

A NEW STUDY ON ASPHALTENE ADSORPTION IN POROUS MEDIA

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Abstract

Asphaltene adsorption is an important problem in petroleum field. In this work, asphaltene adsorption has been investigated in porous media using different adsorption isotherm models. The results show that multilayer isotherms can predict more accurately the asphaltene experimental data in comparison to the two and three parameter isotherm models in particular in carbonate samples with the absolute average deviation 0.9-1.4 %. Also, the three parameters isotherm models can predict the asphaltene experimental data with absolute average deviation 4.1-5.7 %. The two parameter isotherm models can predict the asphaltene experimental data with the absolute average deviation 6.2-11.1 %. Therefore at higher concentrations multilayer isotherm models can predict more accurately the asphaltene experimental data in comparison to the two and three parameter isotherm models.

Key words: Asphaltene; Adsorption; Isotherm; Petroleum; Porous media.

1. Introduction

Asphaltenes are the polar fractions of crude oil that can be separated by addition of low molecular weight n-alkanes. By definition, asphaltenes are the fraction of a crude oil that is soluble in toluene and insoluble in an n-alkane, typically pentane or heptane. These fractions are formed by molecules with a poly aromatic structure containing paraffinic and naphthenic chains, as well as oxygen, nitrogen and sulfur as functional groups or heteroatom. In the other hand, asphaltenes are heavy hydrocarbon molecules that are stabilized by resins adsorbed on their surface in the oil. Asphaltenes can reduce the hydrocarbon effective mobility by:

- Blocking pore throats thus reducing the rock permeability.
- Alteration the formation wettability from water-wet to oil-wet, therefore decreasing the effective permeability to oil and increasing the irreducible oil saturation.
- Increasing the reservoir fluid viscosity.

The majority of existing work addresses the adsorption of asphaltenes in porous media on various porous media under static conditions. Marczewski ^[1] 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 ^[2]. 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 ^[3]. Szymula described the results of adsorption measurements in terms of physical adsorption on heterogeneous porous media ^[4]. 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 ^[5]. 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 [6]. 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 molecular size [7]. Syunyaev reported that the chemical composition and structural parameters of the porous media surface are the main factors that control the adsorption process [8]. The model of Zhu [9] 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 [10]. Recently the experimental and modeling of asphaltene and wax precipitation and adsorption in Iranian oils was investigated by Jafari Behbahani *et al.* [11-22].

2. Investigation of asphaltene adsorption using adsorption isotherms models

In general, an adsorption isotherm is an invaluable curve describing the phenomenon governing the retention of a substance from the aqueous porous to a solid-phase at a constant temperature. Adsorption equilibrium (the ratio between the adsorbed amount with the remaining in the solution) is established when an adsorbate containing phase has been contacted with the adsorbent for sufficient time, with its adsorbate concentration in the bulk solution is in a dynamic balance with the interface concentration. Typically, the mathematical correlation, which constitutes an important role towards the modeling analysis, operational design and applicable practice of the adsorption systems, is usually depicted by graphically expressing the solid-phase against its residual concentration. Over the years, a wide variety of equilibrium isotherm models

(Langmuir, Freundlich, Brunauer–Emmett–Teller, Redlich–Peterson, Dubinin–Radushkevich, Temkin, Toth, Koble–Corrigan, Sips, Khan, Hill, Flory–Huggins and Radke–Prausnitz isotherm), have been presented in terms of three fundamental approaches. Kinetic consideration is the first approach. Hereby, adsorption equilibrium is defined being a state of dynamic equilibrium, with both adsorption and desorption rates are equal. Whereas, thermodynamics, being a base of the second approach, can provide a framework of deriving numerous forms of adsorption isotherm models, and potential theory, as the third approach, usually conveys the main idea in the generation of characteristic curve. However, an interesting trend in the isotherm modeling is the derivation in more than one approach, thus directing to the difference in the physical interpretation of the model parameters.

2.1. Two parameter isotherms

2.1.1. Langmuir isotherm model

Langmuir adsorption isotherm assumes monolayer adsorption (the adsorbed layer is one molecule in thickness), with adsorption can only occur at a finite (fixed) number of definite localized sites, which are identical with no lateral interaction between the adsorbed molecules. In its derivation, Langmuir isotherm refers to homogeneous adsorption, which each molecule possess constant enthalpies and sorption activation energy (all sites possess equal affinity for the adsorbate). Graphically, it is characterized by a plateau, an equilibrium saturation point where once a molecule occupies a site, no further adsorption can take place. Moreover, Langmuir theory has related rapid decrease of the intermolecular attractive forces to the rise of distance. The Langmuir isotherm model can be represented as follows [23]:

