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A comparative study to evaluate the performance of coated Fe$_3$O$_4$ nanoparticles for adsorption of asphaltene from crude oil in bench scale

Narjes Setoodeh, Parviz Darvishi, and Asghar Lashanizadegan

Chemical Engineering Department, School of Engineering, Yasouj University, Yasouj, Iran

ABSTRACT

The present study was conducted to evaluate the performance of magnetic Fe$_3$O$_4$ nanoparticles coated with polythiophene (PT), Mil-101 (Cr) (MOF), graphene oxide (GO), SiO$_2$, and chitosan for adsorption of asphaltene from crude oil in a bench scale setup. All nanoparticles were synthesized using coprecipitation method. The characteristics of nanoparticles were verified using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), and field emission scanning electron microscope (FESEM) analyses. The concentration of nanoparticles was kept constant at the optimum value of 10g L$^{-1}$. The amount of asphaltene adsorption was determined at different contact times of 0.5, 0.75, 1, 2, and 4 hours. The results showed that the adsorption increased with contact time and reached equilibrium after about 2 hours in both continuous and batch experiments. The amount of asphaltene adsorption was lower in continuous experiments compared to batch experiments. However, it was found that magnetic nanoparticles are applicable for inhibition of asphaltene precipitation under flow conditions. Furthermore, polythiophene coating on magnetic Fe$_3$O$_4$ nanoparticles had the highest capacity for asphaltene adsorption. Besides, by applying a magnetic field, the magnetic nanoparticles that adsorbed asphaltene can be separated from crude oil to prevent asphaltene aggregation and precipitation.

GRAPHICAL ABSTRACT

ARTICLE HISTORY

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KEYWORDS

Asphaltene adsorption; coating; continuous and batch tests; crude oil; Fe$_3$O$_4$ nanoparticle

1. Introduction

Crude oils are a continuum of many different hydrocarbon species. The proportions of the elements in crude oils vary over fairly narrow limits despite the wide variation found in properties of lightest crude oils to highly asphaltenic crudes.$^{[1]}$

Asphaltenes are the most polydisperse, heaviest, and polarizable fraction of crude oil. They are polynuclear molecules made up of condensed aromatic rings, aliphatic side chains, and various heteroatom groups.$^{[2]}$ Asphaltenes are soluble in aromatic solvents such as toluene but precipitate in excess amounts of aliphatic solvents such as $n$-pentane and $n$-heptane.

Asphaltene precipitation is the growth of primary particles from a solution due to supersaturation. Asphaltene precipitation consumes supersaturation until the system reaches an equilibrium asphaltene concentration. It is caused by a number of factors including changes in pressure, temperature, and composition. The two most prevalent causes of asphaltene precipitation in the reservoir are decreasing pressure and mixing of oil with injected solvent in enhanced oil recovery (EOR)
and improved oil recovery (IOR) processes. Drilling, acid stimulation, and hydraulic fracturing activities can also induce precipitation in the near-wellbore region and pipelines. Asphaltene precipitation from crude oil and its deposition during production can cause serious problems, as it can cause plugging of reservoir formation, wellbore, production facilities, and tubing.\(^3\)\(^4\)

Various technologies such as inhibitors, polymers, mechanical and bacterial methods, and nanoparticles have been used for inhibition or removal of asphaltene precipitation.\(^5\) Nanoparticles have been more attractive due to their special properties such as high surface to volume ratio, ability to remain suspended, and high adsorption capacity.\(^6\) Therefore, nanoparticles are able to keep asphaltene molecules suspended in the oil and prevent their aggregation and deposition.\(^7\)

Different metal nanoparticles such as Fe\(_3\)O\(_4\), Fe\(_2\)O\(_3\), TiO\(_2\), MgO, NiO, Co\(_3\)O\(_4\), CaO, and Al\(_2\)O\(_3\) have been used for asphaltene adsorption in the literature.\(^8\)\(^–\)\(^27\) All these studies have been performed using synthetic asphaltene-toluene solutions in batch scale and the nanoparticles used without any applied coating. Magnetic nanoparticles consist of iron, cobalt, and nickel. After adsorption of asphaltene, the nanoparticles can be separated from the sample by applying a magnetic field. Among all metal oxide magnetic nanoparticles, iron oxides have more applications. They are non-toxic, easily found in nature, synthesized in the laboratory, and have high coercive properties. If nanoparticles could be synthesized in sizes smaller than 25 nm, they would have superparamagnetic behavior.\(^28\) However, nanoparticles have a high tendency to aggregate with each other and precipitate.\(^29\) In addition, they are unstable over time. To overcome these defects, proper coatings are applied on the surface of nanoparticles.\(^30\)

