



Original Paper

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Remediation of Cr and Fe from aqueous solution by natural adsorbents

Muhammad B. IBRAHIM^{1*} and Wahab L. O. JIMOH

Department of Pure and Industrial Chemistry, Bayero University, P. M. B. 3011, Kano, Nigeria.

* Corresponding author, Email: bashirmbi2@yahoo.ca

ABSTRACT

Different kinds of low-cost agro based fibres can be used to remove both trace and heavy metals from aqueous solutions. The removal efficiency of maize (*Zea mays*) cob, sawdust and coal coded as MC, SD and CO respectively was investigated in this study for the bioremediation of chromium and iron. Sorption experiments were carried out using batch process in which changes in concentration of the adsorbates were monitored by the use of Shimadzu AA650 Double Beam Atomic Absorption/Flame spectrophotometer. Effects of varying adsorbent dose, adsorbate loading concentration, pH, and adsorbent surface area were studied. At optimum adsorbent dose, remediation of Cr varies according to CO > SD > MC, while that of Fe varies according to MC > CO > SD. However, on individual adsorbents the remediation efficiency is; on MC Cr has 48.5% while Fe has 100%, while on SD Cr has 97.85% while Fe has 95% and lastly on CO Cr has 98.57% and Fe has 98%. This shows that the adsorbent can selectively be employed for the remediation of the ions from the solutions.

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Keywords: Adsorbate, Adsorbent, Coal, Maize cob, % Removal, Sawdust.

INTRODUCTION

The application of low-cost natural adsorbents including carbonaceous materials, agricultural products and waste by-products has been investigated in many previous studies (Ajaero, et al., 2010; El - Nemr et al., 2008; Ramesh et al., 2005), which have been recognized as potential alternative to the conventional technologies such as precipitation, ion exchange, solvent extraction and liquid membrane for removal of heavy metals from industrial wastewater because these processes have technical and/or economical constraints (Wu et al., 2008). Several studies have shown that non-living plant biomass materials are effective for the removal of trace metals from the environment

(Elaigwu et al., 2009; Wang and Lin, 2008). Whereas many previous studies have reported the adsorption of metals by materials of diverse biological origin, these have remained limited to the removal of single metal ion and little information is available for multimetal adsorption systems (Abdel-Ghani et al., 2008). The maize cob is an example of plant residues that are mainly composed of lingo-cellulose materials. They have relatively large surface areas that can provide intrinsic adsorptive sites to many substrates and inherently adsorb waste chemicals such as dyes and cations in water due to columbic interaction and physical adsorption (Sun and Shi, 1998). According to Shukla et al. (2002) the cell walls of sawdust mainly consist of

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cellulose and lignin, and many hydroxyl groups, such as tannins or other phenolic compounds which are all active ion exchange compounds. Lignin, the third major component of the wood cell wall, is a polymer material, which is built up from the phenylpropane nucleus, i.e. an aromatic ring with a three-carbon side chain. Coal is thought to consist of a large polymeric matrix of aromatic structures, commonly called the coal macromolecule. This macromolecule network consists of clusters of aromatic carbon that are linked to other aromatic structures by bridges. Bridges between the aromatic clusters are formed from a wide variety of structures. Most bridges are thought to be aliphatic in nature, but may also include other atoms such as oxygen and sulfur. There are other attachments to the aromatic clusters that do not form bridges. These attachments are referred to as side chains and are thought to consist mainly of aliphatic and oxygen functional groups (Solomon, 1981).

Some metals usually form compounds that can be toxic, carcinogenic or mutagenic, even in very low concentrations (Picardo et al., 2009). Iron is commonly found in rocks and soil. Under proper conditions, iron will leach into the water resources from rock and soil formations. Exceeding iron concentration greater than 0.3 mg/L causes water staining that adversely affect plumbing fixtures, dishware and clothes and produce a yellow to reddish appearance in water. These levels may also impart taste and odour of drinking water. The US Environmental Protection Agency (USEPA) has established a secondary drinking water regulation of 0.3 mg/L for iron (Shokoohi et al., 2009).

