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Experimental Design Methodology Optimization of Nickel (II) Ion Removal from Aqueous Solutions Using Phosphogypsum

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ABSTRACT

The aim of this work is modeling and optimizing the removal nickel ions from aqueous solutions on the phosphogypsum. For this, a physicochemical study of the adsorption was carried out by studying the effect of some parameters on the clearance to aqueous solutions, in particular the adsorbent dosage, contact time and initial Ni(II) concentrations, on the adsorption capacity. The adsorption isotherms according to the model of Langmuir, Freundlich and Temkin were studied. The obtained results show that the adsorption of Ni(II) on the phosphogypsum follows the Freundlich isotherm. A Central Composite Design (CCD) was applied to evaluate the interactive effects of adsorption variables and to optimize the adsorption process of Ni(II) ions from aqueous solutions onto phosphogypsum. The optimal condition obtained was located and the optimum adsorption factors were predicted as a contact time of 19.02 min, initial Ni(II) concentrations of 111.80 mg/l and an adsorbent dosage of 13.90 g/l.

Key words: Phosphogypsum, Nickel, Adsorption, Waste treatment, Central composite design

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INTRODUCTION

The heavy metals may be found in wastewater. Their presences are dangerous for people, are toxic at low concentrations and accumulate in the body. Therefore, treatment of wastewater contaminated by heavy metals is an important environmental concern [1-3]. One of the important heavy metals, Nickel(II) finds its way into the water bodies through effluents from industries. It is toxic at high concentrations. It has harmful effects on the living environment [4,5]. According to recommendations of World Health Organization (WHO) and the French legislation, the limit concentration of nickel in drinking water is 20 mg/l [6]. Therefore, it is necessary to decrease the concentration of heavy metals to their permissible limits before their discharge to the environment. The EPA requires nickel in drinking water not to exceed 0.04 mg/l [7]. Nickel was selected as an adsorbate because its compounds have widespread applications in many industrial processes such as non-ferrous metal, mineral processing, electroplating, batteries manufacturing and copper sulfate manufacture [8-10]. Some nickel compounds, such as nickel carbonyl, are carcinogenic and easily absorbed by the skin [11].

The conventional methods which are commonly used for the removal of nickel from wastewater are physicochemical methods, such as ion exchange, solvent extraction, reverse osmosis and precipitation [12-15]. However, most of these techniques have high operating costs, and in some cases are limited in terms of removal efficiency of metals. Adsorption phosphogypsum is recognized as one of the best wastewater treatment techniques contaminated by heavy metals [16,17].

Central Composite Design (CCD) is undoubtedly a good technique for studying the influence of major process parameters on response factor by significantly reducing the number of experiments and optimization study using Response Surface Methodology (RSM) [18]. In this optimization method, the analyzed parameter is changed; others are kept at a fixed level. The actual design consists of estimation of the coefficients in a mathematical model, predicting the response, and checking the adequacy of the model. Essentially the widely used designs to find out response surfaces are factorial designs and the more complex response surface methodologies [19,20].

In the present work, the adsorption of Ni(II) ions by phosphogypsum was studied by investigating the influence of different process variables on Ni(II) uptake, such as contact time, adsorbent dosage and initial Ni(II) concentration. The Langmuir, Freundlich and the Temkin models were utilized for analysis of the adsorption equilibrium. We model and optimize the process using a CCD. The objective of this study was therefore to examine the phosphogypsum to remove Ni(II) ions from aqueous solutions according to CCD.

MATERIALS AND METHODS

Preparation of adsorbent

The adsorbent phosphogypsum is a waste material of the dihydrate wet process phosphoric acid according to the following reaction:

$$Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O \rightarrow 3(CaSO_4, 2H_2O) + 2H_3PO_4 \qquad (1)$$

The prepared solution was mechanically stirred at 80°C. After 1 h 30 min of maturation, the hot solution is filtered to recuperate the phosphoric acid. Thereafter, the solid was washed with hot bidistilled water and pure acetone. It is finally dried at 80°C. Samples characterization before and after nickel ion removal was conducted using X-ray Diffraction (XDR) and Infrared (IR) Spectroscopy.

