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Structural characterization of dodecyltrimethylammonium (DTMA) bromide modified sepiolite and its adsorption isotherm studies

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ABSTRACT

In this study, dodecyltrimethylammonium (DTMA) bromide was used to modify natural sepiolite via an ion exchange reaction to form DTMA-sepiolite. Sepiolite and DTMA-sepiolite were then characterized by using Brunauer–Emmett–Teller (BET), elemental analysis, XRD, FT-IR, thermogravimetric (TG) and zeta potential analysis techniques. The BET surface area of sepiolite significantly decreased from 152.14 m² g⁻¹ to 88.63 m² g⁻¹, after the modification, due to the coverage of the pores of sepiolite. DTMA was located onto sepiolite according to the differential thermogravimetric (dTG) peaks of DTMA-sepiolite. XRD results confirmed the interaction between DTMA⁺ cations and sepiolite. FT-IR spectra indicated the existence of DTMA functional groups on sepiolite surface. After the characterization was accomplished, adsorption isotherm studies of naphthalene, which is the first member of the polycyclic aromatic hydrocarbons (PAHs), were carried out. The maximum adsorption capacity of DTMA-sepiolite for naphthalene was determined from Langmuir isotherm equation at pH 6 and 20 °C as 1.88×10^{-4} mol g⁻¹ or 24.09 mg g⁻¹.

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1. Introduction

Sepiolite is a fibrous hydrated magnesium silicate and a natural clay mineral with a unit cell formula $[Si_{12}Mg_8O_{30}(OH)_4(H_2O)_4$. 8H₂O] and a general structure formed by the alternation of blocks and tunnels which grow up in the fiber direction. Each block consists of two tetrahedral silica sheets enclosing a central magnesia sheet. However, the silica sheets are discontinued and inversion of these silica sheets gives rise to tunnels in the structure. These characteristics of sepiolite make it a powerful adsorbent for organic molecules. In addition, some isomorphic substitutions in the tetrahedral sheets of the lattice of sepiolite, such as Al³⁺ instead of Si⁴⁺ form negative adsorption sites. Such sites are occupied by exchangeable cations that compensate for the electrical charge [1,2].

Most of clay minerals have high surface areas, but they are hydrophilic and thus they do not have large adsorption capacities for hydrophobic organic compounds [3]. However, clays such as sepiolite may be modified by surfactant coating in a manner that significantly enhances its capability to remove hydrophobic contaminants from aqueous solution [4,5]. This material is known as organoclay since the exchangeable inorganic cations are replaced by organic cations including quaternary ammonium compounds, which have cationic head groups with long chain hydrocarbon molecule forming the surfactant tail, thus it can be effectively used to remove hydrophobic nonionic organic compounds from aqueous solutions [4,6,7].

Natural sepiolite and modified sepiolite can be characterized by Brunauer–Emmett–Teller (BET), elemental analysis, XRD, FT-IR and thermogravimetric (TG) analysis techniques. The BET surface area significantly decreases, when natural sepiolite was modified with a surfactant due to the coverage of the pores of sepiolite.

Sepiolite has two types of water, which are magnesium coordinated water and adsorbed water. It is a trioctahedral type mineral with three divalent magnesium cations filling the three positions of the octahedron. The dehydration and dehydroxylation of the palygorskite clays have been examined by thermogravimetric analysis techniques [8–13].

Often, the combination of both the thermogravimetric (TG) and differential thermogravimetric (dTG) analysis curves may be used to interpret thermal behavior of natural sepiolite and organosepiolite. All mass loss events in natural sepiolite are associated with the loss of water. Up to 200 °C both hygroscopic and zeolitic water are lost. The bound water is released from the structure between 250 and 450 °C; more strongly bound water is left the structure in the temperature range 450–610 °C; and coordinated water is lost in the temperature range 730–860 °C. For sepiolite, the partial dehydration of bound H₂O in the ranges 250–610 and 210–550 °C results in the formation of sepiolite anhydride. Dehydration of the bound water in two steps is attributed to the difference in bonding position



