

Experimental Investigation of Hydrogen Sulfide Adsorption from Drilling Fluid Wastes by Functionalized Carbon Nanotubes

Mona Pourjafar¹, Ali Askari², Ali Salehi Sahl Abadi³, Milad Pourjafar⁴, Seyed Ali Rahimi⁵, Afshar Nemati⁶

¹Department of Health, Safety, and Environment, Iran's National Oil Products Distribution Company, Kermanshah, Iran, ²Department of Occupational Health, School of Public Health, Tehran University of Medical Sciences, Tehran, Iran, Department of Health, Safety, and Environment, OICO Occupational Health Division, Ilam, Iran, ³Department of Occupational Health Engineering and Workplace Safety, Shahid Beheshti University of Medical Sciences, Tehran, Iran, ⁴Department of Health, Safety, and Environment, TESCO HSE Manager, North Azadegan Oil Field Project, Khuzestan, Iran, ⁵Department of Oil Engineering, West Oil and Gas Exploitation Company, Kermanshah, Iran, ⁶Department of Management, OICO Deputy Site Manager, Azar Oilfield Development Project, Ilam, Iran

Abstract

Aim: Hydrogen sulfide is one of the most harmful substances known in the drilling industry. Hydrogen sulfide can cause health, environmental, safety, and damage to property problems. Therefore, we conducted this study on a laboratory scale to make carboxylated carbon nanotubes and investigate their performance in removing hydrogen sulfide from drilling mud. **Materials and Methods:** In the first step, we prepared multi-walled carbon nanotubes with 90%–95% purity. In the next step, we provide the drilling fluid. The fluid used in these experiments was a simple water-based mud consisting of water and bentonite. In the last step, we used the Qualitek-4 software to design experiments, and the Taguchi model was used to investigate the obtained results. **Results:** Results show that pH is the most effective parameter in the adsorption process. Interaction of adsorbent concentration with retention time shows the highest SI = 85.85%. Optimal conditions of H₂S adsorption are adsorbent concentration = 100 ppm, pH = 6, and retention time = 30 min. According to the Langmuir model, the adsorption capacity of carbon nanotube (CNT)-COOH was 2480 (mg/mg). By increasing CNT-COOH concentration from 50 ppm to 100 ppm, the adsorption percent of H₂S increased from 51.6% to 66.1%. By increasing the retention time from 2 min to 30 min, an increase in adsorption will be seen from 57.5% to 65.3%. **Conclusion:** Using functionalized nanocarbon tube with at least 90% efficiency is a reliable method to remove hydrogen sulfide from drilling mud.

Keywords: Adsorbent, carbon nanotube, environmental pollutants, hydrogen sulfide, mud

INTRODUCTION

The oil and gas industry is global, with related operations conducted worldwide.^[1] The upstream petroleum industry, which performs all exploration and production activities, provides vital petroleum products used for various purposes, including transportation and electrical energy.^[2] These uses of petroleum significantly contribute to our current standard of living. However, finding and producing oil can impact the environment, and the most considerable impact arises from the release of pollutants compounds concentrations that are not naturally in the background.^[3] Two primary operations in the upstream petroleum industry can potentially impact the environment: drilling and production. Both operations generate a significant volume of waste.^[4] Environmentally responsible actions require an understanding of these wastes and waste-generated types. Improved processes that minimize

or eliminate adverse environmental impacts can be developed from this understanding.^[5] One of the waste streams associated with the petroleum industry is air emissions. The primary ecological consequences of air pollutants are respiratory difficulties in humans and animals, damage to vegetation, and soil acidification.^[6] As mentioned, one of the significant parts of the oil industry is drilling operations. Drilling fluid waste is one of the environmental concerns in the drilling industry.

Address for correspondence: Dr. Ali Salehi Sahl Abadi, Department of Occupational Health Engineering and Workplace Safety, Shahid Beheshti University of Medical Sciences, Tehran, Iran. E-mail: asalehi529@sbm.ac.ir

