

Modelling of Adsorption of Zinc and Silver Ions on Analcime and Modified Analcime Zeolites Using Central Composite Design

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ABSTRACT: In this study, Response Surface Methodology (RSM) using Central Composite Design (CCD) was employed to optimize the conditions of independent variables (adsorption time and ion solution concentration) for the removal of Zinc (II) and Ag ions from the aqueous solutions using analcime and modified analcime zeolites (Fe-ANA and Ni-ANA) as efficient and low cost adsorbent. The operation conditions were contact time of 1-13 h and ion concentration of 25-250 ppm at ambient temperature. Under these conditions the response (the adsorption capacity of zinc (II) and Ag ions) was fitted by a quadratic polynomial regression model and linear model analysis in five-level-two-factor CCD using Design Expert software. The optimal conditions (high removal efficiency) for zinc (II) and Ag⁺ adsorption were achieved. The analysis of variance demonstrated that ion concentration effect was found to be significant in the adsorption process. Moreover, actual and predicted response plot of ion adsorption in zeolites were investigated.

KEYWORDS Zeolite; Atomic absorption spectroscopy; Response surface methodology; Analcime.

INTRODUCTION

The environmental pollution is often the result of uncontrolled and irrational discharges of toxic substances from various industrial facilities. The many efforts are being made to remove the harmful substances from air and water [1-3]. The cations of heavy metals can be found among these substances whose main sources are steel mills, galvanization and chemical plants and others. Since the heavy metals are non-biodegradable, their concentration in industrial wastewater must be below the law defined limits before being discharged into natural water ways e.g. rivers. Zinc and silver waste cause both environmental and human health problems. Although humans can handle proportionally large concentrations

of zinc, excess zinc can be harmful. The free zinc ion in solution is highly toxic to plants [4]. Zeolites are members of the tectosilicate family of minerals and consist of 4-fold connected TO₄ tetrahedral (T: Si, Al). Zeolites have a large cation exchange capacity and an affinity for heavy metals [5-7].

Response Surface Methodology (RSM) approach was used for predictive model building and optimization of zinc (II) and Ag ions adsorption on analcime and modified analcime zeolites.

RSM can be defined as an optimization technique introduced by G.E. Box in the 1950s, based on two distinct stages modeling and displacement which are

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repeated as many times as necessary in order to reach an optimal area of investigated surface. The modeling is normally done by fitting simple models generally linear or quadratic to responses obtained with factorial designs or augmented factorial designs. In combination with response surface analysis, factorial design enables the supply of reliable information about the process and at the same time minimizes the empiricism of trial-and-error techniques [8-12]. Central composite design is an experimental design, useful in response surface methodology, for building a second order (quadratic) model for the response variable without needing to use a complete three-level factorial experiment. The design consists of three steps consist of : (a) factorial design in the factors studied, each having two levels; (b) a set of center points, experimental runs whose values of each factor are the medians of the values used in the factorial portion; (c) a set of axial points which will take on values both below and above the median of the two factorial levels, and typically both outside their range. The advantages of CCD are satisfactory distribution of information across the experimental region, minimum number of treatment combinations, suitability for blocking and etc. [13-15].

In view of this, the present work was to investigate the effect of various process parameters on zinc and Ag ions adsorption from the aqueous solutions. Both adsorption processes of heavy metal ions were performed at room temperature using analcime and modified analcime as the adsorbents. The CCD was employed to optimize the influence of two independent variables on the response (adsorption capacity).

EXPERIMENTAL SECTION

Synthesis of zeolites

All materials, $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$, SiO_2 , NaOH , $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 16\text{H}_2\text{O}$ in synthesis of zeolites were purchased from Merck (Dramstadt, Germany). Analcime was synthesized from initial molar ratio composition of 6.16 SiO_2 : 0.162 Al_2O_3 : 3.12 Na_2O : 100 H_2O at 160 °C for 96 h and characterized by XRD, FT-IR, SEM, and XRF. Modified zeolites were prepared following a hydrothermal synthesis route, which in the total mole of transition metal (M: iron or nickel) and aluminum incorporated in the initial composition was 0.5 [16,17].

