MACEIÓ - ALAGOAS
EBA 15
15° ENCONTRO BRASILEIRO SOBRE ADSORÇÃO
15th Brazilian Meeting about Adsorption

Study of the potential of composite material based on zeolite and geopolymer as an adsorbent of toxic metals

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Abstract

Water pollution is seen as degradation at various levels, encompassing physical, chemical and biological aspects. Due to the high degree of degradation of water bodies, conventional treatments do not present the necessary efficiency. Adsorption is a well-established treatment technique with a wide range of possibilities, and can be used in the treatment of various contaminants and also because several materials have potential as adsorbents. This work proposes the synthesis and application of economically sustainable adsorbent options for the treatment of water contaminated by toxic metals that can be found in industrial effluents such as electroplating. The adsorption of Cu^{2+} e Ni^{2+} ions on a zeolite synthesized from metakaolin and a composite material formed by a geopolymer matrix and a fraction of the same zeolite was evaluated. The kinetic study showed that the adsorptive process follows pseudo-second order (Ho) kinetics with both materials, the composite presented the best results with both ions, 29,100 $mg.g^{-1}$ for copper with the composite and 21.204 $mg.g^{-1}$ for nickel with the composite. The adsorption equilibrium best fitted the Langmuir model, copper presented the highest q_{max} values in both adsorbents being 50.251 $mg.g^{-1}$ in zeolite and 52.356 $mg.g^{-1}$ in the composite..

Keywords: adsorption; electroplating; water treatment.

1. Introduction

Currently, human actions have played a significant role in the socio-environmental crisis. Although technological advances have improved living conditions, they have also promoted a socioeconomic model that is not sustainable [7]. Understanding environmental quality is important to understand how human beings relate to the environment in which they live. This helps to raise awareness, sensitize and understand the environment in which communities develop [3].

The rapid advancement of modern industry and agriculture has made waste management a vital concern. Every year, a significant volume of industrial wastewater, contaminated with hazardous substances, is produced and discharged by sectors such as metallurgy and pesticide manufacturing [9].

The galvanizing industry is responsible for generating a large volume of toxic metal effluents. The objective of electroplating is to increase the durability and corrosion resistance of materials, while improving their aesthetics. This is achieved by applying a thin metallic layer to the surface [6]. During this process, the parts are subjected to successive washings that result in liquid effluents, gaseous emissions and solid waste, which require specialized treatment [10].

Adsorption is a mass transfer process that analyzes the ability of certain solid materials to attract and retain certain substances found in fluids (liquids or gases) on their surface, thus enabling the separation of the substances present in these fluids [5].

Zeolites are a category of minerals formed by hydrated aluminosilicates, which can be found both in nature and created synthetically. They have a distinct crystalline structure, characterized by a three-dimensional pore system [2]. Zeolite adsorbents are widely used in various industrial applications due to their remarkable selectivity and ability to selectively absorb molecules [1].

Recently, geopolymers have emerged as a promising alternative for the treatment of industrial

wastewater contaminated by toxic metals [8]. These materials consist of three-dimensional amorphous structures composed of negatively charged [AlO4] tetrahedra and neutral [SiO4] tetrahedra. They have demonstrated efficacy in the removal of heavy metal cations from wastewater using a combination of charge neutralization, immobilization, and adsorption. Additionally, geopolymers have mesoporous characteristics, characterized by the abundant presence of pores [4].

2. Experimental procedure

2.1. Zeolite A Synthesis (ZAC)

A mixture of 5 g of metakaolin was made with 60 mL of 2.8 M NaOH until it was completely homogenized. The mixture was left to stand for 18 h at room temperature and then placed in an oven at 100 °C for 4 h in Teflon capsules. Finally, the material was washed with water until it reached a pH lower than 9.0.

2.2. Composite Synthesis (CP)

Initially, 18g of non-magnetic fraction (NMF) of fly ash, 2g of metakaolin and 0.6g of zeolite A were weighed, the materials were mixed while still dry and then 10 mL of 10M NaOH and 10 mL of H_2O_2 were added. The mixture was homogenized, placed in Teflon capsules and heated for 28 days in an oven at 90 ºC.

