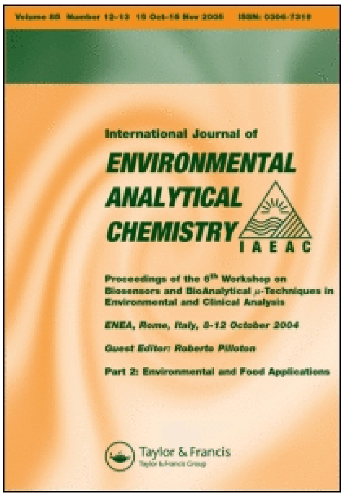

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Binding Cadmium and Copper Ions with Chemically Modified Cellulosic Materials

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Equilibrium sorption of Cadmium and Copper Ions by modified and unmodified maize stalk was studied using a range of metal-ion concentrations and temperatures at various metal ion-substrate contact periods. The amount of metal ion removed from solution depended on the metal ion concentration, the metal ion-substrate contact period and the metal ion type. The level of metal ion uptake reached 15 mg/g of the substrate for cadmium ions at 0°C and was of the order Cd(II) > Cu(II). Modification improved the metal ion binding capacity of the substrate and increased the rate of metal ion uptake. The influence of temperature on the level and rate of metal ion uptake by the substrate was investigated.

INTRODUCTION

The need for effective and economical methods for removing toxic and valuable heavy metal ions from waste waters has resulted in a search for unconventional methods and materials that might be useful.[1] Several workers,[1-6] have reported on the use of agricultural by-products in the sorption of metal ions. The results from these and similar reports indicate a potential for the use of agricultural by-products in removing metal ions from waste-waters. Maize (zea mays) stalk is another commonly available agricultural by-product that might be useful in binding metal ions. This communication reports on the preliminary study of the equilibrium sorption of Cd(II) and Cu(II) ions on chemically modified maize stalk.

MATERIALS AND METHODS

Maize stalks obtained from farms within the campus of the University of Benin, Benin City, Nigeria, were cut to size, air-dried, and powdered in a grinder. The maize stalk meal obtained was further air-dried and sieved through a 300 μm meshscreen. The portion retained on the mesh was further air-dried and part of it was modified by complexation with ethylenediammine tetraacetic acid (EDTA).

A 20 g sample of the maize stalk meal was hydrolysed with 15 times its weight of 7% (v/v) aqueous sulphuric acid for 24 hrs 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 hrs. The reaction mixture was cooled, and after adding 300 mL of deionised water, the mixture was filtered. The EDTA modified substrate was washed several times, first with the filtrate and finally with water.

Equilibrium sorption of Cd(II) and Cu(II) ions by the unmodified and EDTA modified cellulosic materials was performed using various concentrations of the metal ions over a range of metal ion-substrate contact periods. In a typical experiment, a 2 g sample of the substrate was shaken with a 100 mL of a metal ion solution whose concentration had been previously determined. At the end of a given contact period, the mixture was rapidly 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 (making corrections for the metal ion content of the volume of solution retained (absorbed) by the substrate. The effect of temperature on the adsorption behaviour of the metal ions was investigated between 0°C and 50°C.

The fraction of the bound metal ions recoverable with dilute (1% v/v) nitric acid was determined. Air-dried samples of the maize stalk with the adsorbed metal ion was shaken with 50 mL of the dilute acid for 40 mins and filtered. The amount of metal ion in the filtrate was determined chelatometrically.

RESULTS AND DISCUSSION

The variation of the amount of metal ion bound by the modified and unmodified maize stalk with time is shown in Figure 1 (for Cu(II) ions). It shows that the amount of metal ion adsorbed by the substrate increases initially with time and then gradually levels off, reaching equilibrium after about 20 mins. The amount of the metal ions adsorbed per gram of the substrate when equilibrium is attained are shown in Table I. The results indicate that maize stalk can bind substantial amounts of the metal ions and that EDTA modification increases (by up to 40%) the metal ion binding capacity of the cellulosic substrate. The level of metal ion uptake by maize stalk is of the same order of magnitude as the levels reported for other agricultural by-products.[7,8] It can be seen from the results (Table I) that as the initial concentration is increased, the amount of metal ion bound by maize stalk decreases. The amount of Cd(II) ion removed from solution is larger than for Cu(II) ions. This can be explained in terms of the difference in the ionic radii of the metal ions, the difference in the affinity of the metal ions for active groups on the substrate and the nature of the anions of the salt used. For instance,

