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BIOSORPTION OF CR(VI), NI(II) AND FE(II) BY MAIZE (*ZEA MAYS*) COB

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ABSTRACT

The experimental results for the biosorption of Cr(VI), Ni(II) and Fe(II) onto maize cob were reported. The adsorbents efficiency on the bioremediation of these metals was estimated from the change in the percent adsorbate removal with (i) adsorbent dosage (ii) adsorbate initial concentration, (iii) variation in pH of the adsorbate solution and (vi) increase in surface area of the adsorbate. Untreated Maize Cob (MC) was found to demonstrate high affinity for Fe(II) in both granular and powdered form in such a way that 2g Powdered Maize Cob (PMC) was able to remove about 89% whereas a 100% removal was observed with 8g adsorbent. On the other hand MC showed low affinity for Ni(II) in the sense that even with the powdered form, % removal does not vary significantly between 2 and 8g.

Keywords: Zea mays, adsorption, adsorbent, metal ion, % removal

INTRODUCTION

The removal of toxic heavy metal contaminants from wastewater is currently one of the most important environmental issues being researched. Although it has been studied for many years, effective treatment options are still needed.

Several methods such as solvent extraction, reverse osmosis, precipitation, ion exchange, etc. have been employed for the treatment of wastewaters contaminated with heavy metals (Bansal, *et al*., 2009 and Gupta, *et al*., 2003). However, these techniques have certain disadvantages, such as high capital and operational costs or treatment and disposal of the residual metal sludge. Therefore the aforementioned methods are not economically feasible for small and medium industries. Hence an efficient and competitively economical means for the treatment of heavy metals containing wastewaters have been sought for. Adsorption compared with other methods appears to be an attractive process due to its efficiency and ease with which it can be applied in the treatment of heavy metal containing wastewater (Volesky and Holan, 1995). In recent years, a number of adsorptive materials, such as aquatic plants (Axtel, *et* al., 2003), agricultural by-products (Argun and Dursun, 2006), clay (Marquez, *et* al., 2004), zeollite(Alvarez-Ayuso, *et* al., 2003) and microorganisms(Dilek, *et* al., 2002) were used in heavy metal removal from wastewaters. Coconut fiber (Igwe and Abia 2007) and Sawdust (Baral, *et* al., 2006) were equally employed for the bioremediation of wastewaters.

In this work, biosorbent (Maize Cob) simply defined as adsorbents of biological origin has been employed for the treatment of heavy metal containing effluent.

MATERIALS AND METHODS

All glasswares and plastic containers were washed with detergents, rinsed with distilled water and then soaked in a 10% HNO_3 solution for 24hrs. They were then washed with deionised water and dried in an oven for 24hrs at 80°C (Todorovi, *et al*., 2001).

Distilled, deionised water, AnalaR grade reagents used without further purification were employed for the preparation of all stock solutions, and were kept in a refrigerator. Fresh working standards were prepared daily by appropriate dilution of the stock solutions.

Maize (*Zea mays*) cob (MC) adsorbent was 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 different particle sizes and finally kept in plastic containers for subsequent use (Igwe and Abia, 2007).

6M HNO_3 was prepared from conc. HNO_3 (specific gravity 1.490; percentage purity 65% w/v) and 1000mg/L Cr(VI), Ni(II) and Fe(II) were respectively prepared by dissolving 2.8290g of $K_2Cr_2O_7$, 4.0503g of $NiCl_2.6H_2O$ and 4.9780g of $FeSO_4.7H_2O$ in small volumes of distilled deionised water in separate beakers and the solutions were transferred to a 1.0litre volumetric flasks followed by the addition of 100cm^3 of 6M HNO_3 and they were made to mark with more water (Svehla, 2006). Lower working concentrations were prepared from the stock solution by appropriate dilution.

