



Removal of hydrogen sulfide from water-based drilling fluid using titania/carbon nanotubes nano-hybrid: optimization, kinetics, and isotherms

Shiva Khorshidi^a, Samad Sabbaghi^{a,*}, Rahmatallah Saboori^b

^aFaculty of Advanced Technologies, Nano Chemical Engineering Department, Shiraz University, Shiraz, Fars, Iran, Tel. +989171133471; Fax: +9871-36139669; emails: sabbaghi@shirazu.ac.ir/samad.sabbaghi@uwaterloo.ca (S. Sabbaghi), shivakh90@yahoo.com (S. Khorshidi)

^bDepartment of Petroleum Engineering, School of Chemical and Petroleum Engineering, Shiraz University, Shiraz, Iran, emails: ra.saboori@gmail.com (R. Saboori)

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ABSTRACT

Hydrogen sulfide is one of the most dangerous gases known in drilling operations. Hydrogen sulfide can cause problems, such as corrosion in drilling pipes, transportation lines, and storage tanks. In this work, the performance of titania/carbon nanotube nano-hybrid was investigated on the hydrogen sulfide removal from drilling fluid. The nano-hybrids were synthesized by the sol-gel method and were then characterized by X-ray diffraction, Fourier-transform infrared spectroscopy, and scanning electron microscopy. The nano-hybrids were added to the drilling fluid and the removal rate was studied in the drilling fluid set-up. The effects of nano-hybrid concentration, initial hydrogen sulfide concentration, contact time, pH, and the ratio of nano-hybrid were investigated on the adsorption. The results showed that the removal at the optimum condition was 92.86% (obtained in 0.4 wt.% of adsorbent, 800 ppm of initial hydrogen sulfide concentration, pH = 8, 30 min of contact time, and nano-hybrid with the ratio of 1:1). The kinetic adsorption was pseudo-second-order. Isotherm adsorption of hydrogen sulfide was followed by the Langmuir model and monolayer adsorption. The reusability of the nano-hybrid for hydrogen sulfide removal for four cycles was more than 70% and it was found that the nano-hybrid had a good performance for the hydrogen sulfide removal from the drilling fluid.

Keywords: Hydrogen sulfide; Drilling fluid; Removal; Titania/CNT nanohybrid; Optimization; Kinetic

1. Introduction

Hydrogen sulfide is a gas with rather sweet taste, dangerous, foul odor, colorless, heavier than the air, and accumulates in the bottom of confined space [1,2]. Organic material thermal decomposition can produce hydrogen sulfide in underground atmospheres [1,3]. A low concentration of hydrogen sulfide in the oil and gas industry can cause many problems, such as undesirable quality

of products, life-risks, and environmental pollution [4]. Exposure to hydrogen sulfide for a maximum of 8 h and in concentrations of more than 100 ppm would cause bleeding and death. The effects would be irreparable for concentrations more than 600 ppm in less than 3–5 min. Hydrogen sulfide can get into the drilling fluid from oil and gas formation and the ground layers in drilling operations [5]. Corrosion in drilling pipes, transportation lines, and storage tanks, followed by tension fracture and corrosion

* Corresponding author.

cavities in oil and gas installations are some of the consequences of existing this pollutant in the drilling fluid [6–8]. As a result, hydrogen sulfide should be eliminated in some ways to prevent such problems. Different methods could be employed for this purpose, such as biological, electrochemical, physicochemical, and adsorption method [9–12].

Habeeb et al. [13] investigated the effects of using material based on active carbons, such as coconut shell based activated carbon, palm kernel shell activated carbon [14,15], agriculture wastes based activated carbon [16], calcium-coated wood sawdust-based activated carbon [17], eggshell based activated carbon [18], and CaO-eggshells dispersed onto palm kernel shell activated carbon [19] on the adsorption of hydrogen sulfide from wastewater. Results showed that these materials had good potential for hydrogen sulfide removal from wastewater. Samuels studied the effect of using iron oxides on the hydrogen sulfide removal. Results showed that the synthesized magnetic iron oxide had the best performance among iron oxides and were tested for hydrogen sulfide removal [20]. Sayyadnejad et al. [21] experimented on hydrogen sulfide removal using zinc oxide nanoparticles in the drilling fluid. They concluded that zinc oxide nanoparticles are able to eliminate hydrogen sulfide from the drilling fluid in 15 min, while the removal of hydrogen sulfide by the bulk of zinc oxide was found to be 2.5% in up to 90 min [21]. Vaiopoulou et al. [22] studied sulfide removal from wastewater in petrochemical industries by autotrophic denitrification. Their observations were done by using the combination of biological methods. They concluded that H_2S was completely removed and the economic costs were reduced by about 70%. Liu et al. [23] prepared a porous composite of zinc oxide/silica by the sol-gel method and used it for the removal of hydrogen sulfide from the wastewater. Results of this research indicated that 1 g of zinc oxide/silica composite with a ratio of 70%:30% can remove 96.4 mg of hydrogen sulfide from the wastewater. They suggested the nanoscale composite dimension for the better elimination of hydrogen sulfide from the wastewater. Jordan et al. [24] observed that using zinc compounds can make sulfur compounds, especially hydrogen sulfide, in the form of zinc sediments. Moreover, they were looking for some methods to control these zinc sediments in the drilling operations. Morgani et al. [25] investigated the hydrogen sulfide removal from water-based drilling fluid by metal oxide nanoparticle and ZnO/TiO₂ nanocomposite. Hydrogen sulfide concentration was reduced from 800 to 5 ppm (99% removal) by the suggested nanocomposite.

Hydrogen sulfide elimination from wastewater are usually done based on the adsorption method because one or multi components can be separated from the fluid phase and accumulated on the adsorbent by this method. Therefore, adsorption is a suitable method to separate components of wastewater. However, the conditions of the adsorbent and the process should be desirably selected and adjusted [26].

In this study, the performance of titania/carbon nanotube (TiO₂/CNT) nano-hybrid in the removal of hydrogen sulfide from water-based drilling fluid was investigated. Three different ratios of TiO₂/CNT nano-hybrid were synthesized and characterized. The nano-hybrid was then added to the drilling fluid and the removal of hydrogen sulfide was measured. Furthermore, the effects of factors, such as contact

time, hydrogen sulfide concentration, adsorbent concentration, and pH on hydrogen sulfide removal from the drilling fluid were studied and the optimized conditions for the best removal process were proposed. Finally, the kinetic and isotherm removal were investigated.

2. Materials and methods

2.1. Materials

Tetraisopropyl orthotitanate (TTIP, C₁₂H₂₈O₄Ti, 97%), nitric acid (HNO₃, 65%), hydrochloric acid (HCl, 37%), sodium sulfide hydrate (Na₂S, 35%), sodium hydroxide (NaOH), and ethanol (C₂H₅OH, 99.9%) were purchased from Merck Company (Germany). Multiwall carbon nanotube (CNT, >95%, OD: 5–15 nm) was obtained from Nano Tech. (Iran), and deionized water was supplied by Zolal Company (Iran). Bentonite was provided from the National Iranian Oil Company (NIOC) (Iran). Nitrogen gas (>99.9%) was purchased from the Aboughadare Company (Iran). Reagent sulfide (I and II) was obtained from Hach Company (USA).

