Use of radiotracer in adsorption studies of copper on peat

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In this work copper adsorption by peat was studied using ^{64}Cu as tracer considering kinetic and thermodynamic aspects of the process. The study was carried out in agitated batch experiments with copper ion solutions with different initial concentrations at pH 4.5. Adsorption isotherms determined from equilibrium experiments by fitting experimental data to the Langmuir equation showed good correlations. Data obtained from kinetics experiments were fitted to a pseudo-second order model and also in this case a good correlation was obtained. Some parameters calculated from these studies such as rate constant or peat sorption capacity can be used in the development of a waste treatment process based on peat adsorption in batch or in column. The use of the ^{64}Cu radiotracer is presented as a simple, rapid and efficient technique to assess the copper adsorption by the peat.

Introduction

Peat is a dark brown organic sediment widely studied as adsorbent of heavy metals and others hazardous pollutants from wastewaters. The great capacity of peat to adsorb metals in solution is due to its high content of humic substances, where the uptake of metals from the solution is mainly performed by functional groups such as carboxylic and phenolic groups of humic acids.[1] Besides being a highly polar and porous material, peat has some additional characteristics such as low cost and availability making it a good alternative for utilization in wastewater treatment.

In attempts to develop systems for the removal of heavy metals in wastewater the thermodynamics and kinetics of metal ion adsorption to peat has been investigated by several researchers.[2–9] Isotherms based on the Langmuir equation have been used to represent the chemical adsorption of metals on the peat surface.[3,7,8,10] With respect to the kinetics of the process, a pseudo-second order model has been successfully used to describe chemisorption of divalent metals on peat.[9,11]

The estimated total amount of peat in Brazil is about 1.6 billions m^3 distributed on two hundred peatlands toward the country.[12] However, only a few studies have been published on the use of such material to reduce levels of hazardous substances from wastewaters.[13] The aim of this work was to study the adsorption of copper in solution on a Brazilian peat using a radiotracer technique in order to assess the potential use of such peat as a natural low cost adsorbent of metals from wastewaters. Sorption experiments were carried out in the batch mode using ^{64}Cu as tracer to evaluate the behavior of copper ions in solutions submitted to peat contact. Equilibrium experimental data were correlated to Langmuir isotherms. Kinetics of adsorption was studied at different initial concentrations of copper and results were fitted to a pseudo-second order model.[9]

Experimental

Peat description and treatment

The peat used in this study is commercially available in Santa Catarina State, Brazil. Before use in the sorption experiments the peat was submitted to an acid treatment with HCl 1.0 mol·l^{-1} as described in a previous study.[14] The peat was dried at room temperature and sieved to 0.250–2.000 mm particle size. All reagents were of analytical grade.

Radioactive copper solution

^{64}Cu ($T_{1/2} = 12.8$ h) was produced by neutron irradiation of Cu(NO$_3$)$_2$·3H$_2$O in the swimming pool research reactor IEA-R1m for 6 hours at a thermal neutron flux of about $1 \cdot 10^{12}$ n·cm^{-2}·s^{-1}. The irradiated target was dissolved in H$_2$O and diluted to give a concentration of 1 mg·ml^{-1}. Aliquots from 250 μl to 500 μl with the approximate ^{64}Cu activity of $5.5 \cdot 10^4$ cpm were used in copper solutions submitted to peat contact.

Batch experiments

Adsorption experiments were carried out in sealed polyethylene bottles shaken with 160 mg of treated peat in 40 ml of copper nitrate solutions at an initial pH of 4.5 and room temperature (20±0.5 °C). After the appropriate contact time the supernatant solutions were filtered through Whatman No. 41 filter papers and

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subjected to measurement using a Ge (hyperpure) detector from Canberra, with a resolution of 1.0 keV at the 1332.49 keV gamma-peak of ^{60}Co. Spectra were collected with a Canberra S-100 MCA with 8192 channels. Gamma-ray spectrum analyses were carried out using the Genie-2000 NAA Processing Procedure from Canberra.

Equilibrium experiments were carried out for 24 hours with copper solutions at concentrations from 8 to 158 mg·l^{-1}.

