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Adsorption of Lead (II) onto Phosphogypsum from Liquid Effluents

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ABSTRACT

The phosphogypsum is an adsorbent which is used to remove heavy metals in aqueous media. The removal of lead by phosphogypsum was studied as a function of the contact time, the adsorbent dose and the adsorbate concentration. Phosphogypsum was prepared by wet process. The adsorption equilibrium of lead in the phosphogypsum is reached after 5 min and the absorption data have worked well at the Freundlich model. The maximum adsorption capacity of phosphogypsum was found to be 12.38 mg.g⁻¹. The Equilibrium isotherms for the adsorption of Pb (II) were analyzed by the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich models. The Freundlich isotherm model was found to represent better the data of Pb (II) sorption onto phosphogypsum. The results showed that the phosphogypsum is a suitable adsorbent for the removal of lead (II) ions from aqueous solutions.

Keywords: Adsorption, Aqueous solution, Heavy metals, Lead, Phosphogypsum

INTRODUCTION

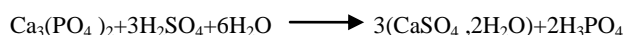
Currently, the environmental pollution by heavy metals affects the most threaten task of water sources and the atmosphere quality. The heavy metals treatment is strongly linked of their retention and persistence in the environment [1]. Lead is a heavy metal that is widely used in industries of various manufacturing processes; in addition, it has a tendency to accumulate in living bodies through the food chain and direct absorption. This can cause hypertension, reproductive disorders, neurological and metabolic problems for humans [2,3].

So, lead (II) has been classified as a hazardous heavy metal of high priority in the perspective of human and environmental risk [4-8]. Lead is also a pollutant because it is usually detected in several industrial wastewaters [9]. The phosphogypsum is a waste material of the dihydrate wet phosphoric acid process. This material used for the elimination of lead of wastewater [10,11]. The removal of lead has been studied by several adsorbents [12]. These adsorbents were used in raw materials or with modified surface [13]. Thus, for the removal of lead from liquid effluents there is a demand to find efficient and low cost adsorbent [14]. The adsorption process has come to the forefront as one of the major techniques for heavy metal removal from wastewaters [15,16].

In this work, we studied the influence of different process variables on the adsorption of lead by phosphogypsum, such as contact time, adsorbent dosage and adsorbate concentration. The adsorption isotherms were obtained and modeled according to Langmuir, Freundlich, Temkin and Dubinin-Radushkevich models. So, the main goal of this work is to use this material to remove Pb (II) from aqueous solutions using the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich models.

MATERIALS AND METHODS

Firstly, phosphogypsum used as adsorbent in this study was obtained according to the wet process of producing phosphoric acid. Using industrial phosphoric acid (30% P₂O₅) for the purpose prepared phosphogypsum by attack of tricalcium phosphate with sulfuric acid by mechanically stirring the prepared solution at a reaction temperature of 80°C [5]. The attack reaction is:



The metal solution was prepared and used in the laboratory as well as the simulated stock solution of Pb (II) was prepared by dissolving the required amount of Pb (NO₃)₂ in distilled water. A quantity of phosphogypsum was mixed with a volume of the solution containing Pb (II) at a temperature T=25°C and pH=5.14. Then we stirred the mixture, after filtration and recovering the solution that we analyzed using atomic absorption spectroscopy.

RESULTS AND DISCUSSION

Effect of contact time

Generally the study of adsorption kinetics is a mandatory prerequisite for determining the contact time or the necessary balance of lead adsorption process on the phosphogypsum that will help us to achieve the following experiences of adsorption isotherms for the metal. The equilibrium time is a significant effect of selecting a wastewater treatment scheme, where the time consumed for wastewater disposal should be measured. As shown in Figure 1 the sorption of Pb (II) onto the phosphogypsum was very fast and equilibrium was reached within 5 min.

