

Use of radiotracer in adsorption studies of copper on peat

S.L.G. Petroni, M.A.F. Pires, C.S. Munita* C.J.A. SEPULVEDA MUNITA

Instituto de Pesquisas Energéticas e Nucleares-CNEN/SP

C.P. 11049 - 05422-970 - São Paulo - SP - Brasil

*E-mail: camunita@curiango.ipen.br

PRODUÇÃO TÉCNICO CIENTÍFICA
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In this work copper adsorption by peat was studied using ^{64}Cu as tracer considering kinetics and thermodynamics aspects of the process. The study was carried out in agitated batch experiments with copper ions solutions at different initial concentrations at pH 4.5. Adsorption isotherm determined from equilibrium experiments was fitted to Langmuir's equation with a good correlation of the experimental data. Results obtained from kinetics experiments were fitted to a pseudo-second order model and also a good correlation of the data was obtained. Some parameters calculated from these studies, such as rate constant or peat capacity, can be used in the development of a treatment process based on peat adsorption in batch or in column. The use of radiotracer ^{64}Cu was 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 humic content, where the uptake of metals in solution is mainly performed by functional

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groups of humic substances, such as carboxylic and phenolic groups of humic acids.¹ Besides being a highly polar and porous material, some of peat's characteristics such as low cost and availability make it a good alternative for utilization in wastewater treatment.

In attempt to develop systems for the removal of heavy metals in wastewater by the peat, sorption of metal ions in solution has been investigated by several researches with great advances related to the comprehension of thermodynamics and kinetics of the process.²⁻⁹ Sorption isotherms well correlated to Langmuir equation have been used to represent the chemical adsorption of metals on 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 m³ 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 is to study the adsorption of copper in solution on a Brazilian peat using 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 batch using ⁶⁴Cu as tracer to evaluate the behavior of copper ions in solutions submitted to peat contact. Equilibrium experimental data were correlated to Langmuir isotherm. Kinetics of adsorption was studied at

different copper initial concentrations and results were fitted to a pseudo-second order model.⁹

Experimental

Peat description and treatment

Peat used in this study is commercially available in Santa Catarina State, Brazil. Before its use in the sorption experiments peat was submitted to an acid treatment with HCl 1.0 mol·l⁻¹ as described in earlier studies.¹⁴ Peat was dried at room temperature and sieved to 0.250–2.000 mm particle size. All reagents were of analytical grade.

Radio-copper solution

⁶⁴Cu ($T_{1/2} = 12.8$ h) was produced by the neutron irradiation of Cu(NO₃)₂·3H₂O in the swimming pool research reactor IEA-R1m for 6 h at a thermal neutron flux of about 1×10^{12} n·cm⁻²·s⁻¹. The irradiated target was dissolved in H₂O and diluted to

give a concentration of $1\text{mg}\cdot\text{mL}^{-1}$. Aliquots from 250 μL to 500 μL were used with copper solutions submitted to peat contact.

Batch experiments

Adsorption experiments were carried out in polyethylene sealed bottles shaken with 160mg of treated peat in 40 mL of copper nitrate solutions at initial pH 4.5 and room temperature (20 ± 0.5 °C). After contact time supernatant solutions were filtered through Whatman 41 filter papers and measurement using a Ge (hyperpure) detector from Canberra, 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 h with copper solutions at initial concentrations from $8\text{mg}\cdot\text{l}^{-1}$ to $158\text{mg}\cdot\text{l}^{-1}$.

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

Results and discussions

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 ^{64}Cu was used as tracer. Adsorption isotherms obtained from equilibrium experimental data are useful to provide information on the adsorption capacity of the adsorbent. Langmuir equation has been used by several authors to describe adsorption of metal ions on peat providing a good correlation of the experimental data.^{3,7,8,10} The equation may be expressed in the form:

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

where C_e is the equilibrium concentration of metal ions in solution in $\text{mg}\cdot\text{l}^{-1}$, 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-peat group complexes formed on peat surface. The values of b and K can be determined using the linearised form of equation (1), as follows:

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

where the ratio b / K provides the theoretical adsorption capacity x_m of the peat⁷ in $\text{mg}\cdot\text{g}^{-1}$. 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

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

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

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

As it can be seen in Fig. 1 peat adsorbed successfully copper ions in solution within the studied concentration range. Adsorption of metal in solution can be classified as favourable 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 represent by Langmuir isotherm characterizing monolayer adsorption on peat surface¹⁷.

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 to the number sites available in the adsorbent's surface. Another important aspect affecting peat's capacity is the pH. Below pH 3.0 peat's capacity decreases rapidly, however,

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 obtained by HO and MCKAY¹⁰ (12.1 mg.g⁻¹) from Langmuir isotherm and by GOSSET et al.² (12.1 mg.g⁻¹) from pH dependence studies with French eutrophic and oligotrophic peat.

