

Adsorption behavior of petroleum asphaltenes dissolved in Toluene by low-cost mineral adsorbents

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ABSTRACT

This paper presents the feasibility of the removal of asphaltenes from aqueous solutions by using low-cost natural adsorbents such as light expanded clay aggregate (LECA), perlite and bentonite. The structure of adsorbents was characterized by XRD, FTIR, and SEM before and after the adsorption of asphaltenes. The effect of the adsorbent type, initial asphaltene concentration, particle size of the adsorbent and temperature on the adsorption capacity was investigated. The results showed that at the initial asphaltene concentration of 125 mg L⁻¹, contact time of 24 h, temperature of 50°C and adsorbent dosage of 1 g, the removal of asphaltenes onto LECA, perlite and bentonite was 53.59, 93.01 and 99.77%, respectively. Also Langmuir and Freundlich models were applied to describe the experimental data. The results indicated a good fit by Langmuir isotherm. Thermodynamic parameters such as ΔH , ΔS and ΔG were also calculated. It was revealed that the adsorption was spontaneous and of exothermic nature, which was evident by decreasing the randomness of the dye at the solid and liquid interfaces. The characteristic results and dimensionless separation factor (RL) showed that perlite and bentonite can be employed as an alternative to commercial adsorbents for the removal of asphaltenes from the aqueous solution and oil.

1. Introduction

The worldwide increase in energy demand dictates the production of light oil fractions. Due to the presence of heavy components in oil and the cracking difficulties, finding proper solutions to overcome asphaltene precipitation and other similar problems seems necessary. Asphaltenes are defined as the components of crude oils that are insoluble in short branched normal alkanes, but are soluble in aromatics such as benzene and toluene. [1-3]. They are composed of aromatic polycyclic clusters variably substituted with alkyl group and contain heteroatoms (N, S, O) and trace metals (e.g., Ni, V, Fe) [4-9]. Any changes in the pressure, temperature and composition of the fluids can cause the asphaltene molecules to associate and form aggregates that may separate and form a new phase [9].

The adsorption of asphaltenes onto various solid surfaces has been investigated from different perspectives [10]. Asphaltenes are problematic components in the oil industry. Unwanted adsorption of asphaltenes onto various natural or industrial surfaces occurs which creates obstacles in the oil recovery, transportation, handling and processing. The adsorption of Asphaltenes on steel surfaces limits the flow of crude oil in piping systems [11]. Also, the adsorption and deposition of asphaltenes on surfaces create problems for the heavy oil recovery and upgrading. The deposition of asphaltenes on mineral surfaces and reservoir rocks changes the wettability of the surfaces and limits the extraction of heavy oils from the reservoirs. Furthermore, asphaltene adsorption onto the catalyst surfaces deactivates the catalysts [10]. These problems motivated the researchers to investigate the characteristics of such adsorptions for better control. Consequently, objectives of the previous studies to overcome these problems can be summarized as follows: 1) enhancing oil recovery by preventing the precipitation and deposition of asphaltenes in reservoirs, 2) improving the flow characteristics of heavy oil, 3) improving the separation of suspended particles from the crude oil, 4) improving the catalytic hydro conversion processes, 5) environmental cleaning and protection as asphaltene adsorption properties affect the way the contamination spreads in the soil, and 6) improving the efficiency of power transformers and preventing their failure [12].

The adsorption of asphaltene and resin have been the concern of a great number of studies [13-18]. In 2002, Ekholm et.al, studied and next tested asphaltene and resin absorption in a solution of toluene, n-heptane solution mixture of toluene and n-heptane (50:50) on a gold surface using the QCM. They observed that the adsorption of asphaltene is more than the absorption of resin on the surface of gold. So, as the amount of toluene increases, the resin adsorption on the surface of gold decreases. He also evaluated and measured changes in terms of frequency and Prandly function of time for the adsorption on the surface of the water like gold for three solutions mentioned above [19]. In 2005, Elbrand et.al, tested the adsorption of asphaltene on stainless steel, iron and aluminum powder using a UV-Vis device. They investigated the effects of resins, temperature and normal ratio of heptane to toluene. Langmuir adsorption was observed in all cases [20]. Similarly, Abdullah and Taylor (2007) studied the asphaltene properties of monolayer adsorption on the surface of stainless steel by using the XPS [21]. Balabyn et al., (2008) also studied the

asphaltene and resin adsorption on the surface of the iron and quartz. In this experiment, they absorbed kinetic and thermodynamic studies using the NIR and AFM devices. They found that the adsorption on the iron and quartz surface was followed by Langmuir's adsorption model and calculated the Langmuir adsorption constants [22]. Later in 2009, Nasser et al., studied the adsorption of asphaltene on metal catalysts: Cos, Co, Ni, Zno and comparing adsorption rates [23]. In the same line Safiwa et al., (2012) studied the adsorption of asphaltene on three dolomite, quartz, and Mica minerals, and obtained kinetic parameters for these three adsorbents [24]. Tarbosh (2014) also investigated the adsorption of asphaltenes in nanoparticles of commercially available particles such as NiO and Fe₂O₃ [25]. In the latest study, Jafari Behbahani (2014), also studied the adsorption of asphaltene at porous surfaces and examined all the adsorption models based on the empirical data [26].

In addition, there are several studies in the literature related to the adsorption of asphaltenes on different minerals including kaolinite, illite, montmorillonite [27]; quartz and silica-rich soil [28]; natural Brazilian quartz, dolomite, calcite and kaolin [29]; Berea sandstone, Bedford limestone and Mexican dolomite rock [30].

In this study, for the first time, we examined the new minerals such as light expanded clay aggregate (LECA), perlite and bentonite as the adsorbents for the removal of asphaltenes from aqueous solution. Structural changes of LECA, perlite and bentonite are discussed by the characterization techniques such as X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). Also, the influence of the various parameters such as type of adsorbent, initial asphaltene concentration, particle size of the adsorbent and temperature on the adsorption was investigated. The isotherm and thermodynamics of the asphaltenes adsorption were also studied.

2. Materials and Methods

2.1. Materials

LECA is a special type of clay that is pelleted and fired in a rotary kiln at very high temperatures. It was purchased from Azerbaijani Company, Kermanshah, Iran with the package price of \$ 28 per cubic meter. The adsorbent perlite was obtained from Tabriz, Iran with the cost per 5000 gr perlite of \$ 1 and bentonite was purchased from Chinikord Company, Kermanshah, Iran (with the cost per 30,000 grams of bentonite \$ 1). The chemical composition of the LECA, perlite and bentonite granules is shown in Table 1. LECA, perlite and bentonite were washed and placed in water for 24 h to be fully saturated. The samples were dried for 24 h at Avon 100 °C.

The asphaltenes used in this study were from Azadegan oil field, Sarvak rock reservoir. The oil had the viscosity of 42.63cP and density of 900 kg m⁻³ at 293 K. The asphaltenes content of the crude oil was about 8.52 wt %. The results of the SARA analysis for the sample, together with the molecular mass of its components, are presented in Table 2. In this study, the filtration method was used to separate the asphaltene from different proportions from the sediment solvent, because in this method pure asphaltenes can be isolated.

The basis of this test is the ASTM D2007-80 method. Modifications were also made to the test to obtain results with high repeatability and precision. [31].