2.3. pH point of zero charge (pH_{pzc})

The immersion method was used to obtain the pH of the zero charge point. 0.05 g of the material was added to 20 mL of 0.1 mol L-1 NaCl solution. The initial pH values were adjusted in the range of 1 to 9 by adding HCl (0.1 mol L-1) or NaOH (0.1 mol L-1) solutions. The system was agitated at 220 rpm on an orbital shaker table for 24 hours. After this period, the final pH of the solutions was measured and a graph of ΔpH versus $pH_{initial}$ was constructed. The pH_{PZC} value was obtained, identified as the intersection point with the $pH_{initial}$ axis.

2.3. Dosage test

A multielement solution containing Ni^{2+} and Cu^{2+} ions at a concentration of 300 ppm and pH equal to 5 was used. It was maintained for 24h and stirred at 220 rpm, Erlenmeyer flasks containing 50 mL of the solution and different masses of adsorbent (10-100mg). Then, the solutions were filtered and the concentration of the ions was determined in an atomic absorption spectrometer, model AA 240 FS Varian.

2.4. Study of contact time

A solution of metal ions with a concentration of 300 ppm was prepared and stirred (220 rpm) with the same mass of adsorbent, remaining in contact for a sufficient time to achieve equilibrium. During this interval, aliquots of the solutions were removed at predefined times and analyzed in an atomic absorption spectrometer, model AA 240 FS Varian, to construct the adsorption profile of the system. The results obtained were treated in the pseudo-first-order Lagergren linear kinetic models (1) and pseudo-second-order Ho (2).

$$ln(q_e - q_t) = ln(q_e) - k_1 \times t \quad (1)$$

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

2.5. Adsorption equilibrium study

The adsorption isotherm studies were conducted based on the Langmuir and Freundlich models.

For the test, a solution of metal ions was prepared in various concentrations, from 10 to 300 mg/L, in contact with the same mass of adsorbent. The systems assembled in Erlenmeyer flasks were kept under constant stirring and temperature for 5h. The equilibrium concentration was determined in an atomic absorption spectrometer, model AA 240 FS Varian.

3. Results and discussion

3.1. pH point of zero charge (pH_{pzc})

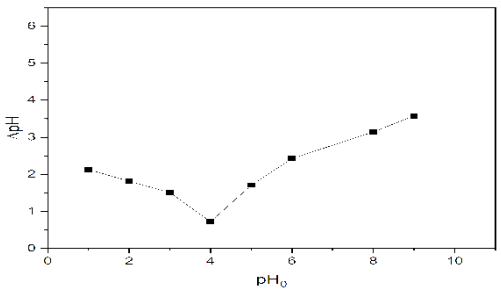

Fig. 1. pH point of zero charge (pH_{PZC}) for the composite.

The value obtained for pH_{PZC} of the composite (fig. 1.) was pHpzc = 4,0.

According to this result, the pH of the solution used in the kinetic and isotherm tests was pH = 5.0; this ensures that the surface of the material will have a charge opposite to the absorbate.

Fig. 2 shows the distribution diagram of Cu(II) in acetic medium. Note that at pH = 5, at which this work was developed, approximately 50% of free Cu(II) predominates, 40% of the species $Cu(CH_3COO)^+$ and 10% of the neutral species $Cu(CH_3COO)_2$. The diagram indicates that approximately 90% of the total Cu in solution is positively charged. The same diagram was made for Nickel (not shown).

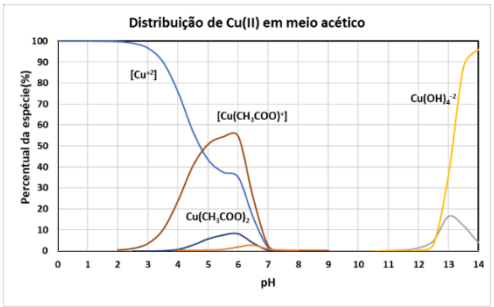

Fig. 2. Diagram of copper distribution as a function of pH.