Coatings have been used in different fields such as wastewater treatment, pharmaceutical industries, and biotechnology.\(^31\)\(^–\)\(^34\) The application of uncoated nanoparticles for asphaltene adsorption from crude oil had been investigated in other studies.\(^8\)\(^,\)\(^25\)\(^,\)\(^35\)\(^–\)\(^37\) In our previous studies, polythiophene (PT) and Metal-organic framework Mil-101 (Cr) (MOF) coatings were used for investigating the potential of magnetic Fe\(_3\)O\(_4\) nanoparticles coated with PT, MOF, GO, SiO\(_2\), and chitosan for adsorption of asphaltene from crude oil under the flow conditions of pipelines and compare their performance with the results obtained in batch scale studies.

2. Materials and methods

2.1. Chemicals

FeSO\(_4\).7H\(_2\)O, FeCl\(_3\).6H\(_2\)O, NH\(_3\) (25%), n-heptane and toluene were purchased from Merck Millipore Company, all in analytical grade. Sarvestan crude oil with the properties given in Table 1 was selected from one of oil fields in southern Iran. The synthesized polythiophene, MOF, graphene oxide, silica, and chitosan were used to coat the nanoparticles. All other chemicals were also of analytical grade and purchased from Merck Millipore Company.

2.2. Preparation of nanoparticles

The suspension of magnetic Fe\(_3\)O\(_4\) nanoparticles was prepared by co-precipitation of FeCl\(_3\).6H\(_2\)O and FeSO\(_4\).7H\(_2\)O in the presence of ammonia solution. The molar ratio of FeCl\(_3\).6H\(_2\)O and FeSO\(_4\).7H\(_2\)O was 2:1. The mixture was added to deionized water and stirred for 1 hour at 353 K with a hot plate magnetic stirrer (M TOPS HSD330, Republic of Korea, Yangju) to dissolve the iron salts in water. To raise the pH of the mixture, the 25 wt.% ammonia solution was added dropwise within one hour under vigorous stirring conditions at 353 K. The formation of magnetic Fe\(_3\)O\(_4\) nanoparticles could be verified using the magnet underneath the vial. Afterward, the collected nanoparticles were washed several times with deionized water. The material collected on filter paper was dried in the oven (Binder FD 115, Germany, Tuttinglen) for 24 hours. Finally, the Fe\(_3\)O\(_4\) nanoparticles were kept at room temperature. The preparation of coated nanoparticles with different coatings was similar to the synthesis of uncoated nanoparticles. At first,

<table>
<thead>
<tr>
<th>Table 1. Properties of the crude oil used in this study.</th>
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<tbody>
<tr>
<td>Density (g cm(^{-3}))</td>
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<tr>
<td>Saturates (wt.%)</td>
</tr>
<tr>
<td>Aromatics (wt.%)</td>
</tr>
<tr>
<td>Resins (wt.%)</td>
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<tr>
<td>Asphaltenes (wt.%)</td>
</tr>
</tbody>
</table>
the specific amounts of coating and deionized water were sonicated for 30 minutes. Then, the mixture was added to the aqueous suspension of iron salts. The further steps were similar to the co-precipitation method of uncoated nanoparticles.[55]

2.3. Characterization of nanoparticles

The X-ray diffraction (XRD) profiles were obtained from synthesized samples using X-ray diffractometer (Bruker D8 Advance, USA, Madison, WI) to determine the crystalline structure. FESEM (MIRA3 TESCAN, Czech Republic, Brno-Kohoutovice) was applied to obtain FESEM bright field images and determine the morphologies and particle size of nanoparticles. FT-IR of samples was conducted using FT-IR spectroscopy (Perkin-Elmer RXI, USA, Waltham, MA) in the frequency interval of 4000 − 400 cm$^{-1}$ to study the functionalization of magnetic nanoparticles with different coatings. The specific surface area ($S_{\text{BET}}$) of nanoparticles was determined by applying Brunauer-Emmett-Teller (BET) method.[56,57] This test was performed using the accelerated surface area and porosimeter (ASAP 2020 Plus Physisorption, USA, Norcross, GA).

