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Binding of Cadmium, Copper, and Lead Ions by Modified Cellulosic Materials

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The need for effective and economical methods for removing toxic and valuable heavy metal ions from sewage and industrial and mining wastewaters has resulted in a search for unconventional methods and materials that might be useful (Kumar and Dara 1981). Many agricultural by-products that are available at little or no cost are capable of binding heavy metals by adsorption, chelation and ion exchange (Ogiwara et al. 1968). Several workers (Freidman et al. 1973, Randall et al. 1978) have reported on the use of some agricultural by-products in the sorption of heavy metal ions. Groundnut (peanut) husk is another commonly available agricultural by-product that might be useful in binding metal ions.

A preliminary study of the removal of heavy metal ions from aqueous solutions by modified cellulosic materials is reported. Cellulosic materials (groundnut husks) were modified by EDTA complexation. The equilibrium and static sorptions of some heavy metal ions (Pb(II), Cu(II), Cd(II) by the modified cellulosic substrate was examined at 28 C over a range of metal ion concentrations. The amount of metal ion adsorbed per gram of the modified substrate depended on both the metal ion type and the initial concentration of the metal ion. In all cases modification resulted in significant improvement in the metal ion binding capacity of the cellulosic materials.

MATERIALS AND METHODS

Fresh groundnuts, Arachis hypogea L. were purchased from open markets in Benin City, Nigeria and dehusked. The husks were air-dried, powdered in a grinder, and sieved through a 300 um mesh screen. The portion retained on the mesh was further air-dried and modified by complexation with ethylenediaminetetraacetic acid (EDTA).

A 20 g sample of the cellulosic materials (portion retained by the sieve) was hydrolysed with 15 times its weight of

7% (v/v) aqueous sulphuric acid for 24 h at 65 C. The mixture was filtered, and the product was washed thoroughly and dried at 50 C. A mixture of 17 g of the hydrolysed material, 300 mL of pyridine and 56.7 g of EDTA was heated under reflux at 70 C for 3 h. The reaction mixture was cooled, and after adding 30 mL of deionised water, the mixture was filtered. The EDTA resin was washed several times, first with the filtrate and finally with water.

Equilibrium sorption of the metal ions by the unmodified and modified cellulosic materials was performed at 28 C by using various concentrations of the metal ions over a range of metal ion substrate contact periods. In a typical experiment, a 5 g sample of the substrate was shaken with 100 mL of a metal ion solution whose concentration had been previously determined. At the end of the contact period, the mixture was filtered (the first 15 mL of the filtrate was discarded), and the final concentration of the metal ion in the filtrate was determined chelatometrically. The difference between the initial and final metal ion concentration was reported as the metal ion adsorbed by the substrate.

Adsorption of metal ions by the substrate in packed columns was examined for both the EDTA-cellulose resin and the unmodified substrate. Sections of 15 mm i.d x 100 cm long glass pipe were used for packed columns. Adsorbent was placed dry into the column, and the column was tapped gently to promote even distribution of packing in the column. Glass beads were added on top of the packing to prevent the adsorbent particles from floating and separating. The packing was wetted with a slow water flow, and was equilibrated for several hours with static water (Randall et al. 1978). Flow of test solutions through the column was by gravity and was controlled (1 mL/minute) by a valve at the bottom of the column.

RESULTS AND DISCUSSION

The variation of the amount of the metal ion bound by the modified material with time is shown in Fig. 1 for Cu II ions. The percentage of metal ion adsorbed by the substrate initially increases slightly with the contact time and then stabilizes, reaching equilibrium after about 20 min.

The amounts of metal ion adsorbed per gram of the substrate when sorption equilibrium is attained is shown in Table 1. The results clearly indicate that groundnut husk can bind substantial amount of heavy metal ions. The amount of metal ion adsorbed per gram of the substrate increases with the increase in the initial metal ion concentration. The difference in the amount of metal ion removed from solution by the substrate can be attributed to the possible difference

