

Bioremediation of Ni(II) and Cd(II) from aqueous solution

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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 was investigated in this study for the bioremediation of nickel and cadmium. Sorption experiments were carried out using batch process and 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 on the percentage removal of the adsorbates were studied. Results revealed that maize cob have higher affinity for Cd than Ni, while the reverse was the case with sawdust and coal, where Ni was found to have higher percentage removal than Cd. Thermodynamic parameters such as ΔH and ΔS were calculated from Van't Hoff plots which subsequently lead to the computation of ΔG . At 60 mg/L adsorbate concentrations, the adsorption process was found to be endothermic, spontaneous and feasible. The enthalpy, entropy and Gibbs energy changes for the removal of Ni onto maize cob were higher than those of Cd and the opposite scenario was observed for sawdust and coal.

Keywords: Adsorbent, Adsorbate, Percentage removal, maize cob, sawdust, coal

Introduction

Generally, metals that form compounds of biological constituents can be toxic, carcinogenic or mutagenic even in very low concentrations (Picardo *et al.*, 2009). Nickel (II) containing wastewaters are common as it is used in a number of industries including electroplating, battery manufacturing such as Ni/Fe storage batteries, mining, metal finishing and forging. It is also used to produce ferrous steel cutlery (Greenwood & Earnshaw, 1993). Higher concentrations of nickel cause cancer of lungs, nose and bone. Dermatitis (Ni Itch) is the most frequent effect of exposure to Ni from coins and jewellery. High concentration of Ni(II) in ingested water may cause severe damage to lungs, kidneys, gastrointestinal distress, nausea, vomiting, diarrhoea, pulmonary fibrosis, renal edema and skin dermatitis (Erdogan *et al.*, 2005; Meena *et al.*, 2005). On the other hand, Cd is mainly used in the industry for coating steel, glass and plastics (including polyvinyl chloride) and also for the Ni-Cd battery production and automotive tires. It has special importance due to its long half life and it can exert toxic effects on almost all systems of the human body (Tsalev, 1993). Under normal conditions, the intake of Cd depends on the cadmium concentration in natural sources such as air, land and water and does not exceed 20 mg/day (Tsalev, 1993). The absorption of Cd from the gastrointestinal tract is quite low; its absorption rate is 3-7% in humans and 2% in experimental animals (Brzoska & Moniuszko-Jakoniuk, 1998). Cadmium could also be shown to be associated with occurrences of Itai-Itai, a disease under which patients show a wide range of symptoms such as low grade of bone mineralization, high rate of fractures, increased rate of osteoporosis and intense bone associated pain (Fridberg *et al.*, 1974; Nogawa *et al.*, 2004).

The presence of heavy metals in the environment is of major concern because of their extreme toxicity and tendency for bioaccumulation in the food chain even in relatively low concentrations. They are highly toxic as ions or in compound forms; they are soluble in water and may be readily absorbed into living organisms. These are facts that necessitate the present work such that cheap and easily available means of removing heavy metals from waters in our environment would be obtained. The work made use of adsorption technique for the removal of the metal ions from the aqueous solution by employing AAS in measuring the residual level of the metal ions.

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 and refrigerated. Fresh working standards were prepared daily by appropriate dilution of the stock solutions. All glassware and plastic containers were washed with detergents, rinsed with distilled water and then soaked in a 10% HNO₃ solution for 24 h. They were then washed with deionised water and dried in an oven for 24 h at 80°C (Todorovi *et al.*, 2001). The adsorbent employed in this work were sawdust, maize cob and coal. Hardwood sawdust collected from a local saw mill 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 particle sizes 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 different particle sizes

