Catecholamine Coated Maghemite Nanoparticles for Asphaltene Adsorption/Desorption Process

Behruz Mirzayi*, Ali Nematollahzadeh, Mohsen Rasouli, Hadi Seyyedbagheri

Chemical Engineering Department, University of Mohaghegh Ardabili, Ardabil, Iran

Abstract
In this study, a nano-layer polydopamine (PDA) coated superparamagnetic maghemite nanoparticles (MNPs) was applied to investigate the asphaltene adsorption/desorption behavior using a model solution. In this process, Fourier-transform infrared spectroscopy of the polydopamine/MNP core/shell (MNP@PDA) before and after asphaltene adsorption was indicated the physical attachment of asphaltene molecules on the polymeric nano-adsorbent surface. The isotherms and kinetics of the asphaltene adsorption process on the MNP@PDA were studied. The good prediction of asphaltene adsorption by the modified Langmuir model indicated that adsorption takes place on an MNP@PDA surface through multilayer adsorption. Also, within the kinetic models, the double-exponential adsorption isotherm model can fit the experimental data well. The obtained results revealed that about 90% removal for asphaltene happened within 30 min which can be acceptable.

Keywords: Asphaltene; Polydopamine; Nanoparticles; Maghemite; Adsorption.

1. Introduction
The most important fossil fuels in the world are heavy oil and bitumen. Due to the rapid progress of various industries, the utilization of these fuels is expected to increase in the close future. For optimal use of these fuels, they need to be upgraded by applying advanced upgrading techniques to produce light and valuable petroleum products. [1]. Accordingly, one of the main problems, which occurs in oil production because of the pressure, temperature, and composition changes, is the heavy organic precipitation such as asphaltene [2, 3]. During the crude oil production and refining, at first asphaltene precipitation/aggregation may be occurred and then deposited in the reservoir rock, wellbore, equipment, and transmission pipes [4]. Moreover, with the increase of asphaltene aggregation rate, the viscosity of oils could be increased and the oil flow has been encountered various problems during the production and transformation process [5]. The adsorption of asphaltene onto rock surfaces can also lead to destructive effects such as pore plugging, permeability reduction, and wettability alteration [6]. By the asphaltene adsorption onto the rock surface, the polar groups in the asphaltene structure cause wettability alteration which could be affected significantly, the oil recovery process [6]. Therefore, using the techniques to control, prevent or remove precipitated asphaltene from the oil is the effective and economical way for overcoming the problems caused by the asphaltene deposition. Recently, nanotechnology has been used as an interesting method to control the asphaltene deposition process [7-9]. Nassar studied asphaltene adsorption onto alumina nanoparticles. He showed that nanoparticles are able to remove asphaltene from the oil successfully, and thus the

1. Corresponding Author
Email: mirzayib@uma.ac.ir
transport of oil will have done without any serious problem. He also showed that upgrading of asphaltenes could be possible in the presence of nanoparticles as a catalyst [10]. Nassar et al. investigated the adsorption of asphaltene onto alumina particles of different sizes. The obtained results showed that the nano-sized alumina has a higher adsorption capacity compared to microparticles [11]. In other works, various metal oxide nanoparticles such as NiO, Co3O4, and Fe3O4 were applied for the removal of asphaltenes extracted from Athabasca oil field [12, 13]. Mirzayi and Shayan investigated the asphaltene adsorption as well as its oxidation onto maghemite nanoparticles [14]. The results of their study showed that the equilibrium condition for asphaltene adsorption onto MNPs is established in less than 2 h, and the adsorption kinetics data fitted well to the pseudo-second-order model. Additionally, their study confirmed that the adsorption isotherms are in good consistency with the Langmuir model. Franco et al. used NiO and PdO nanoparticles deposited on fumed silica for the removal of asphaltene [15]. According to their results, the adsorption isotherms of asphaltene were well fitted by the three-parameter solid-liquid equilibrium (SLE) model [16]. Dopamine (DA) is one of the catecholamine families, which could be polymerized to polydopamine (PDA) at a slightly alkaline pH. The polymerization process involves the reaction of dopamine hydrochloride in Tris-HCl solution as an alkaline buffer. Because of the different functional groups, polydopamine coatings is one of the interesting topics in the last decade of studies [17]. The active surface of polydopamine enables it to adhere easily to the other material's surface for different purposes. For example, polydopamine coated nanoparticles have been used for environmental remediation [17], drug delivery [18, 19], biomedical [20], biosensors [21], etc.