2.4. Experimental setup

To mimic the simulated conditions of asphaltene precipitation in pipelines of petroleum industry, a homemade apparatus (Figure 1) was used to investigate the potential of asphaltene adsorption onto Fe$_3$O$_4$ magnetic nanoparticles with different coatings. The setup consisted of a pipeline (ID = 1/2" galvanized iron), a gear pump (Alvand CF: 3, Iran, Tehran), an electromotor (Stream Y3 90S -4, China, Tianjin), inlet and output ball valves, and nine strong disk neodymium magnets (Grade N42, 1280-1340 mT, D10*2). An electronic board was used to control the operation of electromotor and pump. The inlet and output valves directed the mixture into the pipeline, discharged it from the pipeline, and took the samples. Nine neodymium magnets were placed on three magnet belts. The belts were movable and could be placed anywhere along the pipeline to apply the magnetic field for separation of nanoparticles.

2.5. Batch tests for adsorption of asphaltene from crude oil

Batch adsorption experiments were carried out with initial nanoparticle concentration of 10g L$^{-1}$ to investigate the capacity of coated nanoparticles for adsorption of asphaltene from crude oil. The optimum nanoparticle concentration of 10g L$^{-1}$ was obtained from our recent studies that were carried out in asphaltene-toluene solution models.[38,39] The mixture of crude oil and nanoparticle was mixed at a speed of 250 rpm in a shaking water bath (Daian Wisebath WSB-18, Republic of Korea, Seongbuk-gu) at constant temperature of 298 K. In the case of each coated nanoparticle, the tests were carried out for contact times of 0.5, 0.75, 1, 2, and 4 hours. Then, the mixture was poured into the tube, and the neodymium magnets were placed around the tube. The nanoparticles, which had adsorbed asphaltenes from crude oil, would stick to the wall of the tube through the magnetic field applied by these magnets. The supernatant was discharged from the tube through the outlet valve at the bottom of tube. This mixture was analyzed using IP-143 procedure.[58] in soxhlet apparatus to determine the amount of remaining asphaltene in the supernatant. The amount of adsorbed asphaltene on nanoparticles (mg m$^{-2}$) was calculated using the amounts of asphaltene in the initial crude oil and supernatant:

$$q_t = \frac{(C_0 - C_f)}{AM}$$  \[1\]

Where $A$ is the surface area per unit mass of nanoparticles (m$^2$g$^{-1}$), $M$ is the ratio of nanoparticle mass to solution volume (g L$^{-1}$), $C_0$ is the initial asphaltene concentration (mg L$^{-1}$), and $C_f$ is the asphaltene concentration (mg L$^{-1}$) in the solution at time $t$. For each coating, five $q_t$ values would be calculated for contact time of 0.5, 0.75, 1, 2, and 4 hours in batch tests.

2.5. Bench scale tests for adsorption of asphaltene from crude oil

The initial concentration of nanoparticles in the crude oil was 10g L$^{-1}$. The experiments were performed with uncoated and coated Fe$_3$O$_4$ nanoparticles of PT, MOF, GO, SiO$_2$ and chitosan. For each coating, the circulation time of mixture in the pipeline was considered as 0.5, 0.75, 1, 2, and 4 hours. The mixture of crude oil and nanoparticle was injected into the pipeline and circulated by turning on the electromotor. The flow rate of mixture was set at 40 L min$^{-1}$. After circulation of the mixture for a specified time, the magnets were placed on the pipe just before the output valve. This caused the nanoparticles containing asphaltene stick on the inner wall of the pipeline and remove from crude oil. Then, the remaining oil was discharged from the pipeline through the outlet valve. This oil was analyzed using the IP-143 procedure in the soxhlet apparatus. The percentage of asphaltene in the crude oil showed the amount of unadsorbed asphaltenes on the surface of nanoparticles. The amount of adsorbed asphaltene could be calculated from the difference between the initial and final values of asphaltene content in crude oil.
3. Results and discussion

3.1. Characterization of nanoparticles

The prepared uncoated and coated Fe₃O₄ nanoparticles were characterized using XRD, FESEM, FT-IR, and BET surface area tests. The results are presented in the following subsections.