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The drilling fluid discharged in the mud pit has considerable heavy metals such as Cd, Cr, Al, and Hg. These heavy metals are toxic and can spread over land, surface, and groundwater.^[7] Another important pollutant in the oil industry is the production of large amounts of hydrogen sulfide.^[8] H₂S is a problem in the drilling industry. It is incredibly toxic to human and animal life and is highly corrosive to most metals.^[9] Various studies confirm the known effects of hydrogen sulfide on human health. Studies show that this gas is lethal in acute exposures and has an extensive chronic and subacute impact on human health, such as decreased heart rate, fatigue, insomnia, eye irritation, respiratory problems, and effects on the nervous system.^[9-12] After releasing in the environment, hydrogen sulfide is absorbed from the air into the soil and foliage of plants. This substance dissolves in water and oil, so groundwater and wet soils enter and thus travel long distances in surface water, causing changes in the chemical characteristics of waters, and increasing biological oxygen demand and chemical oxygen demand values. Hydrogen sulfide can quickly evaporate from the water surface due to temperature and pH; low and high temperatures accelerate evaporation. Due to its high solubility in water, it is transported in wet soils and marine environments, absorbing clay and soil organic matter. Some soil and water microorganisms can convert hydrogen sulfide to elemental sulfur, and its half-life in these environments is from 1 to several hours. Furthermore, this gas, in addition to environmental pollution, can lead to corrosion in surface and underground equipment.^[13-15] During drilling, oil and gas H₂S can come into the drilling mud.^[9,10] On the other hand, one of the significant problems in the drilling industry is the cost of drilling fluid loss, as an average of 15% of the cost of operations is related to this sector.^[9] According to the above, removing hydrogen sulfide gas from drilling mud is necessary due to environmental aspects, adverse human health effects, and increasing costs of drilling fluid loss and surface and subsurface equipment corrosion. Hence, we used a carboxylated carbon nanotube to remove hydrogen sulfide from the drilling fluid in this study. The carbon nanotube (CNT)-COOH was used for H₂S uptake and to investigate the effect of various experimental conditions, such as solution pH, time, and adsorbent concentration, on adsorption rate.

MATERIALS AND METHODS

We divided the methods and approaches of the experiments done in this research into five main parts. The first part is the functionalized carbon nanotubes which were done in the Research Institute of Petroleum Industry (RIPI). The second part is the process of preparing the mud. The third part explains the design of the experiment method. The fourth part is all the adsorption experiments on the drilling mud that were done in the Abadan Faculty of the Petroleum University of Technology. This part expresses hydrogen sulfide concentration measurements in mud samples that were done in Abadan Refinery Company. The last part explains the mathematical adsorption study.

The chemicals used in this study were carbon nanotube functionalized with a carboxylic group (SKC, England), Triton X-100 (Sigma-Aldrich, USA), sodium sulfide (Sigma-Aldrich, USA), bentonite (Merck, Germany), HCl (Merck, Germany), and NaOH (Merck, Germany).

The following equipment and devices were used: Mechanical Mixer (R100CL model), ultrasonic processor (UP200H model), electronic pH meter (Jenway 3510), Rotary Incubator (IKA KS 4000IC control model), balance, hydrogen sulfide detector tube (Kitagawa), and Gas aspirating pump (Kitagawa AP-20 Air Sampling Blue Pump Kit), and Bentonite (Merck, Germany).

Nanoparticles preparation

We prepared multi-walled carbon nanotubes (MWCNTs) from the RIPI with 90% to 95% purity prepared by an enhanced chemical vapor deposition over a Co-Mo supported MgO nanoporous catalyst at a reasonable temperature of 1173K, consisting of high-purity methane (99.999%) as a carbon source in a 1.5-m horizontal two pass fixed-bed tubular (Quartz) reactor placed in a 100 cm long and programmable tubular furnace. In the next step, these tubes were sonicated at 60°C with a solution of HNO₃ (65% purity) and H₂SO₄ (98% purity) (3:1, v/v) for 3 h to enhance the functionalization of multi-walled carbon nanotubes (MWCNTs) carboxyl group.^[16,17]

Drilling fluid synthesis

The drilling fluid used in these experiments was a simple water-based mud consisting of water and bentonite. The procedure of preparing the drilling mud is as follows: First, a specific volume of distilled water was taken in a graduated cylinder and moved into a clean 1-L beaker mixed by a mixer with 700 rpm [Figure 1]. A definite amount of bentonite was weighed carefully and added to water gradually. Then, they were mixed well for about 20 min and prepared for measuring their properties.^[3]

Experiments design

In this study, the Taguchi method and also Qualitek-4 software, we used to design and analyze experiments. Experimental design