Table 1. Chemical composition of LECA, perlite and bentonite granules

Compounds	Composition (%wt.)		
	LECA	Perlite	Bentonite
L.O.I*	0.35	4.42	3.95
Na ₂ O	1.735	2.215	0.32
MgO	3.165	0.882	0.287
Al ₂ O ₃	17.263	15.044	21.121
SiO ₂	61.51	67.866	70.75
P ₂ O ₅	0.195	0.19	0.116
SO ₃	0.387	0.036	0.381
Cl	0.103	0.046	-
K ₂ O	3.544	2.983	1.567
CaO	4.061	3.19	0.489
TiO ₂	0.678	0.392	0.443
MnO	0.129	-	-
Fe ₂ O ₃	6.739	2.662	0.53
Rb	0.009	-	-
Sr	0.104	0.055	0.027
Zr	0.028	0.018	0.02

*L.O.I: Loss On Ignition

Table 2. Specifications of oil 2 Azadegan oil field, Sarvak

Resin ratio to asphaltenes	Asphaltene	Resin	Aromatic	Saturation	density (API)	Crude oil components
2/1	8.52	18.1	42.1	31.28	25.57	(%Wt)
Colloidal instability index (CII)	Mw of Asphaltene		Mw of resin		Mw of oil	
0.7	gr/mol 1248		628		340	

2.2. Solution preparation

The initial solution containing asphaltene at a concentration of 3 g / l was prepared by dissolving 0.75 g dry asphaltenes in 250 ml of toluene. The mixture was left in a thermo-stated ultrasonic bath for 1 h to ensure a complete dissolution. Finally, model solutions with different concentrations were prepared by dilution.

2.3. Adsorption analysis

According to the results reported in the literature, in each adsorption experiment, 10 mL of dye solution with a known concentration was added to 1 g of LECA, perlite and bentonite in a 50 mL glass-stoppered flask at 25 ± 0.5 °C. The mixture was stirred on a mechanical shaker and concentrations were measured after 24 h equilibration. After 24 h mixing, the samples were centrifuged at 6000 rpm for 5 min to remove the mineral particles containing adsorbed asphaltenes from the liquid media. The concentration of asphaltenes in the supernatant was determined using a UV-Vis spectroscopy. Toluene solvent identical to those involved in the experiments was used as blank. The wavelength range of 190-1100 nm was covered. The absorbance at 420 nm was considered for the measurement of asphaltene concentration. The adsorption isotherms were studied in the concentration range of 100-1000 mg L⁻¹. All experiments were carried out twice, and the given concentrations were average values.

The adsorption performance was evaluated by the amount of asphaltene adsorbed per unit mass of adsorbent q_e (mg g⁻¹) as below:

$$q_e = \frac{C_0 - C_e}{m} V \quad (1)$$

Where, C_0 and C_e are the initial and equilibrium asphaltene concentration (mg L⁻¹), respectively, V is the asphaltene solution volume (mL), and m is the mass of adsorbent (g). Moreover, the amount of asphaltenes removal was calculated by Eq. (2):

$$\text{Asphaltene removal \%} = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

2.4. Characterization techniques

Scanning electron microscopy (SEM, HITACHI-S4160 Japan), X-ray diffraction (XRD, PHILIPS, XPERT MPD) and Fourier transformed infrared spectroscopy (FTIR, MB160 ABB BomemInc Canada) analyses were used to characterize the physico-chemical properties of LECA, perlite and bentonite.

3. Results and Discussion

3.1. Adsorbent characterization

The likely structural changes brought about by heat treatments were studied using the XRD analysis. Figure 1 shows the XRD profiles of LECA, perlite and bentonite samples. This analysis revealed that labradorite and quartz were dominant in the LECA structure. The typical characteristic peak in the diffraction pattern ($2\theta \approx 30.93$) is related to quartz. The broad powder X-ray

diffraction pattern of perlite in this figure confirms the absence of any ordered crystalline structure, which is typical of the amorphous solids. The typical characteristic peak in the diffraction pattern ($2\theta \approx 32.65^\circ$) is related to Al_2O_3 and quartz along with a broad peak at $2\theta = 32-90^\circ$ confirming the amorphous nature of silica [32]. The XRD pattern of bentonite is also presented in Figure 1. The analysis showed that kaolinite and quartz were dominant in the bentonite structure. The typical characteristic peak in the diffraction pattern ($2\theta \approx 30.01$) is related to quartz.

The FTIR spectra of LECA and loaded asphaltenes were recorded. As shown in Figure 2, several characteristic bands at 453, 623, 794, 1067, 1633, 3475 and 3682 cm^{-1} can be observed. The peak observed at 453 cm^{-1} is attributed to the Si-O bending vibration. The peak at 623 cm^{-1} is indicative of the perpendicular vibration of the octahedral cations R-O-Si (R= Fe, Al, Mg, etc.). Another peak at 794 cm^{-1} is assigned to the stretching vibration of Al-Mg-OH group [33, 34]. The band at 1000-1100 cm^{-1} is ascribed to Si-O stretching, and its variation in intensity and broadness is due to the structural changes in the tetrahedral cations. The peak at 1635 cm^{-1} is related to the bending vibrations of water molecules physisorbed on the LECA surface. Finally, the broad peak at 3475-3682 cm^{-1} is associated to the vibration of high amount of physisorbed water as Al-O-H [35].

The FT-IR spectra images of perlite and loaded asphaltenes were also recorded (Figure 3). In the FT-IR spectra of perlite, the peak at 3625 cm^{-1} might be due to the presence of uncondensed -OH groups. The peak at 1000 cm^{-1} is due to Si-O stretching vibrations in the Si-OH bond. The asymmetric stretching vibrations of Si-O-Si bridges were observed at 1191 cm^{-1} . The peak at 829 cm^{-1} indicates the presence of Al-OH-Mg bonds [36].

The FTIR spectra of bentonite and loaded asphaltenes were also recorded (Figure 4). As shown here, several characteristic bands can be observed at 480, 531, 611, 694, 796, 820, 1048, 1630, 3558 and 3675 cm^{-1} . The peak observed at 480 cm^{-1} is attributed to the Si-O bending vibration. The peak at 611-694 cm^{-1} is indicative of the perpendicular vibration of the octahedral cations R-O-Si (R= Fe, Al, Mg, etc.). The peak at 796 cm^{-1} is also assigned to the stretching vibration of Al-Mg-OH group [33, 34]. The band at 1000-1100 cm^{-1} is ascribed to Si-O stretching that its variation in intensity and broadness was due to structural changes in the tetrahedral cations. The peak at 1630 cm^{-1} is related to the bending vibrations of water molecules physisorbed on the bentonite surface. Finally, the broad peak at 3558-3675 cm^{-1} is associated to the vibration of high amount of physisorbed water as Al-O-H. Slight reductions in the peaks at 3700 cm^{-1} and 1000 cm^{-1} are seen but the peak positions have not been changed for any of the adsorbents. This clearly indicates the adsorption of asphaltenes on the adsorbents by the physical forces instead of the chemical combination [37].

As shown in Figure 5(a-f), the SEM images of LECA, perlite and bentonite were recorded. In the SEM micrograph 5 (a, c, e), the bright spots show the rough and porous surface of the adsorbents, which is one of the factors that increases the adsorption capacity. The loaded SEM images further show the adsorption of asphaltenes on LECA, perlite and bentonite (Figure 5(b, d, e)), depicting the surfaces of particles after the adsorption. It is clearly seen

that the caves, pores and surfaces of the adsorbents are covered by the asphaltenes; consequently, the surfaces have become smooth. It is evident that upon adsorbing the asphaltenes, the adsorbents' structure has changed.