$$q_e = \frac{Q_0 b C_e}{1 + b C_e} \quad (1)$$

2.1.2. Freundlich isotherm model

Freundlich isotherm is the earliest known equation describing the non-ideal and reversible adsorption, not restricted to the formation of monolayer. This empirical model can be applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface. Freundlich isotherm is widely applied in heterogeneous processes especially for organic compounds or highly interactive species on polar porous media. The Freundlich isotherm model can be shown as follows [24]:

$$q_e = k_F C_e^{\frac{1}{n}} \quad (2)$$

2.1.3. Dubinin–Radushkevich isotherm model

Dubinin–Radushkevich isotherm is an empirical model conceived for the adsorption of subcritical vapors onto micro pore solids following a pore filling mechanism. It is applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface. This model has successfully fitted high solute activities and the intermediate range of concentrations data well, but does not predict the Henry's law at low pressure. One of the unique features of the Dubinin–Radushkevich isotherm model lies on the fact that it is temperature-dependent, which when adsorption data at different temperatures are plotted as a function of logarithm of amount adsorbed vs the square of potential energy, all suitable data will lie on the same curve, named as the characteristic curve. The Dubinin–Radushkevich isotherm model can be shown as follows [25]:

$$q_e = (q_s) \exp(-k_{ad} \varepsilon^2) \quad (3)$$

2.1.4. Temkin isotherm model

Temkin isotherm contains a factor that explicitly taking into the account of adsorbent–adsorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage. As implied in the equation, its derivation is characterized by a uniform distribution of binding energies. The Temkin isotherm model can be presented as follows [26]:

$$q_e = \frac{RT}{b_T} \ln A_T C_e \quad (4)$$

2.1.5. Flory–Huggins isotherm model

Flory–Huggins isotherm model express the feasibility and spontaneous nature of an adsorption process. In this respect, θ is the degree of surface coverage, where K_{FH} and n_{FH} are the indication of its equilibrium constant and model exponent. Its equilibrium constant, K_{FH} , used for the calculation of spontaneity free Gibbs energy. The Flory–Huggins isotherm model can be shown as follows [27]:

$$\frac{\theta}{C_0} = K_{FH} (1 - \theta)^{n_{FH}} \quad (5)$$

2.1.6. Hill isotherm model

Hill equation was postulated to describe the binding of different species onto homogeneous substrates. The model assumes that adsorption is a cooperative phenomenon, with the ligand binding ability at one site on the macromolecule, may influence different binding sites on the same macromolecule. The Hill isotherm model can be presented as follows [28]:

$$q_e = \frac{q_{sH} C_e^{n_H}}{K_D + C_e^{n_H}} \quad (6)$$

2.2. Three parameter isotherms

2.2.1. Redlich–Peterson isotherm model

Redlich–Peterson isotherm is a hybrid isotherm featuring both Langmuir and Freundlich isotherms, which incorporate three parameters into an empirical equation. The model has a linear dependence on concentration in the numerator and an exponential function in the denominator to represent adsorption equilibria over a wide concentration range, that can be applied either in homogeneous or heterogeneous systems due to its versatility.

In the limit, it approaches Freundlich isotherm model at high concentration (as the exponent γ tends to zero) and is in accordance with the low concentration limit of the ideal Langmuir condition. The Redlich–Peterson isotherm model can be presented as follows [29]:

$$q_e = \frac{k_R C_e}{1 + a_R C_e^\gamma} \quad (7)$$

2.2.2. Sips isotherm model

Sips isotherm is a combined form of Langmuir and Freundlich expressions deduced for predicting the heterogeneous adsorption systems and circumventing the limitation of the

rising adsorbate concentration associated with Freundlich isotherm model. At low adsorbate concentrations, it reduces to Freundlich isotherm; while at high concentrations, it predicts a monolayer adsorption capacity characteristic of the Langmuir isotherm. The Sips isotherm model can be shown as follows [30]:

$$q_e = \frac{K_s C_e^{\beta_s}}{1 + a_s C_e^{\beta_s}} \quad (8)$$

2.2.3. Toth isotherm model

Toth isotherm model is another empirical equation developed to improve Langmuir isotherm fittings and useful in describing heterogeneous adsorption systems, which satisfying both low and high-end boundary of the concentration. The Toth isotherm model can be shown as follows [31]:

$$q_e = \frac{K_T C_e}{(a_T + C_e)^{1/t}} \quad (9)$$

2.2.4. Koble–Corrigan isotherm model

Koble–Corrigan isotherm [32] incorporated both Langmuir and Freundlich isotherm models for representing the equilibrium adsorption data. The isotherm constants, A, B and n are evaluated from the linear plot using a trial and error optimization. The Koble–Corrigan isotherm model can be shown as follows:

$$q_e = \frac{A C_e^n}{1 + B C_e^n} \quad (10)$$

2.2.5. Khan isotherm model

Khan isotherm is a generalized model for the pure solutions. At relatively high correlation coefficients and minimum ERRSQ or chi-square values, its maximum uptake values can be well determined [33]:

$$q_e = \frac{q_s b_K C_e}{(1 + b_K C_e)^{a_K}} \quad (11)$$

2.2.6. Radke–Prausnitz isotherm model

The Radke–Prausnitz isotherm can be shown as follows [34]:

$$q_e = \frac{a_{RP} r_R C_e^{\beta_R}}{a_{RP} + r_R C_e^{\beta_R} - 1} \quad (12)$$