Preparation of adsorbate solution

The concentrations of nickel in the solutions before and after equilibrium were determined by atomic absorption spectrometer. The pH of solution was measured with a Hanna pH meter using a combined glass electrode.

Adsorption isotherm

Batch adsorption experiments were carried out in a 250 ml stopper conical flask by adding 1 g/100 ml- 6 g/100 ml of adsorbent and 200 mg/l of nickel nitrate solution of specific concentration. The concentration of Ni(II) solution was varied from 20-300 mg/l. All experiments were done at ambient temperature. The samples were shaken in a mechanical shaker for a contact time ranging from 2-180 min. After each experiment, the contents were filtered through a filter paper. Concentrations of nickel ions in the filtrate were then determined by atomic absorption spectrometer. The amount of nickel adsorbed using the adsorbents phosphogypsum at equilibrium, Q_e (mg/g), was calculated by the following mass balance relationship:

$$Q_e = \frac{(C_0 - C_e).V}{m} \qquad (2)$$

Where, C_0 and C_e are the initial and equilibrium liquid-phase concentrations of nickel, respectively (mg/l), V the volume of the solution (L), and m is the weight adsorbate used (g).

Adsorption isotherm models

Adsorption isotherms are important to describe the adsorption mechanism of a solute on adsorbent surface thus aid in optimizing the design of a specific adsorption process. In this study, Langmuir, Freundlich and Temkin adsorption models were used to determine the adsorption capacity of phosphogypsum for Ni(II). The following equations were used for describing the Langmuir, Freundlich and Temkin isotherms:

Langmuir isotherm

The Langmuir adsorption isotherm assumes that adsorption occurs at specific homogeneous sites within the adsorbent and the capacity of the adsorbent is finite [21]. The Langmuir isotherm is given by Equation 3:

$$\frac{C_e}{Q_e} = \frac{1}{bQ_m} + \frac{C_e}{Q_m} \qquad (3)$$

Where, Q_e (mg/g) is the amount of adsorbed species per unit weight of adsorbent and C_e (mg/l) is unadsorbed concentration in solution at equilibrium. b (L/mg) is the Langmuir equilibrium constant and Q_m (mg/g) the maximum adsorption capacity.

Freundlich isotherm

The Freundlich equation is an empirical model that was first used to describe gas and solute adsorption; it has also been used to describe ion retention by adsorption and precipitation processes. This model does not predict an adsorption maximum and implies that the adsorption energy of a surface varies with surface coverage [22]. The Freundlich isotherm is given by Equation 4:

$$\log Q_e = \log K_F + \frac{1}{n}\log C_e \qquad (4)$$

Where, K_F $[(mg/g)/(mg/L)^{1/n}]$ and n are Freundlich isotherm constants that correspond to adsorption capacity and adsorption intensity, respectively.

Temkin isotherm

The Temkin adsorption isotherm is based on the assumption that the heat of adsorption decreases linearly with the coverage due to the interaction between adsorbate and adsorbent [23]. The Temkin isotherm is given by Equation 5:

$$Q_e = B \ln A_T + B \ln C_e \qquad (5)$$

Where, B (RT/b_T, J/mol) is a constant related to the heat of adsorption, b_T is a Temkin isotherm constant, R (8.314 $J.mol^{-1}.K^{-1}$) is the gas constant, T (K) is the absolute temperature, and A_T (L/g) is the Temkin isotherm equilibrium binding constant related to maximum binding energy.