Herein, in the present study, the surface of the synthesized maghemite nanoparticles (MNPs) was coated with a bio-based polymer (i.e., polydopamine, PDA), and the prepared polydopamine/MNPs core/shell (MNP@PDA) was examined to adsorb the asphaltene from a model solution for the first time. By conducting different batch-mode experiments, the kinetics, isotherm, and thermodynamic properties change of asphaltene adsorption onto MNP@PDA were investigated. The core/shell nanoparticles prepared in this research are proposed, for the first time, as potential candidates for the removal of asphaltene from crude oils.

2. Experimental

2.1. Materials and Methods

The materials used in this work, were purchased from Sigma-Aldrich and Merck companies. These include, dopamine (DA), Tris, ammonia solution, toluene, n-heptane HCl, FeCl3, and FeCl2·4H2O. The crude oil is also taken from one of the oil fields in Iran. The well-known IP-143 standard was used to extract the asphaltenes from the crude oil sample. The co-precipitation method by using ferric and ferrous salts was also applied for synthesizing maghemite nanoparticles (MNPs) [22]. This is a simple and low cost method, which will be discussed briefly in the next section.

2.2. Synthesis of Polydopamine Coated γ-Fe2O3 Nanoparticles (MNP@PDA)

First, the hydrochloric acid, ammonia, FeCl3, and FeCl2·4H2O solutions were prepared. Then, the iron salt solution was added dropwise into ammonia solution under agitation within 20 min. The prepared black nanoparticles were separated from the solution by using a magnet. Then, to synthesized the polydopamine coated maghemite nanoparticles (MNP@PDA), dopamine was added to the MNPs in Tris buffer solution (pH=8.4, 10 mM) [17, 23]. Finally, the product was washed with deionized water and dried at 40 °C. Polydopamine polymerization and surface coating of MNP have been illustrated in Fig. 1.

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2.3. Adsorption Experiments

Adsorption of asphaltene onto MNP@PDA was performed at temperatures 25, 40, and 60 °C. The adsorption experiments were done in a batch system, in which a certain mass of MNP@PDA was added to the asphaltene-toluene solution so that a ratio of 10:1 (g/L) was achieved. The prepared samples were agitated at 200 rpm at the above-mentioned three temperatures for 24 hours in an incubator. To separate the nanoparticles containing adsorbed asphaltene a strong magnetic field was applied. The asphaltene in the supernatant solution was evaluated using a UV-vis spectrophotometer at a wavelength of 297 nm. By using the mass conservation low for asphaltene before and after the adsorption process, one could be calculated the amount of adsorbed asphaltene ($q_t$) onto MNP@PDA as Eq. 1:

$$q_t = \frac{(C_0 - C_t)}{m} V$$

where, $C_0$ and $C_t$ (mg/L) are the asphaltene initial and time-dependent concentrations, respectively, $m$ (g) is the nanoparticles mass, and $V$ (L) is the volume for the adsorption medium.

2.4. Adsorption Isotherms Models

Base on the trend of experimental data and the literature the adsorption isotherm models were chosen. Therefore, the isotherms for the asphaltene adsorption onto MNP@PDA were obtained
using several models such as the Langmuir, Freundlich, modified Langmuir, and solid–liquid equilibrium (SLE) models. The expression of the models was illustrated in Table 1.

### Table 1. Isotherm models expression

<table>
<thead>
<tr>
<th>Isotherm model</th>
<th>Expression</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freundlich</td>
<td>( q_e = K_F C_e^{1/n} )</td>
<td>( n, K_F \text{ (mg/g)(L/mg)}^{1/n} )</td>
</tr>
<tr>
<td>Langmuir</td>
<td>( q_e = q_m \frac{K_L C_e}{1 + K_L C_e} )</td>
<td>( q_m \text{ (mg/g)}, K_L \text{ (L/mg)} )</td>
</tr>
<tr>
<td>Modified Langmuir</td>
<td>( q_e = q_m \frac{K_s C_e^x}{1 + K_s C_e^x} )</td>
<td>( x, q_m \text{ (mg/g)}, K_s \text{ ((L/mg)}^{1/x} )</td>
</tr>
</tbody>
</table>