Procedure of zinc and silver adsorption

Batch adsorption of zinc (II) or Ag^+ was performed independently of each other at room temperature in the flask of 500 cm^3 . Zeolites were used as the efficient adsorbent for removing these ions from aqueous solutions. The samples are mixed on a magnetic stirrer. After adsorption of heavy metal ions from water, the particles of zeolites were removed by filtration. The obtained filtrates were analyzed using Atomic Adsorption of spectrophotometric (AAS) method. The effect of two process factors (contact times, Ag concentration and Zn concentration) was investigated. The ion adsorption capacity (mg/g) of zeolites was calculated using the following equation:

$$q = \frac{(C_{\text{initial}} - C_{\text{final}})V}{m_{\text{zeolite}}} \quad (1)$$

Where C (ppm), V (L) and m (gr) are ion concentration, volume of ion solution and the amount of zeolite, respectively.

Central Composite Design

RSM was used for modeling and optimization of the adsorption procedures. In CCD model each process variables were varied in 5 levels: $+\alpha$, $-\alpha$ (axial points), $+1$, -1 (factorial points) and 0 (central point). The α -value of the used design was 1.68 (as shown in Table 1 and Table 2).

In order to get true functional relationship between independent variables and the response, a second order polynomial (Eq. (2)) was used to describe the effect of variables in terms of linear, quadratic and cross product terms.

$$Y = b_0 + \sum_{i=1}^n b_i x_i + \sum_{i=1}^n b_{ii} x_i^2 + \sum_{i < j}^n b_{ij} x_i x_j + \varepsilon \quad (2)$$

Where i and j are linear and quadratic coefficients; b_0 is constant coefficient, b_i is linear coefficient, b_{ii} is interactive coefficient and b_{ij} is quadratic coefficient. Each variable is investigated for individual and interactive effect on removal process.

It is also important to check the adequacy of the developed model. The analysis of variance (ANOVA) technique was applied to identify significant variables and their individual and interactive effect on the zinc and silver ions removal process. Significance of process variables was checked by p-value and F-value.

Table 1: Coded and actual values of independent variables in zinc (II) adsorption.

Variables	Variable levels				
	$-\alpha$	-1	0	+1	$+\alpha$
C (ppm)	6.4	19	49.5	80	92.6
t (h)	1.1	3	7.5	12	13.9

Table 2: Coded and actual values of independent variables in Ag⁺ adsorption.

Variables	Variable levels				
	$-\alpha$	-1	0	+1	$+\alpha$
t (h)	1.1	3	7.5	12	13.9
C* (ppm)	100.8	135	217.5	300	334.2
C** (ppm)	23.25	45	97.5	150	171.75

* Ion concentration adsorbed by ANA zeolite

** Ion concentration adsorbed by Fe-ANA and Ni-ANA zeolites

RESULTS AND DISCUSSION

Experimental design methodology involves changing all variables from one experiment to the next. The reason for this is the parameters can influence each other, and the ideal value for one of them can depend on the values of the others. RSM usually contains three stages: (i) design and experiment, (ii) response surface modeling through regression, and (iii) optimization. The main advantage of RSM is the reduced number of experiments needed to describe the effects of multiple parameters and their interactions [18]. RSM was used to develop mathematical model and optimize process parameters for Cr (IV) removal by Bajpai et al. [4]. In this study, pH parameter disregarded in experimental design because it is obvious H⁺ ion can compete with Ag⁺ and Zn²⁺. The obtained results showed that the higher pH was the higher adsorption capacity.

