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The Removal of Zinc in an Aqueous Solution by the Phosphogypsum: Modeling and Optimizing

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ABSTRACT

Background: This work is devoted to study the removal of Zn (II) by phosphogypsum which is a waste from the manufacture of phosphoric acid. Therefore we can use it in the removal of some impurities such as Zn (II). Our method is based on modeling the adsorption of Zn (II) on the phosphogypsum, by the contribution of Langmuir, Freundlich and Temkin isotherms, in the first hand. In the second hand, we are going to model and optimize with experimental design: Box-Behnken Design. The factors that affect this study are: the contact time between the adsorbate and adsorbent, the concentration of the metal ion Zn (II) and the concentration of the phosphogypsum. **Objective:** Modeling and optimization the removal of Zn^{2+} from the aqueous solution by the phosphogypsum. **Results:** The adsorption of Zn (II) on the phosphogypsum follows the Freundlich isotherm. The modeling and the optimization by Box-Behnken give that the best elimination of Zn (II) requires a contact time equal 12,5 min and the adsorbed quantity is equal to 9,30 mg of Zn^{2+} by gram of phosphogypsum. **Conclusion:** The adsorption follows the Freundlich isotherm and The optimum given by Box-Behnken is 152, 6 mg / L of $[Zn^{2+}]$ for 16, 4 g/L of phosphogypsum. The phosphogypsum can be used for the treatment of the aqueous solutions polluted by Zn (II).

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INTRODUCTION

Most of heavy metal ions are toxic to living organisms, and have the ability to accumulate all along the food chain (Saidi, 2010; Benguella and Benaissa, 2002; Youcef and Achour, 2006). Among these metals is zinc which toxicity symptoms can be gastric disturbance, cardiac arrhythmia among others (Salgueiro *et al*., 2000; Joseph *et al*., 2013). Increased serum and urine levels of zinc were observed in humans and animals after oral inhalation and dermal exposure to zinc (Bentley and Grubb, 1991; Brandao-Neto *et al*., 1990). The world health organization has recommended that the concentrations of this ion in drinking water mustn't exceed 0,5mg/L. The same recommendation is applicable to industrial effluents containing this heavy metal before it is released to the environment (Joseph *et al*., 2013). Consequently, it is essential to eliminate the zinc ion from the aqueous solution on the one hand.

In fact, Morocco has three quarters of global reserves of phosphate ores and ranks first in the export. Moroccan phosphate sedimentary series contains relatively large amounts of associated minerals (Chafik *et al*., 2013; Bilali *et al*., 2001). The manufacture of wet phosphoric acid is obtained by a sulfuric acid attack of the phosphate rock (Govere *et al*., 1995; Bchitou *et al*.; 1998). This attack generates the acid and the phosphogypsum which is a waste, therefore the manufacture of one ton of the phosphoric acid produces about 5 tons of phosphogypsum (Sfar Felfoul *et al*., 2002), on the second hand, it is necessary to use the phosphogypsum for the removal of some impurities such as Zn^{2+} from the aqueous solution and this is the objective of our research in this article.

The influential factors are: the contact time between the adsorbate and adsorbent, the concentration of the metal ion Zn^{2+} and the concentration of phosphogypsum. In Part One, we have studied the effects of these factors using the Langmuir isotherm model, Freundlich and Temkin. The adsorption models are shown in table 1.

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Table 1: Adsorption models

Isotherm model	Equation	Linear expression	Plot	Parameters	Reference
Langmuir	$q_e = \frac{b\,q_0 C_e}{1+bC_e}$	$\frac{Ce}{qe} = \frac{Ce}{q_0} + \frac{1}{bq_0}$	$\frac{Ce}{qe}$ vs Ce	B and q_0	Langmuir (1918)
Freundlich	$q_e = K_F Ce^{1/n}$	log q_e = Log K_F + 1/n log Ce	log q_e vs log Ce	K_F and n	Freundlich (1926)
Temkin	$q_e = B.\ln(A_T Ce)$ $B = R_T/b_T$	$q_e = B \ln A_T + B \ln Ce$	q_e vs ln Ce	B and A_T	Temkin (1940)

In second Part, we are going to model and optimize the adsorption of Zn^{2+} on the phosphogypsum by Box-Behnken experimental design (Chafik *et al*., 2014; Bchitou *et al*., 1996; Goupy, 1988; Sado and Sado, 1991; Amenaghawon *et al*., 2013**;** Tekindal *et al*., 2012).

MATERIALS AND METHODS

Preparation of phosphogypsum:

The attack of tricalcium phosphate by the sulfuric acid produces the phosphoric acid and the phosphogypsum according to the following reaction:

$$Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O \xrightarrow[T=80°\,C]{H_3PO_4(30\%)\ P_2O_5} 3(CaSO_4{,}2\,H_2O) + 2H_3PO_4$$

The prepared solution was mechanically stirred at temperature of 80 ° C. After one hour and half 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 for 24 hours at a temperature of 80 ° C.