Batch Biosorption Studies

In batch (static) adsorption studies, the same solution remains in contact with a given quantity of adsorbent. As the amount of solute adsorbed on the adsorbent increases and the solute concentration in solution reduces, the driving force for adsorption decreases with time accompanied by a reduction in the adsorption capacity. The adsorption process continues however, till equilibrium between the adsorbate concentration in solution, and the adsorbate adsorbed per unit weight of adsorbent, is reached. This equilibrium established is static in character, as it does not change further with time. The static equilibrium behaviour is characteristic of the nature of the adsorbent, the adsorbate, the solvent and the temperature (Rajgopal and Kapoor, 2001).

All batch sorption experiments conducted in this work were carried out at room temperature, i.e 30 ± 2°C and agitation period of one hour. The percent adsorbate removals were calculated from the relation $\left(\frac{C_o - C_t}{C_o} \times 100\right)$, where C_o and C_t are the initial and final adsorbate concentrations respectively (Bhattacharya, *et al.,* 2008).

Effect of Adsorbent Dose

The effect of adsorbent dose on the removal of Cr(VI) ions was studied using 2, 4, 6 and 8g of the *Zea mays* cob adsorbent weighed separately into 250cm^3 screw capped conical flasks. Each weight of the adsorbent was contacted with 100cm^3 of 20mg/L of the aqueous Cr(VI) solution. The mixture was agitated on a shaker (Model: Innova 4000, from New Brunswick Scientific) at a speed of 290rpm for a period of one hour. Immediately, the samples were separately filtered using Whatman number 1 filter paper rejecting the first few millilitres, and the filtrates collected were taken for AAS measurements at the National Research Institute for Chemical Technology (NARICT), Zaria (El – Nemr, *et al.*, 2008).

Effect of Adsorbate Initial Concentration

The effect of variation of initial Cr(VI) ion concentration for a fixed amount of adsorbent was investigated by contacting 30, 40, 50 and 60mg/L of the Cr(VI) solution to 8g of the MC adsorbent, and the mixture was shaken for a period of 1 hour. Fractions were collected through filtrations (El – Nemr, *et al.*, 2008).

Effect of pH of the Adsorbate Solution

The effect of the pH of the test metal solution on its adsorption by the MC was studied by contacting 60mg/L of Cr(VI) solutions whose pH have been adjusted to 2, 4, 6, 8 and 10 using 0.1M HCl or 0.1M NaOH solutions to 8g of the MC separately and agitated for a period of 1 hour. Fractions for AAS measurements were collected in a similar way (El – Nemr, *et al.*, 2008).

Effect of Increase in Surface Area

2, 4, 6, and 8g of powdered maize cob were employed. Each weight of the adsorbent was contacted with 100cm^3 of 20mg/L of the aqueous Cr(VI) solution for an agitation period of 1 hour. Also 8grams of the powdered MC were contacted with 30, 40, 50 and 60mg/L of the Cr(VI) solutions separately to observe the effect of increase in the test ion concentration (El – Nemr, *et al.*, 2008). Steps 2.2.1 to 2.2.4 were repeated separately with Ni(II) and Fe(II) solutions.

RESULTS AND DISCUSSION

Although a detailed characterization of the nature of the binding sites on the *Zea mays* materials was not conducted, from the nature of heavy metal ions and the cob materials, it can be speculated that ion exchange may be the principal mechanism for the removal of heavy metal ions. The affinity of the adsorbent to the different adsorbates as highlighted from Fig. 1 increases with increase in the amount of the granular maize cob (GMC) at the same initial adsorbates concentration of 20mg/L. This is consistent with the fact that for every increase in the adsorbent, there is a corresponding increase in adsorption sites (El-Nemr, *et al.*, 2008) of the GMC. Within the adsorbates, sorption capacity varies according to the order Fe(II) > Cr(VI) > Ni(II), in which with 4g of the adsorbent about 97% of Fe(II) has been removed which is nearly 50% more than Cr(VI) and 70% Ni(II). The removal capacity reaches its maximum with 8g of the GMC in which almost 100% of Fe(II) has been removed. This show the high affinity of the GMC to Fe(II) compared to the other ions.

