

## Optimization of Ni<sup>2+</sup> adsorption on 13X zeolite using box-behken design

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**Abstract.** In this study, the elimination of Ni<sup>2+</sup> using 13X sorbent due to an electrostatic interaction was reported. The significant factors including pH, time and 13X sorbent amount were investigated using Box-Behnken design (BBD). In the optimum experimental conditions, the linear rang and limit of detection of the proposed method were 0.1-20 and 0.102 mg L<sup>-1</sup>, respectively. The precision as RSD% was 1.3% for concentration of 2 mg L<sup>-1</sup>. Concerning the excellent recoveries in a short time with highly efficient sample clean-up and removal, this method may be a very powerful and innovative future sample removal technique. To the best of our knowledge, this is the first report on using BBD for optimizing the parameters affected the removal of Ni<sup>2+</sup> by 13X zeolite sorbent.

**Keywords:** Ni<sup>2+</sup> ion removal; 13X zeolite sorbent; box-behken design; sea water; wastewater

### 1. Introduction

Heavy metals are one of the essential contaminants in water, and they have become a public health concern (An *et al.* 2001). Due to their tendency to accumulate in living organisms and induce harmful effects to natural resources, the elimination of heavy toxic metals such as nickel, cadmium, mercury, and lead present in water has been given much attention in the last decades (Gao *et al.* 2009).

In phosphate fertilizers, cadmium–nickel battery, mining, stabilizers, pigments, and alloys industries, nickel is widely used which find its way to the aquatic environments through wastewater discharge. The industrial discharge limit of Ni<sup>2+</sup> in wastewater and the acceptable limit of Ni<sup>2+</sup> in drinking water are 2 mg/L and 0.01 mg/L, respectively (Pandey *et al.* 2007). Nickel has been considered as a teratogen and embryo toxin. Poisoning effects like headache, nausea, dizziness, extreme weakness, dry cough, tightness of the chest, vomiting, shortness of breath, chest pain, rapid respiration, cyanosis, and even cancer of lungs, nose, and bone can be caused by higher concentration of nickel (Borba *et al.* 2006). Therefore, a systematic study on the removal of nickel from water is of considerable significance from an environmental point of view.

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To eliminate nickel from water, methods such as precipitation, membrane separation, ion exchange, solvent extraction, and electrochemical reduction can be used. However, these methods are often ineffective and costly. For instance, when the contaminations are present in trace amounts, precipitation is not practical and also a large amount of sludge is produced. Ion exchange is expensive. Electrochemical reduction and solvent extraction are cost-effective only for more concentrated solutions (Bhattacharyya and Gupta 2008). In contrast to most of these methods, adsorption has been proved to be one of the simplest, feasible, and efficient method for elimination of nickel from contaminated water (Leung *et al.* 2000). Zeolite, mineral, industrial by-products, organic or biological origin, biomass, agricultural wastes, activated carbon, and polymeric materials are some adsorbent candidates (Barakat 2011). So far, the most popular material in wastewater treatment for nickel elimination is activated carbon. The energy consuming for regeneration and high cost of this material makes its application less economically attractive on an industrial scale (Babel and Kurniawan 2003). The search for alternative adsorbents has intensified in recent years. Due to cost-effectiveness and good selectivity for nickel, zeolites, as alternative materials, are very attractive. They have aluminosilicate structures contain exchangeable metal cations such as K, Na, Mg, and Ca that during the ions exchange, the structure practically does not change. Zeolites can be used in adsorption, catalysis, and separation processes, electronics, medicine, magnetism, agroindustry, chemical sensors, and biochemistry. In addition to natural zeolites, there are wide variety types of synthetic zeolites such as zeolite A, X, and Y (according to the kind of cation exists in frame and Si to Al ratio). Zeolites have large empty spaces or cages that allow cations, such as calcium, sodium, barium, potassium, and even relatively large molecules and cation groups such as ammonia, water, nitrate ions, and carbonate ions to incorporate into their structures. Sources of silica and alumina such as lithium slag (Chen *et al.* 2012), bentonite (Ma *et al.* 2014), high silicon fly ash (Kazemian, Naghdali *et al.* 2010), waste porcelain and kaolinite (Wang *et al.* 2014), and coal fly ash (Tanaka and Fujii 2009) were used in order to minimize the cost of synthetic zeolites. Zeolite X is a very attractive material for environmental and technological usages. 13X, which has an elliptical-shaped internal cavity of 13 Å in diameter with a pore diameter of approximately 8 Å and Si to Al ratio about 1-1.5, is a sodium crystalline zeolite and has wide range applications in separation, catalysis, and ion exchange. There has been a growing interest in the synthesis of 13X (Ma *et al.* 2014). Most of these synthesis methods are not appropriate in industrial scales. Since, sodium silicate is inexpensive; here we synthesized 13X from sodium aluminate and sodium silicate in a closed hydrothermal system with defined temperature and autogenous pressure (Bandarchian and Anbia 2015).

