Removal of Pb (ii) Ions from Water Sources in Kadna Using Sawdust/$MnFeo_4$ Continuous Column Adsorption

Balogun Ebenben Joyce and M.D.Yahya

Department of Chemical Engineering, Federal University of Technology Minna, Nigeria
Extract from an ongoing M.Eng. Research thesis By Balogun Ebenben Joyce
*Corresponding author: Balogun Ebenben Joyce, Department of Chemical Engineering, Federal University of Technology Minna, Nigeria
Email: balogunjoyce@yahoo.com

Abstract: The research entitled The Removal of Pb (Ii) Ions from Water Sources in Kadna Using Sawdust/$MnFeO_4$ Continuous Column Adsorption was carried out with the aim of removing heavy metals from water sources in Kadna using continuous adsorption column method. At the end of the research, the result was analysed and some parameters were determined. The moisture content was 11.41 %, the ash content was 4.46 %, the crude fibre gave 46.15 %, crude protein resulted in 4.825 % and oil extract 6.22 %. The BET results reveals surface area, pore volume and pore size. The surface area of the composite was found to be 341.612m^2/g, Pore volume= 0.1741 and Pore size= 2.138**.** Deducing from the result of analysis, the use of sawdust/$mnfeo_4$ as a medium in the process of removing Pb (ii) ions was very effective. The result proved that the method is reliable, efficient and if adopted for the removal of similar characteristics heavy metals in water bodies, will be very economical, available and cheap

key words: Lead (ii) ions, Water sources, Adsorption, Sawdust, $MnFeO_4$, Minerals and mining

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1 INTRODUCTION

Nigeria is a great country, so endowed with abundant natural recourses such as minerals; these resources, have contributed greatly to the development of the nation's social, infrastructure and economy. There are vast reserves of solid minerals; these include precious deposits like gold diamond and silver, industrial raw materials, energy minerals and metals. Between 1960 and early 1970, Nigeria used to be one of the major exporter of minerals such as tin and coal. Activities in this sector however began to fall immeasurably by the middle of 1970s as a result of political and economic factors. The discovery of crude oil and the potential as a source of foreign exchange remarkably changed the initial focus on exportation of solid minerals. Meanwhile, Nigeria's market worth of solid minerals is about hundreds of trillions of dollars. This can be found in different parts of the country. On a yearly basis, Nigeria loses over fifty billion dollar coupled with the fact that there are no facilities to know accurately the rich deposits of minerals especially in the case of gold exploration. (Omoh, 2016). In recent years, various classes of solid minerals which consists of precious metals, industrial minerals such as limestone, coal, tin; precious stones and many other minerals in large deposits are found in Nigeria (Nwadialor, 2011, Musa, 2013, Fayemi, 2015). These mineral deposits are found in different locations in the country, which accounts for diverse forms of mining activities. However these minerals are far from being fully explored because various scientists have said there are over forty various types under the Nigeria soil (Merem*et al.,* 2017).

Mining of solid mineral provides variety of socio-economic benefits such as job creation; environmental cost if not well handled could result in massive degradation of land, alteration of habitat, pollution of water, land and air. Next to crude oil production, the mining sector is the second source of pollution in Nigeria (Adekoya, 2003). Lead poisoning in Zamfara State left dire consequences on human health and livestock, another serious effect of pollution resulting from mining activities. In Bukuru area of Plateau State and Pandogari in Niger State, abandoned mining sites have resulted in large areas of land degradation, which has lead to changes and in most cases total eradication of natural habitats (Merem et al., 2017). The sector is resource intensive and generates high concentrations of waste and effluents. In recent time and presently still ongoing, the blasting of rocks by Chineses companies scattered all across the Federal Capital Territory especially in Mpape and Bmuko both in the Bwari Area Council of Abuja have adversely affected the population living within these areas. It also results in the defacement of the landscape, increased rate of soil erosion and deforestation. The noise and vibration caused by blasting of rocks with explosives (dynamite) have caused adverse effect on buildings and people leaving within the surrounding communities. Mining, mineral processing and metallurgical extraction are the three principal activities of gold mining industries which produce wastes. Mineral processing also known as beneficiation aims to physically separate and concentrate the ore mineral(s) using physical, chemical and sometimes

microbiological techniques. Metallurgical extraction breaks the crystallographic bonds in the ore mineral in order to recover the desired element or compound (Lottermoser, 2007). Large quantities of waste are produced during this activity particularly in gold mines which release over 99% of extracted ore as waste to the environment (Adler and Rascher, 2007).

