

Optimization Study of Adsorption of Nickel(II) on Bentonite

B. Medjahed, M. A. Didi, B. Guezzen

II. EXPERIMENTAL

Abstract—This work concerns with the experimental study of the adsorption of the Ni(II) on bentonite. The effects of various parameters such as contact time, stirring rate, initial concentration of Ni(II), masse of clay, initial pH of aqueous solution and temperature on the adsorption yield, were carried out. The study of the effect of the ionic strength on the yield of adsorption was examined by the identification and the quantification of the present chemical species in the aqueous phase containing the metallic ion Ni(II). The adsorbed species were investigated by a calculation program using CHEAQS V. L20.1 in order to determine the relation between the percentages of the adsorbed species and the adsorption yield. The optimization process was carried out using 2³ factorial designs. The individual and combined effects of three process parameters, i.e. initial Ni(II) concentration in aqueous solution (2.10⁻³ and 5.10⁻³ mol/L), initial pH of the solution (2 and 6.5), and mass of bentonite (0.03 and 0.3 g) on Ni(II) adsorption, were studied.

Keywords—Adsorption, bentonite, factorial design, Nickel(II).

I. INTRODUCTION

THE increasing discharge of industrial wastewaters containing heavy metals to the environment has been on the increase as a result of rapid intensification of industries. This is a critical problem because heavy metals at high concentrations are toxic causing unsafe effects on the environment and human health [1]. High concentrations of nickel in humans can cause health trouble such as liver damages, headache, dermatitis, and skin irritation [2], [3].

Numerous techniques have been used for the removal of heavy metals from industrials effluents such as ion exchange, reverse osmosis, adsorption, precipitation, phyto-extraction and ultra-filtration [4].

The adsorption technique has been found to be one of the most efficient methods for the elimination of metal ions from solution [5]. Adsorption is the usually preferred method for elimination heavy metal ions in terms of simplicity of design, initial cost, availability of different adsorbents, simplicity of operation, and the insensitivity to toxic pollutants [6].

B. Medjahed Laboratory of Separation and Purification Technology, Tlemcen University (13000), Faculty of Sciences, University, Saida (20000), Algeria (phone: +213661133380; e-mail: medjahedbaghdad@yahoo.fr).

M. A. Didi, Laboratory of Separation and Purification Technology, Faculty of Sciences, Tlemcen University, Tlemcen (13000), Algeria (e-mail: madidi13@yahoo.fr).

B. Guezzen Laboratory of Separation and Purification Technology, Tlemcen University (13000), Faculty of Sciences, University, Saida (20000), Algeria (e-mail: b_guezzen@yahoo.fr).

A. Reagents

Nickel sulfate and sodium sulfate were purchased from Aldrich. Sulfuric acid and sodium hydroxide were provided from Fluka.

B. Adsorbent

The adsorbent used in this research is natural bentonite clay from deposits in the area of Maghnia, Algeria.

The chemical composition of bentonite was determined by X-ray fluorescence spectroscopy (Philips PW 3710), the results of the chemical analysis are shown in Table I.

TABLE I
CHEMICALS ANALYSIS OF BENTONITE CLAY BY XRF

Composition	Content (wt. %)
SiO ₂	62.48
Al ₂ O ₃	17.53
TiO ₂	0.22
Fe ₂ O ₃	1.23
MgO	3.59
CaO	0.57
Na ₂ O	0.39
K ₂ O	0.82

C. Apparatus

The aqueous solution was analyzed with a Perkin-Elmer atomic absorption spectrophotometer assisted by micro-computer (Model A Analyst 300).

The pH of the aqueous solution was adjusted by adding small amounts of H₂SO₄ or NaOH. The equilibrium pH was measured with a Consort C831 pH meter. All the distribution equilibrium studies were carried out at 25±1 °C.

D. Evaluation

The adsorption efficiency (*E*) of Nickel(II) was calculated by

$$E(\%) = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

where *C_i* and *C_e* are the initial concentration and equilibrium concentration of Ni(II), respectively.

E. The Investigated Parameters

The effects of parameters such as contact time, stirring speed, initial concentration of Ni(II), masse of clay, initial pH of aqueous solution, temperature and ionic strength were reported in order to determine the optimal conditions of adsorption.

