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RADIOTRACER TECHNIQUE IN ADSORPTION STUDY OF ZINC AND CADMIUM ON PEAT

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ABSTRACT

Adsorption of zinc and cadmium ions on Brazilian peat was investigated. The study was carried out in batch experiments using ^{65}Zn and ^{115}Cd as radiotracers. Adsorption isotherms were determined at pH 4.5 at 20°C and Langmuir equation was fitted to the results with a correlation coefficient 0.99.

Key Words: Peat; Adsorption; Radiotracer; Zinc; Cadmium; Langmuir isotherm.

Abbreviations: CEC, cation exchange capacity; NMR, nuclear magnetic resonance.

INTRODUCTION

The existing methods to reduce levels of heavy metal pollutants from liquid effluents are usually expensive and have their efficiency limited for practical applications (1). Over the past two decades peat has been widely studied as a biological sorbent for the removal of these toxic substances from wastewaters (2,3). The potential of such inexpensive plentiful material

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has been verified to be a good alternative to solve many of the environmental problems related to heavy metal contamination (4).

Peat is a dark brown organic soil formed by the partial decay of the plant matter in poorly oxygenated wetlands, where the accumulation of the plant matter is greater than its decomposition. It is a highly polar and porous material and it has a high adsorption capacity for transition metals and polar organic molecules (5). The strong attraction of peat for most of the metallic ions in solution is mainly due to its high humic substances content. These substances, known as natural polymers, are rich in negatively charged functional groups such as carboxylic acids and phenolic hydroxides which play the main role during the adsorption of metallic ions in solution (3,6).

Adsorption of metal ions on peat has been extensively studied by several authors (7–16). Peat potential for such use has been successfully verified considering kinetic and thermodynamic parameters, pH best conditions and peat treatment advantages.

The estimated total amount of peat in Brazil is about 1.6 billions m^3 distributed on two hundred peatlands toward the country (17). However, only a few studies have been published on the use of such material to reduce levels of hazardous substances from wastewaters.

The aim of this work was to evaluate the adsorption of zinc and cadmium ions on Brazilian peat using radiotracer technique in an attempt to develop a wastewater treatment process in batch or in column. In previous studies (18), pH dependence of the adsorption process was investigated in column experiments. In this work, equilibrium parameters were determined in batch experiments for Langmuir isotherms. The study of metal ion behaviour in solutions submitted to peat contact was carried out using ^{65}Zn and ^{115}Cd radiotracers solutions. Zinc and cadmium ions were chosen because of the availability of their radioisotopic forms as tracers and of their environmental significance.

Theory

Adsorption can be defined as the accumulation of ions at the solid-liquid interface due to different types of forces (8). Adsorption isotherms developed from theoretical and/or empirical considerations are used to quantify such processes. This can be made by relating the solute concentration in liquid and solid phase at equilibrium conditions. Langmuir equation has been used by several authors to describe adsorption of metal ions on peat providing a good correlation of the experimental data (8–10,14,15). The equation may be expressed in the linearised form as:

$$C/X = 1/b + KC/b \qquad (1)$$

C = equilibrium concentration of metal ions in solution (mmol L^{-1})

X = equilibrium concentration of adsorbed metal ions on peat (mmol g^{-1})
b = Langmuir constant (L g^{-1})
K = relative equilibrium constant of the adsorption process (L mol^{-1})
where the constant K is related to the equilibrium between metal ion in solution and metal-peat group complexes formed on peat surface. The values of b and K can be determined from the linear plot of C/X versus C, where the ratio b/K provides the monolayer capacity X_0 for each adsorbed species in mmol g^{-1}.

A thermodynamical evaluation of the process may be performed by calculating the free energy of monolayer adsorption (ΔG^0_{ads}) using the following equation (19,20):

$$\Delta G^0_{ads} = -RT \ln K \quad (2)$$

where R and T have their usual significance and K must be expressed in units of L mol^{-1}.