Industrial activities like electroplating, metal cleaning and dyeing processing, cement and leather tanning are the major sectors that play role in releasing chromium into the environment. Chromium in the hexavalent form is very toxic. It is quite intriguing that contaminated field by industrial effluent show a mobilization ratio of less than 5 (potentially toxic) for selected plant species. Surprisingly, the mobilization ratios for weeds become

greater than 5, which have healthy morphology in the early flowering stage (Belay, 2010). A study done by Marchese et al. (2008) about the rate of accumulation of chromium in four fresh water plant species, clams, crabs and fishes showed that, all the four fresh water species and animals were found with high concentration of chromium which is an indication of its high accumulation potential. This clearly indicates that this problem become more serious and toxic to human beings which are found at the top of the food web due to its toxicity and bioaccumulation effect.

This study aims at exploring the feasibility of using maize cob, sawdust and coal as adsorbents for the remediation of chromium and iron from aqueous solution. Furthermore, the effects of various factors on the % removal were examined with a view to optimize removal conditions.

MATERIALS AND METHODS

The water used throughout this work was initially distilled and then passed through a deionizer. AnalaR grade reagents were employed for the preparation of all stock solutions, which after preparation were kept in a refrigerator. Fresh working standards were prepared daily by appropriate dilution of the stock solutions. All glasswares and plastic containers were washed with detergents, rinsed with distilled water and then soaked in a 10% HNO₃ solution for 24hrs. They were then washed with deionised water and dried in an oven for 24 hrs at 80 °C (Todorovi et al., 2001).

The adsorbent employed in this work were Sawdust, Maize cob and Coal. Hardwood sawdust from Mahogany (*Khaya senegalensis*) collected from a local sawmill was air dried in sunlight until almost all the moisture evaporated, then it was washed several times with distilled water in order to remove the water soluble tannins, after which it was dried in air and then in an oven at 80 °C. The material was allowed to cool and it was then ground to different working particle sizes (850 µm and powdered form) and kept in

a plastic container for subsequent use. Maize cob was similarly collected from local farm in Minjibir, Kano State, Nigeria. They were cut into small pieces, washed several times with water, air – dried and ground to the working particle sizes and finally kept in plastic containers for subsequent use. Coal was directly obtained from Kano Railway Station and was ground to the working particle sizes and kept for subsequent use.

All batch sorption analyses were carried out at room temperature, i.e 30 ± 2 °C by shaking various amounts of the adsorbents (2 – 8 g) with 100 cm³ of the aqueous solutions of the adsorbates (in a screw capped Erlenmeyer flasks) with initial loading concentrations ranging from 20 – 60 mg/L on an Innova 4000 shaker from New Brunswick Scientific at a speed of 290 rpm for a period of one hour. The pH of the adsorbate solutions (prepared from K₂Cr₂O₇ and FeSO₄.7H₂O) were adjusted with help of 0.5M HCl and 0.5M NaOH solutions. Immediately after the shaking process, the samples were separately filtered using Whatman number 1 filter paper, and the filtrates collected in polyethylene bottles were taken for AAS measurements for the residual adsorbate level using Shimadzu AA650 Double Beam Atomic Absorption/Flame spectrophotometer.

RESULTS AND DISCUSSION

Effect of adsorbent dose

The efficiency of three natural biosorbents viz., maize cob (MC), sawdust (SD) and coal (CO) were tested for the bioremediation of Cr and Fe ions from their aqueous solutions. Increase in the adsorbent dose from 2 to 8 g during the adsorption process (Figure 1) results in a general increase in % removal of the two ions. This can be explained as the higher the adsorbent dose the higher the available contact surface offered for the adsorption. This observation is in close agreement with that reported by Al – Anber and Al – Anber (2008) in the adsorption of iron (III) by olive cake. Also noticeable from the Figure is the low affinity of maize cob to Cr in relation to Fe, in that if not for lower

adsorbent dose an averagely 40% difference in the removal efficiency in favour of Fe is obtained. At optimum adsorbent dose, the removal efficiency of the adsorbents varies in the order; CO > SD > MC for Cr and MC > CO > SD for Fe.