F. Experimental Design

In order to optimize the adsorption of Ni(II) on bentonite clay and to examine the interaction between the studied factors, by varying three key variables, namely the initial pH (X_1), initial metal concentration C_0 (X_2) and mass clay m (X_3), the factorial design of the type 2^3 has been applied in suitable parameter ranges [7], [8]. Two variation levels for each parameter were considered as summarized in Table II.

In this work, we have applied Response surface methodology (RSM), using the software Statgraphics Centurion XVI. 27, which is an empirical statistical technique employed for multiple regression analysis by using quantitative data obtained from properly designed experiments to solve multivariate equations simultaneously [9], [10].

Experiments were carried out to investigate the experimental domain, four experiments were added to investigate the performance in the center of the experimental domain.

TABLE II
LEVELS OF THREE INDEPENDENT VARIABLES CONSIDERS FOR THE ADSORPTION OF NICKEL(II)

Variable	Range and Levels	
	Low (-1)	High (+1)
pH, X_1	2	6.5
C_0 (mM), X_2	2	5
m (g), X_3	0.03	3

III. RESULTS AND DISCUSSION

A. Parametric Study

1. Effect of Contact Time

The effect of stirring time on Ni(II) adsorption yield was examined in the range from 1 to 60 minutes.

The results presented in Fig. 1 showed that the adsorption kinetics of the Ni(II) on bentonite clay is fast, a stirring time of 5 minutes correspond to a maximum yield of adsorption.

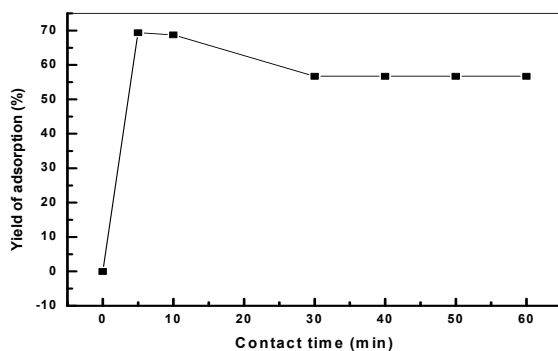


Fig. 1 Effect of contact time

2. Effect of Stirring Speed

The experimental results presented in Fig. 2 show that a maximum yield of Ni(II) is obtained for an agitation speed equal to 560 rpm.

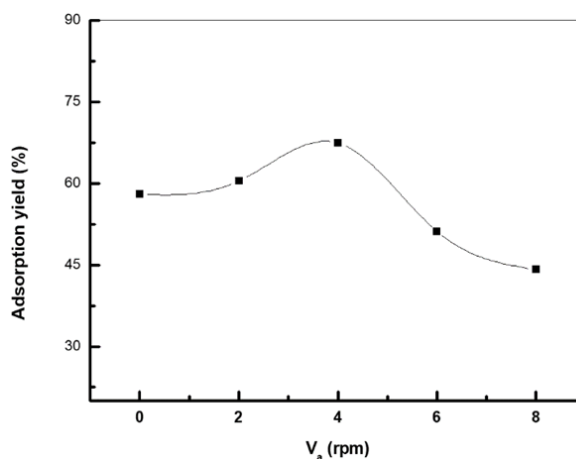


Fig. 2 Effect of stirring speed

3. Effect of Initial Metal Ion Concentration

The effect of the initial concentration of Ni(II) on the adsorption yield was studied in the range $2 \cdot 10^{-3}$ - $1 \cdot 10^{-2}$ M. The results presented in Fig. 3 shows that the initial concentration of Ni(II), for a better adsorption yield, corresponds to a value equal to $5 \cdot 10^{-3}$ M.