EXPERIMENTAL

Peat Description and Treatment

Peat used in this study is commercially available in Santa Catarina State, South of Brazil. Before its use in the adsorption experiments peat was submitted to a preliminary acid treatment in order to leach the samples from metallic cations and to increase peat's CEC (7). Peat treatment was performed using the following procedure: i) air drying at room temperature; ii) hand sorting removal of roots and branches; iii) washing with deionized water, 25 g L^{-1} agitated in sealed bottles for 2 h; iv) separation of the settled portion and discard of the suspended material; v) 24 h drying at 70°C; vi) dry sieving to 0.074–1.000 mm particle size; vii) acidification with 1.0 mol L^{-1} HCl solution, agitated for 2 h, 10 mL HCl per g peat; viii) washing with deionized water in büchner funnel until filtrate reaches pH 5; ix) 24 h drying at 70°C. All reagents used were of analytical grade. Sample characterization was reported in earlier studies (18) in attempt to identify the peat according to suitable experimental procedures of soil analysis (see Table 1).

Tracers Solutions

Stock solutions containing ^{65}Zn ($T_{1/2}$ = 243.9 d) and ^{115}Cd ($T_{1/2}$ = 53.46 h) were prepared by irradiation of ZnO and $Cd(NO_3)_2$, separately, in the swimming pool research reactor IEA-R1m at a thermal neutron flux of about 1×10^{12} n cm^{-2} s^{-1} for 8 h. The irradiated target (ZnO) was dissolved in diluted HNO_3 solution. Aliquots from 25 to 50 μL of $^{65}Zn^{2+}$ and $^{115}Cd^{2+}$ were submitted to peat contact.

Table 1. Peat Characterization

Humification (von Post class)	H6–H8
pH (in $CaCl_2$ 0.01 mol l^{-1})	3.6
Organic carbon (dr wt %)	39
Organic matter (dr wt %)	67
Ash (dr wt %)	7
CEC *in natura* (meq g^{-1})	0.97
CEC treated (meq g^{-1})	1.84

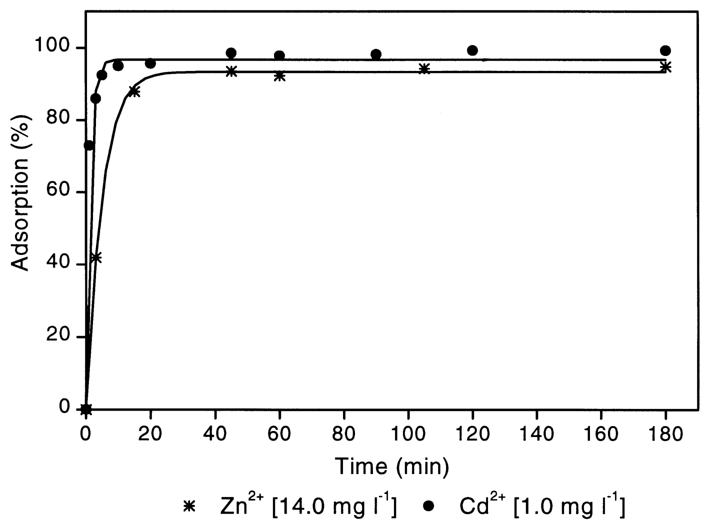

Figure 1. Percent adsorption of zinc and cadmium on peat.

Adsorption Experiments

Equilibrium isotherms were determined in batch experiments by shaking 0.5 g of treated peat with 25 ml of Zn^{2+} or Cd^{2+} solutions at different initial concentrations in Pyrex sealed bottles at 200 rpm. Solutions were buffered to pH 4.5 and temperature was maintained constant at $20 \pm 0.5°C$. After contact time supernatant solutions were filtered through Whatman 41 filter papers and analysed for their γ-activity with the help of a NaI(Tl) scintillation detector (Nuclear Chicago) coupled with a single channel analyser. The total amount of adsorbed ions was calculated by the difference between the counting of initial and final solution activities.

Equilibrium time was determined in kinetic experiments by using a similar procedure, in which the percentage of adsorbed ions was calculated by analysing aliquots of supernatant solutions withdrawn at different time intervals varying from 0 to 180 min. The results obtained are plotted in Figure 1, where it can be clearly observed that equilibrium was attained in approximately 30 min for both elements. Thus, to assure this condition in isotherms experiments, contact time was adopted in three hours.