Experimental data on kinetics were obtained by calculating copper concentration in solutions submitted to peat contact at different time intervals from 2.5 to 180 minutes. The influence of copper concentration upon kinetics was studied in experiments carried out at different initial metal concentrations (13.2, 36.9, 62.4 and 128.0 mg·l^{-1}).

Results and discussion

Adsorption isotherms obtained from equilibrium experimental data are useful to provide information on the adsorption capacity of the adsorbent. The Langmuir equation has been used by several authors to describe adsorption of metal ions on peat providing a good correlation with the experimental data.[3,7,8,10] The equation may be expressed in the form:

$$q_e = \frac{bC_e}{1 + KC_e} \qquad (1)$$

where C_e is the equilibrium concentration of metal ions in solution in mg·l^{-1}, q_e is the equilibrium concentration of adsorbed metal in mg per gram of peat, b is the Langmuir constant, and K is the relative equilibrium constant of the adsorption process related to the equilibrium between metal in solution and metal-functional group complexes formed on the peat surface. The values of b and K can be determined using the linearized form of Eq. (1), as follows:

$$\frac{C_e}{q_e} = \frac{1}{b} + \frac{K}{b}C_e \qquad (2)$$

where the ratio b/K provides the theoretical adsorption capacity x_m of the peat[7] in mg·g^{-1}. The spontaneity of the process and its physical or chemical character may be quantified by the free energy of adsorption (ΔG_{ads}), calculated using the following equation:[15]

$$\Delta G_{ads} = -RT \ln K \qquad (3)$$

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

The adsorption isotherm of copper on peat is shown in Fig. 1. The experimental data are plotted on a theoretical isotherm calculated from linear regression according to Eq. (2). Equilibrium parameters and correlation coefficient r^2 obtained from the linear regression are presented in Table 1.

As can be seen in Fig. 1, the peat adsorbed copper ions in solution successfully within the studied concentration range. Adsorption of metal in solution can be classified as favorable considering the shape of the curve in this figure.[16] The correlation coefficient $r^2 = 0.9985$, calculated in Table 1 shows that the process was well represented by a Langmuir isotherm characterizing monolayer adsorption on the peat surface.[17]

The adsorption capacity x_m is useful in the first steps of a process design in batch or in column. Variations in this parameter are normally attributed to the nature of the adsorbate as well as to the number of sites available on the adsorbent's surface. Another important factor affecting the adsorption capacity is pH. Below pH 3.0 the capacity decreases rapidly, whereas within the range of 3.6 to 8.5, peat can adsorb efficiently most heavy metals up to 4% of its dry weight.[18] The value of x_m (11.7 mg·g^{-1}) was similar to the one obtained by HO and MCKCAY[10] (12.1 mg·g^{-1}) from a Langmuir isotherm and by GOSSET et al.[2] (12.1 mg·g^{-1}) from pH dependence studies with French eutrophic and oligotrophic peat.
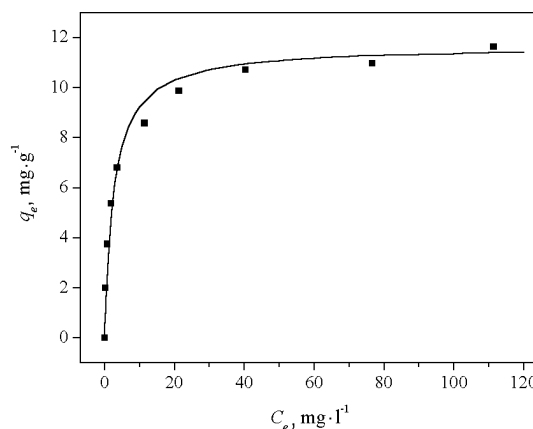

Fig. 1. Adsorption isotherm of copper on peat

Table 1. Equilibrium parameters obtained for adsorption isotherm of copper on peat

r^2	b, l·g^{-1}	K, l·mg^{-1}	x_m, mg·g^{-1}	ΔG_{ads}, kJ·mol^{-1}
0.9985	4.40	0.377	11.7	−24.6

Adsorption of heavy metals in solution by the peat is attributed not only to humic substance functional groups, but also to other organic constituents with similar functional groups, such as cellulose and lignin.[19] An example on formation of a strong complex between Cu^{2+} in solution and functional groups on the humic matter is shown in Fig. 2.[20] Considering the chelates and linkages formed, the heat of adsorption ranges from over 400 kJ·mol^{-1} to less than 80 kJ·mol^{-1}.[21] Once the adsorption is invariably exothermic and accompanied by a decrease in entropy, the negative value of $-\Delta G_{ads}$ calculated in Table 1 indicates the spontaneous nature and the chemical character of the process.