Experimental design and development of regression model of zinc and silver adsorption

Batch experiments were performed for the removal of zinc (II) and Ag (I) from aqueous solution using analcime and modified analcime zeolites based on CCD. A CCD model was generated for describing the observed adsorption process consisting of 4 factorial points, 4 axial points and 5 replicates at center. The 13 runs (Eq. (3)) as per experimental design obtained from Design Expert software are presented in Table 3.

$$N = 2^n + 2n + n_c = 2^2 + (2 \times 2) + 5 = 13 \quad (3)$$

Wang et al. determined adsorption capacities for zinc on pure X and A zeolites ranged 156-220 mg/g [18].

The regression model was developed in terms of process variables affecting zinc (II) adsorption (Eq. (4) to Eq. (6)).

$$q_{\text{ANA}} = 0.39 + 0.028C + 0.028t + 3.27 \times 10^{-4}C - 1.87 \times 10^{-4}C^2 - 1.7 \times 10^{-3}t^2 \quad (4)$$

$$q_{\text{Fe-ANA}} = 26.13 + 0.12C - 0.48t \quad (5)$$

$$q_{\text{Ni-ANA}} = 17.72 + 0.029C - 0.4t \quad (6)$$

Savic et al. studied on removal of lead(II) and zinc(II) from aqueous solutions using bentonite clay. A CCD model was used to optimize the conditions of independent variables by a quadratic polynomial regression model [2]. Quadratic model was selected for analcime as suggested by the software compared to linear model obtained for modified zeolites. It is clear the positive sign of the coefficients in equations indicates the synergistic effect, whereas negative sign suggests antagonistic effect. ANOVA test for above models is presented in Table 4. The statistical parameters values, such as Sum of Squares (SS), degree of freedom (df), Mean Square (MS), F and p-values for equation terms were calculated. The p values less than 0.0500 indicate the significant model terms, while p-values greater than

Table 3: The experimental runs of CCD for zinc(II) adsorption from aqueous solutions.

Std	Run	C(ppm)	t(h)	q _{ANA} (mg/g)	q _{Ni-ANA} (mg/g)	q _{Fe-ANA} (mg/g)
13	1	49.50	7.50	1.57	19.59	29.95
2	2	80.00	3.00	1.60	19.8	31.6
11	3	49.50	7.50	1.50	19.65	30.1
7	4	49.50	1.14	1.25	19.32	30.4
8	5	49.50	13.86	1.62	19.85	19.72
10	6	49.50	7.50	1.55	19.62	29.93
1	7	19.00	3.00	1.16	18.70	26.4
5	8	6.37	7.50	0.48	17.22	20.7
9	9	49.50	7.50	1.60	19.73	29.87
4	10	80.00	12.00	1.80	20.20	30.5
6	11	92.63	7.50	1.82	20.6	33.4
3	12	19.00	12.00	1.18	19.00	25.2
12	13	49.50	7.50	1.63	19.75	29.85

Table 4: ANOVA test for CCD in the case of zinc(II) adsorption.

Zeolite	parameter	SS	Df	MS	F	P
ANA	Model	1.38	5	0.28	12.97	0.0020
	C	1.09	1	1.09	51.26	0.0002
	t	0.069	1	0.069	3.24	0.1148
	Ct	8.100×10^{-3}	1	8.100×10^{-3}	0.38	0.5569
	C ²	0.21	1	0.21	9.93	0.0161
	t ²	7.068×10^{-3}	1	7.068×10^{-3}	0.33	0.5826
	Residual	0.15	7	0.021		
	Lack of Fit	0.14	3	0.046	18.95	0.0079
	Pure Error	9.800×10^{-3}	4	2.450×10^{-3}		
	Core Total	1.53	12			
Fe-ANA	Model	139.11	2	69.56	10.68	0.0033
	C	101.25	1	101.25	15.55	0.0028
	t	37.86	1	37.86	5.81	0.0366
	Residual	65.12	10	6.51		
	Lack of Fit	65.08	6	10.85	1118.16	< 0.0001
	Pure Error	0.039	4	9.700×10^{-3}		
	Core Total	204.23	12			
Ni-ANA	Model	6.53	2	3.26	19.81	0.0003
	C	6.27	1	6.27	38.02	0.0001
	t	0.26	1	0.26	1.59	0.2355
	Residual	1.65	10	0.16		
	Lack of Fit	1.63	6	0.27	56.32	0.0008
	Pure Error	0.019	4	4.820×10^{-3}		
	Core Total	8.18	12			