Effect of adsorbate loading concentration

The % removal of the adsorbates onto the three adsorbents (Figure 2), with the exception of the adsorption of Fe onto MC, shows a general increase with increase in the adsorbate loading concentration. It is generally expected that as the concentration of the adsorbate increases the metal ions removed should increase according to Okeimen and Onyenkpa (2000). From the figure, the trend is in agreement with the expected phenomenon. It is believed that increase in concentration of the adsorbate bring about increase in competition of adsorbate molecules for few available binding sites on the surface of the adsorbent hence increasing the amount of metal ions removed (Elaigwu et al., 2009). However, the decrease observed in the case of the adsorption of Fe onto MC, according to Ibrahim and Jimoh (2008) can be explained by the fact that the adsorbent has a limited number of active (exchangeable) sites, which become saturated above a certain concentration. Also increase of the adsorbate loading concentration results in a decrease in the initial rate of external diffusion and increase in the intraparticle diffusion rate (El- Nemr et al., 2008). Similarly, the involvement of high energy sites in the adsorption process at low concentration and the subsequent use of low energy sites at high metal ion concentration may be linked to the decrease in % removal observed at high concentrations (Bhattacharya et al., 2008).

Effect of pH of the adsorbate solution

The pH of aqueous solution and hence wastewater effluents affects a number of reactions that takes place in these solutions. The effect of pH on heavy metal adsorption from aqueous solutions has been reported by

many workers such as Gang and Weixing (1998), Igwe et al. (2005), and Zouboulis et al. (1992). In all cases, it was found that removal of heavy metal ions was pH dependent at the different pH ranges that were tested. For this reason, in this work, the pH of the test solution was varied from 2 to 10 in order to determine the optimum pH value for the removal of the metal ions onto the different adsorbents. The % removal of Fe from Figure 3 shows a gradual increase from lower to higher pH values. This suggests that adsorbents' surface become more negatively charged which resulted in a more favourable electrostatic attraction forces and so, enhanced cationic metal ion adsorption which allows metal ions to be complexed at the adsorbent surface as pH increased (Chaiyasith et al., 2006; Opeolu et al., 2009). However, for Cr, it can be observed that the optimum pH (i.e. equilibrium pH) for adsorption onto the three adsorbents occurs at pH 2. This is because adsorption of hexavalent chromium varies as a function of pH. Although dichromate anion ($\text{Cr}_2\text{O}_7^{2-}$) from $\text{K}_2\text{Cr}_2\text{O}_7$ was employed as the

source of Cr(VI) in the adsorbate solutions used in this study, it undergoes hydrolysis in aqueous solutions as follows;



Therefore, at pH of 2, HCrO_4^- ion is the dominant ion while the surface charge of the adsorbent is positive at low pH, and this may promote the binding of the negatively charged HCrO_4^- ions. According to Nameni et al. (2008), the HCrO_4^- species are most easily exchanged with OH^- ions at active surfaces of the adsorbents under acidic conditions as below; $\text{AdOH} + \text{HCrO}_4^- + \text{H}^+ \rightarrow \text{AdHCrO}_4 + \text{H}_2\text{O} \dots\dots\dots (2)$

where Ad is the adsorbent surface.

Effects of increase in surface area

The comparison of Figures 4 and 5 with Figures 1 and 2 shows the effect of increase in surface area by using powdered adsorbents on the removal efficiencies of the different adsorbents. It can be observed that in