Figure 1: Drilling fluid preparation

is a strategy to gather empirical knowledge, i.e., knowledge based on the analysis of experimental data and not on theoretical models. Design of experiments (DOE) using the Taguchi approach is a standardized form of experimental design technique (referred to as classical DOE) introduced by R. A. Fisher in England in the early 1920s. Typical areas of application of the method are optimize designs using analytical simulation studies, select better alternatives in development and testing, optimize manufacturing process designs, determine the best assembly method, and solve manufacturing and production problems.^[4-6]

Main effects and interaction

Calculating the average performance of factor a in level 1, the total obtained results from the experiments for A are divided by the number of these experiments. The difference between average performances is essential to select the main effect factor. The larger the difference, the stronger the influence (negative values are ignored). Interaction between factors: QT4 displays interaction plots between any two elements. QT4 calculates $N(N - 1)/2$ possible pairs of interactions for N factors and ranks them by the severity of their presence (severity index, 0%–100%). That SI 100% is for 90 degrees angles between the lines, and 0% is for the parallel line.

Analysis of variance (ANOVA) was used to analyze the experiment's results and determine the variation due to each factor.

Projection of the optimum performance

Equation 1 was used to calculate the optimum performance of experiments.

$$Y_{opt} = T/N + (\bar{A}2 - T/N) + (\bar{E}1 - T/N) + (\bar{I}2 - T/N) \quad (1)$$

Where: *T*: Grand total of all results, *N*: Total number of results, and *Yopt*: Performance at optimum condition;

Adsorption experiment

Adsorption condition

Among parameters that can affect the adsorption conditions, the amount of adsorbent (CNT-COOH), pH, and retention time is critical, so we investigated the three mentioned parameters at different levels [Table 1].

Experimental method

We did several experiments in different pH and retention time conditions with varying amounts of nanotubes to determine optimum conditions for the nanotube adsorption process. All these experiments were accomplished at 25°C. Furthermore, according to the below reaction (Equation 2), a specific amount of sodium sulfide (Na₂S) was added to mud samples to define arbitrary H₂S concentration in solution media.



Drilling mud pH was adjusted by 0.1 M HCl (MERK) and 0.1 M NaOH (MERK) and measured by an electronic pH meter. In this experiment, we examined three parameters at three

different levels. In the next step, we designed nine tests by the Taguchi methods, which are summarized in Table 2.

First, we put 300 ml of the drilling mud in a 500 ml flask to do these experiments. The required amount of adsorbent was weighted by a balance with 10⁻⁴ accuracy. Then, to disperse nanotubes uniformly and improve their adsorption capabilities, a 100-ml beaker was used. Finally, triton and distilled water were added, and the beaker was placed in the ultrasonic processor for about 5 min [Figure 2].

Then, they were added to the mud sample, and after setting the pH, Na₂S was added to the Erlenmeyer flask [Figure 3], and it was shaken on the orbital shaker for the required time in tests.

H₂S concentration measurements

The H₂S concentration in the prepared samples in the previous section was determined by the Kitagawa hydrogen sulfide detector tube. The H₂S concentration in the prepared samples in the previous section was determined by the Kitagawa hydrogen sulfide detector tube. Each detector tube is formulated with high-purity reagents that absorb and react with the target gas or measured vapor. A colorimetric stain is created that is proportional in length to the concentration. For most tubes, the concentration is read directly off the measurement scale on each tube^[17-19] [Figure 4].

Gas aspirating pump, sampling and measurement

We used the Kitagawa Air Sampling Pump (model AP-20) Figure 5. First, we break both ends of the detector tube. The detector tube was securely inserted into the aspirating pump, and the sample was put on the heater mixer. The tube of the Erlenmeyer flask was attached to the detector tube, and the gas path was opened. The pump handle was pulled at a full stroke until it was locked and holed for 1 min or until the completion of sampling was confirmed with the flow indicator of the

Table 1: Parameters and levels description

Parameters	Level 1	Level 2	Level 3
Adsorption (ppm)	50	75	100
pH	2	6	10
Time (min)	2	30	60

Table 2: Experiments conditions

Test number	Adsorbent (ppm)	pH	Retention time (min)
1	50	2	2
2	75	6	30
3	100	10	60
4	50	2	30
5	75	6	60
6	100	10	2
7	50	2	60
8	75	6	2
9	100	10	30