2.2. Synthesis of TiO₂/CNT nano-hybrid

Synthesis of TiO₂/CNT nano-hybrid was done by the sol-gel method. CNT was added to ethanol (10 mL) and was then mixed by vigorous stirring at the ambient temperature (25°C) for 25 min. The mixture was sonicated with high power (400 W and 20 kHz) for 15 min to prepare a stable suspension. TTIP was then added to the suspension and stirred vigorously at the ambient temperature for 10 min. At the end of the process, diluted nitric acid was added to the solution and was mixed for 10 min. As a result, the sol and gel were formed. The formed gel was dried at the ambient temperature. Finally, the powder was calcined in the reactor under nitrogen at 400°C for 4 h. This procedure was done for three ratios (3:1, 1:1, and 1:3) of TiO₂/CNT nano-hybrid. Amount of materials for the synthesis of TiO₂/CNT nano-hybrid with different ratios are shown in Table 1.

2.3. Drilling fluid preparation

To prepare water-based drilling fluid containing H₂S, bentonite (10 g) was added to the deionized water (250 mL) and mixed by Hamilton batch mixer (USA) with 35,000 rpm for 20 min. A certain amount of Na₂S (equivalent to a certain concentration of H₂S in the drilling fluid) was added to the mixture and mixing was continued for another 20 min (solution A). The nano-hybrid was added to deionized water (100 mL) and mixed by magnetic stirrer with

Table 1
Amount of materials used in the synthesis of TiO₂/CNT nano-hybrid with different ratio

Ratio TiO ₂ /CNT nano-hybrid	TTIP (mL)	CNT (g)	Diluted acid (mL)
1:1	1	0.280	1.500
1:3	1	0.042	1.500
3:1	3	0.014	1.500

1,800 rpm for 20 min and then sonicated by cell ultrasonic (400 W, 20 kHz) at the ambient temperature for 20 min (solution B). Finally, solution A and B were mixed by Hamilton batch mixer (USA) for 10 min.

2.4. Removal activity evaluation of nano-hybrid

The removal activity of the TiO₂/CNT nano-hybrid was investigated on the removal of hydrogen sulfide from the drilling fluid at different hydrogen sulfide concentrations, adsorbent concentration, contact time, drilling fluid pH, and ratio of TiO₂/CNT nano-hybrid. In the experimental test, calculated amounts of the adsorbent and hydrogen sulfide (sodium sulfide dehydrate) were added to the water-based drilling fluid at a certain pH value and were then mixed for defined contact time at the room temperature. At the end of the experiment, 10 mL of the drilling fluid was sampled, filtered, and centrifuged to separate the adsorbent and bentonite from the drilling fluid. The concentration of hydrogen sulfide was determined by adding reagent 1 and 2 followed by spectroscopically monitoring the absorbance at the wavelength of 690 nm [25]. Fig. 1 shows the adsorption procedure of hydrogen sulfide from the drilling fluid. The sulfide removal percentage was calculated according to the following equation:

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

where C_0 (mg/L) and C_t (mg/L) are the concentration of hydrogen sulfide in the drilling fluid at $t = 0$ and at a given time interval.

2.5. Experimental design and data analysis

In this study, the effect of four independent parameters, including the nano-hybrid concentration (A), initial hydrogen sulfide concentration (B), contact time (C),

solution pH (D), and ratio of TiO₂/CNT nano-hybrid (E) on the removal of hydrogen sulfide in drilling fluid was investigated using Design-Expert software (version 10.0.0), I-optimal method. I-optimal design was applied to decrease the number of experiments, the effect of each parameter, and their interactions on sulfide removal and also to find optimum conditions. Each parameter was set to certain levels that were determined using pre-test experiments (Table 2). Based on certain levels of parameter, the software suggested 32 experimental runs. Details of experimental tests are shown in Table 2.

2.6. Characterization

X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and field emission scanning electron microscopy (FE-SEM) were utilized to characterize TiO₂/CNT nano-hybrid. By analyzing the XRD pattern information regarding distributed crystalline sizes and confirmation of synthesized nanoparticle, it could be indicated that Bruker D8 diffractometer (Germany) was used in this work. FTIR was examined via Shimadzu 8300 FTIR spectroscopy (Japan) for bonds of synthesized nano-hybrid. In addition, TESCAN VEGA3 FE-SEM (Czech Republic) was used to determine the morphology of synthesized nano-hybrids. Jasco V-730 spectrophotometer (Japan) was used to measure the hydrogen sulfide removal from water-based drilling fluid. It is noteworthy to state that sulfide reagent was used to measure the removal rate by the spectrophotometer.

3. Results and discussion

3.1. Characterization of the nano-hybrid

XRD of synthesized TiO₂/CNT nano-hybrid with ratios of 1:1, 1:3, and 3:1 are demonstrated in Fig. 2. It is obvious in the XRD spectrum that peaks of 2θ equal to 25°, 37°, 48°, 54.2°, 53.1°, 62.1°, 67.1°, and 69.2° are related to the plates of (101), (004), (200), (105), (211), and (204). These peaks are

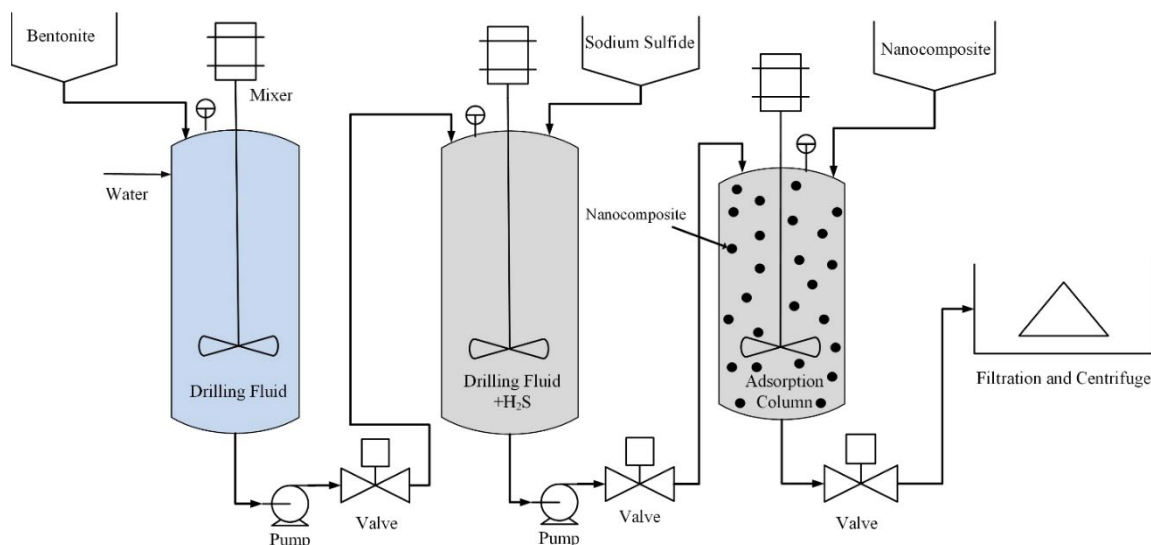


Fig. 1. Schematic of hydrogen sulfide removal from drilling fluid.