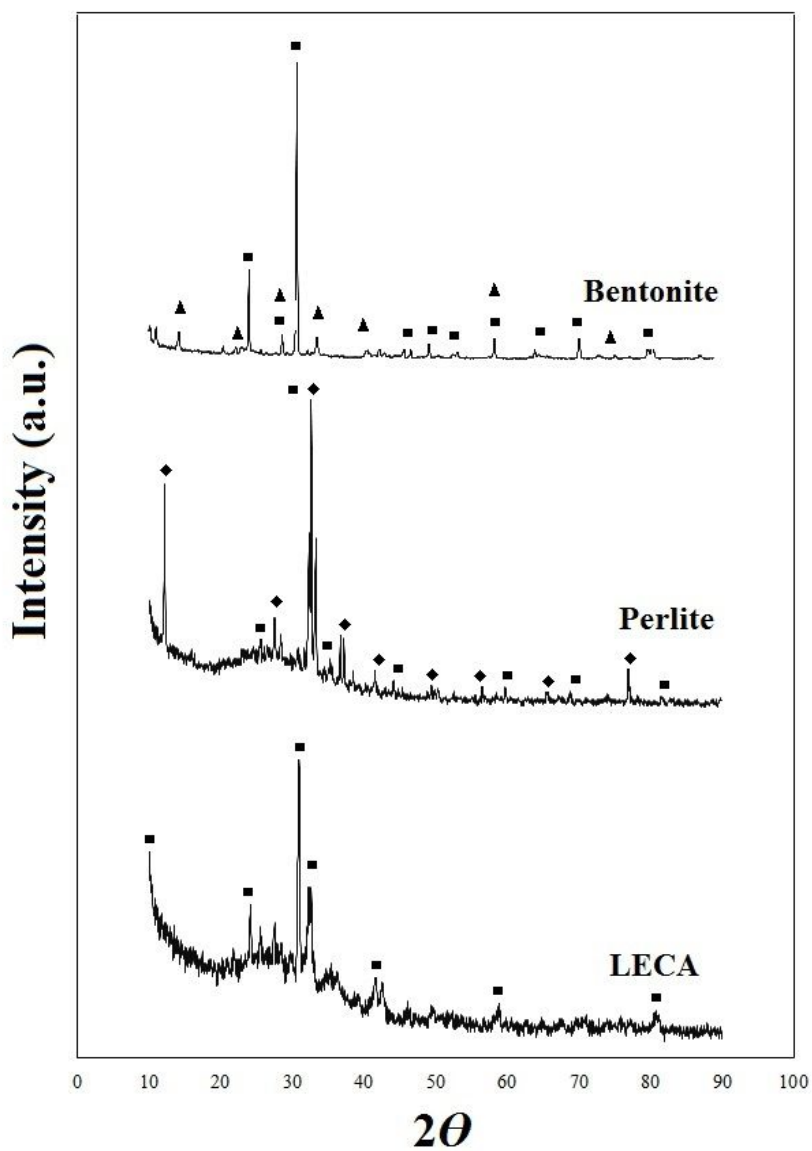


Figure 1. XRD spectrum of LECA, perlite and bentonite adsorbents. (SiO₂ (■), Al₂Si₂O₅(OH)₄ (▲) and Al₂O₃ (◆))

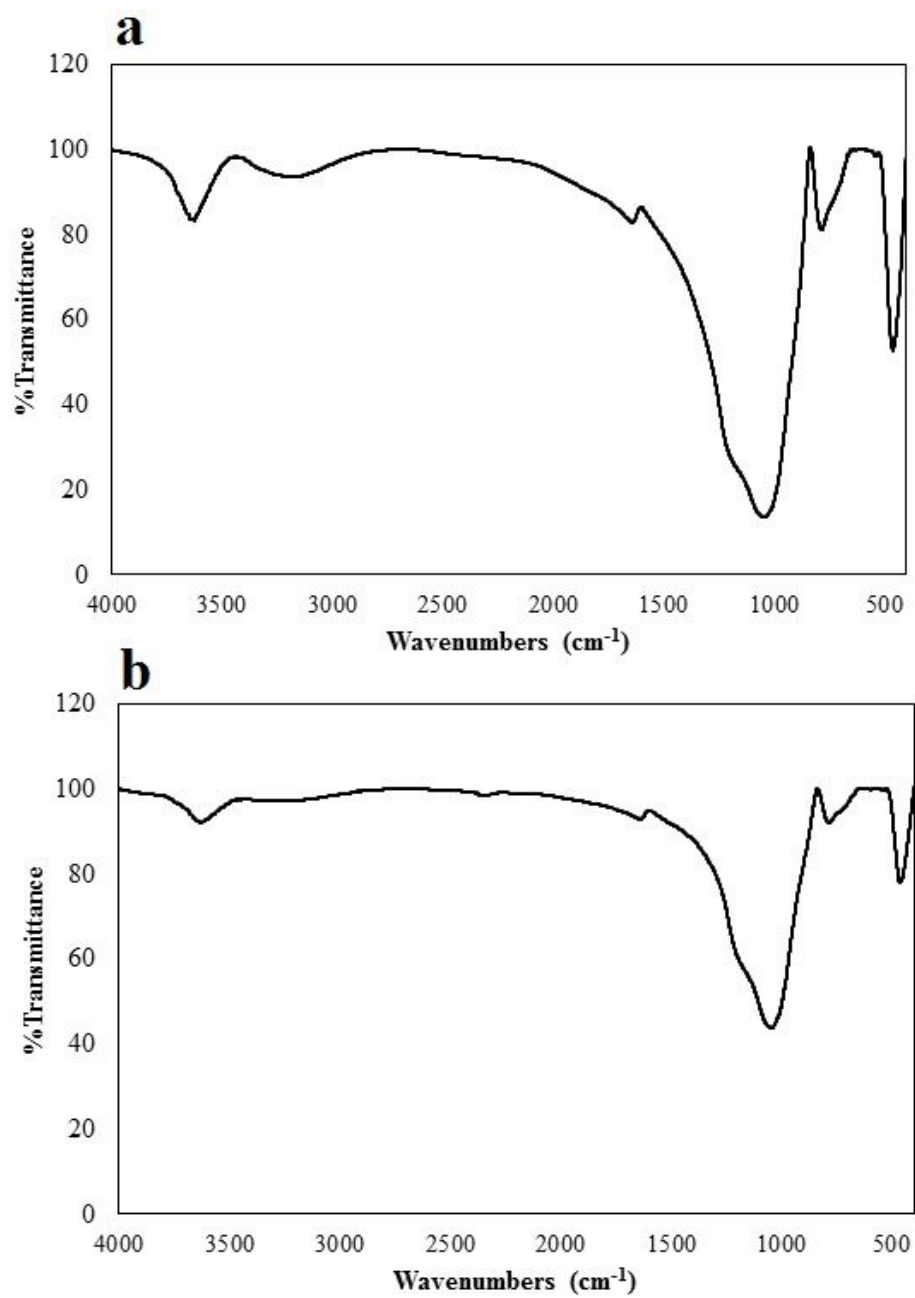


Figure 2. Fourier transformed infrared spectroscopy (FTIR) of LECA: (a) before adsorption and (b) after adsorption