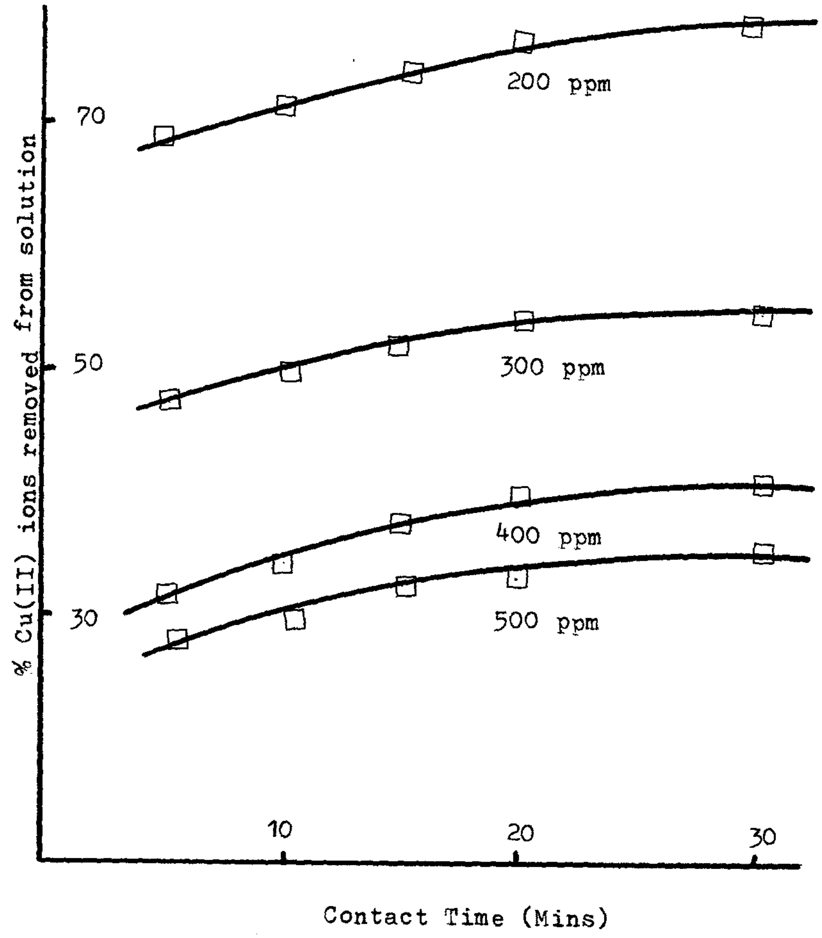

Fig. 1. Adsorption of Cu(II) ions on modified groundnut husks.

in the affinity of the metal ions for the active groups on the substrate, the nature of the anion of the salt, and the difference in the ionic radii of the metal ions. For instance, the level of divalent metal ion uptake by polymerized onion skin has been shown to be significantly increased if an acetate salt, rather than a nitrate, sulphate or chloride salt is used (Kumar and Dara 1981). The level of metal ion uptake by the unmodified substrate is shown in Table 1. The metal ion binding capacity of the substrate is greatly enhanced by modification.

The variations of the amount of metal ions removed from solution with metal ion type and with the initial metal ion concentration for the column experiments (dynamic sorption) are shown in Table 2. As with the equilibrium sorption

Table 1. Equilibrium sorption of metal ions by modified groundnut husks.

Aqueous salt solution	Initial concentration mg/L	amount of metal ion adsorbed mg/g EDTA resin	Unmodified groundnut husk
$Pb(NO_3)_2$	500	6.06	4.20
	400	5.58	-
	300	5.17	2.55
$CuCl_2$	500	4.28	2.29
	400	3.62	-
	300	2.95	-
	200	2.32	1.20
$CdSO_4$	500	3.26	-
	400	3.26	1.65
	300	2.65	-
	200	2.08	-

experiments, the amount of metal ions removed from solution is Pb(II) > Cu(II) ≫ Cd(II).

The amounts of the metal ions adsorbed by the EDTA resin in the column experiments are comparable with the values obtained from the equilibrium experiments. Although column adsorption represents an equilibrium system at each theoretical zone, the continuous removal of metal ions as the solutions move from one zone to another in the column should ensure that a higher proportion of metal ions is removed from the solution than in the equilibrium experiments. It is however possible that adsorption of metal ions by groundnut husks is a two-stage process: an initial high adsorption rate (possibly by ion exchange) followed by a slow chemical reaction of the metal ions with active groups on the adsorbent. It would therefore seem that the metal ion - adsorbent contact time for both the equilibrium and dynamic sorption experiments are relatively shorter than would be required for chemical combination of the metal ion with the active groups on the adsorbent to become significant. Factors that would influence chemical combination of the metal ions with active groups on the substrate include the particle size of the substrate, the nature and distribution of the active groups on the substrate, and the substrate - metal ion contact period. The results from this study indicate a potential for the use of modified groundnut husks for removing heavy metal ions from wastewaters.

Table 2. Dynamic sorption of metal ions by modified groundnut husks

Aqueous salt solution	Initial concentration mg/L	Final concentration mg/L	Metal ion sorbed mg/g
$Pb(NO_3)_2$	500	186	6.3
	400	135	5.3; 3.4[a]
	300	93	4.1
	200	62	2.8
$CuCl_2$	500	303	4.0
	400	203	3.9; 1.8[a]
	300	152	3.0
	200	102	2.0
$CdSO_4$	500	322	3.6
	400	225	3.5; 1.0
	300	165	2.7
	200	112	1.8

a) metal ion adsorbed (mg/g) by unmodified groundnut husk.

REFERENCES

Freidman P, Harrison CS, Ward WH, Lundgsen HP (1973) Sorption behaviour of mecuric and methyl mecuric salts on wool. J Appl Polym Sci 17: 377-390.

Kumar P, Dara SS (1981) Binding heavy metal ions with polymerised onion skin. J Polym Sci 19: 397-402.

Ogiwara Y, Ogiwara Y, Kubota H (1968) The mechanism of consumption of ceric salt with cellulosic materials. J Polym Sci A-1 6: 1489-1499.

Randall JM, Hautala E, Mcdonald G (1978) Binding of heavy metal ions by formaldehyde polymerised peanut skins. J Appl Polym Sci 22: 379-389.

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