3.2. Dosage test

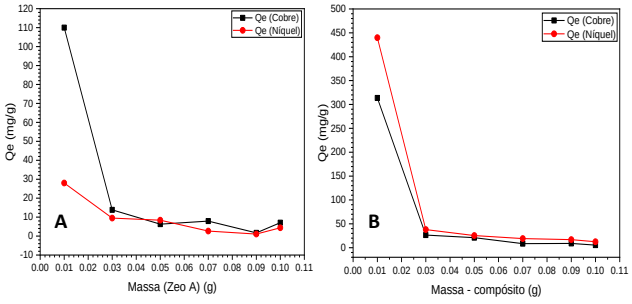

Fig. 3. Dosage test: (A) zeolite A - 300 mg/L, pH = 5; (B) composite - 300 mg/L, pH = 5.

What was observed in the results of both materials is that the increase in the adsorbent mass, from 30 to 100 mg, does not significantly affect the adsorptive capacity of metal ions. It is concluded that there is no need to use quantities greater than 30 mg and since the solution volume was 50 mL, the working dosage is 0.6 g/L.

3.3. Study of contact time

The contact time tests with both materials showed a better fit with the Ho kinetic model (pseudo-second order), indicating the occurrence of chemisorption. This result is consistent due to the nature of the adsorbents used, which have molecular structures capable of interacting with metal ions.

The two materials showed greater adsorptive capacity for Cu^{2+} ions; the kinetic parameters are presented in Table 1.

3.4. Adsorption equilibrium study

The results of the adsorption isotherms were compared with the theoretical values obtained from the Langmuir and Freundlich models.

The Langmuir model was the best fit in all the tests, according to which adsorption occurs in monolayers and in specific sites of uniform energy. Copper presented the highest q_{max} values in both adsorbents, being 50.251 $mg.g^{-1}$ in the zeolite and 52.356 $mg.g^{-1}$ in the composite.

Table 1. Kinetic parameters for the Langergren model of pseudo first order and Ho model pseudo second order: Kinetic constant (k), adsorptive capacity (qe), correlation coefficient (R^2). Ni^{2+}/Cu^{2+} concentration 300mg/L. Adsorbent dosage of 0,6 g/L.

Adsorbent	$q_{e\ exp}$ (mg.g^{-1})	1st Order			2nd Order		
		k_1 (min^{-1})	q_e (mg.g^{-1})	R^2	k_2 (L.mg^{-1}.min^{-1})	q_e (mg.g^{-1})	R^2
CP/Cu	29.100	-	-	-	0.0132	28.57	0.9976
CP/Ni	21.204	0.0253	25.685	0.9768	0.0019	24.270	0.9958
ZAC/Cu	21.800	0.0454	14.092	0.9818	0.0023	24.272	0.9963
ZAC/Ni	16.100	0.0183	20.662	0.9852	0.00504	17.212	0.9975

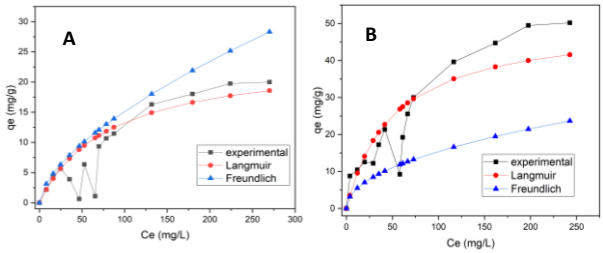

Fig. 4. Adsorption isotherm: (A) zeolite-nickel, 29 ºC; (B) zeolite-copper, 29 ºC.

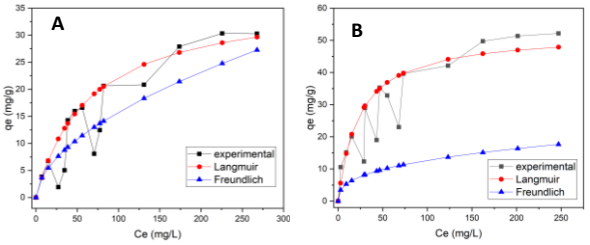

Fig. 5. Adsorption isotherm: (A) composite-nickel, 29 ºC. (B) composite-copper, 29 ºC.

Acknowledgement

The authors would like to thank Programa de Pós Graduação em Química da UFC, a lab LANAGUA, UFC Campus do Pici, and CAPES for the financial support provided to the research.

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