RESULTS AND DISCUSSION

Characterization of adsorbent before and after nickel ions removal

The graph in Figure 1 indicates the results of Fourier Transforms Infra-Red (FTIR) analysis of the adsorbents before and after reaction. The water in phosphogypsum is detected at 3501, 3398, 1683 and 1617 cm^{-1}. The first region is explained by the presence of deformation modes of shear type which indicates the existence of types of water molecules. Consequently, water molecules in calcium sulfates are symmetric. In the other side, spectral region between 1683 and 1617 cm^{-1} indicates H-O-H bending vibration. The sulfate group determines the symmetry with respect to the water molecules and is a high symmetry tetrahedral structure. In the case of phosphogypsum, sulfate peak is detected at 1095 cm^{-1} (Table 1). The absorption band is asymmetric stretching band (ν_a SO_4). Peaks at 664 and 594 cm^{-1} of sulfate, respectively, are assigned to the bending vibrations of phosphogypsum. The difference between the two intensities indicates that the symmetry is weakened by bounds with the water molecules.

The decreasing vibration intensity around 3605, 3555 and 1617 cm^{-1} Indicated the chemical interaction of Ni(II) with the O-H groups of phosphogypsum. Thus, the nickel atoms species mainly present as $Ni(OH)^+$ and $Ni(OH)_2$ were sorbed. The apparition of shoulder bands at different intensities indicates the formation of new compounds and the modification of phosphogypsum crystalline structure. The insertion of nickel on the surface of phosphogypsum particles led to the modification of characteristic absorption band of sulfate groups around 1083 cm^{-1}.

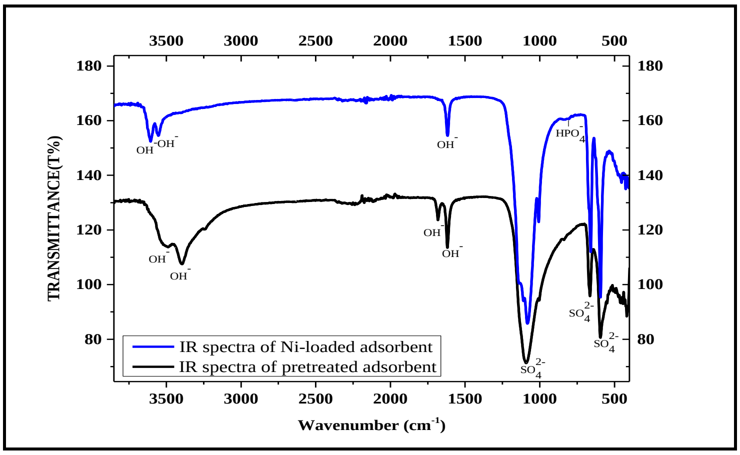

Figure 1: Infrared spectra of adsorbent before and after adsorption of nickel ions

Table 1: IR frequencies of adsorbent before and after adsorption

Functional group	Pretreated adsorbent	Ni-loaded adsorbent
O-H symmetric stretch	3501,13 cm^{-1}	3605,26 cm^{-1}
O-H asymmetric stretch	3398,92 cm^{-1}	3555,12 cm^{-1}
O-H bending vibration	1683,55 cm^{-1}	-
O-H asymmetric elongation	1617,98 cm^{-1}	1617,90 cm^{-1}
SO_4 asymmetric stretch	1095,36 cm^{-1}	1083,79 cm^{-1}
P-OH symmetric stretch	836,95 cm^{-1}	805,13 cm^{-1}
SO_4 asymmetric elongation	664,35 cm^{-1}	648,92 cm^{-1}
SO_4 asymmetric stretch	594,93 cm^{-1}	601,50 cm^{-1}

The XRD patterns of before and after adsorption of nickel ions is shown in Figure 2. The XRD shows that the major constituents of the pure phosphogypsum are calcium sulfate di-hydrate ($CaSO_4.2H_2O$), located at 2θ=11°, 21°, 24°, and 29°, corresponding to the (0 2 0), (-1 2 1), (0 4 0) and (-1 4 1) crystallographic planes, respectively, the hemi-hydrate ($CaSO_4.1/2\ H_2O$), located at 2θ=26° and the characteristic peaks of brushite ($CaHPO_4.2H_2O$), located at 2θ=48°. After adsorption of nickel ions on phosphogypsum we observed the change in intensity; especially peaks at 2θ=21°, 24°, and 29°. Therefore, the shifts in the position of peaks indicate that Ni(II) ions are well associated with surface functionality of phosphogypsum.

