

Optimization of sulfate removal from wastewater using magnetic multi-walled carbon nanotubes by response surface methodology

Vahid Alimohammadi, Mehdi Sedighi and Ehsan Jabbari

ABSTRACT

This paper reports a facile method for removal of sulfate from wastewater by magnetic multi-walled carbon nanotubes (MMWCNTs). Multi-walled carbon nanotubes and MMWCNTs were characterized by X-ray diffraction, Raman, transmission electron microscopy, Fourier transform infrared spectroscopy, and vibrating sample magnetometry. The results of the analysis indicated that MMWCNTs were synthesized successfully. The MMWCNTs can be easily manipulated in a magnetic field for the desired separation, leading to the removal of sulfate from wastewater. Response surface methodology (RSM) coupled with central composite design was applied to evaluate the effects of D/C (adsorbent dosage per initial concentration of pollutant ($\text{mg}_{\text{adsorbent}}/(\text{mg/l})_{\text{initial}}$)) and pH on sulfate removal (%). Using RSM methodology, a quadratic polynomial equation was obtained, for removal of sulfate, by multiple regression analysis. The optimum combination for maximum sulfate removal of 93.28% was $\text{pH} = 5.96$ and $\text{D/C} = 24.35$. The experimental data were evaluated by the Langmuir and Freundlich adsorption models. The adsorption capacity of sulfate in the studied concentration range was 56.94 (mg/g). It was found out that the MMWCNTs could be considered as a promising adsorbent for the removal of sulfate from wastewater.

Key words | isotherm models, magnetic, multi-walled carbon nanotubes, RSM, sulfate removal

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INTRODUCTION

As clean water resources are vital and are becoming low, water pollution is a critical topic for human existence and ecosystems. Several media have declared that water contamination is the main reason for the death of more than 14,000 people daily (Water Standards & World Health Organization 2006; Alimohammadi *et al.* 2017). Wastewater treatment serves two main objectives: protecting the environment and conserving freshwater resources (Bukhari 2008). Sulfate anions are hazardous ions when they exceed certain limits in the water. Sulfates are discharged into the water from mines and smelters and from kraft pulp and paper mills, textile mills, and tanneries (Hassan *et al.* 2010). The damage caused by sulfate emissions is not direct since sulfate is a non-toxic compound. However, the high sulfate concentration can unbalance the natural sulfur cycle (Li *et al.* 2011). Sulfate is a major anion occurring in natural water and industrial effluents, such as inorganic chemical industry wastewater and acid mine drainage (Cao *et al.* 2011). In the wastewater purification, little

consideration has been focused on the mitigation of dissolved sulfate; this may be attributed to its lower environmental risks and regulatory standards when compared to those for acidity and dissolved metals. Consuming drinking water containing sulfate concentrations in the excess of 600 mg/l commonly results in laxative effects. The taste threshold for the most prevalent sulfate salts ranges from 250 to 500 mg/l. While the World Health Organization does not propose a health-based guideline for sulfate in drinking water, it does recommend that health authorities are notified if sulfate concentrations exceed 500 mg/l (Haghsheno *et al.* 2009). When discharged untreated, it poses a threat to the quality of freshwater resources and consequently the well-being of humans and the environment at large (Singh *et al.* 2011). Established methods for the removal of sulfate from industrial effluents include chemical precipitation, biological treatment, reverse osmosis, dialysis and ion exchange and adsorption technologies. Chemical precipitation, for example, to add barium or

