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Binding Nickel and Zinc Ions with Activated Carbon Prepared from Sugar Cane Fibre (*Saccharum officinarum* L.)

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Abstract: Activated carbon was prepared from sugar cane fibre by carbonizing at 500°C for 30 min. This was followed by activation with ammonium chloride. The activated carbon was characterised in terms of pH, bulk density, ash content, surface area and surface charge. Equilibrium sorption of nickel and zinc ions by the activated carbon was studied using a range of metal ion concentrations. The sorption data was observed to have an adequate fit for the Langmuir isotherm equation. The level of metal ion uptake was found to be of the order: $Ni^{2+} > Zn^{2+}$. The difference in the removal efficiency could be explained in terms of the hydration energy of the metal ions. The distribution coefficient for a range of metal ion concentration of the metal ions at the sorbent water interface is higher than the concentration in the continuous phase.

Key words: Nickel, zinc, activated carbon, sugar cane fibre, Langmuir isotherm

INTRODUCTION

Heavy metals are persistent contaminants that tend to accumulate in the environment (Nriagu, 1996). Due to their toxicity, accumulative behaviour and effects on human health, heavy metal pollution has become a problem of increasing concern (Arowolo, 2004). The removal of these heavy metals from industrial and mining waste waters has received much attention in recent years (Ikhuoria and Uyanmadu, 2001; Marzal *et al*., 1996). Precipitation and ion-exchange, the two removal techniques that are generally applied, require the use of chemicals and/or synthetic resins, which are expensive. Over the last few years, adsorption has been shown to be an economically feasible alternative method for removing metal ions in waste water (Marzal *et al*., 1996; Seco *et al*., 1997; Lee *et al*., 2004; Zhou *et al*.,). Recently, emphasis has been given to the treatment of waste water through adsorption technology using activated carbon (Wartelle and Marshall, 2001; Ikhuoria and Etiuma, 2005; Rajukumar *et al*., 2005). Many researchers (Toles *et al*., 1997; Ikhuoria and Okieimen, 2000; Ricordel *et al*., 2001; Mkayula and Matumbo, 1994) have reported on the development of activated carbon from agricultural by products. In continuation of our studies on the potential application of agricultural by products in the production of activated carbon for environmental pollution monitoring and control, we report on the use of activated carbon obtained from sugar cane fibre for the removal of nickel and zinc ions from aqueous solution.

MATERIALS AND METHODS

Preparation of activated carbon from sugar cane fibre: The sugar cane stem was obtained from an open market in Benin City. They were washed crushed and oven dried at 150°C for the removal of moisture and ground.

The finely ground sugar cane fibre was mixed with an aqueous solution of NH_4Cl. The mixture was boiled in a 100 mL beaker for 2-3 h and the resulting paste dried in an oven for 3-6 h at 110°C. The dried sample was carbonized at 500°C for 45 min, in a tubular furnace under nitrogen. After cooling to room temperature, the sample was washed with dilute hydrochloric acid followed by distilled water to remove the activating chemical. The activated carbon was left overnight in the oven to dry at 110°C (Mkayula and Johns, 1994).

Characterization of sugar cane fibre carbon (SCFC)
pH determination: The pH of the carbon was determined by immersing 1.0 g sample in 100 mL of distilled/deionised water and stirring for 1 h.

Bulk density: The bulk density of the SKFC was determined by the tramping procedure (Ahmedna *et al*., 1997).

Determination of total surface charge: The determination of the total surface charge was a modification of the Boehm method (Toles *et al*., 2000). The results are expressed as mmol H^+ neutralized by excess OH^- per gram sample.

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Surface area determination: The surface area of the SKFC was determined by the iodine adsorption method (Okieimen *et al*., 1991). The amount of iodine adsorbed from aqueous solution was estimated by titrating a blank with standard thiosulphate solution and compared with titrating against iodine containing the sample.

