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Relationship between Asphaltene Adsorption on the Surface of Nanoparticles and Asphaltene Precipitation Inhibition During Real Crude Oil Natural Depletion Tests

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Highlights

- Using nickel-zeolite oxide nanoparticles for adsorbing asphaltene on their surface;
- Using nickel-zeolite oxide nanoparticles for solving asphaltene precipitation problems;
- Obtaining the relationship between asphaltene adsorption on the surface of nickel-zeolite oxide nanoparticles and asphaltene precipitation inhibition;
- Surveying Langmuir and Freundlich isotherm models in the presence of nickel-zeolite oxide nanoparticles.

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Abstract

Using nanoparticles for adsorbing asphaltene is an efficient method for upgrading actual oil samples compared to other expensive mechanical treatments or even solvents, such as n-pentane and n-heptane, and surfactants. This study uses nickel-zeolite oxide nanoparticles for asphaltene adsorption and solving asphaltene precipitation problems. Although nickel-zeolite oxide nanoparticles have been used in previous studies as an asphaltene adsorbent, observing the relationship between asphaltene adsorption on their surface and asphaltene precipitation in the presence of nanoparticles during the actual process is not covered. For addressing this relation, we performed a series of experiments included Fourier-transform infrared spectroscopy (FTIR), CO₂-oil interfacial tension tests, Langmuir and Freundlich isotherm models, and natural depletion tests in the presence of nickel-zeolite oxide nanoparticles. The Langmuir model better fitted the adsorption data than the Freundlich model, which shows that the adsorption occurs on a homogeneous surface with monolayer coverage. Based on the CO₂-oil interfacial tension results, there are two different slope forms in interfacial tension readings as pressure increases from 150 to 1650 psi. Due to asphaltene aggregation, the second slope (900–1650 psi) is slower than the first one (150–900 psi). Three pressures of 1350, 1500, and 1650 psi and nickel-zeolite oxide nanoparticles at a concentration of 30 ppm were selected for the natural depletion tests, and the basis of selection was high-efficiency adsorption at these points. As pressure decreased from 1650 to 1350 psi, asphaltene precipitation changed from 8.25 to 10.52 wt % in the base case, and it varied from 5.17 to 7.54 wt % in the presence of nickelzeolite oxide at a concentration of 30 ppm. Accordingly, nickel-zeolite oxide nanoparticles adsorbed asphaltene on their surface correctly, and the amount of asphaltene precipitation decreased in the presence of nickel-zeolite oxide nanoparticles.

Keywords: Adsorption, Asphaltene, CO₂-oil interfacial tension tests, Isotherm models, Nickel-zeolite oxide nanoparticles.

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1. Introduction

One of the main problems in the oil industry, especially during production, which occurs during changes in composition, pressure, and temperature, is related to the precipitation of asphaltene in crude oil (Kralova et al., 2011; Östlund et al., 2003). Asphaltenes are insoluble in paraffins such as pentane and heptane and soluble in aromatics such as toluene (Yarranton et al., 2000; Hemmati-Sarapardeh et al., 2013; Rudyk et al., 2014). Tubing and oil transferring through pipes face serious problems such as plugging due to the precipitation of this solid phase (Thawer et al., 2004; Valter et al., 2001). Surfactants and solvents were known for solving asphaltene precipitation problems using mechanical treatments, while these methods are too expensive. Thus, nanoparticles have recently been used for oil upgrading and solving asphaltene precipitation problems (Karimi et al., 2012; Trbovich et al., 1991; Naghdi et al., 2015; Franco et al., 2013; Hashemi et al., 2013; Nassar et al., 2011; Olvera et al., 2014; Hashemi et al., 2013). The presence of pyridinic (C_5H_5N), carboxylic (C(=O)OH), thiophenic (C_4H_4S), and pyrrolic (C_4H_5N) functional groups in asphaltene is known as the main reason for the adsorption of asphaltene on solid surfaces, and non-metallic and metallic surfaces are used for asphaltene adsorption (Pernyeszi et al., 1988; Bantignies et al., 1988; Pernyeszi et al., 2001; Balabin et al., 2011; Nassar et al., 2010; Nassar et al., 2011; Franco et al., 2013; Alboudwarej et al., 2005).