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of water in the structure of this mineral. The amount of water uptake of sepiolite depends on the relative humidity of the environment to which they are exposed. Organo-cations can be located on the surface of sepiolite according to the differential thermogravimetric (dTG) analysis curve [14]. X-ray diffraction (XRD) analysis is conducted to evaluate the changes that occur in the interlamellar distance of sepiolite as a result of their interaction with hydrophobic organic compounds. Intercalation of a larger size of the surfactant cations is compared with that of the replaced cations among layers of clays not only changes the surface properties from hydrophilic to hydrophobic, but also greatly increases the interlamellar distance (basal spacing) of the layers, thus easing the attraction of hydrophobic organic molecules. The alkylammonium cations in modified sepiolite are arranged in monolayers, bilayers, pseudotrimolecular arrangements, as well as paraffin-type structures in the interlayer [15–17]. FT-IR spectra indicate functional groups of natural sepiolite and surfactant modified sepiolite.

Hydrophobic organic contaminants, e.g. polycyclic aromatic hydrocarbons (PAHs), are mainly generated during the incomplete burning of coal, oil, gas, wood, garbage, tobacco and charbroiled meat. They are well known one of the environmental pollutants and notable amounts produced and emitted. They are toxic, carcinogenic and mutagenic and can cause both short- and long-term health problems. Lower molecular mass PAHs e.g. naphthalene are not carcinogens and can cause short-term toxicity problems via inhalation and are characterized by high volatility; on the contrary, high molecular mass PAHs such as benzo(a)pyrene are known as human carcinogen. PAHs have also accumulated in the air, water bodies, soil and foods. Once inside the human body, PAHs can easily pass through cell membranes and are readily adsorbed into cells and therefore, the immune system converts PAHs to diolepoxides and epoxide hydrolase, which react to DNA and block its synthesis [18-20]. PAHs can enter natural water sources via atmospheric fallout, urban run-off, municipal wastes, industrial effluents and oil spillage or leakage. Although they also take place naturally, high levels of PAHs are mainly attributed to the anthropogenic sources, including oil spills, automobile exhaust, industrial processes, natural-gas consumption, coal refining processes, domestic heating systems, incinerators and smoke; and natural sources such as volcanic eruptions and forest fires [20–27].

Naphthalene is a natural constituent of coal tar and generally used as a wool preservative, moth repellent, and raw material for the production of fine chemicals. The source of naphthalene is mainly from the burning of fossil fuels. It, which is the simplest PAHs, has less toxicity than other PAHs and is easily found in the environment. In this study, naphthalene is chosen as a target compound to view as the primary method of inquiry dealing with complicated PAHs.

Various physical, chemical and biological techniques such as adsorption, microbial biodegradation, liquid-liquid extraction, steam stripping, and chemical oxidation have been attempt the removal of PAHs [28]. Liquid-liquid extraction is not feasible because it involves the introduction of another solvent in the waste stream. Microbial biodegradation is also not suitable for highly refractory organic compounds. Steam stripping is especially not practiced for compounds with boiling points higher than water. One of the most popular methods, which is namely adsorption, can be used the removal of PAHs from aqueous solutions. Although the most promising adsorbent for the adsorption method is activated carbon, which has a high surface area and high adsorption capacity, it is expensive and the regeneration stage alone can contribute to 80% of the operating cost, which limits their usage [28,29]. In this manner, there is a need to find the low-cost, locally available adsorbents, which can be an alternative to the activated carbon. Clays such as sepiolite, zeolite and montmorillonite are being considered alternative low-cost adsorbents for this purpose.

In this study, initially, natural sepiolite and dodecyltrimethylammonium (DTMA) bromide modified sepiolite were characterized by using various characterization methods. After that, the adsorption isotherm studies from aqueous solutions were accomplished. The experimental data were fitted into the Langmuir, Freundlich and Dubinin Radushkevich (D-R) isotherm equations to determine which isotherm gives the best correlation with the experimental data. The calculated thermodynamic parameters from the Langmuir isotherm constant (K_L) were also used to explain the nature of adsorption.

2. Materials and methods

2.1. Materials

Naphthalene was obtained from Merck and was used in the adsorption experiments. The adsorbent, which is sepiolite, was provided from Eskişehir-Turkey. It was crushed, ground and sieved through a 63 μ m size sieve. Then the samples were collected from under the sieve and dried in an oven at 110 °C for 2 h before use.