Adsorption kinetics of a solute on a solid surface is typically described by derivation of the Lagergren pseudo-first order rate equation.[8] However, HO and MCKAY[11] demonstrated that for a large number of adsorbents, including peat, the use of a pseudo-second order model provides the best correlation to the experimental data. The rate law[9] may be represented as a function of the metal ions concentration in solution at any time t as follows:

$$\frac{C_t}{C_0} = 1 - \frac{kt(C_0 - C_e)^2}{C_0(m_s + kt(C_0 - C_e))} \quad (4)$$

where C_0 and C_t are both metal concentrations in solution at $t = 0$ and $t = t$, k is the rate constant and m_s is called peat dose,[9] adopted in this work as 4.0 g·l^{-1} (see experimental section). Equation (4) describes the decay of metal in solution in a batch system for a given value of the initial concentration C_0, and it may be written in the linearized form:

$$\frac{t}{C_0 - C_t} = \frac{m_s}{k(C_0 - C_e)^2} + \frac{1}{C_0 - C_e}t \quad (5)$$

where C_e and k can be calculated from the linear plot of $t/(C_0 - C_t)$ vs. t.

In Fig. 3 the kinetics of copper adsorption is shown through the plot of C_t/C_0 vs. t. The solid lines in this figure were obtained using Eq. (4) with the help of k and C_e calculated from the linear regression of experimental data according to Eq. (5) (Fig. 4). Table 2 shows the correlation coefficient, r^2, calculated for the linear regression and the k and C_e values obtained from the experiments performed at different initial concentrations C_0.

Copper removal from solution within the studied time interval is shown in Fig. 3. The influence of the initial concentration on kinetics can be clearly observed in this figure. The removal of copper was calculated as 99.9%, 84.2%, 58.9% and 38.6%, respectively, for initial concentrations of 13.2 mg·l^{-1}, 36.9 mg·l^{-1}, 62.4 mg·l^{-1} and 128.0 mg·l^{-1}. The time required to reach the adsorption equilibrium increased with the increase in C_0 (Fig. 3).

Table 2. Kinetic data obtained at different initial solution concentration

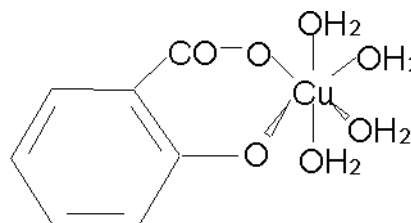| C_0, mg·l^{-1}	k, g·mg^{-1}·min^{-1}	C_e, mg·g^{-1}	r^2
13.2	0.090	0.0014	0.9998
36.9	0.016	5.832	0.9989
62.4	0.011	25.64	0.9968
128.0	0.006	78.64	0.9961

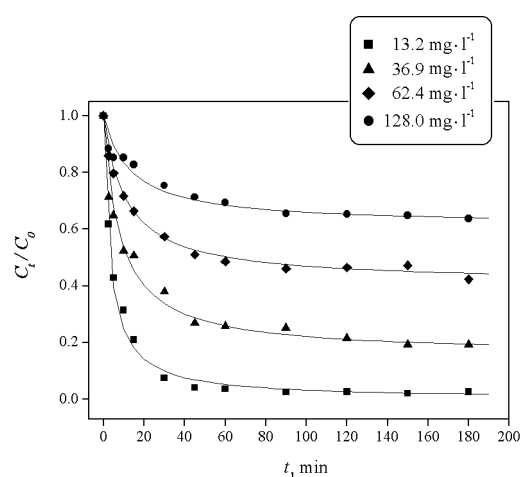Fig. 2. Interaction between humic substance functional group and copper in solution[21]

