

Kinetic Study of the Removal of Residual Copper(II) on Activated Carbon and Alternative Adsorbents

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Abstract The objective of this study was to adjust the kinetic data of the adsorption of residual copper(II) to the pseudo-first-order model, pseudo-second-order model, intraparticle diffusion and Elovich. The waste contained copper(II), generated in the analysis of protein determination at Departamento de Ciência dos Alimentos, of Universidade Federal de Lavras, Brazil. The concentration of copper(II) was 11.39 mg L^{-1} , determined by atomic absorption spectrometry, and the value found for pH was 13. Adsorption was studied employing kaolinite, advanced oxidation process (AOP) sludge and cotton lint as alternative adsorbents. Results of the percentage removal of copper(II) were compared with adsorption onto commercial activated carbon. The adsorption process was conducted at room temperature ($25 \pm 1^\circ\text{C}$), using 0.10 g of adsorbent and 10.0 mL of waste. The percentage removal of residual copper(II) obtained for the adsorbents active carbon, kaolinite, AOP sludge and cotton lint was 95.1, 94.5, 77.2 and 82.1%, respectively. The results showed that kaolinite was the most adequate alternative adsorbent. In this case, the final concentration of copper(II) was lower than the allowed by the Brazilian law for effluent discharge, which is 1.0 mg L^{-1} . The adjusted results showed that the model proposed by Elovich was more adequate for removal onto active carbon and cotton lint while, for adsorption onto kaolinite and AOP sludge, the most adequate was the pseudo-second-order model.

Keywords Adsorption, Alternative adsorbents, Chemical waste, Copper, Kinetic models

1. Introduction

Heavy metals are substances considered persistent in the environment, making them a major cause of pollution, since they are not appropriately discarded [1].

Copper is an important element in industry (galvanizing processes, wood treatment and conservation, production of textile dyes, synthetic dyes and metal alloys [2]; in agriculture (fungicides [3]), besides being a micronutrient present in metalloproteins [4] and aiding in the metabolism of carbohydrates and nitrogenous compounds in vegetables [5].

However, copper can cause two diseases, as a result of genetic mutations: Menkes disease is responsible for neurologic complications, and can lead to death, especially in childhood, and Wilson's disease, which results in the toxic accumulation of copper in the liver and, in some cases, in the brain [6]. In addition, the improper application of pesticides containing heavy metals and organic compounds with a high contamination capacity into the biota, as well as the disposal

of untreated waste, have resulted in the pollution of soil and water bodies [7].

According to the World Health Organization (WHO), the maximum concentration of copper for drinking water is 1.0 mg L^{-1} . At higher concentrations, copper makes water inadequate for consumption, since it causes an unpleasant taste, in addition to effects to the organism. In Brazil, the National Council for the Environment (Conselho Nacional de Meio Ambiente, CONAMA) states, in its resolution n°. 430 of 13 May 2011, that the maximum concentration for the discharge of effluents for dissolved copper is 1.0 mg L^{-1} [8].

In order to meet the requirements of the law, so that there is no damage to the environment and to any living organism, several processes in the removal of metal ions have been studied, thus minimizing the generation of contaminants in effluents containing such substances. Among the most widespread processes, adsorption, which has been an efficient process in the treatment of effluents, stands out [9].

Alternative adsorbents, such as kaolinite, which is a clay mineral [10], are abundant in nature, in addition to by-products of agricultural or industrial processes. These materials have a high efficiency in the removal of various contaminants, besides having a low cost; therefore, they are promising adsorbents, capable of replacing commercial activated carbon, making the effluent treatment process less

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costly [11].

2. Material and Methods

2.1. Adsorbate

The waste generated by the analyses of protein content performed in the Department of Food Science of Universidade Federal de Lavras (UFLA) was used as an adsorbate, and it was collected by the Chemical Waste Management Laboratory (LGRQ). The residue, which had pH 13, consisted of CuSO₄, K₂SO₄, H₂SO₄ and NaOH.

2.2. Adsorbents

Natural kaolinite was provided by Mineradora Química e Minérios (Ijaci, MG, Brazil) and did not undergo any previous treatment, being sieved in the fraction corresponding to 0.425 mm.

Cotton lint was a residue from research activities performed by the Seed Pathology Laboratory, in the Department of Forestry of UFLA. Once emulsified in sulfuric acid, it was first washed with distilled water to reduce the acidity of the starting material. The residue was then left at rest and subjected to drying. The sample was subsequently vacuum filtered until the pH of the last wash was kept at around 7, followed by drying in an oven at 70°C for 24 hours. Cotton lint was previously sieved in a fraction corresponding to 0.425 mm, in order to be used as an adsorbent material.

