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Use of Nanoclay as an Adsorbent to Remove Cu(II) from Acid Mine Drainage (AMD)

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In this research, the adsorption of copper ions from acid mine drainage (AMD) using nanoclay as an adsorbent, was studied. To obtain the nanoclay, a montmorillonite (MMT) was modified with hexadecyltrimethyl ammonium (HDTMA) bromide. It was characterized by XRD and BET by adsorption of N_2 to 77K. The AMD was taken from an abandoned mine located in Jauja, Peru, which was analyzed by ICP-MS and gave a copper concentration of 38 mg/L. To determine the appropriate dosage, the nanoclay mass required for adsorption was determined, being 0.07 g/mL. The adsorption experiments were performed in batch system, at pH from 3 to 8 and contact times from 30 to 90 minutes, at room temperature, in aqueous solutions of 50 mg/L of Cu(II). The highest percentage of Cu(II) removal was given at pH 8 and 30 minutes of contact time, with 96% of removal. The mechanism of adsorption was studied at several initial concentrations of copper, using the models of Langmuir and Freundlich, finding that the one that best suited this process was the Langmuir isotherm. The adsorption capacity of the nanoclay, calculated by the Langmuir isotherm for Cu(II) was 7.53 mg/g. Finally, this procedure was applied to samples of AMD, obtaining a final concentration of 0.4 mg/L for Cu(II) after the treatment.

1. Introduction

The contamination of water by heavy metal ions is becoming an environmental problem due to the high toxicity of some of these elements and their tendency to accumulate through the food chain, affecting all living organisms and the ecological system. Some of important metal contaminated effluents are found in mining areas. Despite the negative environmental impact of mining, it is still a worldwide important industrial sector of economy (Baltazar et al., 2018). The acid mine drainage (AMD) is a strong acidic wastewater rich in high concentrations of dissolved ferrous and non-ferrous metal sulphates, and salts (Macingova et al., 2012) and if AMD is left untreated, it can contaminate ground and surface watercourses, damaging the health of plants, humans, wildlife, and aquatic species (Filion et al., 1990).

One of the metals that are found in AMD is copper, that is an essential trace element needed for human body and well known micronutrient for plants and animals but it is toxic if it exceeds the limit specified. Excessive concentration of copper may cause vomiting, diarrhea, stomach cramp coma, jaundice, gastrointestinal distress and nausea (Sudha et al., 2018).

Nowadays, adsorption is identified as an effective and economic method for the heavy metal wastewater treatment (Patterer, 2017). Adsorption is considered very attractive considering its pollutant removal efficiency in dilute solutions. This technique generally involves the use of conventional adsorbents, such as activated carbon (Lima et al., 2017), zeolite, clay and other silica-alumina materials (Kyzas and Bikiaris, 2015). Clay minerals have drawn much attention due to their distinctive features, such as ion exchange properties, its large specific surface area, high sorption capacity, swelling, intercalation behavior and their lower cost compared to synthesized materials (e.g. silica gel, zeolite) (Sahidu et al., 2008). One of the modified materials that can be obtained from clay is the nanoclay. It can be obtained from montmorillonite by intercalating it with organic compounds such as amines, thus enhancing its adsorbing properties. Currently, nanoclays have been studied to remove heavy metals and proved to be a great adsorbent.

The aim of this study was to investigate the removal of Cu (II) from AMD using nanoclay obtained from montmorillonite (MMT) that was modified with hexadecyltrimethyl ammonium (HDTMA) bromide. First, the

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experiments were done in aqueous solutions of copper using batch system and then in real AMD. Also, the effect of different variables on adsorption of copper ions was investigated and optimum conditions were recognized. Langmuir and Freundlich isotherm models were applied.

2. Methodology

2.1. Preparation of nanoclay

The natural bentonite was collected from the deposit located in Chongos Bajo, Junín, Peru. To obtain the montmorillonite, previously, the bentonite was purified according to Stokes's sedimentation law. The cation exchange capacity (CEC) was determined by the sodium saturation method, it was 80 meq/100g of clay. The synthesis of nanoclay was conducted by the following procedure. An amount of 2 g of montmorillonite previously dried was dispersed with 200 mL of distilled water for 24 h using a magnetic stirrer at temperature room (Shirzad-Siboni et al., 2015). Then, add 0.7 g of hexadecyltrimethyl ammonium bromide to the MMT solution, mix it for 5 hours at a temperature of 80 °C. Centrifuge the solution until the excess of water is eliminated. Dry the obtained nanoclay at 90 °C in an oven for 24 h. The nanoclay was ground, sieved and stored. The X-ray diffraction (XRD) characterization of nanoclay was performed with a Philips-X´Pert XRD instrument. Physicochemical characterization was recorded on a surface area analyzer and porosity (Micromeritics-Gemini VII 2390) equipment.