Zeolites are a reliable adsorbent of asphaltene, and hydrated aluminosilicate (Al₂SiO₅) is the most critical part of zeolites. Moreover, due to positive characteristics such as their stability, zeolites have many applications as catalysts (Kosinov et al., 2018; He et al., 2018; Fakeeha et al., 2013). On the other hand, nickel oxide (NiO) has unique chemical and physical characteristics in adsorption processes, and it is available and reasonable in terms of cost (Li, 2018; Kazemzadeh et al., 2015; Lei et al., 2020; Nassar et al., 2011; Hosseinpour et al., 2014; Hosseinpour et al., 2013; Kashefi et al., 2018). Accordingly, this study used nickel-zeolite oxide nanoparticles to survey the relationship between asphaltene adsorption on the surface of nanoparticles and asphaltene precipitation inhibition. Although nickel-zeolite oxide was used in previous studies for asphaltene adsorption, observing adsorption behavior during CO₂-oil interfacial tension (IFT) tests and matching the results with actual natural depletion tests have not been covered to the best of our knowledge. Thus, this study used natural depletion as the primary source of making asphaltene precipitation by changing pressures for obtaining this relationship, and the main points in natural depletion tests were selected based on the interfacial tension tests of CO2 and oil. Two tests of CO2-oil interfacial tension and ultraviolet-visible spectroscopy (UV–Vis) were used for describing asphaltene adsorption on the surface of nanoparticles, and two different isotherm models, namely Langmuir and Freundlich isotherms, were surveyed entirely in the presence of nickel-zeolite oxide nanoparticles.

2. Materials and methodology

2.1. Laboratory equipment

Crude oil was collected from one of the oil reservoirs in Iran with an oil density of 0.864 g/cm³ and viscosity of 9.9 cP at 40 °C. Table 1 lists the results of the saturate-aromatic-resin-asphaltene (SARA) test and crude oil specifications.

The specifications of the crude oil and SARA test.					
Components	Reservoir oil (Mol %)	Components	Reservoir oil (Mol %)		
H ₂ S	0.01	iC4	1.23		
N_2	0.08	nC4	5.77		
CO ₂	0.56	iC5	3.70		
C ₁	3.44	nC5	5.30		
C2	1.88	C ₆	5.92		
Сз	3.45	C7+	68.67		

Table 1

Note: Other crude oil properties: GOR: 237.00 SCF/STB, Molecular weight of residual oil: 232.00, Saturate: 50.20%, Aromatic: 30.10%, Resin: 4.70%, and Asphaltene: 15.00%.

The standard IP143 method (ASTM D6560-17, 2017) was used to extract asphaltenes, and normal heptane 99%, toluene 99%, ethanol 99%, and Watson paper grade 42 with a thickness of 0.22 micrometer were purchased from Merck Company.

2.2. Methodology

a. Synthesis of ZSM-5 and NiO/ZSM-5

The below procedures are used to synthesize ZSM-5 (Sedighi et al., 2018):

- 1- Dissolving NaOH (1.4 g) in bio-cadaverine (8 mL) and distilled water (65 mL);
- 2- Adding silicic acid (13.1 g) and stirring the product;
- 3- Aging the mixture at 100 °C for 10 h;
- 4- Putting the mixture at 180 °C for 40 h;
- 5- Filtering, drying, and calcinating the obtained mixture.

For synthesizing NiO/ZSM-5, the steps are as follows:

- 1- Adding Ni (NO₃)2.6H₂O to the prepaid ZSM-5:
- 2- Putting the mixture at 100 °C for 12 h;
- 3- Putting the obtained sample in a muffle at 550 °C for 5 h.

For preparing nanofluid, specific amounts of nickel-zeolite oxide nanoparticles (10, 20, or 30 ppm) were stirred in solution and sonicated for 30 min, where nickel-zeolite oxide nanoparticles remained stable in the solution. Probe ultrasonic (24 kHz and 400 W) set-up was used for sonication and braking nanoparticle agglomerates (Sedighi et al., 2018).

b. Interfacial tension test

Figure 1 shows a schematic of the HPHT interfacial tension apparatus used to measure the interfacial tension between CO₂ and oil at different pressures. All the experiments were performed at 40 °C.



A schematic of the HPHT interfacial tension apparatus.