Adsorption of metal ions: A series of the metal ion solutions (0.5-2.5 mmol L^{-1}) were prepared by dilution of the stock solutions (10 mmol L^{-1}) of the metal ions with distilled/deionised water. One gram of the SKFC was stirred for 2 h in 100 mL of the metal ion solution. The pH of the slurry was recorded at the start and at the end of the experiment. Residual metal ion concentration was determined by atomic absorption spectrophotometer (969 solar A-A). The quantity of adsorbed metal ion on SKFC was calculated as the difference between the initial concentration and the concentration at equilibrium.

RESULTS AND DISCUSSION

Characteristics of the sugar cane carbon (SCFC): A study on the physico-chemical properties of activated and non-activated carbon prepared from sugar cane fibre has been made. These properties are given in Table 1. These results compare favourably with literature data (Johns *et al*., 1999) on commercial activated carbon. Surface area is a single most important characteristic of activated carbon designed for adsorption of compounds from liquid media. The surface area of the activated sugar cane fibre carbon was found to be 835.77 m^2 g^{-1} and this compares favourably with commercial activated carbon which is about 850-1000 m^2 g^{-1}. Large surface area is generally a requirement for good adsorbent (Okieimen *et al*., 1991). The surface area of the activated and non-activated carbon was found to be 835.77 and 602.8 m^2 g^{-1}, respectively. This shows that chemical activation increased the surface area of sugar cane fibre carbon.

The type and net charge of fundamental groups bonded to carbon surface is important in understanding the mechanisms of adsorption of ionic molecules on activated carbons. The total surface charge of SCFC is comparable with values reported for some commercial grade activated carbon.

Adsorption capacity of sugar cane fibre carbon (SCFC): Table 2 result shows that chemical activation with NH_4Cl increased the activity of the carbon. The results also show that the amount of Zn^{2+} adsorbed on the activated and non-activated carbon is higher than that of Ni^{2+}. The difference in the amount of metal ion adsorbed at a given

Table 1: Physico-chemical properties of activated and non-activated carbon from sugar cane fibre

Properties	Activated	Non-activated carbon
pH	6.8	7.2
Bulk density (g mL^{-1})	0.0806	0.0694
Ash content %	5.92	5.72
Surface area (m^2 g^{-1})	835.77	602.84
Surface charge (mmol+ g^{-1} C)	1.62	0.812

Table 2: Adsorption of Ni^{2+} and Zn^{2+} on activated and non-activated carbon prepared from sugar cane fibre

Initial metal ion concentration (mmol L^{-1})	Amount of Zn^{2+} adsorbed (mmol g^{-1})		Amount of Ni^{2+} adsorbed (mmol g^{-1})	
	Activated	Non-activated	Activated	Non-activated
0.5	0.072	0.064	0.053	0.039
1.0	0.162	0.082	0.091	0.063
1.5	0.213	0.176	0.152	0.096
2.0	0.294	0.203	0.198	0.128
2.5	0.302	0.251	0.216	0.142

Table 3: Distribution coefficient, k_D, of metal ions at 29°C

Metal ion	Distributed coefficient, k_D (g L^{-1}) Non-activated carbon	Activated carbon
Ni^{2+}	1.106-0.842	1.812-1.264
Zn^{2+}	1.346-1.002	2.637-1.561

equilibrium concentration might be explained on the bases of their ionic radii, hydration energy, ionic mobility and diffusion coefficient (Ricordel *et al*., 2001).

Hydration energy is an important parameter to take into account since the hydrolysis of the metal ions occurs by the replacement of water ligands in the inner co-ordination sphere with hydroxo groups (Marzal *et al*., 1996; Ikhuoria and Omomhenle, 2001). Adsorption may be related directly to the loss of the outer hydration spheres that precedes hydrolysis. According to these parameters Zn^{2+} will lead to a higher extent in the adsorption process. Similar tendency has been reported by other workers using various raw materials (Okiemien and Onyenkpa, 1989; Seco *et al*., 1997; Johns *et al*., 1999).

Sorption coefficient: The relative effectiveness of an adsorbent in removing metal ions from waste water may be assessed in terms of the distribution coefficient. Distribution coefficient is defined as the ratio of the metal ion adsorbed to the amount in the liquid phase and it provides an estimate of sorption efficiency. Values of the distribution coefficient lower than 1 indicates low sorption efficiency (Ikhuoria and Udo, 1992). The values of the distribution coefficient of metal ion between the activated carbon and continuous aqueous phases are dependent on the initial metal ion concentrations and are higher than 1.0 as shown in Table 3. These values suggest high efficiency of the activated carbon, which means that limited sorption cycles will be required in the treatment of waste water containing the metal ions with activated carbon from sugar cane fibre.