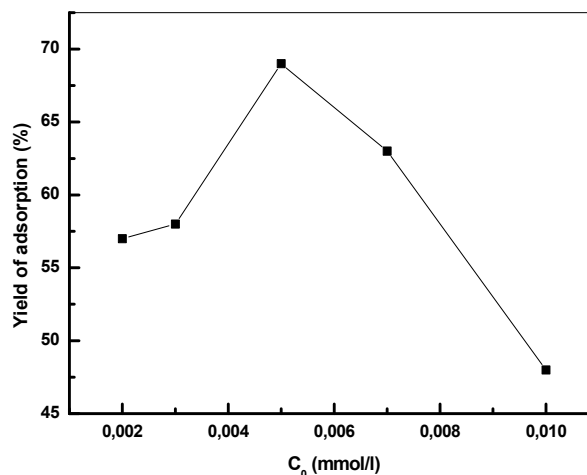


Fig. 3 Effect of initial metal ion concentration

4. Effect of Clay Mass

In order to study the effect of adsorbent dosage on the adsorption of Ni(II) on bentonite clay, a series of adsorption experiments were carried out with different adsorption dosages varying from 0.01 to 0.5 g at initial concentration of Ni(II) equal to $5 \cdot 10^{-3}$ M. The volume used of the aqueous solution containing the metal ion is equal to 10 ml.

The experimental results presented in Fig. 4 show that the optimum value of the mass of clay, corresponding to a maximum yield of absorption, is 0.2 g.

The effect of adsorbent dosage was found, from 0.2 g of bentonite clay in 10 ml of the aqueous solution, to decrease by increasing the adsorbent dose. This may be due to the fact that

as the amount in grams of adsorbent is increased, the total surface area accessible for the adsorption of Ni(II) reduces as a result of aggregation of adsorption sites [11].

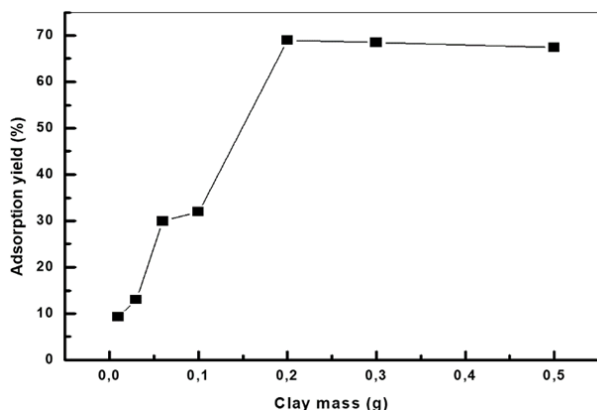


Fig. 4 Effect of clay mass

5. Effect of Initial pH of Aqueous Solution

To study the effect of initial pH on Ni(II) adsorption, the values of the operating parameters used are: $[\text{NiSO}_4] = 5 \cdot 10^{-3}$ M, equilibrium contact time $t = 5$ min, $V_a = 560$ rpm, clay

mass $m = 0.2$ g in 10 ml of the aqueous solution and $T = 25$ °C.

pH values were varied from 2 to 10. Fig. 5 shows that the optimum pH value of the aqueous phase containing the metal ion is 6.5.