Figure 2: Ultrasonic processor



Figure 3: Sample preparation

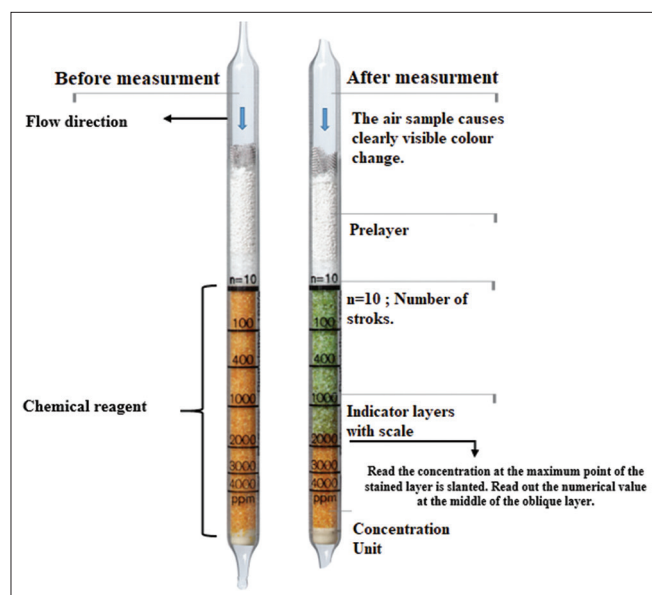


Figure 4: Detector tube

pump [Figure 6]. On completion of the sample, the scale at the maximum point of the stained layer was read.^[7]

Mathematical Adsorption Study

The amount of hydrogen sulfide molecules adsorbed was calculated according to Equation 3.^[8,9]

$$qe = V(C_0 - C_e)/m \quad (3)$$

Where

q_e : Equilibrium amount of H_2S adsorbed on the adsorbent (mg/g)

V : Volume of solution (L)

C_0 and C_e : Initial and equilibrium concentrations in solution (mg/L)

m : The mass of adsorbent (g)

The uptake efficiency of H_2S adsorbed on CNT-COOH was calculated from the difference of H_2S concentration before

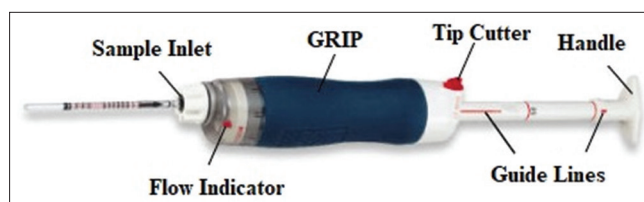


Figure 5: Kitagawa Air Sampling Pump

and after the experiment. The uptake efficiency was calculated based on Equation 4.

$$E = \frac{C_0 - C_e}{C_0} \times 100 \quad (4)$$

Where, E is uptake efficiency.

RESULTS

Characterization of adsorbent

We characterized the crystalline structure of multi-walled carbon nanotubes by transmission electron microscopy (TEM), scanning electron microscopy (SEM), and Fourier-transformed infrared (FTIR) analyses.

The TEM images of prepared multi-walled carbon nanotubes in Figure 7 were prepared at different magnifications. The cylindrical and hollow structure of MWCNT is apparent in these figures.

SEM image as shown in Figures 8 revealed that the average diameters of carbon nanotubes synthesized for this study vary from 40 to 70 nm and their length from 5 to 15 μm . This image shows the cylindrical structure of carbon nanotubes and their uniform distribution. This suggests the high surface area of CNT, which means that CNT has a high adsorption capacity.

The FTIR analysis of carboxylated MWCNTs is presented in Figure 9. As shown in Figure 10, the band around 1569 is attributed to the graphitic structure of MWCNTs. The presence of carboxylic $C = O$ ($\sim 1720 \text{ cm}^{-1}$) and $C-O$ ($\sim 1199 \text{ cm}^{-1}$)



Figure 6: H₂S Sampling and measurement

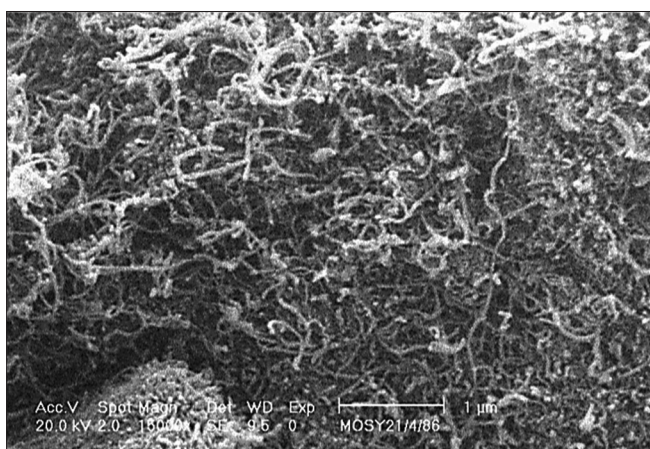


Figure 8: MWCNT SEM images. MWCNT: Multi-walled carbon nanotube, SEM: Scanning electron microscopy