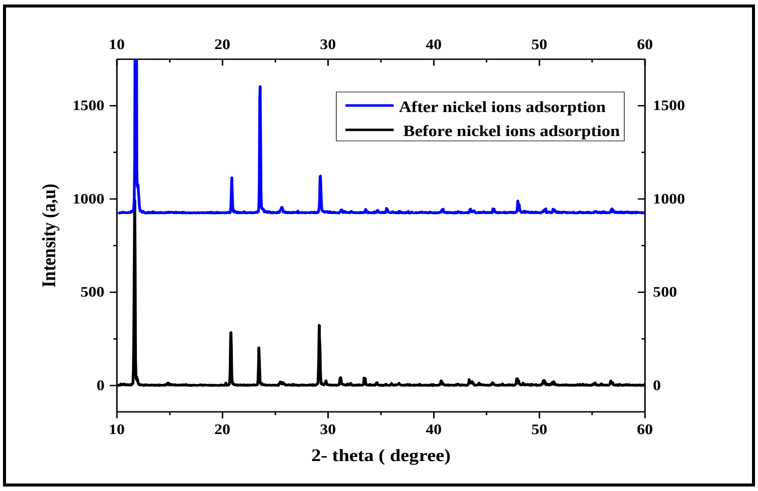

Figure 2: X-ray diffraction patterns of adsorbent before and after the adsorption process

Effect of contact time

Figure 3 is showing the result of the optimization of contact time. The maximum removal was found at 30 minu and beyond this no appreciable improvement in removal was observed; therefore time optimized was 30 min.

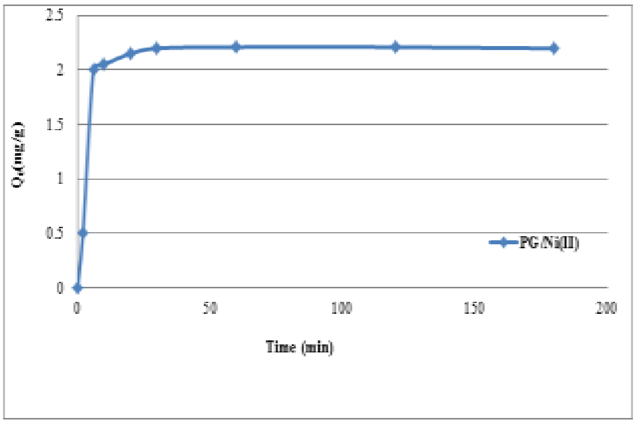

Figure 3: Effect of initial contact time (Initial concentration of Ni(II), 200 mg/l; phosphogypsum dosage, 2 g/100 ml; pH 7.01)

Effect of adsorbent dosage

Figure 4 shows the effect of phosphogypsum concentration on Ni(II) adsorption. The amount of Ni(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 adsorbent [24].

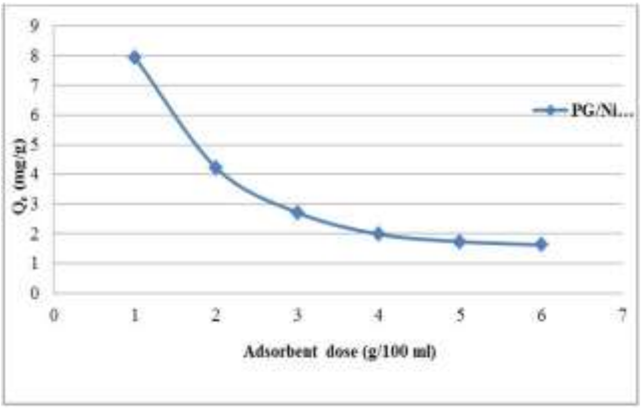

Figure 4: Effect of phosphogypsum dosage (Initial concentration of Ni(II), 200 mg/l; Contact time: 40 min, Ph 7.01)

Effect of initial concentration

The effect of initial adsorbate concentration on the adsorption was investigated by varying the initial concentration of Ni(II) between 20 and 300 mg/l. The experimental data were illustrated in Figure 5. It was observed that Ni(II) adsorption increased with the increase in Ni(II) concentration for the concentration range of 20-300 mg/l. This increase may be due to the higher adsorption rate and the utilization of all the active sites available for the adsorption at higher concentration [25,26].

