

Carbon Nanotubes Characterization and their Potential for Increased Hydrocarbon Production

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Abstract

Increasing the hydrocarbon recovery rate is one of the most important objectives in the field of hydrocarbons. The elimination of problems that obstruct the flow, such as sulfates or barium sulfate deposits, will increase hydrocarbon recovery. In this work, carbon nanotubes are used to solve the sulfate problem. To avoid the precipitation of barium sulfate. Multiwalled carbon nanotubes (MWCNT) were prepared by chemical vapor deposition of gas condensation at 1000 °C and oxidized with an acid mixture at 115 °C for 2 hours, then applied as an adsorbent for the removal of sulfates. The variables Effects such as temperature, adsorbent dose, time, and agitation speed, as well as their interactions during adsorption, were determined and optimized using the response surface methodology (RSM) via a central composite factorial design (CCF). The experimental data were examined by analysis of variance (ANOVA) and fitted to a second-order polynomial equation. The optimal conditions were an initial concentration of 800 mg/L, an adsorbent dose of 0.14447 g, a pH of 7, and a temperature of 74.21 °C, 530 rpm for 240 min, and a maximum sulfate removal of 96% was achieved. Isotherm models were studied to describe the sulfate adsorption data, and a higher model fitting the Langmuir isotherm was found. Kinetic studies have shown that the adsorption followed a pseudo-second-order reaction. Overall, MWCNTs are promising adsorbents for water treatment and have great potential for application in oil fields to reduce the tartar ion content at the source.

Keywords: Adsorption, Sulfate Ion, Carbon Nanotubes, Recovery Rate, Removal of Deposits

Introduction

When the reservoir pressure decreases, one of the enhanced oil recovery (EOR) methods offers the possibility of bringing crude oil to the surface by injecting fluids and chemicals into the wells to improve and increase the amount of oil recovered [1]. In the simplest case, oil is extracted by creating pressure gradients in the reservoir that cause the oil to flow through the interconnected pores towards one or more production wells. Pressure gradients are maintained by injecting either chemical, gas, steam, heat, or water into the well. Reservoir through injection wells. [2]. Due to its simplicity and reliability, the water injection technique (secondary recovery) has been implemented worldwide and has been considered for most conventional oil reservoirs to extract more oil after the primary recovery process [3]. The main problems associated with the use of water injection to enhance oil

recovery are the corrosion of surface and subsurface equipment and the possible reaction of the injected water with the reservoir and its contents, which leads to the formation of new undesirable deposits. These deposits are precipitated as a result of a disturbance in the system's pressures and temperatures and the mixing of incompatible waters. Many oil fields encounter precipitation problems, although barium sulfate deposits are the most dangerous. If the sulfate comes from the injected water, then the barium comes from the reservoir waters ($\text{Ba}^{2+} + \text{SO}_4^{2-} \rightarrow \text{BaSO}_4$) [4]. As a new member of the carbon family, carbon nanotubes (CNT) have been considered promising adsorbents at both research and technological levels for the removal of pollutants from the environment due to their physical, optical, and mechanical characteristics [5, 6]. CNTs could strongly adsorb organic and inorganic chemicals and consequently modify their chemical mobility,

size and pore distribution, and the specific surface curvature of the tubes. As well as the operational parameters of adsorption types of CNT (single-walled CNT (SWCNT) or multi-walled CNT (MWCNT)) are used in adsorption, and MWCNT have become popular due to their ease and cheaper synthesis methods, unique structure, and excellent mechanical, electrical, and thermal properties. Therefore, this work aims to study the potential use of MWCNTs as an adsorbent for the removal of sulfate ions from injected water. The combined effect of the adsorbent dose, contact time, agitation, the rate and temperature of sulfate ion removal by water flooding with MWCNT.

Experimental

Adsorption

In the present study, batch adsorption experiments were conducted to obtain the optimal operating conditions for the removal of sulfate ions from simulated polluted water injected as the adsorbed solution. The preparation of the standard sulfate reserve solution: 800 mg were weighed and dissolved in pure deionized water contained in a beaker, the volume was adjusted to 1000 ml in a volumetric flask. A 250 ml solution with a known initial

concentration (800 mg/l) was taken from 500 ml Erlenmeyer flasks, and a known quantity of MWCNT as an adsorbent was added to the solutions and the mixture was stirred mechanically at different speeds using a heating plate equipped with batch water circulation to maintain the temperature at the desired degree (25°C to 80°C). The effect of dosage, contact time, temperature, and agitation of MWCNT on the adsorption rate of sulfate ions was determined. The samples were then centrifuged to collect the MWCNT to determine the absorbance of sulfate ions in each solution. After achieving adsorption equilibrium, the concentration of sulfate ions in the solution was determined and the amount of adsorption at equilibrium (q_e , mg/g) was calculated according to equation (1). [7]

$$ae = \frac{(C_0 - C_e)}{m} v \quad 2$$

Where C_0 represents the initial concentration of sulfate ions (mg/l); C_e represents the residual concentration of sulfate ions (mg/l); V represents the volume of sulfate ion solution (l); and m represents the dosage of MWCNT (g). In this work, the adsorption kinetics and adsorption isotherm data are linearly fitted using the Origin software and evaluated by the average of the correlation coefficient R^2 . The morphologies of the adsorbents were studied using a scanning electron microscope (SEM, FEI QUANTA 600 W) and high-resolution transmission electron microscopy (HRTEM, Jeol ARM 200 F) combined with energy dispersive spectroscopy. The elemental composition of the synthesized materials was determined using energy-dispersive X-ray spectroscopy.