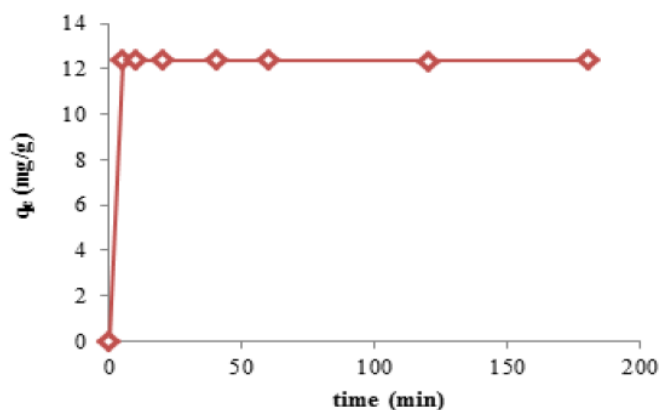


Figure 1: Effect of contact time on adsorption of Pb (II)

Effect of adsorbent concentration

The study of the effect of phosphogypsum concentration varies from 5-35 g/l to determine the optimum amount that would need to be used in a volume of the contaminated contraction solution of 652 ppm. The results obtained in this study are illustrated in Figure 2.

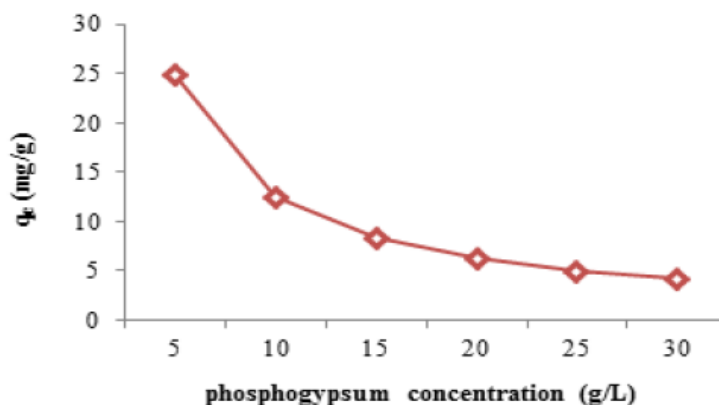


Figure 2: Effect of phosphogypsum concentration on adsorption of Pb (II)

The results show that the absorption of the Pb ions decreases with the increase of the phosphogypsum mass.

Effect of initial concentration of heavy metal

The adsorption isotherm was performed with different initial concentration of metal studied for an adsorbent dose of 10 g/l. The contact time is 1 h. Figure 3 illustrates the adsorption of the isotherm of lead on the phosphogypsum.

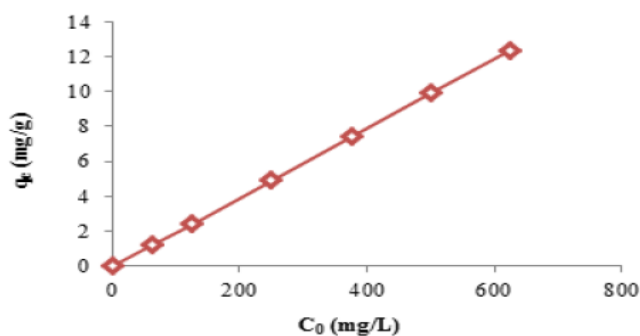


Figure 3: Effect of initial concentration on adsorption of Pb (II)

From the results of this figure, it can be seen that the percentage of elimination increases with the increase of initial concentration. Sufficient adsorption sites are available at higher initial concentrations.