2.2. Material characterization

Natural sepiolite was characterized with respect to its cation change capacity (CEC) by the methylene blue method [30]. The BET surface area of natural sepiolite was determined from N₂ adsorption isotherm with a surface area analyzer (Quantachrome Instruments, Nova 2200e). The chemical analysis of natural sepiolite was conducted using an energy dispersive X-ray spectrometer (EDX-LINK ISIS 300) attached to a scanning electron microscope (SEM-Cam Scan S4). The crystalline phases present in sepiolite were determined via X-ray diffractometry (XRD-Rigaku Rint 2000) using Cu K α radiation.

Natural sepiolite and DTMA-sepiolite were analyzed by X-ray powder diffraction equipment (XRD-Bruker D8 Advance), before and after the modification procedure to observe the intercalation of surfactant into the sepiolite layers.

FT-IR spectra were recorded on transmission mode by using KBr pellets with a Jasco FT/IR-300E model Fourier transform infrared spectrometer to see functional groups of natural sepiolite and DTMA-sepiolite. Infrared spectroscopy with attenuated total reflection (ATR) technique was also performed to observe possible interactions between KBr and DTMA-sepiolite by using Bruker IFS 66v/S Model Infrared Spectrophotometer.

The elemental analysis (Vario EL III Elemental Analyzer, Hanau, Germany) of DTMA-sepiolite was performed to determine C/N ratio in DTMA-sepiolite. Thermal analysis (Setaram) was done to observe the modification of DTMA⁺ cations onto sepiolite. The analyses for natural sepiolite and DTMA-sepiolite were carried out in the temperature range 25–1000 °C and at a heating rate of 10 °C min⁻¹. Zeta potentials for natural sepiolite and DTMA-sepiolite in the presence of naphthalene were measured using Malvern Zetasizer Nano Series (UK) instrument.

2.3. Preparation of DTMA-sepiolite

The Na-exchanged form of sepiolite was prepared by stirring samples for 24 h with a 1 M aqueous solution of NaCl. Excess NaCl and other exchangeable cations were removed from the exchanged sepiolite by washing the latter several times with deionized water. Sepiolite was then re-suspended and filtered until a negative chloride test was obtained with 0.1 M AgNO₃.

The Na-saturated sepiolite (30 g) was dispersed in 0.8 dm³ of deionized water and DTMA-sepiolite prepared by adding DTMA-bromide at twice the cation-exchange capacity of sepiolite

and stirring for 24 h. After the treatment procedure, DTMA-sepiolite was washed with deionized water until free of salts and a negative bromide test had been obtained with 0.1 M AgNO₃ [31–35]. It was further used for naphthalene adsorption experiments.

2.4. Adsorption experiments

The pH experiments were conducted by mixing 50 ml of a 10 mg dm^{-3} aqueous naphthalene solution with 1 g dm^{-3} of DTMA-sepiolite concentration at 20 °C and various pH values in the range of 1.5–7.0. The solution pH was carefully adjusted by adding a small amount of HCl or NaOH solution and measured using a pH-meter (Fisher Accumet AB15), while naphthalene solutions contained in 100 ml Erlenmeyer flasks closed with glass stoppers to avoid evaporation, then they were stirred using a magnetic stirrer. The blank experiments were also carried out to observe the effect of vaporization of naphthalene. The amount of vaporization during the experiments was subtracted from the experimental data. Once the optimum pH had been attained as 6.0, contact time was determined at this pH value for the increasing periods of time, until no more naphthalene was removed from the aqueous phase and the equilibrium had been achieved. After such time (60 min), the samples were filtered and the equilibrium concentrations were ascertained by spectrophotometer (Shimadzu UV-2101PC) at the respective λ_{max} value, which is 219 nm for naphthalene. The amount of naphthalene adsorbed onto DTMA-sepiolite was determined by the difference between the initial and remaining concentrations of naphthalene solution. The adsorption capacity was determined by using the following equation taking into the concentration differences of the solution at the beginning and equilibrium accounts:

$$q_{\rm e} = (C_{\rm i} - C_{\rm e})V/m \tag{1}$$

where C_i and C_e are the initial and the equilibrium naphthalene concentrations (mg dm⁻³), *V* is the volume of solution (dm³) and *m* is the amount of adsorbent used (g).