2.2. Acid Mine Drainage (AMD) sampling

The AMD sample was taken from an abandoned mine located in Jauja, Peru, which was analyzed by Mass Spectrometry with Inductively Coupled Plasma (ICP-MS), the initial concentration of copper was 38 mg/L, also present large quantities of iron.

2.3. Removal of Cu (II) with nanoclay

An aqueous solution of 50 mg/L of Cu (II) was prepared from a standard solution of 1000 mg/L of Cu (II) of the Merck brand.

Experiments were performed to determine the optimal dosage of the adsorbent by means of a mass curve, using different amounts of nanoclay, from 1.0 to 9.0 g/L. The study of the influence of pH was done adjusting the pH of the process in a range of 3 to 8. The parameters of operation were as follows, agitation speed of 200 rpm, volume of the solution of copper 40 mL at room temperature. The pH of solutions was regulated with 1.0 and 0.1 M HCl or 1.0 and 0.1 M NaOH, and measured by a pH meter (Analytics, Handylab). The obtained solutions were analyzed in an Atomic Absorption Spectrophotometer (Varian-220FS).

The dependence of the initial concentration of copper ions in the adsorption process was studied, performing experiments at different concentrations of copper ions in a range of 10 to 50 mg/L.

The amount of copper ions adsorbed per nanoclay mass unit, q_e (mg/g) was calculated by the following equation:

$$q_e = \frac{V(C_o - C_e)}{m\,x\,100} \tag{1}$$

Where, $\mathrm{C_0}$ and $\mathrm{C_e}$ are the initial and equilibrium concentration of copper in the solution respectively; q_e is the amount of copper ion adsorbed at equilibrium, V is the volume of the solution in liters, and m is the mass of nanoclay.

The Langmuir and Freundlich models were used to determine the adsorption isotherms. Adsorption isotherms are used to describe the interaction between the metal ion and the adsorbent. The Langmuir isotherm model suggests that the adsorption of the metallic ion occurs uniformly by a monolayer adsorption on a homogeneous surface, with no interaction between the adsorbed ions (Langmuir, 1918). The linear form of the Langmuir model can be written as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m k_L} + \frac{C_e}{q_m} \tag{2}$$

Where $\mathrm{C_e}$ and $\mathrm{q_e}$ are the equilibrium concentrations (mg/L) and the amount of copper ions adsorbed at equilibrium (mg/g), respectively, $\mathrm{k_L}$ is the Langmuir constant (L/g), and $\mathrm{q_m}$ (mg/g) represents the adsorption capacity of the monolayer in equilibrium.

The Freundlich equation (Freundlich, 1906) is an empirical equation based on a heterogeneous system and a multilayer adsorption, which assumes the relationship between the concentration of the adsorbate in equilibrium, and the level of adsorption is logarithmic. It also assumes that adsorption sites are distributed exponentially with respect to adsorption energy (Ibrahim, 2009). This model is expressed by the following equation:

$$\log q_e = \log k_F + \frac{1}{n \log C_e} \tag{3}$$

Where k_F (mg/g) and n are the constants of the Freundlich model that indicate the capacity and intensity of adsorption, respectively.

3. Results and discussion

3.1 Characterization of nanoclay

X-ray diffraction (XRD)

The X-ray diffraction has been used to study the changes in the surface properties of montmorillonite clay through the changes in the basal spacing of montmorillonite. XRD patterns of montmorillonite and nanoclay samples are shown in Figure 1. As seen in Figure 1, with an addition of surfactant hexadecyltrimethyl ammonium bromide, the basal spacing of the resultant nanoclay increases from 15.3 Å to 22.57 Å. The amount of added surfactant has a direct effect on the interlayer expansion of montmorillonite. In addition, the X-ray diffraction analysis also indicates the presence of montmorillonite minerals in nanoclay (Uddin, 2008).

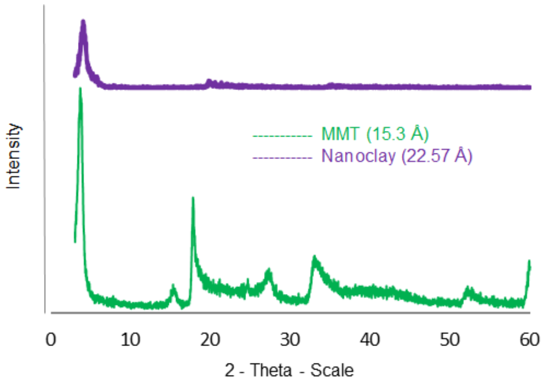

Figure 1: X-ray diffraction pattern of montmorillonite (MMT) and nanoclay

BET analysis by adsorption of N_2

The BET surface area of natural bentonite was determined as 70.7 m^2g^{-1} and of the nanoclay was 21 m^2g^{-1}. The BET surface area significantly decreased after the modification due to the coverage of the pores of natural bentonite.