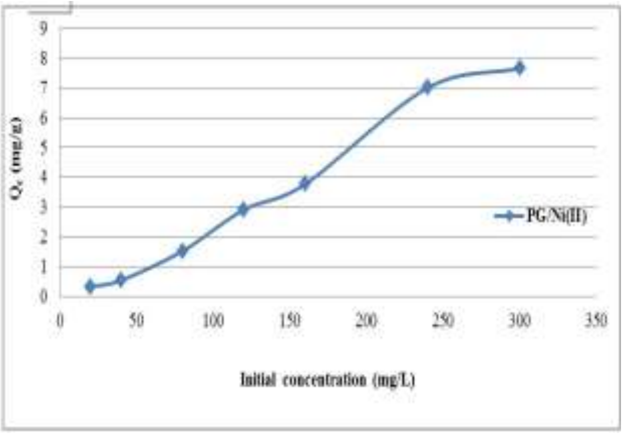

Figure 5: Effect of initial Ni(II) concentration (phosphogypsum dosage, 2 g/100 ml; Contact time: 40 min, pH 7.01)

Isotherm study

Figure 6 shows the adsorption isotherms for the adsorption of Ni(II) ions onto phosphogypsum adsorbent at optimum conditions with some Ni(II) concentrations ranging from 20 to 300 mg/l. The equilibrium adsorption isotherm models such as, Langmuir; Freundlich and Temkin isotherms were applied to interpret the experimental data and understanding the adsorption mechanism.

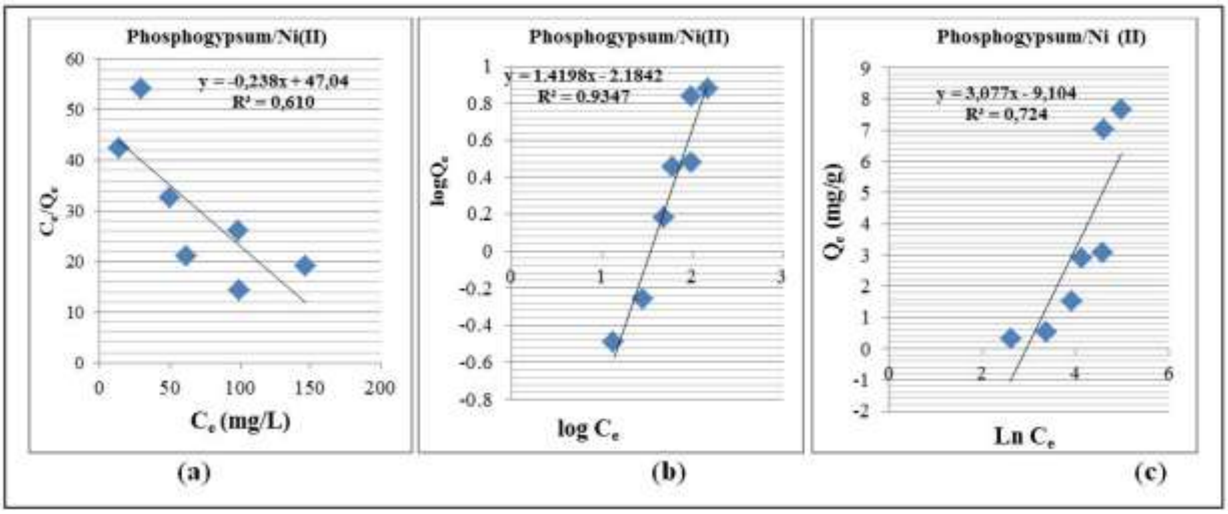

Figure 6: The equilibrium isotherms (a) Langmuir, (b) Freundlich, (c) Temkin, for adsorption of Ni(II) ions on phosphogypsum