Adsorption of heavy metals in solution by the peat is attributed not only to humic substances functional groups, but to other organic constituents with similar functional groups, such as cellulose and lignin.¹⁹ An example of how a strong complex is formed between Cu²⁺ in solution and humic substance functional group 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 one solute on solid surface is typically described by the derivation of Lagergren pseudo-first order rate equation.⁸ However, HO and MCKAY¹¹ demonstrated that for a large number of adsorbents, including the peat, the use of a pseudo-second order model provides the best correlation of the experimental data. The rate law is represented as function of the amount of adsorbed metal ions per g of peat q_t , at any time t as follows:⁹

$$q_t = \frac{t}{1/kq_e^2 + t/q_e} \quad (4)$$

which has the linearised form:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \quad (5)$$

where k is rate constant and q_t and q_e may be written as:

$$q_t = \frac{C_0 - C_t}{m_s} \quad (6)$$

$$q_e = \frac{C_0 - C_e}{m_s} \quad (7)$$

C_0 and C_t are both metal concentrations in solution at $t=0$ and $t=t$ and m_s is called peat dose⁹, adopted in this work in $4.0 \text{ g} \cdot \text{l}^{-1}$ (see experimental section).

Substituting (6) and (7) in (5) gives:

$$\frac{t}{C_0 - C_t} = \frac{m_s}{k(C_0 - C_e)^2} + \frac{1}{C_0 - C_e}t \quad (8)$$

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

Equation (8) may be rearranged and written as a function of C_t / C_0 , as follows:

$$\frac{C_t}{C_0} = 1 - \frac{kt(C_0 - C_e)^2}{C_0(m_s + kt(C_0 - C_e))} \quad (9)$$

Equation (9) describes the decay of metal in solution in a batch system for a given value of initial concentration C_0 .

In Fig. 3 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 equation (9) with

the help of k and C_e calculated from the linear regression of experimental data according to equation (8) (Fig. 4). Table 2 shows the coefficients correlation 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 was verified within the studied time interval in Fig. 3. The influence of initial concentration upon kinetics can be clearly observed in this Figure. Percent removal was calculated in 99.9 %, 84.2 %, 58.9 % and 38.6 % respectively for 13.2 mg.l⁻¹, 36.9 mg.l⁻¹, 62.4 mg.l⁻¹ and 128.0 mg.l⁻¹ initial concentrations. The time required to reach the equilibrium of adsorption increased with the increase in C_0 (Fig. 3). The rate constants k calculated in Table 2 were found to decrease between 0.090 g.mg⁻¹.min⁻¹ to 0.006 g.mg⁻¹.min⁻¹ with the increase in the copper initial concentration from 13.2 mg.l⁻¹ to 128.0 mg.l⁻¹.

The transport mechanisms of one solute from liquid along the solid surface are: a) diffusion of the solute through the bulk solution to the outer surface of the adsorbent, b) intraparticle 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 negligible, adsorption of divalent metals on peat occur in two stages.¹¹ In the initial stage, intraparticle diffusion appears to be the rate-limiting step where, for the first 20 minutes,

initial experimental data are well correlated to 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 equation¹¹. In Table 2, correlation coefficients r^2 higher than 0.996 indicate that 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 other kinetic study of copper adsorption by peat⁹, where the increase in C_0 from 25 mg·l⁻¹ to 200 mg·l⁻¹, resulted in the decrease of r^2 from 1.00 to 0.996. Considering the heterogeneous nature of peat surface, this slight deviation of the model can be explained by the relative decrease in the number of adsorption sites with the increase of adsorbate concentration in liquid phase.

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 adsorbate's concentration.²¹ When intraparticle diffusion limits the kinetics, this rate is proportional to the square root of the initial concentration.⁵ In order to verify if intraparticle diffusion is the limiting step in 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 the different initial copper concentrations. The evidence that the process is not only controlled by the intraparticle diffusion is illustrated by the nonlinear 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 tracer. Equilibrium isotherm was fitted to Langmuir equation providing good correlation of the experimental data. Peat's capacity was determined from Langmuir isotherm in 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. Evidences 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 intraparticle diffusion. The kinetic model proposed by HO and MCKAY¹¹ can be highly effective and applicable for peats of 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 on the study of copper adsorption by the Brazilian peat.

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The authors wish to thank CAPES, FAPESP and University of São Paulo for financial support.

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

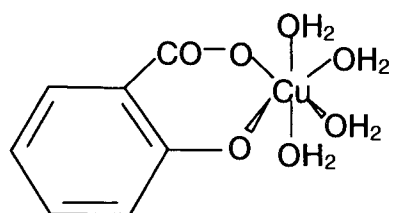
r^2	b (l·g ⁻¹)	K (l·mg ⁻¹)	x_m (mg·g ⁻¹)	ΔG_{ads} (kJ·mol ⁻¹)
0.9985	4.40	0.377	11.7	- 24.6

Table 2. Kinetic data obtained at different initial solution concentration.