#### 2.5. Adsorption Kinetics Models

To study the kinetics of the adsorption process, the adsorption of asphaltene onto MNP@PDA was conducted for 12 h at an initial asphaltene concentration of 500 mg/L, and a temperature of 25 °C. Using the obtained data, the adsorption kinetics were modeled using several well-known adsorption models such as pseudo-first-order, pseudo-second-order, and double-exponential models (DEM) [24, 25]. The efficiency of the grafted adsorbent was evaluated by studying the adsorption kinetics. The studied kinetics models were summarized in Table 2.

### Table 2. Kinetics models expression

<table>
<thead>
<tr>
<th>Kinetics model</th>
<th>Expression</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first-order</td>
<td>( q_t = q_e (1 - e^{-K_1 t}) )</td>
<td>( q_e \text{ (mg/g)}, K_1 \text{ (1/min)} )</td>
</tr>
<tr>
<td>Pseudo-second-order</td>
<td>( q_t = (K_2 q_e^2 t) / (1 + K_2 q_e t) )</td>
<td>( q_e \text{ (mg/g)}, K_t \text{ (g/mg.min)} )</td>
</tr>
<tr>
<td>Double-exponential</td>
<td>( q_t = q_e - \frac{D_1}{m_a} \exp (-K_1 t) - \frac{D_2}{m_a} \exp (-K_2 t) )</td>
<td>( q_e \text{ (mg/g)}, K_1, K_2 \text{ (1/h), D_1, D_2 (mg/g)} )</td>
</tr>
</tbody>
</table>

#### 2.6. Recycling Experiment

For conducting the desorption experiment, the nanoparticles were dispersed into 10 mL of chloroform/methanol (70/30 Vol. %) solution and shaken at 300 rpm for 4 h. After spending the desired time, the nanoparticles were collected using a magnetic and washed with the solution. The concentration of asphaltene in the residual solution was determined using UV–vis spectrophotometer. After drying the nanoparticles in a vacuum oven at 40 °C, they were re-dispersed in a known concentration of asphaltene solution to investigate the adsorption ability of the retrieved removal agent. The recovery rate was calculated using Eq. (2):
\[ R(\%) = \frac{C_r}{C_0 - C_e} \times 100 \]  

(2)

where \( C_0 \), \( C_e \), and \( C_r \) are the concentration of asphaltene in initial, equilibrium, and eluent solutions, respectively.

3. Results and discussion

3.1. Characterization of MNP and MNP@PDA

The specific surface area, chemical structure, morphology, and size of MNP@PDA could be found in the previous work [23]. Briefly, the average size of MNP@PDA was determined using TEM analysis to be about 10 nm, and the theoretical surface area was about 30 m\(^2\)/g. The Fourier transform infrared (FT-IR) spectroscopy was also applied for revealing the presence of chemical interactions between the maghemite nanoparticles (MNPs) and polydopamine (PDA) [17, 23]. Therefore, in the present work, the characterization of the adsorbed material onto MNP@PDA was accomplished by FT-IR spectroscopy. FT-IR analyses of as-prepared MNP@PDA [23], and asphaltene adsorbed MNP@PDA were performed and shown in Fig. 2. The FT-IR spectrum of nanoparticles before asphaltene adsorption shows two main peaks at 439 and 575 cm\(^{-1}\). These peaks indicate the stretching vibration of Fe-O band in the structure of the nanoparticles. The other peak appears at 3430 cm\(^{-1}\), which confirms the existence of water and OH groups on the MNP surface [17]. The other three peaks are also observed at 1292, 1490, and 1624 cm\(^{-1}\). The peak at 1624 cm\(^{-1}\) is related to the vibration of C-C, the peak at 1490 cm\(^{-1}\) shows the N-H stretching vibration, and the peak at 1292 cm\(^{-1}\) is attributed to the C-O-H stretching–bonding vibration. Several new peaks have been created in the FT-IR spectrum of MNP@PDA after asphaltene adsorption, which is as follows: (1) the absorbance band at 1273 cm\(^{-1}\) is related to connectors ether and ester in the surface of nanoparticles, (2) the band at 1460 cm\(^{-1}\) assigned to the existence bending of the CH\(_3\) and CH\(_2\), (3) the peak at 2354 cm\(^{-1}\) absorption bands is related to C=O and C=N=O bonds is in conjunction with carboxylic connections or strong bond C=O, (4) the peak at 2856 cm\(^{-1}\) is attributed to the C-H bond, and (5) the peaks at 2920 and 3403 cm\(^{-1}\) are related to CH\(_3\)-CH and N-H bonds, respectively, that the latter may be attributed to the sharing of electron between nitrogen atoms available in the asphaltene structure and hydrogen atoms located on the surface of the nanoparticles.
3.2. Adsorption isotherms