Results and Discussion

Effect of Parameters on Sulfate Adsorption

Effect of Contact Time

The increase in reaction time, Figure 1(a), the sulfate ion removal rate and the unit adsorption capacity gradually increased and consequently reached a stable state. In the 120 minutes following the reaction, the sulfate removal rate increased significantly, as did the adsorption capacity. The reason for this phenomenon

may be due to the presence of numerous active and vacant adsorption sites on the surface of MWCNT in the initial stages of the reaction, which increased the adsorption efficiency. However, with the progression of the reaction and for contact times exceeding 180 minutes, there is repulsion between the sulfate molecules adsorbed on the surface of the MWCNT and those present in the solution, making the remaining sites on the surface difficult to occupy.

Effect of Temperature

The influence of temperature (from 20°C to 80°C) on adsorption is illustrated in Figure 1(b). The adsorption of sulfate strongly depends on temperature, indicating that the adsorption of SO₄²⁻ on MWCNT is more favorable at higher temperatures, reflecting an endothermic adsorption process, thereby allowing a more critical diffusion of sulfates into the pores of the MWCNT. In other words, an increase in temperature leads to a rapid diffusion of sulfate ions through the external boundary layer and the internal pores of the adsorbent particles due to a lower resistance offered by the viscous forces in the aqueous phase, and at higher temperatures.

Effect of the Adsorbent Dose

A given amount of adsorbent has the capacity to adsorb only a fixed amount of adsorbate species. Figure 1(c) shows the effect of MWCNT dosage on the adsorption of sulfate ions in the range of 0.01 g to 0.2 g. The results showed that the amount of sulfate adsorbed increased with the increase in the adsorbent dose from 0.01 g to 0.1 g. This behavior was attributed to the availability of more vacant surface sites and larger surfaces with the increase in dosage, which led to the increase in the sulfate ion removal rate. As a result, the performance improves with an adsorbent dose. Nevertheless, the adsorption rate remains constant above a dose of 0.1 g of carbon nanotubes in 250 ml of simulated sulfate water.