The adsorption constants and correlation coefficients of the Langmuir, Freundlich and Temkin isotherm were given in Table 2. The correlation coefficients of Langmuir, Freundlich and Temkin models are 0.610, 0.934 and 0.724, respectively. The results showed that Freundlich model with the highest value of correlation coefficient (R^2=0.934) fitted better than other isotherm models, indicating that adsorption process occurs as multilayer coverage on the heterogeneous surface of adsorbent due to the diversity of adsorption sites [27]. From Table 1 the Freundlich constants K_f and n were found to be 0.006 and 0.70 respectively. As a result, it can be concluded that as the 1/n ($1/n > 1$) value for the adsorption by phosphogypsum is more than unity, a physical adsorption rather than chemical is probably dominant in Ni (II) adsorption by phosphogypsum.

Table 2: Isotherm constant parameters and correlation coefficients calculated for the adsorption Ni(II) ions on phosphogypsum

Isotherm model	Parameters	Ni(II)
Langmuir	Q_{max} (mg/g) b (L/mg) R^2	-4,20 -0.005 0,610
Freundlich	n k_F (mg/g)/(mg/l)$^{1/n}$ R^2	0,70 0,006 0,934
Temkin	B A_T (L/g) R^2	3,077 0,05 0,724

Modeling and optimization of Ni(II) sorption

In the present study, a CCD was employed for determining the optimum conditions for the adsorption of nickel by phosphogypsum. According to this design, the total number of treatment combinations was $2^k+2.k+N_0$ where 'k' is the number of independent variables and 'N_0' is the number of repetitions of the experiments at the centre point. For this study, a 2^3 factorial design with six star points and six replicates at the central points were employed to fit the Second order polynomial model, which indicate that 20 experimental were required for three factors (Adsorbent dosage, contact time and initial Ni(II) concentration). The amount of nickel removal (Y) was taken as the response of the design experiments. The quadratic equation for the independent variables was expressed as follows:

$$Y = a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_{12}X_1X_2 + a_{13}X_1X_3 + a_{23}X_2X_3 + a_{11}X_1^2 + a_{22}X_2^2 + a_{33}X_3^2 \pm \varepsilon. \qquad (6)$$

Where a_0 represents the interception coefficient, a_1, a_2 and a_3 are the linear coefficients, a_{11}, a_{22} and a_{33} are the quadratic coefficients, a_{12}, a_{13} and a_{23} is the cross-product coefficients, X_1, X_2 and X_3 represent the independent variables studied and ε is the random error. The various factors that influence the adsorption of Ni(II) on the adsorbent is shown in Table 3.

Table 3: Coded and actual values for nickel (II)

Factors	Variables	Range and levels (coded)				
		-1.682	**-1**	**0**	**+1**	**+1.682**
[PG] (g/l)	X_1	6.59	10	15	20	23.40
t (min)	X_2	3.18	10	20	30	36.81
[Ni(II)] (mg/l)	X_3	65.91	100	150	200	234.08

Tables 4 and 5 present the various experiments based on the central composite design for various factors and the results of calculations of the model coefficients respectively, that influence the adsorption of Ni(II) on the phosphogypsum.