To obtain the maximum amount of asphaltene adsorbed onto MNP@PDA and determine the isotherm model constants, the adsorption tests were conducted at different temperatures. The parameters of the models and obtained $R^2$ values from adsorption isotherms at different temperatures are outlined in Table 3. As can be inferred, the results show that the modified Langmuir type isotherm could cover the experimental data well with $R^2$ values of greater than 0.999. This result proves that the adsorption of asphaltene onto MNP@PDA occurs by multilayer adsorption. The adsorption isotherms of asphaltene according to the modified Langmuir model are depicted in Fig. 3. Based on this figure, the model fits well the experimental data and the good consistency of the experimental data and prediction results could be seen in the figure.
Table 3. Isotherm models parameters

<table>
<thead>
<tr>
<th>Isotherm model</th>
<th>T (°C)</th>
<th>Model parameters</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$l/n$</td>
<td>$K_f ((mg/g)(L/mg)^{1/n})$</td>
</tr>
<tr>
<td>Freundlich</td>
<td>25</td>
<td>0.3369</td>
<td>5.0292</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.3377</td>
<td>5.1572</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.3428</td>
<td>5.5842</td>
</tr>
<tr>
<td>Langmuir</td>
<td>25</td>
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</tr>
<tr>
<td></td>
<td>40</td>
<td>51.25</td>
<td>0.0133</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>56.17</td>
<td>0.0142</td>
</tr>
<tr>
<td>Modified Langmuir</td>
<td>25</td>
<td>0.7738</td>
<td>56.82</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.7722</td>
<td>58.66</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.6162</td>
<td>78.09</td>
</tr>
</tbody>
</table>

Fig. 3. Modified Langmuir model adsorption isotherm of asphaltene

3.3. Adsorption kinetics

The kinetics of the asphaltene adsorption onto MNP@PDA were modeled and the adsorption capability of the modified adsorbent was evaluated using the three adsorption kinetics models. Fig. 4 shows the changes in the amount of adsorbed asphaltene onto MNP@PDA versus the contact time. It can be concluded that the adsorption is very fast so that the equilibrium was observed within 30 min. According to the obtained results, the main part of asphaltene removal occurred in the first half-hour. The results depicted in Fig. 4 shows that the double-exponential model is a powerful model to represent the experimental data. This model considers the adsorption process in two-steps, including fast and slow steps. The steps were described by the parameters with subscripts 1 and 2. The fast step happened in the first half-hour and the most
of adsorption was occurred during this step, whereas on the next step, the adsorption was happened so slowly.

![Fig.4. Evaluation of kinetic models for the asphaltene adsorption onto nanoparticles](image)

The kinetic model parameters were determined and reported in Table 4 together with the $R^2$-values. According to the $R^2$-values, it can be inferred that the adsorption obeys from the double-exponential model.

**Table 4. Kinetic models parameters for asphaltene adsorption**

<table>
<thead>
<tr>
<th>Kinetic model</th>
<th>Parameters</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Double-exponential</td>
<td>$q_0$ (mg/g)</td>
<td>$m_0$ (g/L)</td>
</tr>
<tr>
<td></td>
<td>43.3283</td>
<td>10</td>
</tr>
<tr>
<td>Pseudo-second-order</td>
<td>$q_e$ (mg/g)</td>
<td>$K_2$ (g/mg.min)</td>
</tr>
<tr>
<td>Pseudo-first-order</td>
<td>$q_e$ (mg/g)</td>
<td>$K_1$ (1/min)</td>
</tr>
</tbody>
</table>
3.4. Desorption and regeneration of the adsorbent

The variation in the adsorption/desorption efficiency concerning the cycle number is depicted in Fig. 5. As can be seen in Fig. 5, the adsorption/desorption cycle does not remarkably change during the three cycles. Consequently, the synthesized nanoparticles could be successfully reused without a considerable loss of their adsorption efficiency. The recovery tests demonstrated that we can use polymer at the surface of the nanoparticle as recyclable adsorbents for asphaltene removal.