In order to study the adsorption isotherms a 0.05 g of DTMAsepiolite were kept in contact with 50 ml of naphthalene solution at various concentrations to allow attainment of the equilibrium at constant temperatures of 10, 15 and 20 °C.

The adsorption data were analyzed to see whether the isotherm obeyed the Langmuir [36], Freundlich [37] and Dubinin-Radushkevich (D-R) [38] isotherm models. The Langmuir isotherm theory is based on the assumption that adsorption on a homogeneous surface possessing identical sites equally available for adsorption and with equal energies of adsorption involves with the adsorbent being saturated after one layer of adsorbate molecules has formed on the surface. The linear form of the Langmuir isotherm equation is represented by the following equation:

$$1/q_{\rm e} = 1/q_{\rm max} + (1/q_{\rm max}K_{\rm L})1/C_{\rm e}$$
⁽²⁾

where q_e is the equilibrium naphthalene concentration on the adsorbent (mol g⁻¹), C_e is the equilibrium naphthalene concentration in the solution (mol dm⁻³), q_{max} is the monolayer capacity of the adsorbent (mol g⁻¹), and K_L is the Langmuir constant (dm³ mol⁻¹) and related to the free energy of adsorption. The plots of $1/q_e$ versus $1/C_e$ for the adsorption of naphthalene onto DTMA-sepiolite give a straight line of slope $1/q_{max}$ K_L and intercept $1/q_{max}$.

The Freundlich isotherm describes adsorption when the adsorbate has a heterogeneous surface with adsorption sites that have different energies of adsorption. One limitation of the Freundlich model is that the amount of adsorbed solute increases indefinitely with the concentration of solute in the solution. The energy of adsorption varies as a function of the surface coverage (q_e) and is represented by the Freundlich constant K_F (dm³ g⁻¹) in the following equation:

$$\ln q_{\rm e} = \ln K_{\rm F} + 1/n \ln C_{\rm e} \tag{3}$$

where *n* (dimensionless) is the heterogeneity factor which has a lower value for more heterogeneous surfaces. The fit of the experimental data to the Freundlich model was explored by plotting $\ln C_e$ versus $\ln q_e$ to generate the values of K_F and *n*.

The Dubinin-Radushkevich (D-R) isotherm is more general than the Langmuir isotherm since it does not assume a homogeneous surface or constant adsorption potential. It was applied to distinguish between the physical and chemical adsorption of adsorbate. The linear form of D-R isotherm equation is

$$\ln q_{\rm e} = \ln q_{\rm m} - \beta \varepsilon^2 \tag{4}$$

where β is a constant related to the mean free energy of adsorption per mole of the adsorbate (mol² kJ⁻²), q_m is the theoretical saturation capacity, and ε is the Polanyi potential, which is equal to $RT \ln (1 + 1/C_e)$, where R (kJ mol⁻¹ K⁻¹) is the gas constant, and T (K) is the absolute temperature. Hence by plotting $\ln q_e$ versus ε^2 it is possible to obtain the value of q_m (mol g⁻¹) from the intercept, and the value of β from the slope.

3. Results and discussion

3.1. Characterization of adsorbents

In this study, sepiolite and DTMA-sepiolite were characterized by using Brunauer–Emmett–Teller (BET), elemental analysis, XRD, FT-IR, thermogravimetric (TG) analysis and zeta potential techniques.

3.1.1. Cation exchange capacity and surface area of adsorbents

Cation exchange capacity (CEC) of sepiolite was found to be as 544.3 mmol kg⁻¹. The BET surface areas of natural sepiolite and DTMA-sepiolite were 152.14 m² g⁻¹ and 88.63 m² g⁻¹, respectively. Since the interparticle pores of sepiolite are covered and the interlamellar spaces are blocked leading to the inhibition of the passage of N₂ molecules, therefore the BET surface area has decreased nearly two times with the modification.

3.1.2. Elemental analysis

The ratio of C/N for DTMA-sepiolite from elemental analysis results is 12.40 and the calculated value of C/N ratio is 12.86. These results confirm that the modification of sepiolite with DTMA-bromide was accomplished.