AOP sludge was obtained from the degradation, via photo-Fenton reaction, of organic waste collected by the LGRQ. AOP sludge was sun-dried, sieved in a fraction corresponding to 0.425 mm, and was subsequently used as an adsorbent.

For comparison purposes, the adsorption test was carried out with powdered activated carbon (Cromoline, Brazil).

2.3. Adsorption Kinetics

Adsorption experiments were conducted in batch at room temperature (25 ± 1°C) in a shaking table at 120 rpm. 10-mL aliquots of the residue were placed in contact with 0.100 ± 0.005 g of the adsorbents in a kinetics monitored between 0 and 360 minutes. Samples removed at defined time intervals were filtered, and the remaining concentrations were determined by flame atomic absorption spectrometry (FAAS), in an AA 110 Varian Spectra equipment, at a wavelength of 325 nm.

The percentage removal of copper(II) was calculated according to Equation 1:

$$\text{Removal}(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

Where C₀ and C_t are the concentrations of copper(II), initial and at time t, respectively.

3. Results and Discussion

One of the most important parameters for the evaluation of adsorption efficiency is the kinetic, which studies the time-evolution of a physical phenomenon.

The kinetic models that were used to evaluate the efficiency of the adsorbent in metal removal and to predict the mechanisms of adsorption process by pseudo-first-order, pseudo-second-order and Elovich.

The pseudo-first-order kinetic model described by Lagergren (1898) [12] is often used to understand the adsorption mechanism of adsorbates in liquid phase, and is represented by Equation 2:

$$q_t = q_e [1 - \exp(-k_1 t)] \quad (2)$$

Where q_t and q_e are the amounts of copper(II) removed at time t and at equilibrium (mg g⁻¹), respectively, k₁ is the rate constant (min⁻¹) and t is the contact time (min).

The pseudo-second-order kinetics proposed by Ho & McKay (1999) [13] is described by Equation (3):

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (3)$$

Where k₂ is the pseudo-second-order constant (g mg⁻¹ min⁻¹), q_t and q_e are the amounts of copper(II) removed at time t and at equilibrium (mg g⁻¹), respectively.

Although pseudo-first-and pseudo-second-order models consider the adsorption steps, they do not provide a definitive mechanism [14].

The model proposed by Elovich describes adsorption governed by chemisorption, whose application is associated with slow kinetic processes. Equation 4, which is frequently evaluated for systems in which the adsorbent surface is heterogeneous, is represented below:

$$q_t = \frac{1}{\beta} \ln(1 + \alpha \beta t) \quad (4)$$

Where α is the initial adsorption rate (mg g⁻¹ min⁻¹) and β is the ratio between the degree of surface coating and the activation energy involved in chemisorption (g mg⁻¹) [15].

The adjustment results of the experimental data to the kinetic models studied are described in Table 1.

By the analysis of Table 1, it was possible to observe, through the values of coefficient of determination (r²), that the results obtained for activated carbon and cotton lint were adjusted more adequately to the Elovich model, while the results for kaolinite and AOP sludge followed the pseudo-second-order model.

Although the Elovich equation describes predominantly chemical adsorption on highly heterogeneous adsorbents, the equation does not propose any definite mechanism for adsorbate-adsorbent interaction. The coefficients are significantly depending on the amount of adsorbent with α being more sensitive.

On the other hand, the results were better adjusted to the pseudo-second-order model when kaolinite and AOP sludge were employed as adsorbents, showing that the removal capacity is associated with adsorption in specific sites, in a pseudo-chemical reaction, which involves electron transfer. These results also suggested that adsorption of copper(II) by kaolinite is a rate-limiting step and are similar with others described in Table 2.

Table 1. Adjustment of the experimental data to the kinetic models

Kinetic model	Activated carbon	Kaolinite	AOP sludge	Cotton lint
Pseudo-first order				
q_e (mg g^{-1})	1.0182	1.0184	0.8569	0.8765
k_1 (min^{-1})	0.0885	0.0832	0.0596	0.0748
r^2	0.9761	0.9783	0.9918	0.9669
Standard error	0.0528	0.0504	0.0263	0.0541
Pseudo-second order				
q_e (mg g^{-1})	1.0687	1.0689	0.9094	0.9292
k_2 ($\text{g mg}^{-1}\text{min}^{-1}$)	0.1562	0.1484	0.1152	0.1384
r^2	0.9948	0.9962	0.9928	0.9930
Standard error	0.0247	0.0213	0.0246	0.0249
Elovich				
α ($\text{mg g}^{-1}\text{min}^{-1}$)	50.0491	44.2356	4.0347	7.9794
β (g mg^{-1})	11.1868	11.0928	10.4822	10.915
r^2	0.9990	0.9958	0.9700	0.9976
Standard error	0.0106	0.0223	0.0506	0.0144