calcium salts, is rapid and effective, but it may produce another kind of pollution and secondary treatment for the solid phase is necessary (Haghsheno *et al.* 2009; Cao *et al.* 2011). Biological sulfate reduction processes have been used to treat a wide range of sulfate-rich wastewaters including acid mine drainage, tannery and textile wastewater, and landfill leachate. The biodegradation of phenolic and other persistent organic contaminants by sulfate-reducing bacteria culture has also been studied (Rasool *et al.* 2013). Although reverse osmosis has a high performance for wastewater treatment, the accumulation of matter may occur during the membrane filtration of surfactants, resulting in severe flux decline (Mai *et al.* 2016). Selecting the wastewater treatment method is usually based on the type of wastewater, removal rate, the waste concentration and cost of the treatment (Haghsheno *et al.* 2009). The adsorption method may be preferred for its rapid and high selectivity, and sulfur can be recovered (Cao *et al.* 2011). Adsorption is proven to be an economical and effective method for the removal of a number of contaminants from wastewater (Perić *et al.* 2004; Deliyanni *et al.* 2007; Liu *et al.* 2008; Yang *et al.* 2009; Moba-sheerpour *et al.* 2012). Adsorption methods are the most applied in the removal of sulfate from wastewaters since they can produce high-quality water and also are economically feasible processes (Tait *et al.* 2009). Zero-valent iron (ZVI) is a reductive material that can serve as an electron donor for both sulfate reduction and methanogens. ZVI has been used as a permeable reactive barrier in the underground water treatment to simultaneously immobilize heavy metals by enhancing sulfate reduction and mineralize organochlorine pesticides through enhanced methanogens (Zhang *et al.* 2011). Multi-walled carbon nanotubes (MWCNTs) have been widely used for the removal of various contaminants from wastewater due to their large surface area, light mass density, high porosity and hollow structure, small size, and strong interaction between the pollutant molecules and MWCNTs (Di *et al.* 2004; Chen & Wang 2006; Wang *et al.* 2007; Chen *et al.* 2009; Kabbashi *et al.* 2009; Shao *et al.* 2010; Ren *et al.* 2011; Zhang *et al.* 2012; Al-Hakami *et al.* 2013; Gu *et al.* 2013; Laoui *et al.* 2015; Al Amer *et al.* 2016). Among the various technologies, magnetic adsorption is a new method to remove sulfate from industrial wastewaters, since it can produce high-quality water and also is a process that is economically feasible (Madrakian *et al.* 2011). The MWCNTs have received more and more consideration for their unique structure and excellent mechanical, electrical, and thermal properties. The MWCNTs have attracted researchers' interest as a new type of powerful solid-phase extraction adsorbent (Qu *et al.* 2008). The MWNTs/Fe₃O₄

nanocomposites could respond rapidly to a permanent magnet, and after adsorption, the nanocomposites could be separated from solution easily by an external magnet (Song *et al.* 2011). Also, iron oxide nanoparticles that are attached to MWCNTs do not separate from the magnetic multi-walled carbon nanotubes (MMWCNTs) during blending with wastewater and the presence of iron on the MWCNT does not cause the removal of sulfate by the Fenton reaction (see Appendix, available with the online version of this paper). In this paper, we wish to report an eco-friendly method for the removal of sulfate using MMWCNTs extract without any stabilizer or surfactant. We synthesized and characterized the magnetic carbon nanotubes and investigated the adsorption behavior of the MWCNTs/Fe₃O₄ for the removal of sulfate in wastewater. Thus, the aim of this study was to report systematically the effect of the pH and D/C ratio (adsorbent dosage per initial concentration of pollutant (mg_{adsorbent}/(mg/l)_{initial})) on the removal of sulfate by MMWCNTs. In addition, the response surface methodology (RSM) was applied as a systematic experimental design method to predict the maximum percent of sulfate removal. The targeted usage of MMWCNT is completely new and promising for this field of investigation.

MATERIALS AND METHODS

The MWCNTs (the lengths were a few micrometers and the average outer diameter was 10–30 nm) were used in this study. MWCNTs were bought from Nano Port Co. Ltd (Shenzhen, China). FeCl₃·6H₂O, FeCl₂·4H₂O, NH₃·H₂O and Na₂SO₄ of analytical grade were obtained from Merck and Fluka. A Metrohm model 713 pH-meter was used for pH measurements. All glassware were soaked in dilute nitric acid for 24 h and finally washed three times with distilled water before use. A neodymium magnet was used in producing the magnetic field for sulfate-water separation (maximum field strength theory: 13.2 kG).

Synthesis of MWCNT/Fe₃O₄ magnetic nanoparticle

The MWCNTs were dispersed in concentrated sulfuric acid and concentrated nitric acid (a 3:1 volume ratio) to modify the MWCNTs surface by ultrasonication for 4 h. This acid mixture containing MWCNTs was diluted to 20% of its original concentration. The oxidized MWCNTs were filtered with a polytetrafluoroethylene filter membrane (Alltech, 0.45 μm pore size) with the aid of a vacuum pump; then it was washed by double-distilled water until the filtrate was

neutral. MWCNTs were dried in the oven at 80 °C for 12 h. Thirty-five milligrams of functionalized MWCNTs were dissolved in 22 ml of distilled water by ultrasonic irradiation for 36 min. Then 25 mg of FeCl₃·6H₂O was added under stirring. After the mixture was stirred vigorously for 30 min under N₂ atmosphere, 37 mg of FeCl₂·4H₂O was added and the mixture stirred under N₂ atmosphere for 25 min. Six millilitres of concentrated NH₃·H₂O diluted with 16 ml of distilled water was added to the mixture drop by drop. The adding of NH₃·H₂O aqueous solution was finished in 90 min and then the solution was heated to 100 °C and reacted for 3 h. The whole process must be under N₂ atmosphere. The reaction mixture was then filtered, washed with distilled water and dried at 60 °C for 24 h (see Figure S1 and Scheme S1 in Appendix, available with the online version of this paper).