Table 4: Central composite design experiments and experimental results

Experiment number	Real values (coded values)			Responses (Q(mg/g))		
	X_1([PG])	X_2(t)	X_3([Ni(II)])	$Y_{experimental}$	$Y_{calculi}$	Y_{exp}-Y_{calc}
1	10 (-1)	10 (-1)	100 (-1)	3.17	2.83	0.33
2	20 (+1)	10 (-1)	100 (-1)	1.42	2.22	-0.80
3	10 (-1)	30 (+1)	100 (-1)	2.22	2.16	0.05
4	20 (+1)	30 (+1)	100 (-1)	1.62	2.19	-0.57
5	10 (-1)	10 (-1)	200 (+1)	8.74	8.77	-0.03
6	20 (+1)	10 (-1)	200 (+1)	4.32	4.99	-0.67
7	10 (-1)	30 (+1)	200 (+1)	8.73	8.54	0.18
8	20 (+1)	30 (+1)	200 (+1)	4.44	5.39	-0.95
9	6.59 (-α)	20 (0)	150 (0)	2.87	3.48	-0.61
10	23.40 (+α)	20 (0)	150 (0)	1.82	0.33	1.49
11	15 (0)	3.18 (-α)	150 (0)	3.99	3.59	0.40
12	15 (0)	36.81 (+α)	150 (0)	3.84	3.37	0.47
13	15 (0)	20 (0)	65.91 (-α)	4.84	4.55	0.29
14	15 (0)	20 (0)	234.08 (+α)	12.82	12.23	0.58
15	15 (0)	20 (0)	150 (0)	3.81	3.84	-0.03
16	15 (0)	20 (0)	150 (0)	3.83	3.84	-0.01
17	15 (0)	20 (0)	150 (0)	3.82	3.84	-0.02
18	15 (0)	20 (0)	150 (0)	3.82	3.84	-0.02
19	15 (0)	20 (0)	150 (0)	3.82	3.84	-0.02
20	15 (0)	20 (0)	150 (0)	3.82	3.84	-0.02

Table 5: ANOVA test for central composite design model Ni(II) adsorption

Parameter	Coefficient estimate	t. exp.	Signification (%)
a_0	3.845	1491	$< 0.01^{***}$
a_1	-0.939	-548.76	$< 0.01^{***}$
a_2	-0.065	-38.18	$< 0.01^{***}$
a_3	2.286	1336	$< 0.01^{***}$
a_{11}	-0.684	-410.66	$< 0.01^{***}$
a_{22}	-0.129	-77.49	$< 0.01^{***}$
a_{33}	1.609	965.55	$< 0.01^{***}$
a_{12}	0.160	71.55	$< 0.01^{***}$
a_{13}	-0.795	-355.53	$< 0.01^{***}$
a_{23}	0.108	48.08	$< 0.01^{***}$

The result of the quadratic model in the form of ANOVA showed small probability value ($< 0.01^{***}$) indicating the individual terms in the model have signification on the effect (The associated signification % value for the model is lower than 5% (α=0.05 or 95% confidence) indicates that the model is considered to be statistically signification. The non-signification value is more than 5%) (Table 5). The empirical relationship between nickel ion removal (Y) and the three test variables in coded units obtained is given by:

$$Y= 3.84– 0.93X_1 + 0.06X_2 + 2.28X_3 + 0.16\ X_{12} – 0.79X_{13} + 0.10X_{23} – 0.68X_1^2 – 0.12X_2^2 + 1.60X_3^2 \quad (7)$$

Effect of process variable on nickel ion adsorption

The mathematical model above is found for plotting the response surfaces which are shown in Figure 7a-c which respectively represent the isoresponse adsorption curves in the plans: ([PG] (X_1)* (Contact time) (X_2)), ((Contact time) (X_2)* [Ni (II)] (X_3) and [Ni (II)] (X_3) *([PG] (X_1)).