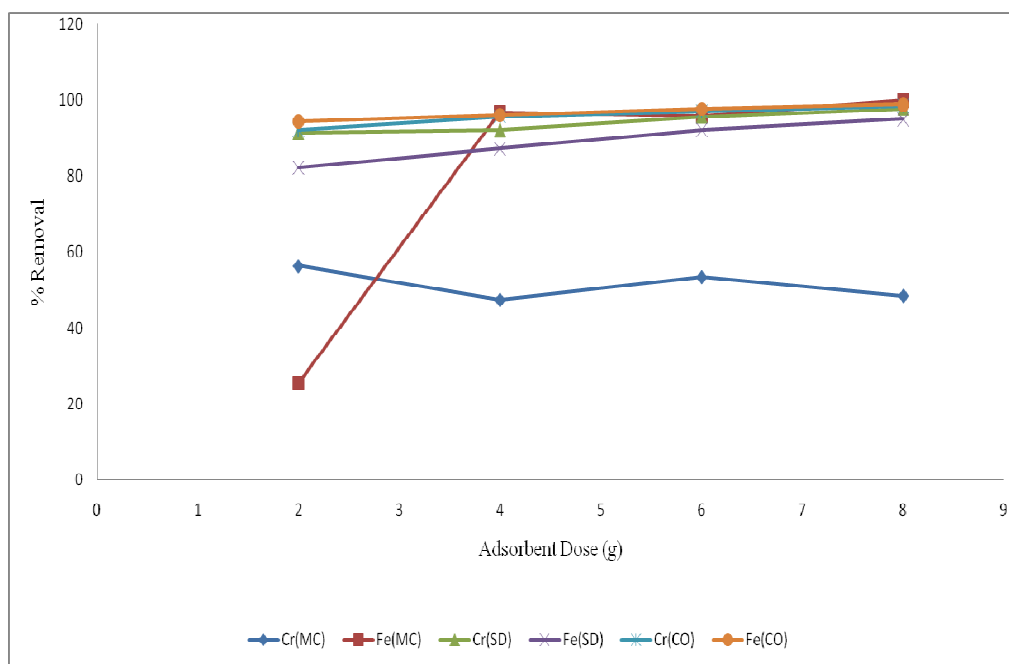


Figure 1: Variation of % removal with increase in adsorbent dose.

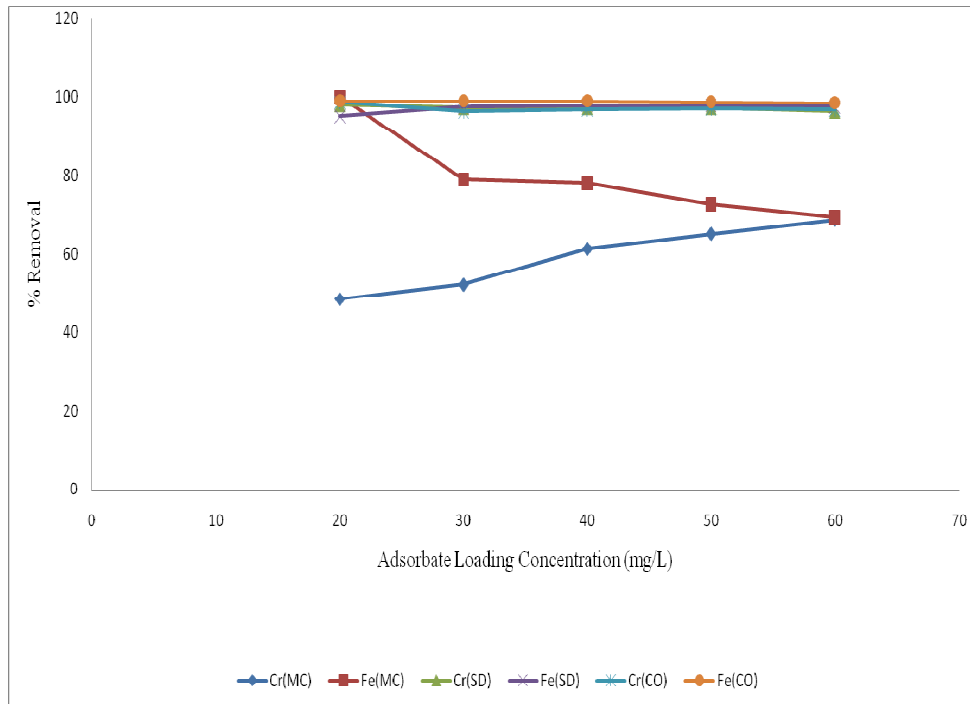


Figure 2: Variation of % removal with adsorbate loading concentration for the various adsorbents.