Characterization

The chemical structure of γ-Fe₃O₄ nanoparticle functionalized with MWCNT was investigated by X-ray diffraction (XRD). The XRD measurements were carried out using a Philips powder diffractometer type PW 1373 goniometer (Cu Kα = 1.5406 Å). The Raman, Fourier transform infrared (FTIR) and magnetic properties analysis are shown in the Appendix. Transmission electron microscopy (TEM) studies were carried out on a JEOL JEM 2200FS field emission electron microscope (equipped with an energy-dispersive spectrometer) at 200 kV. The specific surface area and pore size of MWCNTs and MMWCNTs were determined by nitrogen adsorption/desorption porosimetry at (77.4 K) using a porosimeter (Bel Japan, Inc.).

Solution preparation

Sulfate stock solution containing 147.9 mg Na₂SO₄/l was prepared by dissolving sulfate salt (analytical reagent grade) in distilled water that contains 100 ppm of SO₄. The pH value of the sulfate working solution was adjusted with 0.1 M HCl and 0.1 M NaOH solutions before adsorption experiments.

Adsorption study

The adsorption of sulfate on MMWCNT was studied under batch conditions. For this work, a series of 12 solutions, each containing 50 ml wastewater sample and of various concentrations varying from 3.33 to 10 mg/l of sulfate, with 5 mg of the nanocomposite were agitated for 90 min in 100 ml bottles kept in a shaker rotating at rpm of 200.

The temperature was kept at 25 °C in preliminary experiments. After magnetic separation using the permanent magnet, a single beam UV-VIS spectrophotometer (UV-DR5000, Hach) was used for determining sulfate concentration in the solutions. The absorbance was read at 450 nm. The sulfate removal efficiency was determined using the following expression:

$$R\% = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (1)$$

where C₀ and C_t represent the initial and final concentrations in mg/l. All the experiment were carried out at room temperature. All experiments were performed in triplicate to ensure the repeatability of the results. The supernatant solutions were analyzed spectrophotometrically at 450 nm wavelength. The effect of pH value on adsorption was investigated by using an initial pH value varying in the range 3–10. The Langmuir and Freundlich isotherms were studied to calculate the adsorption capacity and the kind of adsorption.

RESULT AND DISCUSSION

Characterization of MWCNTs/Fe₃O₄ nanocomposites

Phase investigation of the crystallized product was performed by powder XRD measurements and the powder diffraction pattern of MWCNTs is presented in Figure 1(a). The diffraction peaks at 2θ = 25.55° and 44.49° are consistent with (002), (100) planes of the MWCNTs. Figure 1(b) represents the XRD pattern of MMWCNTs, which contains all the carbon nanotube and iron oxide nanoparticle peaks. The peaks at 2θ = 29.74, 35.25, 43.09, 57.09 and 62.67° were identified as the (220), (311), (400), (511) and (440) crystal planes of the spinel phase of Fe₃O₄ (JCPDS No. 65-3107), respectively (Wang *et al.* 2014). The XRD results confirm

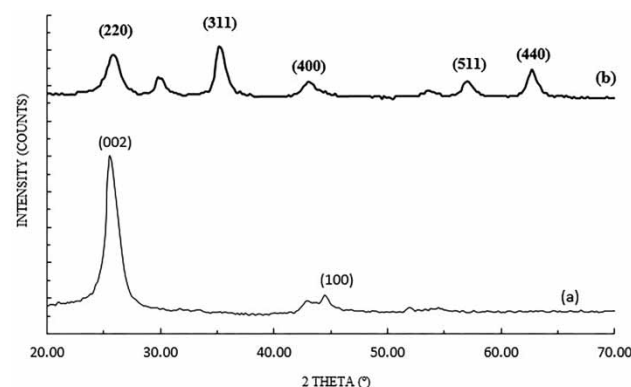


Figure 1 | XRD patterns of (a) MWCNTs, (b) MMWCNTs.

that MWCNTs/Fe₃O₄ nanocomposites were successfully synthesized by a facile hydrothermal method. No crystalline impurities were detected and the existence of Fe₃O₄ nanoparticles in the nanocomposites was confirmed.

Figure 2 shows the TEM images of the magnetic carbon nanotubes. Most of the carbon nanotubes were loaded with iron oxide nanoparticles. Figure 2(a) indicates that no separated nanoparticles were present, which suggests that the unattached nanoparticles have been completely removed from the product. The image of MWCNTs/Fe₃O₄ nanocomposites (Figure 2(b)) illustrates that some nanoparticles assembled on the MWCNTs but still adhered stably on the tube surface. It indicates the high efficiency of our synthesis method.