3.1.1. X-ray diffraction

The XRD pattern of synthesized uncoated and coated Fe₃O₄ nanoparticles is shown in Figure 2. The diffraction peaks correspond to reflection planes at 220, 311, 400, 422, 511, 440, 620, and 622 are the same for uncoated and coated nanoparticles. This demonstrates that coated nanoparticles were successfully prepared and the structure of Fe₃O₄ nanoparticles was not changed by applying the coatings. The results also indicate that the structure of nanoparticles is crystalline. The mean crystalline diameter of nanoparticles is calculated from Debye-Scherrer equation:

\[ D = \frac{k\lambda}{\beta \cos \theta} \]  

Where \( \theta = 35.73^\circ \), \( k = 0.9 \), and \( \lambda = 1.542 \) Å. The mean diameters of uncoated Fe₃O₄, PT-Fe₃O₄, MOF-Fe₃O₄, GO-Fe₃O₄, SiO₂-Fe₃O₄, and chitosan-Fe₃O₄ nanoparticles were 10.9, 12.8, 11.5, 16.6, 10.4, and 18.5 nm, respectively.

3.1.2. The size and morphology of nanoparticles

FESEM images of uncoated and coated nanoparticles are presented in Figure 3 to show the morphology and particle size of synthesized nanoparticles. The shape of particles is spherical, and their sizes are in the range of 10 – 23 nm. So, they exhibit super magnetic properties (<25 nm). The coated nanoparticles showed more dispersion properties. The variation of diameter between uncoated and coated nanoparticles is low that is indicative of the thin coating layer on Fe₃O₄ nanoparticles.

3.1.3. Fourier transform infrared spectroscopy

Figure 4 shows the FT-IR spectra of PT, MOF, GO, SiO₂, and chitosan coatings. In Figure 4a for PT, the peaks at 543.43, 603.68, 624.86, and 665.97 cm⁻¹ signified the presence of C-S-C ring and C-S functional groups. The stretching vibration peaks at 1707.92 and 1401 cm⁻¹ attributed to asymmetric and symmetric C=C bands of thiophene ring, respectively. The C-H bending and C-H in plane vibrations were characterized with the peaks at 1088.11 and 1159.36 cm⁻¹, respectively. In Figure 4b for MOF, the peaks at 1385.11, 1405.68, and 1507.96 cm⁻¹ are assigned to the vibration of O-C-O functional group that is indicative of dicarboxylate in MOF. In addition, the stretching vibration peaks at 1624.27 and 3412.52 cm⁻¹ correspond to the presence of water molecules in MOF. The absorption peak at 1541.28 cm⁻¹ presents the aromatic ring in the MOF structure. As shown in Figure 4c for GO, the peak at 1420.15 cm⁻¹ can be attributed to C=O (carboxyl) bond. The absorption bands at 1116.56 and 1241.95 cm⁻¹ are ascribed to alkoxy C-O and epoxy C-O stretching vibrations, respectively. The peak located at 3423.89 cm⁻¹ is characteristic for the framework of O-H stretching vibration in the C-OH groups and water. The peak at 1618.01 cm⁻¹ may be attributed to the presence of C=C (aromatics) in GO. In Figure 4d for

![Figure 2. XRD patterns of (a) Fe₃O₄ (b) PT-Fe₃O₄ (c) MOF-Fe₃O₄ (d) GO-Fe₃O₄ (e) SiO₂-Fe₃O₄ (f) chitosan-Fe₃O₄ nanoparticles.](image-url)
SiO₂, three peaks at 473.68, 808.68, and 1102.30 cm⁻¹ indicate the vibrations of Si-O bending, symmetric stretching, and Si-O-Si asymmetric stretching band, respectively. The broad peak at 3425.95 cm⁻¹ belonged to O-H group, which is related to water molecule in SiO₂.