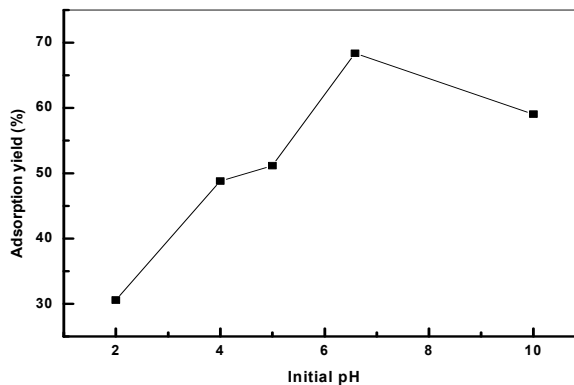


Fig. 5 Effect of initial pH of aqueous solution

$$[\text{Ni}^{2+}]_{\text{TOT}} = 5.00 \text{ mM}$$

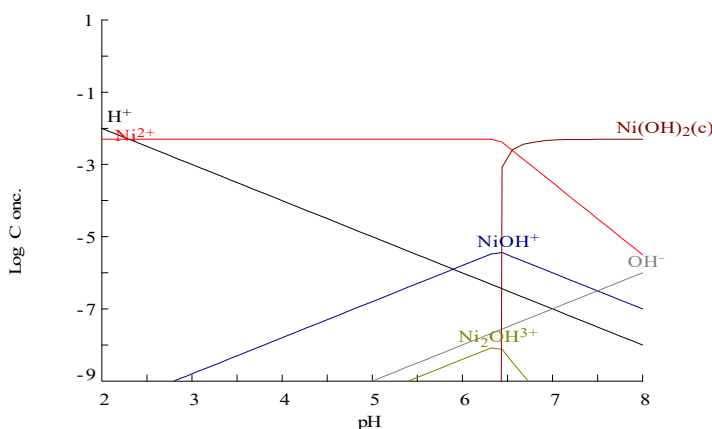


Fig. 6 Distribution diagrams of Ni(II) ($5 \text{ mmol} \cdot \text{L}^{-1}$) in sulfate media using Medusa and Hydra programs [12]

From Fig. 8, it can be seen that, for pH values greater than 6.5, there is a decrease in the rate of free Ni(II) ion and the beginning of hydroxide formation, which explains the decrease in the adsorption yield.

6. Effect of Temperature

The effect of temperature on the adsorption of the Ni(II) ions was studied under optimum conditions. The results presented in Fig. 7 showed that the adsorption reaction of the Ni(II) is disfavored by an increase in temperature.

The best adsorption of Ni(II) was obtained at $T=25$ °C, stirring time of 5 min, stirring speed of 560 rpm, clay mass 0.2 g in 10ml of the aqueous solution with $[\text{NiSO}_4] = 5 \cdot 10^{-3}$ M and initial pH of aqueous solution equal to 6.5.

7. Effect of Addition of Sodium Sulfate

The influence of the ionic strength on the adsorption yield of Ni(II), was studied by adding the salt of sodium nitrate to the aqueous phase.

The results, presented in Fig. 8, showed that the addition of amount of the sodium sulfate to the aqueous solution, in the range 0.01-0.1 M, has a negative effect on the yield of adsorption.

The identification and the quantification of the present chemical species, in aqueous phase, were obtained by the use of a software called Chemical Equilibrium in Aquatic System (CHEAQS) [13].

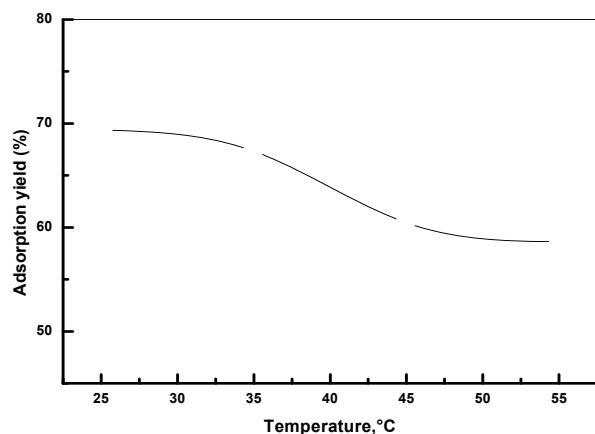


Fig. 7 Effect of temperature

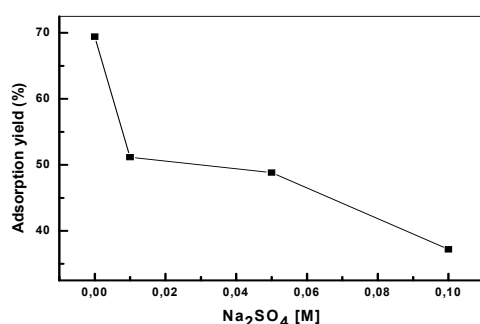


Fig. 8 Effect of addition of sodium sulfate

Fig. 9 represents the variation of the chemical species percentage present in the aqueous solution as a function of the concentration of the added salt. The results show that the increase of Ni(II) concentration is accompanied by a decrease of the Ni(II) species rate and a relative increase of the $\text{Ni}(\text{SO}_4)_{\text{aq}}$ and $\text{Ni}(\text{SO}_4)_2^{2-}$ species rate.

The decrease of the adsorption yield can be explained in this case by the competition phenomenon existing between these species.

