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Removal of Copper from Phosphoric Acid by Adsorption on Tunisian Bentonite

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Abstract

This experimental study was articulated around the efficiency of the technique of adsorption as a method for the elimination of copper from phosphoric acid by using bentonite as a support. Several parameters such as the effect of the initial concentration of the pollutant, the isotherms and the retention capacity of bentonite, was investigated. The adsorption was modeled by simples' models of Langmuir, Freundlich. The results obtained have proved that the adsorption of copper follow the Freundlich Model.

Keywords: Copper; Phosphoric acid; Bentonite; Adsorption

Introduction

Several studies carried out have shown that the clay has a very important role as a powerful adsorbent for removing heavy metals contained in phosphoric acid, due to their high availability and relatively lower costs compared to industrial adsorbents. A study was conducted by Mellah and Jaffar [1], on the adsorption of heavy metals from phosphoric acid by an Algerian activated bentonite. Some tests of zinc (II), cadmium (II) and chromium (III) adsorption contained in 5.5 M phosphoric acid pretreated (30% P_2O_5) were performed. The results showed a removal of 88% for zinc (II) and 89% for Cd (II) and chromium (III) of the initial concentrations (Table 1). In the same context, another study by Omri et al. [2] in the purification of Tunisian phosphoric acid, using various types of clays in their natural state or modified for the adsorption of cadmium, fluorine, carbon and organic chlorides. The experimental results show good fixation of these impurities on these adsorbents. For cadmium is of about 50%, fluorine and chloride about 98%, and finally for organic carbon can close to 85%. According to data in a study developed by El-Bayaa et al. [3] for the elimination of iron (III) ions and of uranium (VI) ions from 5 M phosphoric acid (52% P_2O_5) through silica sand. The maximum removal of iron (III) ion was 84% with a dose of 60 g of adsorbent/l and for uranium (VI) ions was 75% with a dose of 200 g of adsorbent/l. El-Sofany et al. [4] studied the cadmium, copper, zinc and lead removals from phosphoric acid by the use of impregnated charcoal. The removal rate was 43.7% for the (Cd), 36.74% for the (Zn), 27.45% for the (Cu) and 9.12% for (Pb).

The objective of this study is to achieve the possibility of the maximum elimination of copper from phosphoric acid by adsorption on bentonique Tunisian clay [5]. The effect of the initial concentration of copper, the different isotherms and the retention capacity of bentonite to remove copper.

Materials and Methods

Preparation of solutions and used reagents features

Main solutions: We have prepared a solution of 1M phosphoric acid from a standard stock solution (Fischer, Analar Normapur, France) of 85% purity with a density of 1.692 and a molecular weight of 98 g/mol, while injecting the adequate amount of copper sulfate ($CuSO_4$, $5H_2O$) with a molar mass 249.69 g/mol. The various studied solutions are prepared by adding copper to the main solution of 1M phosphoric acid, as a range of the metal concentrations in the North African phosphoric acid.

Elements studied	Cu (ppm)
Algerian rock [5]	6-26
Tunisian rock [6]	1-3
Marocan rock [7]	35

Table 1: Phosphoric acid composition (28% P_2O_5).

Experimental protocol: Our experimental study is based on the purification of contaminated phosphoric acid solutions assigns a range of initial copper concentration of 3 to 32 ppm. The first step was started by mixing the appropriate amount of clay (0.5 to 3 g) with a volume of 100 ml for each of the acid solution to be treated and then is subsequently stirred at 25°C and with a speed of 450 rpm for 120 minutes. After centrifugation step in a centrifuge-type Grosseron, MICRO 22, for 10 minutes at 6000 rpm, the solutions were filtered in a Buchner vacuum filter while using filters based on a cellulose membrane 0, 45 microns.

The analysis of the filtrate is made by an atomic absorption apparatus air-acetylene flame of mark (VARIAN AA140 Atomic Absorption Spectrophotmeter) lamp cathode (copper) is used to determine the adsorption capacity and the removal efficiency [6].

Bentonites tested: The clay that we used is a rich montmorillonite bentonite and from south-eastern Tunisian deposits (Hicha El Hamma). It is a calcium, grey bentonite and in powder form. Its specific surface area is around 70 m^2/g. Table 2 presents some characteristics.

