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Comparative Performance of MOCZ and FOCZ in the Removal of Fe and Mn from Aqueous Solutions: Optimization Using RSM

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Abstract

The adsorption performance of manganese oxide-coated zeolite (MOCZ) and iron oxide-coated zeolite (FOCZ) for the removal of Fe and Mn from aqueous solutions was evaluated. Response Surface Methodology (RSM) based on the Box-Behnken design was used to assess the effect of independent variables on the response function and prediction of the best response value. Analysis of variance (ANOVA) was used to analyze the responses. MOCZ and FOCZ were characterized by scanning electron microscopy (SEM) and X-Ray Diffraction (XRD) techniques. The effect of parameters such as pH, time, and concentration was studied at different values. Under the optimized conditions (pH 8, contact time 120 min, initial concentration 3 mg/L), MOCZ achieved 96.1% Mn and 92.5% Fe removal. While FOCZ reached 88.5% Mn and 75.9% Fe removal, confirming the superior performance of MOCZ. The experimental data for the variables showed high correlations, with coefficient of determination (R^2) values of 0.93 and 0.90 for Mn and 0.92 and 0.45 for Fe. These results indicate that MOCZ is a more effective adsorbent for Fe and Mn removal compared to FOCZ under the evaluated conditions.

Keywords: Adsorption, FOCZ, Fe and Mn, MOCZ, Response Surface Methodology

Introduction

The discharge of metal pollutants in the environment poses a serious challenge for numerous industries due to its impact on human health and nature. Wastewaters containing dissolved metal ions such as Iron and Manganese are released into the aquatic environment from a variety of sources like electroplating, metal finishing, metallurgy, chemical manufacturing, mining and battery manufacturing [1, 2]. Groundwater is currently a widely used resource for drinking water supply; however, one of the major concerns associated with groundwater is the lack of efficient treatment methods for large quantities of Fe- and Mn-contaminated water. Elevated levels of these heavy metals in groundwater have been linked to multiple adverse health effects, including renal, pulmonary, and gastrointestinal disorders, and their compounds are suspected carcinogens and contributors to oliguria[3]. These metals can cause irreversible damages to the nervous system and other pathologies as pneumonia, circulatory collapse, edema of the respiratory treating[1]. Therefore, standard drinking water, the recommended maximum contaminant level of Fe and Mn by US Environmental Protection Agency is 0.3 and 0.05 mg/L. Currently, adsorption is believed to be a simple and effective technique for water and wastewater treatment. Also, the success of the technique largely depends on the development of an efficient adsorbent. over the past decades, Clinoptilolite samples from various regions show different sorption and ion-exchange behavior, the difference being mainly caused by different composition of zeolitic tuffs [4]. Because of its low-cost and nontoxic nature of clinoptilolite, the adsorption technology has been widely applied into treatments of variant pollutant waters around the world. The effectiveness of this technology in removals of Pb, Zn, Ar and dye from water and wastewater has been confirmed by some recent studies [5, 6].

The removal efficiencies of metals in adsorption systems are often influenced by many parameters such as the adsorbent scheme size, concentration of heavy metal, time, and pH of solution. Therefore, using of the method for optimization of parameters is necessary. Recently, one of the methods for optimization is Response Surface Methodology (RSM) technique [7]. RSM is a collection of mathematical and statistical technique that can be used for studying the effect of several factors. Unlike one-factor-at-a-time experiments, RSM employs a statistical design of experiments based on multivariate nonlinear models, in which all parameters are varied simultaneously over a defined set of experimental runs. This approach simplifies process modeling and improves efficiency in terms of time and resource utilization [8, 9].

The novelty of this study was in the comparative evaluation of manganese oxide-coated zeolite (MnO_2–zeolite, MOCZ) and iron oxide-coated zeolite (FOCZ) under identical optimized conditions using RSM. This approach provids new insight into selecting efficient adsorbents for simultaneous Fe and Mn removal that an important contribution to practical groundwater treatment applications. So, this study aimed to determine the effectiveness of MOCZ and FOCZ to remove Fe and Mn from water.

