Modeling and Optimization of Adsorption and Removal of Cd(II) from Aqueous Solution by Phosphogypsum

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Received: 1 July 2014;

Accepted: 10 October 2014;

Published online: 1 December 2014;

AJC-16410

The aim of this work is the modeling and the optimization of the adsorption and the removal of cadmium by the phosphogypsum from aqueous solution. Generally, the attacks of the phosphate rock react with sulfuric acid to produce a major product phosphoric acid and phosphogypsum as a by product. This latter could be used for removing inorganic heavy metal impurities such as cadmium from aqueous solutions. We have applied two techniques for the modeling and the optimization of the removal of cadmium: First, we have used the technique of isotherms of Langmuir, Freundlich and Temkin in order to evaluate the metal quantity adsorbed. Second, we adopted the technique of Box-Behnken design experiments. The determining factors for the processes are the contact time, the concentration of Cd(II) and the phosphogypsum. The optimum concentration of Cd(II) adsorbed and phosphogypsum is 125 mg/L and 15 g/L, respectively at pH = 5, 84 and T = 22 °C.

Keywords: Cadmium, Phosphogypsum, Adsorption, Removal, Aqueous solutions and Box-Behnken design experiments.

INTRODUCTION

The pollution of aqueous solutions (water and waste water) with heavy metals is considered dangerous because of the great toxicity and non-biodegradability. These pollutants can be accumulated through the food chain even at a low concentration rate which is liable to lead to serious problems on aquatic life as well as to animal, plant life and human health¹⁻³. Particularly, Cd(II) is common metal ions found in effluents of a large number of industries⁴, therefore, it is necessary to design processes to effectively minimize the pollution caused by Cd(II) discharges and to reduce the risks associated with its presence in the environment. While looking for a potential tool to remove the Cd(II), we have used the phosphogypsum which is a byproduct of commercial production of phosphoric acid. About 5 tons of phosphogypsum are produced for every ton of the phosphoric acid⁵. We can use phosphogypsum to remove some impurities such as Cd(II) by adsorption which is dangerous for the health of humans, animals and for the environment⁶. The parameters that can influence the adsorption are the contact time, the adsorbate [Cd(II)] and the adsorbent (phosphogypsum). The main objective of this research is to determine and to evaluate the effects of these factors using the adsorption isotherms Langmuir, Freundlich and Temkin. Then the chemometrics methods will be used for the modeling and

optimizing the adsorption of Cd(II) on the phosphogypsum by Box-Behnken design experiments.

EXPERIMENTAL

The phosphogypsum produced during the wet process manufacture of phosphoric acid by attack of tricalcium phosphate by the sulfuric acid, the reaction is:

The prepared solution was mechanically stirred at 80 °C. After 1 h 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 h at 80 °C.

Later, a fixed quantity of phosphogypsum was dissolved with a volume of the sample solution containing a fixed concentration of Cd(II) at a temperature T = 22 °C and pH maintained at 5, 84. And the contact time varied from 0 to 2 h. In the next step, the same work for the varied cadmium concentration was carried out with 0, 2-1 g/L and the same work for the varied phosphogypsum was carried out with 10-50 g/L, to find out the effect of these parameters on the adsorption and the removal of Cd(II), after the solution is filtered and retrieved. The amount of cadmium was analyzed by ICP-AES.

RESULTS AND DISCUSSION

Effect of contact time: Fig. 1 shows the influence of the contact time on the adsorption on the phosphogypsum. The analysis of the kinetic curve shows that the adsorption of cadmium on the phosphogypsum is changing rapidly during the first minutes of the reaction. This explains probably that the rate of adsorption decreases in the later stages of the adsorption due to the slow pore diffusion of the solute ion into the bulk of the adsorbent.

Fig. 1. Effect of the contact time on the adsorption of Cd(II) on the phosphogypsum, $[Cd^{2+}] = 1$ g/L, $V = 50$ mL, $pH = 5$, 84 ; $T = 22$ °C

Effect of phosphogypsum concentration: Fig. 2 shows the effect of phosphogypsum concentration on Cd(II) adsorption. The amount of Cd(II) adsorbed by unit weight of the adsorbent decreased. The decrease in the adsorbed amount with the increase in adsorbent concentration may result from the electrostatic interactions, interference between binding sites and reduced mixing at higher concentration adsorbent⁷.