Gold mining could either be open-pit or deep shaft. This is however combined with heavy metals like copper (Cu), silver (Ag) and lead (Pb). The location of a mining site determines the mining technique to be used and also the quantity of effluent generated. In the past, wastes generated by mining activities were smaller because higher grade ores were being exploited. There was also limited capacity to move large quantities of materials and so the effluents generated were discarded a few meters from the mine opening or pit. Open-pit mining results in eight to ten times as much waste as underground mines. This is because great amount of topsoil are overburden and barren or waste rock has to be removed (Fashola*et al.,* 2016). Tailings are the major effluents that are produced from gold extraction and they contain high amounts of heavy metals (HM). Heavy metals leach into surrounding environments unchecked; on exposure to water or through dispersal by wind. The presence of elevated concentrations of these metal ions in the environment is a serious health issue worldwide due to their non-degradable nature making them persistent and thereby exerts long-term effects on the ecosystem (Singh *et al.,* 2011). In most cases, the aquatic habitat is the ultimate recipient of almost all effluents released. These effluents contain diverse contaminants as well as heavy metals. This has long been recognized as a serious problem (Farombi, 2007). Heavy metals could be found in water at the trace levels. Nonetheless, constituents of the effluents are sometimes very toxic and tend to accumulate over a long period of time if they are not treated before they are disposed. They find their way to the food chain. Consumption of heavy metals by human beings can have adverse effect on the health hence there is a need to treat these effluents before they are released into the environment. There is also a need to know the concentration of heavy metals in water sources because of its daily usage by man (Adebayo, 2017).

There is a desire to remove these toxic metals from effluents which find their way into the water bodies supplying water to these mining environments. A number of techniques have been used for the removal of metals from aqueous solutions. These techniques include membrane separation processes, precipitation, reverse osmosis, flocculation, solvent extraction, ion exchange and electrodialysis. These methods however have their advantages and disadvantages. The disadvantages include amongst others, high cost of operation and complexity of treatment (Bernard *et al.,* 2013). However, adsorption is recognized as the most effective amongst other methods. This is as a result its operations, the equipment used, its efficiency, low-cost, no pollution, and high adsorption capacity (Kong *et al.,* 2014). It is widely used to remove contaminants in polluted water bodies (Liu *et al.,* 2017). Various adsorptive materials have being explored such as zeolite, agricultural by-products, clay, chitosan, industrial by-products, aquatic plants as well as micro-organisms. In this present research work, a composite consisting of sawdust and $MnFe_2O_4$ will be prepared by co-precipitation (Podder and Majumder, 2016) and used remove one of the heavy metals that are present in the water. The heavy metal isPb(II). Sawdust is in abundant supply, it is a waste in most sawmills in and around Minna, Niger State. They are either burnt or left indiscriminately in dumb sites. Sawdust has been combined with various materials to form activated carbon, used for the removal of heavy metals from aqueous solutions. This has varying levels of successes recorded. The compositions of sawdust are lignin, cellulose, extractives, starches, simple sugars and hydrocarbons. Carboxylic, alcohols, and phenolic acids groups are their functional groups; these are used in metal ion complexion. As a result of the involvement of metal ion complexion with the functional groups, different biosorption techniques have being done by many researchers using spectroscopic methods.

2.0 MATERIALS AND METHODS

2.1 Methodology

3.2. Pre-treatment of adsorbent

The sawdust was collected from sawmill in Minna, Niger State. It was washed several times to remove all forms of impurities. Thereafter, it was rinsed carefully with distilled water and finally dried at 100 °C for 12 h.

