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Application of Box-Behnken Design for the removal of copper in aqueous solutions by phosphogypsum

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Abstract

In this experiment we are going to study the removal of Cu (II) ion from aqueous solution by phosphogypsum. The removal capacity of phosphogypsum was studied as a function of the influential factors like the contact time between the adsorbate and adsorbent, the concentration of the metal ion Cu (II) and the concentration of phosphogypsum. The method is based on modeling and optimizing by Box-Behnken Design. The maximum adsorption is 9,49 mg/ g of Cu (II) in the phosphogypsum and the equilibrium time was attained at 12,5 min.

Keywords: Phosphogypsum, adsorption, copper, aqueous solutions and Box-Behnken Design.

Introduction

The elimination of heavy metals from aqueous solution is important to protect public health [1-3], since, most of the metal ions are toxic to living organisms, and have the ability to accumulate all along the food chain [4, 5]. Among these metals, there is copper. The international regulations impose a limit concentration of copper which is 1mg / L in waters and wastewaters [6-8]. It was found that the accumulation of copper in the brain, liver, pancreas and human myocardium may cause Wilson's disease [9, 10]. The objective of this work is to study the possibility of removing the copper existence in aqueous solutions by adsorption on the phosphogypsum. The influential factors are the contact time between the adsorbate and adsorbent, the concentration of the metal ion Cu (II) and the concentration of phosphogypsum. We model and optimize the adsorption of Cu (II) on the phosphogypsum using Box Behnken experimental design [11-16].

2. Materials and methods

We prepare the phosphogypsum per attack of tricalcium phosphate with sulfuric acid with the presence of industrial phosphoric acid (30% P_2O_5). The attack reaction is:

$$Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O \longrightarrow 3(CaSO_4, 2\ H_2O) + 2H_3PO_4$$

The prepared solution was mechanically stirred at a reaction temperature of 80 ° C. After one hour of maturation, the solution is filtered hot, to retrieve the first filtrate which is phosphoric acid. Then the phosphogypsum was washed with hot water double distilled and pure acetone. It is finally dried in an oven overnight at a temperature of 80 ° C.

The metal solution has been prepared and used in the laboratory. Simulated stock solution of Cu (II) was prepared by dissolving required quantity of copper sulfate ($CuSO_4$, $7H_2O$) salt in the distilled water. The stock solution was further diluted with distilled water to desired concentrations.

We mix a quantity of phosphogypsum with a volume of the solution containing Cu (II) at a temperature T = 21, 8 ° C and pH = 5, 25. Then we agitate the mixture, after filtration and recovery of the solution which we'll analyze by the atomic absorption spectroscopy.

3. Results and discussion

3.1. Adsorbent: Phosphogypsum.

The powder x-ray diffraction pattern of phosphogypsum is reported in figure 1, and Figure 2 presents the infrared spectra of phosphogypsum prepared.

The analysis of diagrams given by the diffraction of the X-rays shows that the main observed phases are the sulfate of calcium hemihydrate ($CaSO_4.1/2\ H_2O$) and dihydrate ($CaSO_4.2H_2O$), and these phases are always mixed by the brushite ($CaHPO_4,2H_2O$). The analysis of IR spectra confirms the existence of the phases quoted above [17].

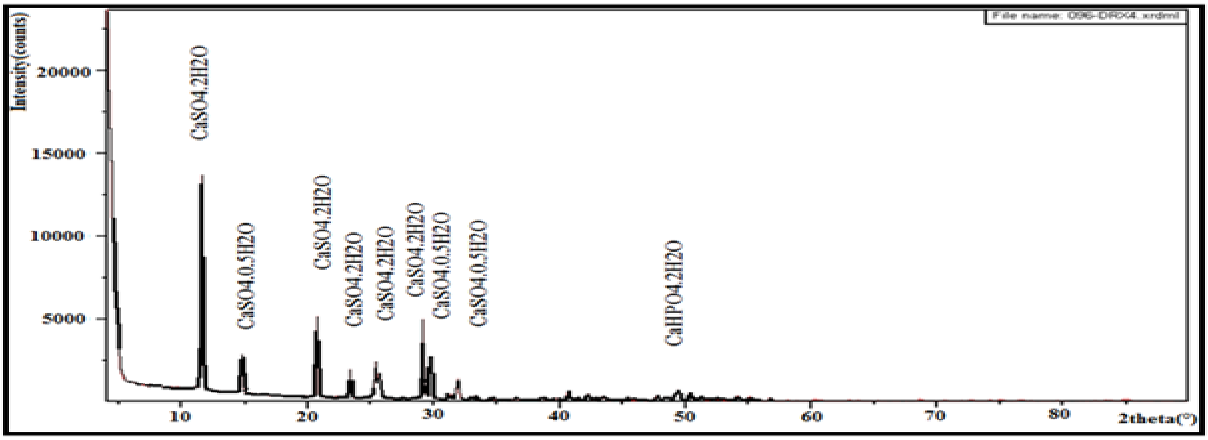

Figure 1: The powder X-ray diffraction pattern of phosphogypsum.