C: ion concentration, t: time, SS: sum of squares, df: degree of freedom, MS: mean square

Table 5: The experimental runs of CCD for Ag (I) adsorption from aqueous solutions by analcime zeolite.

Std	Run	C(ppm)	t(h)	q _{ANA} (mg/g)
10	1	217.5	7.50	27.1
11	2	217.5	7.50	27.04
3	3	135	12	19.36
6	4	334.2	7.50	32.8
5	5	100.8	7.50	14.02
4	6	300	12	31.2
8	7	217.5	13.86	27.34
13	8	217.5	7.50	26.95
9	9	217.5	7.50	27.20
12	10	217.5	7.50	27.04
7	11	217.5	1.14	25.60
2	12	300	3	30.00
1	13	135	3	18.47

0.1000 indicate the insignificant model terms. It is clear from Table 3 that F value of model is higher than p value. It implies that the model is significant and can appropriately explain the relationship between response and independent variables.

Also, the effects of the independent variables on Ag (I) sorption using zeolites was examined by batch tests (Tables 5 and 6).

The relationship between independent variables and adsorption capacity of zeolites was drawn by quadratic model (Eq. (7) to Eq. (9)).

$$q_e = -3.97 + 0.19C + 0.33t + 2.09 \times 10^{-4}Ct - 2.7 \times 10^{-4}C^2 - 0.017t^2 \quad (7)$$

$$q_e = -2.86 + 0.23C + 0.18t - 9.52 \times 10^{-5}Ct - 7.33 \times 10^{-4}C^2 - 9.9t^2 \quad (8)$$

$$q_e = -2.65 + 0.24C + 0.11t - 4.97 \times 10^{-4}Ct - 7.44 \times 10^{-4}C^2 - 0.011t^2 \quad (9)$$

ANOVA technique was applied to the significance of each parameter in Eq. (7) to (9) is presented in Table 7. The large F-value shows the significant of parameter and p-values less than 0.005 indicate the significant model terms. ANOVA studies showed that initial concentration of Ag has the most significant effect on Ag removal in ANA, Fe-ANA and Ni-ANA.

The normal probability plot of the residuals in Zn and Ag adsorption were shown in Figs. 1 and 2, respectively. These plots show systematic variance from the assumption and errors are normally distributed and independent of each other. Fairly good value of correlation coefficient R^2 (0.90) was obtained in Zn adsorption using ANA zeolite (Eq. 4) while moderate values were obtained for Fe-ANA and Ni-ANA generated using Eqs. (5) and (6). This could be due to coverage of wide range of process variables in limited number of CCD experiment design.

The good correlation coefficient R^2 (0.99) in Ag adsorption using ANA zeolites show a good agreement of predicted and actual values by Eqs. (7-9).

Combined effect of process variables

Three dimensional (3D) response surface plots were obtained to investigate the effects of two parameters, *i.e.* contact time and initial concentration of ion solution on Zn^{2+} and Ag^+ removal (shown in Fig. 3 and Fig. 4).

The amount of zinc in investigated solution is more important factor than adsorption time. The increase of zinc concentration leads to increasing the adsorbed amount of ions. The maximal adsorbed amount of zinc (II) was achieved in concentration of 80 ppm.