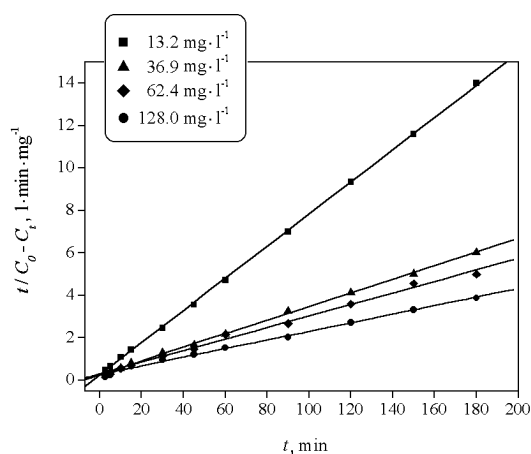Fig. 3. Kinetics of copper removal by the peat

Fig. 4. Kinetics of copper removal in solution linearized according to the pseudo-second order rate equation

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The rate constants k calculated in Table 2 were found to decrease between 0.090 and 0.006 g·mg^{-1}·min^{-1} with an increase in the initial copper concentration from 13.2 to 128.0 mg·l^{-1}.

The transport mechanisms of a solute from the liquid to the solid surface are: (a) diffusion of the solute through the bulk solution to the outer surface of the adsorbent, (b) intraparticular diffusion in the internal pores of the adsorbent surface, and (c) binding of the adsorbate on the activated sites on the interior of the pores through chemical reactions.[21] Considering diffusion of metal through the bulk solution to be negligible, adsorption of divalent metals on peat occur in two stages.[11] In the initial stage, intraparticular diffusion appears to be the rate-limitting step where, for the first 20 minutes, initial experimental data are well correlated to the Lagergren pseudo-first order equation. In the second stage, for longer periods of time, chemical reactions become significant in the rate-limiting step and the overall process is best described by the pseudo-second order equation.[11] In Table 2, correlation coefficients r^2 higher than 0.996 indicate that the kinetics of copper removal by the peat was well represented by the pseudo-second order model. The decrease in r^2 values from 0.9998 to 0.9961 with the increase in C_0 was observed (Table 2). The same trend was observed in another kinetic study of copper adsorption by peat,[9] where the increase in C_0 from 25 to 200 mg·l^{-1}, resulted in a decrease of r^2 from 1.00 to 0.996. Considering the heterogeneous nature of the peat surface, this slight deviation from the model can be explained by a relative decrease in the number of adsorption sites with the increase of adsorbate concentration in the liquid phase.

The concentration dependence of the rate of adsorption is also used to define the rate-limiting step in the process. In simple diffusion-controlled processes, the rates of adsorption are expected to be proportional to the first power of the concentration of adsorbate.[21] When intraparticular diffusion limits the kinetics, this rate is proportional to the square root of the initial concentration.[5] In order to verify if intraparticular diffusion is the limiting step during the initial minutes of the adsorption, the relation between the rates of adsorption and $C_0^{1/2}$ was tested in this work. The rates of adsorption were calculated from the linear regression of the plot of q_t vs. $t^{1/2}$ for the initial 15 minutes of the adsorption.[5] Table 3 shows the values of these rates obtained for different initial copper concentrations. The evidence that the process is not only controlled by the intraparticular diffusion is illustrated by the non-linear relationship between the rate of adsorption and $C_0^{1/2}$ in Fig. 5.

Conclusions

Copper adsorption by a Brazilian peat was evaluated in terms of equilibrium and kinetics parameters using ^{64}Cu as a tracer. An equilibrium isotherm fitted to the Langmuir equation provided good correlation with the experimental data. The adsorption capacity of the peat was determined from Langmuir isotherm to be 11.7 mg Cu per g of peat. The process was spontaneous and mainly governed by chemisorption. Kinetics data were obtained at different initial concentrations and correlated to a pseudo-second order model with correlation coefficients greater than 0.996. The rate-controlling step of the adsorptive process was found to be chemisorption. Evidence based on the non-proportionality of the rate of adsorption with initial copper concentrations demonstrated that for the first minutes of adsorption the process was not only limited by intra-particular diffusion. The kinetic model proposed by HO and MCKAY[11] can be highly effective and applicable for peats from different origins in the design and/or in the operation of a treatment process for the removal of metals from liquid effluents. The use of radiotracer was presented as a simple and efficient technique for the study of copper adsorption by the Brazilian peat.