As shown in Figure 1, the main parts for obtaining CO_2 -oil interfacial tension are the CO_2 cylinder, primary cell, capillary tube, oil pump, heating jacket, light source, temperature sensors, digital camera, and acquisition system with interfacial tension calculation software (Kashefi et al., 2018). The main procedure for measuring the interfacial tension are summarized below:

- 1. Flushing the high-pressure cell with N₂ gas;
- 2. Applying CO₂ gas to the primary cell at a specific pressure and temperature;
- 3. Pumping the oil (or oil with nanoparticles) and capturing oil droplets with a digital camera at equilibrium;
- 4. Calculating the interfacial tension with software (Kashefi et al., 2018).

c. Natural depletion tests

Figure 2 shows the set-up for measuring asphaltene precipitation during natural depletion, and the basis of measuring was filtration methods. The main parts are the hydraulic pump, recombination cell, PVT cell, metal filter for extracting asphaltene, sampling cell, CO₂ cylinder, needle valves, pressure gauges, and an oven for setting temperature. Briefly, the below procedures were used to perform the natural depletion tests:

- 1. Transferring the crude oil sample to the primary cell at a specific pressure;
- 2. Allowing the system to remain for 24 h at a specific pressure and temperature;
- 3. Passing the sample through a 0.22 µm metal filter;
- 4. Calculating the asphaltene content with the IP143 method;
- 5. Obtaining asphaltene precipitation by subtracting the previous step from the initial asphaltene content.



The set-up for performing the natural depletion tests.

d. Batch adsorption experiment

Surveying the adsorption of asphaltene on the surface of nickel–zeolite oxide nanoparticles was performed with batch adsorption tests in the presence of toluene solution. The below procedure was used in this work:

- 1. Adding specific amounts of nickel-zeolite oxide nanoparticles;
- 2. Shaking solution at 200 rpm for 4 h (Kashefi et al., 2018);
- 3. Using centrifuge at 3000 ppm for 30 min to separate asphaltene adsorbed on the surface of nickel-zeolite oxide nanoparticles.
- 4. Measuring remaining asphaltene concentration at a wavelength of 410 nm;
- 5. Calculating the amount of adsorbed asphaltene on the surface of nanoparticles by Equation (1).

$$Q = \frac{(C_o - C_e)}{m} * V \tag{1}$$

where C_o is the asphaltene initial concentration in the toluene solution (mg/L), C_e indicates the concentration of asphaltene in the equilibrium conditions (mg/L), V denotes the volume of the solution (L), and m represents the mass of the nickel–zeolite oxide nanoparticles (mg).

3. Results and discussions

Figure 3a and 3b shows the asphaltene characterization with the Fourier transform infrared (FTIR) tests and scanning electron microscopy (SEM) image of nickel–zeolite oxide nanoparticles, respectively. There are six different peaks in the FTIR spectrum, indicating O–H and N–H, C–H in CH₂ and CH₃, C–H in aldehyde hydrogen, C=O, C=C, and C–H in CH₃, respectively (Derrick et al., 1999; Mayo et

al., 2003; Stuart et al., 2005; Silverstein et al., 2005; Field et al., 2008). The presence of heteroatoms such as N and O in asphaltene structure is a very efficient parameter in asphaltene adsorption on the surface of nanoparticles, and the main reason is that the heteroatom is sufficiently exposed to the active sites of the adsorbent (Gonzalez et al., 2007; Lopez-Linares et al., 2006). Nickel–zeolite oxide nanoparticles have a rough and riveted surface, and the catalyst has been adequately synthesized with an approximate size of 15 nm. As shown in Figure 4b, nickel particles are observable on the zeolite surface.



Figure 3

(a) The asphaltene FTIR and (b) the SEM image of the nickel-zeolite oxide nanoparticle.

3.1. Asphaltene adsorption in the presence of nickel-zeolite oxide nanoparticles

Langmuir and Freundlich's isotherm models used in this study are expressed in Equations (2) and (3) (Ahmadi et al., 2018; Mansouri et al., 2021).

$$Q_e = Q_m \frac{K_L C_e}{1 + K_L C_e}$$
(2)

$$Q_e = K_F C_e^{1/n}$$
(3)

Equations (4) and (5) are expressed in a linear form:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{Ce}{Q_m} \tag{4}$$

$$Ln\left(Q_{e}\right) = Ln\left(K_{F}\right) + \frac{1}{n}Ln\left(C_{e}\right)$$

$$\tag{5}$$

where Q_e is the amount of asphaltene adsorbed onto the nanoparticles (mg/g), C_e represents the asphaltenes concentration in the equilibrium condition (mg/L), Q_m indicates the maximum amount of

adsorbed asphaltenes per unit gram of nanoparticles (mg/g), and K_L is the Langmuir equilibrium adsorption constant (L/mg). Furthermore, K_F , i.e., the adsorption capacity ([mg/g] [L/mg]), and 1/n, i.e., the adsorption intensity factor (unitless), are Freundlich constants.