The optimization of nickel adsorption can be performed by two different ways. The first, conventional univariate methodology represented by a process where “one variable is studied at each time”, needs more effort, materials and time (Bezerra *et al.* 2008). The other way named multivariate or response surface methodology (RSM). The RSM is faster, more effective and economical than univariate methodology and considers the possible interactions. Furthermore, in this approach, simultaneous optimization of several variables is possible (Leardi 2009). Therefore, detection of the main factors and the interactions among them are possible which providing the most information with minimal number of runs and without sacrificing the quality of the results (Singh *et al.* 2011). The Box-Behnken design (BBD), a kind of RSM, is a second-order experimental design method that received widespread application in optimization of experimental conditions. The required number of experiments (N) in this design is defined as  $N = 2k(k-1) + C_0$ , where (k) is the factor number and  $C_0$  is the replicate number of the central point (da Silva *et al.* 2008).

In our previous work, 13X sorbent effectively used to adsorb trace amounts of H<sub>2</sub>S from gas stream (Bandarchian and Anbia 2015). To expanding the usage of this sorbent, in the present study, we used the 13X sorbent for removal of Ni<sup>2+</sup> from aqueous solutions. To the best of our knowledge, there has not been any report on the usage of the BBD to optimize the key factors and to investigate the interactions among the factors influencing the extraction efficiency of Ni<sup>2+</sup> from aqueous solutions using 13X sorbent, which is more renewable, economic, and environmental-friendly than other sorbents.

## 2. Experimental

### 2.1 Chemicals and materials

Hydrochloric acid, sodium hydroxide, NiSO<sub>4</sub>·6H<sub>2</sub>O, and other chemicals were purchased from Merck (Darmstadt, Germany). NaAlO<sub>2</sub> (Al<sub>2</sub>O<sub>3</sub>:50-56%, Na<sub>2</sub>O:40-45% anhydrous) was purchased from Sigma-Aldrich (Steinheim, Germany). Sodium silicate (10.54 wt. % Na<sub>2</sub>O, 26.53 wt. % SiO<sub>2</sub>, 62.93 wt. % H<sub>2</sub>O) was purchased from ATDM Co. (Iran). Doubled-distilled water was used to prepare the samples. Proper amount of NiSO<sub>4</sub>·6H<sub>2</sub>O was dissolved in water to obtain stock solutions of the Ni<sup>2+</sup> with a concentration of 1 mg mL<sup>-1</sup>. Other diluted standard solutions were freshly prepared by diluting the standard solution of the Ni<sup>2+</sup> with doubled-distilled water. For optimization of pH solution, pH was adjusted to desired values with 0.1 M hydrochloric acid and sodium hydroxide solutions.