The effect of increase in the initial metal ion concentration, with a fixed weight of adsorbent, on the adsorption process as revealed by Fig. 2 shows a gradual decrease in the % adsorbate removal with increase in the initial metal ion concentration for the metal with high affinity (Fe(II)). This agrees closely with the fact that all adsorbents have a limited number of active sites, which would have become saturated above a certain concentration and hence the percentage removal of metal ions which is a function of the initial concentration decreases(Nameni, *et al.*, 2008). However, the gradual increase in the % removal of Cr(VI) and Ni(II) is suggestive of the concentration range with which the removal of the these metals with MC will be effective.

Fig. 3 depicts how metal biosorption is critically linked with pH in the sense that Fe(II) which happens to exhibit high affinity to the adsorbent shows a more reduced adsorption at lower pH. This may be attributed to the fact that at low pH high concentration of H$^+$ leads to a competition between the proton and the metal cations for binding sites on the adsorbent surface, which consequently results in lower metal ion uptake, but increasing the pH to 8 and above lead to an accelerated adsorption rate, a case similar to what has been reported elsewhere in the literature (Omar and Al – Itawi, 2007). The result also shows a steady uptake in Cr(VI) and Ni(II) at pH 6 and above with Ni(II) showing about 10.6% increase in uptake over what has been reported earlier (Bansal, *et al.,* 2009). Summarily, this shows that there is a favourable pH range for the adsorption of every metal on a certain adsorbent.

Something that is clearly evident from Figs. 4 and 5 is the improvement in the removal capacity of the adsorbent for all the metals under both conditions. This is because by using the powdered maize cob (PMC) a reduction in particle size is noted which leads to increase in surface area and then increase in adsorption opportunity at the outer surface of the adsorbent. Besides, there is also the possibility of intraparticle diffusion from the outer surface into the pores of the adsorbent.

CONCLUSION

This work has demonstrated the possibility of using *Zea mays* cob in the treatment of heavy metal contaminated effluents. Also surmised in the work is the benefit that would open-up to food agriculture in that new market would be opened for the cob.