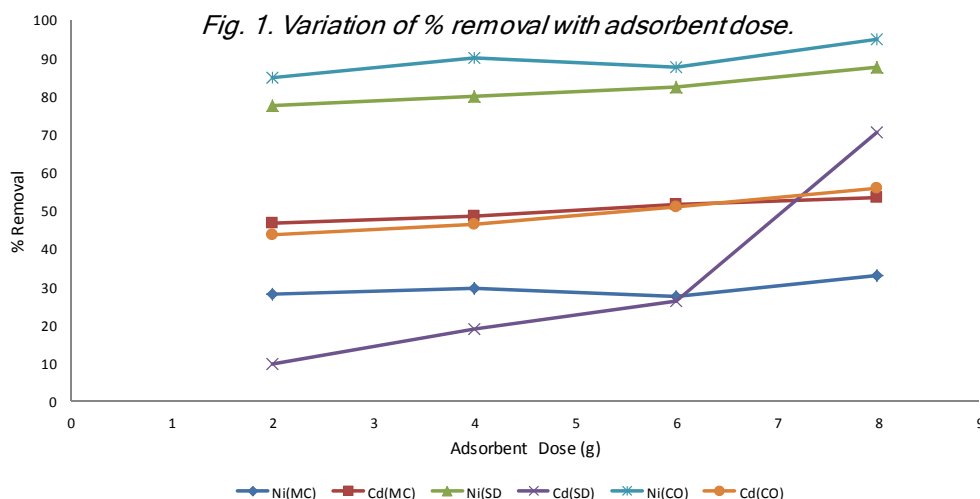
and finally kept in plastic containers for subsequent use. Coal was directly obtained from Kano railway station and was ground to different sizes and kept for subsequent use.

All batch sorption analyses were carried out at room temperature, i.e $30 \pm 2^\circ\text{C}$ by shaking various amounts of the adsorbents (2-8 g) with 100 cm^3 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 1 h. The pH of the adsorbate solutions were adjusted with help of 0.5 M HCl and 0.5 M NaOH solutions. Immediately after the shaking process, the samples were separately filtered using Whatman No. 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.

(2009) similarly reported that increasing adsorption with adsorbent weight can be attributed to increased number of unsaturated active sites on the adsorbents as well as high accessibility of the various ions to the binding sites. Also from Fig. 1 it can be observed that MC has higher affinity for Cd(II) compared to Ni(II), on which percentage removal for Ni varied from 28.1 to 33% whereas that of cadmium ion varied from 46.6 to 53%, a situation which is similar to that reported by Akporhonor and Egwaikhide, (2007) for the removal of similar metals onto chemically modified maize cob. However, for SD and CO the percentage removal of Ni(II) were higher in relation to those of Cd(II). On SD the percentage removal of Ni(II) ranges from 77.5 to 87.5% and on CO from 85% to 95%. On the other hand percentage removal of Cd on SD varied from 9.8% to 70.4% while on CO it varied from 43.7 to 55.7%. Obvious from this is that the adsorbents can be employed for the selective removal of the different adsorbates from their aqueous solutions.

Effect of adsorbate loading concentration

Adsorbate loading concentration is one of the effective factors on adsorption efficiency. The percentage removal of the adsorbates onto the 3 adsorbents (Fig. 2) shows a general increase with increase in the adsorbate loading concentration in which for MC at 20 mg/L adsorbate concentration, Cd has 53% and Ni 33% which gradually increases to 77% and 65% respectively at 60 mg/L. While for SD Ni has 87.5% which subsequently increases to 90% at higher adsorbate concentration.