Figure 4e shows the FT-IR spectrum for chitosan. A broad peak at 3462.11 cm⁻¹ represents the vibrations of N-H₂ and O-H functional groups. A peak at 1609.45 cm⁻¹ can be ascribed to the carbonyl group C=O. The stretching vibrations of C-H and C-O are characterized with the peaks at 1159.05 and 1094.08 cm⁻¹. The peak located at 894.97 cm⁻¹ is attributed to the saccharide structure of chitosan.

The FT-IR spectra of Fe₃O₄, PT-Fe₃O₄, MOF-Fe₃O₄, GO-Fe₃O₄, SiO₂-Fe₃O₄, and chitosan-Fe₃O₄ magnetic nanoparticles are shown in Figure 5. The peaks at 577.83 and 1624.87 cm⁻¹ in Figure 5a are attributed to stretching vibrations of Fe-O and FeOO', respectively. The figure shows that the synthesis procedure of Fe₃O₄ magnetic nanoparticles was precise and without fault. The spectra observed between 550 and 600 cm⁻¹ in Figures 5b–f demonstrate that the structure of Fe₃O₄ would not change after coating. The hydroxyl functional group due to water absorption by nanoparticles was observed at 3434.57 and 3427.40 cm⁻¹ in Figure 5a and 5b, respectively. The peak at 2922.45 cm⁻¹ in Figure 5b
corresponds to C-H stretching vibration. The absorption band at 1622.80 cm\(^{-1}\) is assigned for C=C stretching vibrations of the thiophene ring. In the C-H plane, the aromatic bending vibrations of thiophene ring are presented by the very weak peak at 1088 cm\(^{-1}\). Because of the coating of Fe\(_3\)O\(_4\) with polythiophene, the peaks related to C-S and C-S-C would not be observed in Figure 5a. In the case of MOF-Fe\(_3\)O\(_4\) in Figure 5c, the stretching vibrations located at 1534.26, 1638.41, and 3416.21 cm\(^{-1}\) are assigned for aromatic rings, O-H, and N-H bands, respectively.

In Figure 5d for GO-Fe\(_3\)O\(_4\) nanoparticles, the peaks at 1104.89, 3415.70, and 1626.63 correspond to C-O, O-H, and C=C vibrations of GO coating, respectively. Figure 5e for SiO\(_2\)-Fe\(_3\)O\(_4\) nanoparticles shows the typical characteristic stretching vibrations of Si-O, Si-O-Si, and O-H for SiO\(_2\) coating on Fe\(_3\)O\(_4\) nanoparticles at about 776.75, 1026.89, and 3438.23 cm\(^{-1}\), respectively. Finally, in Figure 5f for chitosan, the peaks at 3426.51, 1579.15, 1148.19, and 1057.84 cm\(^{-1}\) are assigned for N-H\(_2\), C=O, C-H, and C-O vibrations, respectively.

### 3.1.4. Estimating the surface area of nanoparticles

The BET surface areas for Fe\(_3\)O\(_4\), PT-Fe\(_3\)O\(_4\), MOF-Fe\(_3\)O\(_4\), GO-Fe\(_3\)O\(_4\), SiO\(_2\)-Fe\(_3\)O\(_4\), and chitosan-Fe\(_3\)O\(_4\) magnetic nanoparticles were calculated to be 71.64, 73.63, 74.43, 69.46, 74.63, and 70.25 m\(^2\)g\(^{-1}\), respectively. The synthesized nanoparticles exhibit large amount of active surface functionality per unit mass of nanoparticle that promotes the adsorption capacity of particle.

### 3.2. Adsorption of asphaltene from crude oil in batch tests

Figures 6–11 show the amounts of asphaltene adsorption onto Fe\(_3\)O\(_4\), PT-Fe\(_3\)O\(_4\), MOF-Fe\(_3\)O\(_4\), GO-Fe\(_3\)O\(_4\), SiO\(_2\)-Fe\(_3\)O\(_4\), and chitosan-Fe\(_3\)O\(_4\) magnetic nanoparticles, respectively. The adsorption of asphaltene from crude oil was performed in batch experiments for contact times of 0.5, 0.75, 1, 2, and 4 hours. The results show that the amount of adsorption increases with contact time. The mixture reached the equilibrium conditions after about 2 hours, and then the amount of asphaltene adsorption stays constant. The trend of asphaltene adsorption from crude oil with time is similar to that of adsorption from synthetic asphaltene-toluene solutions in our previous works\(^{[38,39]}\). As the amount of initial asphaltene
in crude oil (1.38 wt.%) is higher than asphaltene-toluene solutions, the $q_t$ values would be certainly higher in tests of adsorption from crude oil.