2.3 Preparation of sawdust/$MnFe_2O_4$ composite

Sawdust/MnFe2O4 composite was prepared by chemical co-precipitation (Shao et al.2012).The amount of sawdust was adjusted to obtain a mass ratio of sawdust to MnFe2O4; 2:1. The prepared sawdust was added into a 250 mL solutioncontaining manganese (II) chloride (2mmol) and ferric chloride (4 mmol) at room temperature. Under vigorousmagnetic–stirring and at an increased temperature 70 °C, NH_3 solution was added drop wise to raise the suspension pH toaround 10 and the stirring was continued for 1 hour. The suspension was further heated in a hot bath at 100^0C for 2 hours (Podder and Majumder, 2017). It was left to cool down for a while, there after the magnetic composite was washed several times with distilled water and oven dried at 105 °C for 2 hours.

2.4 Characterisation of Adsorbent

The physical properties were determined by Fourier transform-infrared spectrophotometer FT-IR for functional group of the raw adsorbent and after it had treated. The Brunauer-Emmett-Teller (BET) test of raw adsorbent was also done to determine the surface area and pore volume analysis.

2.5. Fourier transform-infrared spectrophotometer FT-IR

The FT-IR spectra of sawdust and the sawdust/MnFe2O4 composite were examined to identify the functional groups which are responsible for metal uptake and frequency changes of the functional groups in the composite. This was carried out in the Chemistry Advanced Laboratory in SHEDA Science and Technology Complex (SHESTCO), Sheda at Abuja

2.6 Brunauer-Emmett-Teller (BET) Analysis

The specific surface area and the pore volume analysis were carried out on the sawdust/MnFe2O4 composite using BET surface area Nitrogen adsorption procedure. The adsorbent that was prepared was outgassed under a vacuum for three hours at a temperature of 300^0C. This was done to remove moisture content for the surface of the adsorbent. Surface area measurements and the pore volume of the adsorbent were obtained using nitrogen adsorption at 77K by a NovaWinQuantachrome, in Step B Center, Federal University of Technology, Bosso Campus, Minna.

2.7 Point Of Zero Charge

The point of zero charge determines the surface charge of the sawdust/MnFe2O4 composite at a given pH. This also indicates the possible electrostatic interactions between the adsorbent and the chemical species of the metal to be adsorbed. There are three different method used to achieve to the point of zero charge of an adsorbent. There are potentiometric mass titration (PMT) technique, mass titration (MT) and immersion technique (IT) (Fiol and Villaescusa, 2007). In this work potentiometric mass titration technique was used to determine the point of zero charge ofsawdust/MnFe2O4 compositeused for adsorption.

Different suspensions of three masses of sawdust/MnFe2O4 composite2g/L, 5g/L and 10g/L were placed in contact with a 0.03M KNO3 solution. The mixtures were agitated for 12 hours in a rotary shaker at 205rpm while checking for changes in pH of the mixture. Vigorous agitation was used in order to ensure homogenization of the suspension (Fiol, et al 2008). When the pH was at equilibrium, the agitation was stopped. 2mL of 1M NaOH was added to the suspension to deprotonate surface sites before titration commenced. The suspensions were titrated by adding 0.05mL of HNO3 of concentration 0.1M under continuous agitation. After each addition, the pH value was recorded as a function of the added volume of titration solution. The procedure was repeated for blank solution of 0.03M of KNO.

2.8 Proximate Analysis

The proximate analysis of sawdust/MnFe2O4 composite for moisture content, ash content, crude protein, crude fibre and oil extract were determined.The proximate analysis of the samples for moisture, ash and carbohydrate contents were determined as described by AOAC (2005). Crude protein, fibre and fat contents were determined by the methods of Pearson (1976)

2.9 Treatment of the wastewater

2.9.1 Analysis of the Water before Treatment

Water from the source of water supply in Kadna, Chanchaga are of Minna, Niger State was collected and taken to the laboratory to determine the initial concentration of heavy metals before treatment using Atomic adsorption Spectrophotometer at the Chemistry Advanced Laboratory in SHEDA Science and Technology Complex (SHESTCO), Sheda at Abuja.