In Fig. 4, the significant effect on the Ag adsorption has the amount of ion in solution. The maximal adsorbed

Table 6: The experimental runs of CCD for Ag (I) adsorption from aqueous solutions Fe-ANA and Ni-ANA zeolites.

Std	Run	C(ppm)	t(h)	q _{Ni-ANA} (mg/g)	q _{Fe-ANA} (mg/g)
1	1	45	3	6.4	6.33
11	2	97.5	7.5	13.38	14.02
6	3	171.75	7.5	16.57	16.90
2	4	150	3	15.02	16.94
8	5	97.5	13.86	13.5	13.08
13	6	97.5	7.5	13.29	13.85
7	7	97.5	1.14	13.20	14.50
12	8	97.5	7.5	13.40	13.65
3	9	45	12	6.63	5.50
5	10	23.25	7.5	2.85	3.41
10	11	97.5	7.5	13.42	13.88
9	12	97.5	7.5	13.45	13.72
4	13	150	12	15.16	15.64

Table 7: ANOVA test for CCD in the case of Ag (I) adsorption.

Zeolite	parameter	SS	Df	MS	F	P
ANA	Model	338.72	5	67.74	341.43	< 0.0001
	C	311.61	1	311.61	1570.54	< 0.0001
	t	2.59	1	2.59	13.05	0.0086
	Ct	0.024	1	0.024	0.12	0.7381
	C ²	24.42	1	24.42	123.08	< 0.0001
	t ²	0.82	1	0.82	4.14	0.0813
	Residual	1.39	7	0.20		
	Lack of Fit	1.35	3	0.45	53.26	0.0011
	Pure Error	0.034	4	8.480×10 ⁻³		
Core Total	340.10	12				
Fe-ANA	Model	229.78	5	45.96	165.09	< 0.0001
	C	198.28	1	198.28	712.31	< 0.0001
	t	2.14	1	2.14	7.69	0.0276
	Ct	0.055	1	0.055	0.20	0.6695
	C ²	29.29	1	29.29	105.23	< 0.0001
	t ²	0.38	1	0.38	1.37	0.2794
	Residual	1.95	7	0.28		
	Lack of Fit	1.87	3	0.62	29.85	0.0034
	Pure Error	0.083	4	0.021		
Core Total	231.73	12				
Ni-ANA	Model	195.53	5	39.11	160.27	< 0.0001
	C	167.02	1	167.02	684.46	< 0.0001
	t	0.079	1	0.079	0.32	0.5875
	Ct	2.025×10 ⁻³	1	2.025×10 ⁻³	8.299×10 ⁻³	0.9300
	C ²	28.41	1	28.41	116.43	< 0.0001
	t ²	0.28	1	0.28	1.15	0.3190
	Residual	1.71	7	0.24		
	Lack of Fit	1.69	3	0.56	153.80	0.0001
	Pure Error	0.015	4	3.670×10 ⁻³		
Core Total	197.24	12				