### 3.3. Adsorption of asphaltene from crude oil in continuous tests

Figures 6–11 also show the amounts of asphaltene adsorption onto Fe$_3$O$_4$, PT-Fe$_3$O$_4$, MOF-Fe$_3$O$_4$, GO-Fe$_3$O$_4$, SiO$_2$-Fe$_3$O$_4$, and chitosan-Fe$_3$O$_4$ magnetic nanoparticles in continuous experiments. The residence time for the mixture of crude oil and nanoparticles in the tests was 0.5, 0.75, 1, 2, and 4 hours, similar to contact times considered for batch experiments. The same trends as batch tests were achieved for all nanoparticles and coatings. The amount of asphaltene adsorption in continuous tests was less than batch experiments. However, the results of continuous experiments were satisfactory and did not make much deviation from batch results. In the first part of curves in Figures 6–11, the difference between the batch and continuous performance data is low, and with more time, the difference becomes greater. This can be attributed to the fact that initially, the active sites of nanoparticles are empty and asphaltenes can interact with nanoparticle surfaces and adsorb on active sites in both cases. After occupying the underlying layers, due to the low shear force between the surrounding fluid and nanoparticles in batch tests, asphaltenes can adsorb on the next layers of nanoparticle surfaces. However, the higher fluid velocity in continuous tests prevents asphaltenes to adsorb on the outer layers of nanoparticle surfaces. This leads to a higher amount of asphaltene adsorption in batch
GO-Fe3O4, SiO2-Fe3O4, and chitosan-Fe3O4 magnetic and chitosan-Fe3O4 magnetic nanoparticles, respectively. Each nanoparticles versus contact time are plotted in Figures 6–11 The variations in the amount of adsorbed asphaltenes onto asphaltene precipitation in the conditions of crude oil flow experiments. The continuous experiments were performed to investigate the potential of coated nanoparticles for inhibition of asphaltene precipitation in the conditions of crude oil flow in pipelines of petroleum industry. The contact and residence times of crude oil and nanoparticles were considered 0.5, 0.75, 1, 2, and 4 hours in both batch and continuous cases. After 2 hours, the asphaltene adsorption reached its equilibrium.

3.4. Adsorption kinetics

The variations in the amount of adsorbed asphaltenes onto nanoparticles versus contact time are plotted in Figures 6–11 for Fe3O4, PT-Fe3O4, MOF-Fe3O4, GO-Fe3O4, SiO2-Fe3O4, and chitosan-Fe3O4 magnetic nanoparticles, respectively. Asphaltene adsorption was investigated with initial nanoparticles concentration of 10g L−1 at 298 K for 4 hours. The adsorbed asphaltenes reached to equilibrium after 2 hours in accordance with other reported works.[6,10,13–15,27] The experimental data for Fe3O4, PT-Fe3O4, MOF-Fe3O4, GO-Fe3O4, SiO2-Fe3O4, and chitosan-Fe3O4 magnetic nanoparticles in batch and continuous tests were modeled according to Eqs. (3) and (4) using the pseudo-first-order Lagergren[59] and the pseudo-second-order Lagergren[60] models:

\[ \frac{dq_t}{dt} = k_1(q_e - q_t) \]  

\[ \frac{1}{q_t} - \frac{1}{q_e} = \frac{k_1}{q_e^2} t \]  