Materials and methods

Materials and reagents

In this study, potassium permanganate ($KMnO_4$, Scharlau) and hydrochloric acid (HCl, Synth) were used to prepare the MOCZ. Iron nitrate [Fe $(NO_3)_2$] and manganese nitrate [Mn $(NO_3)_2$] (Chemlab) were used in the preparation of manganese synthetic solutions for the adsorption study, and used directly without any further purification. All the reagents were prepared with deionized water. The solution for adsorption experiments were prepared from stock solution to the desired concentration by successive dilutions. The Clinoptilolite used in the present investigation comes from a layer situated in Semnan, Iran. According to its chemical composition, the material was identified as clinoptilolite with the empirical formula $(Na_{0.52}K_{2.44}Ca_{1.48})\ (Al_{6.59}Si_{29.41}O_{72}).28(H_2O)$.

Preparation of MnO_2 – zeolite and FeO – zeolite

Prior to modification, the zeolite was converted to its sodium form by suspending 30 g of zeolite in 500 mL of a 1 M NaCl solution for 24 h. The resulting Na–zeolite was dried in an oven at $100C^0$ for 24 h before use. The preparation of MnO2-coated zeolite was performed as follows: (1) the raw zeolite was sieved to obtain different sets of mesh size; (2) the latter was ion-exchanged with potassium permanganate, placed in a beaker, followed by drop-wise addition of hydrochloric acid (37.5%). After stirring for 1 h, the suspension was filtered, washed several times using distilled water (to remove free potassium and chloride ions); (3) the material was then dried in an oven at $100C^0$ for 24 h. For the preparation of FeO – zeolite (1), 30 g clinoptilolite was added to 60 ml of solution containing 2% $Fe\ (NO_3)_3{\cdot}9H_2O$. The pH of the mixture was adjusted to the desired value with NaOH; (2) the mixture was stirred for 1 h; (c) dried at 105 C° for 20 h, and (3) then washed with deionized water to remove unattached oxide until the pH was constant (pH 7–8). The FOCZ was dried at 105 C° for 24 h and stored in a capped bottle.

Adsorbent characterization

MOCZ and FOCZ were characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses. SEM images of all samples were taken, using KYKY (EM-3200) microscope. XRD analysis was performed on the zeolite to confirm the crystal structure and to determine its mineralogical composition.

Batch adsorption studies

Batch adsorption experiments were conducted to investigate the effects of three controllable factors: initial pH, initial concentration (C_0), and contact time. The factors and their levels are listed in Table 1. Experimental conditions were designed according to RSM. The design was composed of three levels (low, medium and high, being coded as -1, 0 and 1) and a total of 15 runs were carried out in optimize the level of chosen variables based on the three center points per block, such as concentration (1–5 mg/L), pH (4–8), contact time (5–120 min) and removal percent of Fe and Mn was taken as response of the system. In this study, the software Minitab 16.0 was used to design the experiments and analyze the experimental data. The results were analyzed by applying the coefficient of determination (R^2), response plots, and analysis of variance (ANOVA).

Table 1. Level of various independent variables at coded values of the response surface methodology

Symbol	Independent variables	Coded levels		
		-1	0	1
X_1	pH	4	6	8
X_2	Contact Time, min	5	30	120
X_3	Concentration, mg/L	1	3	5

Analytical quantification of Fe and Mn

The concentrations of dissolved Fe and Mn were determined using flame atomic absorption spectrophotometry (AAS, PerkinElmer AAnalyst 400). Samples were first filtered through 0.45 µm cellulose nitrate membrane filters to remove suspended solids before analysis. Calibration curves were established using standard Fe and Mn solutions in the range of 0.1–10 mg/L, prepared from analytical-grade $Fe(NO_3)_3$ and $Mn(NO_3)_2$ stock solutions. Instrument calibration was verified every 10 samples using mid-range standards, and quality assurance/quality control (QA/QC) was ensured by analyzing blanks and duplicates in each batch (variation $< 5\%$). The method detection limits were 0.02 mg/L for Fe and 0.03 mg/L for Mn.