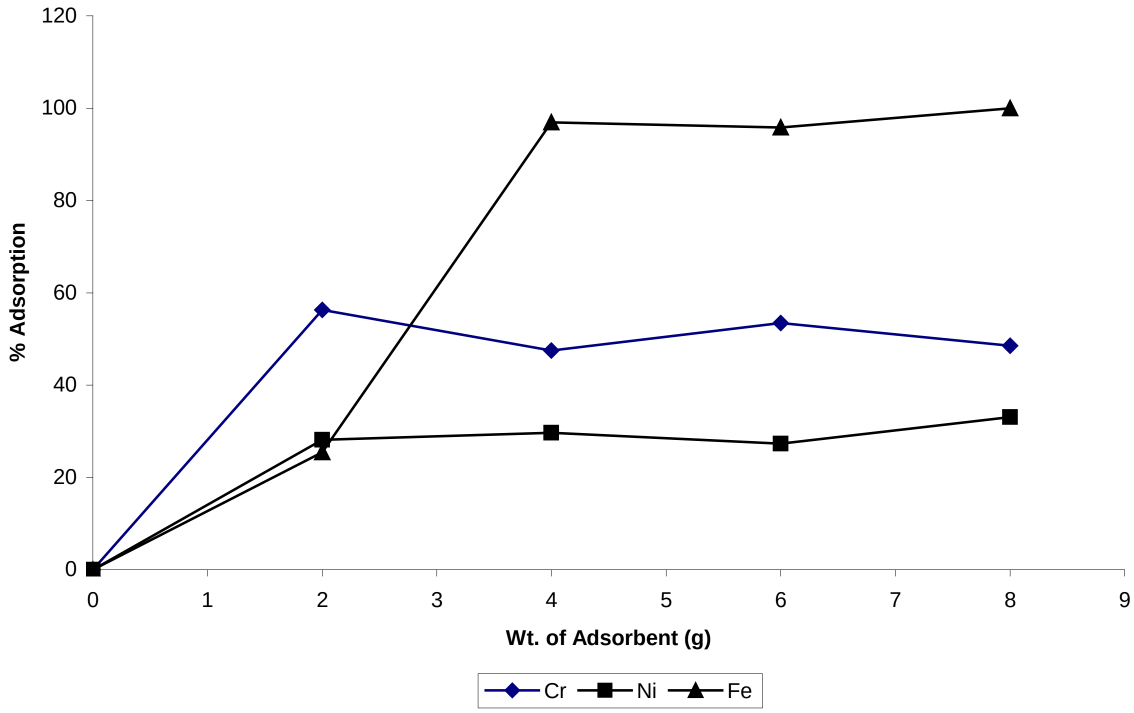

Fig. 1: Variation of the % Adsorbate Removal with Weight of Adsorbent (GMC)

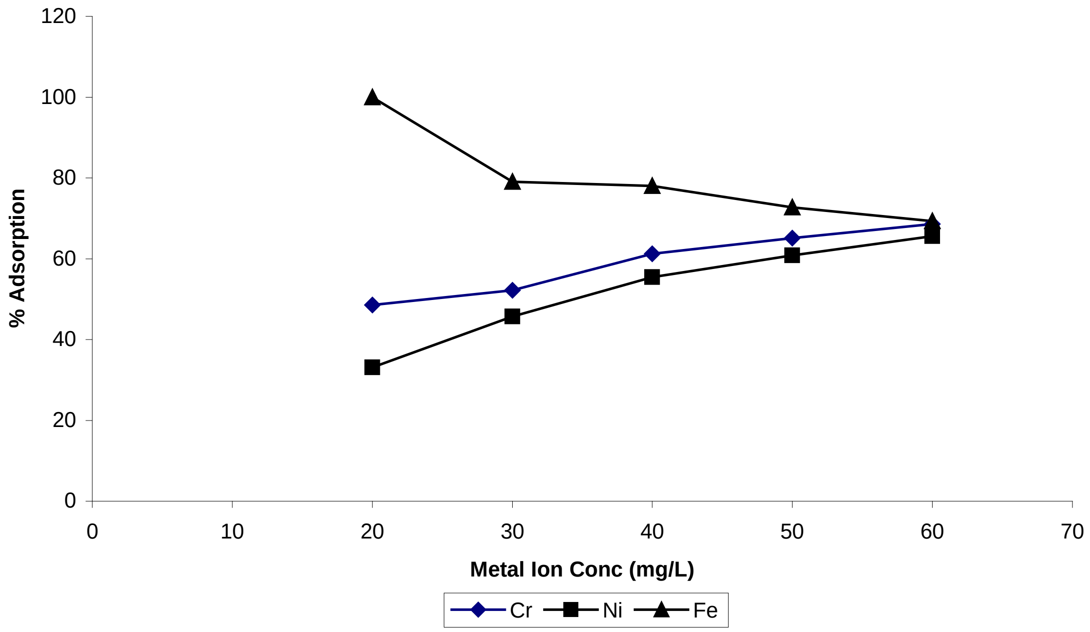

Fig. 2: Variation of % Adsorbate Removal with Increase in Initial Metal Ion Conc. Using (GMC)