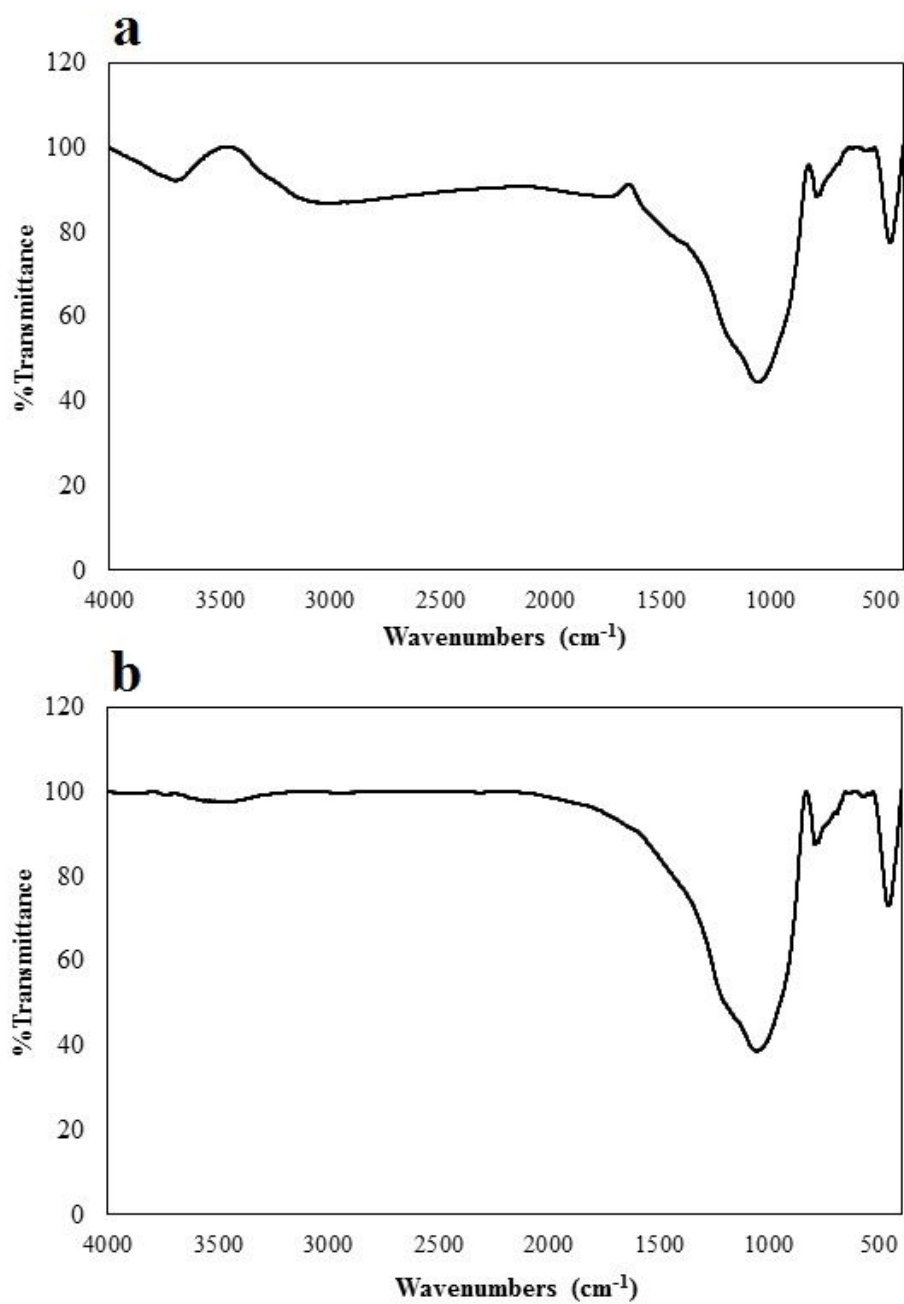


Figure 3. FTIR of perlite: (urea) before adsorption and (b) after adsorption

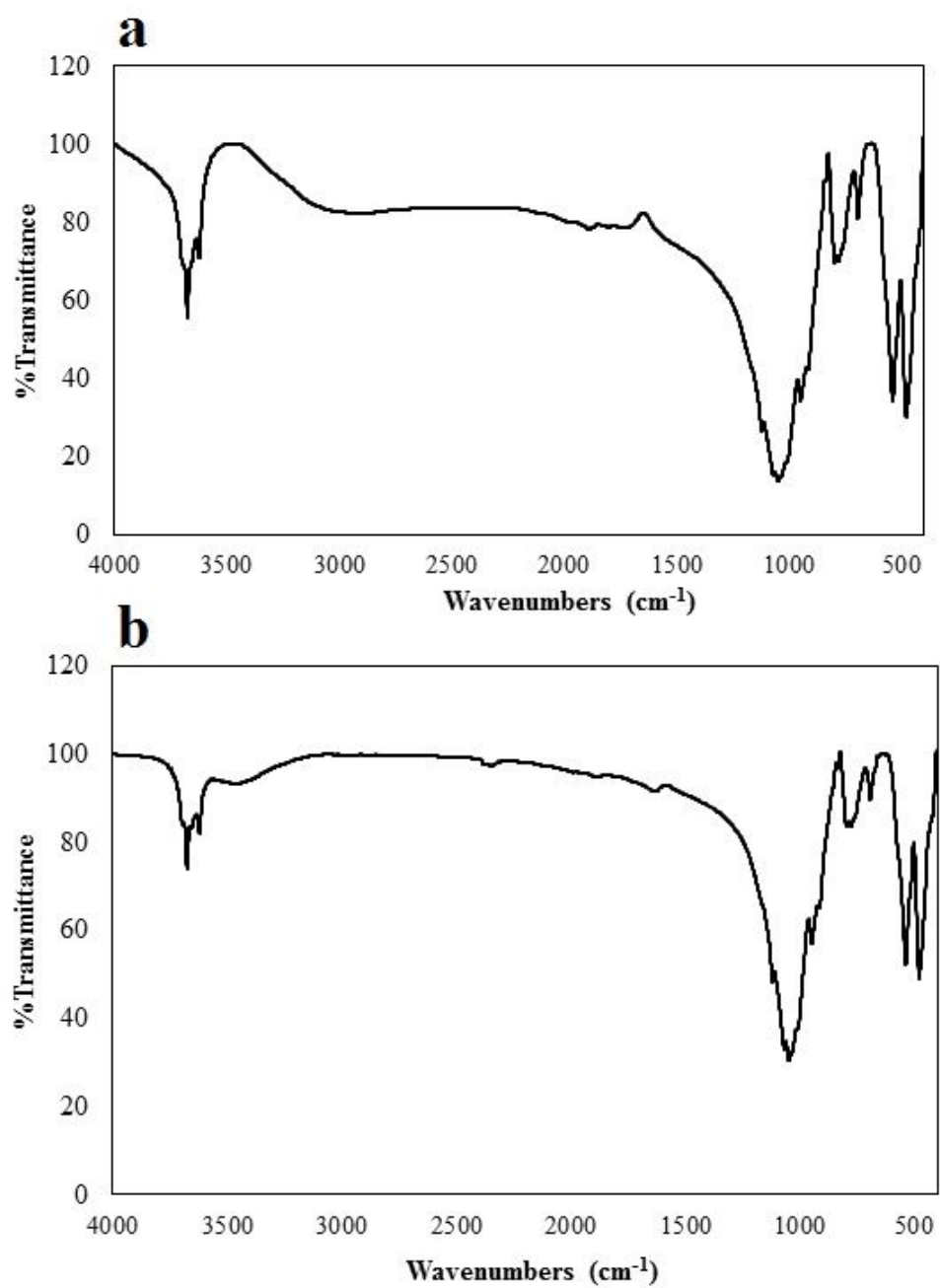


Figure 4. FTIR of bentonite: (a) before adsorption and (b) after adsorption

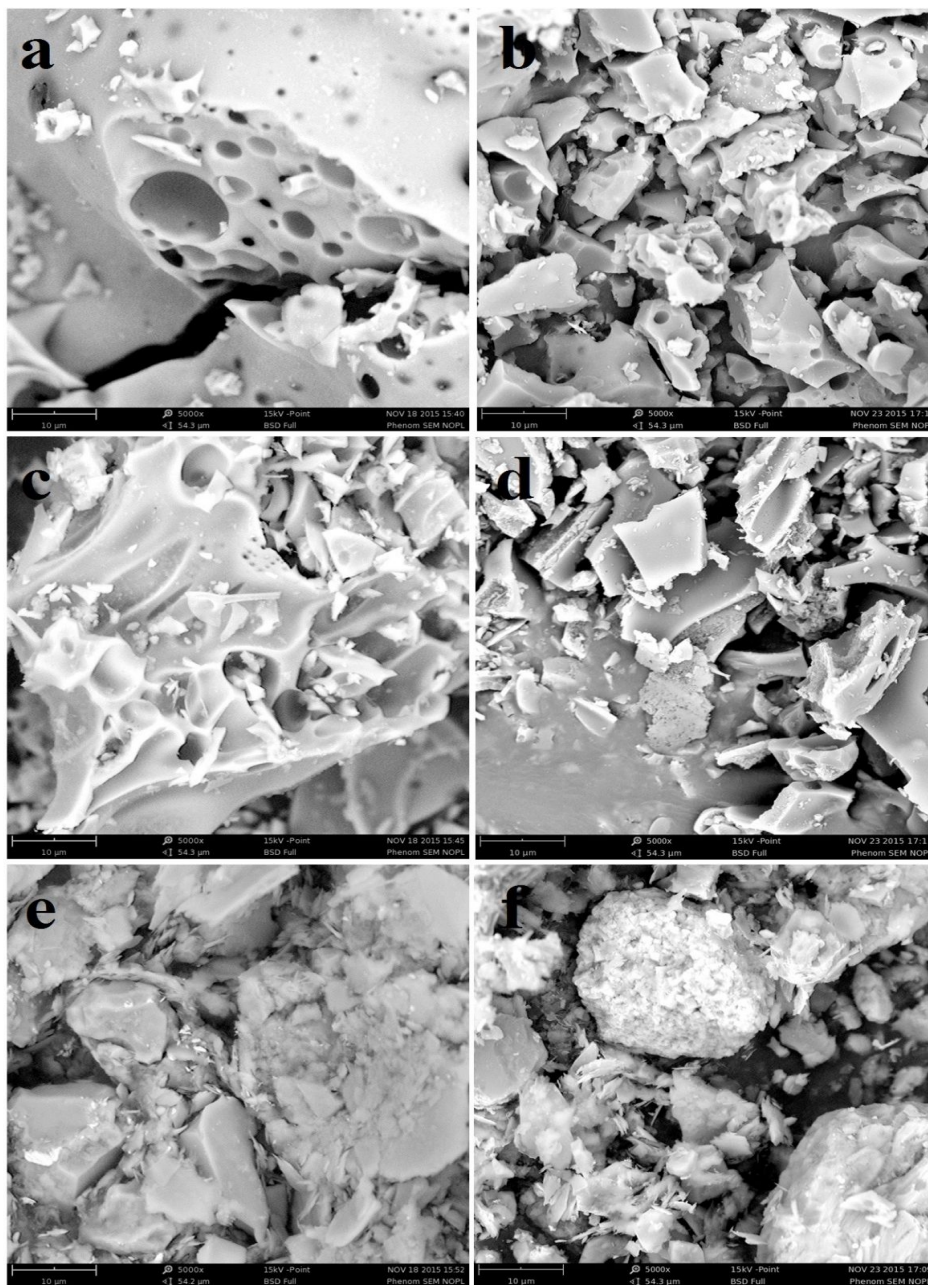


Figure 5. Scanning electron microscopy (SEM) of LECA, perlite and bentonite: (a) SEM image of LECA before the adsorption, (b) after the adsorption; (c) SEM image of perlite before the adsorption, (d) after the adsorption; (e) SEM image of bentonite before the adsorption and (f) after the adsorption

3.2. Effect of the adsorbent type

The surface chemistry and morphology of minerals and the chemical nature of asphaltenes and their solubility in toluene determine the nature of bonding mechanisms as well as the strength of the adsorption. The adsorption capacities of asphaltenes onto the three different selected mineral particles shown in Figure 6 suggest that the magnitude of the adsorption capacity was in

the order of bentonite > perlite > LECA. The results of SEM images in Figure 5 clearly show the caves, pores and surfaces of the adsorbents in order of bentonite> perlite> LECA. The BET surface area of LECA, perlite and bentonite was found to be 0.8, 2.6 and 41m²/g, respectively [38, 39].