RESULTS AND DISCUSSION

The use of tracers offers several advantages such as high sensitivity, speed and simplicity and easy automation that can be detected and monitored in the course of the analytical procedure. In this paper ^{65}Zn and ^{115}Cd were used as tracers. In Figure 2 adsorption isotherms of Zn^{2+} and Cd^{2+} on peat are shown; the experimental data were fitted to Langmuir isotherms according to equation (1). Equilibrium constants (*b* and *K*), correlation coefficient (*r*), peat's capacity (X_0) and adsorption energy ($-\Delta G^0_{ads}$) calculated from this graph are presented in Table 2.

The results obtained showed that peat adsorbed zinc and cadmium ions from solution at pH 4.5 successfully. The good correlation of the experimental data for Zn^{2+} and the acceptable correlation obtained for Cd^{2+} in

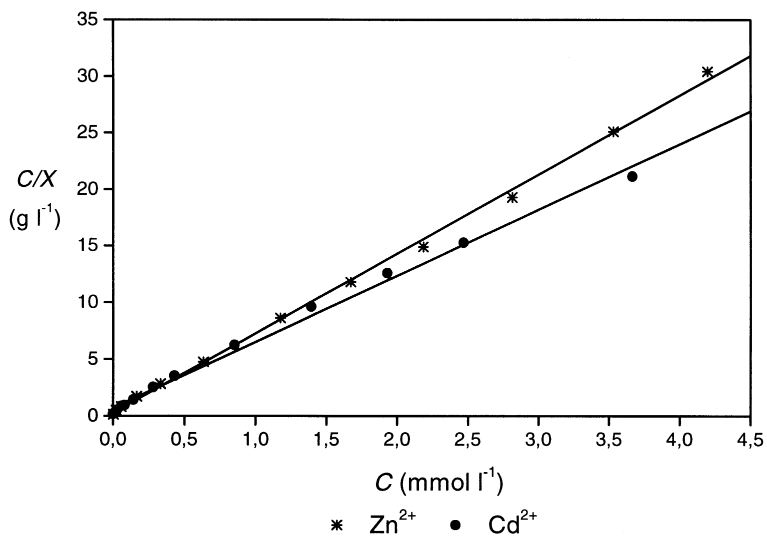

Figure 2. Langmuir isotherms for the adsorption of zinc and cadmium on peat.

Table 2. Parameters Obtained from Langmuir Isotherm

Metal ion	b ($L\,g^{-1}$)	K ($L\,mol^{-1}$)	R	X_0 ($mmol\ g^{-1}$)	$-\Delta G^0_{ads}$ ($kJ\,mol^{-1}$)
Zinc	3.49	24.40×10^3	0.999	0.143	24.6
Cadmium	1.45	8.47×10^3	0.997	0.171	22.0

the considered concentration range (Figure 2), demonstrated that the process was well represented by Langmuir's model which characterizes monolayer adsorption on homogeneous surface (21). The second assumption of the model should be explained for this case as the uptake of metals performed by the same type of binding sites or functional groups.

At suitable pH conditions, peat can adsorb most heavy metals up to 4% of its dry weight (5). Peat treatment must be pointed out as an important step to improve the adsorption capacity. The increase on metal removal efficiency with peat acid treatment was verified by some authors (10,11). In this work, as it can be seen in Table 1, acid treatment improved peat CEC of 92%. Preliminary tests of Petroni and Munita (unpublished) revealing higher metal adsorption in columns of treated peat support our observations in such experiments.