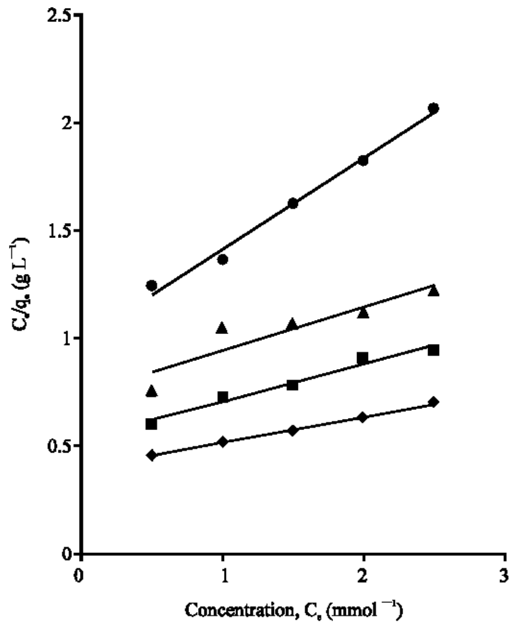

Fig. 1: Equilibrium sorption of Zn^{2+} on activated (●) and non-activated (▲) and Ni^{2+} on activated (■) and non-activated (♦) sugar cane fibre carbon

Sorption isotherm: Sorption data is usually modeled by using the classical Langmuir and Freundlich adsorption isotherms as shown in Eq. 1 and 2, respectively.

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (1)$$

$$q_e = k_f C_e^{\frac{1}{n}} \quad (2)$$

Here, C_e is the equilibrium concentration, q_e is the amount of metal ion adsorbed, Q_0 and b are constants of the Langmuir's isotherm related to maximum binding capacity and energy of adsorption respectively, while k_f and n are the coefficient and exponent of the Freundlich equation and they incorporate all the factors affecting adsorption capacity and intensity. In the removal of metal ion by SCRC, the application of Langmuir isotherm model was more appropriate than that of Freundlich model. Figure 1 shows the linear plots of the sorption data for zinc and nickel as C_e/q_e versus C_e. Q_0 and b were determined from the slope and intercept of the plots and are given in Table 4. The maximum metal ion binding capacity of the activated and non-activated carbon samples was found to be 0.174 and 0.12 mmol g^{-1} for nickel and 0.412 and 0.20 mmol g^{-1} for zinc ions, respectively. The essential characteristics of the Langmuir isotherm model can be expressed in terms of dimensionless constant, separation factor, R_L, which is given by Treyball (1980), as:

Table 4: Langmuir isotherm constants for the sorption of the metal ions

Parameters	Ni^{2+}	Zn^{2+}
Q_0 (mmol g^{-1})	0.174 (0.12)	0.42 (0.20)
b (g L^{-1})	0.529 (0.392)	0.99 (0.74)
R_L	0.314 (0.208)	0.625 (0.421)

Values for the non-activated carbon in parenthesis

$$R_L = 1/(1 + bCo)$$

Where: Co is the initial metal ion concentration. It has been established that the R_L values of between 0 and 1 are indicative of favourable adsorption of the metal ions onto the adsorbate (Treyball, 1980). The R_L values obtained in this study as shown in Table 4 are indicative of favourable adsorption onto the adsorbate.

CONCLUSIONS

Activated carbon prepared from sugar cane fibre has been used for the adsorption of Ni^{2+} and Zn^{2+} over a range of initial metal ion concentration. From the results, the sorption capacity of the metal ions was found to be of the order: $Zn^{2+} > Ni^{2+}$. This result shows that sugar cane fibre, an agricultural by product of no commercial value can be usefully utilized to scavenge metal ions from aqueous effluents. Thus, with this process, the money that would have been spent on commercial activated carbon or other chemicals used in conventional effluent treatment is conserved.

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