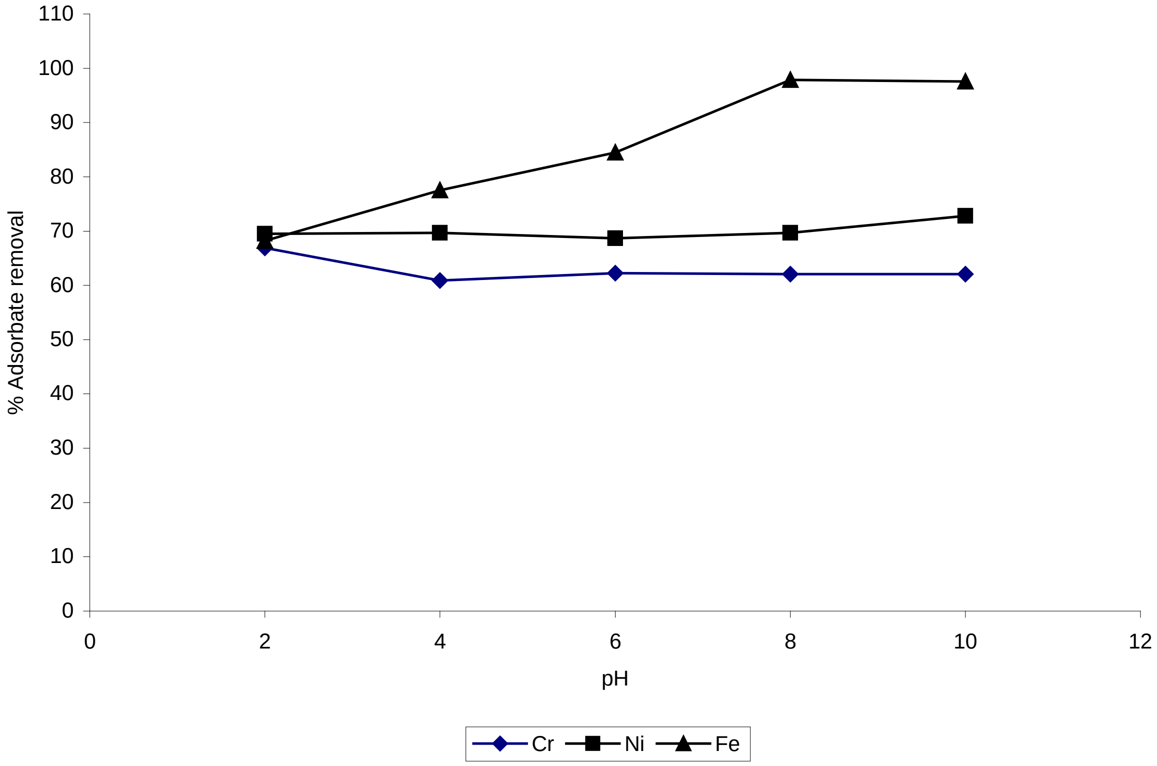

Fig. 3: Variation of % Adsorbate Removal with pH of the Metal Ion Solution using (GMC)