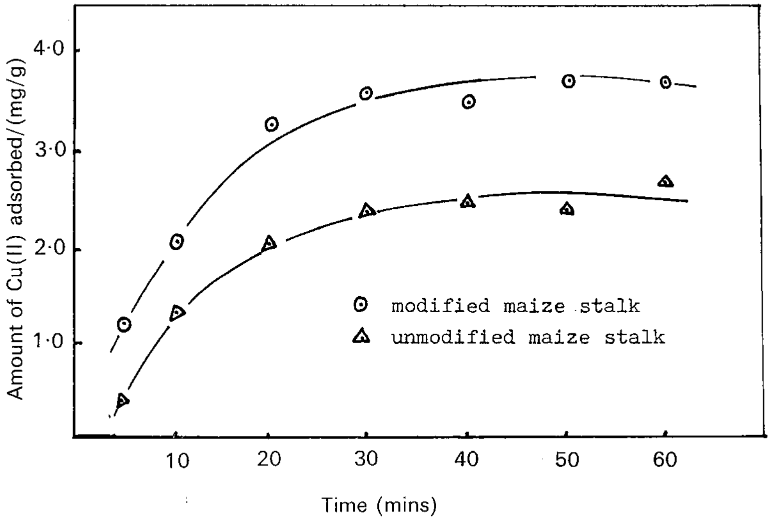

FIGURE 1 Equilibrium sorption of Cu(II) ions by maize stalk at 0°C.

TABLE I

Levels of cadmium and copper ions uptake by modified maize stalk

Initial concentration (mg/L)	Amount of metal ion adsorbed (mg/g)							
	0°C		29°C		40°C		50°C	
	Cd(II)	Cu(II)	Cd(II)	Cu(II)	Cd(II)	Cu(II)	Cd(II)	Cu(II)
100.0	5.3(3.7)	3.5(2.3)	4.6(2.9)	3.2(2.0)	3.9(2.2)	2.1(1.7)	3.0(2.0)	2.1(1.5)
300.0	11.5(8.4)	8.7(5.5)	9.9(6.6)	7.1(4.5)	7.7(6.3)	5.1(4.0)	7.2(4.8)	5.1(3.3)
500.0	15.9(12.0)	12.0(8.1)	14.6(10.2)	9.8(6.6)	11.8(9.8)	7.8(5.3)	10.6(8.2)	7.6(5.0)

Levels of metal ions uptake by unmodified maize stalk in brackets. Salts used: $CdSO_4$ *and* $CuCl_2$.

the binding of different metal ions by cellulosic substrates has been shown to be significantly improved if an acetate salt is used instead of a nitrate, sulphate or chloride salt.[1] Besides, for EDTA modified substrate, the stability of the metal ions-substrate interaction would be expected to vary with the metal ion type.

The influence of temperature on the adsorption isotherm of Cd(II) ions is shown in Figure 2. It shows that an increase in temperature is accompanied by a reduction in the time required for adsorption to reach equilibrium and a reduction (by up to 40%) of the amount of metal ion removed from solution when equilibrium is attained. The uptake of metal ions by maize stalk can be brought about by Vonder Waals interaction, chelation and ion-exchange,[9] acting sim-