Table 2
Influential factors in hydrogen sulfide removal from water-based drilling fluid by TiO₂/CNT nano-hybrid

Parameter	Symbol	Unit	Range				
Nano-hybrid (Adsorbent) concentration	A	wt.%	0.05	0.1	0.2	0.3	0.4
Hydrogen sulfide concentration	B	ppm	200	400	600	800	–
Contact time	C	min	5	10	15	20	30
pH	D	–	8	10	12	–	–
Ratio of TiO ₂ /CNT	E	–	1:3	1:1	3:1	–	–

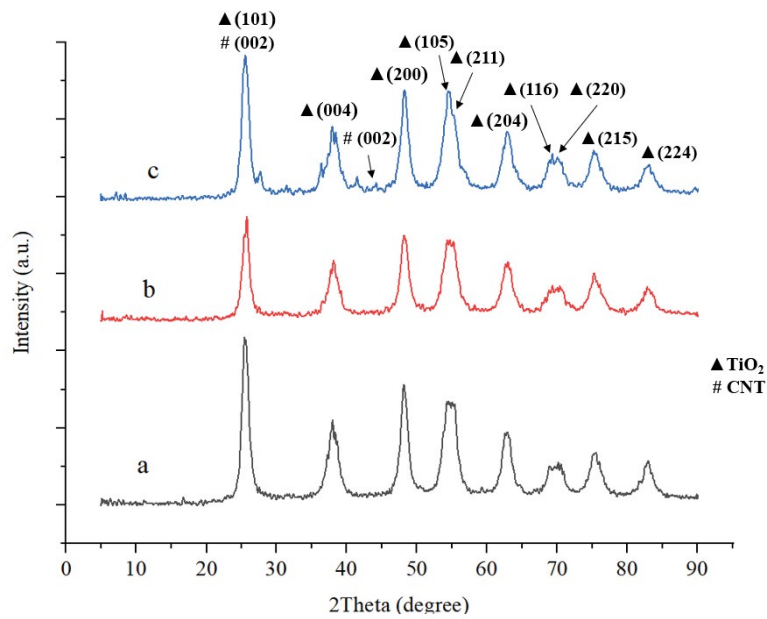


Fig. 2. XRD pattern of TiO₂/CNT nano-hybrid with ratios of (a) 3:1, (b) 1:1, and (c) 1:3.

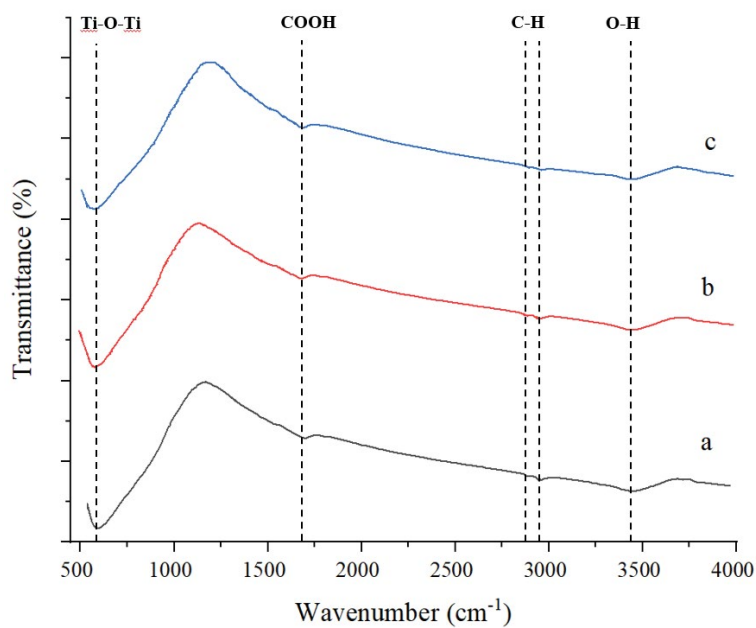


Fig. 3. FTIR pattern of TiO₂/CNT nano-hybrid with ratio of (a) 3:1, (b) 1:1, and (c) 1:3.

similar to those that can be detected for TiO₂ nanoparticle and are clearly observable in three ratios of nano-hybrid. Peak of $2\theta = 25^\circ$ is related to the plane of (101) and was emerged in the three ratios; a weak peak in $2\theta = 43^\circ$ for ratio of 1:3 and 1:1 nano-hybrid, and a much weaker peak in the $2\theta = 80^\circ$ for ratio of 1:3 and 1:1 of nano-hybrid are dedicated to CNT. Therefore, the presence of the peaks in Fig. 2 that are dedicated to both TiO₂ and CNT confirms the synthesis of nano-hybrids [27–30].

FTIR spectra of TiO₂/CNT nano-hybrid with ratios of 3:1, 1:1, and 1:3 are illustrated in Figs. 3a–c. This spectrum is in the wave range of 450–4,000 cm⁻¹. In this spectrum, the peak at 586.34 cm⁻¹ corresponds to the bending vibration of Ti–O–Ti, and the peak at 3,426.83 cm⁻¹ is the result of bending and stretching vibrations of O–H group. The peaks in the wave range of 2,800–2,900 cm⁻¹ are allocated to the symmetrical and asymmetrical C–H and are corresponding to the –CH₂ and –CH₃ vibrations, respectively. In addition, the specified spectrums of –COOH group in the wave range of 1,460–1,720 cm⁻¹ correspond to the C–H asymmetrical form which belongs to –CH₃ group vibrations and are due to the existence of CNT. The mentioned spectrums can be observed in all three ratios of the nano-hybrid [28,29,31,32].

FE-SEM image of TiO₂/CNT nano-hybrid with the ratios of 1:1, 1:3, and 3:1 are illustrated in Figs. 4a–c. Particles with rodlike shape and semispherical shape correspond to CNT and TiO₂ nanoparticles, respectively. TiO₂ nanoparticle can be seen on the surface of CNT. These images confirm that the nano-hybrid was successfully synthesized.

3.2. Design of experiments

The number of designed experiments, conditions, and results of hydrogen sulfide removal related to each experiment are given in Table 3. To determine the effective parameter and the interaction between parameter and the best model for the removal as of hydrogen sulfide from drilling fluid, *P* and *F*-value were used. Parameters with *P* < 0.05 were considered potentially significant and important. Additionally, the effective role of these parameter decreases with the increase of *F*-value parameter. Their values are shown in Table 4. It is noteworthy to state that the analysis of variance (ANOVA) was provided by the Design Expert software. According to Table 4, the parameter of *A*, *B*, *C*, and *D* had the most influence on the removal rate of hydrogen sulfide from the drilling fluid. *CE*, *B*², *D*², *DE*, and *BE* were also effective interaction parameters. Furthermore, standard deviation *R*² values, adjusted *R*², and predicted *R*² are 0.98, 0.96, and 0.93, respectively. Models for the hydrogen sulfide removal (second-order polynomial) from the drilling fluid by nano-hybrids ratio of 3:1, 1:1, and 1:3 are proposed by Eqs. (2)–(4) (in terms of actual parameter). It should be noted that these equations indicate hydrogen sulfide removal without considering the type of nano-hybrid. However, Eq. (5) is suggested as a general equation (in terms of coded factors) for hydrogen sulfide removal with the percent of nano-hybrid parameter type.