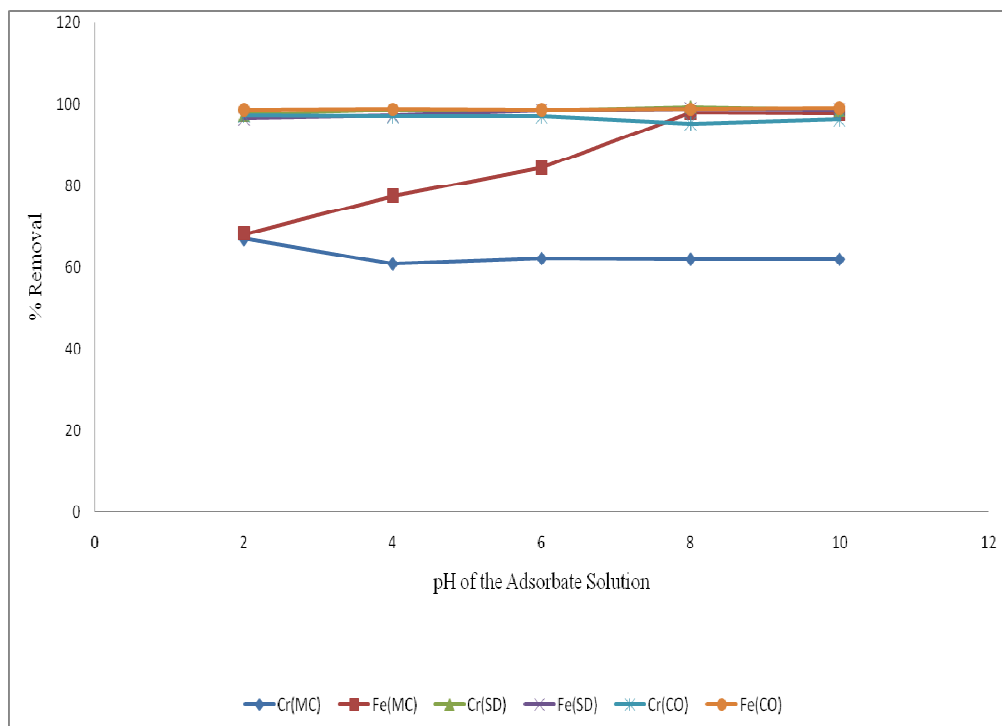


Figure 3: Variation of % Removal with pH of the Adsorbate Solution for the Various Adsorbents.