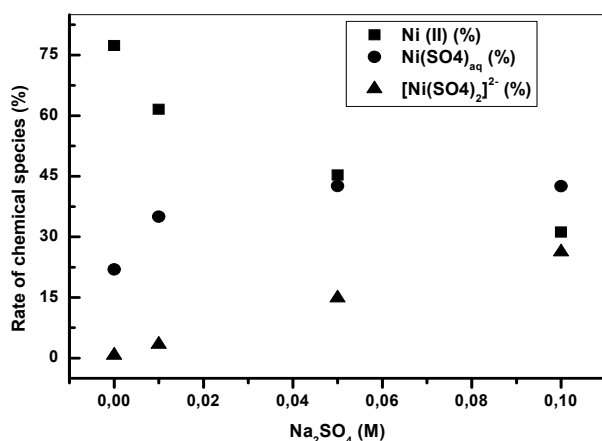


Fig. 9 Rate of chemical species present in the aqueous solution

B. Factorial Design Study

The experiment design was given in Table III along with experimental data and predicted responses. The adsorption yield (E) of Ni(II) was chosen as experimental response. The ANOVA table partitions the variability in yield into separate pieces for each of the effects.

TABLE III
EXPERIMENTAL DATA

Run	Factors levels			Response function	
	X1	X2	X3	Observed Value (E %)	Fitted Value
1	-1	-1	-1	20.14	21.85
2	-1	-1	+1	44.13	45.84
3	-1	+1	-1	30.23	31.94
4	-1	+1	+1	64.50	66.21
5	+1	-1	-1	59.30	61.01
6	+1	-1	+1	59.60	61.31
7	+1	+1	-1	19.35	21.06
8	+1	+1	+1	61.15	62.86
(9,10,11,12) ^a	0	0	0	(49.78;50.45;49.18;50.37)	46.51

Note: ^a Four additional test at the central point (0,0,0) for the calculation of the Student and Fisher's tests.

It then tests the statistical significance of each effect by comparing the mean square against an estimate of the experimental error [14]-[16]. In this case, four effects have P-values less than 0.05, indicating that they are significantly different from zero at the 95.0% confidence level.

The R-Squared statistics indicates that the model as fitted explains 97.2708% of the variability in yield. The adjusted R-squared statistics, which is more suitable for comparing models with different numbers of independent variables, is 92.4948%. The standard error of the estimate shows the standard deviation of the residuals to be 4.23195. The mean absolute error (MAE) of 2.28667 is the average value of the residuals. The Durbin-Watson (DW) statistics tests the residuals to determine if there is any significant correlation based on the order in which they occur in our data file.

Table IV (ANOVA table) shows the analysis of variance model for the adsorption yield (E) of Ni(II). In this case, four effects have P values less than 0.05, indicating that they are significantly different from zero at the 95.0% confidence level.

TABLE IV
STATISTICAL PARAPETRS FOR 2³ DESIGN

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A:X1	204.02	1	204.02	11.39	0.0279 ^a
B:X2	7.88045	1	7.88045	0.44	0.5434
C:X3	1259.02	1	1259.02	70.30	0.0011 ^a
AB	592.712	1	592.712	33.10	0.0045 ^a
AC	32.6432	1	32.6432	1.82	0.2483
BC	335.146	1	335.146	18.71	0.0124 ^a
ABC	121.836	1	121.836	6.80	0.0595
Total error	71.6375	4	17.9094		
Total (corr.)	2624.89	11			

$R^2 = 97.2708$, $R^2_{\text{adj}} = 92.4948$; a: significant variable

Polynomial model that describes the Ni(II) adsorption on

bentonite clay of the fitted model is:

$$E(\%) = 46.515 + 5.05X_1 - 0.992X_2 + 12.545X_3 - 8.607X_1X_2 - 2.02X_1X_3 + 6.472X_2X_3 + 3.902X_1X_2X_3 \quad (2)$$

IV. CONCLUSION

The experimental parametric study of the Ni(II) adsorption on the bentonite clay revealed the optimal operating conditions.

The study of the effect of ionic strength on adsorption shows that the chemical species Ni(II) ions are the most adsorbed.

The second part of this study showed that factorial experimental design approach could successfully be used to develop empirical equation for the prediction of Ni(II) adsorption yield. Absolute values and the signs of each coefficient give an idea of the intensity and tendency of each effect as well as the combined effects of the parameters studied. The results showed that the most influential combined effect on the adsorption yield is that between the initial concentration of Ni(II) and the value of the clay mass.