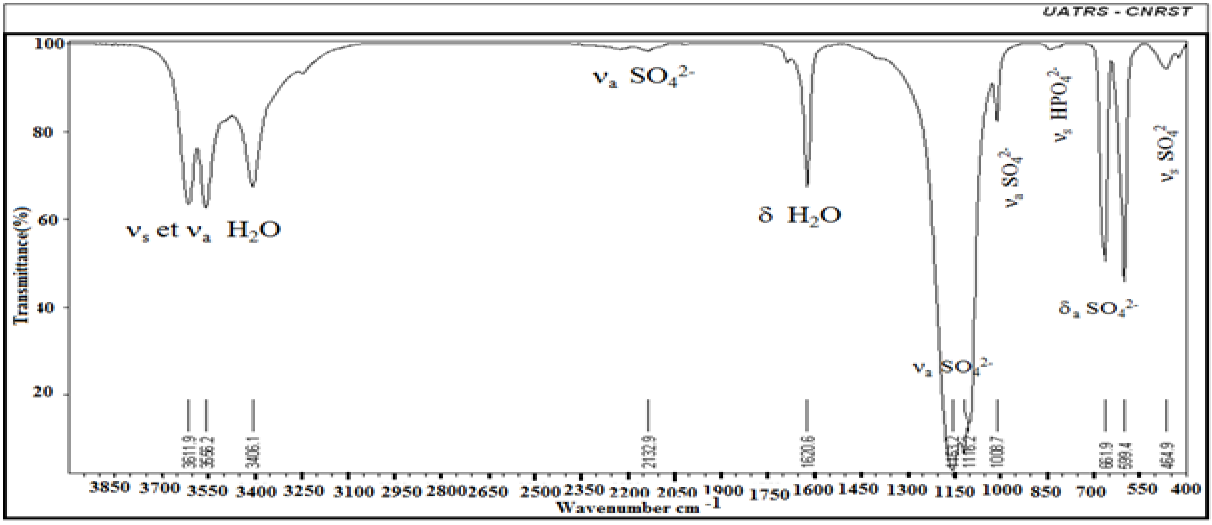

Figure 2: Infrared absorption spectrum of phosphogypsum.

3.2. Isotherms: Langmuir, Freundlich and Temkin

The equilibrium data obtained were described by the following three widely used isotherms. Langmuir isotherm is: $Ce/qe = 1/bq_0 + (1/q_0)\ Ce$, With Ce is the equilibrium concentration ($mg \cdot L^{-1}$) and q_e is the mass of copper adsorbed per unit mass of phosphogypsum (mg · g-^{1}), b is the equilibrium constant adsorbate-adsorbent and q_0 is the maximum adsorption capacity [18].

Freundlich isotherm is: qe = kf Ce$^{1/n}$ Where K_F and n are Freundlich constants, the linear expression is: log q_e = Log K_F + 1/n log Ce [19].

Temkin isotherm is: q_e =(R_T/b_T). ln(A_TC_e), Where b_T and A_T are Temkin isotherm constants. R: ideal gas constant (8,314 K J/ mol). 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 Ce [20].

Figures 3 (a), (b) and (c) represent the isotherms adsorption of Cu^{2+} on the phosphogypsum: Langmuir Freundlich and Temkin, and Table 1 shows the parameters of these isotherms.

The correlation coefficients of Langmuir, Freundlich and Temkin models are 0,037, 0,964 and 0,908 respectively. Therefore, the Freundlich equation can be fitted with a desirable R^2 =0,964. We can conclude that the adsorption of Cu^{2+} of phosphogypsum follows very well the model of Freundlich.

