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Box-Behnken Design of Experiments Investigation forAdsorption of Cd^{2+} onto carboxymethyl Chitosan Magnetic Nanoparticles

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Abstract

The main objective of the present study is to investigate the feasibility of using Carboxymethyl chitosan magnetic nanoparticles (CCMN) for the adsorption of Cd^{2+}. The study also reports important parameters, which affect the adsorption process, i.e., pH, adsorbent dose, contact time and concentration of Cd^{2+}, using Box-Behnken designs. Firstly, functional carboxymethyl chitosan magnetic nanoparticles (about 33 nm) was prepared by chemical coprecipitating and characterized by means of scanning electron microscope (SEM), X-ray diffraction (XRD), Fourier Transform infrared spectroscopy (FTIR). Then, CCMN was used as the adsorbent for the treatment of effluent. The ANOVA result of the full model shows that pH, adsorbent dosage and metal concentration had a significant effect on metal removal. In addition, this parameters indicates which contact time variable does not have a significant effect ($p>0.05$).

Keywords: *experimental design; nano magnetic; carboxymethyl chitosan; Cd^{2+}.*

1. Introduction

The removal of polluting heavy metals from wastewater is one of the most important concerns due to their harmful effects on human health and environment [1]. Heavy metal ions such as Cr(II), Cd(II), and Ni(II) are toxic and carcinogenic at even relatively low concentrations [2]. They are not ecologically friendly and can accumulate in living organisms [3]. Therefore, these heavy metals can be considered as one of the most important pollutants for waters and wastewaters [4]. Heavy metal pollutants mainly come from industries including mining, electric device manufacturing, metal plating, and so on [5].

Recently, magnetic nanoparticles have widely been studied. Superparamagnetic iron oxide (Fe_3O_4) nanoparticles have attracted researchers invarious fields such as biology, physics, medicine and materials sciences due to their multifunctional properties such as low toxicity, small size, biocompatibility and Superparamagnetic, etc. [6, 8]. Compared to the traditional treatment systems, such as chemical precipitation, ion exchange, coagulation, electrolysis and reverse osmosis processes [9], the magnetic nanoparticles possess optimal magnetic properties and high surface areas, which lead to high removal rate of contaminants, high adsorption efficiency, rapid and easy separation of adsorbent from solution via magnetic field.

Numerous types of magnetic nanoparticles for heavy metalremoval could be tailored by using functionalized synthetic or natural polymers to impart surface reactivity [10]. Shashwat et al. [10] utilized gum Arabic modified magnetic for the removal and recovery of Cr(VI) from wastewater, and Kochen et al. [11] used magnetic polymer resin for the removal of Actinides and other heavy metals from contaminated water. The removal of copper ions by chitosan-bound Fe_3O_4 magnetic nanoparticles was reported by Chang et al. [12] and Ngomsik et al. reported the removal of Nickel ions from aqueous solution by magnetic alginate microcapsules [13].

The natural polysaccharide–carboxymethyl chitosan was favored to modify the magnetite nanoparticles because of excellent features such as biodegradability, biocompatibility, hydrophilicity, and notable affinity for metal ions [14,15].

In the present study magnetic carboxymethyl chitosan nanoparticles were synthesized and used for the removal of Cd^{2+} from wastewater samples. Box-Behnken Design was used to optimize the removal of Cd^{2+} from wastewater samples by magnetic carboxymethyl chitosan nanoparticles.

Traditional experiments require more effort, time, and materials when a complex formulation needs to be developed. In general usage, various experimental designs are useful in developing a formulation requiring less experimentation and providing estimates of the relative significance of different variables.

pH (X_1), dosage of magnetic nano adsorbents (X_2), contact time (X_3), concentration of metal ions (X_4) were selected as independent variables to evaluate their separate and combined effects on percentage removal of Cd^{2+}.

2. Experiment

2.1. Materials

Chitosan polymer (medium viscous) was obtained from Chito Tech Company (IRAN). Mono-chloroacetic acid (Merck, Ger) was used as a solvent for the chitosan polymers and cyanamide (Aldrich, USA) was used as the cross-linker. All chemicals were of analytical grade and no further purification was required.