ADSORPTION ISOTHERMS

Langmuir isotherm

Langmuir indicates the equilibrium distribution of metal ions between the solid and liquid phases [17]. The Langmuir isotherm is admissible for single-layer adsorption on a surface containing a finite number of similar sites. The model assumes uniform energies of adsorption on the surface and no adsorbate transmigration in the plane of the surface (Figure 4). Based on these assumptions, the following equation was represented by Langmuir:

$$C_e/q_e = 1/bq_0 + (1/q_0) C_e$$

Where, C_e =Equilibrium concentration of the adsorbate (mg/L^{-1}), q_e =Amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g), q_0 =Maximum adsorption capacity (mg/g), b =Equilibrium constant adsorbate-adsorbent.

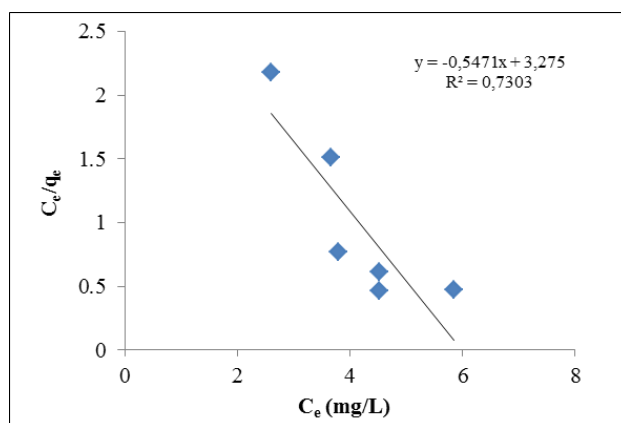


Figure 4: Langmuir adsorption isotherms

Freundlich isotherm

This is conventionally used to describe the adsorption characteristics for the heterogeneous surface (Figure 5). These data often correspond to the empirical equation allocated by Freundlich [18]:

$$q_e = k_f C_e^{1/n}$$

Where, K_f =Freundlich isotherm constant (mg/g), n =Adsorption intensity, C_e =Equilibrium concentration of adsorbate (mg/L), q_e =Amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g). The linear expression is:

$$\log q_e = \log K_f + (1/n) \cdot \log C_e$$

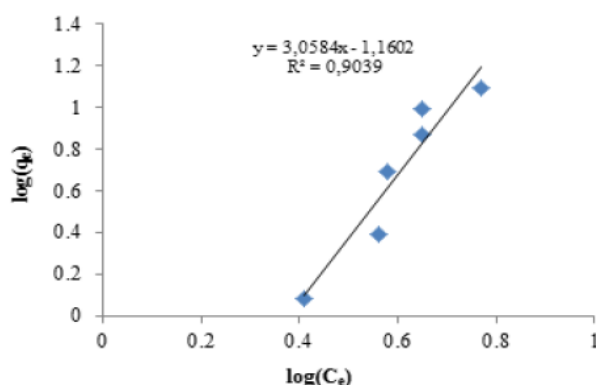


Figure 5: Freundlich adsorption isotherms

Temkin isotherm

This isotherm has a factor that explicitly takes into account the adsorbent-adsorbate interactions (Figure 6). By ignoring the very low and high value of the concentrations, model augurs that the heat of adsorption (function of temperature) of all the molecules of the layer would decrease linearly rather than logarithmically with coverage. As is implicit in the equation, the derivation is determined by a uniform distribution of binding energies (up to a certain maximum bonding energy), by tracing the sorbed quantity q_e against $\ln(C_e)$ and the constants were determined from slope and intercept. The model is given by according to equation [19]:

$$q_e = (R/b_T) \cdot \ln(A_T C_e)$$

Where, b_T and A_T are Temkin isotherm constants, R : Constant gaz universel ($8.314 \text{ J.K}^{-1}.\text{mol}^{-1}$), C_e : the equilibrium concentration of metal ions (mg/l), T : the absolute temperature. The linear expression is:

