The Sorption of Heavy Metals with Corncob Hydroxylate–Red Onion Skin Resins

The disposal of organic wastes is becoming a serious problem in this part of the world, having arisen through rapid urbanization of an increased population and public awareness on the quality of the environment, although, in the past, the problems were less severe because of high rural population. Today much of the waste materials generated is cellulosic and over the years there has been active research into uses for these materials, especially crop residues which can serve as substrates for demineralization of waste water.

Recently, studies have been reported on the removal of toxic heavy metal ions from effluents by treating with various agricultural products such as tree bark,[1] peanut waste,[2] cotton,[3] and polymerized red onion skins.[4] However, these studies concerning programs that convert organic wastes, mainly agricultural residues to useful products, treat each type as an independent entity. As a result many concentrations are deemed too small to support waste conversion systems. If, however, wastes from dissimilar sources are combined, this problem may be overcome. Thus, the combined use of corn-cob hydroxylate (source of furfural) and red onion skin (source of phenolic compounds) deserves serious considerations. The present study is an attempt in this direction.

This report, therefore, demonstrates the preparation and properties of ion exchange substrate based on corncob–red onion skins as potential material for scavenging heavy metal ions from waste streams.

EXPERIMENTAL

Materials

The dry corncob and red onion skins used in this experiment were procured locally, ground, and sieved over 100–200-mesh screen to separate the fibers which were rejected. All chemical reagents used throughout this work were of the purest grade available except otherwise specified.

Preparation of Exchanger

To prevent color leaching and to insolubilize the tannin molecules, two parts of onion skins was treated with one part corncob hydroxylate, 1 part formaldehyde, and 20 parts $0.2M\ H_2SO_4$. The mixture was then refluxed for 3 h at 60°C and, thereafter, filtered, washed to a pH of 4.64, and dried in an oven overnight at 50°C.

RESULTS AND DISCUSSION

Static Tests

One hundred milliliters of metal ions solution and 1 part sorbent were added into a flask and shaken at room temperature for 24 h. After filteration the M^{2+} ion was determined in the filtrate chelatometrically. The results obtained are listed in Table I. As can be seen, the final pH is always less than the initial pH. Accordingly, it was concluded that the corncob–onion skin material acts as an acidic ion exchanger since H^+ ions are released into the solution as metals are bound. Thus, the equilibrium attained corresponds to a solution at lower pH than that of the original test solution. Similar observation was reported by Randall et al.[2] For the metal salts of acetate anion, no reasonable lowering pH was obtained owing to the buffering effect of the acetate ion. As expected for normal sulphonic acid cation exchangers, the ad-

Journal of Applied Polymer Science, Vol. 30, 2715–2719 (1985)

CCC 0021-8995/85/062715-05$04.00

TABLE I
Removal of Heavy Metal Ions from Solutions with Corn Cob Hydrozylate–Onion Skin Resin by Static Tests

Compound	Initial Concn (ppm)	Initial pH	Final pH	Cation sorbed (ppm)	Final Concn (ppm)	% cation sorbed
$Zn(OAC)_2$	355.00	6.02	5.32	274.40	80.60	77.30
$MgSO_4$	142.00	5.55	3.56	100.30	41.70	70.40
$NICl_2$	449.60	5.26	3.29	366.10	83.50	81.40
$Pb(NO_3)_2$	625.40	5.61	3.59	525.00	100.00	84.21
$CdCl_2$	614.00	5.23	3.09	501.60	112.40	81.60
$CaCl_2$	360.00	5.86	3.23	222.00	138.00	61.90
$HgCl_2$	740.00	5.30	3.54	523.00	217.00	70.60
$MnSO_4$	325.00	5.52	3.12	215.00	110.00	65.40

sorption of various M^{2+} ions from their solutions on the substrate is characterized by the following decreasing order: $Pb^{2+} > Cd^{2+} > N_i^{2+} > Zn^{2+} > Ca^{2+} > Hg^{2+} > Mg^{2+} > Mn^{2+}$. Abnormal sorption pattern displayed by some metal ions may be due to the extent of dissociation of their salts and probably to the stability of the complexes formed with tannin molecules of the onion skins.

Effect of pH

Figure 1 concerns the uptake of Zn^{2+} metal ion over a range of pH conditions under static test. From the graph, it may be seen that the highest pH at which Zn^{2+} ions will quantitatively be retained and optimum separation achieved is 6.0. At pH 2.5, the Zn^{2+} ion adsorption is low and decreased further with decrease in pH, as has been found for peanut waste.[2] The effect of pH is made more evident by the observation that the metal binding efficiency on the substrate increases with increase in pH, at least to a level where the ions might begin to precipitate.

Adsorption Isotherm

An illustration of the effect of initial metal ion concentration on the uptake of metal by the substrate from solution is given by an adsorption isotherm for Zn^{2+} ion (Fig. 2). It can be

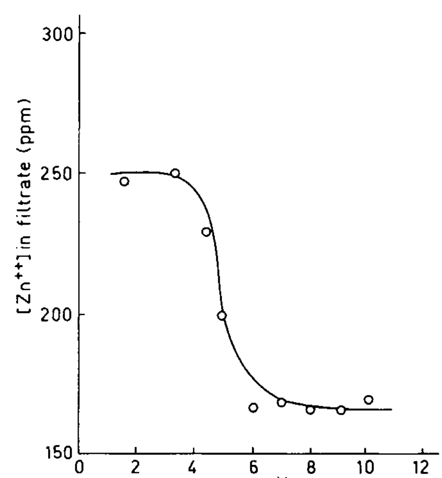

Fig. 1. Effect of pH on the adsorption of zinc ions from zinc acetate solution using corn cob hydroxylate–onion skin resin.