2.2. Preparation of Mangnetic Nanoparticles

Magnetite was prepared using the modified Kang method [16]. $FeCl_2.4H_2O$ and $FeCl_3.6H_2O$ [Fe^{2+}: Fe^{3+}= 1:2] were dissolved in about 10 ml HCl (0.1M), and stirred under strong ultrasonic agitation. Next, this iron solution source was drop-wised into NaOH solution with the temperature of 70°C for 30 minutes, and N_2 gas was bubbled through. Black Fe_3O_4 particles were decanted by permanent magnet and cleaned by deionized water several times.

2.3. Preparation of Carboxymethyl Chitosan

Carboxymethyl Chitosan (CCs) was prepared by use of Sun et.al. 2008 method. [17], briefly, 10 g chitosan and 10 g sodium hydroxide were added into 100 ml of isopropanol/water (50/50) mixture to swell and alkalize for 1 h. Then, 20 ml of 0.75 gml^{-1} chloroacetic acid solution was drop-wised into the reaction mixture. After reaction for 4 h, ethyl alcohol was added to stop the reaction. The solid was filtered, rinsed with ethyl alcohol (80%) and vacuum dried to get Na salt CC. Na-CC (1 g) was suspended in ethyl alcohol aqueous solution (100 ml, 80%), and stirred for 30 min. Finally, hydrochloric acid (10 ml, 37%) was added and stirred to desalt.

2.4. Preparation of Fe_3O_4 Nanoparticles Coated with Carboxymethyl Chitosan

The binding of carboxymethyl chitosan (CCs) was conducted following the Chang and Chen method [18]. First, Fe_3O_4 nanoparticles were added to 2 ml of buffer A solution (0.003M phosphate, pH 6, 0.1 M NaCl). Then, the reaction mixture was sonicated for 10 minutes after adding 0.5 ml of carbodiimide solution. Finally, 2.5 ml of Carboxymethyl chitosan solution was added and the reaction mixture was sonicated for 60 minutes. The chitosan-bound Fe_3O_4 nanoparticles were recovered from the reaction mixture by magnetic barand washed with water and ethanol.

2.5. Characterization Methods

Powder X-ray diffraction (XRD) patterns were obtained at room temperature by X′Pert MPD, Philips, Holland, using Co kα radiation. The dimension and morphology of magnetic chitosan nanoparticles were observed by scanning electron microscopy (SEM) (XL30, Philips, Netherlands). The nano-magnetic particles were also characterized using Fourier-Transform Infrared Spectroscopy (FTIR) (Tensor 27, Burker).

2.6. Adsorption Experiments

2.6.1. Batch Experimental Programme

For each experiment, 25 ml of wastewater containing Cd^{2+} ions was added to the magnetic nanoadsorbents. This mixture was agitated in a temperature-controlled shaking water bath, at a constant speed for all experimental runs. The percentage removal of metal ions was calculated using the following equation:

$$\text{Percentage removal} = 100\,(C_0 - C_t)/C_0 \qquad (1)$$

where C_0 and C_t are the initial and the equilibrium concentration of Cd^{2+} ions (mg/L) repectively.

2.6.2. Box-Behnken Design

Box-Behnken Design requires a lower numbers of actual experiments to be performed[19]. This facilitates probing into possible interactions between the parameters studied and their effect on the percentage removal of metal ions. Box-Behnken is based on a spherical, revolving design; it consists of a central point and the middle points of the edges of a cube circumscribed on a sphere [20, 21]. It contains three interlocking 22 factorial designs and a central point. It has been applied for the optimization of several chemical and physical processes, and the number of experiments is decided accordingly.