Specific surface area (SSA) is analyzed commonly by the Brunauer, Emmett, and Teller (BET) method. The SSA of the sample is measured by the physical adsorption of a gas on the surface of the solid and by measuring the amount of adsorbed gas corresponding to a monomolecular layer on the surface (Madrakian *et al.* 2011). The BET measurements found that the SSA of MWCNTs and MWCNT/Fe₃O₄ was 127.91 m²/g and 112.26 m²/g, respectively. When the Fe₃O₄ particles are added to the MWCNTs, the surface area of the MMWCNTs decreases slightly (Qu *et al.* 2008).

Experimental design

The study carried out involved the employment of a central composite design (CCD) in investigating the adsorption process owing to its suitability to fit quadratic surface,

which usually works well for process optimization. The CCD is the most frequently used under RSM design (Can *et al.* 2006). We selected pH (X₁) and D/C (X₂) as control variables. The Design Expert 7.1.3 software was used for the regression and graphical analyses of the experimental data. The design consists of two-level full factorial design (2² = 4), four star points, and one center point. Furthermore, we performed three reproductions at the central point to evaluate the pure error among each experiment. To lower the uncontrolled effect of factors, the order of experiments was randomized. A quadratic polynomial equation was developed to predict the responses as a function of independent variables involving their quadratic interactions and squared terms. The chosen independent variables used in this study were coded according to Equation (2):

$$x_i = \frac{X_i - X_0}{\Delta X_i} \quad i = 1, 2, 3, \dots, k \quad (2)$$

The data were fitted as a second order equation. The response equation in a two variable design is given in Equation (3):

$$Y = \beta_0 + \sum_{j=1}^3 \beta_j X_j + \sum_{j=1}^3 \beta_{jj} X_j^2 + \sum_{i < j} \beta_{ij} X_i X_j \quad (3)$$

Multiple regression analysis techniques included in the RSM were used to estimate the coefficients of the models. Table 1 shows the five-level two-factor CCD which has been employed in this optimization study; each of the parameters was coded at

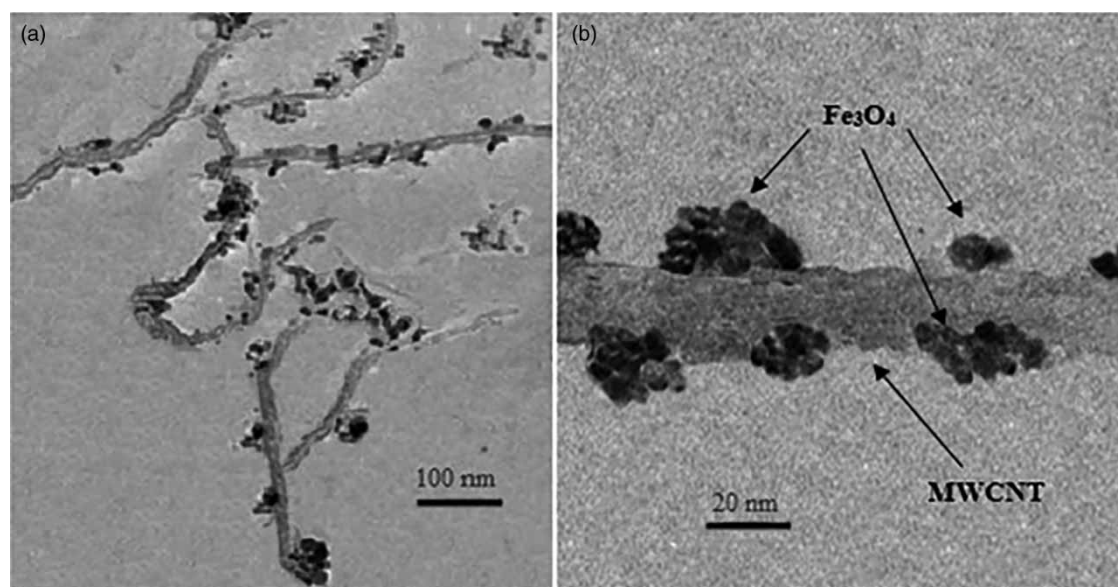


Figure 2 | Representative TEM image of MWCNT/Fe₃O₄ nanocomposites.

Table 1 | Factors and levels for CCD study

Level	pH, X_1	D/C, X_2
$-\alpha$	3.00	10.00
-1	4.03	12.93
0	6.50	20.00
+1	8.97	27.07
$+\alpha$	10.0	30.00

five levels: $-\alpha$, -1, 0, +1 and $+\alpha$.; meanwhile, the design matrix with the corresponding results is listed in Table 2.