vibrations, the spectrum of oxidized MWCNTs indicated that carboxyl groups are introduced to the tip and sidewalls of the MWCNTs.

Experimental results

Table 3 shows the results obtained from the experiments, which were entered in Qualitek-4.

The main objectives of employing the Taguchi methodology are to understand the influence of factors individually and in combination on adsorption and establish the optimum conditions with the selected elements for effective performance. The difference between values is shown in Table 4. The larger the difference, the stronger the influence (negative values are ignored). Levels two and one (L2–L1) of each factor indicated the relative impact on the performance.

Table 5 shows three interactions between factors. Interaction of adsorbent concentration with retention time shows the highest SI (85.85%).

The ANOVA is summarized in Table 6. This table is the output of Qualitek software. Among the factors considered, the most

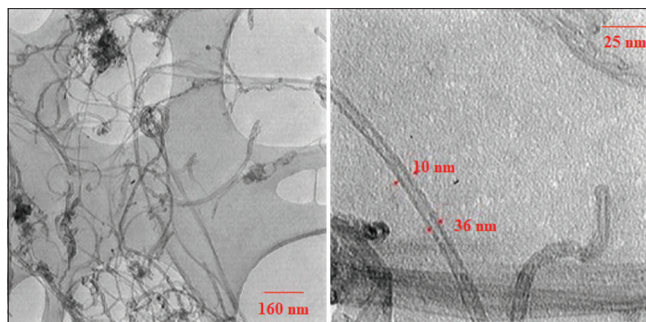


Figure 7: MWCNT TEM images. MWCNT: Multi-walled carbon nanotube, TEM: Transmission electron microscopy

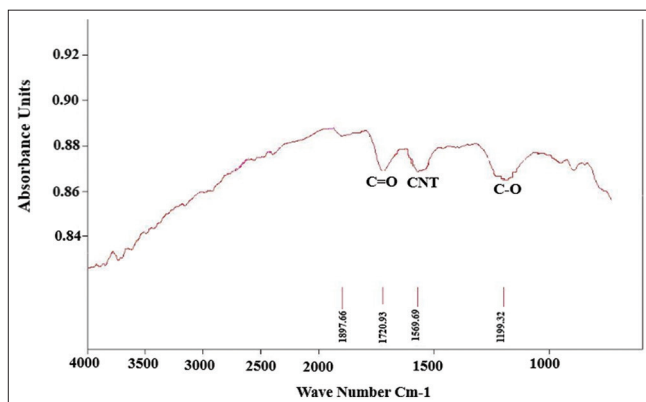


Figure 9: The FTIR spectra of MWCNTs functionalized with the carboxyl group. FTIR: Fourier transformed infrared, MWCNTs: Multi-walled carbon nanotubes

Table 3: Experiments result

Trial	Adsorbent (ppm)	pH	Retention time (min)	Results
#1	50	2	2	0
#2	75	6	30	0.99
#3	100	10	60	0.56
#4	50	2	30	0.05
#5	75	6	60	0.94
#6	100	10	2	0.76
#7	50	2	60	0.10
#8	75	6	2	0.965
#9	100	10	30	0.92

Table 4: The parameters with main effects in this study

Factors	Level 1	Level 2	Level 3	L2-L1
C (ppm)	0.516	0.583	0.661	0.066
pH	0.05	0.964	0.746	0.913
Time (min)	0.575	0.653	0.533	0.078

influential is pH, with a 93.843% contribution, followed by adsorbent concentration (0.982%) and time (0.335%). The error is calculated by software at 4.84%

The optimum conditions derived from DOE analysis showed effective H₂S adsorption in the presence of pH (level 2)

using the concentration of CNT-COOH (level 3) for retention time (level 2) [Table 7].

Optimal conditions of the factors show that H₂S uptake by CNT-COOH is predicted by software 1.104 indicating complete uptake. The confirmation test condition was performed after calculating the optimal conditions according to Table 8.