In the present study, the three-level, four-factorial Box-Behnken experimental design is applied to investigate and validate adsorption process parameters, which affect the removal of Cd^{2+} ions onto magnetic nano-adsorbents. Table 1. represents a 27-trial experimental design, where each variable was tested in three different coded levels: low (-1), middle (0) and high (+1). The coded values correspond to X_1: -1(4), 0(6), +1(8), X_2: -1(30 mg), 0(75 mg), +1(120 mg), for X_3: -1(20), 0(40), +1(60) and for X_4: -1(43 mgl^{-1}), 0(100 mgl^{-1}), +1(157 mgl^{-1}). The whole set of experiments was performed in triplicate and mean response was used for analysis. A second order polynomial equation was then fitted to the data using the Minitab (ver. 16) software [22].

Table 1. Experimental and predicted values of Cd^{2+} adsorption (Y%) on the surfaces of nanoparticles

Run	pH	abso	Time	ppm	Y_{exp}	Y_{pre*}	E
1	8	75	40	157	98.82	99.30	-0.474
2	8	75	20	100	98.98	99.10	-0.116
3	6	120	40	43	86.94	86.77	0.167
4	6	30	40	157	92.35	91.68	0.675
5	6	120	20	100	89.13	89.72	-0.584
6	4	75	40	43	81.01	81.09	-0.083
7	6	120	60	100	88.85	90.05	-1.20
8	6	30	40	43	84.24	84.03	0.218
9	6	75	60	43	87.16	86.92	0.248
10	6	30	20	100	88.82	88.17	0.644
11	6	75	20	43	84.73	85.35	-0.621
12	8	75	60	100	99.52	99.88	-0.368
13	6	75	20	157	92.37	92.90	-0.533
14	6	120	40	157	92.52	91.90	0.624
15	6	75	40	100	88.82	88.86	-0.043
16	4	75	20	100	88.87	87.66	1.210
17	4	30	40	100	83.66	85.03	-1.369
18	6	75	40	100	88.74	88.86	-0.122
19	8	120	40	100	99.41	98.33	1.083
20	4	75	40	157	92.52	93.15	-0.628
21	8	75	40	43	98.65	98.85	0.071
22	4	75	60	100	88.64	87.68	0.958
23	6	75	60	157	92.48	92.14	0.335
24	4	120	40	100	88.75	88.84	-0.089
25	6	75	40	100	89.02	88.86	0.165
26	8	30	40	100	98.98	99.18	-0.197
27	6	30	60	100	88.66	88.64	0.028

3. Results and Discussions

3.1. Characterizations of the Magnetic Nanoparticles

3.1.1. SEM analysis

The SEM micrographs of Fe_3O_4 and Fe_3O_4-CCs nanoparticles are shown in Figure 1. From the micrographs it is clear that the CCs-bound Fe3O4 nanoparticles are essentially monodispersed. As CCs was employed in the preparation of composites, the obtained magnetic Fe_3O_4–CCs nanoparticles were almost spherical or ellipsoidal. The nanoparticles had a mean diameter of 33 nm, i.e. smaller than the nanoparticles produced using conventional techniques.

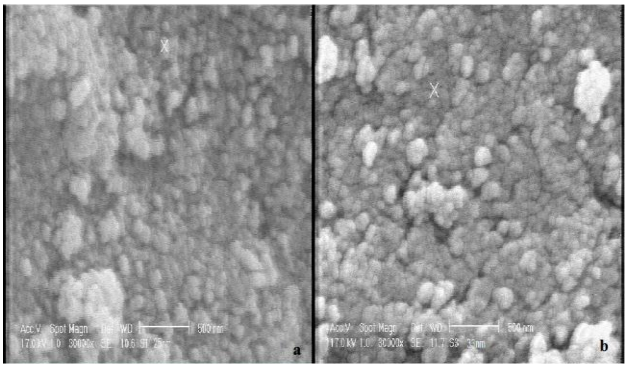

Figure 1. SEM micrographs of (a) Fe_3O_4 and (b) Fe_3O_4-CCs nanoparticles.