The initial conditions are \( q_t = 0 \) at \( t = 0 \) and \( q_t = q_e \) at \( t = t_e \). Where \( q_t \) and \( q_e \) are the amount of asphaltene adsorbed on nanoparticles (mg m⁻²) at time \( t \) (h) and equilibrium, respectively. The rate of adsorption is proportional to saturation concentration based on the pseudo-first-order Lagergren model. However, chemical adsorption is the controlling step of adsorption process in the pseudo-second-order model. Integrating Eqs. (3) and (4) gives the following equations:

\[ \ln(q_e - q_t) = \ln(q_e - q_t) - k_1 t \]  

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \]  

\( k_1 \) (h⁻¹) and \( k_2 \) (mg m⁻²h⁻¹) and \( q_e \) are determined from the slopes and intercepts of the lines \( \ln(q_e - q_t) \) and \( t/q_t \) versus \( t \), respectively, which are given in Table 2. The calculated results showed that the pseudo-first-order and pseudo-second-order Lagergren models were in good agreement with experimental data. Also, \( R^2 \) values demonstrate that the pseudo-second-order Lagergren model matches better with experimental data. It indicates that chemical adsorption is the dominant mechanism in asphaltene adsorption onto the nanoparticles.

In continuous tests, the residence time of particles was used in Equations (5) and (6).

4. Conclusion

In this study, Fe3O4 magnetic nanoparticle was synthesized using co-precipitation method. It was coated with PT, MOF, GO, SiO2, and chitosan coatings as modifiers to enhance its properties for asphaltene adsorption. The synthesized nanoparticles were verified using the XRD, FESEM, FT-IR, and BET surface area tests. The experiments of asphaltene adsorption from crude oil were conducted in a continuous setup for the first time, and the results were compared with batch experiments. The continuous experiments were performed to investigate the potential of coated nanoparticles for inhibition of asphaltene precipitation in the conditions of crude oil flow in pipelines of petroleum industry. The contact and residence times of crude oil and nanoparticles were considered 0.5, 0.75, 1, 2, and 4 hours in both batch and continuous cases. After 2 hours, the asphaltene adsorption reached its equilibrium.
The amount of asphaltene adsorption increased with time and was lower in continuous tests compared to batch tests. The results of adsorption kinetics showed that pseudo-second-order Lagergren model was in better agreement with experimental data than the pseudo-first-order Lagergren model. Based on the results obtained, polythiophene coating on magnetic Fe₃O₄ nanoparticles had the highest capacity for asphaltene adsorption, and MOF-Fe₃O₄, GO-Fe₃O₄, chitosan-Fe₃O₄, uncoated Fe₃O₄ and SiO₂-Fe₃O₄ were ranked afterward. The promising results of this study show the application of magnetic nanoparticles for inhibition of asphaltene precipitation from crude oil in pipelines of petroleum industry and using a magnetic field for separation of nanoparticles from crude oil. Applying an appropriate coating on the surface of nanoparticles would establish a baseline to enhance the inhibition of asphaltene precipitation.

**Nomenclature**

- \( A \): Surface area per unit mass of the nanoparticles (m²g⁻¹)
- \( C_0 \): Asphaltene initial concentration in solution (mg L⁻¹)
- \( C_t \): Asphaltene concentration in the solution at the time \( t \) (mg L⁻¹)
- \( D \): Crystalline size of nanoparticles (nm)
- \( K \): Scherrer constant
- \( k_1 \): First-order adsorption rate constant (h⁻¹)
- \( k_2 \): Second-order adsorption rate constant (mg m⁻² h⁻¹)
- \( M \): Ratio of mass of nanoparticles to the solution volume (g L⁻¹)
- \( q_e \): Amount of asphaltene adsorbed on nanoparticles at equilibrium (mg m⁻²)
- \( q_t \): Amount of asphaltenes adsorbed on nanoparticles, (mg m⁻²)
- \( t \): Time (h)

**Abbreviations**

- BET: Brunauer-Emmett-Teller
- EOR: Enhanced oil recovery
- FESEM: Field emission scanning electron microscope
- FT-IR: Fourier transform infrared spectroscopy
- GO: Graphene oxide
- IOR: Improved oil recovery
- MOF: Metal organic framework
- PT: Polythiophene
- XRD: X-ray diffraction

**Greek letters**

- \( \beta \): Peak width at half of the maximum height of the peak
- \( \theta \): Diffraction angle
- \( \lambda \): X-Ray wavelength

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**References**