Table 1 Analytical conditions of the atomic absorption spectrometer

Parameters	values
Wavelength (nm)	231
Lamp current (mA)	10
Slit width (nm)	0.2
Acetylene flow rate (L min <sup>-1</sup> )	7
Air flow rate (L min <sup>-1</sup> )	1
Flame height (mm)	5
Burner length (cm)	10

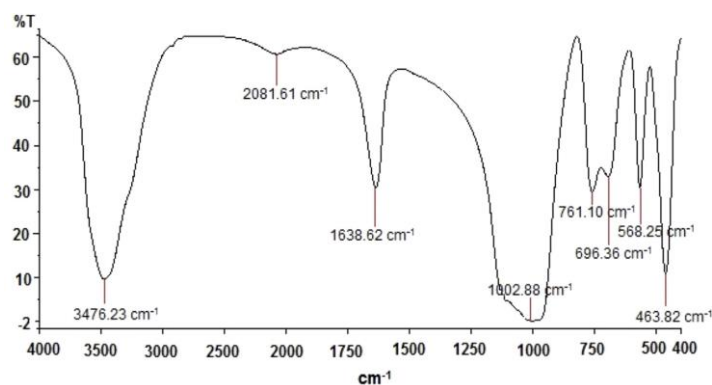


Fig. 1 FTIR spectra of 13X

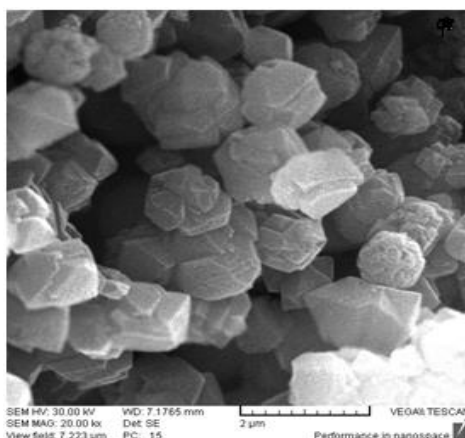


Fig. 2 SEM image of 13X

## 2.2 Experimental set-up

Detection of the  $\text{Ni}^{2+}$  was performed by an atomic absorption spectrometer (SPECTRO AA 200) containing nickel hollow cathode lamp and used an air-acetylene flame. Analytical conditions of this spectrometer can be seen in Table 1. All experiments were carried out at ambient temperature. Centrifugation was performed by Kokusan centrifuge (Japan). All pH measurements were performed using a pH-meter Metrohm 744 (Switzerland).

## 2.3 Preparation of the 13X adsorbent

Powder 13X preparation and characterization were described in the previous report (Bandarchian and Anbia 2015). Briefly, hydrothermal reaction between sodium  $\text{NaAlO}_2$ , sodium silicate, sodium hydroxide and water was used for synthesis of 13X adsorbent. The obtained gel was stirred (300 rpm) at room temperature for 40 min. Then for crystallization, it was transferred to an autoclave. After cooling to room temperature, the solid product was filtered, washed until pH of supernatant reached to 8 and dried in oven. Finally, the resulting white powder of the 13X was cooled in a desiccator. Granules 13X was obtained kindly from Pars Petrochemical Co (Iran). The FT-IR spectra and SEM micrograph of used 13X are depicted in Figs. 1 and 2 respectively.

## 2.4 Nickel adsorption using 13X sorbent

Schematic representation of nickel ion removal and detection are shown in Fig. 3. 50 mL of the  $\text{Ni}^{2+}$  solution ( $1000 \text{ mgL}^{-1}$ ) was filled into a 100 mL beaker and, according to the experimental design, the pH of the solution was adjusted by HCl or NaOH solutions. Then, a defined amount of 13X (according to the BBD) was added to the above solution. By using a magnetic stirrer (100 rpm), the solution was stirring for a defined time. After that, the 13X was removed from the solution by a filter paper. The obtained solution was kept in centrifuge machine for 5 min (3000 rpm). Finally, the supernatant solution was carefully removed and, transferred to the atomic absorption spectrometer for  $\text{Ni}^{2+}$  concentration determination. The obtained concentrations used as the response in experimental design.