2.9.2 Treatment of the water

2.9.3 Batch adsorption studies

A preliminary batch adsorption was done until equilibrium was reached. The experiment was done by placing 15mL of digested effluent of known concentration in six different conical flasks having varying pH of the water to be treated, by added either HCl or NaOH to the water (Onyeji and Aboje, 2011). The various pH were 2, 4, 6, 8, 10 and 12. 1g of sawdust/MnFe2O4 composite was placed in each solution. The suspension was stirred using a rotary shaker at a constant speed of 150 rpm at room temperature (37^0C) for 2 hours. They were then filtered using filter paper and the filtrate was taken to for analysis to determine the percentage of Pb(II) removed and at what pH has the highest removal.

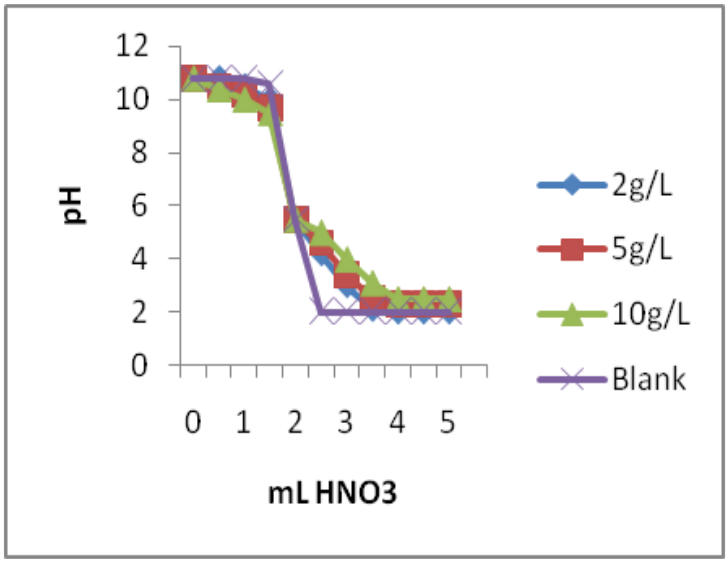
2.9.4 Column Analysis

Dynamic column studies were carried out in a glass column of 3.8cm internal diameter and column height of 28cm. A peristaltic pump was used to maintain the desired flow rate. In the bottom side 0.05 cm thick glass wool was placed to prevent any loss of adsorbent and was to give mechanical support to the adsorbent bed. The experiment was carried out at room temperature. Effects of process parameter like flow rates (2.8, 6.4, and 9.8 mL/min), bed depth (4.7, 9.4 and 14.2cm), and concentration (2, 4 and 7.8mg/L) were investigated. Samples were collected every 20 minutes from the bottom of the column and were tested to know the Pb (II) concentrations. The column performance was investigated by calculating the breakthrough time and adsorption capacity.

3.0 RESULTS AND DISCUSSION

3.1 Result of Potentiometric Mass Titration (PMT)

Equilibrium pH values were plotted as a function of acid volume added to obtain the potentiometric curves. The point of zero charge (pHpzc) was identified as the intersection point of the potentiometric curves with the blank. Equilibrium pH values were plotted as a function of acid added to obtain the potentiometric curves. pHpzc was identified as the intersection point of the potentiometric curves with the blank as shown in the fig below.



Potentiometric mass titration curves for
From the figure obtained, the point of zero charge was found to be 5.5.

3.2 Results Proximate Analysis

The proximate analysis carried out on the composite gave the following results on an average. They were conducted two times. The moisture content was 11.41%. the ash content was 4.46%, the crude fibre gave 46.15%, crude protein resulted in 4.825% and oil extract 6.22%.