Total amount of adsorbed ions was estimated through X_0 values (Table 2) as approximately 2% (dr wt). A slightly greater peat capacity for cadmium than for zinc could be observed. This same order was obtained by other authors (14) using Langmuir isotherms with very similar results: 0.179 mmol $Zn^{2+}\,g^{-1}$ and 0.188 mmol $Cd^{2+}\,g^{-1}$, this trend was supported by some properties of metal ions, such as electronegativity and standard reduction potential. Other similar results of maximum peat capacities were obtained in batch metal removal studies (7): 0.170 to 0.200 mmol $Zn^{2+}\,g^{-1}$ and 0.180 to 0.200 mmol $Cd^{2+}\,g^{-1}$. In these studies best adsorption conditions were attained at pH 4.7 to 6.7 for both elements. The influence of pH on the adsorption process can be observed from other studies in literature (10,11), where the best removal efficiencies are verified within the range of pH 3.5 to 8.5; below pH 3.0 peat capacity decreases; above pH of about 6.5 most of the metal ion species precipitate and at pH 9.0 peat degrades due to the solubilization of humic substances (3). The influence of pH was previously investigated in column experiments (18), where 99% of removal was obtained for both elements in the range of pH between 3.7 and 6.5. Below these values retention was strongly affected and was almost nil for pH 2.0, where metals are displaced by H^+ with pH decreasing (22). At pH 9.0 peat degradation was revealed by the dark-yellow colour of the effluent solutions. For wastewater treatment purposes, recovery studies of adsorbed metals with acid solutions ($pH < 2$) for regeneration of saturated peat may be suggested considering cost advantages and environmental benefits.

Peat has a complex structure in which humic substances participate together with other organic constituents such as cellulose and lignin to the adsorption of heavy metals in solution (23). The contribution of these substances is also attributed to polar functional groups with characteristics similar to those of humic substances. In Figure 3 is shown an example of how Cu^{2+} could interact with humic substance functional groups in aqueous solution (6). According to this reference, binding of metal would occur mainly at those sites that form strong complexes like chelate structures (I) or coordi-

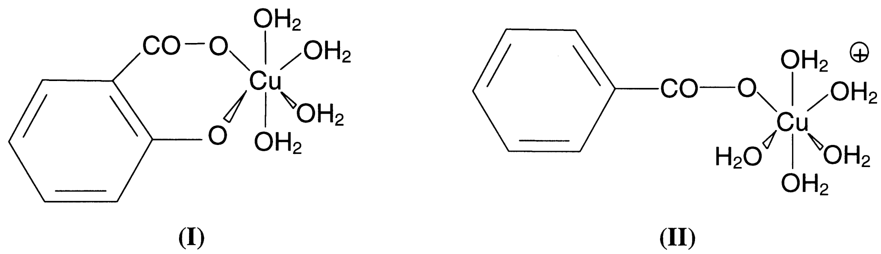

Figure 3. Cu^{2+} interactions with humic substances functional groups (6).

nated linkages (II). The chemical character of the process may be predicted by the thermodynamic evaluation of the adsorption isotherms (Figure 2). In chemisorption, due to the chelates and linkages formed, adsorption energies are in the range of 40 to 400 kJ mol^{-1}. In physical adsorption these values decrease down to 300 to 3,000 J mol^{-1} (24). Considering the order of magnitude of $-\Delta G^0_{ads}$ values in Table 2, chemical adsorption may be assumed as the predominant binding mechanism, the negative sign characterizing the spontaneous nature of the process.

Adsorption was found to be very similar for both elements when considering parameters like peat capacity or adsorption energy. Nevertheless, the relative equilibrium constant K calculated in Table 2 was about three times greater for zinc than for cadmium. This indicates that, although peat exhibits a slightly greater capacity to adsorb cadmium, somewhat stronger complexes are formed with zinc ions. In fact, more conclusive information would be provided by detailed NMR-spectroscopic investigations of the interactions between the studied metals and the functional groups of peat.

CONCLUSION

This study presented a preliminary evaluation of Brazilian peat as an adsorbent of zinc and cadmium ions from aqueous solution. Adsorption was evaluated in terms of Langmuir isotherms. The observed uptake of ions in solution was very similar for both elements up to equilibrium concentration 4,5 mmol l^{-1}. Equilibrium time was attained in 30 min and peat adsorbed each metal in approximately 2% of its dry weight. Zinc adsorption was better represented by Langmuir's model compared to cadmium. The relative equilibrium constant gave the indication that stronger complexes are formed with zinc ions and $-\Delta G^0_{ads}$ values showed that the process is spontaneous and mainly governed by chemisorption. The use of radiotracer technique allowed the efficient evaluation of zinc and cadmium adsorption by the peat. The results obtained indicate a good potential of Brazilian peat as an adsorbent of zinc and cadmium in solution encouraging further studies on the utilization of this material in wastewater treatment.

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