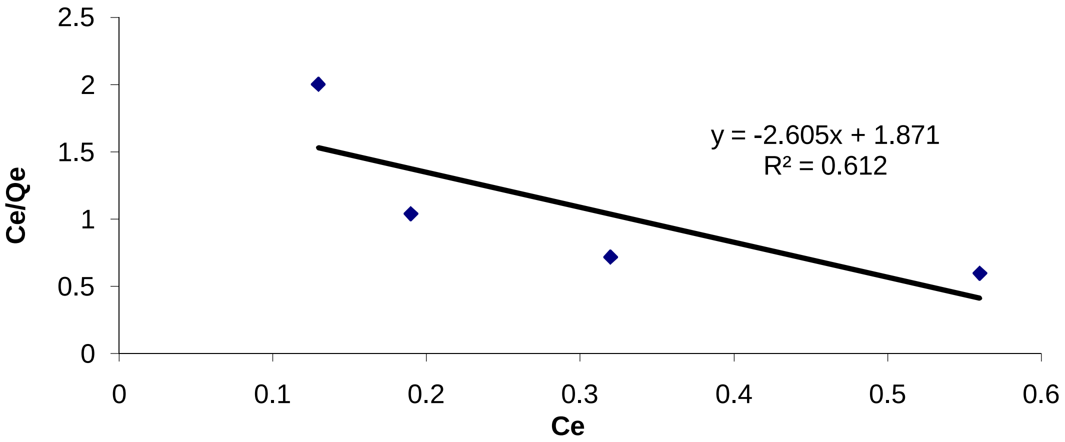

Figure 9. Langmuir adsorption isotherm for cadmium at neutral pH and initial Concentration of 10 mg kg^{-1} and 25^{o}C.

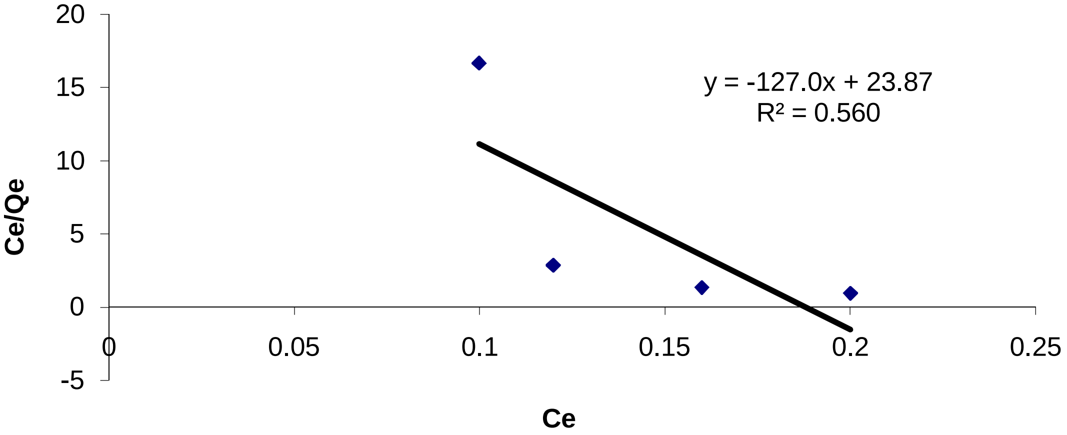

Figure 10. Langmuir adsorption isotherm for lead at neutral pH and initial concentration of 10 mg kg^{-1} and 25^{o}C.

CONCLUSION

This study clearly suggest that the use of maize-cobs as sorbent is much economical, effectual and more viable. It can be efficiently used to remove ions from aqueous solution. The different operational parameters observed during the process of investigations reveal that the adsorption of manganese, cadmium and lead ions was dependent on initial rate concentrations, solution pH, ionic strength and contact-time with same magnitude in their removal but different adsorption capacities. The long contact time of 2hrs at which equilibrium for manganese, cadmium and lead ions was reached indicated that the predominant mechanism is physisorption. The maximum adsorption capacity was attained at pH_{max} of 6.0, 5.0 and 4.0 for Mn^{2+}, $Cd^{2+}$and Pb^{2+}respectively. It is common to describe the goodness of it in terms of R^2, which is the square of the correlation coefficient. Langmuir isotherm shows an inadequate fit of experiment data in the whole range of concentrations generally giving the R^2 values lower than 0.90. The adsorption of the metals ions conform with Freundlich isotherm of heterogeneous adsorption but non linear with Langmuir equation and the coefficient of distribution (R^2) decreases from Mn^{2+}, $Cd^{2+}$and Pb^{2+}respectively. As a result of this study, it may be concluded that maize cob may be used as alternative and effective material for elimination of heavy metal pollution from waste waters since it is low cost, abundant and locally available adsorbent.

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