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ADSORPTION OF HEAVY METALS ON MODIFIED SNAIL (*ARCHACHATINA MARGINATA*) SHELL

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Abstract

The adsorption of cadmium and lead ions on modified powdered snail shell was examined by equilibrium sorption studies at 29 °C. The amounts of metal ions removed from solution depended on the type of metal ion and its ionic size. The adsorption was enhanced by modification with EDTA (per cent N = 12.05). The distribution coefficient, K_d, of the metal ions between the adsorbent phase and the bulk aqueous phase was determined.The sorption process fitted the Langmuir isotherm equation. The maximum metal ion binding capacities, X_m of the EDTA-modified powdered snail shell were found to be 0.042 mmol g^{-1} and 0.125 m mol g^{-1} for cadmium and lead ions, respectively. The adsorption of lead ions on the keratinous sorbent was found to be higher than that of cadmium ions.

Résumé

IKHUORIA, E. U. & UYAMMADU, C.: *Adsorption des métaux lourdes sur le coquille modifié d'escargot* (Archachatina marginata). L'adsorption de cadmium et ions de plomb sur le poudre de coquille modifié d'escargot était étudiée par les études d'absorption équilibre à 29 °C. Les quantités d'ions métaux enlevés de solution dépendait de type d'ion métal et sa dimension ionique. L'adsorption était améliorée par la modification avec EDTA (% N = 12.05). Le coefficient de distribution, K_d, d'ions métaux entre la phase adsorbante et la phase aqueuse en grosse quantité était trouvé. Le processus d'absorption était apte à l'équation isotherme de Langmuir. Les capacités maxima attachant les ions métaux, X_m de EDTA - poudre de coquille modifié d'escargot étaient trouvées d'être 0.042 mmol g^{-1} et 0.125 mmol g^{-1} respectivement pour cadmium et ions de plomb. L'adsorption d'ions de plomb sur les sorbants kératineux était trouvé d'être plus élevé que l'ion de cadmium.

Introduction

The danger of accumulation of heavy metals in various aspects of the environment has, in recent times, gained prominence and, therefore, drew the attention of some workers (Roberts & Rowland, 1973; Reiniger, 1977; Denny, 1978; Ferguson & Babela, 1974; Okieimen *et al.*, 1985; Randall, Huatala & Medonald, 1978; Okieimen & Orhorhoro, 1986). These workers attributed the incidence of heavy metals to the indiscriminate disposal of industrial and mining waste waters. The need for an effective and an economical method of removing heavy metals from waste waters has resulted in a search for non-conventional methods and materials that may be useful in reducing the levels of accumulation of heavy metals in the environment. Many workers have shown that keratinous materials after suitable pretreatment are effective sequestering agents for metals. In this study, sorption behaviour of cadmium and lead ions on powdered snail shell, modified by the incorporation of ethylene diamine tetraacetic acid (EDTA), are reported.

Experimental

Shells of snails obtained from New Benin market, in Benin City, were ground into powder and sieved through 425 μm and 300 μm mesh screens. The portion of the powdered snail shell retained on the 300 μm screen was steeped in dilute 2% (v/v) nitric acid solution overnight, rinsed with deionised water and air-dried.

Modification of the powdered snail shell

A 20-g sample of the powdered snail shell 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 solid residue was washed thoroughly with deionised water and dried at 50 °C. A mixture of 17 g of the solid residue, 300 ml of pyridine and 56.7 g of ethylene-diamine tetra acetic acid (EDTA) was heated under reflux for 3 h. The reaction mixture was cooled, diluted with 30 ml of deionised water and filtered. The EDTA-modified sorbent was washed with deionised water until free of pyridine odour and then air-dried. The nitrogen contents of both the unmodified and EDTA-modified powdered snail shell were determined by the Kjeldahll method to be 6.44 and 12.05 per cent, respectively.

Equilibrium sorption of metal ions on the powdered snail shell

Determination of sorption of cadmium and lead ions on EDTA-modified snail shell was done at 29 °C using aqueous solution of the nitrates salts of the ions by varying the concentrations of the metal ions. In a typical experiment, 1g of the shell was dispersed in 100 ml of aqueous solution of metal ion with a known initial concentration. The mixture was continuously shaken in a well-stoppered flask for 1 h at room temperature (29 °C). The mixture was filtered and the residual concentration of the metal ion in the filtrate was determined by complexometric titration. The amount of the metal ion removed from solution by the sorbent was determined by the difference between the initial and final concentrations of the metal ions.