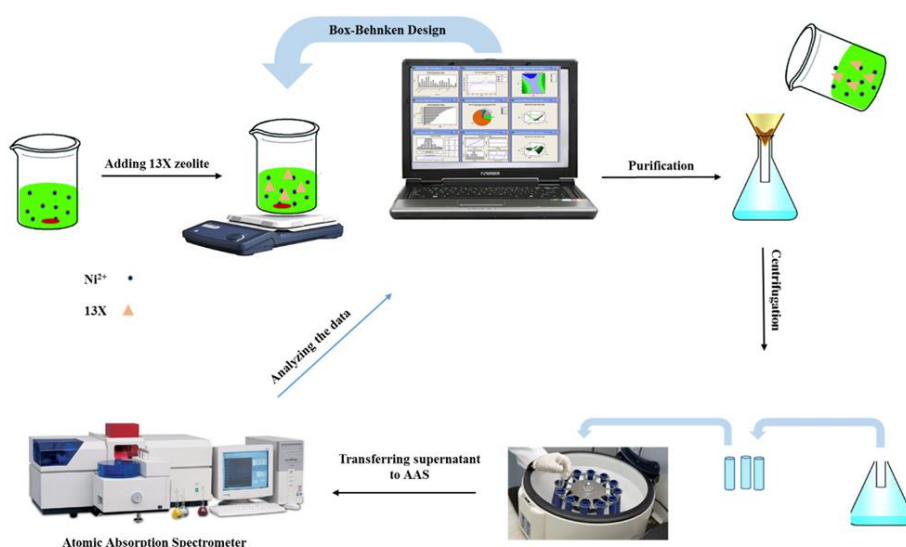


Fig. 3 Schematic representation of nickel ion removal and detection

### 2.5 Experimental design and statistical analysis

The factors (parameters) and the levels were determined based on our previous knowledge about 13X adsorbent. The BBD was applied to study the factors (pH, stirring time and adsorbent amount) and their interactions. The design consisted 15 runs (experiments) including three central points. Design generation and statistical analyses were performed by means of Design Expert software (version 7.0, Stat-Ease, Inc., Minneapolis, USA). The significance of each term in the obtained equation is estimated using ANOVA analysis.

### 2.6 Preparation of real samples

Sea water and industrial wastewater samples were collected from Caspian Sea (north of Iran) and Ranguin Industrial and Chemical Co. manufacturer of paints and protective coatings (Tehran), respectively. The sample solutions were directly spiked with the Ni<sup>2+</sup>. The wastewater samples were diluted 100 times. No additional cleanup step was applied to the samples. 50 mL of sample solution was mixed with 0.55 g of 13X sorbent and the pH of the obtained solution was adjusted to 8. The rest of the adsorption and detection method was similar to section 2.4. The accuracy was demonstrated by using the standard addition method.

Table 2 Experimental variables and levels of the BBD

Factors	Symbol in Eq. 1	Levels		
		Low (-1)	Central (0)	High (+1)
pH of uptake solution	A	5	6.5	8
Stirring time (min)	B	5	32.5	60
13X amount (g)	C	0.1	0.55	1

Table 3 Presentation of 15 experiments with real values for factor levels for the BBD

Standard Order	Run Order	A (pH)	B (Time)	C (13X amount)	Response (R1)
7	1	5.00	32.50	1.00	2.292
12	2	6.50	60.00	1.00	3.864
13	3	6.50	32.50	0.55	33.58
8	4	8.00	32.50	1.00	0.388
15	5	6.50	32.50	0.55	27.74
2	6	8.00	5.00	0.55	27.48
5	7	5.00	32.50	0.10	2.932
1	8	5.00	5.00	0.55	2.84
14	9	6.50	32.50	0.55	35.45
4	10	8.00	60.00	0.55	0.17
3	11	5.00	60.00	0.55	39.51
6	12	8.00	32.50	0.10	0.718
10	13	6.50	60.00	0.10	2.932
9	14	6.50	5.00	0.10	0.32
11	15	6.50	5.00	1.00	5.415

Table 4 Results of analysis of variance for Ni<sup>2+</sup> removal by 13X zeolite