3.1.2. XRD Analysis

Figure 2. showes the XRD patterns for the naked and Fe_3O_4 nanoparticles coated with chitosan. Six characteristic peaks for Fe_3O_4 were observed for both samples. These peaks reveal that the resultant nanoparticles were pure Fe_3O_4 with a spinel structure. It is also explained that the coating process did not result in the phase change of Fe_3O_4.

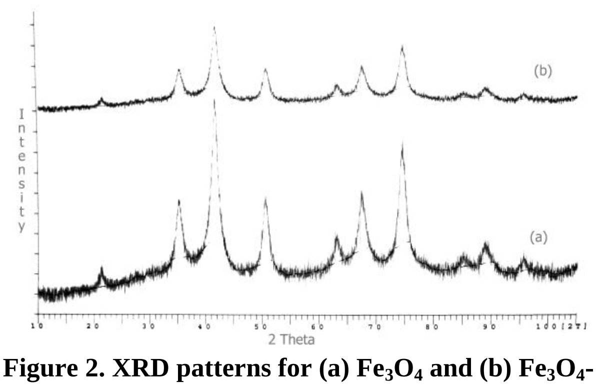

Figure 2. XRD patterns for (a) Fe_3O_4 and (b) Fe_3O_4-CCs.

3.1.3. FTIR Spectra Analysis

To realize the binding mechanism, FTIR spectra of the (a) naked Fe_3O_4, (b) Fe_3O_4– Carboxymethyl Chitosan nanoparticles were examined and the results are shown in Figure 3. For the naked Fe_3O_4 (Figure 3.(a)), the peak at 569 cm^{-1} relates to Fe–O group. This peak shifted to lower amounts on Fe_3O_4 – Carboxymethyl Chitosan nanoparticles. In addition to these, 1558 and 1406cm^{-1} private peaks of Fe_3O_4– Carboxymethyl Chitosan nanoparticles. These results prove that Carboxymethyl chitosan have been coated on magnetite nano-particles.

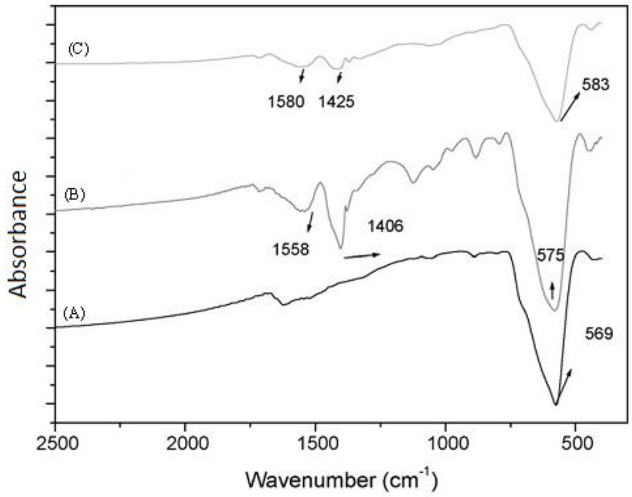

Figure 3. FTIR spectra of the (a) naked Fe3O4, (b) Fe_3O_4-Chitosan and (c) Fe3O4– Carboxymethyl Chitosan nanoparticles.

3.1.4. Model building and Statistical Significance Test

A 27-run Box-Behnken design with four factors and three levels, including three replicates at the center point, was used for fitting a second-order response surface. The three center point runs were added to provide as a measure of process stability and inherent variability. Considerable variation in the removal of mineral wastewater under different condition is shown in Table 2.

Analysis of variance (ANOVA) is a statistical technique that subdivides the total variation in a set of data into component parts associated with specific sources of variation for the purpose of testing hypotheses on the parameters of the model [20]. As Table 3. shows, the $F_{Statistics}$ values for all regressions were higher. The large value of F indicates that most of the variation in the response can be explained by the regression equation. The associated p value is used to estimate whether $F_{Statistics}$ is large enough to indicate statistical significance. A p > F-value, less than 0.05, indicates that the model could explain 95% of the variability. The analysis of variance for the four variables (pH, adsorbent dose, contact time and metal concentration) indicate that removal of metals can be well described by a polynomial model with a relatively high correlation coefficient ($R^2 = 0.95$). The statistical analysis of the full model in Table 3. shows that pH, adsorbent dose and metal concentration have a significant effect on metal removal. The probability value of the coefficient of linear effect of contact time was very high, 0.58. In addition, the interaction coefficients of this variable with other variables were high, which indicates the insignificance of these coefficients.