ACKNOWLEDGMENT

We gratefully acknowledge the ATRST (Agence Thématique de Recherche en Sciences & Technologie-Algérie) (ex. ANDRU) for this financial support.

REFERENCES

- [1] S. S. Ahluwalia, D. Goyal. Microbial and plant derived biomass for removal of heavy metals from wastewater. *Biores Technol* 2007; 98:2243–57.
- [2] S. Wang, X. Shi. Molecular mechanism of metal toxicity and carcinogenesis. *Mol Cell Biochem* 2001; 222:3–9.
- [3] E. Denkhause, K. Salnikov. Nickel essentiality, toxicity and carcinogenicity. *Crit Rev Uncol Hematol* 2002;42(1):35–56.
- [4] T. K. Kurniawan, GYS. Chan, W. Lo, S. Babel. Comparison of low-cost adsorbents for treating wastewaters laden with heavy metals. *Sci Total Environ* 2006; 366:409–26.
- [5] S. Liang, X. Guo, N. Feng, Q. Tian. Isotherms, kinetics and thermodynamic studies of adsorption of Cu²⁺ from aqueous solution by Mg²⁺/K⁺ orange peel adsorbents. *J Hazard Mater* 2010; 174:756–62.
- [6] S. Wang, H. Li. Kinetic modeling and mechanism of dye adsorption on unburned carbon, *Dyes Pigments* 72 (2007) 308–314.
- [7] V. J. P. Vilar, C. M. S. Botelho, R. A. R. Boaventura, Influence of pH, ionic strength and temperature on lead biosorption by gelidium and agar extraction algal waste, *Process Biochem.* 40 (2005) 3267–3275.
- [8] G. E. P. Box, W. G. Hunter, J. Stuart, *Statistics for Experimenters*, second ed., John Wiley and Sons, New York, NY, 2005 p. 633.
- [9] K. Vimalashanmugam, T. Viruthagiri, “Response surface methodology optimization of process parameters for xylanase production by *Aspergillus fumigatus* in SSF using central composite design,” *International Journal of Engineering Research and Applications*, vol.2, pp.277–287, 2012.
- [10] S. J. Nejad, H. Abolghasemi, Mohammad A. Moosaviana, Mohammad G. Maragheh, “Fractional factorial design for the optimization of supercritical carbon dioxide extraction of La³⁺, Ce³⁺ and Sm³⁺ ions from a solid matrix using bis(2,4,4-trimethylpentyl)dithiophosphinic acid + tributylphosphate,” *chemical engineering research and design*, vol. 89, pp.827–835, 2011.
- [11] B. Das and N. K. Mondal, “Calcareous soil as a new adsorbent to remove lead from aqueous solution: equilibrium, kinetic and thermodynamic study,” *Universal Journal of Environmental Research and Technology*, vol. 1, no. 4, pp. 515–530, 2011.
- [12] I. Puigdomenech, “HYDRA (Hydrochemical Equilibrium Constant Database) and MEDUSA (Make Equilibrium Diagrams Using Sophisticated Algorithms) Programs,” Royal Institute of Technology, Sweden. <http://www.kemi.kth.se/medusa>.
- [13] “Program for Calculating Chemical Equilibria in Aquatic Systems,” RIVM, Bilthoven, 2004. <http://www.cheaq.su.se/>. Accessed on 16/05/2016.
- [14] G. P. E. Box, W. G. Hunter, and J.S. Hunter, “Statistics for Experimenters,” 2nd ed., Wiley, Hoboken, NJ, pp. 363–385, 1978.
- [15] B. Guezzen, M.A. Didi and B. Medjahed, “Optimization of Process Parameters using Response Surface Methodology for the Removal of Zinc (II) by Solvent Extraction” *WASET J. International Journal of Chemical, Molecular, Nuclear, Materials and Metallurgical Engineering* Vol:11, No:2, 2017.
- [16] B. Medjahed, M. A. Didi and D. Villemin “Factorial design in optimization of extraction procedure for copper (II) using Aliquat 336 and Tri-nbutylphosphate based supported liquid membrane. *Desalination and Water Treatment* 52 (2014) 3237–3245.