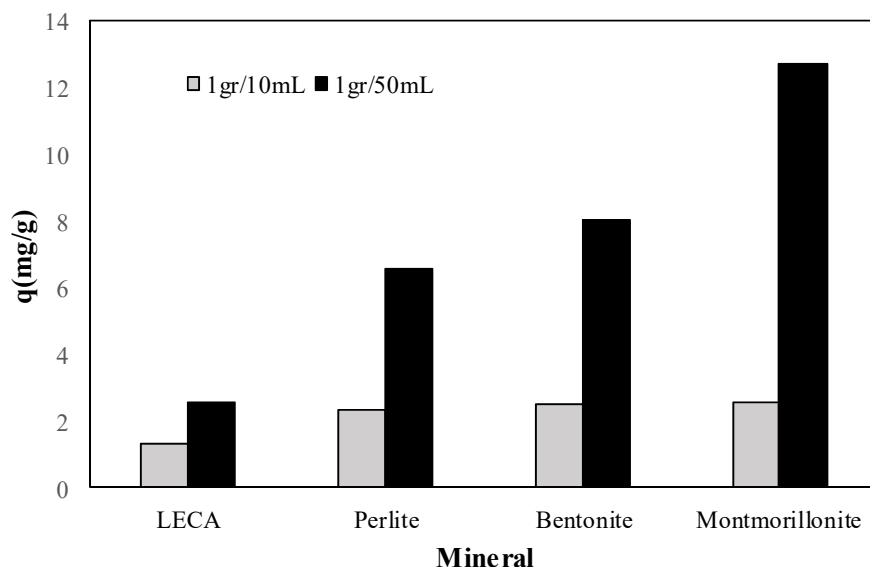


Figure 6. Effect of type of the adsorbent on the asphaltene adsorption (adsorbent dosage=1 g, initial asphaltene concentration =250 mg/L and contact time=24 h)

3.3. Effect of the initial asphaltene concentration

In order to investigate the effect of initial asphaltene concentration, the following tests were conducted with the initial asphaltene concentrations ranging from 100 to 1000 mg/L at the contact time of 24 h, mass mineral to asphaltene solution ratio of 1:10&1:50 and temperature of 25°C (Figure 7). The results showed that the initial asphaltene concentration had a significant effect on the amount of the adsorbed asphaltene. By increasing the initial asphaltene concentration from 100 to 1000 mg/L, the asphaltene adsorption capacity of LECA, perlite and bentonite significantly increased. This may be due to the fact that the higher concentration gradient between the aqueous solution and the adsorbents causes stronger driving force of the adsorption and the higher adsorption capacity.