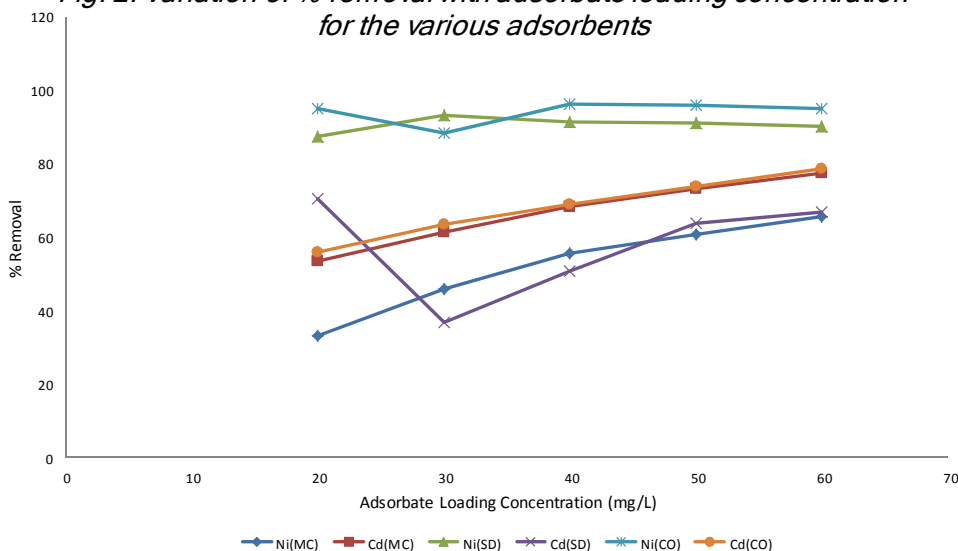


Results and discussion

Effect of adsorbent dose

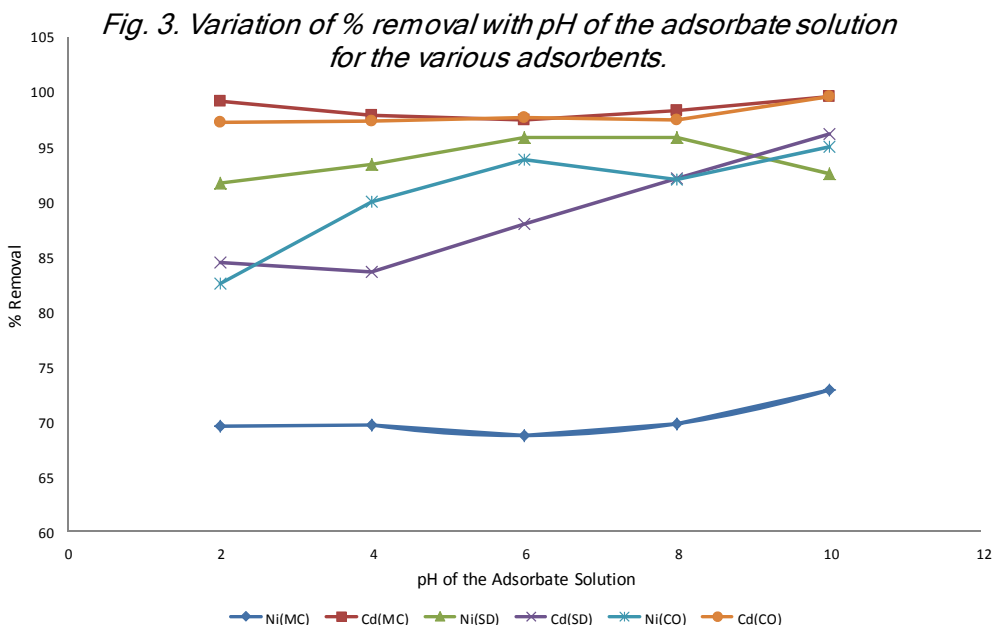
The efficiency of 3 biosorbents namely, maize cob (MC), sawdust (SD) and coal (CO) were tested for the bioremediation of Ni and Cd ions from their aqueous solutions. Changes in the amount of adsorbent during the adsorption process (Fig. 1) showed a general trend of increase in percentage removal as the adsorbent dose increased from 2 to 8 g. This phenomenon according to Mataka *et al.*, (2010) is expected since the metal uptake capacity of the adsorbent increases with the increase in dosage as the number of active sites available for metal increases with increase in the amount of adsorbent. Opeolu *et al.*,

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



However, Cd though with an initial decrease in percentage removal from 20 mg/L to 30 mg/L, it showed a maximum of 66.7% removal at 60 mg/L. On the other hand, on CO the percentage removal varies from 88 and 55.7% to 95 and 78.6% for Ni and Cd respectively. This observed trend of increase in percentage removal with adsorbate loading dose was similarly observed by Mishra *et al.*, (2009) for the adsorption of Ni with municipal sludge. It is generally expected that as the concentration of the adsorbate increases the metal ions removed should increase according to Okeimen and Onyenkpa, (2000). This is because increase in the concentration of the adsorbate brings about increase in chances of the adsorbate molecules to be adsorbed at the available binding sites on the surface of the adsorbent thereby increasing the amount of ions removed (Elaigwu *et al.*, 2009).

pH value required for the adsorption of the metal ion beyond which a decrease will be experienced. According to Baig *et al.* (1999) carboxyl groups (-COOH) to some extent are responsible for the binding of the metal ions. At lower pHs the carboxyl groups retained their protons thereby reducing the probability of them binding to any positively charged ions. Whereas, at higher pHs (above pH 4), the carboxyl groups are deprotonated and as such are negatively charged. The negatively charged carboxylate (-COO⁻) ligands attract the positively charged metal ions and binding occurs. The observed lower percentage removal at lower pH may be related to the competition existing between metal ions and H⁺ ions for the available adsorption sites on the adsorbents (Ibrahim *et al.*, 2006). Also, the observed increase in percentage removal of Ni by MC and Cd removal by the 3 adsorbents with increasing pH had been explained to be due to the hydrolysis of heavy metals and the charge at an active site on the surface of the adsorbents (Chaiyasith *et al.*, 2006). Enhanced percentage adsorption with increasing pH for Cd on SD also suggests that adsorbents' surface become more negatively charged. This resulted in a more favourable electrostatic attractive 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).