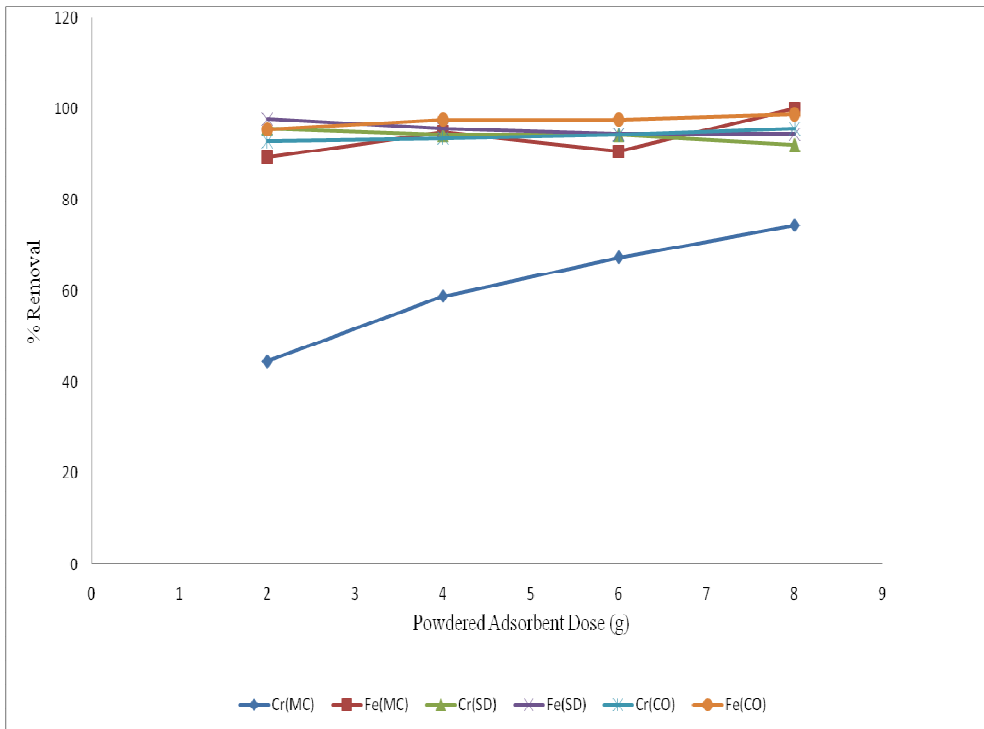


Figure 4: Variation of % removal with increase in powdered adsorbents dose.

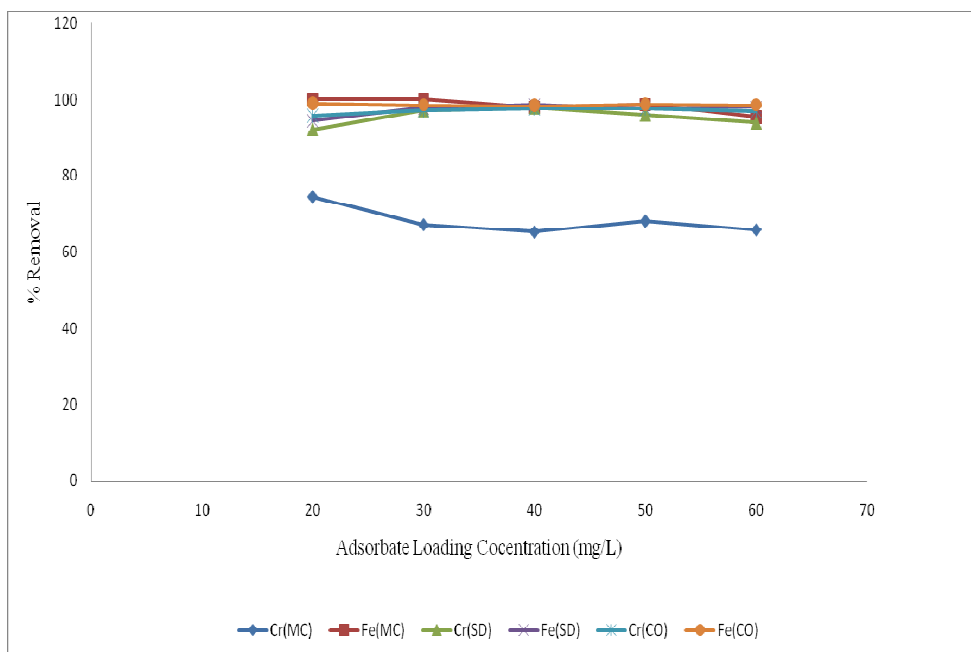


Figure 5: Variation of % removal with adsorbate loading concentration for the various powdered adsorbents.

all the cases where powdered adsorbent was used the % removal for the respective adsorbents for the two adsorbates have increased as a result of the increase in the available surface area for adsorption. These observed increases are obvious as with reduction in particle size of the adsorbent, the active site available for complexation with metal ions increases thereby leading to improved % adsorptions (Shukla, 2002; Kannan and Veemaraj, 2010).

Conclusion

The work has successfully demonstrated the use of natural adsorbents for the remediation of metallic pollutants from their aqueous solution, with the removal efficiencies varying with conditions such as adsorbent dose, adsorbate loading concentration, pH and surface area. For Cr(VI) the optimum pH was found to be 2 while for Fe(II) it was found to be pH 6. At optimum adsorbent weight % removal of Cr(VI) varied as 48.5, 97.85 and 98.57% on the three adsorbents MC, SD and CO respectively. Whereas, for Fe(II) on the same adsorbents the % removal was 100, 95 and 98% respectively.

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