Fig. 5. Adsorption efficiency of asphaltene in adsorption/desorption cycles

3.5. Thermodynamics of asphaltene adsorption

Thermodynamic properties such as Gibbs, enthalpy and entropy change of asphaltene adsorption onto MNP@PDA was determined using the following equations (Eqs. 3 and 4) [26]:

$$
\Delta G_{ads}^{o} = -RT \ln(K) 
$$

(3)

$$
\ln(K) = -\frac{\Delta H_{ads}^{o}}{RT} + \frac{\Delta S_{ads}^{o}}{R}
$$

(4)

In the above equations, the equilibrium constant, $K$, is equal to $K_L C_{sol}$, where $K_L$ (L/mmol) is the Langmuir constant and $C_{sol}$ (mM) is the solvent molar concentration, $R$ is the universal gas constant, and $T$ (K) is the temperature.

The solvent molar concentration can be calculated through the density and molecular weight of toluene. Furthermore, the molecular weight of asphaltene is needed to determine the parameters $K$ and $K_L$. Due to the uncertainty of the molecular weight of asphaltene, it was assumed to be about 800-4500 g/mol. Based on this assumption the parameters $K$ and $K_L$ were calculated and the variation of $\ln(K)$ was plotted as a function of $(1/T)$. The slopes and intercepts of the straight lines were obtained and the enthalpy change ($\Delta H_{ads}^{o}$) and entropy change ($\Delta S_{ads}^{o}$) of adsorption were determined using Eq. 4. The Gibbs energy change of asphaltene adsorption was also obtained directly using Eq. 3.
Table 5 shows the calculated above-mentioned thermodynamic properties for the adsorption of asphaltene onto MNP@PDA. The negative values of $\Delta G_{\text{ads}}^\circ$ demonstrated that this process is spontaneous. The positive values of the enthalpy revealed the endothermic behavior of the adsorption process. Also, the positive values of $\Delta S_{\text{ads}}^\circ$ were attributed to the randomness increasing during the adsorption process.

<table>
<thead>
<tr>
<th>$M_w$ (g/mol)</th>
<th>$T$ (K)</th>
<th>$K$</th>
<th>$\Delta G_{\text{ads}}^\circ$ (kJ/mol)</th>
<th>$\Delta H_{\text{ads}}^\circ$ (kJ/mol)</th>
<th>$\Delta S_{\text{ads}}^\circ$ (J/mol.K)</th>
<th>$R^2$</th>
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<td>800</td>
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<td>603353.38</td>
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</table>

4. Conclusions

In this work, kinetic and isotherm studies of asphaltene adsorption onto maghemite nanoparticle modified with natural polymers nano-layer were investigated experimentally. Characterization of the adsorbed asphaltene was accomplished using FT-IR. The FT-IR spectrum revealed the adsorption of asphaltene onto the modified nanoparticles. Among the adsorption isotherm models, the modified Langmuir type isotherm showed the best fitting to the adsorption experimental data which revealed that the asphaltene adsorption on MNP@PDA occurs in monolayer. To better elucidate the absorption kinetics, three models namely, pseudo-first- and -second-order model, and double-exponential model were used. From the results, it was inferred that the double-exponential model is consistent with the experimental data. The obtained results also revealed that about 90% removal of asphaltene happens within 30 min. The reusability of MNP@PDA was examined using chloroform/methanol as striping solution. The results showed successful reusability of the natural polymer-coated maghemite nanoparticle at least three times, for asphaltene adsorption from the prepared asphaltene-toluene solutions. Furthermore, thermodynamics studies of asphaltene adsorption onto MNP@PDA showed the spontaneous and endothermic nature of the process.
References