The confirmation test showed complete adsorption; this means that the software's optimum performance is confirmed.

Adsorption isotherm

Equilibrium data, called adsorption isotherms, describe how hydrogen sulfide molecules interact with adsorbents. Adsorption experiments were performed for CNT-COOH at different pH. The data from pH = 6 to pH = 10 were modeled by Longmuir [Figure 10] and Freundlich [Figure 11].

Effect of carbon nanotube-COOH concentration on H₂S adsorption

Figure 12 shows the effect of adsorbent concentration on the amount of H₂S adsorption. According to the figure, increasing the concentration to 100 ppm will increase the amount of adsorption.

Effect of pH on H₂S adsorption

Figure 13 shows the distribution of sulfur species as a function of pH in drilling fluid. This study was about the H₂S fraction in the range of pH = 2.0–10.0.

In pH = 2, all the sulfur components in the fluid are the form of H₂S. In these conditions, we cannot get an appropriate response because of the large amounts of H₂S; the surface of the adsorbent will be saturated.

In pH = 6, the compound HS-is appeared. Therefore, the concentration of H₂S will be reduced to a more reasonable amount, which is the ideal pH for this study. Since there is an equilibrium between H₂S and HS-, the adsorbent has enough time to absorb the produced H₂S. In pH = 10, the concentration of H₂S concerning S₂-, HS-is small, and due to the large pH,

the produced H₂S will change into S₂-, HS-quickly, and it takes more time to the adsorbed by the adsorbent.

Effect of retention time on H₂S adsorption

The effect of time on the amount of adsorption of H₂S is represented in Figure 14. An increase in adsorption will be seen by increasing the retention time from 2 min to 30 min. After 30 min, the amount of adsorption will be reduced to reach its minimum in 60 min.

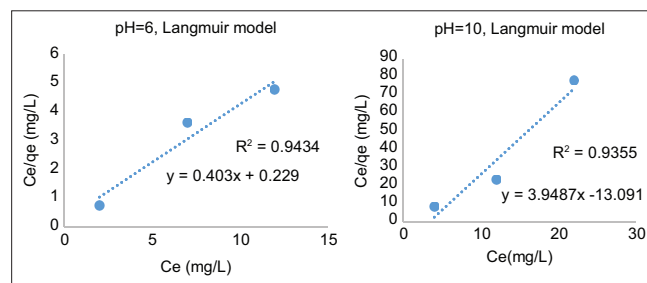


Figure 10: Langmuir isotherm model fitting

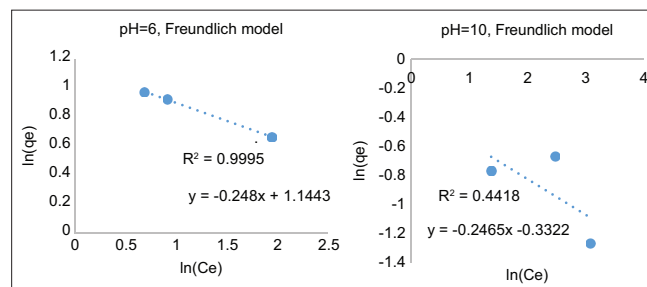


Figure 11: Freundlich isotherm model fitting

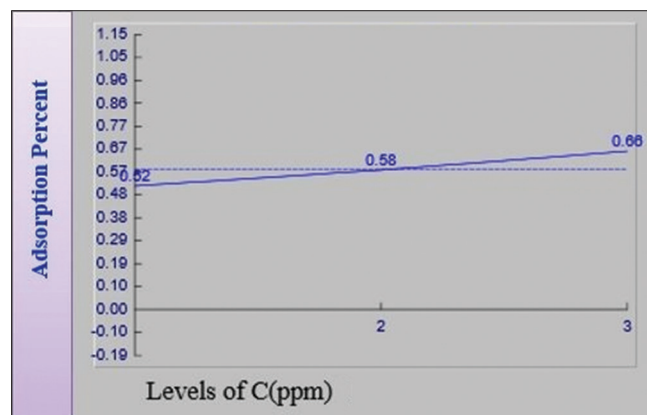


Figure 12: Average effect of concentration (ppm)

Table 5: Interacting factor pairs (order based on SI)

