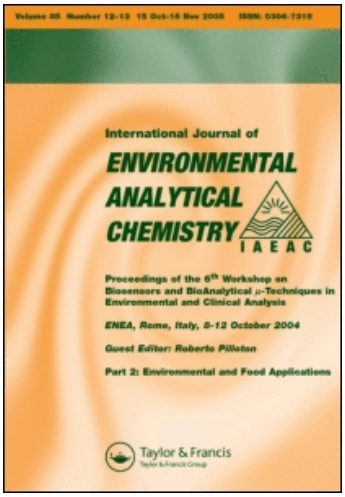

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Okieimen, F. E. , Maya, A. O. and Oriakhi, C. O.(1988) 'Sorption of Cadmium, Lead and Zinc Ions on Sulphur-Containing Chemically Modified Cellulosic Materials', International Journal of Environmental Analytical Chemistry, 32: 1, 23 — 27
To link to this Article: DOI: 10.1080/03067318808079074
URL: http://dx.doi.org/10.1080/03067318808079074

Intern. J. Environ. Anal. Chem., Vol. 32, pp. 23–27
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Printed in Great Britain

Sorption of Cadmium, Lead and Zinc Ions on Sulphur-Containing Chemically Modified Cellulosic Materials

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(*Received 11 November 1986; in final form 5 June 1987*)

Cellulosic materials containing 1.7% and 3.3% thiol groups were prepared by treating maize cobs meal with thioglycollic acid solution at 29 °C. Equilibrium sorption studies of cadmium, lead and zinc ions from aqueous solutions on the unmodified and thiolated cellulosic materials were carried out at 29 °C using various concentrations of the dilute metal ions solutions. The metal ion binding capacity of the cellulosic material was significantly improved by the incorporated thiol groups. The influence of pH of the metal ion solutions on the uptake levels of the metal ions by the cellulosic substrate was examined.

INTRODUCTION

The removal and recovery of toxic and/or valuable metals from aqueous effluents have received much attention in recent years. Precipitation and ion-exchange, the two removal/recovery techniques that have found wide application require the use of chemicals and synthetic resins which are expensive. Many agricultural by-products that are available at little or no cost have been reported to be capable of removing substantial amounts of metal ions from aqueous solutions.[1–5]

More recently, we reported on the binding of heavy metal ions by

cellulosic materials modified by the introduction of nitrogen-containing moieties.[6-8] The increased levels of metal ions uptake reported for the modified cellulosic materials required that other modification methods capable of enhancing the metal ion binding capacity of cellulosic materials be investigated. In this communication, we report on a preliminary study of the removal of heavy metal ions from aqueous solutions by cellulosic materials containing thiol groups.

MATERIALS AND METHODS

Maize (Zea mays) cobs were obtained from a Maize mill in Benin City. They were cut into small pieces, air-dried and powdered in a grinder. The maize cobs meal obtained was air-dried and sieved through a 300 μm screen. The portion of the maize cobs meal retained on the mesh was soaked in dilute nitric acid solution (2% v/v) overnight, rinsed with deionised water and air-dried.

The cellulosic material was modified by treatment with thioglycollic acid solution at 29 °C. A 25 g portion of the maize cobs meal was stirred in dilute thioglycollic acid solution (0.3 M and 1.0 M) for 24 h at 29 °C in a well ventilated hood. The mixture was filtered and the cellulosic material was thoroughly washed with deionised water and air-dried. The thiol content of the cellulosic material was determined by reacting 0.5 g sample of the thiolated material with excess iodine at neutral pH followed by back titration of the unreacted iodine with thiosulphate solution.

Equilibrium sorption of cadmium, lead and zinc ions on the unmodified and thiolated cellulosic material was carried out using 100 ml of various concentrations (10.0 mg/100 mL–50.0 mg/100 mL) of the metal ions at constant metal ion-substrate contact period (1 h) at 29 °C. The details of the experimental procedure were as described previously.[6-8] The uptake levels of the metal ions from acidic solutions (H^+ concentration of between 0.01 M and 0.001 M) were examined.