Source	Sum of squares	df	Mean square	F-ratio	p-Value Prob > F
Model	3187.25	9	354.14	28.99	0.0009
A-pH	44.26	1	44.26	3.62	0.1153
B-Stirring time	13.57	1	13.57	1.11	0.3401
C-13X amount	3.20	1	3.20	0.26	0.6307
A×B	1023.04	1	1023.36	83.78	0.0003
A×C	0.024	1	0.024	1.967E-003	0.9663
B×C	4.33	1	4.33	0.35	0.5775
A×A	245.46	1	245.46	20.09	0.0065
B×B	160.99	1	160.99	13.18	0.0151
C×C	1872.67	1	1872.67	153.31	< 0.0001
Residual Error	61.08	5	12.22		
Lack-of-Fit	28.73	3	9.58	0.59	0.6774
Pure Error	32.35	2	16.17		

### 3. Results and discussion

#### 3.1 Optimization of Ni<sup>2+</sup> adsorption by 13X zeolite

To fully understand the way in which experimental parameters affect the adsorption and extraction of nickel ion by 13X, individual factors and nonlinear effects and interaction terms must

be considered. The BBD is probably the most widely used experimental design for fitting a second-order response surface. The design is characterized by set of points lying at the midpoint of each edge of a multidimensional cube and center point replicates whereas the ‘missing corners’ help the experimenter to avoid the combined factor extremes (Ghambarian *et al.* 2011). One of the main advantages of BBD matrix is that it does not contain combinations for which all factors are simultaneously at their highest or lowest levels. So this design is useful to avoid experiments performed under extreme conditions. Initially, three factors were selected while they were potentially affecting the Ni<sup>2+</sup> adsorption by 13X zeolite (Table 2). The selected levels of pH refer to our knowledge about safe 13X structure and rang of Ni<sup>2+</sup> deposition in solution. Other levels considered economically and design set in one block. Therefore, 15 experiments were performed. The design matrix of the variables in natural units together with the experimental results of concentration of Ni<sup>2+</sup> in solutions (mgL<sup>-1</sup>) after adsorption (R1) is given in Table 3.

The adequacy of the model was investigated using the analysis of variances (ANOVA) and the results are shown in Table 4.

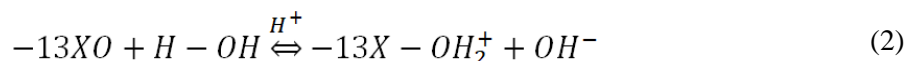
Using the ANOVA table, the model was found to be statistically significant. The F-value of 28.99 confirms this claim. There is only a 0.09% chance that a “Model F-Value” this large could occur due to noise. Values of “Prob>F” less than 0.0500 indicate model terms are significant. In our study AB, A<sup>2</sup>, B<sup>2</sup>, C<sup>2</sup> are significant model terms. The “lack-of-fit F-value” of 0.59 implies the lack of fit is not significant relative to the pure error and the value shows that the quadratic model is valid.

The quality of fit of a polynomial model was expressed by the coefficient of determination (R<sup>2</sup>). Joglekar and May proposed that R<sup>2</sup> should be at least 0.80 for a good fit of a model (Joglekar and May 1987). In our study, the R-Squared was 0.9812, which means that the obtained equation has good adequacy for correlating the experimental results to the response. The “Pred R-Squared” of 0.8361 is in reasonable agreement with the “Adj R-Squared” of 0.9474. “Adeq Precision” measures the signal to noise ratio. A ratio greater than 4 is desirable. Our ratio of 13.537 indicates an adequate signal. The multiple regression analysis gives the following second-order polynomial equation which explains the relation of absorption of Ni<sup>2+</sup> with significant factors and interactions.

$$R1 = -238.83748 + 58.7968 A + 3.18160 B + 125.72642 C - 0.38776 (A \times B) + 0.11481 (A \times C) - 0.084101 (B \times C) - 3.62376 (A^2) - 8.73152E-003 (B^2) - 111.21337 (C^2) \quad (1)$$

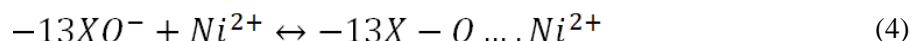
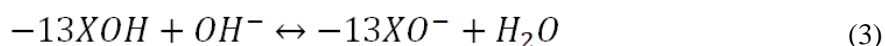
In this equation A, B and C were pH of solution, stirring time for removal nickel ion by sorbent, and 13X zeolite amount, respectively.