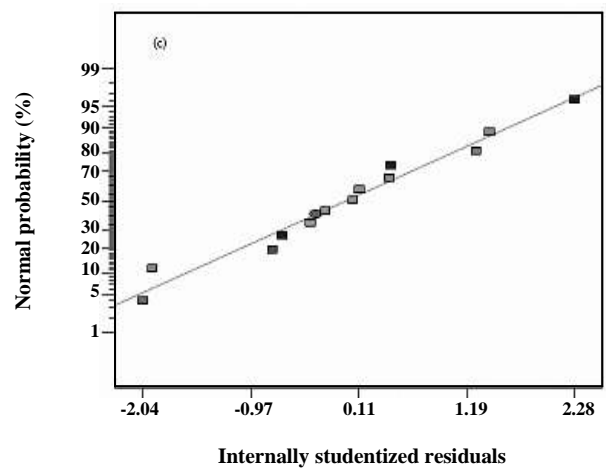
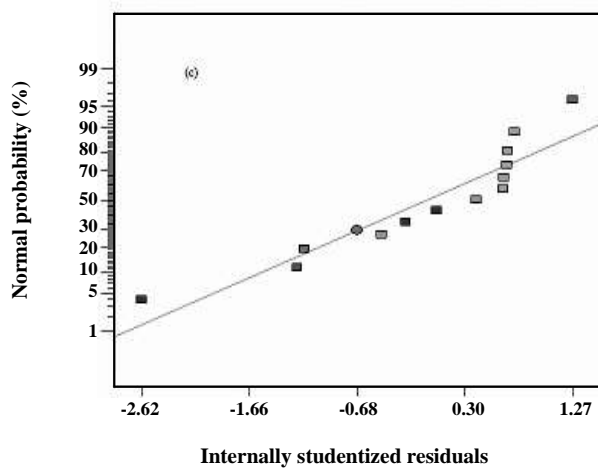
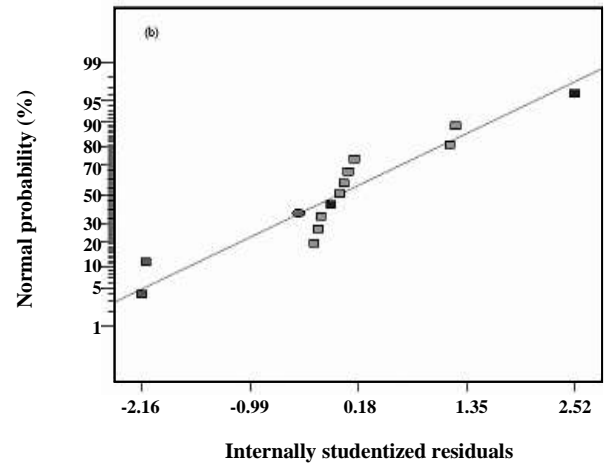
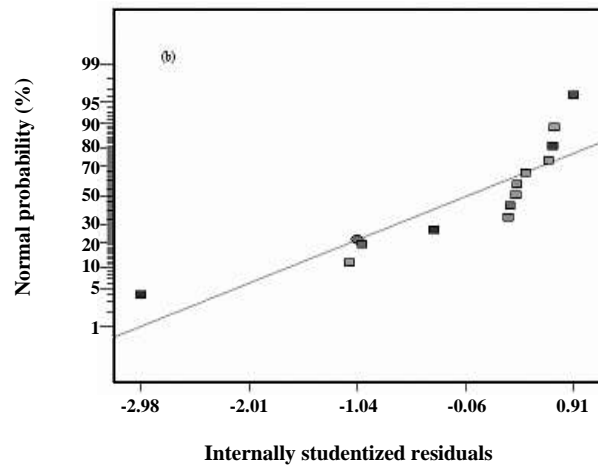
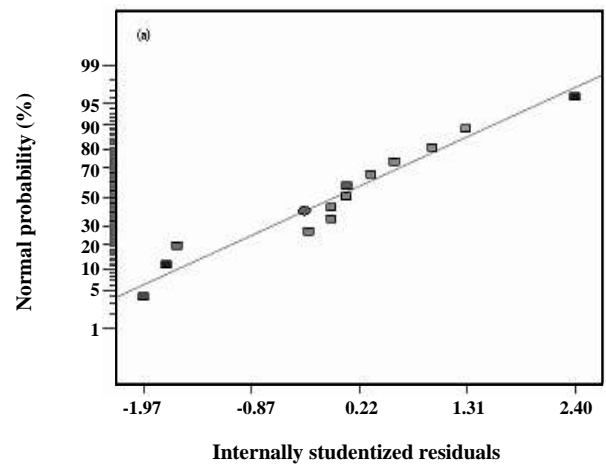
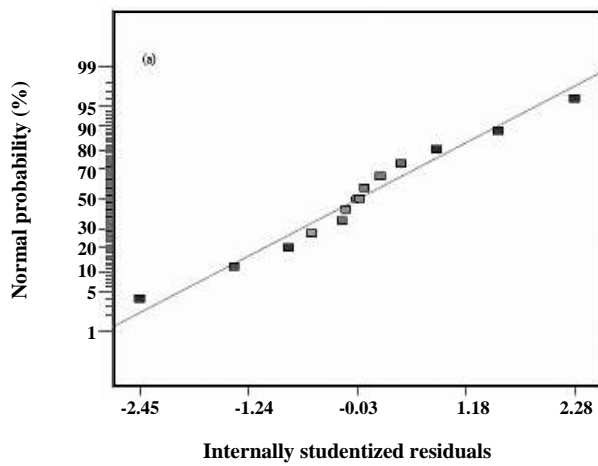