$$\text{Adsorption}(\%) = -18.28 + 57.38A + 4.22 \times 10^{-3}B + 1.23C + 17.07D - 5.10 \times 10^{-5}B^2 - 0.95D^2 \quad (2)$$

$$\text{Adsorption}(\%) = +16.08 + 57.38A + 0.02B + 0.46C + 14.50D - 5.10 \times 10^{-5}B^2 - 0.95D^2 \quad (3)$$

$$\text{Adsorption}(\%) = -12.86 + 57.38A + 0.01B + 0.77C + 16.60D - 5.10 \times 10^{-5}B^2 - 0.95D^2 \quad (4)$$

$$\text{Adsorption}(\%) = +81.35 + 10.04A - 11.42B + 10.25C - 5.96D + 3.75E + 2.71BE - 4.5CE - 3.11DE - 4.59B^2 - 3.81D^2 \quad (5)$$

3.3. Effect of parameters on hydrogen sulfide removal

Nano-hybrid concentration is one of the most important factors in the removal process of hydrogen sulfide from the drilling fluid. Surface of the nano-hybrid and surface availability for the removal have huge effects on the efficiency of the removal. Fig. 5 shows the effect of TiO₂/CNT nano-hybrid concentration on the removal of hydrogen sulfide from the drilling fluid. Raising the nano-hybrid concentration increases availability of the surface for removal. Therefore, hydrogen sulfide can have contact with these surfaces and help to increase the removal of hydrogen sulfide. Figs. 5a–c confirms the increase in removal of hydrogen sulfide by raising the nano-hybrid concentration from 0.05 to 0.4 wt.% for three ratios of the nano-hybrid. Removal of hydrogen sulfide increases from about 61%–80%, 71%–92%, and 62%–82% for nano-hybrid ratios of 3:1, 1:1, and 1:3, respectively (at 500 ppm hydrogen sulfide concentration, pH of 10, and contact time of 10 min).

Results of ANOVA table indicate the importance of contact time factor for the removal of hydrogen sulfide from the drilling fluid. Figs. 6a–c demonstrates the impact of contact time on removal of hydrogen sulfide for all studied ratios of the nano-hybrid. By increasing the contact time, removal of hydrogen sulfide increases. The main reason for this increase in the hydrogen sulfide removal is that hydrogen sulfide has more opportunity to be removed from the adsorbent surface in the higher contact time. It is noteworthy to state that the removal rate in all nano-hybrid ratios have the same trends. However, adsorbent ratio of 1:1 resulted in the most hydrogen sulfide removal rate compared to the case in which ratios of 1:3 and 3:1 are used (for contact time range of 5–30 min).

The effect of initial hydrogen sulfide concentration on its removal in the range of 200–800 ppm is illustrated in Fig. 7. This Fig. 7 shows that the removal efficiency decreases by increasing the initial hydrogen sulfide concentration. This result may be due to the reduction of nano-hybrid active site to hydrogen sulfide in high concentrations. It is also important to state that the removal increases and reaches to the maximum rate of 200 ppm in initial hydrogen sulfide concentrations of less than 200 ppm because of being high active site to hydrogen sulfide ratio. The removal was then decreased and the maximum removal rate was found to be for the nano-hybrid ratio of 1:1 in a hydrogen sulfide concentration range of 200–800 ppm.

Figs. 8a–c shows the effect of pH on the hydrogen sulfide removal. It is obvious in these figures that raising pH

Table 3
I-Optimal experiments by design expert software and removal amount

Run	A (wt. %)	B (ppm)	C (min)	D (-)	E (-)	Removal (%)
1	0.40	800	15	8	3:1	74.32
2	0.10	400	30	8	1:3	84.43
3	0.05	800	30	12	1:3	52.34
4	0.05	600	5	10	3:1	50.33
5	0.10	200	5	10	3:1	70.22
6	0.30	400	5	10	1:1	88.45
7	0.40	400	30	12	1:1	90.65
8	0.30	400	15	8	3:1	86.10
9	0.30	400	5	10	1:1	83.34
10	0.30	800	30	10	3:1	84.51
11	0.10	600	20	12	3:1	63.96
12	0.30	800	20	12	1:1	60.40
13	0.05	800	5	12	1:1	45.33
14	0.40	600	20	10	1:3	85.23
15	0.05	800	20	8	3:1	50.31
16	0.05	200	30	8	3:1	95.20
17	0.40	200	15	12	3:1	88.23
18	0.05	800	15	10	1:3	46.45
19	0.05	200	10	12	1:1	64.19
20	0.40	800	30	8	1:1	93.67
21	0.40	800	5	10	3:1	54.97
22	0.40	600	20	10	1:3	84.33
23	0.05	400	15	10	1:3	71.33
24	0.30	200	20	8	1:1	98.97
25	0.40	200	5	8	1:3	84.33
26	0.20	600	20	8	1:1	88.26
27	0.10	600	30	10	1:1	80.97
28	0.20	800	10	8	1:3	60.30
29	0.20	200	30	12	1:3	86.00
30	0.05	400	5	8	1:1	75.34
31	0.30	600	5	12	1:3	60.10
32	0.40	600	5	8	1:3	74.52

A: adsorbent concentration, B: H₂S concentration, C: contact time, D: pH, E: ratio of TiO₂/CNT nano-hybrid.

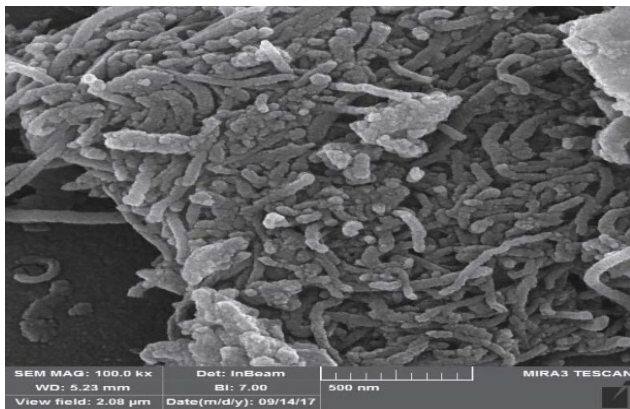
(from 8 to 12) decreases the hydrogen sulfide removal. According to zeta potential results of TiO₂/CNT nano-hybrid [33,34], getting the surface charge of TiO₂/CNT nano-hybrid to the acidic pH can lead zeta potential to become more negative. Based on the attraction law of unlike charges and negative surface charge of sulfide, the more TiO₂/CNT nano-hybrid charge becomes positive, the more absorption will be occur. Therefore, hydrogen sulfide removal in pH of 8 is more than the removal rate in the pH range of 10–12 and this trend is the same for all ratios of TiO₂/CNT (Fig. 8).

