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# A new model based on multilayer kinetic adsorption mechanism for asphaltenes adsorption in porous media during dynamic condition

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ABSTRACT

In this work, a new model based on multilayer kinetic adsorption mechanism has been proposed to account asphaltene adsorption in porous media under dynamic condition and the model was verified using experimental data obtained in this work and also with those reported in the literature. In the proposed model two steps are considered for asphaltene adsorption. The first step is taken as adsorption of asphaltenes on the surface of the porous media and the second step is taken as adsorption of asphaltenes on the asphaltenes already adsorbed on the porous media. The Crank-Nicholson method, central difference in space and trapezoidal rule in time, giving second order convergence in time was applied to develop a computer program using MATLAB software. Also, the Rung-Kutta fourth order scheme has been applied to calculate the volume fraction of asphaltene adsorption. The results show that the proposed model based on multilayer adsorption kinetic mechanism of aphaltene with the absolute average deviation 0.7% can predict more accurately the asphaltene adsorption experimental data in comparison to the previous models based on the monolayer adsorption kinetic and equilibrium mechanism. Sensitivity analysis shows that the proposed model is more sensitive to the first step of adsorption than the second step of adsorption. Also, a series of experiments was carried to investigate the asphaltene adsorption using UV–vis spectroscopy in order to study the effect of different parameters on asphaltene adsorption mechanisms during dynamic condition in porous media such as concentration, asphaltene composition, flow rate and type of porous media. The experimental results show that adsorption is controlled by the type of porous media rather than the asphaltene concentration of solution. Also, it was found that the adsorption process in porous media is controlled by kinetics mechanism during dynamic condition.

## 1. Introduction

The flow of fluid in porous media is controlled by porous media-fluid interactions. A number of interaction forces, individually or in combination with each other, can be responsible for this interaction. The interaction between asphaltenes and reservoirs rock alters the wettability of porous media from water-wet toward more oil-wet conditions. The majority of existing work addresses the adsorption of asphaltenes in porous media on various porous media under static conditions [1–10]. The irreversible adsorption [5,11,12] and reversible adsorption [13] have been investigated in literature. Marczewski [6] reported the typical shape of asphaltene adsorption isotherms for several systems with the characteristic steps which indicate changes in the state of asphaltene molecules in the solution and at the mineral surface. Dudasova found that adsorption depends on particle type with H-bond formation and proposed a correlation between amount of nitrogen in asphaltene sample and its adsorbed amount on the particle [14,15]. Gonzalez reported that the final dynamics adsorption seems to be dependent on the nature and specific content of heteroatom, which allows them to interact stronger and faster with the porous media surface [16]. Szymula described the results of adsorption measurements in terms of physical adsorption on heterogeneous porous media [17]. Castro presented a molecular thermodynamics approach for the modeling of adsorption isotherms of asphaltenes adsorbed on berea sandstone, bedford limestone and dolomite samples, using a model for bulk asphaltenes precipitation and a quasi-two-dimensional approach for confined fluids [18]. Acevedo observed that the rate of adsorption decreases and the adsorption capacity increases by increasing the asphaltene concentration as a result of different adsorption kinetics for aggregates as compared to monomers [11]. Lopez-Linares found that the rate of asphaltene adsorption on different porous media increases with increasing aromaticity and nitrogen content of asphaltene and decreasing its

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**Nomenclature**

| | |
|---|---|
| $\Gamma$ | amount of adsorbed substance in mol/L |
| $C$ | experimental concentration value in mol/L |
| $k_1$ | first step adsorption parameter (this step is considered as adsorption of asphaltenes from solution to the surface of the rock) |
| $k_2$ | second step adsorption parameter (this step is taken as adsorption of asphaltenes from solution to those asphaltenes already adsorbed to the rock) |