Factors	Columns	SI (%)	Column	Optimization
C (ppm) × time (min)	1×3	85.85	2	[1,2]
C (ppm) × pH	1×2	5.05	3	[1,2]
pH × time (min)	2×3	1.26	1	[2,2]

SI: Severity index

Table 6: Variance analysis results

Factors	DOF	Sum of squares	Variance	F-ratio	Pure sum	Percent
C (ppm)	2	0.031	0.015	1.812	0.014	0.982
pH	2	1.370	0.685	78.573	1.352	93.843
Time (min)	2	0.022	0.011	1.277	0.004	0.335
Other/error	2	0.016	0.008	-	-	4.840
Total	8	1.441	-	-	-	100.000

DOF: Degree of freedom

DISCUSSION

Hydrogen sulfide is one of the most harmful substances known in the drilling industry.^[10] Numerous restorative technologies control the H₂S, such as physicochemical, chemical, biological, and electrochemical approaches.^[11] In the meantime, nanotechnology has already donated significantly to technological advances in the oil and gas industry. Nanotechnology has the potential to inset a possible revolution in different aspects of the drilling industry.^[12] One of the most important applications of nanotechnology is its use to develop a variety of adsorbents.^[11,12] In the present study, we made an adsorbent for this purpose using nanotechnology and considering the importance of removing hydrogen sulfide from drilling mud. We characterized the crystalline structure of multi-walled carbon nanotubes by TEM, SEM, and FTIR analyses. The cylindrical and hollow structure of MWCNT was apparent in TEM images, and SEM analysis indicated a high absorption of CNT. Finally, The FTIR analysis showed that carboxyl groups were introduced to the tip and sidewalls of the MWCNTs. As stated in the methods section, the parameters affecting adsorbents' optimal performance, including pH, adsorbent, and retention times, were investigated. One of the most significant parameters influencing the uptake capacity of adsorbent materials is the pH value.^[13] Table 4 PH showed a more substantial

influence among the factors studied, followed by CNT-COOH concentration and retention time. According to Table 4, factor 1 (concentration of CNT-COOH) responded to adsorption at level 3 favorably (66.1%). Individually, pH (level 2) depicted effective adsorption (96.4%) compared to the other two pH studies. Among the retention time levels, level 2 characterized superior adsorption efficacy (56.3%) compared to the different groups. Furthermore, results [Figure 13] show that NCT-COOH in PH = 6 has an optimum condition. In a study by Almasvandi *et al.*,^[20] on removing hydrogen sulfide from crude oil, the results showed that the ideal pH for removal is <5.5. Furthermore, based on Alimohammadi *et al.*'s^[21] study, understanding the optimum pH is fundamental since pH influences the surface amount of adsorption and the degree of ionization and speciation of adsorbent during the reaction. Considerable studies confirm the effect of pH on nano-adsorbents' efficiency for different adsorption conditions and purposes.^[22-24] The second parameter studied is the concentration of adsorbent. Studies in various fields of adsorbent manufacturing show that this parameter has a significant effect on determining the optimal adsorption conditions.^[24,25] In this present study, considering the physical adsorption definition, by increasing the concentration of CNT-COOH [Figure 12], more adsorbent surfaces will be exposed to the H₂S gas molecules. Hence, the concentration of 100 ppm is the ideal concentration of the adsorbent in this study. The number of available adsorption sites grows when the dosage is increased, enhancing the removal effectiveness by increasing the concentration. As a result, the increased removal efficiency with the increasing amount of adsorbent is attributed to the adsorbed procedure' isomerization of adsorption sites. Another essential parameter that was investigated is retention time. In some implemented investigations on nano-adsorbents, as time rises, ions evolve more likely to contact the functional groups in the adsorbent structure, and the adsorption rate increases.^[26,27] In this study, after 30 min, the amount of adsorption will be reduced to reach its minimum in 60 min [Figure 14]. To explain this condition, we can say that during retention time, these samples are continuously shaken at the rate of 350 rpm. After 30 min, the dissolved H₂S in the fluid, which CNT-COOH does not yet adsorb, is released into the gas phase. Furthermore, due to the importance of pH, adsorption experiments were

Table 7: Optimum condition and performance results

Factors	Level description	Level	Contribution
C (ppm)	100	3	0.074
pH	6	2	0.377
Time (min)	30	2	0.066
Total contribution from all factors			0.517
Current grand average of performance			0.587
Expected result at optimum condition			1.104