3.4. Effect of interaction parameters on the hydrogen sulfide removal

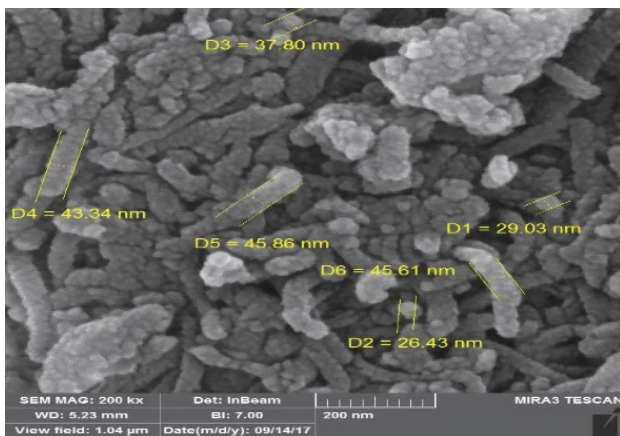
One of the advantages of using Design Expert software is that this software considers the interaction between main parameters and the effect of these interactions on the removal

Table 4
Analysis of variance

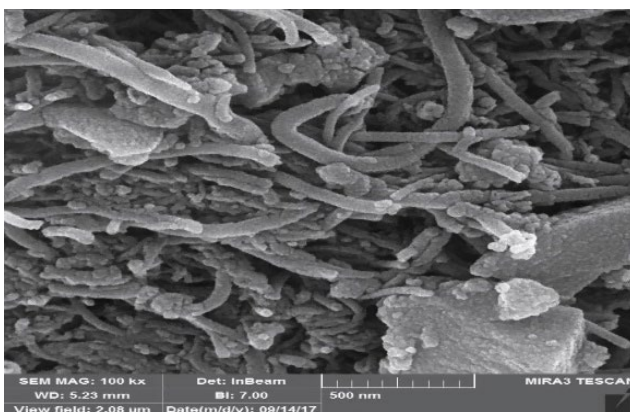
Source	Sum of squares	F-value	P-value (Prob. > F)
Model	7,496.00	57.47	<0.0001
A	1,726.07	185.27	<0.0001
B	2,446.24	262.58	<0.0001
C	1,531.02	164.34	<0.0001
D	708.63	76.06	<0.0001
E	331.64	17.80	<0.0001
BE	81.58	4.38	0.0293
CE	244.90	13.14	0.0004
DE	98.73	5.30	0.0163
B ²	111.00	11.91	0.0030
D ²	85.19	9.14	0.0077



(a)



(b)



(c)

Fig. 4. FE-SEM image of the TiO₂/CNT nano-hybrid with ratio of (a) 1:3, (b) 1:1, and (c) 3:1.

of hydrogen sulfide. The interaction occurs when the effect of a parameter depends on the surface of the other one and both of these parameters have an effect on the removal rate. The interaction between hydrogen sulfide concentration and ratio of nano-hybrid, contact time, nano-hybrid ratio, and between pH and ratio of adsorbent on hydrogen sulfide

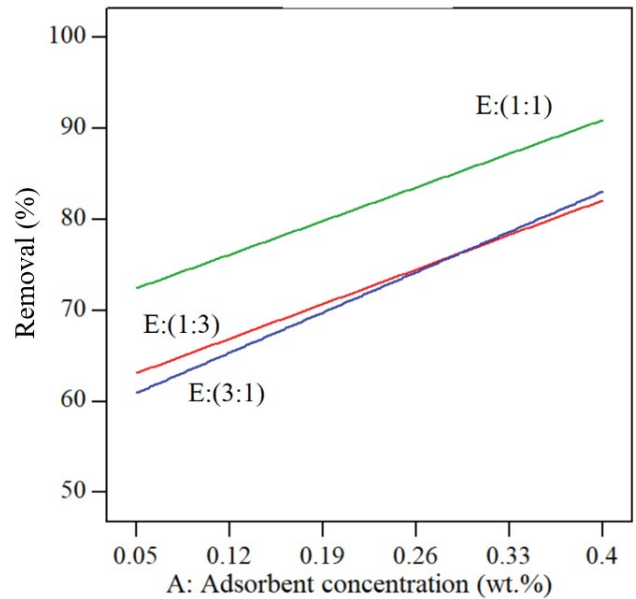


Fig. 5. Effect of adsorbent concentration on hydrogen sulfide removal efficiency at pH = 10, hydrogen sulfide concentration = 500 ppm, and contact time = 10 min and for different ratio of TiO₂/CNT nano-hybrid.

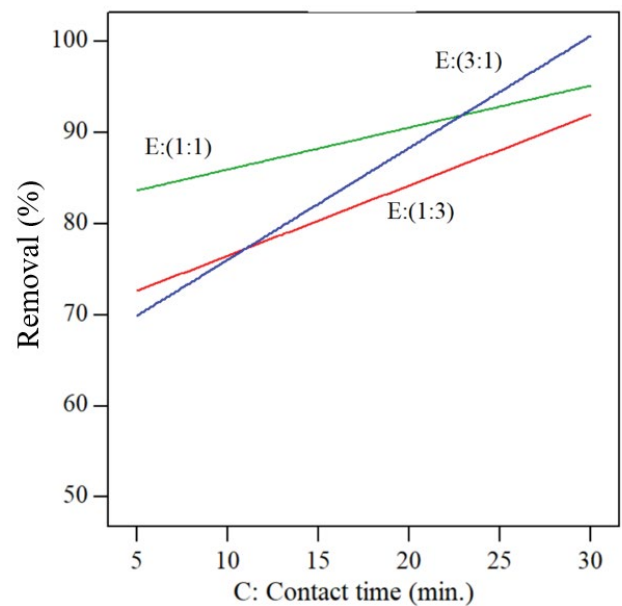


Fig. 6. Effect of contact time on hydrogen sulfide removal efficiency at pH = 10, nano-hybrid adsorbent concentration = 0.3 wt.%, hydrogen sulfide concentration = 500 ppm, and for different ratio of TiO₂/CNT nano-hybrid.

removal are illustrated in Figs. 9a–c. This Figure shows that raising the contact time and reducing the initial hydrogen sulfide concentration and pH will increase the removal rate for all nano-hybrid ratios. In addition, the nano-hybrid with the ratio of 1:1 had the most effect on the hydrogen sulfide

removal from the water-based drilling fluid, compared to the cases in which other ratios of nano-hybrid are used.

3.5. Optimum point for the hydrogen sulfide removal

To find the optimum condition for the hydrogen sulfide removal, nano-hybrid concentration, contact time, pH, and ratio of nano-hybrid were set in some ranges (Table 2). Initial hydrogen sulfide concentration was 800 ppm and removal rate was set to the maximum. At the optimum condition, maximum removal of hydrogen sulfide from water-based drilling fluid was found to be 92.86% (Fig. 10). Furthermore, maximum desirability in optimum condition was 0.941. This optimum condition was repeated three times in the drilling fluid laboratory and the removal rate was reported to be 91.85%.

3.6. Isotherm and kinetics of hydrogen sulfide removal

One of the most important parameters in the process of hydrogen sulfide removal from the drilling fluid is the prediction of absorption rate which is controlled by kinetics of absorption. To describe the kinetics of hydrogen sulfide removal (onto TiO₂/CNT nano-hybrid with different ratios) from the water based drilling fluid, pseudo-first-order [Eq. (6)] [35] and pseudo-second-order [Eq. (7)] [36] models are used [37,38]. Figs. 11a and b and Table 5 illustrate regression results of pseudo-first- and second-order models. It is obvious that R² for pseudo-first-order (0.960) is more than pseudo-second-order (0.997). Therefore, pseudo-second-order is suggested for the removal of hydrogen sulfide from drilling fluid.