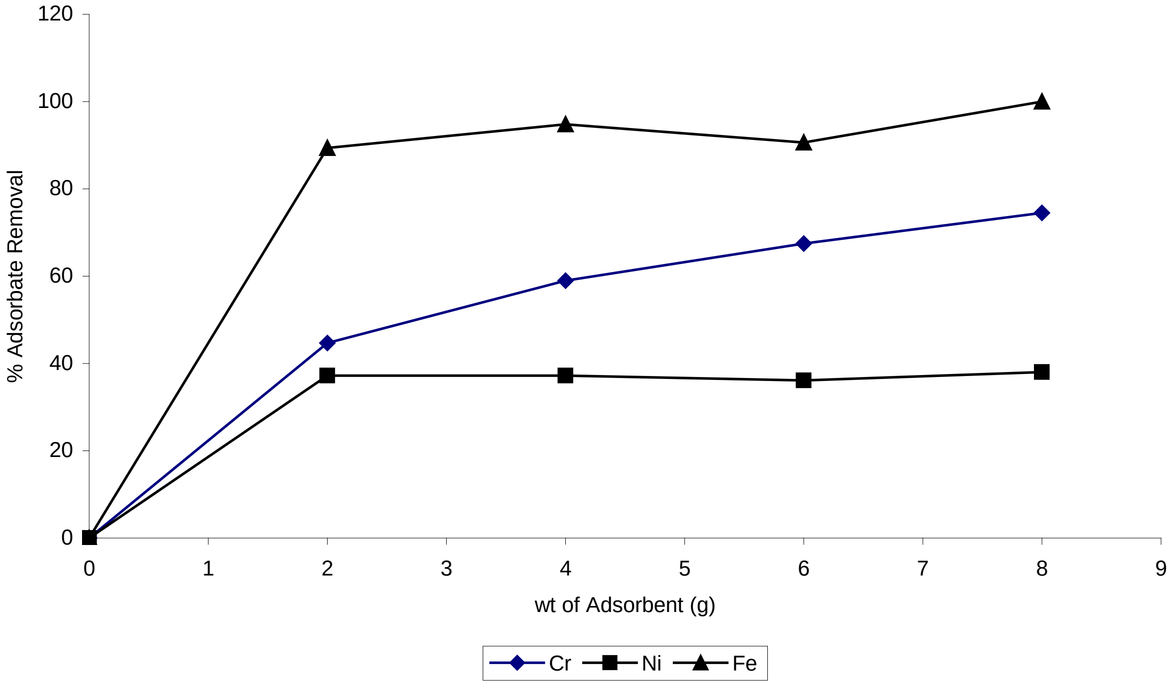

Fig. 4: Variation of the % Adsorbate Removal with Increase in Weight of Adsobent (PMC)

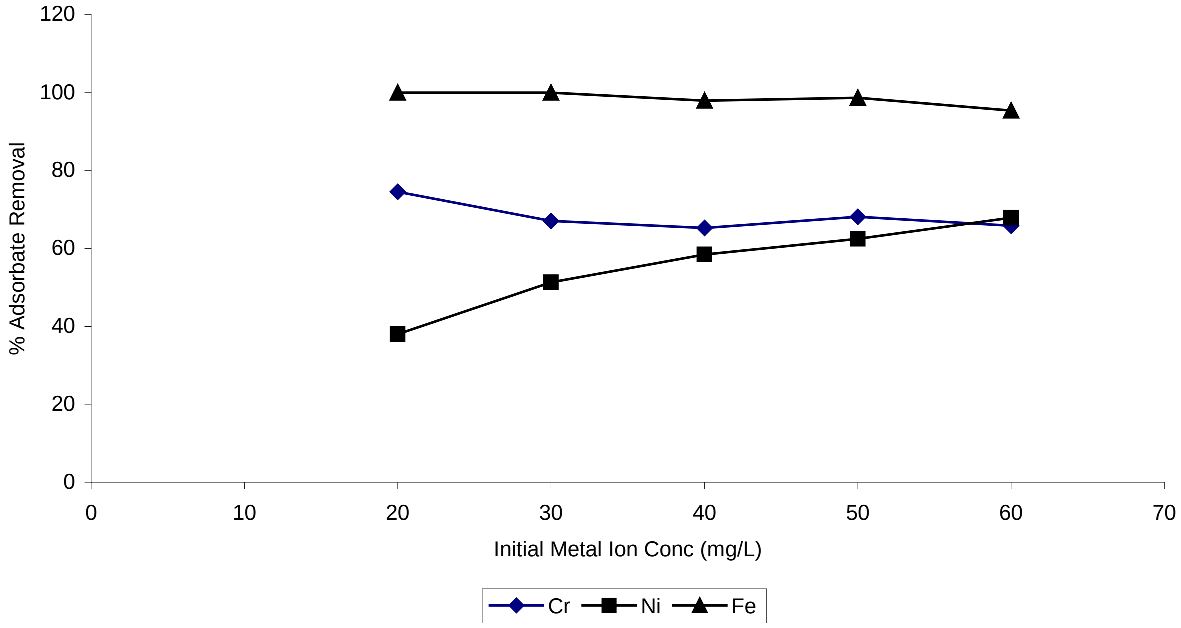

Fig. 5: Variation of the % Adsorbate Removal with Increase in Initial Metal Ion Conc. using (PMC)

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