Dynamic sorption of Pb(II) ions on the unmodified shell

Sorption of Pb(II) ions on the unmodified husk in packed columns was examined using different volumes of the metal ion solution with a known initial concentation. Sections of 0.5 cm × 35 cm long glass pipes were used for packed columns. Glass beads were added on top of the column to prevent the sorbent particles from floating and separating. The packing was wetted with water and equilibrated for 4 h (Randall, Huatala & Medonald, 1978). The metal ion solution was allowed to flow through the column by gravity at a controlled rate of 1 ml min^{-1}. The fraction of the bound metal ion recoverable with dilute (2% v/v) nitric acid was determined. Air-dried samples (1-2 g) of the powdered snail shell with the sorbed metal ion was shaken with 50 ml of 0.01*M* HC1 for 40 min and then the mixture was filtered. The amount of the metal ion in the filtrate was determined by complexometric titration.

Results and discussion

Sorption capacity

The variation in the levels of metal ion uptake by the powdered snail shell with initial metal ion concentration is shown in Table 1. It can be seen from the equilibrium sorption studies on Cd(II) and Pb(II) ions that the metal ions removed from solution is greatly enhanced, by the modification with EDTA. The differences in the amount of metal ions removed from solution by the keratinous sorbent can be explained in terms of the difference in the ionic size of the metals, the metal ion type, the nature and distribution of the active groups on the keratinous sorbent and the mode of interaction of the metal ions with the sorbent (Freidman *et al.*, 1973).

The influence on the sorption of Pb(II) ion of *p*H(2) of the metal ion solution is shown in Table 1. It can be seen that the levels of Pb(II) ions uptake are significantly reduced as the *p*H of the metal ion solution is reduced from about 6.0 to 2.0. Lead nitrate in aqueous solution and in the absence of complexing agents gives divalent lead ions. In the presence of excess chloride ions, as a result of the 0.1*M* HC1, chloride compounds of lead with oxidation number greater than two may be formed. This is because lead can exhibit valences of 2 and 4. In the 2-valent state the 2s electon are inert, taking no part in chemical bonding (Liptrot, 1984). The decrease in the ionic radius associated with the formation of such chlo-

TABLE 1
Equilibrium sorption of metal ions on powdered snail shell at 29 °C
pH of the metal ion solution is approximately 6.0

Initial metal ion concentration (mg/100 ml)	*Amount of metal Cd(II) adsorbed (mmol/g)*	*Amount of Pb (II) ion adsorbed (mmol/g)*
10.0	0.24[a] (8.25)[b]	0.69[a] (0.90)[b] (0.82)[c]
20.0	0.68[a] (1.02)[b]	1.42[a](1.87)[b] (1.48)[c]
30.0	1.43[a] (1.86)[b]	2.12[a] (3.21)[b] (2.96)[c]
40.0	2.16 (2.24)[b]	2.76[a] (3.78)[b] (3.06)[c]
50.0	2.52[a] (3.12)[b]	3.80[a] (4.01)[b] (3.31)[c]

Level of metal ion uptake by EDTA-modified shell in parenthesis.
(a) Uptake levels by unmodified keratinous sorbent
(b) Uptake levels by EDTA-modified sorbent
(c) Uptake Pb(II) ions from 0.01*M* HCl solution at *p*H of 2

ride compounds would explain the reduction in the uptake of Pb(II) ions at low *p*H.

Besides, the mechanism of interaction of metal ions with the sorbent suggests that sorption occurs primarily by preferential solubilisation of the metal ions (Freidman *et al.,* 1973). It may, therefore, be expected that a reduction in *p*H of the solution may lead to changes in the nature of the active sites which acting independently or in conjunction with changes in the oxidation states of Pb(II) ions may reduce the solubilisation process by the sorbent. The *p*H dependence of the uptake of Pb(II) ions by the powdered snail shell as observed in Table I by comparing columns (a) and (c) suggested that quantitative recovery of adsorbed metal ions could be achieved in acid medium.

Table 1 shows the effect of EDTA modification on the uptake levels of Cd(II) and Pb(II) ions on powdered snail shell. It has been found that EDTA moieties get incorporated into the powder during the modification process. The enhanced levels of metal ion uptake associated with EDTA modification could, therefore, be explained in terms of the increased number and type of reactive groups on the keratinous substrate, which can interact with the metal ions. It has been established that EDTA modification is associated with large increase of up to 100 per cent in the nitrogen content of the modified material (Kumar & Dara, 1981).

Sorption coefficient

Separation data of sorption processes may be expressed in terms of the distribution or sorption coefficient, K_d, which may be defined as the concentration of the solute in the adsorbent phase divided by the concentration of the solute in the bulk - liquid phase. The value of K_d is of practical significance in the treatment of heavy metals present in waste waters. Primarily, K_d affords the determination of the number of cycles of equilibrium sorption processes required to reduce the levels of metal ions in aqueous effluents to acceptable levels.

Table 2 shows the sorption coefficient, K_d of the metal ions on the keratinous sorbent. The results show that the concentration of the metal ions at the sorbent-water interface is markedly higher than the concentration in the bulk aqueous phase. A relatively high K_d values was obtained from this study by dividing the concentra-

tion of the metal ion at the shell water interface by the concentration in the bulk aqueous phase. This shows that the treatment of aqueous effluents contaminated at moderate levels (500 ppm) with heavy metals, would require a fairly small number of equilibrium sorption cycles, to quantitatively reduce the metal ions to acceptable levels.