2.3. Multilayer physisorption isotherms

Brunauer–Emmett–Teller (BET) isotherm is a theoretical equation [35]:

$$q_e = \frac{q_s C_{BET} C_e}{(C_s - C_e) [1 + (C_{BET}/C_s) C_e]} \quad (13)$$

Meanwhile, Frenkel–Halsey–Hill (FHH) isotherm [36], another multilayer adsorption derivation from the potential theory may be written as:

$$\ln\left(\frac{C_e}{C_s}\right) = -\frac{\alpha}{RT} \left(\frac{q_s}{q_e d}\right)^r \quad (14)$$

Similarly, MacMillan–Teller (MET) isotherm model [37] interpreted from the inclusion of surface tension effects in the BET isotherm is termed as:

$$q_e = q_s \left(\frac{k}{\ln(C_s/C_e)}\right)^{1/3} \quad (15)$$

As a note, the empirical isotherm is reasonable fit to Frenkel–Halsey–Hill (FHH) or MacMillan–Teller (MET) isotherms for relative pressures higher than 0.8 and approximately Brunauer–Emmett–Teller (BET) isotherm for relative pressures lower than 0.35.

Jafari Behbahani *et al.* [38] a new model based on multilayer adsorption mechanism proposed to account asphaltene adsorption in porous media.

In the proposed model two steps are considered for asphaltene adsorption.

- The first adsorption step is taken as adsorption of asphaltenes in solution to the surface of the porous media.
- The second adsorption step is taken as the adsorption of asphaltenes in solution to those asphaltenes already adsorbed to the porous media.

Based on the multilayer adsorption mechanism, the monolayer kinetic adsorption model was modified as follow:

$$\frac{\partial \Gamma}{\partial t} = \Gamma_{\infty} k_1 (C^n^{-1} + k_2 C^n) - \Gamma [k_1 C (1 + k_2 C^{n-1}) + 1] \quad (16)$$

The proposed model included four parameters.

- k_1 is the first adsorption step parameter.
- k_2 is the second adsorption step parameter.
- n is the mean aggregation number of the adsorbed asphaltenes on porous media.
- Γ_{∞} is the maximum possible adsorption of asphaltene.

3. Results and Discussion

The main objective of this section is to compare the performance of adsorption isotherm models using the experimental data given in the literature [39] for calculating asphaltene adsorption in porous media. The absolute average deviation of the predicted adsorbed asphaltene weight percent values obtained for the studied adsorption isotherm models from their experimental values was calculated by following relation

$$AAD\% = \frac{\sum_{i=1}^N [w_{exp} - w_{model}] / w_{model}}{N} \quad (17)$$

Table 1 shows the average absolute deviation (AADs) of the asphaltene adsorption weight percent from the experimental data for studied crude oil using two parameter isotherm models.

Table 1 Absolute Deviation of the predicted asphaltene adsorption amount from the experimental results using the two parameter isotherm models

Asphaltene concentration(ppm)	Langmuir	Freundlich	Dubinin-Radushkevich	Temkin	Flory-Huggins	Hill
1000	9.8	6.8	8.5	9.5	9.1	7.6
2000	9.5	6.2	9.2	8.3	8.4	8.2
3000	10.2	7.1	8.7	9.2	9.4	8.6
4000	10.8	7.3	8.2	9.9	9.7	9.1
5000	11.1	6.5	9.6	8.4	8.6	8.7

Table 2 shows the average absolute deviation (AADs) of the asphaltene adsorption weight percent from the experimental data for studied crude oil using three parameter isotherm models.

Table 2 Absolute Deviation of the predicted asphaltene adsorption amount from the experimental results using the three parameter models

Asphaltene concentration(ppm)	Redlich-Peterson	Sips	Toth	Koble-Corrigan	Khan	Radke-Prausnitz
1000	4.5	5.1	4.9	5.2	4.8	5.3
2000	5.2	5.6	5.3	5.6	4.6	4.1
3000	4.8	6.3	4.1	5.7	4.1	5.2
4000	4.6	5.4	4.7	5.1	4.7	4.9
5000	5.8	6.7	4.6	5.1	5.1	4.6

Table 3 shows the average absolute deviation (AADs) of the asphaltene adsorption weight percent from the experimental data for studied crude oil using multilayer isotherm models.