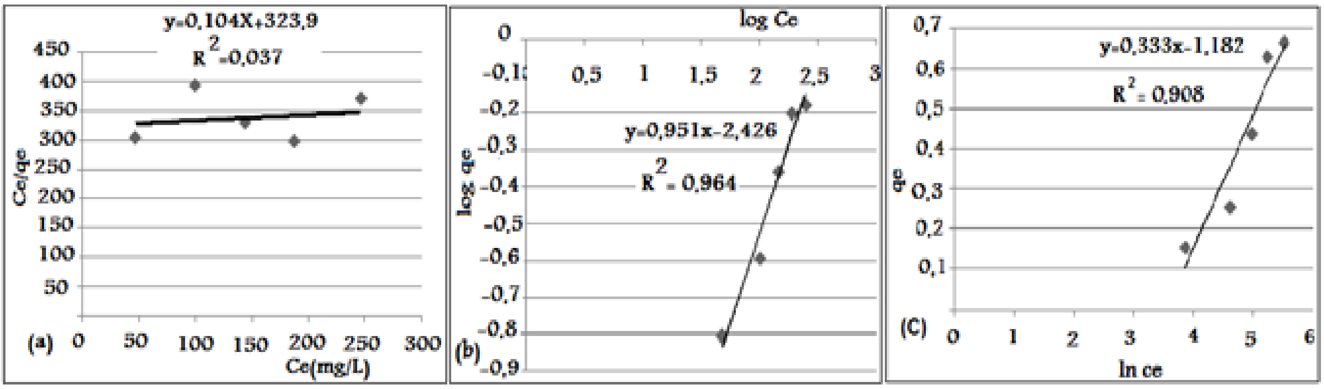

Figure 3: Isotherm model for Cu (II) adsorption on phosphogypsum: (a) Langmuir plot, (b) Freundlich plot, **(c)** Temkin plot.

Table 1: The isotherm parameters of Langmuir, Freundlich and Temkin

Langmuir parameters	q_0 (mg/g)	b (L/mg)	R^2
	9.6154	0.0003	0.0370
Freundlich parameters	K_F	n	R^2
	0.0037	1.0515	0.9640
Temkin parameters	A_T (L/g)	B	R^2
	0.0287	0.333	0.9080

3.3. Modeling by the plans of experiments: Box-Behnken design.

The influential factors are the contact time between the adsorbate and adsorbent, the concentration of Cu (II) and the concentration of phosphogypsum. The entire experimental domain is defined by the coded variables Xi and natural variables xi which are shown in Table 2.

Table 2: The Factors affecting the adsorption of Cu (II) ion in the phosphogypsum

Coded variables Xi	X_1, X_2, X_3	-1	0	1
Natural variables xi	x_1=time (min)	10	15	20
	x_2=[Cu^{2+}] (mg/L)	100	150	200
	x_3= [PG] (g/L)	10	15	20

Table 3 presents the different experiences depending Box-Behnken design for different factors influencing the adsorption of Cu (II) on the phosphogypsum and table 4 shows the analysis of variance.

The equation of the model:

$$Y= 0.007+0.0325X_1 + 0.0025X_2 – 0.0725X_3 + 0.003 X_1X_3 - 0.02X_2X_3 – 0.0725X_1^2 + 0.0825X_2^2 + 0.2325 X_3^2$$

For an estimate of 63 % the model is:

$$Y= 0.007 + 0.0325X_1 + 0.0025X_2 + 0.003 X_1X_3 - 0.02X_2X_3$$

Table 3: Three factor Box-Behnken design with experimental as well as predicted responses of dependent variable

N° test	X_1	X_2	X_3	Y (mg/g)
1	-1	-1	0	0.07
2	1	-1	0	0.07
3	-1	1	0	0.09
4	1	1	0	0.09
5	-1	0	-1	0.08
6	1	0	-1	0.15
7	-1	0	1	0.25
8	1	0	1	0.44
9	0	-1	-1	0.63
10	0	1	-1	0.66
11	0	-1	1	0.15
12	0	1	1	0.10
13	0	0	0	0.09
14	0	0	0	0.06
15	0	0	0	0.06

Table 4: Analysis of variance

Source	**Response value**
Rsquare	0.511585
Rsquare Adj	-0.36756
Root Mean Square Error	0.241143
Mean of Response	0.199333
Observations (or Sum Wgts)	15

Results of variance analysis are presented in Table 5. From the regression model of adsorption of Cu (II) on phosphogypsum, the model terms X_1 and X_2 were significant with a probability superior to 63 %. The terms X_1X_3 and X_2X_3 were also significant indicating that there was interaction between contact time and phosphogypsum concentration as well as phosphogypsum concentration and copper concentration. The interaction between the terms X_1 and X_2 however had no significant effect on the adsorption. Also the terms X_3, X_1^2, X_2^2, X_3^2 had no significant effect.