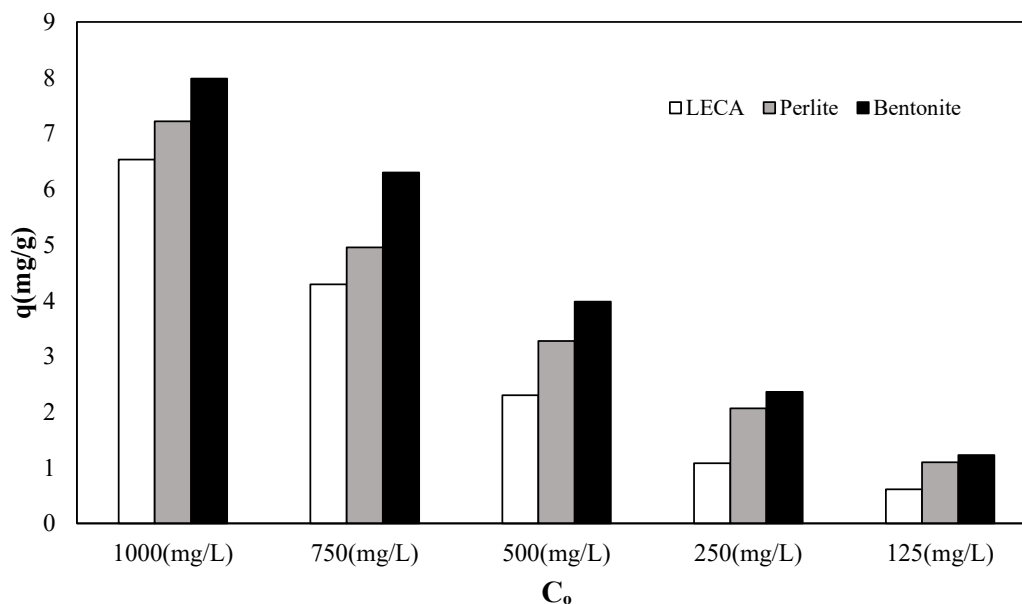


Figure 7. Effect of initial concentration on the asphaltene adsorption by LECA, perlite and bentonit, (adsorbent dosage=1 g/L and contact time=24

3.4. Effect of the size of adsorbent particles

To study the effect of particle size, the adsorbent particles with sizes 595 μm , 250 μm and 100 μm were used. In each study, 1g of the adsorbent in 10 mg L^{-1} of asphaltene solution was agitated to the equilibrium time of 24 h. Then, the adsorbent was separated, and the supernatant solution was analyzed for the asphaltene concentration. The amounts adsorbed for 595 μm , 250 μm and 100 μm particle size LECA, perlite and bentonite adsorbents were 1.08, 1.14, 1.34, 2.201, 2.33, 2.35, 2.43, 2.47 and 2.49 mg g^{-1} , respectively. It is evident from Figure 8 that an increase in the particle size decreased the percentage of the removal. At a fixed adsorbent dosage, the decrease in the particle size also increased the adsorbent uptake. The increase in the uptake by smaller particles is due to the greater accessibility to pores and to the greater surface area for the bulk adsorption per unit mass of the adsorbent.

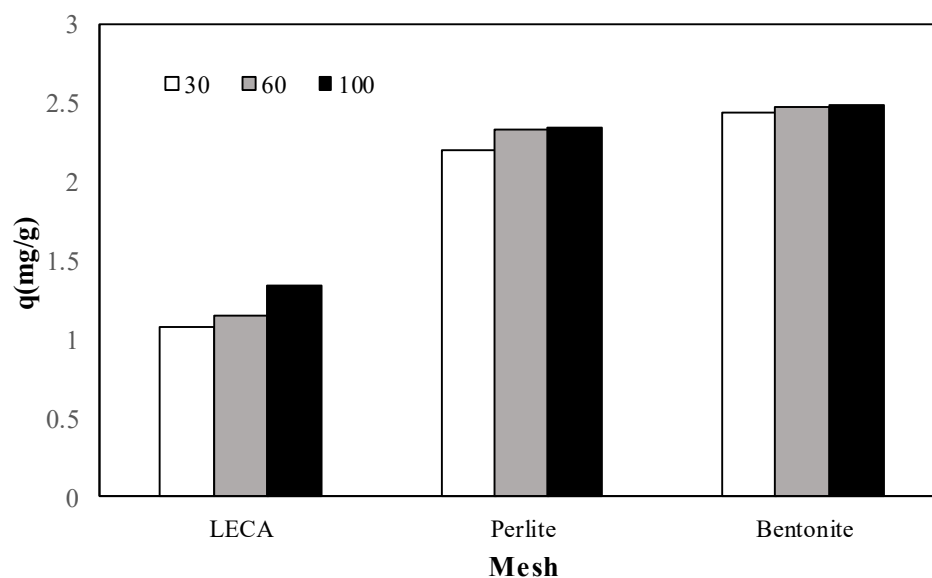


Figure 8. Effect of the size of mineral particles on the adsorption capacity of LECA, perlite and bentonite), (adsorbent dosage=1 g, initial asphaltene concentration =250 mg/L and contact time=24 h)

3.5. Effect of temperature

The effect of temperature on the asphaltene adsorption by LECA, perlite and bentonite was studied at the temperatures of 25, 50 and 75°C, the initial concentration of 250 mg L⁻¹, and the adsorbent dosage of 1 g L⁻¹ during 24 h. The results showed that when the temperature increased from 25 °C to 75 °C, the adsorption capacity of asphaltenes onto LECA, perlite and bentonite increased (Figure 9). Therefore, we can conclude that higher temperature facilitates the adsorption of asphaltenes on LECA, perlite and bentonite.

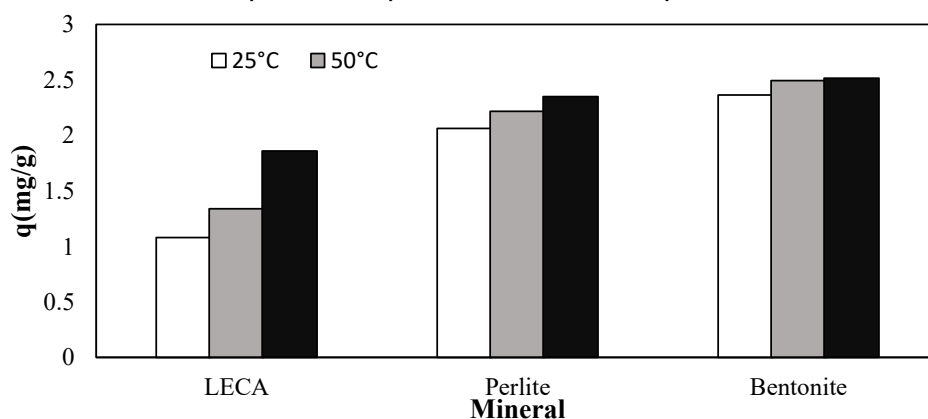


Figure 9. Effect of temperature on the asphaltene adsorption by LECA, perlite and bentonite, (adsorbent dosage=1 g, initial asphaltene concentration =250 mg/L and contact time=24 h)

3.6. Adsorption isotherms

The study of the equilibrium behavior of an adsorbent is necessary to design and optimize the adsorption systems. In this study, we analyzed the adsorption isotherms of all the adsorbent samples using Langmuir and Freundlich isotherms.

The concentration measurement was performed by UV device. In this device, the concentration is less than the greater accuracy considering the laboratory temperature. For this purpose, several experiments with initial concentrations of 250 mg L⁻¹, temperature of 25°C, and adsorbent dosage of 1 g L⁻¹ were conducted. The parameters of Langmuir and Freundlich isotherm models and their correlation coefficients are presented in Table 3.

Langmuir isotherm is based on monolayer coverage of the adsorbent's homogenous surfaces with the constant adsorption heat for all active sites, and its linear form is as follows [40]:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e \quad (3)$$

Where, q_e and q_m represent the amount of asphaltenes adsorbed at equilibrium and the maximum sorption capacity (mg g⁻¹), respectively. C_e is the asphaltene concentration in the solution at equilibrium (mg L⁻¹), and K_L is the Langmuir constant (L mg⁻¹). The maximum monolayer adsorption capacity obtained from the Langmuir plots for the LECA, perlite and bentonite adsorbents was 2.789, 4.050 and 4.275 (mg g⁻¹), respectively (Table 2).

The dimensionless separation factor (R_L) is the essential characteristic of Langmuir isotherm [39]:

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

Where, C_0 is the initial concentration (mg L⁻¹) and K_L is the Langmuir constant (L mg⁻¹). According to Table 1, variation of R_L for LECA, perlite and bentonite adsorbent is 0.6803, 0.1413 and 0.0303, respectively.