Fig. 2. Effect of phosphogypsum concentration. $[Cd^{2+}] = 1$ g/L, $V = 50$ mL, $pH = 5$, 84 , $T = 22$ °C, Contact time: 60 min

Langmuir, Freundlich and Temkin adsorption isotherms:

The Langmuir adsorption isotherm represents the distribution equilibrium of metal ions between the solid and liquid phases⁸. It is valid for monolayer adsorption onto a surface containing a finite number of identified sites. Langmuir proposed the following model⁹:

$$q_e = \frac{b \cdot q_0 \cdot C_e}{1 + b \cdot C_e}$$

The linear isotherm equation is represented as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_0} + \frac{1}{b \cdot q_0}$$

where:

- C_e the equilibrium concentration of adsorbate ($mg\ L^{-1}$)
- q_e = The amount of metal adsorbed per gram of the adsorbent at equilibrium ($mg\ g^{-1}$)
- q_0 = Maximum adsorption capacity ($mg\ g^{-1}$)
- b = Langmuir isotherm constant ($L\ mg^{-1}$)

The Freundlich adsorption isotherm¹⁰ is commonly used to describe the adsorption characteristics of the heterogeneous surface¹¹. The proposed equation is: $q_e = K_F C_e^{1/n}$

The linear form is: $\log q_e = \log K_F + 1/n \log C_e$
 K_F and n are Freundlich constants.

The derivation of the Temkin isotherm assumes that the fall in the heat of adsorption is more linear rather than logarithmic, as implied in the Freundlich equation¹². The model is given by the following equation¹³:

$$q_e = (R_T/b_T) \ln(A_T C_e)$$

The linear form is: $q_e = B \ln A_T + B \ln C_e$.

- A_T = Temkin isotherm equilibrium binding constant ($L\ g^{-1}$)
- b_T = Temkin isotherm constant
- R = Universal gas constant ($8,314\ J\ mol^{-1}\ K^{-1}$)
- T = Temperature
- B = Constant related to heat of sorption ($J\ mol^{-1}$).

Figs. 3-5 represent the isotherms adsorption Langmuir, Freundlich and Temkin of Cd(II) on the phosphogypsum and Table-1 shows the parameters of these isotherms.

The adsorption of Cd(II) on the phosphogypsum follows the isotherm of Freundlich. The determination coefficient (R^2) of the model was 0,936 (Table-1). It indicates that 93, 6 % of the variability was explained by the model and it represents the real relationship between the variables under consideration. Note also that $n = 1.61 > 1$ explains that the adsorption isotherm of Cd(II) on the phosphogypsum can be chemical.

Fig. 3. Langmuir isotherm of Cd(II) adsorbed on phosphogypsum

Fig. 4. Freundlich isotherm of Cd(II) adsorbed on phosphogypsum

Fig. 5. Temkin isotherm of Cd(II) adsorbed on phosphogypsum

TABLE-1
LANGMUIR, FREUNDLICH AND TEMKIN ISOTHERM
CONSTANTS FOR THE ADSORPTION OF Cd(II)
FROM AQUEOUS SOLUTIONS

Langmuir	q_0 (mg g ⁻¹)	b (L mg ⁻¹)	R^2
	1.022	1.82×10^{-3}	0.812
Freundlich	K_F	n	R^2
	1.32×10^{-4}	1.610	0.936
Temkin	A_T (L g ⁻¹)	B	R^2
	1.08×10^{-2}	1.181	0.766

Box-Behnken design: Modeling is to define an empirical model that describes the variations of the response Y as a function of various factors that may affect these changes¹⁴⁻¹⁶. Our research allowed to identify the factors that affect the amount of cadmium adsorbed (Y) on the phosphogypsum which are: the contact time between the adsorbate and adsorbent, cadmium concentration and phosphogypsum concentration, using Box-Behnken design experiments^{17,18}. The entire experimental domain is defined by the coded variables X_i and natural variables x_i which are shown in Table-2. The theoretical equation of the model:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2$$

where Y (Amount of cadmium adsorbed) is the predicted response, X_1 , X_2 and X_3 are the independent variables, b_0 is the offset term, b_1 , b_2 , b_3 are the linear effects and b_{12} , b_{13} and b_{23} are the interaction terms.