Preparation of metal ion Zn^{2+}

The solution of Zn^{2+} was prepared by dissolving required quantity of zinc sulfate ($ZnSO_4$, $5H_2O$) salt in the distilled water. The stock solution was further diluted with distilled water to desired concentrations.

Finally, we mixed a quantity of phosphogypsum with a volume of the solution containing Zn^{2+} at a temperature T = 21, 8 ° C and pH = 6, 57. Then we agitated the mixture, after filtration and recovery of the solution, it was analyzed by the atomic absorption spectroscopy.

RESULTS AND DISCUSSIONS

The influence of agitation time and the density of the phosphogypsum on the adsorption of Zn^{2+} on phosphogypsum:

Fig. 1 shows the influence of the contact time on the adsorption of Zn^{2+} on the phosphogypsum and fig. 2 represents the percentage of adsorption depending on the density of phosphogypsum.

The analysis of the kinetic curve shows that the adsorption of Zn^{2+} on the phosphogypsum is changing rapidly during the first minutes of the reaction. The fast adsorption kinetics can be explained by the fact that at the beginning of adsorption, the number of the active sites available on the surface of the adsorbing material is much more important than that of the sites remaining after.

For the optimum influence of the phosphogypsum concentration, we note that the more this quantity is high the more the adsorption of Zn (II) is higher.

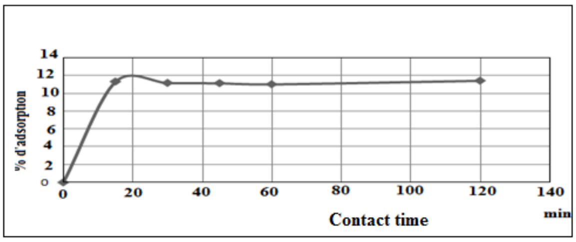

Fig. 1: Influence of the contact time on the adsorption of Zn^{2+} on the phosphogypsum; $[Zn^{2+}]$= 1000 mg/L, V=50mL, pH=6,57, T=21,8°C.

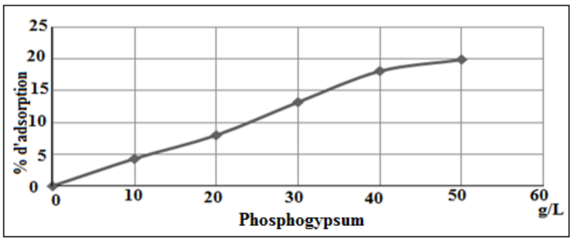

Fig. 2: Influence of phosphogypsum density on the adsorption of Zn (II); $[Zn^{2+}]$= 1000mg/L, V=50mL, pH=6,57, T=21,8°C, contact time: 1H.

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Isotherms: Langmuir, Freundlich and Temkin:

Fig. 3, 4 and 5 represent respectively the isotherms of Langmuir, Freundlich and Temkin of the adsorption of Zn^{2+} on the phosphogypsum (PG) and table. 2 illustrates the parameters of these isotherms.

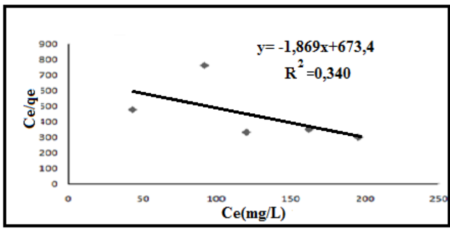

Fig. 3: isotherm models for Zn (II) adsorption on PG: Langmuir plot.

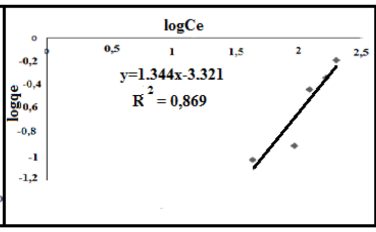

Fig. 4: isotherm models for Zn (II) adsorption on PG: Freundlich plot.

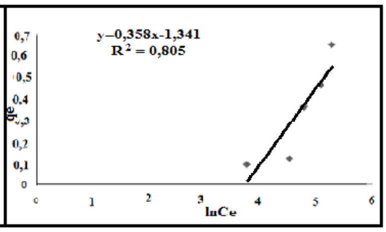

Fig. 5: isotherm models for Zn (II) adsorption on PG: Temkin plot.

Table 2: The parameters of the isotherms of Langmuir, Freundlich and Temkin

Parameters of Langmuir	q_0 (mg/g)	b (L/mg)	R^2
	-0,535	-0,0027	0,340
Parameters of Freundlich	KF	n	R^2
	0,00047	0,744	0,869
Parameters of Temkin	A_T (L/g)	B	R^2
	0,0236	0,358	0,805

We notice that the adsorption of Zn (II) on the phosphogypsum follows the isotherm of Freundlich. We can conclude that the phosphogypsum is the best method to remove Zn (II) from the aqueous solution.