3.3 Results FTIR Analysis of Adsorbent

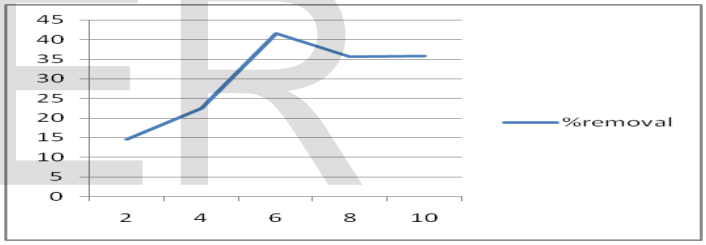
The FT-IR spectra of precursor and composite was examined to determine the vibration frequency changes in the functional groups of the adsorbent walnut shell as show in figure below. The spectra was measured within the range of 500– 4000cm−1 wavelength. The results indicated the presence of the following functional groups; hydroxyl, carboxylic acids, alcohol, carboxylate and carbonyl groups (Garg et al., 2008). The hydroxyl functional group play an important role in the biosorption process as reported by various researchers (Ebrahim and Rasheed, 2013). The FTIR spectra sawdust/MnFe2O4 composite showed a board band of 3421.85cm^{-1} which is close to the broad band 3413cm^{-1} as reported by Hashemian and Hidarian, 2014. This showed the presence of both free and hydrogen bonded OH groups on the sawdust surface. The broad bands 2923.92cm^{-1} assigned to C=H Stretching frequencies. A peak is seen around 1641. This is attributed to hydrogen bending vibrations of water. Hence, FTIR of sawdust/MnFe2O4 indicated an increase in the presence of peaks having close range as that of the Sawdust and MnFe2O4.

3.4 The BET Result

The BET results reveals surface area, pore volume and pore size. The surface area of the composite was found to be 341.612m^2/g
Pore volume= 0.1741
Pore size= 2.138

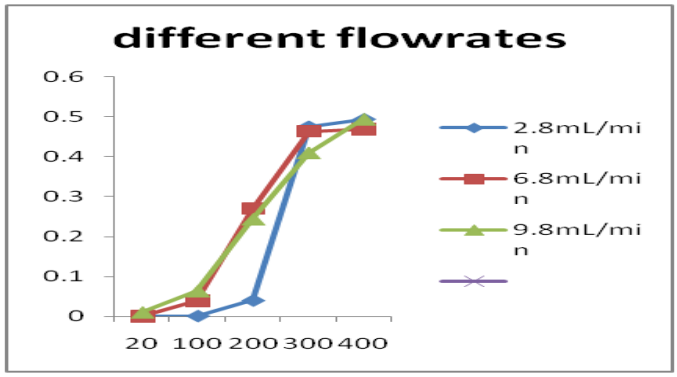
3.5 Batch Adsorption Studies

This was carried out to determine the effect of pH on the Pb(II) ions adsorption on sawdust/$MnFeO_4$ composite adsorbent. The experiment was carried out with dose of 1g/15ml solution. The intialPb(II) ions concentration was 7.8mg/L. it was given a contact time of 120minutes and placed in a rotary shake at 150rpm at room temperature. The pH were 2, 4, 6, 8 and 10.
Results revealed that at lower pH values, the H^+ concentration was high so the proton can compete with the metal ions for surface sites. This resulted in low adsorption for the Pb(II) ions at pH of 2. At higher pH between 5 and 6, more adsorption occurred. However when alkalinity increased, the rate of adsorption dropped.
Based on the results obtained, the water to be treated pH was adjusted to 5.5 for the column adsorption analysis.
A graph representing the removal is shown below