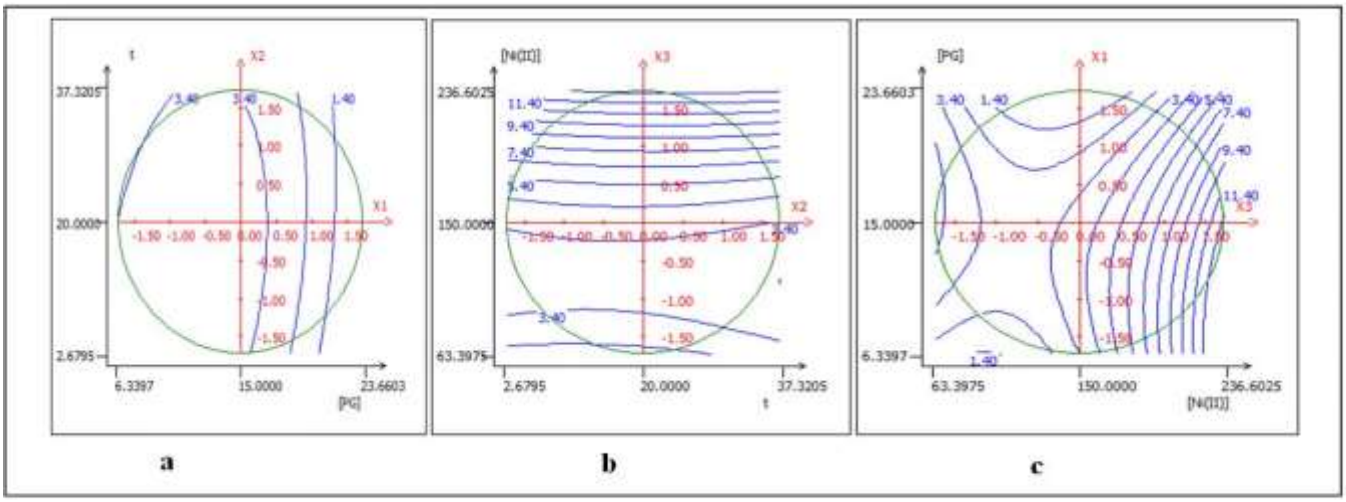

Figure 7: Isoresponse curves adsorption of nickel (II) on phosphogypsum: (a) Effect of adsorbent dosage and contact time ([Ni (II)] initial=150 mg/l); (b) Effect of contact time and initial Ni(II) concentration ([PG]=15 g/l); (c) Effect of initial Ni(II) concentration and adsorbent dosage on the amount of nickel (mg/g) (t=20 min)

From this figure we see that:

- The amount of nickel Q_e (mg/g) increases with increasing the initial nickel ion concentration and decrease with increase in adsorbent dosage
- The effect of contact time has no effect on the amount of nickel Q_e (mg/g).
- The model equation is useful in indicating the direction in which the variables should be changed in order to optimize the removal efficiency of Ni(II). A combination of optimum experimental values in coded form was found for each parameter by differentials for removal efficiency of Ni (II) as follows:

$$\left\{\begin{array}{l} \frac{\partial Y}{\partial X_1} = 0 \to X_1 = -0.21 \text{ (coded values)} \\ \frac{\partial Y}{\partial X_2} = 0 \to X_2 = -0.19 \text{ (coded values)} \\ \frac{\partial Y}{\partial X_3} = 0 \to X_3 = -0.76 \text{ (coded values)} \end{array}\right\} \quad (8)$$

Thus, the working conditions at the optimum point for removal efficiency of Ni(II) were determined as follows:

[PG]=13.90 g/l

t=19.02 min

[Ni(II)]=111.80 mg/l

CONCLUSION

The phosphogypsum powder is an effective adsorbent for the removal of Ni(II) from aqueous solutions. The study indicates the performance of this material in terms of adsorbent dosage, contact time and initial Ni (II) concentration. The maximum removal of Ni(II) is obtained at equilibrium time of 30 min white a minimal dosage of absorbent. The uptake capacity of Ni(II) increased with the increase in initial metal ions concentration and decrease with increase in adsorbent dosage. Freundlich model gives a better fit. An experimental design methodology (CCD) was applied to evaluate the interactive effects of adsorption variables and to optimize the adsorption process of Ni(II) ions from aqueous solutions onto phosphogypsum. The optimal condition obtained was located and the optimum adsorption factors were predicted as a contact time of 19.02 min, an adsorbent dosage of 13.90 g/l and initial Ni(II) concentrations of 111.80 mg/l. Under these adsorption conditions, a maximum removal of 3.08 mg/g (± 0.01) amount of nickel removal was demonstrated. Hence, the phosphogypsum can be used for effluent containing Ni (II) ions.

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