The R_L parameters between 0-1 represent that the asphaltenes adsorption by LECA, perlite and bentonite is propitious. Table 3 also indicates that the R_L value approaches zero as the severity of perlite and bentonite increases, meaning that the adsorption of asphaltenes onto LECA, perlite and bentonite is more favorable at high concentrations of the solution. In addition, the values of R_L prove that perlite and bentonite are more potential adsorbents for the adsorption of asphaltenes from aqueous solution in comparison to LECA.

Freundlich isotherm model is derived from the multilayer adsorption model and is applicable to high heterogeneous surfaces. The linear form of this model is as below [40]:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

Where, q_e is the amount of asphaltenes adsorbed at equilibrium (mg g⁻¹), C_e is the concentration of asphaltenes in the solution at equilibrium (mg L⁻¹),

K_F is the Freundlich constant (mg g^{-1}), and $1/n$ is the intensity of adsorption process (heterogeneity factor). The slope and intercept of the linear plot of $\log q_e$ versus $\log C_e$ are used to determine the heterogeneity factor ($1/n$) and Freundlich constant (K_F), respectively. The magnitude of the exponent $1/n$ indicates whether the adsorption is good ($0.1 < 1/n < 0.5$), moderately difficult ($0.5 < 1/n < 1$), or poor ($1/n > 1$) [41]. As can be seen in Table 2, the values of $1/n$ for all experiments are smaller than 1 which represent a favorable adsorption process. Additionally, by comparing the results of the correlation coefficient (R^2) values, it can be concluded that Langmuir model yields a better fit than Freundlich model, meaning that the asphaltene adsorption by perlite and bentonite samples has a monolayer nature with uniform distribution of the adsorption sites on their surfaces. On the other hand, it can be concluded that Freundlich model yields a better fit than Langmuir model which implies that the asphaltenes adsorption by LECA samples has a multilayer nature with the uniform distribution of adsorption sites on their surfaces.

3.7. Thermodynamic parameters

In engineering practice, the values of thermodynamic parameters such as enthalpy change (ΔH), entropy change (ΔS) and Gibbs free energy change (ΔG) must be taken into consideration in order to determine the spontaneity of a process. Based on Eq's 5-7, the thermodynamic parameters for LECA, perlite and bentonite were calculated at various temperatures and at optimum experimental conditions:

$$\Delta G = RT \ln K_d \quad (5)$$

$$K_d = \frac{C_e}{q_e} \quad (6)$$

$$\ln K_d = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (7)$$

Where, K_d is the distribution coefficient, q_e is the amount of asphaltene adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of asphaltene in the solution (mg L^{-1}), T is the temperature (K) and R is the ideal gas constant equal to $8.31 \text{ J mol}^{-1}\text{K}^{-1}$. By linear plotting of $\ln K_d$ versus T^{-1} , the values ΔH and ΔS can be estimated from the slopes and intercepts, respectively (Figure 10-12). The values of thermodynamic parameters for the adsorption of asphaltenes on LECA, perlite and bentonite samples are given in Table 4. For all samples at all temperatures, the values of ΔH were negative, indicating that the adsorption process was exothermic in nature. Also, the negative values of the entropy change suggest that the randomness decreases the removal of asphaltenes on LECA, perlite and bentonite [40]. Changes in the Gibbs free energy (ΔG) were negative for all the modified adsorbents at all temperatures, suggesting the spontaneous nature of the asphaltenes adsorption. In the case of untreated bentonite, it was observed that the value of ΔG was positive at 323 and 348 K. It means that increasing the temperature causes more unspontaneous and unfavorable asphaltenes adsorption by the untreated bentonite.

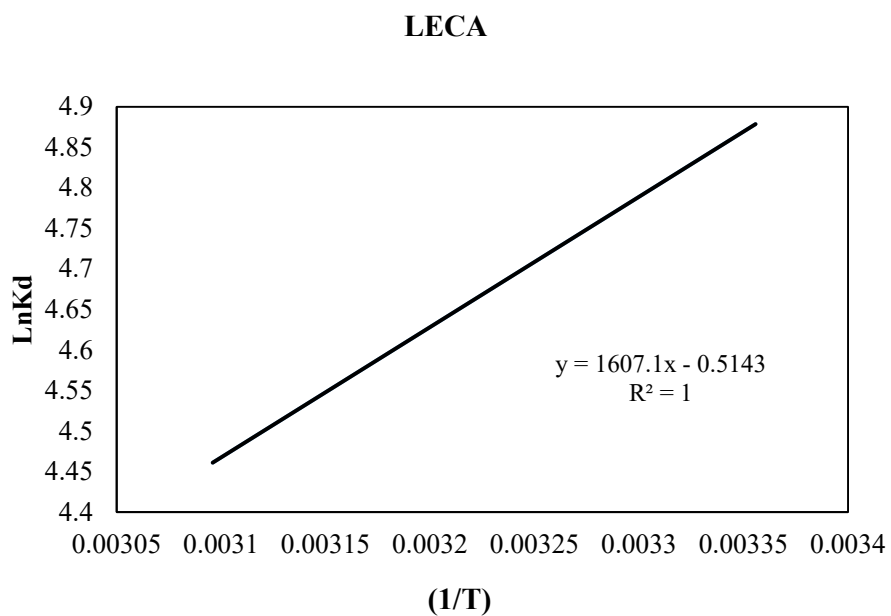


Figure 10. $\ln K_d$ vs. $1/T$, (slope = $\Delta H/R$ and intercept = $\Delta S/R$) for Leca

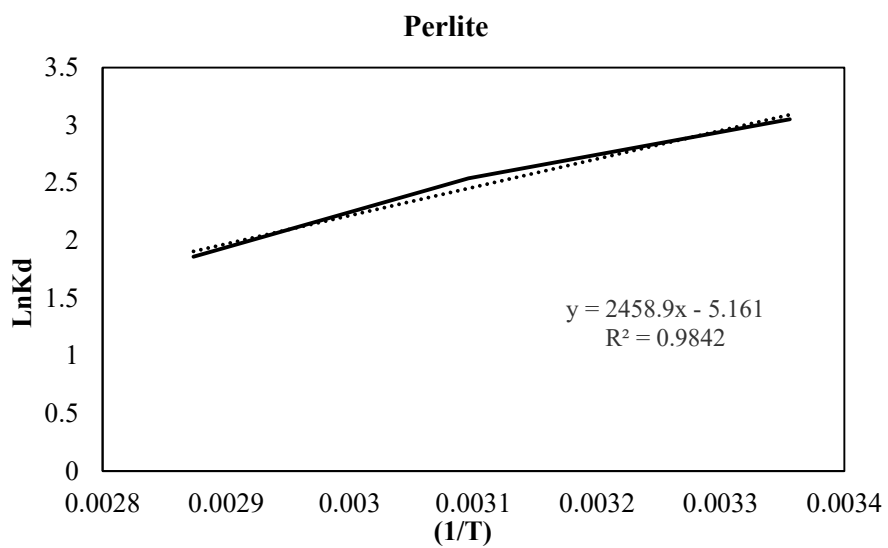


Figure 11. $\ln K_d$ vs. $1/T$, (slope = $\Delta H/R$ and intercept = $\Delta S/R$) for Perlite