Description of the adsorption tests on bentonite

The tests were realized in a batch reactor, where the acid solutions at different initial copper concentrations (3 to 32 ppm) are brought into contact with increasing doses of clay ranging from 0.5 g/100 ml acid to 3 g/100 ml acid. Tests were stirred at a speed of 450 rpm and maintained at a temperature of 25°C for two hours. When equilibrium is reached, samples will be centrifuged, filtered and analyzed.

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Chemical compound	specific area (m2/g)	CaO	SiO2	Al2O3	Fe2O3	SO3	K2O	MgO	Na2O	MnO	P2O5	TiO2
Composition (%)	70	2,52	48,92	19,31	13,13	0,28	1,06	2,53	1,21	0,05	0,19	1,63

Table 2: Physico-chemical characteristics of bentonite.

Model	Langmuir			Freundlich		
Dose (g/l)	R2	Qm (mg/g)	KL (l/mg)	R2	n	KF (l/mg)
5	0,9537	0,5903	0,0163	0,9962	2,156	0,0623
15	0,9083	0,3405	0,0472	0,9953	1,329	0,0212
30	0,7886	0,1257	0,0108	0,9904	0,7305	0,0077

Table 3: Parameters of Langmuir and Freundlich isotherms.

During our tests, some parameters were studied to see their effects on the performance of the adsorption: the influence of dose of clay added the effect of treatment by the clay on the concentration of phosphoric acid and the effect of the initial copper content [7].

Results and Interpretation

Effect of the amount of bentonite

We followed the evolution of the removal efficiency of copper with initial concentrations of copper (5-32 mg/l) while varying each time the dose of bentonite (5-30 g/l). Measuring the residual copper content of the treated samples was made after 120 minutes contact with the bentonite.

From the results shown in Figure 1, we can see that the removal efficiency of copper increased with increasing dose of bentonite introduced whatever the initial concentration of the copper present in the phosphoric acid. Note that for small amounts of clay (5 and 15 g/l), the best yields (14-20%) are for initial copper concentrations of 3 ppm. But for large dose of clay (30 g/l), the best yield obtained (43%) is for high copper concentration (32 ppm). On the adsorption phenomenon produced, it can be justified by Basta and Tabatabai's [8] proposed the following mechanism for the adsorption of metals:

$$M^{2+} + H_2O \rightleftharpoons MOH^+ + H^+$$

$$MOH^+ + X^- \rightleftharpoons XMOH$$

X: surface; M: metal.

Effect of initial copper content

We conducted tests for initial copper contents varying from 3 to 32 ppm doses of clay (5 to 30 g/l) to see its effect on the removal efficiency.

The results shown in Figure 2, we can see that the performance is gradually improving with the initial copper content for a high clay dose (3 g/l). But for both low doses (5 and 15 g/l) we see that the efficiency decreases with the initial copper content.

These results demonstrate that treatment with bentonite is not very effective for a low initial concentration of copper. The removal of copper was 23%, obtained for an initial concentration of 3 ppm copper. While for high initial concentrations (32 ppm) was used a high dose of bentonite to get a good removal efficiency of about 43%.

Treatment effect of bentonite on the concentration of phosphoric acid

We made the assays acid before and after treatment to see its influence on the rate of P_2O_5. We studied the effect of the dose of clay on the loss of P_2O_5 and found that there's a slight decrease (0.03%) on the initial concentration of phosphoric acid to a low dose of bentonite (5 g/l) and decreased more for larger doses (15 and 30 g/l), which varies between 0.05 and 0.07% (Figure 3).

Adsorption isotherms of copper

To study of the isotherms of adsorption of copper by bentonite, volumes of 100 ml of different initial concentrations of pollutants from (3 to 32 mg/l) are contacted with a mass of 0.5 g of the adsorbent. The fixed amount of copper per gram of adsorbent (mg/g) is given by the following relationship:

$$Qe = (C_0 - C_e) * \frac{v}{m}$$

Where Qe the fixed amount of copper in mg per gram of adsorbent, C_0 and C_e: are respectively the initial and instantaneous concentrations of copper (mg/l), V is the volume of the solution, m the mass of adsorbent used (g). Figure 4 shows the isotherm of copper for clay dose of 5 mg/l.