The reduced second-order polynomial equation by multiple regressions (Y) and the significant terms ($p < 0.05$) obtained:

$$Y=79.520 +6.415X_1+0.136X_2+0.246X_4+1.052X-0.012X_1X_2-0.024X_1X_4$$

Where X_1, X_2 and X_4 represent codified values for pH, adsorbent dosage and metal concentration respectively.

The three replicated center points in the Box-Behnken experimental design made it possible to assess the pure error of the experiments and enabled the model's lack of fit to be checked. In this study, the model was checked for lack of fit for the responses. For lack of fit P values we obtained 0.408, hence the current model provided a satisfactory fit to the data ($P > 0.05$) and had no lack of fit.

Table 2. ANOVA table for Y

Source	Sum of Squares	d.f.	Mean Square	F-Value	P	Remark
Regression	706.991	14	50.4993	59.051	0.001	Significant
linear	548.510	4	20.870	24.410	0.001	Significant
pH	419.051	1	17.707	20.741	0.001	Significant
adsorbent dosage	6.594	1	6.128	7.170	0.002	Significant
Time	0.481	1	0.269	0.312	0.585	-------
metal concentration	122.385	1	31.170	36.450	0.002	Significant
Square	117.849	4	29.462	34.451	0.002	Significant
pH*pH	115.436	1	94.548	110.56	0.001	Significant
adsorbent dosage* adsorbent dosage	0.750	1	0.268	0.313	0.585	---------
Time*Time	1.685	1	1.396	1.633	0.226	---------
metal concentration* metal concentration	0.009	1	0.0089	0.012	0.921	----------
Interaction	40.630	6	6.771	7.920	0.001	Significant
pH*abso	5.418	1	5.418	6.342	0.027	-----------
pH*Time	0.150	1	0.150	0.182	0.683	-----------
pH*metal concentration	32.102	1	32.102	37.54	0.004	Significant
abso*Time	0.004	1	0.0042	0.001	0.945	------------
abso* metal concentration	1.604	1	1.6037	1.883	0.196	------------
Time* metal concentration	1.352	1	1.352	1.583	0.233	-----------
Residual error	10.262	12	0.0855	--------	----------	-----------
Lack-of-fit	10.218	10	1.021	46.323	0.408	-----------
pure error	0.004	2	0.022	----------	-----------	----------
Total	717.25	26	--------	---------	-----------	-----------

A normal probability plot and a dot diagram of these residuals are shown in Figure 4. The data points on this plot lie reasonably close to a straight line, lending support to the conclusion that X_1, X_2, X_4, X^2_1, X_1X_2, and X_1X_4 are the only significant effects and that the underlying assumptions of the analysis are satisfied.

Figure 5. shows the relationship between the actual and predicted values of *Y* for adsorption of Cd^{2+} onto CCs-Fe_3O_4. It is seen in Figure 5. that the developed models are adequate because the residuals for the prediction of each response are minimum, since the residuals tend to be close to the diagonal line.