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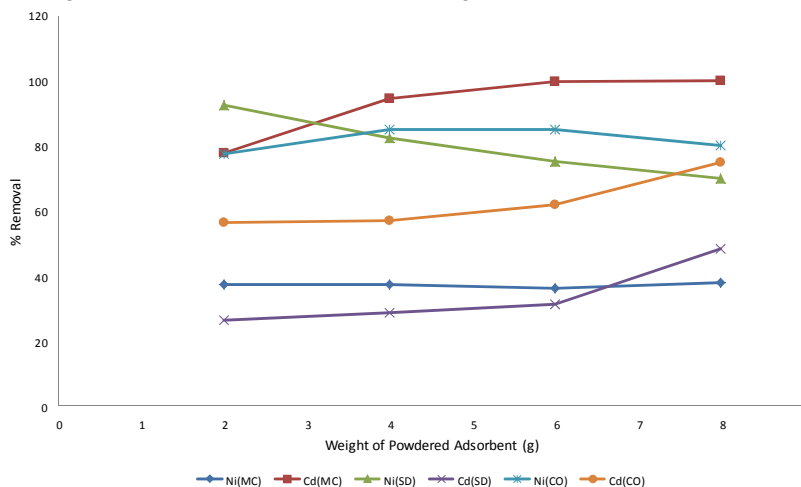
Effects of increase in surface area

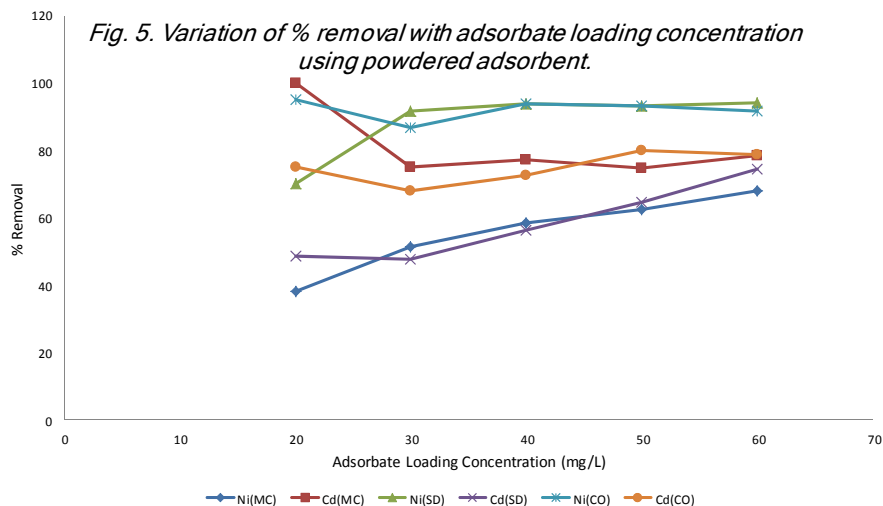
Fig. 4 reveals the effect of increase in surface area by using powdered adsorbents on the percentage removal of the different adsorbents. With the

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 Wiexing, (1998), Zouboulis *et al.* (1992) and Igwe and Abia (2003) etc. 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 percentage removal of Ni from Fig. 3 showed a gradual increase from pH 2 to pH 6 (for SD & CO) and then followed by a decrease at higher pH values. This indicates that there is an optimum

Fig. 4. Variation of % removal with weight of powdered adsorbents.





exception of the adsorption of Ni onto sawdust, when compared with Fig. 1 it can be observed that in all the cases where powdered adsorbent was used the percentage removal for the respective adsorbates increased. However, the decrease observed in the case of Ni removal by sawdust had been explained as due to the overcrowding of adsorbent particles (Garg *et al.*, 2003; Najua *et al.*, 2008). Moreover, the high adsorbent dosage could impose a screening effect on the dense outer layer of the cells, thereby shielding the binding sites from the metal ion (Pons & Fuste, 1993). The same increase (though with some initial decrease) in percentage removal can be observed in Fig. 5 for a situation where powdered adsorbents were used with increase in adsorbate loading concentration. 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 percentage adsorptions.