From Figure 4, we observed that the amount of adsorbed copper increases more or less rapidly at low concentrations in solution, then decreases to reach a plateau corresponding to a saturation adsorption sites, resulting in a monolayer adsorption. The isotherm obtained is L-type according to the classification of Giles [9].

The results show that the adsorption capacity for bentonite decreases with the solid/liquid ratio of 5 to 15 g/l and increases with the initial contents of Copper. For a high dose of bentonite (30 g/l) of the maximum adsorption capacity (0.47 mg / g) is obtained for an initial copper concentration of 32 mg/l and 0.28 mg/g for a dose of 5 g/l (Figure 5).

Linearization of adsorption isotherms: We have adopted the classic models of Langmuir and Freundlich isotherms adsorption, which allow linear regression to obtain the values of their constants (Q_m, K_L, 1/n, K_F), to better interpret the results of adsorption.

The Langmuir model [10] is based on the following assumptions:

Forming a single layer of adsorbate on the surface of the adsorbent, the existence of the defined sites of adsorption, the surface is uniform with no interaction between the adsorbed molecules.

Freundlich model [11] is based on an empirical equation reflects a change in energy with the adsorbed amount. This distribution of the interaction energies can be explained by heterogeneity of adsorption sites. Unlike the Langmuir model, the Freundlich equation does not provide higher adsorption which restricts its application to dilute media limit. However, this model admits the existence of interactions between the adsorbed molecules [12].

In fact, we remember different linearization equations for each model:

Langmuir relation:

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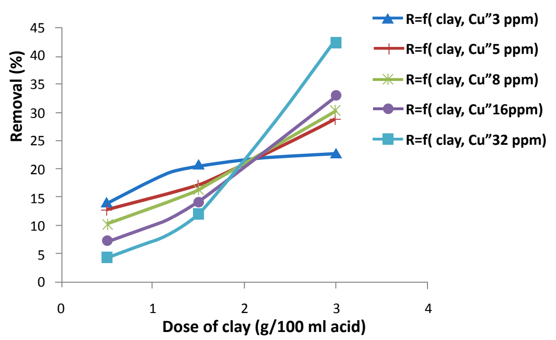

Figure 1: Effect of the dose of bentonite on the removal efficiency of copper.

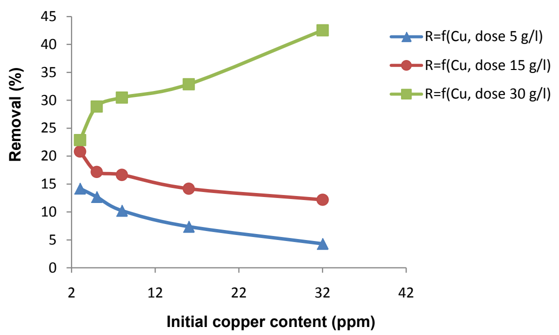

Figure 2: Variation of removal efficiency as a function of the initial copper content.

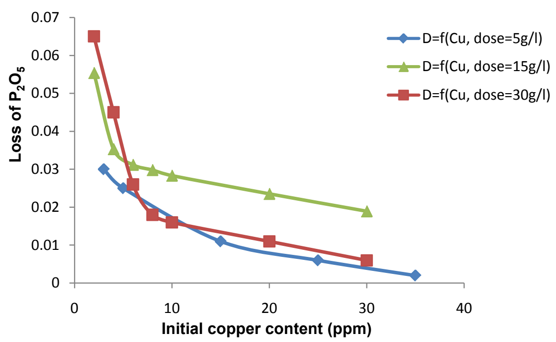

Figure 3: Effect of clay dose on loss of P_2O_5.

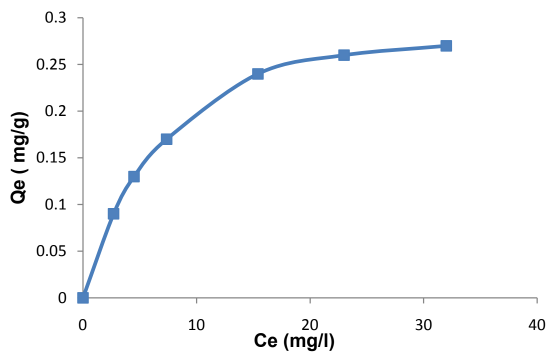

Figure 4: Isothermal adsorption of Cu2+ on the bentonite clay to a dose of 0.5 g to 25°C.