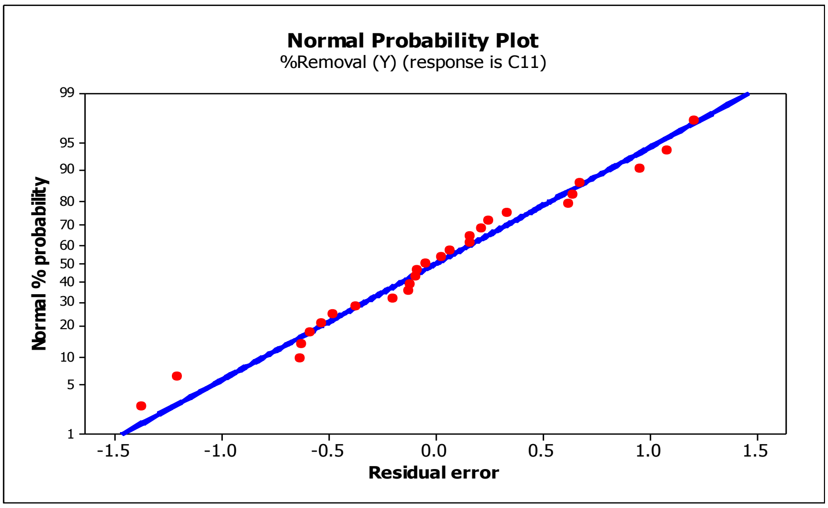

Figure 4. Normal % probability versus residual error.

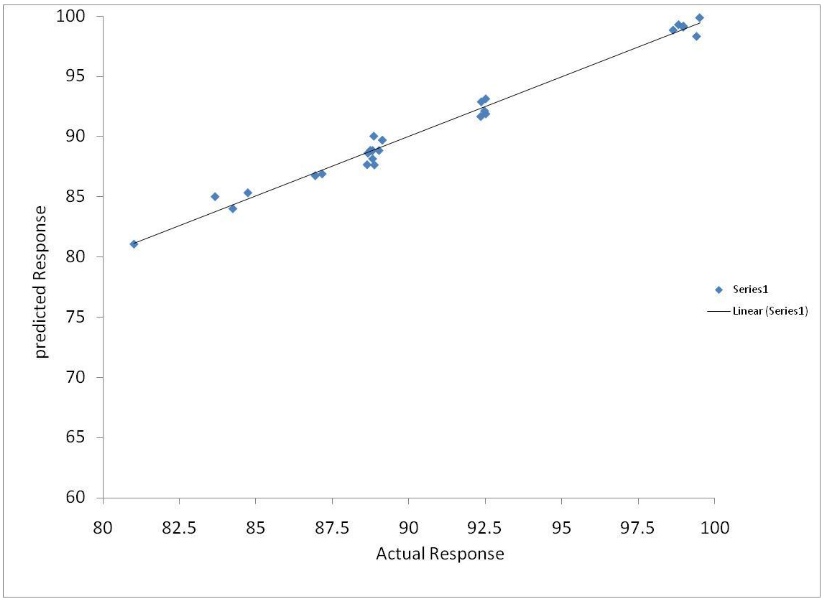

Figure 5. Scatter diagram of predicted response versus actual response for the Cd^{2+} /nanomagnetic chitosan adsorption system.

The main results of this study are presented in counter plots, which representthe relationship between the dependent and independent variables.
The effects of X_1 and X_4 with their interaction on removal percentage at a fixed level of X_2 (medium level) are shown in Figure. 6(a). The plots were found to be nonlinear up to 92% removal, but above this value, the plots were found to be linear indicating a linear relationship between X_1 and X_4. It was determined from the contour plot that a higher value of removal (≥92%) could be obtained with an X_1 level range from –6.75 to 8.0, and an X_4 level range from 50 to 150. It is evident from the contour that the high level of both X_1 and X_4 favors removal of Cd^{2+} ions from solution. pH is present in a higher proportion at the high level of X_1, resulting in high removal metal ions.
When the coefficient values of 2 key variables, X_1 and X_4, were compared, the value for variable X_1 (β_1=6.415) was found to be higher, indicating that it contributes most in predicting the removal of Cd^{2+}.
Figure. 6 (b) shows the contour plot drawn at a 0 level of X_4. The contours were found to be linear from 96 to 88% and indicated that a high value of removal (96%) can be obtained for a combination of the 2 independent variables, the X_1 level in the range of 7.5 to 8, and the X_2 level in the range of 30 to 120.
The surface plots of this study are presented in Figure 7., which represents the expected removal response and correlation between variables in three dimensional plots. Figure. 7(a) shows non-additive effects of pH and Metal concentration due to the significant interaction between them. Figure. 7(b) shows that the effects of pairs of factors were additive since there are no interactions.
By additivity of the two-factor effects it is meant that the effect of one factor on the response does not depend on the level of the other factor. Figure. 7(b) illustrates that increasing pH value to pH 8 at each level of adsorbent dose lead to maximum removal Cd^{2+} ions.