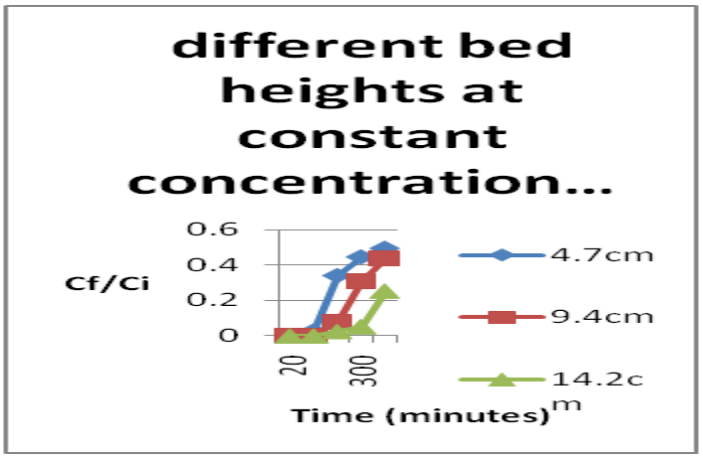
EFFECT OF PH ON PB (II) ADSORPTION

The effect of concentration of the water on the column is shown in the graph above.



Effect of flowrate. At lower flowrate, the adsorbent takes a longer time to get saturated. At a higher flowrate, saturation

occurs faster

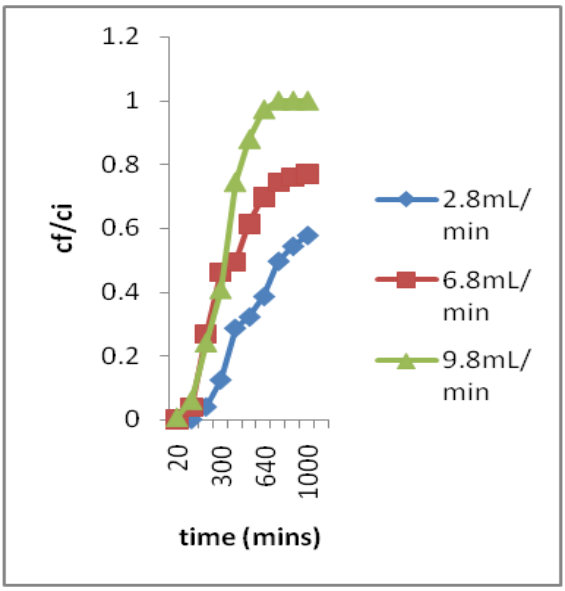


The effect of bed height is shown in the graph above. At lower bed height, the S- slope is achieved in least time, while higher bed height the s- slope takes a longer time.