$$\frac{Ce}{Qe} = \left(\frac{1}{Q_m}\right) * Ce + \frac{1}{(K_L * Q_m)}$$

Freundlich relation: $\ln Qe = \left(\frac{1}{n}\right) \ln Ce + \ln K_F$

With:

C_e: Concentration in liquid phase at equilibrium (mg/l)

Q_e: Quantity adsorbed at equilibrium (mg/g)

Q_m: maximum adsorption capacity of the monolayer (mg/g)

K_L: Parameter Langmuir (l/mg)

K_F: Distribution coefficient Freundlich on the total sorption capacity of the solid (l/mg) and

n: constant characterizing the Freundlich adsorption affinity.

Figures 6 and 7 show the performance of the isotherms in their linearized forms.

From Figure 6, we note that the linearization of the adsorption isotherms of copper bentonite is satisfactory with good correlation coefficients. We can say that the Freundlich model is adequate for a good description of the adsorption isotherms. The various constants derived equations of the lines obtained are summarized in Table 3.

Note that according to the R^2 values of different models studied the adsorption of copper in phosphoric acid follows the Freundlich model.

The application of the linearized forms of Langmuir and Freundlich laws has verified that the latter model was applicable and that the removal efficiency of copper varies in the same direction with the Freundlich model.

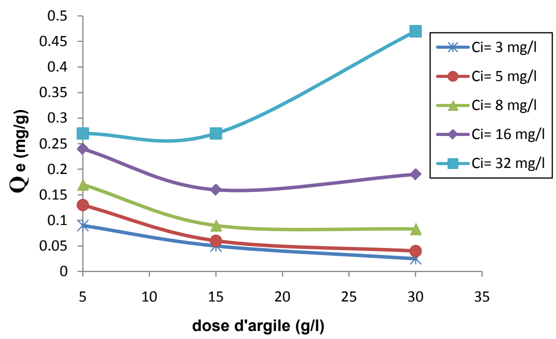

Figure 5: Effect of solid/ iquid ratio on the adsorbed amount of Cu^{2+} for different initial concentrations of copper at 25°C.

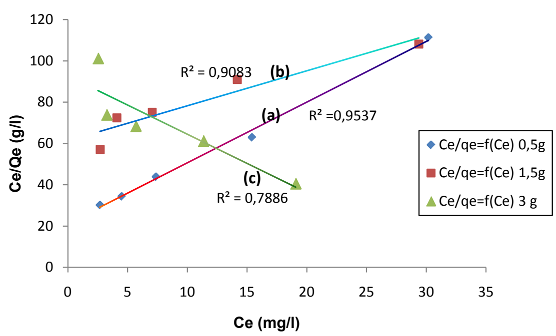

Figure 6: Modeling of adsorption isotherms of copper by the bentonite according to the Langmuir model at 25°C.

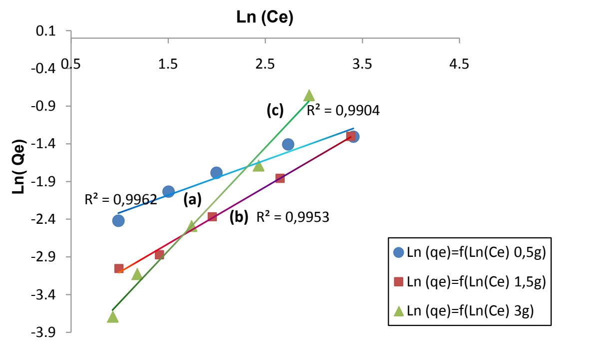

Figure 7: Modeling of adsorption isotherms of copper by the bentonite according to the model of Freundlich at 25°C.

Conclusion

Bentonite that we used in this study was moderately effective for the removal of copper from phosphoric acid. She gave us a yield of 23% removal for low initial concentrations of copper in varying doses of 5 to 15 g/l and a yield of 43% for an initial content of 32 ppm copper and a dose of 30 g of clay. The maximum retention capacity of copper to an initial copper concentration of 32 mg/l is 0.47 mg/g for a clay dosage of 30 g/l and 0.28 mg/g to a dose of 5 g/l.

The adsorption isotherms of copper on the bentonite are satisfactorily described by the Freundlich model, while the Langmuir model cannot describe our experimental results over the entire concentration range studied.

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