$$q_e = B \ln(A_T) + B \ln C_e$$

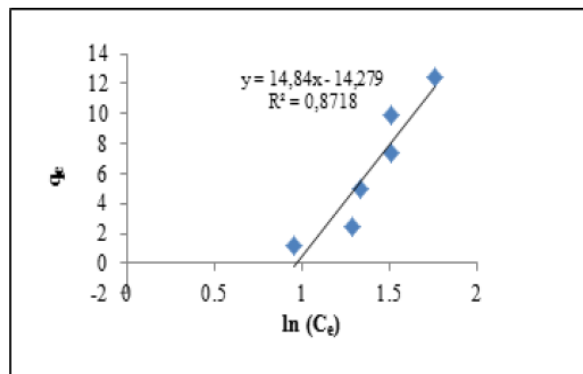


Figure 6: Temkin adsorption isotherms

Dubinin–Radushkevich isotherm

The Dubinin-Radushkevich isotherm is an empirical model that has been stated for the adsorption process according to a filling pores mechanism. It is commonly applied to present the adsorption process on homogeneous and heterogeneous surfaces (Figure 6). The nonlinear expression of the Dubinin-Radushkevich isothermal model can be named by equations (a) and (b) [20]:

$$q_e = (q_s) \exp(-K_{ad} \epsilon^2) \quad (a)$$

$$\epsilon = RT \ln(1 + 1/C_e) \quad (b)$$

Where, q_s (mg P/g) is a constant in the Dubinin-Radushkevich isotherm model which are united to the adsorption capacity, K_{ad} (mol^2/kJ^2) is a constant in allied to the mean free energy of adsorption, R ($\text{J.K}^{-1}.\text{mol}^{-1}$) is the gas constant T (K) is the absolute temperature (Figure 7).

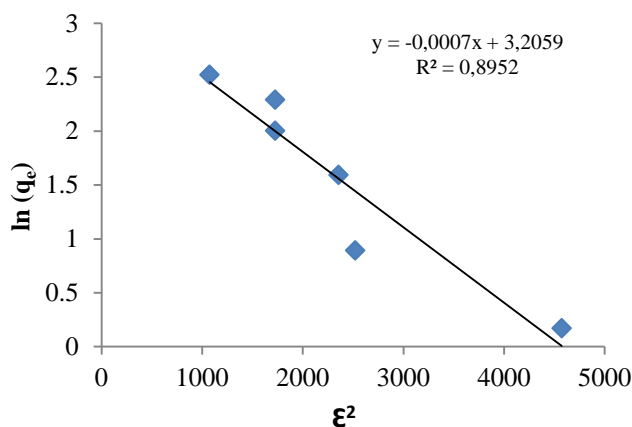


Figure 7: Dubinin–Radushkevich adsorption isotherms

The correlation coefficients of Langmuir, Freundlich, Temkin and Dubinin-Radushkevich models are respectively, 0,7303; 0,9039; 0,8718 and 0,8952. Therefore, The Freundlich equation can be escaped from a desirable $R^2=0,9039$. We can conclude that the adsorption of Pb (II) on phosphogypsum follows very well the model of Freundlich (Table 1).

Table 1: Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm parameters

Langmuir parameters	$ q_0 $ (mg/g)	$ b $ (L/mg)	R^2
	1,828	0,167	0,7303
Freundlich parameters	K_f	n	R^2
	0,069	0,327	0,9039
Temkin parameters	A_T (L/g)	B	R^2
	2,616	14,84	0,8718
Dubinin-Radushkevich parameters	q_s (mg P/g)	K_{ad} mol^2/kJ^2	R^2
	24,68	0,0007	0,8952

CONCLUSION

In present study, it was investigated that the lead adsorption process is dependent on phosphogypsum dosage and initial Pb (II) concentration. Freundlich model is the better method to remove lead. It concluded that phosphogypsum can be used effectively to remove Pb (II) from aqueous media and can be seen as an alternative approach for the treatment of Pb (II) polluted aqueous solutions. Indeed, the results of this article have shown the potential of phosphogypsum as an economical and excellent adsorbent for the removal of metal ions from infected waters.

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