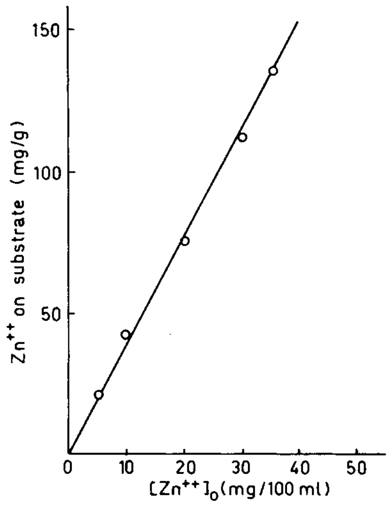

Fig. 2. Adsorption isotherm for adsorption of zinc ions from zinc acetate solution using corn cob hydroxylate–onion skin resin (mass of Zn^{2+} absorbed by unit mass of resin vs. initial concentration of Zn^{2+}). For detailed conditions see Table IV.

TABLE II
Removal of Heavy Metal Ions from Solutions on a Packed Column of Corn Cob Hydrozylate–Onion Skin Resin

Metal ion	Zn^{2+}	Cd^{2+}	Pb^{2+}	Hg^{2+}	Cu^{2+}
Concn of cation in feed (ppm)	213	293	438	443	140
Concn in effluent (ppm)	21	25.2	23.65	76.2	19.40
Rate of flow (mL/min.)	3.0	3.0	3.0	3.0	3.0
Initial pH	5.72	6.43	5.02	5.43	5.93
Final pH	3.40	3.72	3.09	3.54	3.72
Cation sorbed (ppm)	192.9	267.8	414.3	366	120
% sorbed	90.6	91.4	94.6	82.8	86.4

TABLE III
Maximum Exchange Capacity of Corn Cob Hydrozylate Onion Skin Resin for Heavy Metal Ions

Metal ion (M^{2+})	Zn^{2+}	Cu^{2+}	Ca^{2+}	Pb^{2+}
Concn of M^{2+} in feed (ppm)	344	396	260	731
Concn of M^{2+} in effluent (ppm)	1.33	2.86	5.27	2.30
Flow rate (mL/min)	2.5	2.5	2.5	2.5
Maximum concn M^{2+} on packing (mg m^{2+}/g substrate)	35.70	44.76	27.80	125.24
Maximum exchange capacity of M^{2+} on packing (meq/g)	1.09	1.41	1.39	1.21

TABLE IV
Effect of Initial Zinc Ion Concentration on the Amount of Zn^{2+} Ion Adsorbed by the Resin

Initial Zn^{2+} ion Concn.		Final Zn^{2+} ion Concn.		Amount of Zn^{2+} adsorbed		Amount of Zn^{2+} adsorbed per gram of Resin (mg/g)	% Zn^{2+} ion removal
mg/100 ml	$\times 10^{-5}$ (mol/L)	mg/100 ml	$\times 10^{-5}$ (mol/L)	mg/100 ml	$\times 10^{-5}$ (mol/L)		
5	3.82	1	0.76	4	3.05	20	80
10	7.6	2	1.53	8	6.12	40	80
20	15.3	5	3.82	15	11.4	75	75
30	23.0	8	6.12	22	16.8	110	73.3
35	26.7	12	9.17	23	17.5	135	65.6

[a] Amount of resin = 0.1 g; total volume = 50 ml; metal salt = Zn $(OAC)_2$.

seen that an increase in the concentration of Zn^{2+} ion gives a corresponding increases in the binding action of the substrate and absolute percentage of metal ion decreases, as seen in Table IV.

Dynamic (Column) Experiments

The sorption profile of the corncob–onion skin substrate in packed columns are given in Table II. For all metals tested the effluent pH is always less than the feed pH. The metal ion removal for Pb^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, and Hg^{2+} were 94.6%, 91.4%, 90.6%, 86.4%, and 82.8% as seen in Table II.

The maximum capacity of the corncob–onion skin sorbent for several divalent metal ions was obtained by eluting packed columns of the substrate with large quantities of the metal solutions as shown in Table III. Maximum capacities per gram of the corncob–onion skin substrate for Zn^{2+}, Cu^{2+}, Ca^{2+}, and Pb^{2+} were 1.09, 1.41, 1.39, and 1.21 meq, respectively.

References

1. J. M. Randall, R. F. W. Reuter, V. Garrett, and A. C. Waiss, *Prod. J.*, **24**, 80 (1974).
2. J. M. Randall, F. W. Reuter, and A. C. Waiss, *J. Appl. Polym. Sci.*, **19**, 1563–1571 (1975).
3. E. J. Roberts and S. P. Rowland, *Environ. Sci. Technol.*, **7**, 552–555 (1973).
4. P. Kumar and S. S. Dara, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 397–402 (1981).

THOMAS ODOZI
ROWLAND EMELIKE

Department of Applied Chemistry
Faculty of Chemical Sciences
University of Port Harcourt
Port Harcourt, Nigeria

Received January 17, 1984
Accepted September 27, 1984