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Short Communication

Removal of selected metal ions from aqueous solution by adsorption onto chemically modified maize cobs

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Maize cob carbon was prepared by pyrolysis at 300 and 400°C for 35 min. This was followed by steeping in saturated ammonium chloride. The activated carbon which was characterized for bulk density, surface area, surface area charge, abrasion resistance and pH was used in the removal of Cd^{2+}, N_1^{2+}, Cd^{2+} and Zn^{2+}. The surface areas of the maize cob carbon at 300 and 400°C were 0.010 and 0.021 g sample per mg iodine, respectively. The effectiveness of the modified maize cobs in removing the metal ions from solution was found to be Zn >Ni> Cd. The removal efficiency of the metal ions is depended on the metal ion concentration and temperature of carbonization.

Key words: Maize cobs, activated carbon, pyrolysis, steeping,carbonization.

INRODUCTION

Industrial activities and mining operations have exposed man to the toxic effects of metals (Carrein and Becker, 1984). Heavy metals are present in the soil, natural water and air, in various forms and may become contaminants in food and drinking water (Forsther, 1977). Some of them are constituents of pesticides, paints and fertilizer application (Ikhuoria and Okieimen, 2000). Hazards associated with the contamination of water have led to the development of various technologies for wastewater purifycation namely filtration and ion exchange, precipitation with carbonate or hydroxide (Arowolo, 2004).

Man's exposure to heavy metals comes from industrial activities like mining, smelting, refining and manufacturing processes (Nriagu, 1996). Heavy metals constitute an important part of environmental pollutants and source of poisoning (Okieimen and Onyenkpa, 1989). The presence of strong chelating agents makes precipitation process ineffective (Ricordel et al., 2001). Although these methods are effective for removing metals from contaminated waters, they are either expensive or time consuming and have their inherent limitations (Marshall and Johns, 1996). The need for economical and effective methods of removing heavy metals from wastewater has resulted in the search for unconventional materials that may be useful in reducing the levels of accumulation of heavy metals in the environment (Egwaikhide et al., 2002).

MATERIALS AND METHODS

Maize cobs carbonization and characterization

Maize cobs were collected from a dump site in Ihievbe, Edo State, Nigeria. They were air-dried, powdered with a grinder and sieved through a 250 µm mesh size and retained by 90 µm mesh size. The portion that was retained in the 90 µm mesh was steeped in ammonium chloride solution for 24 h. After which, it was drained and air dried for a period of 6 days, to ensure proper drying and divided into 2 portions. The first portion was carbonized at 300°C and the second portion at 400°C to obtain fine particles sizes of the two portions. The pH of the carbon was determined by immersing 1.0g sample in 100ml of distilled/deioni-sed water and stirring for 1 h. The bulk density of the maize cob carbon was determined by tramping procedure (Ahmedna et al., 1997). The determination of the total surface charge was a modification of Boehm method reported by Toles et al. (2000). The results were expressed as mmol H^+ neutralized by excess OH per gram sample. The surface area of the maize cob carbon was determined by the iodine adsorption method (Okieimen et al., 1991). The amount of iodine adsorbed from aqueous solution was estimated by titrating blank with standard thiosulphate solution and compared with titrating against iodine containing the sample.

Metal ions adsorption by carbonized maize cobs

Zinc ion adsorption: 1 g each of samples carbonized at 300 and 400°C were placed in 5 different flasks to which 100 ml of varied concentrations of the Zn^{2+} standard solutions were added and shaken at intervals for a period of 60 min to ensure optimum adsor-

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Table 1. Some characteristics of activated carbon carbonized at 300°C and 400°C prepared from maize cob.

Parameters	300°C	400°C
pH	6.7± 0.32	6.4 ± 0.46
Bulk density (g/ml)	0.560 ± 0.09	0.602 ± 0.04
Surface area (g C/mg I_2)	0.010 ± 0.60	0.021 ± 0.64
Abrasion resistance (%)	16.41 ± 0.80	18.10 ± 0.64
Surface area charge (mmol H^+/g C)	1.60 ± 0.02	1.71 ± 0.06

ption. It was then filtered and 25 ml of the filtrates were used in the determination of the amount of Zn^{2+} adsorbed by the sample using complexometric titration with EDTA. Deionized water was used to dilute the 25 ml of the Zn^{2+} filtrate to 100 ml mark of the flask. 2 ml of buffer solution were added with a few drops of solochrome black indicator. This was then titrated against EDTA solution until colour changed to blue. The titre value was recorded: 1 ml of 0.1 M EDTA = 6.538 mg Zn.

Nickel ion adsorption: 1 g each of the samples carbonized at 300 and 400°C were placed separately in 5 different flasks of 25 ml capacity. 100 ml each of the various concentration of the Ni^{2+} standard solution were added and shaken for a period of 60 min for optimum adsorption to take place. It was then filtered and from the filtrate, 25 ml was taken for the complexometic titration to determine the amount of Ni^{2+} adsorbed by the sample. 25 ml of Ni^{2+} solution was diluted up to 100 ml with deionized water, 5 drops of murexide indicator were added and then 2 ml of buffer solution, which turned the solution yellow. These were then titrated against 0.1 m EDTA solution until it turned violet. The volume of EDTA used was then recorded: 1 ml of 0.1 M EDTA = 5.87 mg of Ni.