Figure 4 shows the asphaltene adsorption onto the surfaces of nickel–zeolite oxide nanoparticles at different initial asphaltene concentrations, including 25–400 ppm (Ahmadi et al., 2020). The adsorbed amount of asphaltene onto nickel–zeolite oxide nanoparticles increased dramatically up to an asphaltene concentration of 105 ppm, while the adsorbed amount of asphaltene onto nickel–zeolite oxide nanoparticles reached a constant value at higher concentrations. Langmuir and Freundlich's isotherms were investigated, and the Langmuir model fitted the adsorption data better than the Freundlich model. The primary Langmuir model assumption is that asphaltene adsorption occurs on a homogeneous and monolayer surface. In contrast, the Freundlich model assumes a heterogeneous surface with different adsorption energy sites (Balabin et al., 2011).



Figure 4

Asphaltene adsorption models (Langmuir and Freundlich) for nickel-zeolite oxide nanoparticles.

Figures 5 and 6 show the Langmuir and Freundlich linear plots for nickel–zeolite oxide nanoparticles, respectively. The Langmuir model isotherm parameters for nickel–zeolite oxide nanoparticles well matched the experimental data.







Freundlich model constants for the nickel-zeolite oxide nanoparticles.

Table 2 presents the isotherm parameters for both Langmuir and Freundlich models in the presence of nickel–zeolite oxide nanoparticles. Q_m values were 72.992 mg/g for nickel–zeolite oxide nanoparticles. Moreover, the value of the Freundlich constant (K_F) for nickel–zeolite oxide nanoparticles implied that the adsorption capacity was 1.822 ([mg/g] [L/mg]^{1/n}).

			Table	2		
	The	constants of th	ne Langmui	r and Freundlich mode	els.	
	Longmuir Constants			Freundlich Constants		
Nanoparticles	$Q_m (\mathrm{mg/g})$	Kl (L/mg)	R^2	$K_F [mg/g][L/mg]$	1/n (Unitless)	R^2
Nickel–zeolite oxide	72.9927007	0.01918	0.9977	1.822369849	0.4152	0.9787

3.2. Effect of the concentration of nickel–zeolite oxide nanoparticles and pressure on CO₂–oil interfacial tension

Figure 7 shows CO₂–crude oil interfacial tension versus pressure at three different concentrations of the nickel–zeolite oxide nanoparticles: 10, 20, and 30 ppm. There are two different pressure changes: 150–900 psi and 900–1650 psi. The interfacial tension decreased with increasing pressure in the first region due to dissolving carbon dioxide gas in crude oil. The aggregation of asphaltene makes the slope of the second region milder. After adding the nickel–zeolite oxide nanoparticles at different concentrations of 10, 20, and 30 ppm, the slope steepened compared to the base case. Change of the slope in the presence of nickel–zeolite oxide nanoparticles indicates the adsorption of asphaltene on the surface of the nanoparticles.



The effects of pressure and the concentration of nickel-zeolite nanoparticles on CO₂-oil interfacial tension.

Table 3 lists the relation between CO₂-crude oil interfacial tension in terms of pressure and the secondto-first ratio slope after adding the nickel-zeolite oxide nanoparticles. Based on the results, the base second-to-first ratio was 16.7%. Adding the nickel-zeolite oxide nanoparticles to the crude oil did not change the slope of the first region (150–900 psi) significantly but increased the slope of the second region (900–1650 psi). As nickel-zeolite oxide nanoparticles were added from 10 to 30 ppm, the second-to-first ratio, 16.7% in the base case, increased from 25.0% to 39.5%, respectively. Therefore the agglomeration process was delayed due to adding nickel-zeolite oxide nanoparticles. On the other hand, more asphaltene adsorbed on the nanoparticles by increasing the concentration of the nickelzeolite oxide nanoparticles from 10 to 30 ppm. To examine this effect on the asphaltene precipitation, we designed a series of natural depletion tests in the presence of the nickel-zeolite oxide nanoparticles.