Fig. 4 depicts the experimental results of concentration of Ni<sup>2+</sup> in solutions (mgL<sup>-1</sup>) after adsorption (R1) as a function of pH and stirring time. The optimal values were obtained by solving the regression equation and by analyzing the response surface plots. As can be seen from this figure, increasing the time of adsorption of nickel ion by 13X sorbent led to increase the signal. In the same manner, using higher pH values can increase the response signal. In low pH, Ni<sup>2+</sup> ions compete with H<sub>3</sub>O<sup>+</sup> ions for filling the active sites of the 13X sorbent and, hence, working at low pH will decrease the signal of nickel absorption (Sprynskyy *et al.* 2006, Malamis and Katsou 2013). Furthermore, in acidic pH, oxygen atoms at the surface of 13X zeolite react with H<sub>2</sub>O and make some positive-charge complexes (Sen Gupta and Bhattacharyya 2008)



where the “-13X” is the 13X zeolite sorbent surfaces. The positive charges at the surface of 13X

sorbent prevent nickel ion to approach the zeolite and this explain the decrease in extraction efficiency of sorbent. In low basic and neutral environments, the surface of 13X has negative charge and electrostatic interaction between nickel ion and the sorbent will increase the extraction efficiency



but in pH higher than 9 the  $Ni^{2+}$  ions precipitate as  $Ni(OH)_2$ .

The interactions of pH and sorbent amounts can be seen in Fig. 5. Here, at appropriate and optimum conditions, numerous active sites and sufficient positive surface charges can enhance the extraction efficiency of nickel ion by 13X sorbent.

Fig. 6 shows R1 as a function of stirring time and sorbent amounts. It is obvious that, with increasing the time and the sorbent amount because of increasing the active sites at the sorbent surface, the signal will increase, but it will not be economical.

Generally, according to Eq. (1) and the response surface methodology, the optimized values for pH, time, and sorbent amounts were found to be 8, 60, and 0.55 g, respectively.

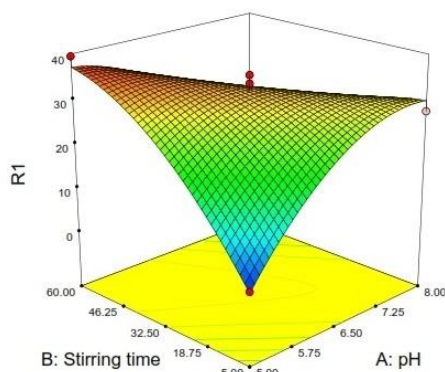


Fig. 4 Response surface for  $Ni^{2+}$  using the Box-Behnken design. The final concentrations of  $Ni^{2+}$  ion as function of pH and time

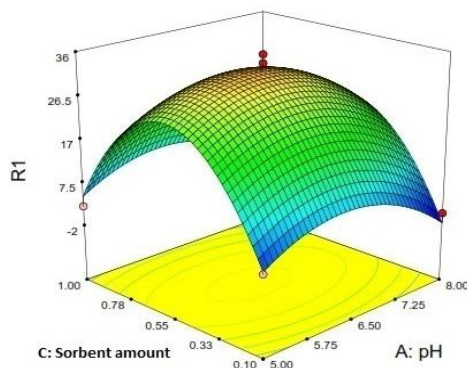


Fig. 5 Response surface for  $Ni^{2+}$  using the Box-Behnken design. The final concentrations of  $Ni^{2+}$  ion as function of pH and 13X amounts



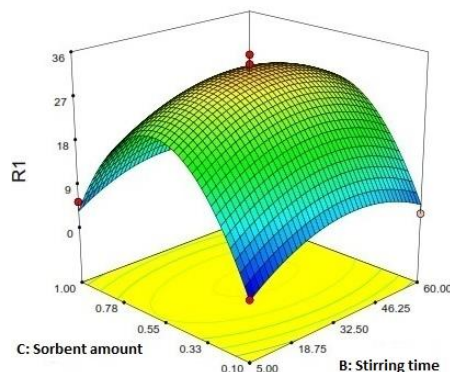


Fig. 6 Response surface for  $\text{Ni}^{2+}$  using the Box-Behnken design. The final concentrations of  $\text{Ni}^{2+}$  ion as function of pH and 13X amounts