Results and discussion

Surface morphology of the modified zeolite

The surface morphology of the modified zeolite is presented in Fig. 1. As observed, the zeolite surface generally exhibit a rough and porous texture. The figure shows that zeolite surface sites were apparently occupied with newborn manganese oxide and iron oxide. A clear difference in the surface morphology of MOCZ and FOCZ may relate to manganese oxide particles that appear to be growing together in surface depressions and coating cracks. This surface morphology of the modified zeolite has turned to show more dense, relatively porous surface and high affinity for diffusion of metal ions (Fe and Mn) in the case of modified zeolite composites [10]. The x-ray diffractogram pattern obtained for MOCZ sample is presented in Fig.2. According to XRD analysis clinoptilolite was the major crystalline phase (~70%). It was found that peaks of clinoptilolite in XRD pattern are in good agreement with data of clinoptilolite. Feldspar sanidine (~19%), quartz (~8%) and Ramsdellite (~3%) were also detected in XRD analysis. The oxide coated on zeolite surface is presented as Ramsdellite (manganese (IV) oxide) with chemical formula of MnO_2

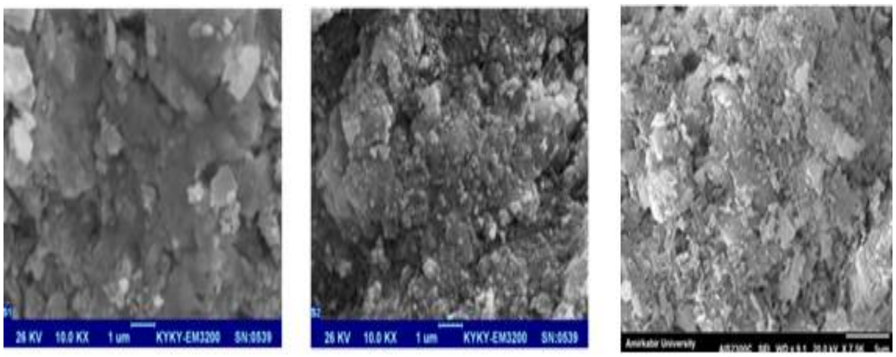

Figure 1. SEM micrograph of zeolite samples. (S_1) Raw zeolite, (S_2) MOCZ, (S_3) FOCZ.

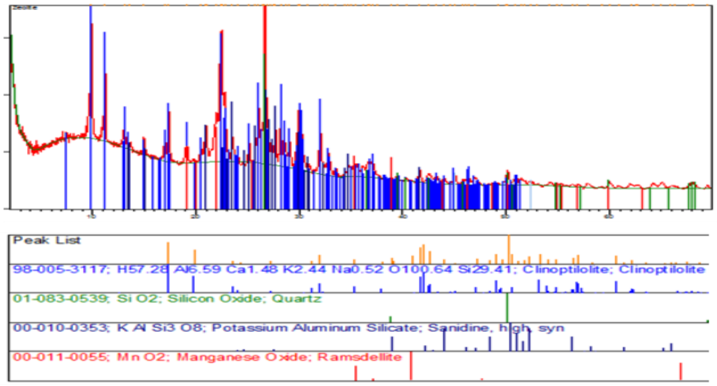

Figure 2. X-ray diffractgram of the MOCZ sample

Response surface estimation for removal of Fe and Mn

The experimental design matrix by the Box–Behnken design is presented in Table (2 and 3) and corresponding experiments were performed.

Table 2. Box–Behnken design and corresponding experimental and predicted responses for Mn with MOCZ (left) and FOCZ (right).