Table 3. Rates of adsorption calculated for the initial 15 minutes of adsorption

C_0, mg·l^{-1}	Rate of adsorption, mg·g^{-1}·min$^{-1/2}$
13.2	0.6846
36.9	1.2191
62.4	1.3674
128.0	1.3753
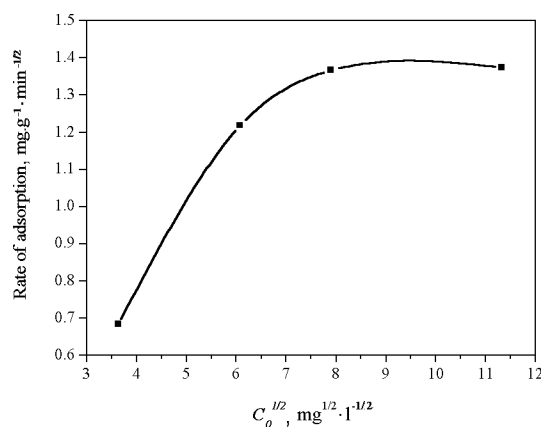
Fig. 5. Non-linear relationship between the rate of adsorption and $C_0^{1/2}$

References

1. D. COUILLARD, Water Res., 28(6) (1994) 1261.
2. T. GOSSET, J. L. TRANCART, D. R. THÉVENOT, Water Res., 20 (1986) 21.
3. M. BENCHEIKH-LEHOCINE, Environ. Technol. Lett., 10 (1989) 101.
4. X. CHEN, T. GOSSET, D. R. THÉVENOT, Water Res., 24 (1990) 1463.
5. Y. S. HO, D. A. J. WASE, C. F. FORSTER, Environ. Technol., 17 (1996) 71.
6. Y. S. HO, G. MCKAY, Water SA, 22(3) (1996) 219.
7. G. MCKAY, J. F. PORTER, J. Chem. Technol. Biotechnol., 69 (1997) 309.
8. Y. S. HO, G. MCKAY, Water Res., 33 (2) (1999) 578.
9. Y. S. HO, G. MCKAY, Water Res., 34 (3) (2000) 735.
10. Y. S. HO, G. MCKAY, Chem. Eng. Sci., 55 (2000) 817.
11. Y. S. HO, G. MCKAY, Proc. Biochem., 34 (1999) 451.
12. MINISTÉRIO DAS MINAS E ENERGIA, Plano 2015. Oferta de energia elétrica, tecnologias, custos e disponibilidades, Projeto 4B, Eletrobrás Centrais Elétricas Brasileiras, Rio de Janeiro, 1993, p. 65.
13. J. S. D'AVILA, C. M. MATOS, M. R. CAVALCANTI, Water Sci. Technol., 26 (9) (1992) 2309.
14. S. L. G. PETRONI, M. A. F. PIRES, C. S. MUNITA, J. Trace Microprobe Tech., 19 (2001) 429.
15. R. O. JAMES, T. W. HEALY, J. Colloid Interface Sci., 40 (1) (1972) 65.
16. J. R. MIHELCIC, Fundamentals of Environmental Engineering, John Wiley & Sons, Inc., New York, 1998, p. 102.
17. W. J. WEBER Jr., Physicochemical Processes for Water Quality Control, Wiley Interscience, New York, 1972, p. 640.
18. B. COUPAL, J. M. LALANCETTE, Water Res., 10 (1976) 1071.
19. S. E. BAILEY, T. J. OLIN, R. M. BRICKA, D. D. ADRIAN, Water Res., 33 (1999) 2469.
20. F. J. STEVENSON, Humus Chemistry: Genesis, Composition, Reactions, John Wiley & Sons, New York, 1994, p. 378.
21. S. D. FAUST, M. A. OSMAN, Adsorption Processes for Water Treatment, Butterworth Publishers, Massachussets, 1987 p. 1; 65.