Absorption mechanisms (monolayer or multilayer and physical or chemical adsorption) of hydrogen sulfide by TiO₂/CNT nano-hybrid from water-based drilling fluid are described by equilibrium adsorption isotherms. The Langmuir and Freundlich are isotherm models [39,40]. Freundlich and Langmuir models assume that hydrogen sulfide covers on nano-hybrid in a multilayer (physical adsorption) and in a monolayer (chemical adsorption) [38,39,41,42]. The experiments of adsorption isotherm model for TiO₂/CNT nano-hybrid are done in conditions of 0.4 wt.% adsorbent concentration, contact time of 30 min, pH of 8, and hydrogen sulfide concentration range of 200–800 ppm. Fig. 12 shows the regression results of comparing the experimental data to the adsorption models and Table 6 indicates the calculated parameters of Freundlich and Langmuir adsorption isotherm. The constants of two models show that Langmuir model (R² = 0.994) is better than Freundlich model for the prediction of hydrogen sulfide removal from the drilling fluid and this model matches well with the experimental data. Therefore, adsorption of hydrogen sulfide on nano-hybrid occurs in a monolayer form.

3.7. Adsorbent performance (reusability)

Reusability test was done in optimum conditions to investigate the adsorbent performance in the continuous processes (cycle), (Fig. 10). Adsorbent was used four times successively in the removal process without washing and drying and the results are shown in Fig. 13. It can be detected in this figure that the removal rate

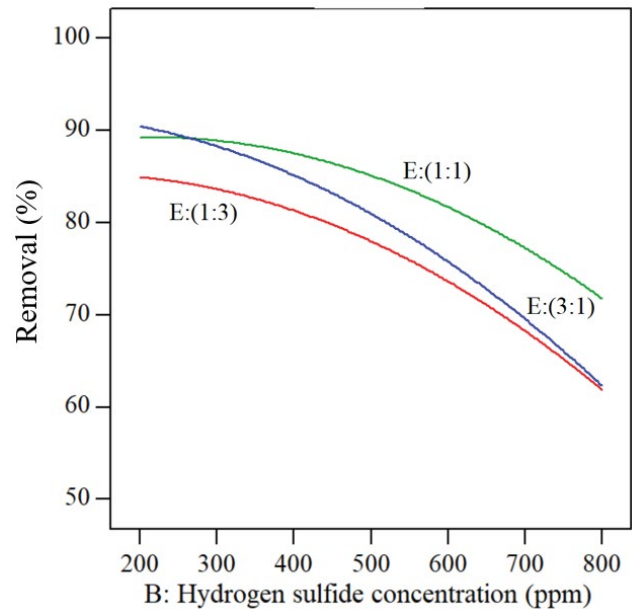


Fig. 8. Effect of pH on the hydrogen sulfide removal from drilling fluid at contact time=10 min, nano-hybrid concentration= 0.3 wt.%, initial hydrogen sulfide concentration=500 ppm, and for different ratio of TiO₂/CNT nano-hybrid.

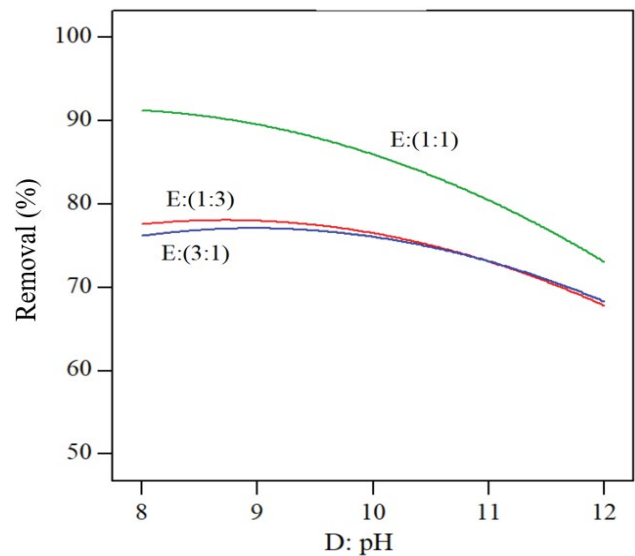


Fig. 7. Initial hydrogen sulfide concentration effect on removal efficiency at pH = 10, adsorbent concentration = 0.3 wt.%, contact time = 10 min, and for different ratio of TiO₂/CNT nano-hybrid.

Table 5
Parameters of kinetic models for the adsorption of hydrogen sulfide onto the TiO₂/CNT nano-hybrid from drilling fluid

Kinetic model	K ₁ (1/min)	K ₂ (g/mg/min)	R ²
Pseudo-first-order	0.061	–	0.960
Pseudo-second-order	–	0.00086	0.997