Run	**pH**	**Time**	**Concentration**	**Response value (Removal %)**	
	X1	X2	X3	Experimental (actual)	Predicted
1	6	30	3	69.00	63.43
2	8	5	3	59.00	64.29
3	6	30	3	62.00	63.43
4	8	30	5	80.00	74.20
5	4	30	5	57.00	59.53
6	6	5	5	59.00	60.38
7	4	120	3	80.40	79.43
8	6	30	3	69.80	63.43
9	4	5	3	47.20	49.61
10	6	5	1	55.40	53.51
11	8	30	1	61.80	67.23
12	6	120	1	83.15	83.33
13	4	30	1	53.60	52.66
14	8	120	3	96.10	94.10
15	6	120	5	85.42	90.20

Run	**pH**	**Time**	**Concentration**	**Response value (Removal %)**	
	X1	X2	X3	Experimental (actual)	Predicted
1	6	30	3	64.2	58.07
2	8	5	3	51.1	58.55
3	6	30	3	63.0	58.07
4	8	30	5	73.0	66.29
5	4	30	5	49.9	52.24
6	6	5	5	48.9	52.71
7	4	120	3	76.0	74.62
8	6	30	3	63.6	58.07
9	4	5	3	40.9	44.50
10	6	5	1	53.0	50.34
11	8	30	1	59.4	63.91
12	6	120	1	79.8	80.46
13	4	30	1	49.0	49.86
14	8	120	3	88.5	88.67
15	6	120	5	78.9	82.83

Table3. Box–Behnken design and corresponding experimental and predicted responses for Fe with MOCZ (left) and FOCZ (right).

Run	pH	Time	Concentration	Response value (Removal %)	
	X1	X2	X3	Experimental (actual)	Predicted
1	6	30	3	68.0	59.74
2	8	5	3	59.5	61.65
3	6	30	3	58.0	59.74

Run	**pH**	**Time**	**Concentration**	**Response value (Removal %)**	
	X1	X2	X3	Experimental (actual)	Predicted
1	6	30	3	50.1	40.38
2	8	5	3	17.0	29.03
3	6	30	3	49.0	40.38

4	8	30	5	73.0	71.52
5	4	30	5	53.0	55.39
6	6	5	5	58.0	57.30
7	4	120	3	76.0	73.83
8	6	30	3	64.1	59.74
9	4	5	3	41.9	45.52
10	6	5	1	50.0	49.87
11	8	30	1	59.4	64.59
12	6	120	1	76.8	78.18
13	4	30	1	49.0	47.97
14	8	120	3	92.5	89.96
15	6	120	5	80.9	85.61

4	8	30	5	23.0	40.63
5	4	30	5	42.9	51.58
6	6	5	5	41.0	40.23
7	4	120	3	75.0	67.00
8	6	30	3	49.0	40.38
9	4	5	3	34.9	39.98
10	6	5	1	48.0	28.78
11	8	30	1	31.0	29.18
12	6	120	1	24.0	55.80
13	4	30	1	34.0	40.13
14	8	120	3	75.9	56.05
15	6	120	5	72.0	67.25