Using the coefficients determined, regression analysis in coded terms of the experimental data yielded the following regression equation for the percentage removal of sulfate (response) (Gusain et al. 2016):

$$R_1 = -49.81 + 14.98X_1 + 8.09X_2 + 0.085X_1X_2 + 1.43X_1^2 - 0.176X_2^2 \quad (4)$$

The effects of the design parameters on sulfate removal can be determined by means of the analysis of variance (ANOVA) results given in Table 3. The F -value, which is a ratio of the mean square due to regression to the mean square due to error, is converted into its corresponding p -value. The model F -value of 19.06 means the model is significant. In the model above, linear and quadratic parameters were significant with The p -value less than 0.05. The predicted R-squared

Table 2 | Design matrix and experimental data of the main products for removal study

Run	Factor		Final removal %
	pH	D/C	
1	4.03	27.07	84.14
2	6.50	20.00	89.21
3	8.97	27.07	75.23
4	6.50	20.00	88.07
5	4.03	12.93	72.14
6	8.97	12.93	57.27
7	6.50	20.00	89.07
8	6.50	30.00	92.28
9	10.00	20.00	66.35
10	3.00	20.00	76.36
11	6.50	10.00	50.19
12	6.50	20.00	90.97

value is found to be 0.9408 for Equation (4). Therefore, R^2 indicates a very good fitting for the experimental data and predicted values.

Contour plots

The simultaneous effects of two independent variables, pH and D/C, on sulfate removal were analyzed. The responses corresponding to the contour plots of the second order predicted model indicated that, for high pH, the percent of sulfate removal increases with increasing D/C (Figure 3). Equation (4) is used to construct the response surface and contour plots. Figure 3 proves that the pH and D/C are important parameters affecting the removal of sulfate. However, sulfate removal increases as pH is increased to 5.96, then decreases as pH further increases to 10. At pH = 10 and D/C = 10, the removal of sulfate reaches a minimum value (29%), while at pH = 5.96 and D/C = 24.35, the removal reaches a the maximum value.

The regression model and perturbation plot of two independent factors (pH and D/C) are indicated in the Appendix (Figure S5, available with the online version of this paper).

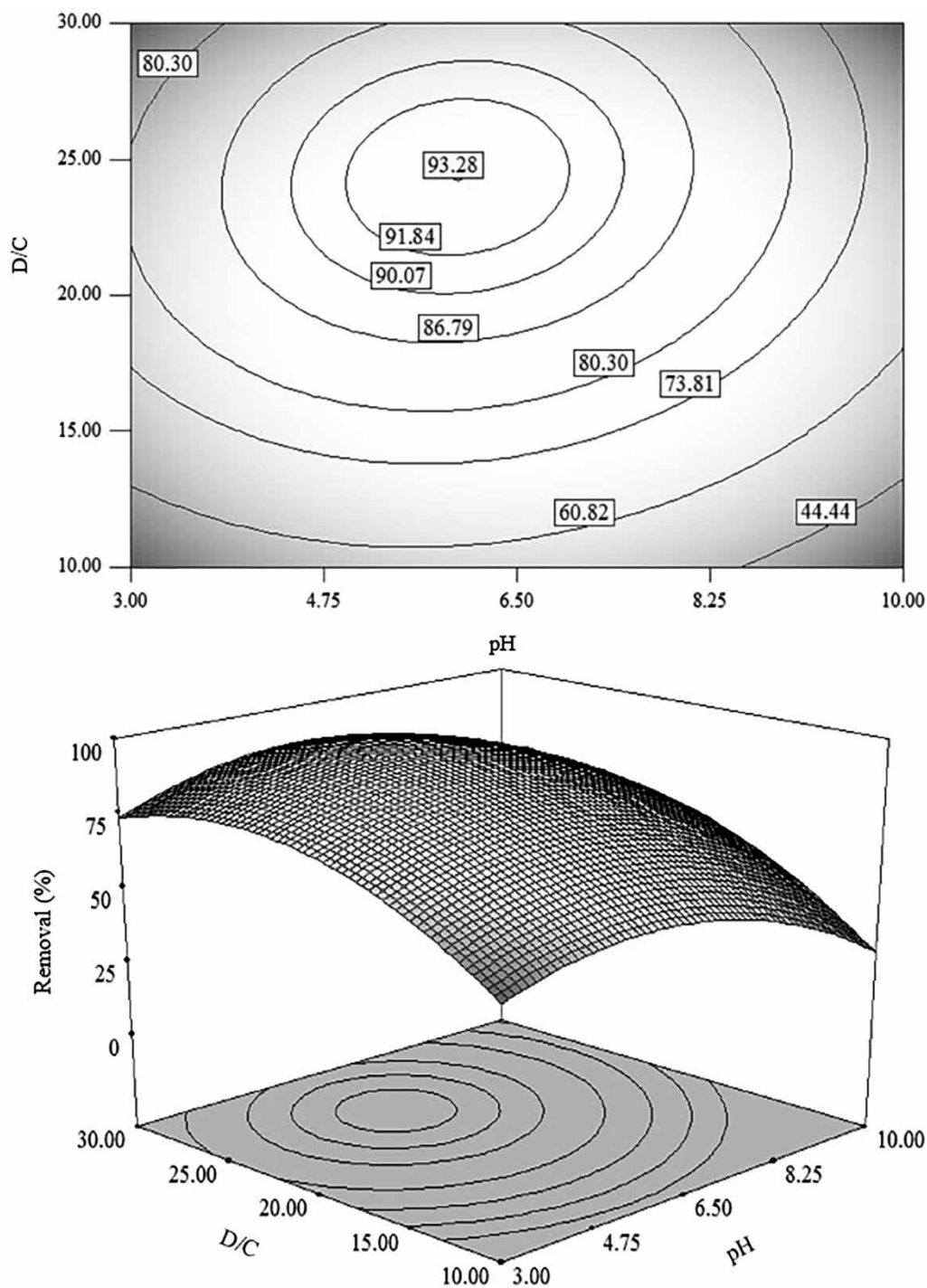
The pH and D/C of a solution are important parameters during the adsorption process. The pH affects the surface charge of the adsorbent and the degree of ionization and specification of adsorbate. In order to establish the effect of pH, the equilibrium studies at different pH and D/C values were carried out in the range of 3–10 and 10–30, respectively. As shown in Figure 4(a), with the increase of D/C at pH = 5.96, the removal of sulfate increased from 57% to 93.28%. Figure 4(b) shows the pH of the solution has a significant effect on adsorption capacity. With an increase of pH from 3 to 10, the removal increased from 81% to 93.28% at D/C = 24.35 and pH = 5.96. The maximum removal of sulfate by MMWCNT was 93.28% at pH = 5.96 and D/C = 24.35. Therefore, the pH and D/C values of the wastewater are important factors for sulfate removal.