Fig. 1: The normal probability plot of the residuals in Zn adsorption of a) ANA b) Ni-ANA and c) Fe-ANA.

Fig. 2: The normal probability plot of the residuals in Ag adsorption of a) ANA b) Ni-ANA and c) Fe-ANA.

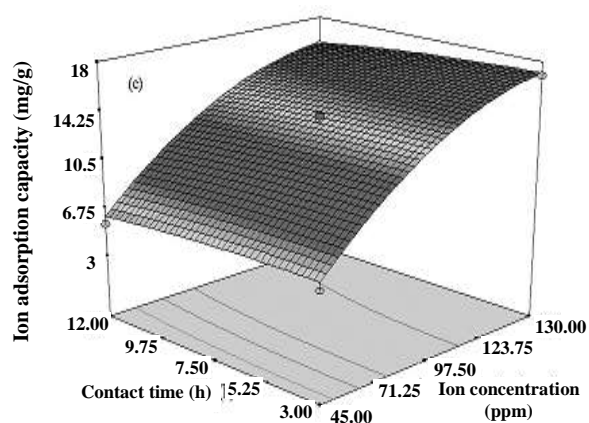
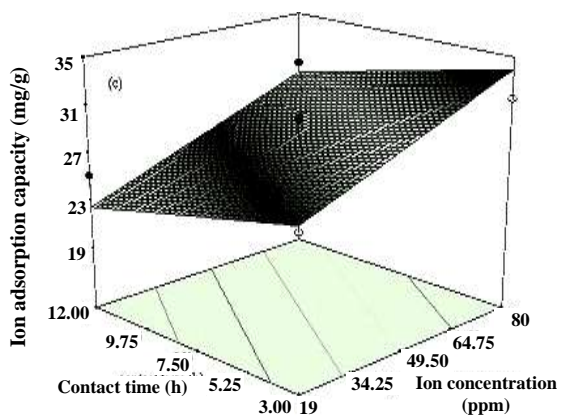
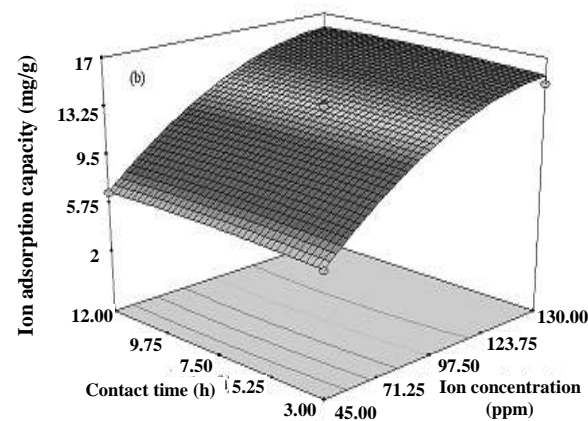
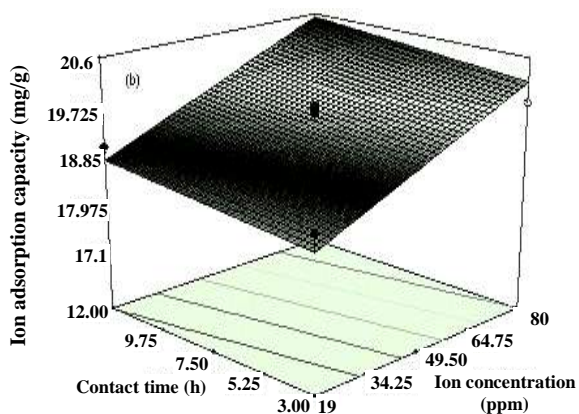
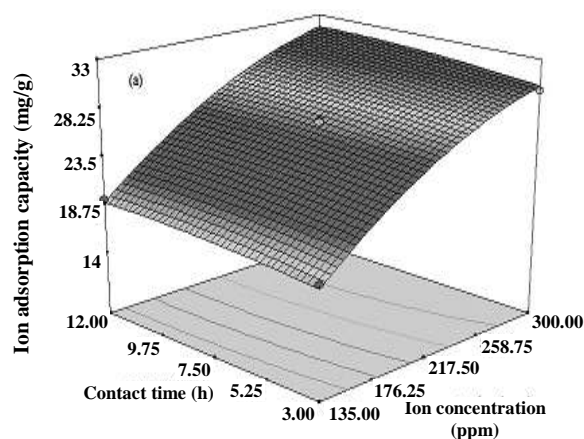
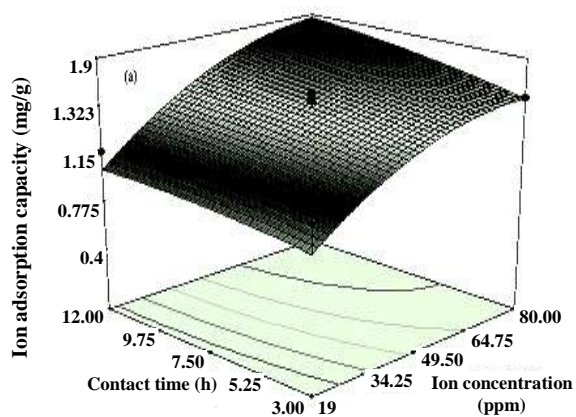