Nanoparticles type	Nanoparticle concentration (ppm)	Region	Equation interfacial tension (mN/m)	The ratio of the interfacial tension slope in the second to the first region (%)
Basa	0	First	IFT = -0.0124 P + 7.64	167
Dase		Second	IFT = -0.0021 P + 26.98	10.7
Nickel–zeolite oxide particles	10	First	IFT = $-0.012 P + 17.13$	25.0
		Second	IFT = $-0.003 P + 8.21$	
	20	First	IFT= $-0.012 P + 26.20$	22.2
		Second	IFT = -0.004 P + 9.44	33.3
	30	First	IFT = -0.0124 P + 25.98	20.5
		Second	IFT = -0.0049 P + 10.35	39.5

 Table 3

 Changes in CO2–oil interfacial tension slope ratio due to adding the nickel–zeolite oxide nanoparticles

3.3. Natural depletion tests in the presence of nickel zeolite oxide nanoparticles

As mentioned in the previous section, natural depletion tests were designed in the presence of nickel– zeolite oxide nanoparticles to examine the relationship between asphaltene adsorption on the surface of nanoparticles and asphaltene precipitation. To this end, three pressures, including 1350, 1500, and 1650 psi, were selected to investigate the precipitation changes during natural depletion at nanoparticle concentrations of 30 ppm. The mentioned pressures were selected based on the results of the previous section: a more remarkable change in the second slope and higher asphaltene adsorption on the surface of nanoparticles compared to the other pressures. A nanoparticle concentration of 30 ppm was selected based on the maximum amount of adsorption between the three tested nanoparticle concentrations of 10, 20, and 30 ppm (Ahmadi et al., 2020). Figure 8 shows the effects of nickel–zeolite oxide nanoparticles on the asphaltene precipitation trends. With decreasing pressure from 1650 to 1350 psi, asphaltene precipitation increased from 8.25 to 10.52 wt %, and reducing fluid power and density were the main reasons. Based on the results, nickel–zeolite oxide nanoparticles decreased asphaltene precipitation compared to the base case, and according to the results of this study and CO_2 –oil interfacial tension tests, both results are in good agreement. In other words, increasing the asphaltene adsorption on nickel–zeolite oxide nanoparticles decreased asphaltene precipitation.



Figure 8 The effects of the nickel–zeolite oxide nanoparticles on asphaltene precipitation during natural depletion.

4. Conclusions

The main goal of this study was to obtain the relationship between asphaltene adsorption on the surface of nickel–zeolite oxide nanoparticles and asphaltene precipitation during natural depletion tests. Accordingly, a series of CO_2 –oil interfacial tension and UV–Vis tests observed the adsorption behavior of crude oil on the surface of nickel–zeolite oxide nanoparticles. Then, based on these results, three pressures of 1350, 1500, and 1650 psi (due to the higher asphaltene adsorption observed at these pressures) and a concentration of the nanoparticles of 30 ppm (due to the maximum amount of adsorption among the tested concentrations) were selected for performing the actual natural depletion tests. The results show that asphaltene was adsorbed on the surface of the nickel–zeolite nanoparticles according to CO_2 –oil interfacial tension and UV–Vis tests. Furthermore, decreasing the pressure from 1650 to 1350 psi increased asphaltene precipitation from 8.25 to 10.52 wt %.

Interestingly, it was seen that after adding the nickel–zeolite nanoparticles, asphaltene precipitation decreased, confirming that the nanoparticles can be used efficiently as an asphaltene inhibitor. The agglomeration process was delayed in the presence of nickel–zeolite nanoparticles. Langmuir and Freundlich's isotherms were used in this study, and the Langmuir model isotherm well fitted the data, demonstrating the monolayer adsorption in the presence of nickel–zeolite oxide nanoparticles. The adsorption capacity and the maximum amount of adsorbed asphaltenes per gram of nickel–zeolite oxide nanoparticles were 72.993 mg/g and 1.822 [mg/g][L/mg], respectively. Nickel–zeolite oxide nanoparticles can be used as an efficient adsorbent for solving asphaltene precipitation during actual crude oil natural depletion, and nickel–zeolite oxide nanoparticles adsorbed asphaltene on their surface correctly.

Nomenclatures

Ce	Equilibrium sorption of asphaltene (mg/g)
Co	Asphaltene initial concentration in the toluene solution (mg/L)
FTIRS	Fourier-transform infrared spectroscopy
IFT	Interfacial tension (mN/m)
K_f	Asphaltene adsorption capacity factor ([mg/g] [L/mg])
K_L	The Langmuir equilibrium (L/mg)
M	Mass of nickel-zeolite oxide nanoparticles (mg)
PVT	Pressure–Volume–Temperature
q_e	Asphaltene absorption in equilibrium time (mg/g)
Q_m	The maximum adsorption capacity of the activated carbon (mg/g)
q_t	Asphaltene absorption at equilibrium time $t (mg/g)$
SARA	Saturates, aromatics, resins, and asphaltenes
SEM	Scanning electron microscopy
V	The volume of solution (L)

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