Effect of pH and contact time on the adsorption of Fe and Mn

Adsorption experiments were conducted according to the selected model within the chosen ranges of the pH and contact time to investigate the combined effect of initial solution pH and contact time on the system. The Mn removal increases with pH from 4 to8 with FOCZ and optimum pH for MOCZ is 7 with maximum adsorption 0.03 mg/g in 15 min. It is evident that both variables have a strong influence on the Fe and Mn removal. Results showed that when pH was increased from 4 to 8 under constant time (15 min) and dosage (1 g/L), the static repulsion force decreases and the Mn adsorption increases. With increased pH range of 4–8, the surface of MOCZ and FOCZ was negatively charged. In comparison to FOCZ, the more negatively charged surface of MOCZ would have a higher affinity towards Mn^{2+} which makes the adsorption more favorable, resulted to a higher adsorption capacity [11]. At high pH values, both ion exchange and aqueous metal hydroxide formation may become significant mechanisms in the metal removal process [12].Furthermore, the enhanced adsorption at higher pH values can be attributed to the predominance of Mn in its anionic form in aqueous solution. This allows Mn to interact with the active sites of MOCZ and FOCZ, facilitating its removal from solution. However, the removal of Fe decreased at high pH with both of absorbent. That is because Fe has a low pK_a of 2.13 in comparison with pK_a=10.6 for Mn, which can hardly be removed by ion exchange. The effect of the process variable “pH” on the removal of Fe indicated that its removal increased with a decrease of pH. This can be explained that when pH is reduced, positive surface phenomena predominated in the mass transfer and as a result, the ion exchange of the Fe got excess. The solute had sufficient time to diffuse throughout the adsorbent mass. Further, it was also observed that the sorption capacity of the Fe was increased with the increase in contact time. It was due to the sufficient time and increased availability of binding sites for sorption. Thus, the combination of lower pH and extended contact time enhanced Fe removal from the solution [13, 14].

Effect of pH and Concentration of Fe and Mn

The combined effects of pH and concentration on Fe and Mn removal are shown in Table.2 and 3. It was observed that the percentage removal of Fe and Mn increased with increasing the amount of concentration as well as pH at a constant time of 15 min. This means that higher values of Fe and Mn removal can be obtained by simultaneous increase in pH and concentration for Mn. This may be due to the saturation of the adsorption sites at lower Mn concentrations. The Mn concentration provides an important driving force to overcome all mass transfer resistance [10]. Also, the maximum removal (96.1% and 92.5%) occurred by MOCZ, and (88.5% and 75.9%) by FOCZ for Mn and Fe, respectively.

Effect of concentration and time

Figure 3 and 4, shows the interaction effects of concentration and time in the response process. The concentration showed a little effect, while a remarkable effect of time on the removal of Fe and Mn by FOCZ is shown in Figure 1 and Table 4. Additionally, the removal of Fe and Mn increased as the concentration increased. That is probably due to the saturation of the adsorption sites at lower Fe and Mn concentrations. The Fe and Mn concentration provides an important driving force to overcome all mass transfer resistance [10]. As shown in Fig. 3 and 4, the maximal Fe and Mn removal of (96.1% and 92.5%) occurred by MOCZ, and (88.5% and 75.9%) by FOCZ were obtained at a concentration of 4 and 5 mg/L and contact time of 120 min, with an initial solution pH (4 and 8), respectively.

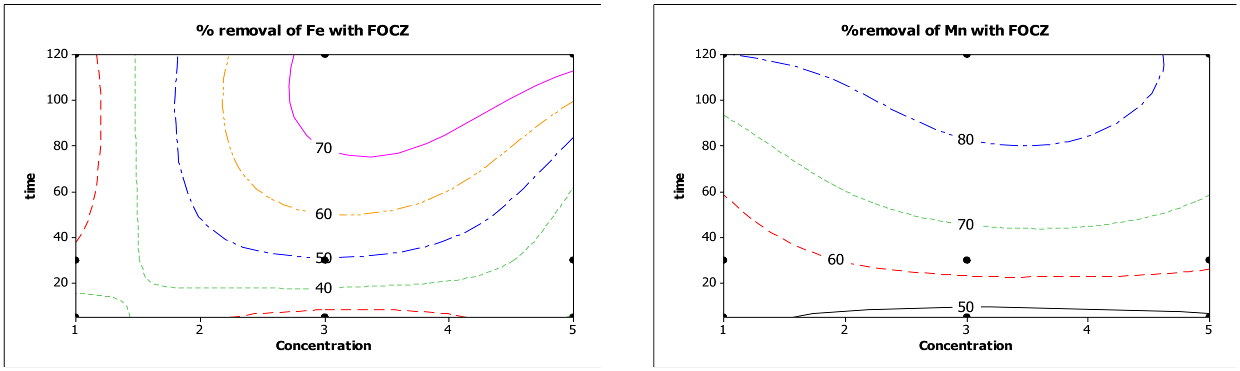

Figure 3. The effect of concentration and contact time on percentage removal of Fe and Mn with FOCZ