The effect of equilibrium concentration on the adsorption of sulfate was investigated at pH 5.96 and D/C 10–30. Results are presented in Figure 4(c). It could be concluded that the maximum adsorption capacity of MMWCNT increased up to approximately 56.94 mg/g.

This can be due to the negative charge of the surface of MMWCNT in a high pH range. The negative charge of the surface of the nanoparticles was also confirmed from the data on the zeta potential (Legodi & De Waal 2007). At the higher pH, the negatively charged parts generally increased, but the electrostatic repulsion from the negatively charged parts of the

Table 3 | ANOVA for the removal of sulfate

Source	Sum of squares (S.S.)	Degrees of freedom	Mean square	F-value	p-value	R ²
S.S. regression	2014.34	5.000	402.87	19.06	0.0013	0.9408
S.S. error	126.81	6.000	21.14			
S.S. total	2141.15	11.00				

**Figure 3** | Contour plots describing the response surface of composite desirability as a function of pH and D/C.

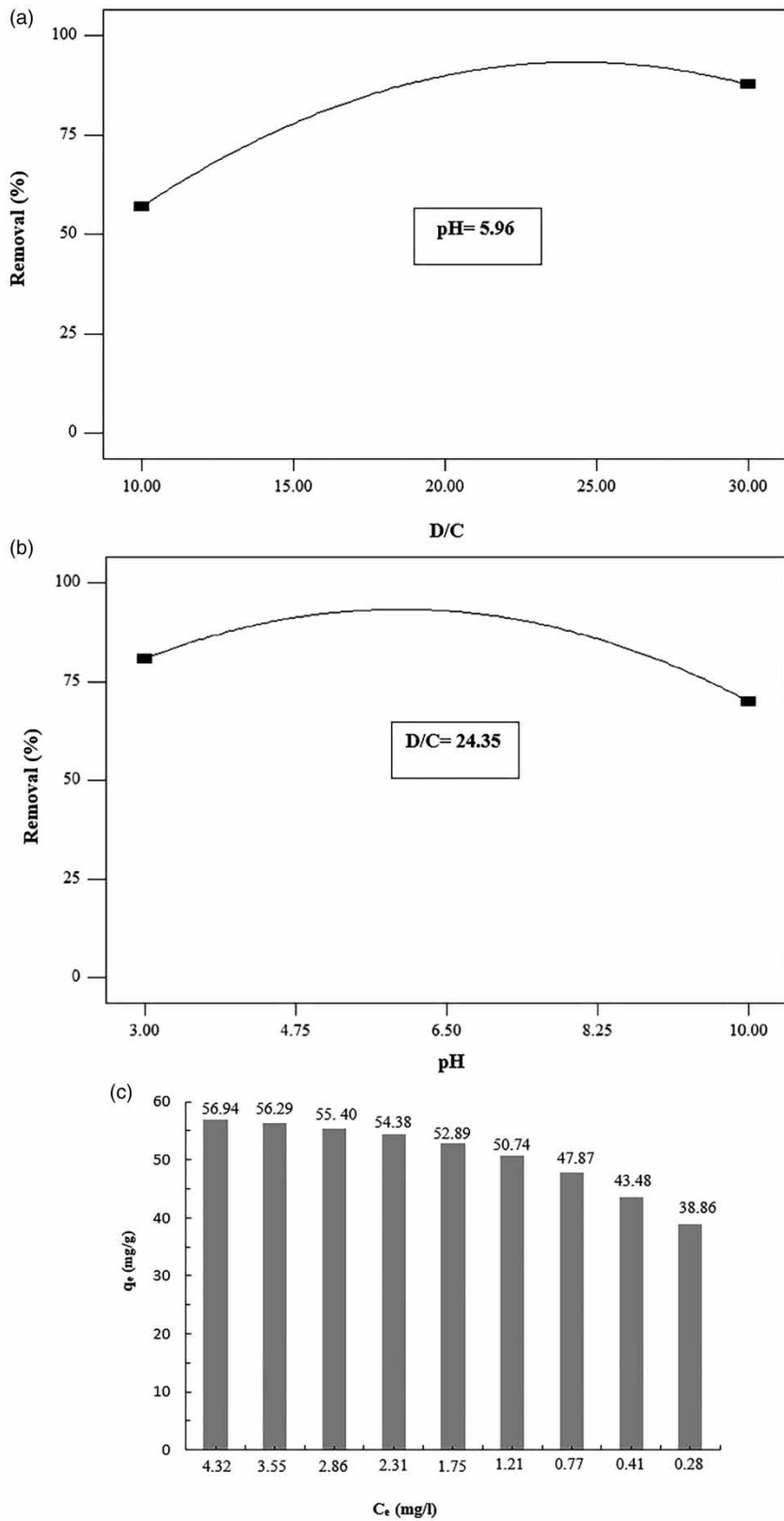


Figure 4 | (a) Effect of D/C and (b) effect of pH on the sulfate removal. (c) Equilibrium adsorption uptake of sulfate on MMWCNT at different equilibrium sulfate concentration and pH 5.96.