Table 3 Absolute Deviation of the predicted asphaltene adsorption amount from the experimental results using the multilayer isotherm models

Asphaltene concentration(ppm)	Brunauer-Emmett-Teller	Frenkel-Halsey-Hill	MacMillan-Teller
1000	1.2	1.3	1.1
2000	0.9	1.1	1.2
3000	1.1	1.4	1.3
4000	1.4	0.9	0.9
5000	0.9	1.1	1.1

Figure 1 shows the performance of adsorption isotherm models in prediction the amount of asphaltene adsorption.

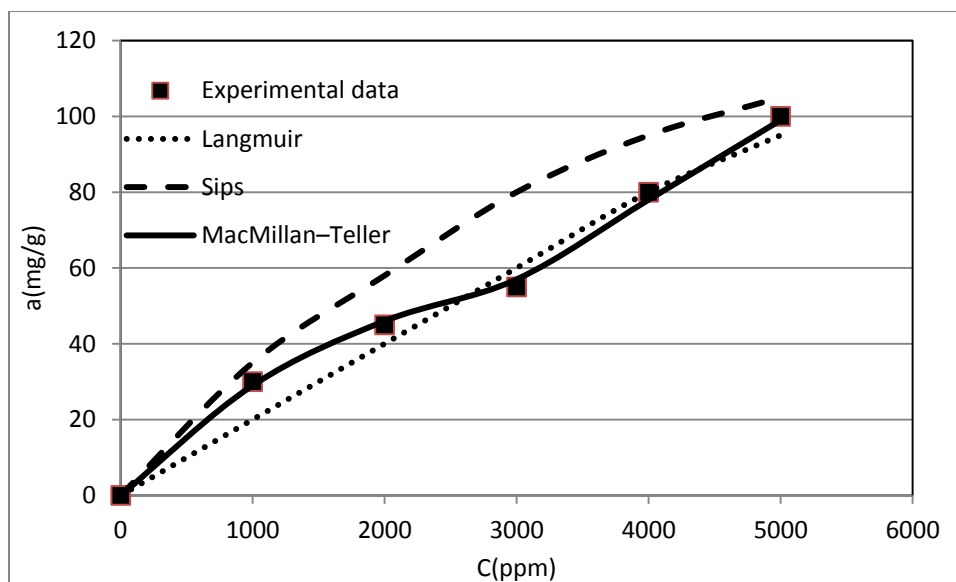


Figure 1 The performance of adsorption isotherm models in prediction the amount of asphaltene adsorption

The results show that the multilayer isotherm models predict the behavior of asphaltene adsorption better than the other two and three isotherm models with AAD less than 0.9-1.4%. Also, the two parameter isotherm models cause the deviation from experimental data and are not accurate for prediction of behavior of the asphaltene adsorption in porous media with AAD 6.2-11.1%. The results show that three parameter isotherm models are capable of prediction the asphaltene adsorption experimental data with the AADs of 4.1-5.7 %. This phenomenon can be justified by the fact that the asphaltene adsorption mechanism, which is related to the interactions between the asphaltenes functional groups and the porous media surface, involves surface polarity, affinity or other attractive forces. Asphaltene is a positive polar component therefore porous media especially carbonate sample have ability to absorb it. It is also known that asphaltene surface groups may be acidic (carboxylic, benzoic, phenolic), and/or basic (pyridine, pyrazine, dimethylsulfoxide) functionality. The adsorption of asphaltenes on porous media is the result of favorable interactions of the asphaltene species or its aggregates with chemical species on the porous media surface. A number of interaction forces, individually or in combination with each other, can be responsible for it. The major forces that can contribute to the adsorption process include electrostatic (Coulombic) interactions, charge transfer interactions, Van der waals interactions, repulsion or steric interactions and hydrogen bonding.

4. Conclusions

In this work, asphaltene adsorption in porous media has been investigated using different isotherm models. Also, the studied models were verified using the experimental data given in literature as follows:

1. The results show that multilayer isotherms can predict more accurately the asphaltene experimental data in comparison to the two and three parameter isotherm models in particular in carbonate samples with the absolute average deviation 0.9-1.4 %.
2. Also, the three parameters isotherm models can predict the asphaltene experimental data with absolute average deviation 4.1-5.7 %.
3. The two parameter isotherm models can predict the asphaltene experimental data with the absolute average deviation 6.2-11.1 %.

Therefore at higher concentrations multilayer isotherm models can predict more accurately the asphaltene experimental data in comparison to the two and three parameter isotherm models.

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