3.4. Optimization of the Cu (II) adsorption on the phosphogypsum

Figure 4(a), (b) and (c) show isoresponse curves adsorption of Cu (II) on the phosphogypsum. The analysis of these curves shows that the contact time is very fast and it is less than 15 min and the best adsorption is given by the figure 4 (b), thus the optimum is given as follows: For a contact time equal to 12, 5 min, the concentration of copper is 150 mg/L and the concentraton of phosphogypsum is 15.80 g/L, whether 9.49 mg/ g of Cu (II) in the phosphogypsum.

Table 5: Analysis of variance for the adsorption of Cu (II) on the phosphogypsum

Source	**Nparm**	**DF**	**Sum of squares**	**F Ratio**	**Prob> F**
X_1-contact time	1	1	0.00845000	0.1453	0.7187
X_2-[Cu^{2+}]	1	1	0.00005000	0.0009	0.9777
X_3-[PG]	1	1	0.04205000	0.7231	0.4339
X_1X_1	1	1	0.01940769	0.3338	0.5885
X_2X_1	1	1	0.00000000	0.0000	1.0000
X_2X_2	1	1	0.02513077	0.4322	0.5400
X_3X_1	1	1	0.00360000	0.0619	0.8134
X_3X_2	1	1	0.00160000	0.0275	0.8748
X_3X_3	1	1	0.19959231	3.4324	0.1231

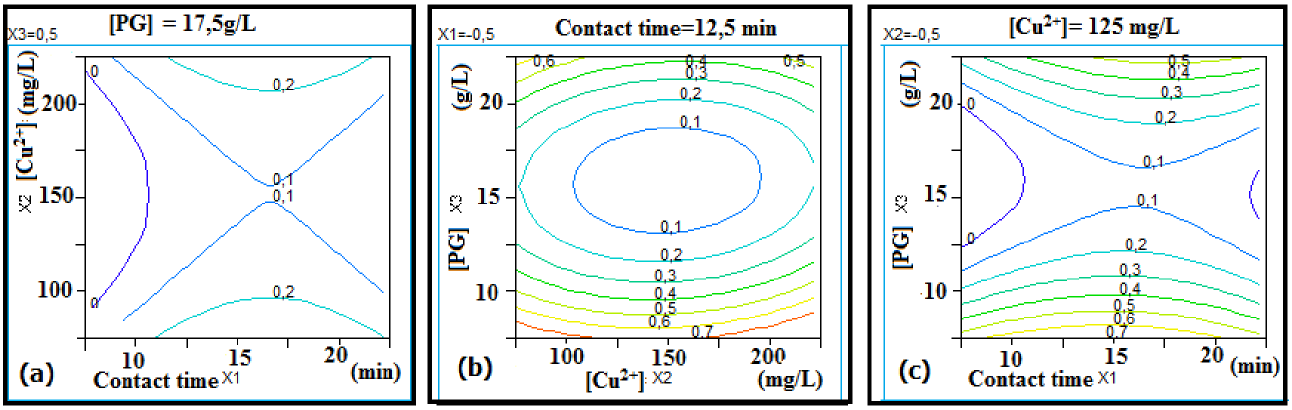

Figure 4: Isoresponse curves adsorption of Cu (II) on the phosphogypsum, (a) Concentration of Cu (II) and contact time, (b) Concentration of phosphogypsum and concentration of Cu II, (c) Concentration of phosphogypsum and contact time.

Conclusion

In this work, we have studied the adsorption of copper in phosphogypsum. The adsorption follows the Freundlich isotherm and it's a very good method to remove some impurities such as copper, which is a toxic element in the aqueous solution if it exceeds the standards. Therefore, the phosphogypsum presents a major advantage of giving low cost recovery processes making them suitable for use in aqueous solutions purification.

The equation of the model given by box Behnken design is:

$$Y= 0.007 + 0.0325X_1 + 0.0025X_2 + 0.003\ X_1X_2 - 0.02X_2X_3$$

At the contact time equal to 12, 5 min, the optimum is 9, 49 mg.g^{-1} of Cu (II) in the phosphogypsum. The same work was made for Zn (II), the optimum was 9.30 mg.g^{-1}[21].

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