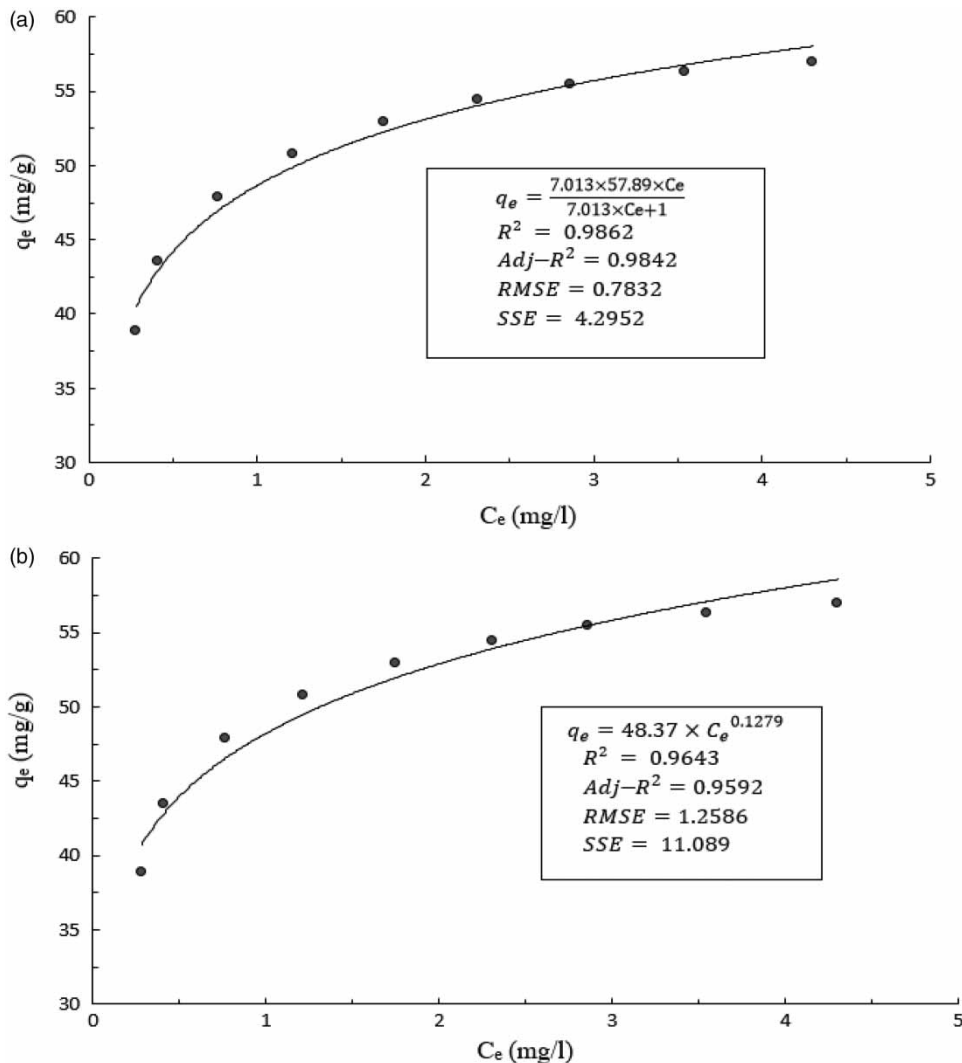


Figure 5 | Adsorption isotherms for the concentration range of sulfate onto MMWCNTs at different initial concentration: Langmuir (a) and Freundlich (b) (volume of sulfate solution: 50 ml, initial concentration of sulfate: 3.33–10 mg/l, adsorbent: 5 mg, pH: 5.96).

adsorbent does not favor absorption of sulfate (Alimohammadi et al. 2016). The results indicate that the nanocomposite is more effective in the acidic pH than high pH.

Result validations of the final optimal point in the multi-responses optimization are presented in Table S3 in the Appendix.

Adsorption isotherms

The isotherms of sulfate adsorption by MMWCNTs in wastewater can be investigated using the Langmuir and the Freundlich adsorption models (Li et al. 2015). In order to optimize the use of MMWCNTs adsorbents, it is important to establish the most appropriate adsorption isotherm. Thus, the

correlation of equilibrium data by either theoretical or empirical models is essential for practical operation. Langmuir and Freundlich equations were used to analyze the experimental data of the MMWCNTs adsorbents for sulfate in our work.

Langmuir adsorption model:

$$q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e} \quad (5)$$

Freundlich adsorption model:

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \quad (6)$$

where q_e is the amount of sulfate adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of sulfate

Table 4 | Langmuir and Freundlich isotherm model parameters and correlation coefficients for adsorption of sulfate onto MMWCNT

Adsorbent (MMWCNT) Q ₀ (mg/g)	Langmuir isotherm model			Freundlich isotherm model		
	R _L	K _L (l/mg)	R ²	K _F	1/n	R ²
57.89	0.014	7.013	0.99	48.37	0.1279	0.96

(mg/l), K_L is the Langmuir adsorption coefficient (l/mg), Q₀ is the maximum amount of solute adsorbed per gram of surface (mg/g), K_F is the Freundlich adsorption coefficient (l/mg), and n represents the measure of the nonlinearity involved. The linear plots for Langmuir and Freundlich isotherms are shown in Figure 5.