A low K_d indicates that the metal ion has little tendency to adsorb onto the sorbent, may be highly mobile or may easily be leached from the adsorbent. A low K_d, therefore, indicates that several equilibrium sorption cycles would be required for the removal of heavy metals in polluted effluents. On the other hand, a high K_d value indicates greater adsorption effectiveness which may result in a smaller number of equilibrium sorption cycles.

TABLE 2
Distribution coefficient (K_d) of metal ions at 29 °C

Metal ion	*Equilibrium concentration of metal ions (mmol dm^{-3})*	*Distribution coefficient (K_d)*
Cd(II)	0.072-0.146	2.10-3.64
	(0.064-0.128)	(2.52- 4.01)
Pb(II)	0.098-0.494	4.22-5.94
	(0.081-0.432)	(4.77-6.41)

Data on EDTA modified sorbent in parenthesis.

K_d = (mmol metal ion/kg sorbent)/(mmol metal ion/dm^3 solution).

Sorption isotherm

Sorption data usually follows Freundlich or Langmuir isotherms (Okieimen *et al.*, 1985, Okieimen, Okundia & Ogbeifun, 1991). The Freundlich and Langmuir isotherms can be mathematically represented, as shown in equations (1) and (2), respectively.

$$\frac{x}{m} = KC_e^{1/n} \quad \text{.....(1)}$$

$$\frac{C_e}{(x/m)} = \frac{1}{bX_m} + \frac{C_e}{X_m} \quad \text{.....(2)}$$

x = amount of adsorbate removed from solution

m= mass of adsorbent

K,n = Freundlich constants (coefficient and exponent of the isotherm respectively)

C_e = equilibrium (residual) concentration of adsorbate

b = constant related to the energy of adsorption

X_m = maximum adsorption capacity (mg/g adsorbent)

If sorption followed the Freundlich isotherm, then the plot of log (x/m) versus log C_e would be linear from which *k* and *n* values could be calculated from the intercept and slope, respectively. Alternatively, if sorption followed the Langmuir isotherm, then a linear relationship would be obtained between $C_e/(x/m)$ and C_e from which the constant b and X_m could be calculated.

Equation (2) predicts that X_m can be deduced from the slope of the linear plots of $\frac{C_e}{(x/m)}$ against C_e. When experimental data fit the Langmuir isotherm equation, a relative index of binding capacity is the apparent equilibrium constant, K, of the sorption process which may be obtained as the products of the values X_m and b. The data from this study fitted the Langmuir-isotherm equation. Fig. 1 shows the plot of the data from this study

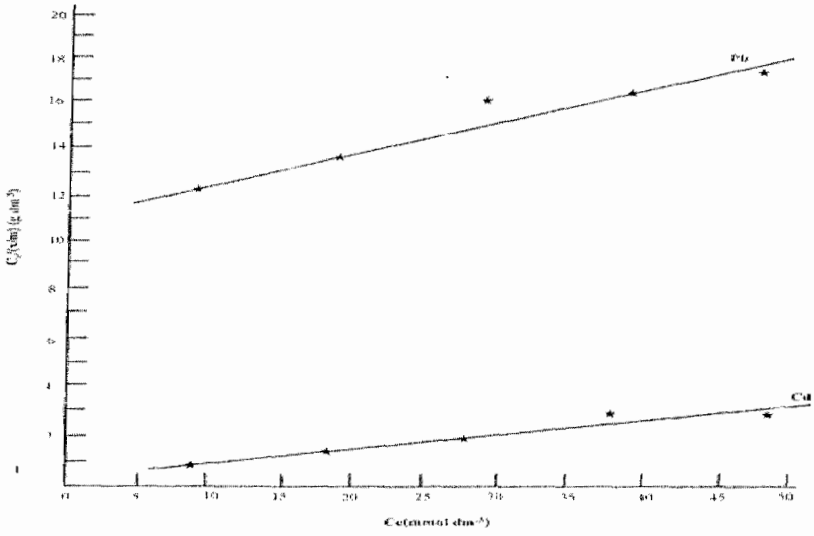

Fig. 1. Maximum binding capacity of EDTA-modified powdered snail shell

as $\frac{C_e}{(x/m)}$ versus C_e.

By least square fit, the values of the maximum metal ion binding capacities, X_m of 0,125 mmol g^{-1} and 0.042 mmol g^{-1} were obtained for Pb(II) and Cd(II) ions, respectively, with the EDTA modified snail shell.

Conclusion

The study generally showed that powdered snail shell, a by-product of no commercial value, may be useful in scavenging traces of heavy metals from waste waters. A packed column of this keratinous sorbent also has a high potential for success as a solvent preconcentration technique, especially when modified with EDTA.

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