TABLE-2
CODED AND REAL LEVELS FOR THREE FACTORS
INVESTIGATED

Coded variables X_i	X_1, X_2, X_3	-1	0	1
Natural variables x_i				
	$x_1 = [\text{PG}]$ (g L ⁻¹)	10	15	20
	$x_2 = [\text{Cd}^{2+}]$ (mg L ⁻¹)	100	150	200
	$x_3 = \text{Time}$ (min)	10	15	20

TABLE-4
ANALYSIS OF VARIANCE FOR THE ADSORPTION OF Cd(II) ON THE PHOSPHOGYPSUM

Source	Nparm	DF	Sum of squares	F Ratio	Prob > F
X_1	1	1	0.0171	0.0382	0.8528
X_2	1	1	0.0015	0.0034	0.9559
X_3	1	1	0.6160	1.3737	0.2940
X_1X_1	1	1	0.3548	0.7912	0.4145
X_2X_1	1	1	0.0004	0.0009	0.9773
X_2X_2	1	1	0.2895	0.6455	0.4582
X_3X_1	1	1	0.0056	0.0125	0.9152
X_3X_2	1	1	0.0240	0.0536	0.8261
X_3X_3	1	1	0.9888	2.2050	0.1977

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

TABLE-3
EXPERIMENTAL MATRIX OF ADSORPTION
MODEL OF Cd ON PHOSPHOGYPSUM

N°	X_1	X_2	X_3	Y (mg g ⁻¹)
1	-1	-1	0	0.22
2	1	-1	0	0.14
3	-1	1	0	0.10
4	1	1	0	0.06
5	-1	0	-1	0.04
6	1	0	-1	0.21
7	-1	0	1	0.45
8	1	0	1	0.77
9	0	-1	-1	1.60
10	0	1	-1	1.91
11	0	-1	1	0.16
12	0	1	1	0.16
13	0	0	0	0.16
14	0	0	0	0.16
15	0	0	0	0.16

The equation of the model is $Y = 0.1600 + 0.0460X_1 + 0.0140X_2 - 0.2770X_3 + 0.0100 X_1X_2 + 0.0370 X_1X_3 - 0.0770X_2X_3 - 0.310X_1^2 + 0.2800 X_2^2 + 0.5170 X_3^2$

The analysis of variance for the adsorption of Cd(II) on the phosphogypsum shows that for an estimate of 80 %, the model is:

$$Y = 0.1600 + 0.0460X_1 + 0.0140X_2 + 0.0100 X_1X_2 + 0.0370 X_1X_3 - 0.0770X_2X_3$$

(± 0.0041) (± 0.0020) (± 0.0006) (± 0.0003)
(± 0.0011) (± 0.0023)

Optimization of the adsorption on the phosphogypsum:

In order to optimize the conditions for the removal of Cd(II) from aqueous solution and to optimize the influential variables on the adsorption, contour plots were used to investigate the effect of all the factors on the responses (Figs. 6-8).

The analysis of the plots shows the quantity of Cd(II) adsorbed on phosphogypsum was low (Figs. 6 and 7) than the amount of cadmium adsorbed in Fig. 8.

It is concluded that the optimum is 125 mg/L of cadmium on 15 g/L of phosphogypsum (Fig. 8).

Conclusion

In this paper, investigation of the equilibrium adsorption was carried out at 22 °C and pH = 5, 84. Other physico-chemical parameters were determined and three adsorption isotherm models were studied.

Fig. 6. Effect of the interaction between contact time and phosphogypsum

Fig. 7. Effect of the interaction between contact time and concentration of Cd(II)

Fig. 8. Effect of the interaction between concentration of Cd(II) and phosphogypsum

This study showed that the adsorption follows the Freundlich adsorption isotherm and the model equation by Box-Behnken design with an estimated 80 % is:

$$Y = 0.1600 + 0.0460X_1 + 0.0140X_2 + 0.0100 X_1X_2 \\ (\pm 0.0041) \quad (\pm 0.0020) \quad (\pm 0.0006) \quad (\pm 0.0003) \\ + 0.0370X_1X_3 - 0.0770X_2X_3 \\ (\pm 0.0011) \quad (\pm 0.0023)$$

The optimum is 125 mg/L from concentration of Cd(II) in 15 g/L for phosphogypsum.

It could be concluded that the phosphogypsum could be considered as a good material and alternative approach for aqueous solutions treatments polluted by Cd(II), a potential and active sorbent for removal of cadmium ions from industrial waste water remediation and a way of the removal of other impurities such as zinc¹⁹ and copper²⁰.

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