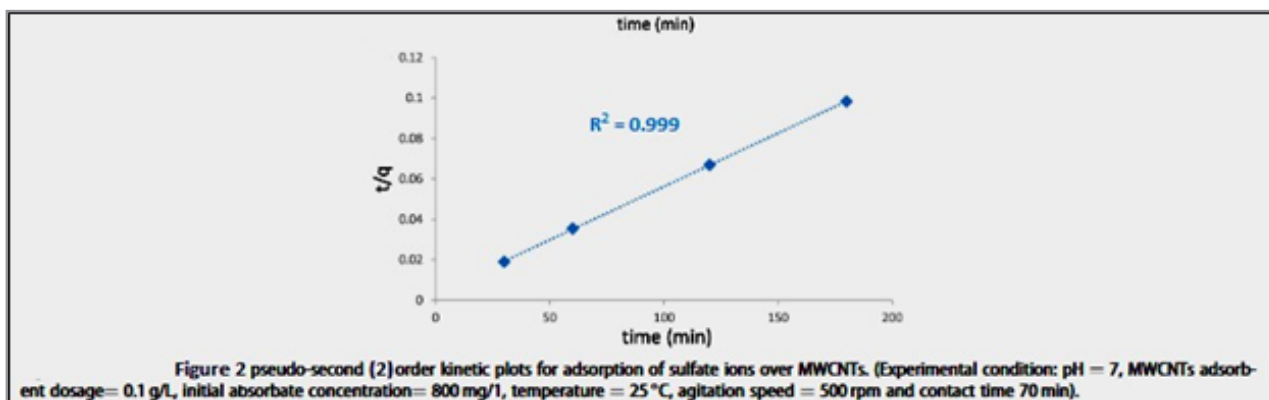
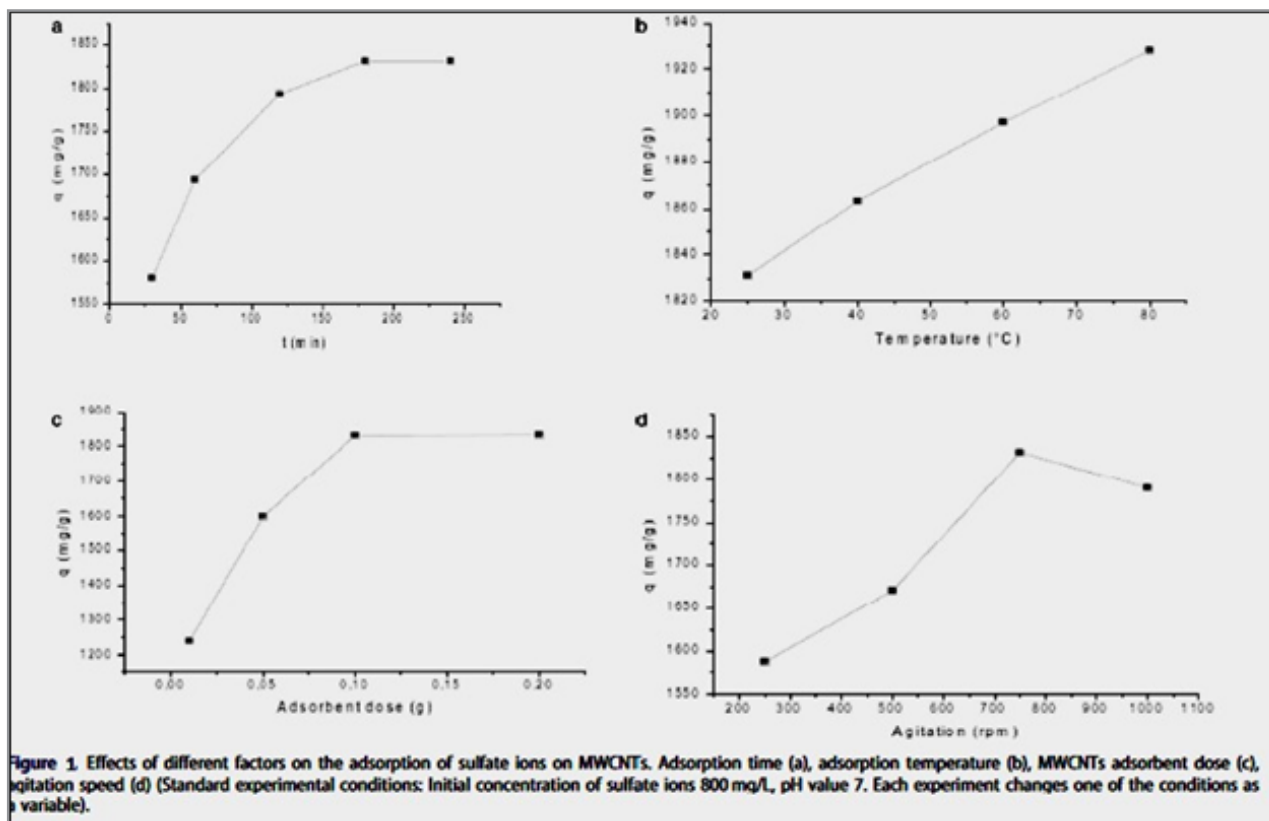
Effect of Stirring Speed

The dose of adsorbent, the initial sulfate ions, the concentration, the contact time, and the temperature were kept constant. The study was conducted by varying the speed from 250 to 1000 rpm using a magnetic stirrer. The effect is shown in Figure 1(d). As can be seen, the adsorption capacity was increased by increasing the stirring speed in the range of 250 to 750 rpm, which is related to the good diffusion of sulfate ions from the bulk liquid to the liquid boundary layer surrounding the MWCNT particle becoming higher due to an increase in turbulence and a decrease in the thickness of the liquid boundary layer. It can be seen in the figure that at 750 rpm, the adsorption capacity of the adsorbent is at its maximum. Beyond that, there is no further increase in the adsorption capacity of the adsorbent. This is probably due to the fact that at a very high agitation speed, the kinetic energy of the adsorbate molecule and the adsorbent particles has increased sufficiently for them to collide with each other rapidly, leading to the detachment of weakly bound adsorbate molecules [8].

Pseudo-second-order Kinetic Equation

Pseudo-second-order kinetic equations are mainly used to describe models including external liquid film diffusion, surface adsorption, and internal particle diffusion. The linearized form of equation t is expressed as follows: [9]

$$\frac{t}{qt} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad 3$$



Conclusion

In this study, MWCNTs were synthesized using the CDV method as a low-cost adsorbent for the adsorption of sulfate from an aqueous solution. The effect of operating parameters and the kinetics of the sulfate removal process was studied. The optimal point was found at a contact time of 240 minutes, a temperature of 74.21 °C, an adsorbent dose of 0.14447 g, and an agitation speed of 530 rpm with a predicted adsorption capacity of 1961.05 mg/g, and the adsorption process can be well described by the pseudo-second order equation. Overall, MWCNTs are an excellent sulfate- adsorbing material to use in water treatment to prevent the precipitation of barium sulfate, which ultimately leads to an increase in production.

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