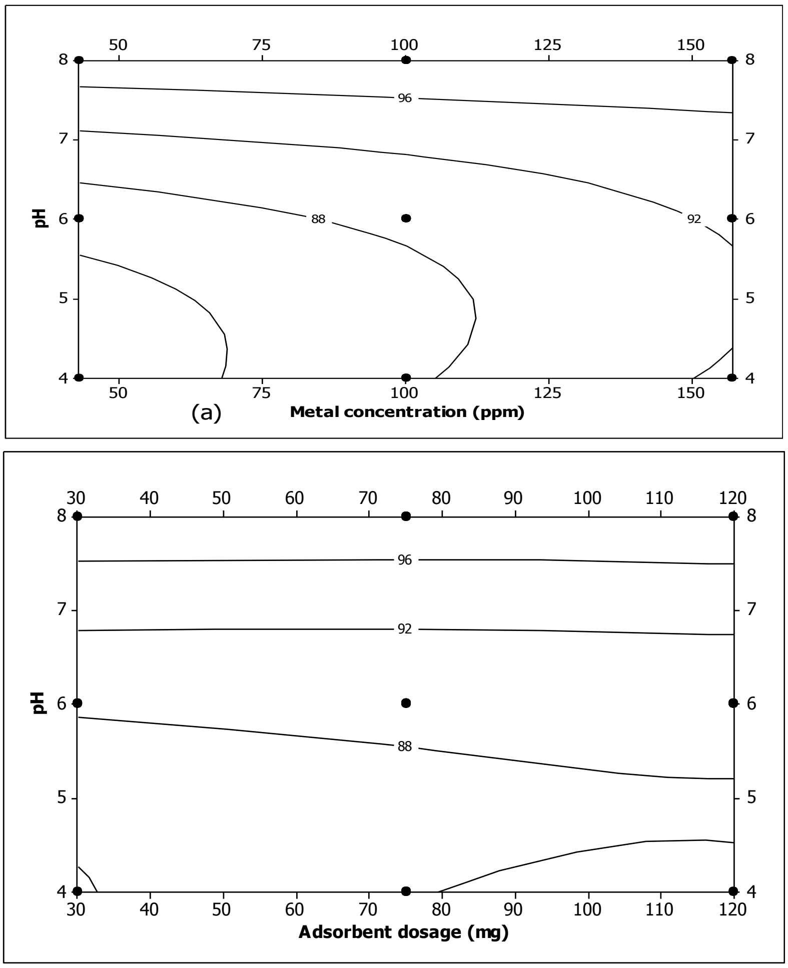

Figure 6. Contour graph of (a) pH versus Metal concentration at a holding adsorbent of 75 mg, (b) pH versus Metal concentration at a holding metal concentration of 100 ppm for the Cd^{2+} /nanomagnetic chitosan adsorption system.