Fig. 3: The combined effect of contact time and initial concentration on zinc removal in a)ANA b)Ni-ANA c)Fe-ANA zeolite.

Fig. 4: Response surface plots of the adsorption capacity versus the effect of contact time and initial concentration on the adsorption of Ag by a) ANA b) Ni-ANA c) Fe-ANA.

ions were higher in analcim zeolite than the modified zeolites. The contact time did not significantly influence on the Ag adsorption.

Optimization of Zn(II) and Ag ions adsorption from solution

It is important to compare and maximize ion removal amount by analcime zeolites. This method was used quadratic and linear models with the objective to maximize adsorption capacity within defined experimental range. The adsorption efficiency of analcime for 73 ppm zinc and 300 ppm Ag removal was 2.5% and 10% at 12 h contact time, respectively. The maximum efficiency of Fe-ANA was 12% at 4 h contact time and 140 ppm of solutions. The optimum adsorption of 80 ppm Zn and 150 ppm Ag solutions using Ni-ANA at 8 h contact time were 25% and 10%, respectively. These results showed Ni-ANA zeolite was more suitable for Zn removal than other zeolites. Also, the maximum removal of Ag ion was achieved by ANA zeolite.

CONCLUSIONS

The adsorption processes of Ag^+ and Zn^{2+} using analcime and modified analcime zeolites were successfully modeled by Central Composite Design. The optimal condition of adsorption was achieved for each zeolite. The obtained results showed the modification of analcime structure using Ni and Fe reduced the capacity of Ag adsorption while increasing Zn adsorption. In the other hand, substitution of Al by Ni and Fe reduce interaction of Ag and investigated zeolites. Also, the concentration of ion solution significantly influences on the adsorption process.

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