### 3.2 Figures of merit

To evaluate the practical applicability of the proposed method, the figures of merit under optimized removal conditions were investigated. The validation of the method was checked under optimum conditions by establishing linearity, limits of detection (LOD), and precision (RSD %). Calibration curves were found to be linear in the range of  $0.1\text{--}20\text{ mg L}^{-1}$  ( $r=1$  in new rational method). The LOD of  $\text{Ni}^{2+}$ , calculated according to the formula  $3s_b/m$ , where  $m$  is the slope of the calibration curve and  $s_b$  is standard deviation of the blank signal, was  $0.102\text{ mg L}^{-1}$ . The repeatability of the peak areas was studied for three-replicate experiments by spiking  $2\text{ mg L}^{-1}$  of  $\text{Ni}^{2+}$ . The relative standard deviation (RSD %) for nickel ion was 1.3%, indicating the good repeatability achieved by this method. It was shown that along with its simplicity, this method exhibited good sensitivity, wide linearity range, and an acceptable reproducibility with an emphasis on the removal time which seems to be short and no need to sample preparation steps.

### 3.3 Real sample analysis

The applicability of the 13X sorbent for elimination of nickel ion and matrix effects was investigated for sea water and wastewater samples. The metal removal was performed under the optimum conditions of pH, time, and 13X sorbent amount. The sea water and wastewater sample solutions were directly spiked with the nickel ion. Wastewater samples were diluted 100 times. No additional cleanup step was applied to these samples. In a typical experiment,  $0.55\text{ g}$  of the 13X was added to  $50\text{ mL}$  of wastewater or sea water samples and the pH of the obtained solution was adjusted to 8. The concentrations of  $\text{Ni}^{2+}$  reduced in sea water and wastewater samples to  $0.828$  and  $2.556\text{ mgL}^{-1}$  and the recoveries were 97.30 and 82.48% respectively.

### 3.4 Comparison of the extraction efficiencies of granule and powder 13X zeolites

Separation and purification of powder sorbents from a large-volume solution encounter some difficulties. To reduce these problems, we used 13X as granules and this sorbent was compared with powder 13X. The optimized values of the parameters in the powder 13X sorbent were also used for granule 13X sorbent. All conditions were the same in powder and granule experiments.

Table 5 Comparison of the extraction efficiencies of granule and powder 13X zeolites

Sample	Sorbent	Concentration (ppm)	RSD%	Removal%
Sea water	Granule	0.444	5.5	46.00
Wastewater	Granule	0.207	12.3	91.90
Sea water	Powder	0.145	12.5	82.48
Wastewater	Powder	0.069	10.4	97.30

Because of presence of some binders in 13X granules, some pores of sorbent have been filled. Thereby, reducing adsorption is predictable. The results obtained from Ni<sup>2+</sup> absorption in real samples by 13X as powder and granule have shown in Table 5. The results demonstrate that elimination of nickel ion by powder 13X sorbent, due to higher surface area, is more effective than that by granule 13X sorbent. However, separation and purification of sorbents from a large-volume solution is more comfortable by using granules.

#### 4. Conclusions

In this paper, the removal of nickel ion using 13X sorbent was successfully performed. The fast time analysis, reduced solvent requirement, and simplification of the whole analytical procedure are major advantages using this method. The factors were optimized and the interaction was investigated using Box-Behnken design. This method can be extended to analyze other heavy metals with little modification. Sea water and wastewater samples were successfully analyzed by the proposed method. Concerning the excellent recoveries in a short time with highly efficient sample clean-up and removal, this method may be a very powerful and innovative future sample removal technique. To use this approach with different heavy metals, research is currently underway in our laboratory that will be published in the future.

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