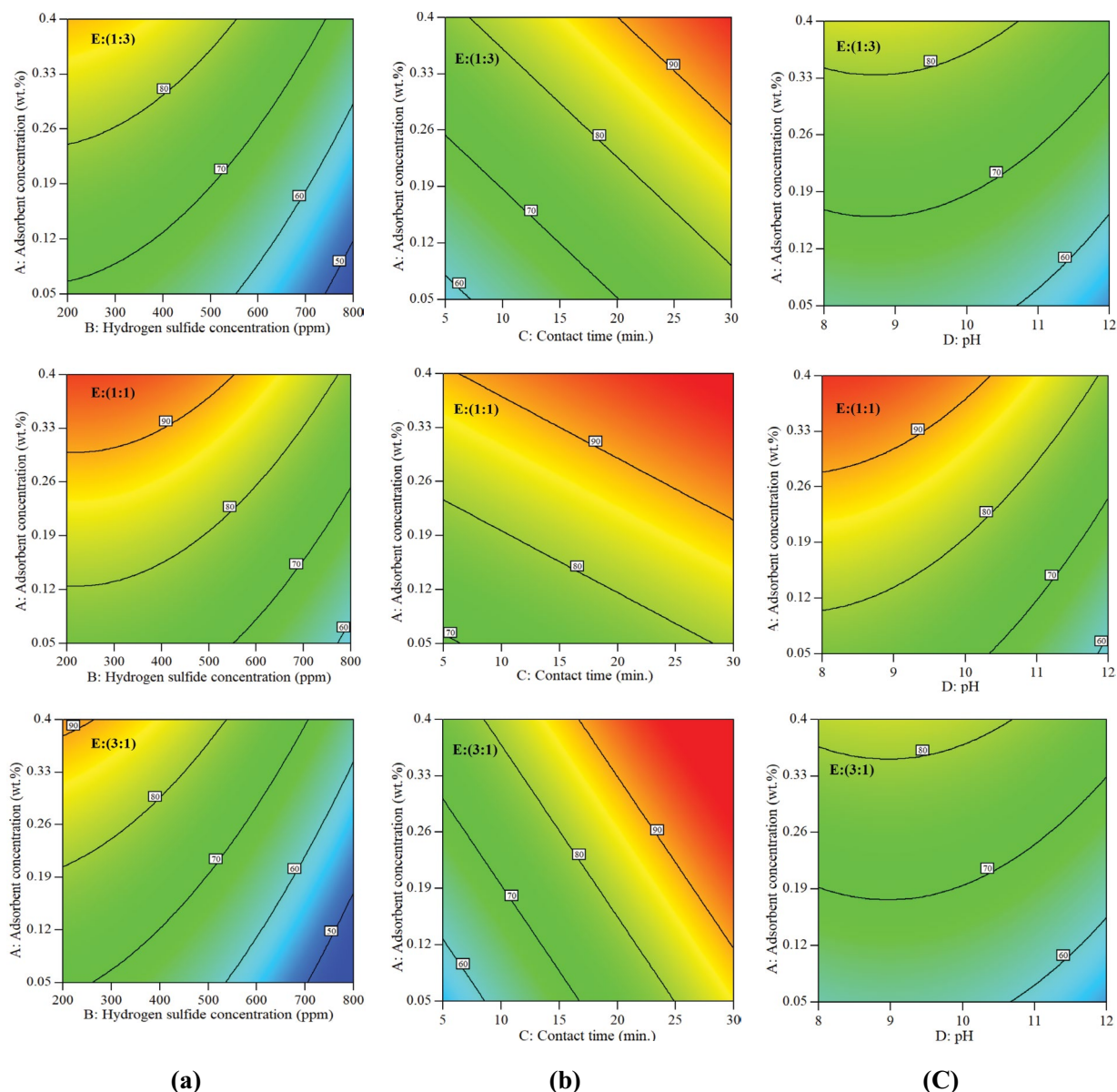


Fig. 9. Effect of interaction between (a) hydrogen sulfide concentration and ratio of nano-hybrid, (b) contact time and ratio of nano-hybrid, and (c) pH and ratio of adsorbent on hydrogen sulfide removal.

reaches 70% after using the adsorbent for four consecutive cycles indicating that this adsorbent has a good performance for the removal process (in case of using TiO_2/CNT nano-hybrid).

Comparison of the results of hydrogen sulfide removal in this work with those of the other works is shown in Table 7. It is obvious that synthesized TiO_2/CNT nanocomposite has a high removal capacity of hydrogen sulfide.

4. Conclusion

To adsorb hydrogen sulfide from water-based drilling fluid, TiO_2/CNT nano-hybrid with ratios of 3:1, 1:1, and 1:3 were synthesized by sol-gel method and were then characterized. Experiments were designed with Design Expert

software and *I*-optimal method. The effect of parameters, such as nano-hybrid concentration, initial hydrogen sulfide concentration, contact time, pH, ratio of nano-hybrid, and interaction between parameters were investigated and optimized for the removal of hydrogen sulfide from drilling fluid. Maximum removal in optimum conditions with initial hydrogen sulfide concentration of 800 ppm, adsorbent concentration of 0.4 wt.%, pH of 8, contact time of 30 min, and TiO_2/CNT nano-hybrid ratio of 1:1 was found to be 92.86%. In addition, study of kinetic model and isotherm removal showed that adsorption of hydrogen sulfide onto nano-hybrid with 1:1 ratio follows pseudo-second-order, Langmuir isotherm model, and monolayer adsorption. TiO_2/CNT nano-hybrid has the ability to be used in at least four consecutive cycles of hydrogen sulfide removal with an efficiency

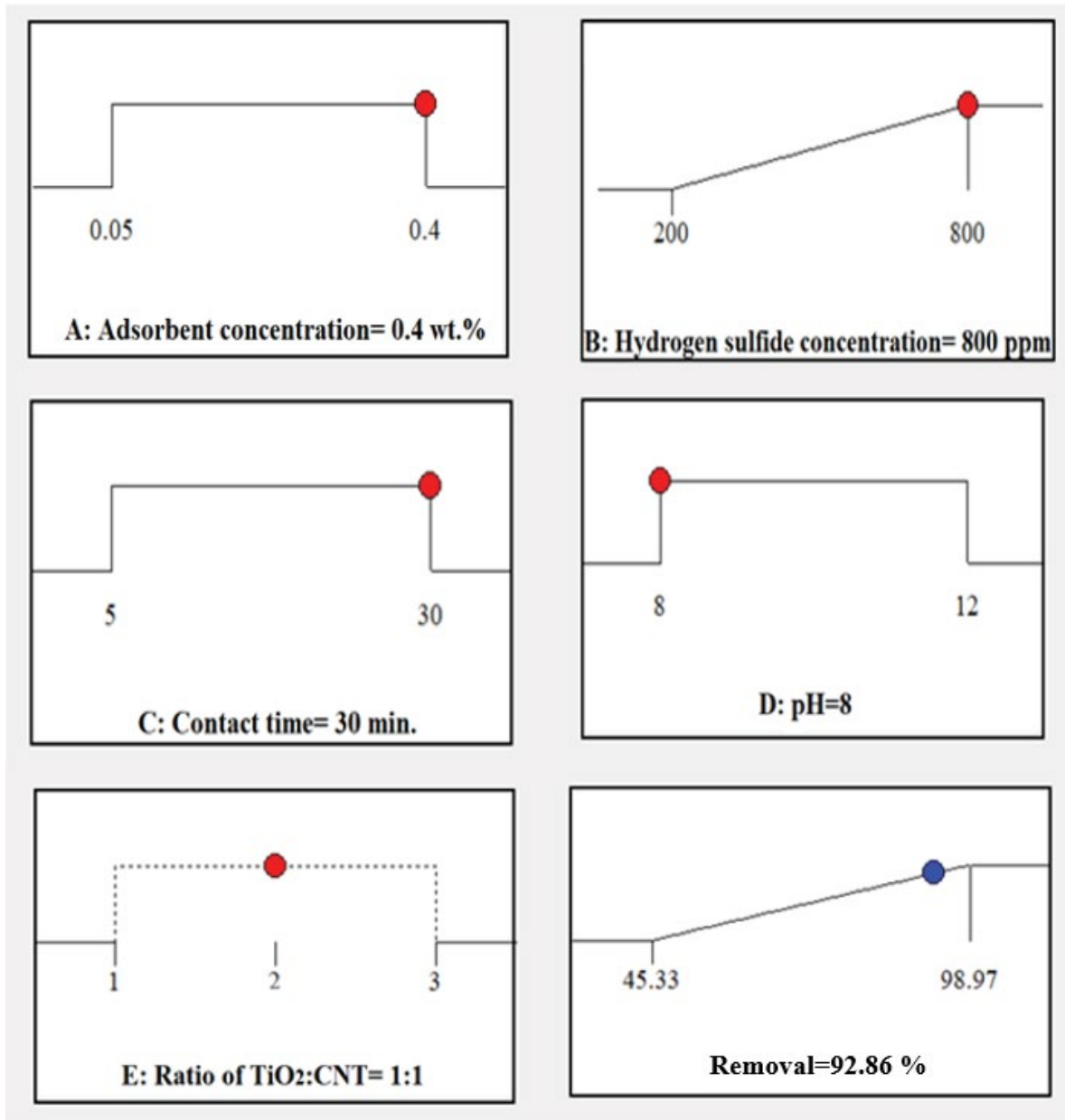


Fig. 10. Optimum condition for maximum removal of hydrogen sulfide from drilling fluid.