Table 8: Confirmation test results

Trial	Concentration of adsorbent (ppm)	pH	Retention time (min)	Result
#10	100	6	30	1.00

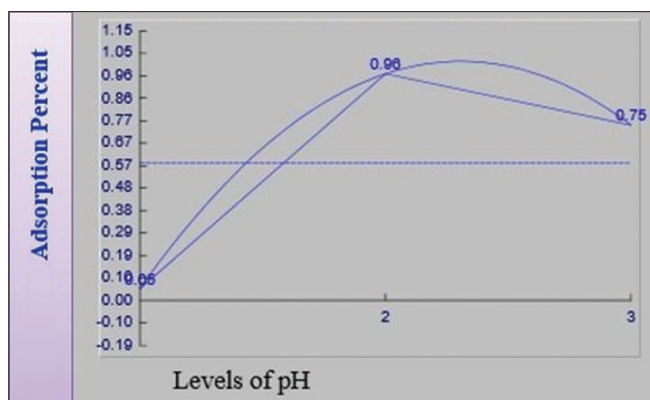


Figure 13: Average effect of pH

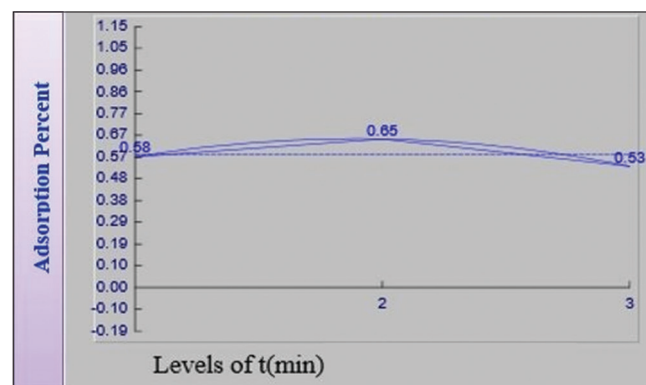


Figure 14: Average effect of retention time (min)

evaluated by Langmuir and Freundlich.^[28,29] Tables 9 and 10 show that the Langmuir model fits the experimental data of adsorption equilibrium better than the Freundlich model for both pHs. Therefore, adsorption can be represented more appropriately by monolayer adsorption. Finally, based on the results of this investigation, we can say pH is the most effective parameter, with a contribution percent = of 93.84%. Interaction of adsorbent concentration with retention time shows the highest SI = 85.85%. Optimal conditions of H₂S adsorption are adsorbent concentration = 100 ppm, pH = 6, and retention time = 30 min. According to the Langmuir model, the adsorption capacity of CNT-COOH was 2480(mg/mg). The adsorption process shows an increase in pH from 2 to 6; the adsorption percent increased from 0.05% to 96.4%, then with a reduction of pH from 6 to 10, the adsorption percent decreased to 74.6%. By increasing CNT-COOH concentration from 50 ppm to 100 ppm, the adsorption percent of H₂S increased from 51.6% to 66.1%. By increasing the retention time from 2 min to 30 min, an increase in adsorption will be seen from 57.5% to 65.3%, and then by increasing the time to 60 min, the adsorption percent decreases to 53.3%.

CONCLUSION

Results show that nanotubes adsorb H₂S from drilling mud. Furthermore, adsorption does not occur in very low pH and acidification ambient, so these conditions are unlikely in the drilling process. However, adsorption occurs at the normal pH. Due to their high surface area, nanotubes can adsorb H₂S well, even in a low amount of CNT-COOH. The Langmuir isotherm is the most appropriate to describe the experimental data for CNT-COOH; this means the adsorption process is monolayer adsorption onto a surface. Software predicts that at optimal conditions, adsorption is complete (100%). The result of the confirmation test shows H₂S completely adsorption.

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Ethics code

4000821/027.

Financial support and sponsorship

The ethical considerations of this study were investigated and approved by the R&D department and research committee of OICO under the 4000821/027 registration number.

Conflicts of interest

There are no conflicts of interest.

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Table 9: Langmuir isotherm parameters for H₂S adsorption

pH	Langmuir (constants)		
	K _l	q _m (mg/g)	R ²
pH=6	1.76	2480	0.94
pH=10	-0.019	250	0.93

Table 10: Freundlich isotherm parameters for H₂S adsorption

pH	Freundlich (constants)	
	K _f	n
pH=6	3.12	-4.03
pH=10	0.72	-4.06

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