3.2 Dosage of nanoclay

To determine the amount of the appropriate nanoclay for the adsorption, the dosage curve was constructed with an initial concentration of Cu (II) of 50 mg/L, and then it interacted with different amounts of adsorbent mass. The curve of dosage of nanoclay is showed in Figure 2. It can be seen that the adsorption reaches equilibrium with 2.8 g of nanoclay, with a removal percentage of 77.3%. this calculated mass was used for the other experiments. Then, the appropriate adsorbent/adsorbate dosage is 7 g/L.

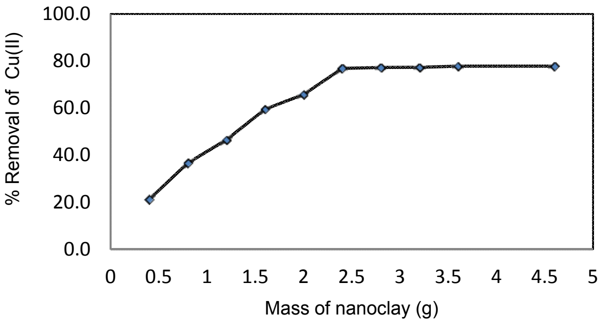

Figure 2: Mass curve for dosage of the nanoclay. C_oCu=50 mg/L

3.3 Effect of pH

The highest percentage of Cu (II) removal was given at pH 8 with 96.3%. Clays are known to have a negative surface charge in solution, as the pH changes, the surface charge also changes, and the adsorption of charged species is affected. At low pH values, there is excess of H_3O^+ ions in solution, there is a competition between positively charged hydrogen ions and metal ions for accessible adsorption sites on the surface of the clay (Soleimani, 2015).

3.4 Isotherm studies

The adsorption isotherm is the equation or curve that relates the concentration of the metal that has been adsorbed on the solid phase with the concentration of the metal in the solution at equilibrium at a defined temperature. The application of experimental data on equations that describe the isotherms is valuable; subsequently the estimation of the system performance and optimization of the use of the adsorbent is obtained. The adsorption equilibrium provides fundamental physicochemical data to estimate the applicability of adsorption procedures as a unitary process. In terms of equilibrium verification, the Langmuir isotherm model is in many cases in accordance with the experimental data, while the Freundlich model has also been used to adjust the experimental data in several cases. The adsorption isotherms are of vital importance in the design of adsorption systems, because they indicate the amount of metal ions present and how they are positioned between the adsorbent and the liquid phase. When the metal ion comes into contact with the adsorbent, the concentration of the metal on the surface begins to increase until a dynamic equilibrium is reached; it is at this point that the distribution of the metal ion between the solid and liquid phases is defined clearly. Figure 3 shows that the percentage of removal of Cu (II) decreased with the increase of the metallic ion concentration.

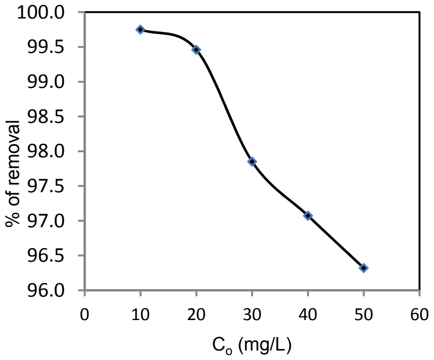

Figure 3: Effect of the initial concentration of Cu (II) on the percentage of removal.

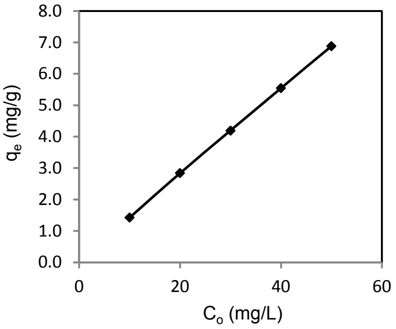

Figure 4: Isotherm of adsorption of Cu (II) with nanoclay.

In Figure 4 it is observed that, when the initial concentrations of Cu (II) varied from 10 to 50 mg/L, the amount adsorbed per unit of mass (q_e) increased with the increase of the concentration of the metal.

Figure 5 shows the Langmuir isotherm for the adsorption of Cu (II) with nanoclay. The Langmuir isotherm is probably the most extensively applied model for an adsorption isotherm, where this model considers that the adsorption energy of each molecule is independent of the surface of the material, occurring in specific places of the adsorbent and without any interaction between the molecules because the heat of adsorption is constant for these sites. Once the ion occupies a place, no further adsorption can occur at this same site, resulting in the formation of a monolayer where the adsorption occurs uniformly on the surface of the adsorbent; in this model, the attraction between the metal ions and the surface of the adsorbent is mainly based on physical forces (electrostatic or Van der Waals forces).