Table 6
Removal parameter of isotherm models for hydrogen sulfide removal onto TiO₂/CNT nano-hybrid from water-based drilling fluid

Langmuir model			Freundlich model		
q_m (mg/g)	K_L (mg/L)	R^2	n	K_f (mg ¹⁻ⁿ L ⁿ /g)	R^2
138.7	0.025	0.994	2.9	15.88	0.837

Table 7
Comparison adsorption capacity of TiO₂/CNT nanocomposite with other adsorbents for removal hydrogen sulfide

Adsorbents	Adsorption capacity (mg/g)	Reference
SBA-15 supported ZnO nanoparticle	436	[9]
Activated carbon from modified palm kernel shell	524.2	[14]
Wood sawdust activated carbon	390	[17]
Calcium coated wood sawdust activated carbon	544.4	[17]
Eggshell based activated carbon	289.3	[18]
CaO-eggshells dispersed onto palm kernel shell activated carbon	543.5	[19]
ZnO/TiO ₂ nanocomposite	118	[25]
Modified eggshells	150.1	[42]
Copper-promoted ZnO-SiO ₂	51	[43]
Copper-zinc oxides supported on mesoporous silica	75	[44]
Carbon nanofilaments functionalized with iron oxide nanoparticle	25.6	[45]
N-modifying AC supported ZnO	62.5	[46]

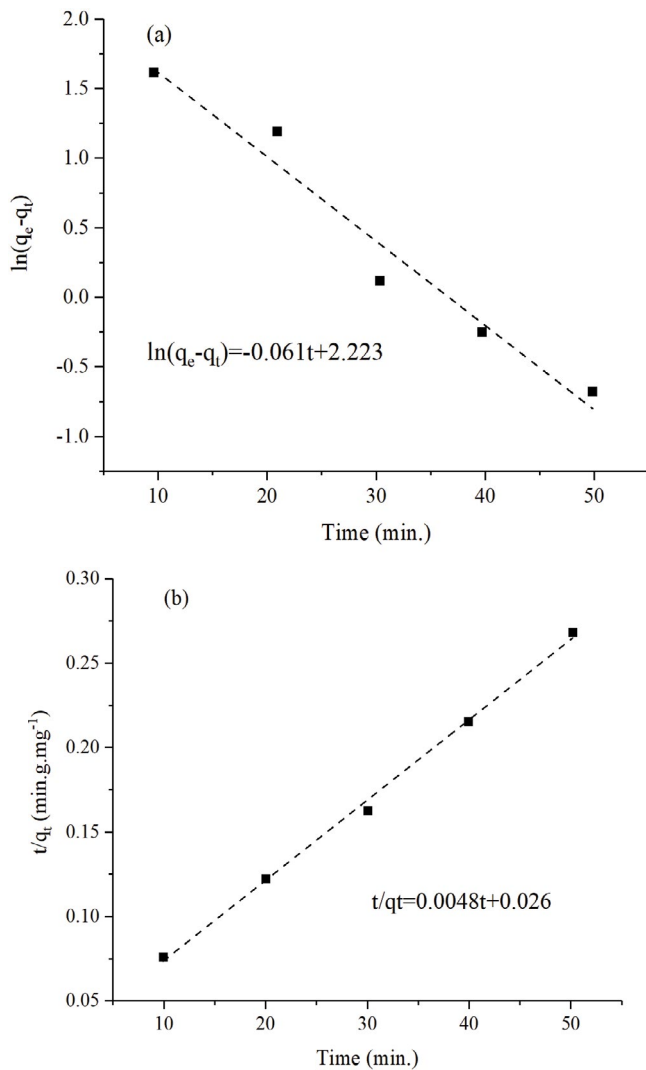


Fig. 11. Result of kinetic study of hydrogen sulfide removal by TiO₂/CNT from water-based drilling fluid (a) the pseudo-first-order and (b) the pseudo-second-order.

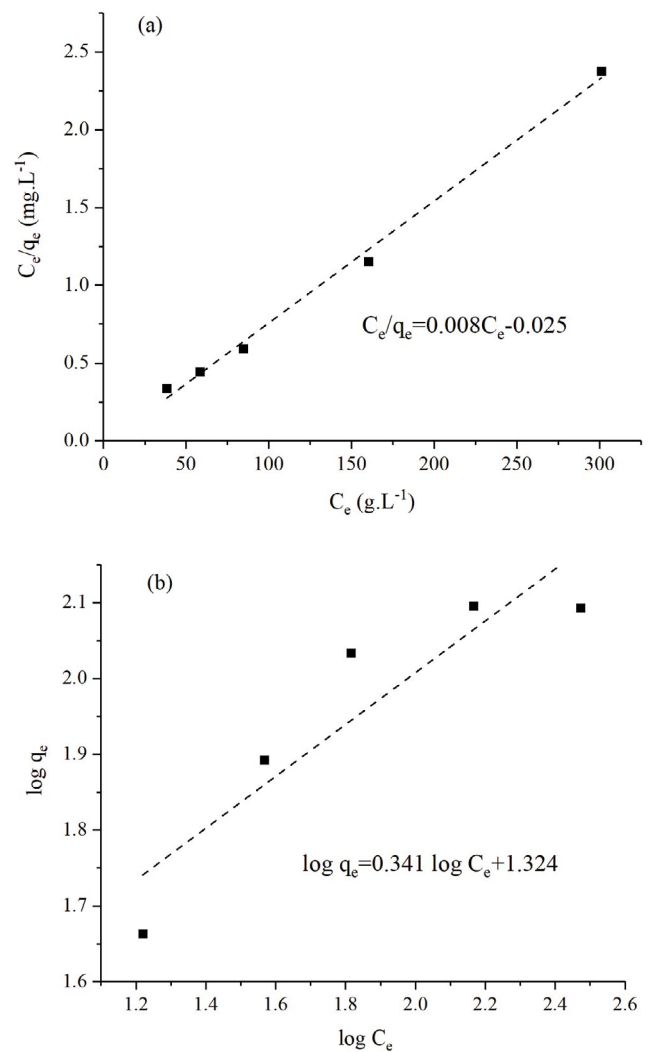


Fig. 12. Isothermal curves for hydrogen sulfide removal onto TiO₂/CNT nano-hybrid from water-based drilling fluid (a) Langmuir and (b) Freundlich model.

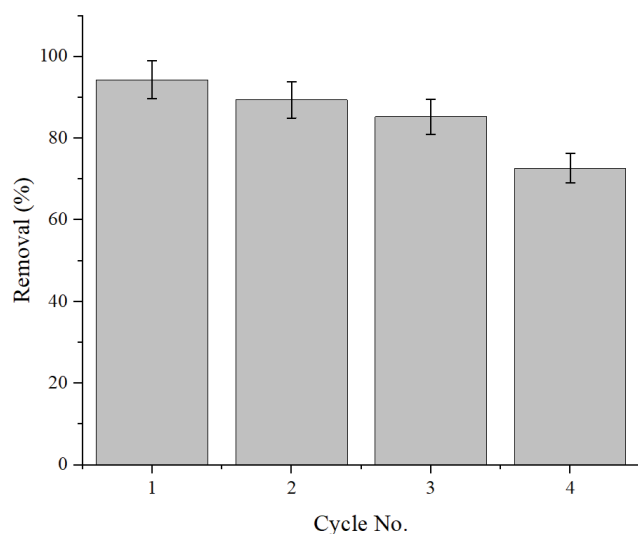


Fig. 13. Synthesized TiO₂/CNT nano-hybrid performance in reusability test at optimization condition.

higher than 70% and nano-hybrid had a good capability for the hydrogen sulfide removal.

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