RESULTS AND DISCUSSION

The uptake levels of Cd(II), Pb(II) and Zn(II) ions from solutions containing various amounts of the metal ions by the unmodified and

thiolated cellulosic materials are shown in Table 1. The results show that the amounts of the metal ions bound by the cellulosic substrate depend on the metal ion type, the concentration of the metal ion solution, and the level of incorporation of thiol groups in the substrate. The level of metal ions uptake is Pb(II) > Cd(II) > Zn(II) ions. The difference in the uptake levels of the metal ions can be explained in terms of the difference in the ionic size of the metal ions, the nature and distribution of active groups on the substrate, and the mode of interaction between the metal ions and the substrate.[7] It can be seen that although the amount of the metal ions removed from solution increases with an increase in the initial concentration of the metal ion solution, the proportion of metal ions removed from solution by the cellulosic materials decreases with increase in the initial metal ion concentration. The results (Table 1) show that the metal ion binding capacity of the cellulosic material is markedly enhanced by the presence of relatively low levels (less than 5%) of thiol groups on the substrate. The improved levels of metal ions uptake by the thiolated cellulosic material is thought to result from the relative ease of exchanging hydrogen atoms of the thiol groups with the heavy metal ions. The levels of metal ions uptake by the thiolated cellulosic materials are much higher than the levels reported for EDTA modified cellulosic materials.[6-8] The practical implications of the relatively high metal ion binding capacity of thiolated cellulosic materials are numerous.

Table 1 Equilibrium sorption of cadmium, lead and zinc ions from aqueous solutions (pH 6.8 approx) by maize cobs meal containing different concentrations of SH-groups (3.3%, 1.7% and 0%) at 29 °C using 100 mL of the metal ion solutions

Metal ion concentration (mg/100 mL)	*Amount of metal ions adsorbed (meq/g)*		
	Cd(II)	*Pb(II)*	*Zn(II)*
10.0	0.06; 0.05[a] (0.02)	0.04; 0.03[a] (0.01)	0.06; 0.05[a] (0.02)
20.0	0.09; 0.09[a] (0.04)	0.09; 0.04[a] (0.03)	0.13; 0.12[a] (0.07)
30.0	0.22; 0.17[a] (0.10)	0.17; 0.12[a] (0.06)	0.27; 0.24[a] (0.22)
40.0	0.27; 0.22[a] (0.19)	0.19; 0.17[a] (0.13)	0.29; 0.29[a] (0.26)
50.0	0.31; 0.30[a] (0.29)	0.24; 0.21[a] (0.17)	0.32; 0.31[a] (0.28)

[a]Levels of metal ions uptake by cellulosic materials containing 1.7% SH-groups. Levels of metal ions uptake by unmodified (0% SH) cellulosic materials in brackets.

Table 2 Uptake of Cd(II) and Pb(II) ions from 0.01 M HNO_3(pH 2), 0.001 M HNO_3 (pH 3) and 0.0001 M HNO_3(pH 4) solutions containing 50 mg/100 mL of the metal ions by maize cobs meals at 29 °C[a]

pH of metal ion solution	*Amount of metal ions adsorbed (meq/g)*					
	Unmodified maize cobs		*Maize cobs with 1.7% SH-groups*		*Maize cobs with 3.3% SH-groups*	
	Cd(II)	*Pb(II)*	*Cd(II)*	*Pb(II)*	*Cd(II)*	*Pb(II)*
2.0	0.29	0.16	0.29	0.16	0.34	0.19
3.0	0.31	0.22	0.30	0.23	0.38	0.23
4.0	0.32	0.25	0.34	0.25	0.39	0.26

[a]The results are obtained by using the average of triplicate titre values. Variations were less than 0.5%.

The influence of pH of the metal ion solution on the sorption of Cd(II) and Pb(II) ions by the unmodified and thiolated maize cobs meals is shown in Table 2. It can be seen that the amount of metal ions removed from the solutions by the cellulosic materials increases as the pH of the metal ion solution is increased from pH 2 to pH 4. The uptake of metal ions from aqueous solutions by cellulosic materials is usually accompanied by a reduction in the pH of the metal ion solution. This is generally believed to be due to the exchange of the hydrogen atoms in the substrate by metal ions. The extent of hydrogen ion exchange would depend on the relative concentration of the exchangeable hydrogens and the hydrogen ion concentration of the medium. It is thought that the presence of a relatively high concentration of H^+ ions in the medium would influence the exchange of hydrogen on the substrate. The observed reduction in the levels of metal ions removed from solution by the cellulosic materials associated with the increase in the hydrogen ion concentration of the metal ion solution therefore indicates that the contribution of hydrogen atom exchange to the overall sorption process at these pH values may be insignificant. The pH dependence of Cd(II) and Pb(II) ions sorption by maize cobs meal suggests that at about pH 2, a large proportion of adsorbed metal ions may be recovered.

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