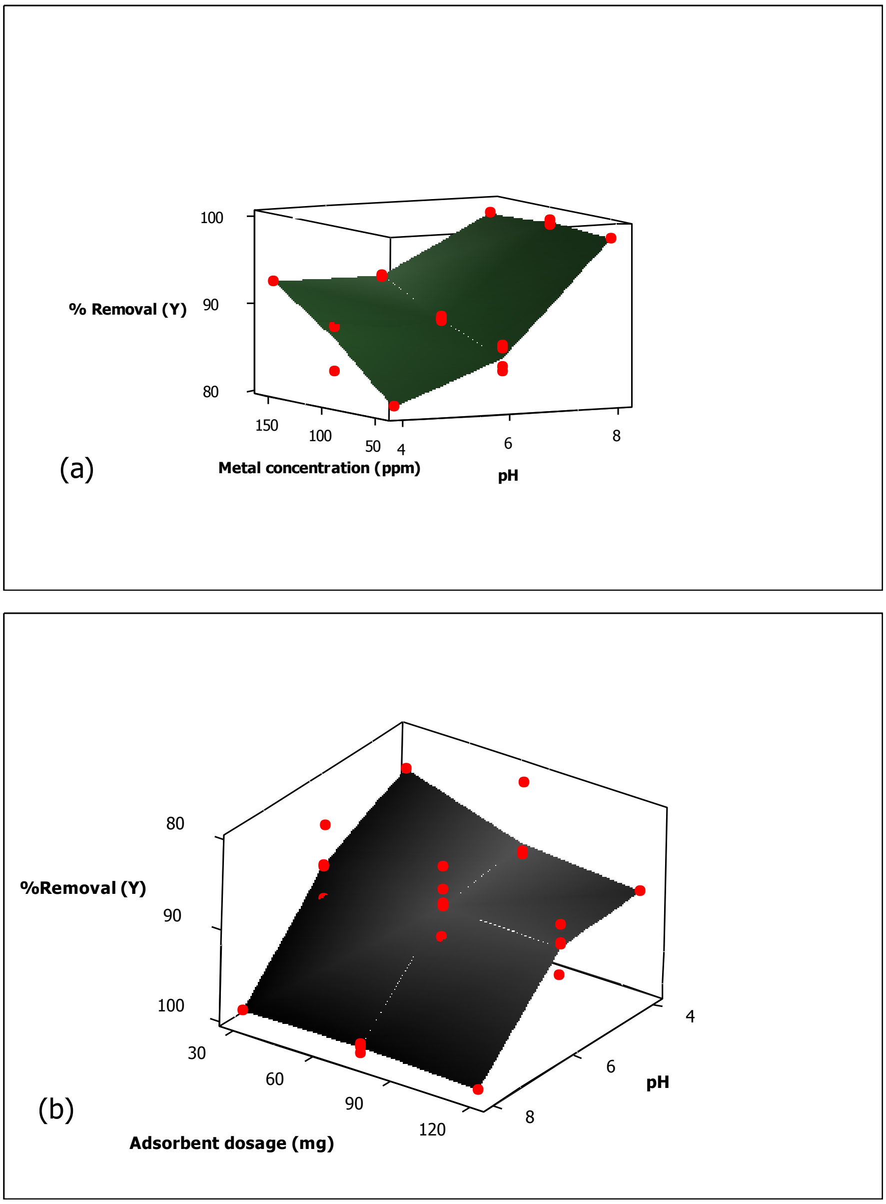

Figure 7. 3D response surface graph of (a) pH versus Metal concentration at a holding adsorbent of 75 mg (b) pH versus adsorbent dose at a holding metal concentration of 100 ppm ppm for the Cd^{2+} /nanomagnetic chitosan adsorption system.

3.1.5 Validation of optimum point

The point predication option in the software is used for the optimization of the process parameters obtained from statistical software. These are listed in Table 4. Table 4 summarizes the experimental conditions and the actual experimental values. For their validation, the experiment was conducted using the optimized parameters obtained.

4. Conclusion

In this study, a magnetic chitosan nano-adsorbent was prepared, characterized and used for the removal of Cd^{2+} from aqueous solution. Cd^{2+} removal from wastewater using nanomagnetic adsorbent requires a proper process parametric study to determine its optimal performance characteristics. Response Surface Methodology (RSM) is one of the advanced statistical analysis techniques for parametric studies involving a minimum number of trials. The Box-Behnken surface statistical design of experiments was carried out with four factors, i.e., pH, Adsorbent dose, contact time and metal concentration between the removal Cd^{2+} and the adsorbent. Analysis of variance for the four variables indicate that removal of metals can be well described by a polynomial model with a relatively high coefficient of determination (R^2 = 0.95). The statistical analysis of the full model shows that pH, adsorbent dose and metal concentration have a significant effect on metal removal.

Acknowledgments

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