Table 2. Comparison with others literatures

Adsorbent	Reference
Chitosan/PVA beads	[16]
Natural clay	[17]
Chemically modified babassu coconut mesocarp	[18]
Alginate-immobilized bentonita clay	[19]
Moringa pods	[20]

As shown in Figure 1, all alternative adsorbents showed a high copper(II) removal, with percentages of 94.5, 82.1 and 77.2% for kaolinite, cotton lint and AOP sludge, respectively, while activated carbon removed 95.1%.

Through the analysis of Figure 1, one can also infer that the adsorption is higher at the beginning of the process, tending to decrease and remain constant close to equilibrium. Increasing the amount of copper(II) removed during the first time intervals for all adsorbents can be associated with the availability of free sites for adsorption, which becomes reduced to the extent that the surface tends to saturation.

The final concentrations of copper(II) were 0.56, 0.63, 2.04 and 2.60 mg L^{-1} , when activated carbon, kaolinite, cotton lint and APO sludge, respectively, were used. These results showed that only in the adsorption on activated carbon and kaolinite, the remaining concentrations of copper(II) were below the maximum limit established by the Brazilian law, which is 1.0 mg L^{-1} .

The difference in the equilibrium times of the adsorbent materials can be attributed to the adsorbents chemical composition as well as the adsorption sites accessibility. The obtained results also showed that the surface charge of adsorbents had an important influence on kinetics.

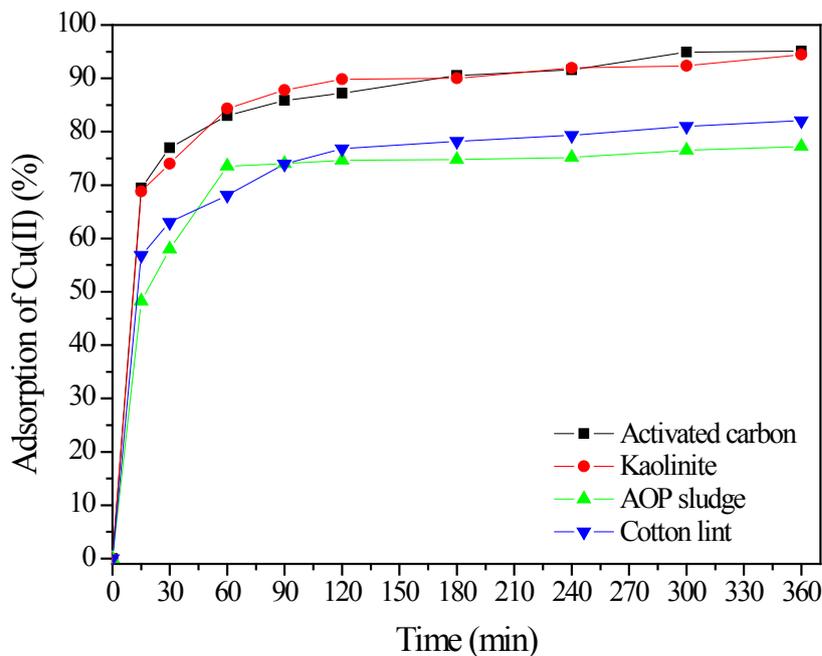


Figure 1. Adsorption kinetics of residual copper(II)

4. Conclusions

The results for the adjustments of the data to the adsorption of residual copper(II) showed that the kinetic profiles followed distinct models, allowing to infer that the removal process involved surfaces with different characteristics. While the model proposed by Elovich was the most suitable for the removal on activated carbon and cotton lint, adsorption on kaolinite and POA sludge followed the pseudo-second-order model.

Kaolinite was the alternative adsorbent with the highest efficiency in copper(II) removal, which was 94.5%, similar to the commercial activated carbon (95.1%).

Additionally, the remaining concentration of copper(II) in the process in which kaolinite was used as an adsorbent was below the maximum limit specified by the Brazilian law. Therefore, this material presented a high potential to replace activated carbon in the treatment of copper(II) waste, generated in protein analyses.

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