These observed increases are obvious as with reduction in particle size of the adsorbent, there is increase in adsorption opportunity at the outer surface of the adsorbent materials. Besides, there is also possibility of intraparticle diffusion from the outer surface into the pores of the adsorbent material. In other word, the active site available for complexation with metal ions increases thereby leading to improved percentage adsorptions (Shukla *et al.*, 2002).

Thermodynamics of the adsorption process

The enthalpy and entropy changes of the adsorption process were estimated from Van't Hoff plots;

$$\ln K_a = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

While the change in Gibbs free energy (ΔG) was calculated from,

$$\Delta G = \Delta H - T\Delta S$$

Where R (8.314 Jmol⁻¹K⁻¹) is the gas constant, T(K) is the absolute temperature (Chen & Wang, 2006; Omar & Al-Itawi, 2007; Zawani *et al.*, 2009). From Table 1, the adsorption process was found to be endothermic. One

possible interpretation of endothermicity of adsorption was that the metal ions were highly solvated in water. In order for these ions to be adsorbed, the hydration sphere must be removed and this process requires energy intake. This energy of dehydration supersedes that required for getting the ions attached to the surface of the adsorbent (Chen & Wang, 2006). The positive nature of the ΔS_{ad} values at higher ionic strength, suggesting spontaneous process. This occurs as a result of redistribution of energy between the adsorbate and the adsorbent. Before adsorption occurs, the metallic ions near the surface of the adsorbent were more ordered than in the subsequent adsorbed state. This increase in randomness at the solid-solution interface during the adsorption process leads to the increase in entropy and hence an overall positive ΔS . The adsorption process is therefore likely to occur spontaneously at normal and high temperatures

Table 1. Thermodynamic parameters for the bioremediation process.

Adsorbent	ΔH (Jmol ⁻¹)		ΔS (Jmol ⁻¹ K ⁻¹)		ΔG (Jmol ⁻¹)	
	Ni	Cd	Ni	Cd	Ni	Cd
MC	1,622.8928	1,276.1990	28.7082	20.0534	-7,075.70	-4,799.97
SD	754.1629	1,868.1558	10.0433	35.6587	-2,288.96	-8,936.44
CO	548.5577	1,425.0196	6.0277	26.0810	-1,277.82	-6,477.53

Conditions: 8 g adsorbent, 60 mg/L adsorbate conc., 1 h contact, 303 K temperature

because $\Delta H > 0$ and $\Delta S > 0$ (Andal & Sakthi, 2010). The Gibbs free energy changes (ΔG) were found to be negative (i.e. feasible & exergonic) as expected for a spontaneous process. The decrease in ΔG (i.e. increase negative) values indicated the increase in the extent of the adsorption. In other words suggesting more efficient adsorption and the ease with which the ions are desolvated (Qadeer, 2005; Chen & Wang, 2006; Hefne *et al.*, 2008). Table 1 also suggested that the strength of adsorption of Ni onto the biosorbents varies in the order MC > SD > CO, while that of Cd varies as SD > CO > MC. However, within the adsorbents, Ni attaches more strongly onto MC compared to Cd, while the reverse is the case on SD and CO adsorbents. This implies that desorption possibilities of Ni from MC will be less when compared to Cd and other way round on SD and CO adsorbents.

Conclusion

Natural organic adsorbents such as maize cob, sawdust and coal have the ability of removing Ni and Cd ions from aqueous solution which increased with the amount of the adsorbent and adsorbate loading concentrations at an optimum pH for each ion. On MC, SD and CO, the percentage removal of Ni ion varied as 28.1 to 33%, 77.5 to 87.5% and 85 to 95% respectively. Whereas, the percentage removal of Cd ion on the same adsorbents (MC, SD & CO) varied as 46.6 to 53%, 9.8 to 70.4% and 43.7 55.7% respectively. Thermodynamic analysis revealed the adsorption process to be endothermic (ΔH being positive),

spontaneous (ΔS being positive) and feasible (ΔG being negative).

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