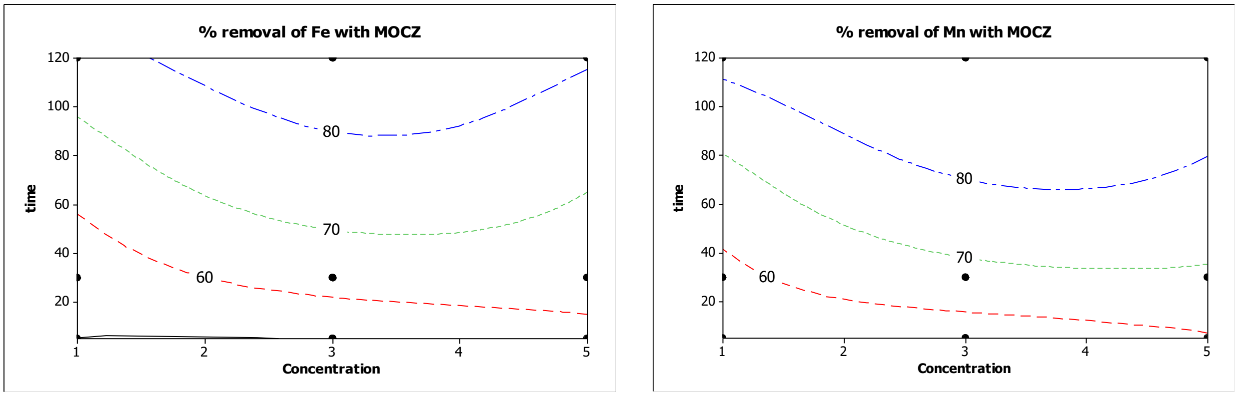

Figure 4. The effect of concentration and contact time on percentage removal of Fe and Mn with MOCZ

Response surface methodology (RSM)

Factorial designs are widely used in experiments when a curvature in the response surface is of concern. All factors have 3 levels in the three- level factorial design. This design requires many runs; as a result, the confounding in blocks can be used. Also, the fractional factorial design can be an alternative approach when the number of factors gets large [15]. The coefficient of determination (R^2) quantifies the goodness-of-fit of the models.The adjusted R^2 (R^2 adj) and predicted R^2 should be within approximately 0.20 of each other to be in reasonable agreement. The close correspondence between R^2 adj and R^2 indicates unnecessary variables have not been included. Acording to Table4, the R^2 values of 0.45 and 0.90, respectively, for Fe and Mn by FOCZ and its 0.92 and 0.93 for Fe and Mn using MOCZ. Beside P-value is used to determine the effects in the model that are statistically significant. The significance of the data is determined by its p-value being closer to zero [16]. The main effect of each factor and the interaction effects are statistically significant when the p-value is less than 0.05 [17]. As can be seen from Table 4, the p-values of X1 and X2 are less than 0.05, which indicates that these variables are significant on the removal of Fe and Mn by both adsorbents, but the p-values of X3 show that these variables are not significant on the removal by FOCZ adsorbent ($p>0.05$). Each level of the factors affects the response differently. Each factor at its high level results in higher mean responses compared to that at the low level of Fe and Mn by two methods, except for factor pH, about Fe removal (low pH= high removal). Alternatively, the factor X1=time has a greater effect on the responses by MOCZ, with a steeply slope. Furthermore, a multiple response method was applied for the optimization of any combination of four goals (pH, contact time, concentration and removal of Fe, and Mn). By searching for 4 starting points, for Mn and Fe the best local maximum response was found to be at initial solution pH 8 and 4, respectively, concentration 5 mg/L, and contact time of 120 min using MOCZ adsorbent. The maximum response (Fe and Mn removal) was 92.5% and 96.1%, respectively.