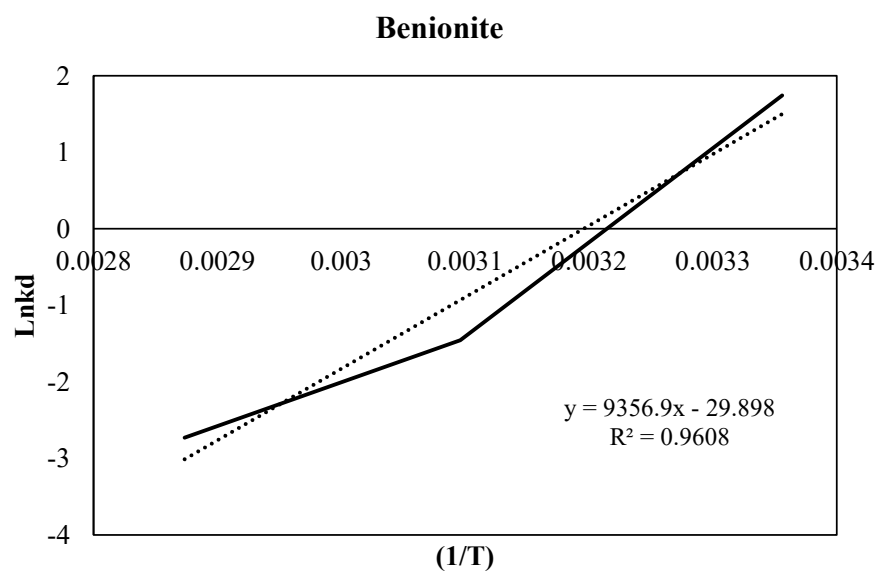


Figure 12. Ln Kd vs. 1/T, (slope = $\Delta H/R$ and intercept = $\Delta S/R$) for Benionite

Table 3. The Langmuir and Freundlich isotherms constants for adsorption of asphaltenes on LECA, perlite and bentonite

Adsorbent	q_{exp} (mg/g)	q_{max} (mg/g)	Langmuir isotherm			Freundlich isotherm		
			K_L	R_L	R^2	K_F	$1/n$	R^2
LECA	1.080	2.789	0.0019	0.6803	0.8064	0.0023	1.297	0.9025
perlite	2.064	4.050	0.0243	0.141	0.9999	0.3512	0.442	0.9736
bentonite	2.364	4.275	0.1280	0.0303	0.9971	0.8933	0.3845	0.9484

Table 4. Change of thermodynamic parameters with temperature

Adsorbent	Temperature (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol.K)
LECA	298	-12.081	-13.355	-0.004274
	323	-11.974		
	348	-10.232		
Perlite	298	-7.554	-20.433	-0.0429
	323	-6.813		
	348	-5.373		
Bentonite	298	-4.318	-77.756	-0.2485
	323	3.906		
	348	7.886		

4. Conclusions

For the first time in this study, new minerals such as leca, perlite and bentonite as adsorbent were investigated to remove asphaltene from the solution. The adsorbent structure characterized by techniques such as XRF, XRD, FTIR, and SEM before and after the absorption of asphaltene was described. Also, the effect of various parameters such as the adsorbent type, initial concentration of the asphaltene, adsorbent particle size and temperature on the absorption was investigated. Finally, the isotherm and thermodynamics of the asphaltene adsorption were also studied. The results of the study are as follows:

1. The surface chemistry and morphology of the minerals and the chemical nature of asphaltenes and their solubility in toluene give the nature of the bonding mechanisms as well as the strength of the adsorption. The adsorption capacities of asphaltenes onto the three different selected mineral particles suggest that the magnitude of adsorption capacity was in the order of bentonite > perlite > LECA. In addition, the results of SEM images in Figure 5 clearly show the caves, pores and surfaces of the adsorbents in order of bentonite > perlite > LECA. The BET surface area of LECA, perlite and bentonite was found to be 0.8, 2.6 and 41m²/g, respectively.
2. The initial concentrations of asphaltene have a significant effect on the asphaltene adsorption, so that with an increase in the initial concentration of asphaltene from 100 to 1000, the asphaltene adsorption rate for leca, perlite, and bentonite significantly increased.
3. In order to study the effect of particle size, adsorbent particles of 595 microns, 250 microns and 100 microns were used. It was observed that with increasing particle size in the adsorbent dose, the percentage of the removal reduced.
4. The effect of temperature on asphaltene adsorption by leca, perlite and bentonite was studied at 25 ° C, 50 ° C and 75 ° C. The results showed

that when the temperature ranged from 25 ° C to 75 ° C, the adsorption capacity of asphaltene increased on leca, perlite and bentonite.

5. Isotherm and thermodynamics of the asphaltene adsorption were also investigated.

6. Adsorption equilibrium was observed to fit well with Langmuir isotherm.

Thermodynamic parameters such as ΔH , ΔS and ΔG were calculated. It was revealed that the adsorption was spontaneous and of an exothermic nature, which was evident by decreasing the randomness of the dye at the solid and liquid interfaces. The characteristic results and dimensionless separation factor (RL) showed that perlite and bentonite can be employed as an alternative to commercial adsorbents for the removal of asphaltenes from aqueous solution and oil.

Nomenclature

XRD	X-ray diffraction
FTIR	Fourier transform infrared spectroscopy
SEM	scanning electron microscopy
cP	Dynamic Viscosity Unit
C_0	Initial concentration of asphaltene, (mg L ⁻¹)
C_e	asphaltene concentration in the solution at equilibrium , (mg L ⁻¹)
V	volume of solution (ml)
m	adsorbent mass , (g)
Θ	X-ray diffraction angle, (°)
q_m	maximum adsorption capacity (mg g ⁻¹)
R	ideal gas constant, $\left(\frac{J}{mol.K}\right)$
T	absolute temperature (K)
q_e	asphaltenes adsorbed at equilibrium) (mg g ⁻¹)
K_L	Langmuir constant , (L Mg ⁻¹)
K_F	Freundlich constant, (mg g ⁻¹)
ΔH	enthalpy change (kJ/mol),
ΔS	entropy change (kJ/mol.K)
ΔG	Gibes free energy change (kJ/mol)
K_d	distribution coefficient (ml)
R_L	dimensionless separation factor

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رفتار جذب آسفالتین محلول در تولوئن توسط جاذب های معدنی کم هزینه

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چکیده

در این مقاله امکان حذف آسفالتین از محلول با استفاده از جاذب طبیعی کم هزینه مانند لیکا، پرلیت و بنتونیت بررسی شد. ساختار جاذب ها توسط تکنیک های XRD، FTIR، SEM قبل و بعد از جذب آسفالتین توصیف شد. اثر نوع جاذب، غلظت اولیه آسفالتین، اندازه ذرات جاذب و دما بر ظرفیت جذب مورد بررسی قرار گرفت. نتایج نشان داد که در غلظت اولیه آسفالتین 1125 mg L⁻¹، زمان تماس ۲۴ ساعت، درجه حرارت ۵۰ درجه سانتی گراد و مقدار ۱ گرم جاذب، مقدار حذف آسفالتین توسط لیکا، پرلیت و بنتونیت به ترتیب ۵۳/۵۹، ۹۳/۰۱ و ۹۹/۷۷ درصد بود، همچنین مدل لانگمویر و فروندلیچ برای توصیف داده های تجربی به کار گرفته شد و نتایج نشان داد که مدل ایزوترم لانگمویر داده ها را بخوبی برازش می کند. پارامترهای ترمودینامیکی مانند ΔH ، ΔS و ΔG محاسبه شد. نشان داد که فرایند جذب خود به خودی و گرمازا است، که با کاهش اتفاقی رنگ در رابط جامد و مایع آشکار شد. نتایج شناسایی جاذب ها و فاکتور جداسازی (RL) نشان داد که از پرلیت و بنتونیت می توان به عنوان یک جاذب تجاری ارزان قیمت برای حذف آسفالتین از محلول و نفت استفاده کرد.

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