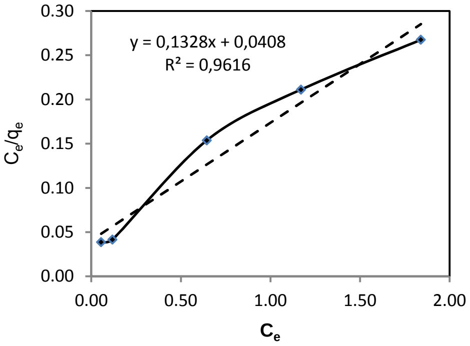

Figure 5: Langmuir isotherm for the adsorption of Cu (II) with nanoclay.

Figure 6 shows the Freundlich isotherm for the adsorption of Cu (II) with nanoclay. In the Freundlich isotherm model, an empirical equation is used, where it proposes a multilayer adsorption with a heterogeneous energy distribution of active sites, accompanied by the interaction of adsorbed molecules, which are first occupied by strong bonds, and this force is decreasing as the active sites are occupied by the adsorbate.

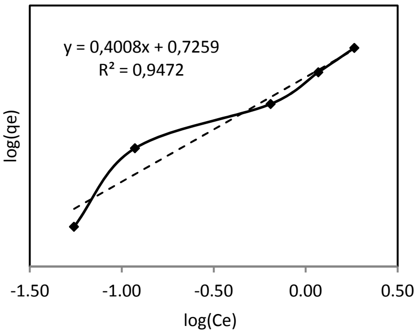

Figure 6: Freundlich isotherm for the adsorption of Cu (II) with nanoclay.

Table 1 shows the parameters of the Langmuir and Freundlich isotherms, derived from Figures 5 and 6.

Table 1: Parameters of the Langmuir and Freundlich isotherms

Adsorbent	Langmuir			Freundlich		
	Q_0 (mg/g)	b (L/mg)	R^2	K_f	n	R^2
Nanoclay	7.53	3.25	0.96	0.04	2.49	0.94

In Table 1 is compared the parameters of the Langmuir and Freundlich isotherms, the Langmuir model is the one that best represents the experimental results. This is verified by the value of correlation coefficient R^2 of 0.96, a value relatively higher than that found by the Freundlich model, being 0.94.

The Langmuir isotherm is frequently used to describe the adsorption of liquid solutions and this model assumes a coverage of the monolayer adsorption surface. The Langmuir adsorption model assumes that the surface is homogeneous, which has a specific number where a molecule can be adsorbed, that is, when all the sites are occupied it is not possible for the adsorption to continue (the system saturates), the adsorption heat is independent of the degree of coating and all sites are equivalent and the energy of the adsorbed molecules is independent of the presence of other molecules.

Finally, according to the parameters calculated in the Langmuir isotherm, the capacity of adsorption of the nanoclay for Cu (II) is 7.53 mg/g.

To apply the treatment carried out in the present investigation, by means of the adsorption process, a sample of Acid Mine Drainage (AMD) was used, coming from an abandoned mine in Jauja - Peru. After a chemical analysis of the AMD by ICP-MS, it gave as initial concentration of copper, 38 mg/L. The experimental tests of copper adsorption in batch system in AMD sample, was done with 2.8 g of nanoclay, at pH 8. The AMD sample after the adsorption treatment was taken to a new analysis by ICP-MS, which gave a final concentration of 0.4 mg/L of copper, which represents the 98.9 % of removal of this metal.

4. Conclusions

Copper ions were reduced from aqueous solutions using nanoclay as an adsorbent, from an initial concentration of 50 mg/L to final concentration of 1.84 mg/L, equivalent to 96.3% removal percentage. The best experiment was given to pH 8.

The model that best described the Cu(II) adsorption mechanism on nanoclay was the Langmuir isotherm, showing an R^2 correlation coefficient of 0.96, a value greater than that obtained by Freundlich's model, being 0.94, consequently the adsorption is given in monolayer on a homogeneous surface. The adsorption capacity of the nanoclay, calculated by means of the Langmuir isotherm for Cu(II), was 7.53 mg/g.

To demonstrate the efficiency of the proposed process, copper ions were removed from a sample of acid mine drainage (AMD) from an abandoned mine in Jauja - Peru. Copper was removed from an initial concentration of 38 mg/L to a final concentration of 0.4 mg/L, which represents the 98.9 % of removal of this metal.

With these results it is shown the great efficiency that nanoclay has when it is applied to the copper removal in real samples of AMD, which also constitutes a proposal for the use of this material that is generally low cost and abundant in the central region of Peru.

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