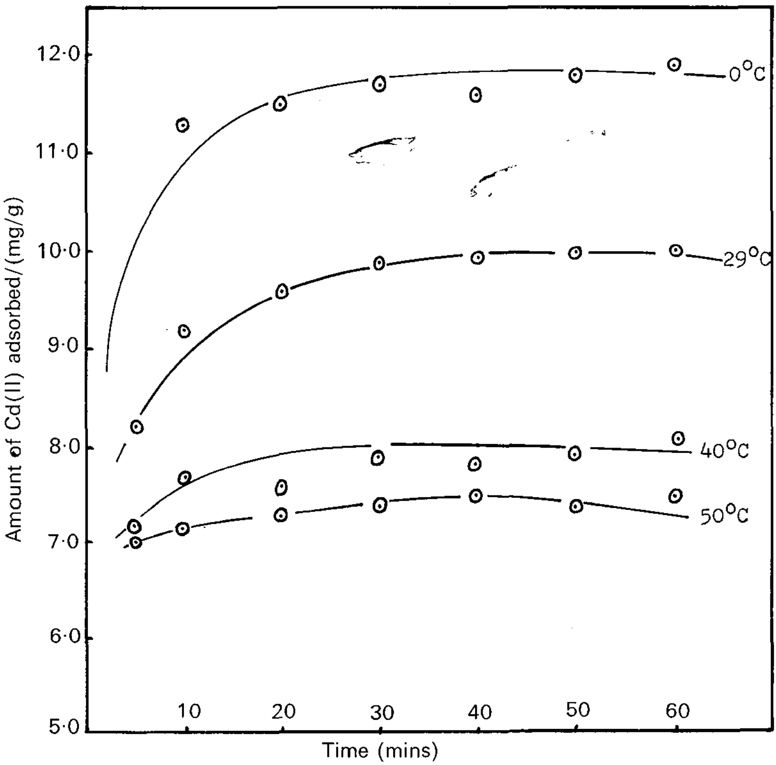

FIGURE 2 Effect of temperature on the equilibrium sorption of Cd(II) ions by chemically modified maize stalk from 300 mg/L solution.

ultaneously or one followed by the other. The uptake of metal ions by maize stalk can be considered to result from interaction of metal ions with reactive groups on the substrate which may differ in activity and distribution. Table I shows the variation of the level of metal ion uptake with temperature. The reduction in the level of metal ion uptake accompanying increase in temperature can be explained in terms of an increase in the average kinetic energy of the metal ions. Increase in the average kinetic energy of the metal ions could accentuate desorption and/or cause the metal ions to bounce off the surface of the substrate instead of colliding and combining with it.

A quantitative estimate of the rate of adsorption was obtained from plots of relative concentration, C/C_0, against time; where C_0 and C are the initial and residual concentrations of the metal ions respectively. The results (Table II) show that the half-times for the uptake of the metal ions are relatively high, varying from about 99.0 mins for Cd(II) ions at 0°C to 1.2×10^3 mins at 40°C. It can be seen that modification substantially increased the rate of metal ion uptake. This is as would be expected! The modification process involved the reduction of the molecular size of the adsorbent molecules through hydrolysis and the introduction of reactive carboxyl and amino groups on the substrate. The reduction in the rate of metal ion uptake with increase in temperature indicates that maize stalk scavenges metal ions from solution by two modes: molecular, non-specific interaction, and chemical combination of the metal ions with reactive groups on the substrate. At low temperatures, both modes of interaction would be taking place simultaneously, whereas at high temperatures, only the slow diffusion controlled chemical combination process can take place and it would be in competition with desorption of the already adsorbed ions.

TABLE II

Rate of Cd(II) ion uptake by modified maize stalk

Temp/°C	0	29	40
$10^3k/(\text{min}^{-1})$	7.0(4.6)	1.9	0.6
$t_{0.4}/(\text{min})$	99.02(150.67)	364.79	1155.16

k and $t_{0.5}$ values for unmodified maize stalk in brackets.

The fraction of adsorbed metal ions recoverable with dilute nitric acid is shown in Table III. The results show that between 20% and 30% of the adsorbed metal ions are retained on the substrate. The relatively high levels of recovery of the bound metal ions indicate that the substrate can be used in the preconcentration of trace quantities of metal ions from aqueous effluents.

TABLE III

Recovery of metal ions adsorbed[a] on maize stalk using 1%(v/v) nitric acid

Metal ion	Amount adsorbed (mg/g)	Amount desorbed (mg/g)	% Recovery
Cd(II)	11.9(10.4)	10.0(9.4)	84.0(90.1)
Cu(II)	3.7(2.5)	2.6(2.0)	70.2(80.4)

[a] Metal ions were adsorbed from 300 mg/L solutions at 0°C. Values for unmodified maize stalk in brackets.

The results from this study show that maize stalk, an agricultural by-product of no commercial value can be used to scavenge metal ions from aqueous effluents.

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