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

Our study allowed us to highlight the factors which influence the adsorption of zinc ion on the phosphogypsum which are: the time of contact, the concentration of the metal ion and the concentration of the phosphogypsum. The whole experimental domain is defined by coded variables Xi and natural xi which are represented in the table 3.

Table 3: The factors which influence the adsorption of the ion Zn^{2+} on the phosphogypsum

coded variables	X_1, X_2, X_3	-1	0	1
Natural variables xi	x_1=t : min	10	15	20
	x_2=[Zn^{2+}] : mg/L	100	150	200
	x_3= [PG] : g/L	10	15	20

The table 4 represents the various experiments realized according to a Box-Behnken plan for the various factors which influence the adsorption of Zn^{2+} on the phosphogypsum.

Table 4: Matrix of the model of the adsorption of Zn^{2+} on the phosphogypsum

N° test	X1	X2	X3	Y(mg/g)
1	-1	-1	0	0,06
2	1	-1	0	0, 06
3	-1	1	0	0,04
4	1	1	0	0,05
5	-1	0	-1	0,06
6	1	0	-1	0,09
7	-1	0	1	0,12
8	1	0	1	0,36
9	0	-1	-1	1,46
10	0	1	-1	1,65
11	0	-1	1	0,05
12	0	1	1	0,03
13	0	0	0	0,05
14	0	0	0	0,05
15	0	0	0	0,04

The model equation is:

$Y= 0{,}0467 + 0{,}035X_1 + 0{,}0175X_2 – 0{,}0875X_3 +0{,}0025\, X_1X_2+ 0{,}0525\, X_1X_3 - 0{,}0525X_2X_3 – 0{,}0671X_1^2 + 0{,}0729\, X_2^2 + 0{,}1779\, X_3^2$

For an estimate of 65% the model will be:

$Y= 0{,}\ 0467 + 0{,}035X_1 + 0{,}0175X_2 +0{,}\ 0025\, X_1X_2+ 0{,}\ 0525\, X_1X_3 - 0{,}0525X_2X_3$.

Optimization:

Fig. 6 represents the isoréponse curves of the adsorption of Zn (II) on the phosphogypse. We notice that for a good adsorption of Zn^{2+} on the phosphogypsum, the concentration of Zn^{2+} is equal to 152, 6 mg / L and the concentration of phosphogypsum is 16,4 g/L For a contact time equal to 12,5 min, whether 9,30 mg of Zn^{2+} per gram of phosphogypsum.

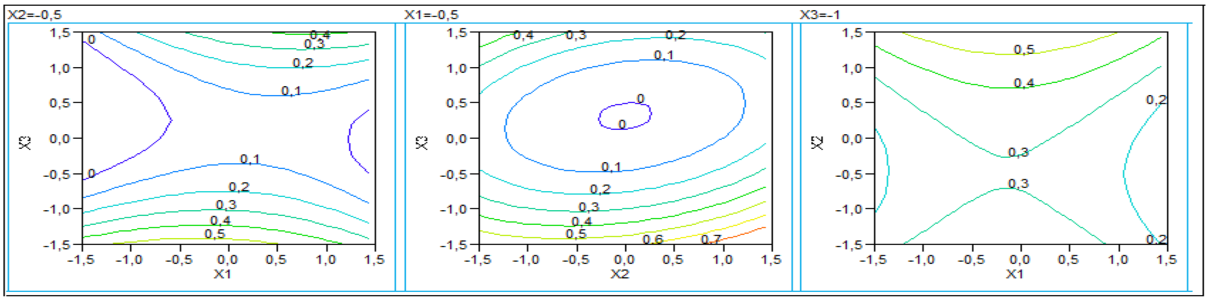

Fig. 6: The isoresponse adsorption curves of Zn (II) on the phosphogypsum, pH = 6, 57, T = 21, 8 ° C.

Conclusion:

This article illustrates the removal of Zn (II) by the adsorption on the phosphogypsum, this study showed that the adsorption follows the Freundlich isotherm and the model given by the plans of experiments (Box-Behnken) with 65 % estimation is the following one:

$Y= 0, 0467 + 0,035X_1 + 0,0175X_2 +0, 0025 X_1X_2+ 0, 0525 X_1X_3 - 0,0525X_2X_3$.

For a contact time equal to 12,5 min, the concentration of Zn^{2+} is equal to 152, 6 mg / L at a concentration of phosphogypsum is equal to 16.4 g / L.

We can conclude that the phosphogypsum can be used for the treatment of the aqueous solutions polluted by Zn (II) and also a way of elimination of the other impurities.

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