molecular size [12]. Syunyaev reported that the chemical composition and structural parameters of the porous media surface are the main factors that control the adsorption process [13]. In addition, they found different rate constants for different particle size of the same material. De la Cruz studied the adsorption mechanisms involved in the interfacial interaction of the asphaltene/porous media system at high asphaltene concentrations [9]. Adsorption isotherms of asphaltenes were obtained by contacting samples of berea sandstone, bedford limestone, and a Mexican dolomite rock sample with an asphaltene fraction dissolved in toluene. At low concentrations, the typical shape of asphaltene adsorption isotherms is similar as that reported in the literature, while at higher concentrations it was found a stepwise-type isotherm, which suggest a qualitative change in the adsorption behavior. Such changes are related to the asphaltene association and their aggregation. The model of Zhu [19] for fitting the whole adsorption isotherm was proposed in order to understand the adsorption behavior at higher concentrations. Piro used a crushed dolomite sample and asphaltene in toluene solution to investigate their dynamic adsorption under different flow rates and found that the amounts of adsorbed asphaltenes are rate-dependent [20]. More recently, the adsorption of asphaltenes on porous media was studied under dynamic conditions using a quartz crystal microbalance with dissipation monitoring (QCM-D) [7,21]. It was shown that the solubility of asphaltenes in the liquid phase affects the mechanical properties of the adsorbed film and the amount of adsorbed asphaltenes can be correlated to their nitrogen content. Adsorption under static conditions can be governed by kinetics and equilibrium phenomena. In the kinetic phenomena, asphaltene adsorption is controlled rate or time-dependent, whereas in the equilibrium phenomena, asphaltene adsorption is instantaneous because of strong interactions between asphaltene and porous media and only the final state of a system is considered [22]. Recently the experimental and modeling of asphaltene and wax precipitation and adsorption in Iranian live oils was investigated by Jafari et al. [23–26]. In processes involving flow through porous media convection-dispersion effects are considered and it is the relative rate of adsorptive and convective-dispersive mass transfer that determines whether adsorption/desorption kinetics or adsorption equilibrium governs the adsorption process. Either adsorption equilibrium or kinetic equations were incorporated into the convection dispersion-adsorption model to simulate the experimental data. Very little work currently exists on the adsorption kinetics of asphaltenes under dynamic conditions in literature. In this work, a new model based on multilayer kinetic mechanism has been proposed to account asphaltene adsorption in porous media under dynamic condition and the model was verified using experimental data obtained in this work and also with those reported in the literature. Also, a series of experiments on different porous media were conducted to investigate adsorption of asphaltenes on porous media under dynamic conditions using different porous media samples.

**Table 1**
Studied live oil compositions.

| Components | Bottom hole live oil (mol%) | Components | Bottom hole live oil (mol%) |
|---|---|---|---|
| $H_2S$ | 0 | n–C5 | 1.59 |
| $N_2$ | 0.3 | C6 | 6.95 |
| $CO_2$ | 1.83 | C7 | 4.1 |
| C1 | 22.7 | C8 | 3.88 |
| C2 | 8.24 | C9 | 2.49 |
| C3 | 6.14 | C10 | 4.03 |
| i–C4 | 1.19 | C11 | 2.85 |
| n–C4 | 3.61 | C12+ | 28.74 |
| i–C5 | 1.38 | Total | 100 |

**Table 2**
SARA test results of the studied oil.

| Type of group | Oil |
|---|---|
| Saturate (wt%) | 32.61 |
| Aromatic (wt%) | 43.48 |
| Resin (wt%) | 7.61 |
| Asphaltene (wt%) | 16.3 |

**Table 3**
Characteristics of the studied asphaltene (elemental analysis) (wt%).

| %C | %H | %N | %$O_2$ | %S |
|---|---|---|---|---|
| 86.91 | 8.12 | 1.31 | 2.38 | 1.28 |

## 2. Materials and methods

### 2.1. Materials

In this work, the asphaltene samples were prepared from a crude oil reservoir on the Southeast region of Iran. The Specific Gravity and viscosity of the oil sample were measured to be 0.9322 and 4.35 cP at the reservoir pressure, respectively. The compositional analysis of studied crude oil using the gas chromatography method was given in Table 1. The asphaltene content of the crude oil was measured to be 16.3 wt% using the SARA analyses. The constituents of crude oil are typically classified by solubility saturates aromatics, resins, and asphaltenes (SARA). The SARA analyses results for studied crude oil are shown in Table 2. The oil was first centrifuged at 2500 rpm to remove any impurities, such as mineral fines, and then filtered with 2 μm filter prior to asphaltene separation. Asphaltenes were precipitated from crude oil using an excess of n-pentane in ratio 1:40 according to the ASTM D2007-80 procedure.

The mixture of crude oil and n-pentane was stirred for 24 h at room temperature. The asphaltenes fraction was filtrated through a 0.45 μm filter and washed with an additional n-pentane. After filtration, the asphaltenes were dried for 48 h and then was controlled by weighting. The extracted asphaltenes were stored in a desiccator for 5 days. In order to characterize the asphaltenes, the elemental analysis was done and the results are given in Table 3. Then asphaltene solutions were prepared by dissolving asphaltenes in dry toluene (HPLC grade, Fisher Scientific) and stirring it for 120 min. Prior to adsorption experiments, toluene and n-heptane used as solvents were dried on a 0.4 nm molecular sieve (Merck AG) to remove any traces of water. In order to reach equilibrium the solutions were stored for at least 12 h. Also, the densities were measured using a DMA45 density meter (Anton-Paar).

### 2.2. Porous media-adsorbents

Four carbonate, dolomite and sandstone rock samples were extracted from the Iranian wells as porous media, then characterized and tested in the Research Institute Petroleum of Industry