The adsorption constants calculated according to the Langmuir and Freundlich adsorption models are shown in Table 4. It can be observed that the sulfate adsorption isotherms of MWCNTs/Fe₃O₄ nanocomposites followed the Langmuir adsorption model better than the Freundlich adsorption model. Initial concentration range of 3.33–10.00 mg/l) is assumed. As shown in Table 4, the experimental data of sulfate removal fit the Langmuir adsorption isotherm well with a correlation coefficient of 0.9862 (0.99).

A comparison with other adsorbents that have been used for removal of sulfate by previous researcher is shown in the Appendix.

CONCLUSION

In conclusion, the authors have indicated an environmentally friendly method for the removal of sulfate from wastewater. The MMWCNTs were shown to be effective adsorbents, which could be employed in wastewater treatment. In addition, the prepared magnetic adsorbent could be well dispersed in the wastewater and can be easily separated magnetically from the solution after adsorption. Modeling and optimization of the removal of sulfate and its stability were studied, using RSM-CCD. Two parameters, namely pH and D/C, were the control factors in this study. One quadratic model for sulfate removal was developed. ANOVA results confirmed that there was a significant agreement between the models and the experimental data. The results show that pH and D/C were the factors with statistically highly significant effect. The optimum point was found at pH = 5.96 and D/C = 24.35 with the predicted removal of 93.28%. MMWCNT is a superior adsorbent for the removal of sulfate from wastewater. Both the Langmuir and

Freundlich isotherm models were investigated to describe the sulfate adsorption data, showing a higher suitability of the Langmuir isotherm model. Overall, the properties of easy regeneration and stable adsorption behavior enable MMWCNTs to be an excellent adsorbent material to use in wastewater purification.

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