Results and discussion of result

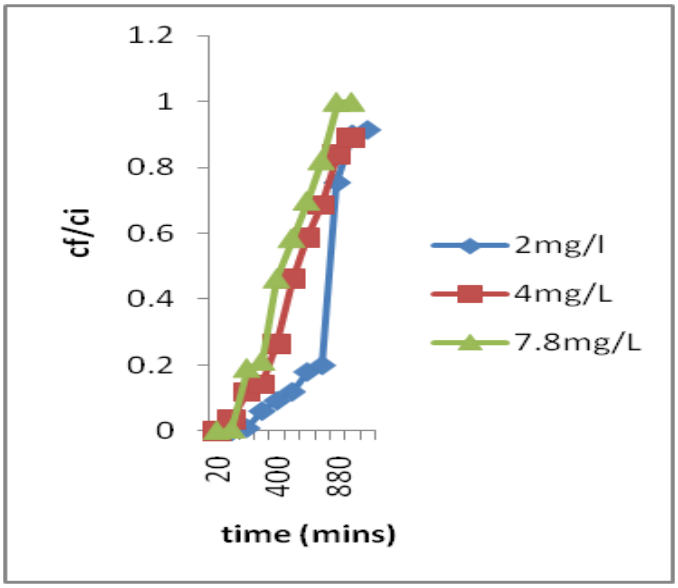
Effect of flow rate

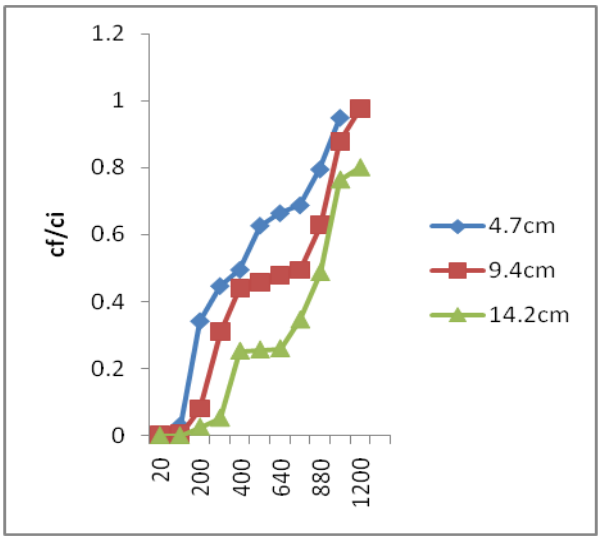
The effect of flow rate on the adsorption of Pb(II) ions at constant initial concentration of 2mg/L and constant bed height of 14.7cm were carried out. The different flow rates were 2.8mL/min, 6.8mL/min and 9.8mL/min. the results are given in the figure below. They indicate that the uptake of Pb(II) ions onto the sawdust/$MnFeO_4$ reduces when the flow rate through the bed increases. This is due to the decrease in contact time between the Pb(II) ions and the sawdust/$MnFeO_4$ at higher flow rates. An early breakthrough curve is the results observed. This is in line with other results obtained also a lower adsorption capacity is obtained (Taty-Costodes et al., 2005)



Effect of initial concentration

The effect of the initial concentration onto the breakthroughcurves with column bed depth set at 14.7cm and flow rate of 2.8mL/min is shownin figure below. The concentrations were 2mg/L, 4mg/L and 7.8mg/L. It can be observed that when the inlet metal concentration was 7.8mg/L,the time the packed bed getssaturated reduces as shown . A high metal concentrationmay saturate the sawdust/$MnFeO_4$ compositemore quickly, thereby decreasingthe breakthrough time. Similar results were also obtained forthe sorption of copper and cadmium ions onto bone char (Ko et al., 2001)and sorption of copper and zinc by the residual biomass ofthe alga Sargassum sp. (Valdman et al.,2001). These results demonstrate thatan increase in the concentration modifies the adsorption ratethrough the bed and increases the bed adsorption capacity. Hence the diffusion process depends on the inletconcentration (Rajagopal and Kapoor, 2001). Nevertheless, the saturation of the adsorbentrequires much more time. However the breakthrough is reached before all the active sites of the sawdust/$MnFeO_4$ composite are occupied by the metallic ions. This implies that the adsorbent in this study a high affinity for lead cations and copper ions under these experimental conditions.





Concentration for Pb(II) ions

Effect of bed depth

The breakthrough curves obtained for lead (II) ions adsorption are illustrated in figure below for the various bed depth of sawdust/$MnFeO_4$ (4.7, 9.4, and 14.7cm), at a constant flow rate of 2.8mL/min. They follow the characteristic "S" shape profile produced in ideal adsorption systems. Results indicate that the breakthrough time varies with bed depth. An increase in the bed adsorption capacity is noticed at the breakthrough point with the increase in bed depth (Table 1). This increase in the adsorption capacity with that in the bed depth can be due to the increase in the specific surface of the adsorbent which supplies more fixation binding sites. Breakthrough time is important parameter of the process. Lower bed height reduces the intra-particulate phenomena in mass transfer and this causes an increase in breakthrough time (Han,et al., 2009 and Fiol et al., 2006).

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EVALUATION OF COLUMN PERFORMANCE

Fixed bed column performance is best described through the concept of breakthrough curve.this is shown

4.0 CONCLUSION

The research entitled the removal of Pb (ii) ions from water sources in kadna using sawdust/$MnFeO_4$ continuous column adsorption was carried out with the aim of removing heavy metals from water sources in Kadna using continuous adsorption column method. Deducing from the result of analysis, the use of sawdust/$mnfeo_4$ as a medium in the process of removing Pb (ii) ions was very effective. The result proved that the method is reliable, efficient and if adopted for the removal of similar characteristics heavy metals in water bodies, will be very economical, available and cheap.

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