Table 4. ANOVAs for response surface model for Fe and Mn removal by MOCZ and FOCZ. (X1=pH, X2= Time and X3= Concentration)

Ion & zeolite	Source	Sum of squares	df	Mean square	F value	p-Value Prob>F
Mn (MOCZ)	Model	2568.52	3	856.17	44.39	0.000
	X1	430.71	1	430.71	2.38	0.001
	X2	2043.49	1	2043.49	36.03	0.000
	X3	94.33	1	94.33	0.46	0.049
	Residual	212.18	11	19.29		
	Lack of fit	175.35	9	19.48		
	Pure error	36.83	2	18.41		
	Cor total	2780.70	14			
R^2=93.4%	R^2(adj) =90.3%	R^2(pred) =86.23%				
Fe (MOCZ)	Model	2471.79	3	823.93	51.87	0.000
	X1	520.0	1	520.0	3.18	0.002
	X2	1841.50	1	1841.50	1841.5	0.001

	X3	110.26	1	110.26	110.26	0.023
	Residual	174.74	11	15.89		
	Lack of fit	123.93	9	13.77		
	Pure error	50.81	2	25.40		
	Cor total	2646.53	14			
R^2=92.2%	R^2(adj) = 90.6%	R^2(pred) =84.88%				
Mn (FOCZ)	Model	2491.35	3	830.45	33.60	0.000
	X1	394.81	1	394.81	2.17	0.002
	X2	2085.26	1	2085.26	39.98	0.000
	X3	11.28	1	11.28	0.05	0.513
	Residual	271.91	11	24.72		
	Lack of fit	271.19	9	30.13		
	Pure error	0.72	2	0.36		
	Cor total	2763.26	14			
R^2=90.2%	R^2(adj) = 87.5%	R^2(pred) =82.96%				
Fe (FOCZ)	Model	2179.6	3	726.5	3.06	0.074
	X1	239.8	1	239.8	0.68	0.423
	X2	1677.6	1	1677.6	7.00	0.020
	X3	262.2	1	262.2	0.75	0.402
	Residual	2615.1	11	237.7		
	Lack of fit	2614.3	9	290.5		
	Pure error	0.8	2	0.4		
	Cor total	4794.8	14			
R^2=45.5%	R^2(adj) = 30.6%	R^2(pred) =0.00%				

Removal pathway

While the optimized pH was set to 6.5 to favor adsorption kinetics, it is acknowledged that competitive precipitation of $Fe(OH)_3$ may contribute to the observed removal efficiency. To account for this potential artifact, parallel experiments were conducted using a non-adsorptive control material (e.g., glass beads) under the same pH and contact time conditions. The results confirm that the removal achieved by MOCZ and FOCZ significantly exceeds the non-specific precipitation contribution, validating the adsorbent-specific mechanism, though precipitation remains a relevant factor that is now discussed explicitly.

Conclusion

In this research, MOCZ and FOCZ were used to remove Fe and Mn from an aqueous solution. A Box-Behnken design was employed to evaluate the effects of pH, contact time and, concentration on the removal efficiency of Fe and Mn. Regression models describe the relationship between the responses and variables accurately. The optimal conditions for Fe and Mn adsorption by MOCZ were determined to be a pH of 8 for Fe and 4 for Mn, with an initial metal concentration of 5 mg/L. The effects of interactions of time and pH on the removal of ions by MOCZ were significant, while the interactions of concentration were not significant.Finally, the results of this study suggest that MOCZ can be considered a more effective adsorbent than FOCZ for the removal of Fe and Mn from aqueous solutions.

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