Cadmium ion adsorption: 1 g each of the sample carbonized at 300 and 400°C was placed in five 25 ml flask. 100 ml of various concentrations of the Cd^{2+} standard solution were added and shaken for a period of 60 min, to ensure optimum adsorption. These were then filtered and 25 ml of the filtrate was pipetted out for the determination of the amount of Cd^{2+} adsorbed. 25 ml of the Cd^{2+} solution filtrate was diluted up to 100 ml with deionized water. 3 drops of xylenol orange indicator were also added. The solution changed to yellow. 1 ml of 0.1 M EDTA = 11.24 mg of Cd.

Determination of surface area of the sample using iodine adsorption method

0.5 g carbonized corn cob was taken in a glass containing 25 ml of 0.05 m iodine solution and centrifuged for 2 min. 20.0 ml of the supernatant was taken in a 250 ml beaker and titrated against 0.1 m sodium thiosulphate until the colour of the solution turned yellow. At that point, 2 ml of starch solution was added, immediately the whole solution changed to blue. Titration with sodium thiosulphate was continued until the solution finally became colourless which is an indication of the endpoint. Iodine value (I.V.) was calculated according to standard methods.

RESULTS AND DISCUSSION

Some characteristics of activated maize cob

Some physical and chemical properties of activated maize cob are given in Table 1. The pH of activated maize cob carbonized at 300 and 400°C were found to be 6.7 and 6.4, respectively. For most applications, carbon pH of 6 - 8 is acceptable (Ahmedna et al., 2000). Bulk density determines the amount of carbon that can be contained in a filter of a given solids capacity and the quantity of the treated liquid that is retained by the filter cake (Hutchin, 1988). The surface areas of activated maize cob were determined by the iodine adsorption method. Large surface area is generally a requirement for good adsorbent. Surface area is a single most important characteristic of activated carbon designed for adsorption of compounds from liquid media (Okieimen et al., 1991).

Low cost adsorbent should not only possess good adsorptive properties, it should also possess high resistance to abrasive forces in batch and column applications for it to be considered for commercial use. The resistance of activated maize cob to mechanical abrasion is comparable with those of carbons, prepared from other agricultural by-products (Toles et al., 2000).

Adsorptive properties of maize cob carbon

The capacity and efficiency of maize cob carbon in removing Zn^{2+}, Ni^{2+} and Cd^{2+} ions from aqueous solutions are given in Table 2. Heavy metal adsorption is usually modeled by using the classical adsorption isotherms. The Langmuir model ($Ce/q_e = 1/Q_o b + C_e/Q_o$) was applied to the sorption data. The linear plots of C_e/q_e versus C_e shows that adsorption obeyed the Langmuir isotherm, suggest the formation of homogenous monolayer of the heavy metals on the surface of the activated carbon (Das et al., 2000) and indicates that the binding of the heavy metals may be caused by interaction with functional groups present on the absorbent (Romero-Gonzalex et al., 2000). Intercepts were extrapolated from the graph; slopes and binding capacities were calculated and the results are as presented in Tables 3 and 4. The tables show that increase in temperature of carbonization also increases the amount of metal ions absorbed. This can be explained by the large surface area and more pores that resulted from increase in carbonization temperature.

We can also deduce from the results that zinc is absorbed more by the sample than nickel and cadmium. The binding capacity (which is the reciprocal of the slope from

Table 2. The capacity and efficiency of maize cob carbon in removing Zn^{2+}, Ni^{2+} and Cd^{2+} ions from aqueous solutions.

Initial metal ion conc. (mmol/l)	Amount of Zn^{2+} adsorbed (mmol/g)		Amount of Ni^{2+} adsorbed (mmol/g)		Amount of Cd^{2+} adsorbed (mmol/g)	
	300°C	400°C	300°C	400°C	300°C	400°C
2.0	0.140	0.152	0.130	0.142	0.169	0.173
3.0	0.210	0.181	0.156	0.170	0.181	0.224
4.0	0.235	0.215	0.242	0.226	0.220	0.261
5.0	0.283	0.294	0.277	0.289	0.278	0.325
6.0	0.303	0.382	0.354	0.316	0.322	0.333

Results are given as a mean of triplicate determinations.

Table 3. Slopes and binding capacities extrapolated from the graph of metal ion adsorbed by 1 g sample carbonized at 300°C against the equilibrium concentration of the metal ions.

Metal ion solution	Slope	Binding capacities
Zinc	2.160	0.214
Nickel	2.850	0.124
Cadmium	2.630	0.101

Table 4. Slopes and binding capacities extrapolated from the graph of metal ion adsorbed by 1 g sample carbonized at 400°C against the equilibrium concentration of the metal ions.

Metal ion solution	Slope	Binding capacities
Zinc	2.160	0.368
Nickel	2.850	0.136
Cadmium	2.630	0.110

Langmuir isotherm equation and the tendency of the metal ions to be retained on the absorbent) is found to be highest in Zn^{2+} followed by Ni^{2+} and Cd^{2+} as shown in Tables 3 and 4. This work shows that carbonized maize cobs were found to be a good adsorbent for heavy metal ions.

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