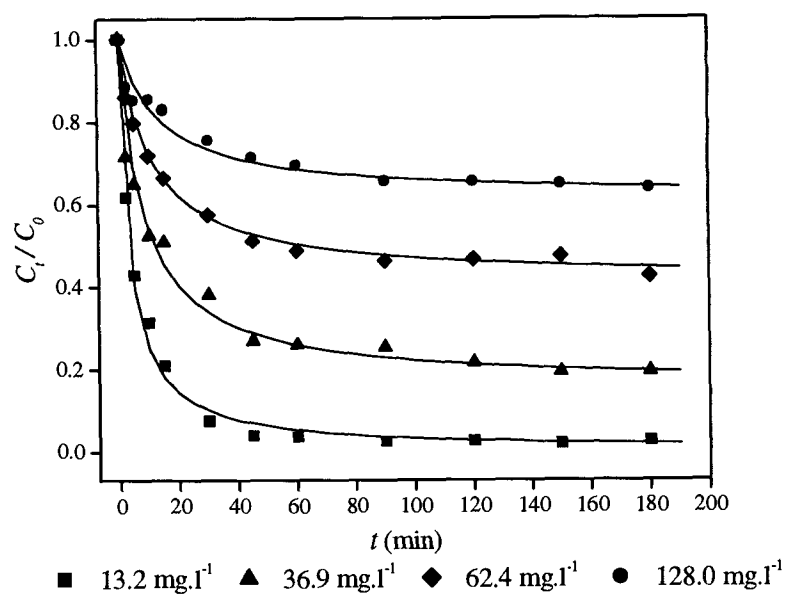
C_0 (mg.l ⁻¹)	k (g.mg ⁻¹ .min ⁻¹)	C_e (mg.g ⁻¹)	r^2
13.2	0.090	0.0014	0.9998
36.9	0.016	5.832	0.9989
62.4	0.011	25.64	0.9968
128.0	0.006	78.64	0.9961

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

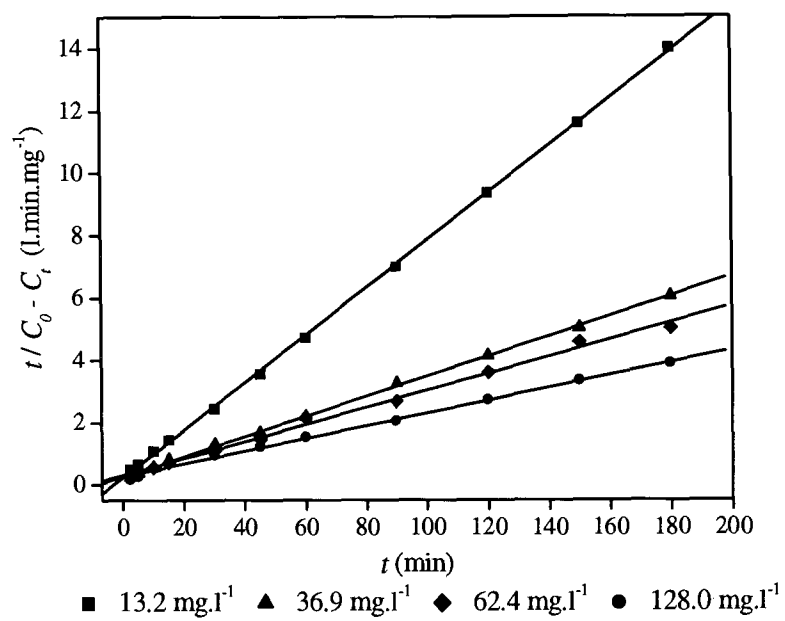
C_0 (mg·l ⁻¹)	(mg·g ⁻¹ ·min ^{-1/2})
13.2	0.6846
36.9	1.2191
62.4	1.3674
128.0	1.3753



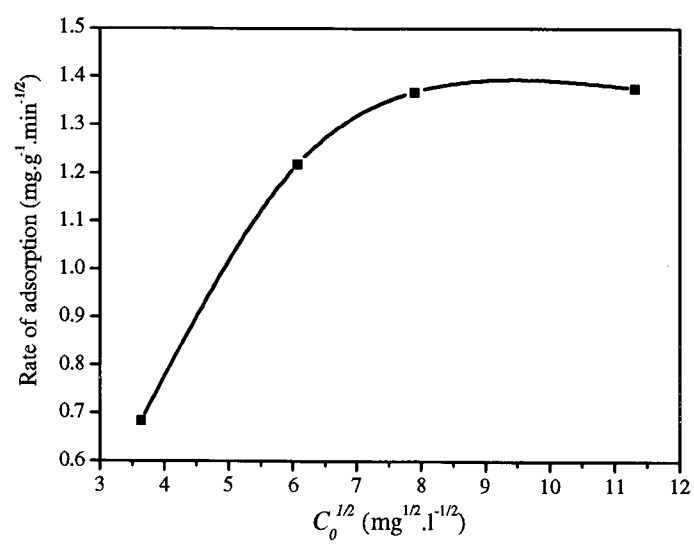
S. L. G. Petroni - Fig.2



S. L. G. Petroni - Fig.3



S. L. G. Petroni - Fig.4



S. L. G. Petroni - Fig.5

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radiotracer, adsorption studies, copper,
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DATA: 26.10.02

15 JUL 2002