3.1.3. Chemical composition of sepiolite

X-ray diffraction (XRD) analysis together with the chemical analysis of sepiolite (29.3% SiO₂, 12.4% MgO, 9.09% CaO, and 34.99% CaCO₃) indicates that sepiolite and dolomite are the major components along with traces of Al_2O_3 (0.175%), K_2O (0.037%) and Fe_2O_3 (0.069%) in the form of impurities and loss of ignition (13.94%).

The XRD patterns of natural sepiolite and DTMA-sepiolite were recorded (Fig. 1) and their basal spaces were observed at 11.92 and 11.97 Å, respectively. The expansion in the basal spacing of the natural sepiolite due to the modification of sepiolite was calculated as $\Delta d = d - 11.92$ Å, where *d* is the basal spacing of the DTMA-sepiolite and 11.92 Å is the thickness of a clay mineral layer. Δd is found to be 0.05 Å. This result suggests that the expansion in the basal spacing of natural sepiolite with DTMA⁺ cations was not exactly observed and therefore it can be said that DTMA⁺ cations attached to the edges of sepiolite.

3.1.4. FT-IR analysis

FT-IR spectra of natural sepiolite and DTMA-sepiolite were illustrated in Fig. 2. The band at 3688 cm⁻¹ that corresponds to



Fig. 1. XRD patterns of: natural sepiolite (a) and DTMA-sepiolite (b).

stretching (v_{OH}) vibrations of hydroxyl groups (belong to Mg₃OH) attached to octahedral Mg²⁺ ions located in the interior blocks of natural sepiolite and DTMA-sepiolite. The band at 3619 cm⁻¹ indicates that assigned to Al–OH or Mg–OH stretching vibrations in both of samples. The broad band at 3418 cm⁻¹, observed each sample, is due to H–O–H vibrations of strongly hydrogen bonded [39].

A pair of bands at 2857 and 2929 cm⁻¹ was only observed with DTMA-sepiolite can be assigned to the symmetric and asymmetric stretching vibrations of the methylene group and their bending vibrations at around 1456 cm⁻¹, supporting the modification of functional groups of surfactant (DTMA⁺) cation, but these stretching bands are not observed in natural sepiolite [39,40]. The band at 1652 cm⁻¹ corresponds to the OH⁻ deformation of water.

The Si–O coordination bands at 1210, 1017, and 983 cm^{-1} are observed as a result of the Si–O vibrations. The intense band at 1017 cm⁻¹ represents the stretching of Si–O in the Si–O–Si groups of the tetrahedral sheet and two peaks at around 689 cm⁻¹ are represent the bending vibration of Mg₃OH in natural sepiolite and DTMA-sepiolite. The bands observed at 502 and 480 cm⁻¹ for natural sepiolite and DTMA-sepiolite related to Si–O–Al (octahedral) and Si–O–Si bending vibrations respectively. These results are also consistent with above elemental analysis results.

Infrared spectroscopy with attenuated total reflection (ATR) attachment was used for the observation of possible interactions between KBr and DTMA-sepiolite. Petit et al. [41] have indicated that the use of the KBr pressed pellet technique can affect NH₄⁺ exchangeability in NH₄⁺-smectites. During pellet preparation NH₄⁺ can be exchanged with K⁺ from KBr. In this manner, ATR-FTIR spectrum was recorded in this study for DTMA-sepiolite and the presence of the band near 1435 cm⁻¹ shows that ammonium ions in the interlayers of the clay mineral did not exchange with potassium from KBr [41,42].

3.1.5. Thermogravimetric analysis

Thermal analysis using thermogravimetric techniques enables the mass loss steps and the mechanism for the mass loss to be determined. The thermogravimetric (TG) analysis curve related to natural sepiolite exhibited mass losses by 1.897%, 0.462%, 5.268% and 22.46% in temperature ranges 25–150 °C, 300–350 °C, 480– 585 °C and 600–822 °C, respectively. Frost et al. [14] found that to natural sepiolite exhibited mass losses by 10.9%, 3.5%, 1.8%, 2.9% and 0.4% in temperature ranges 25–800 °C. The comparison this result with our results, total mass loss was 30.09% in this study and 19.5% in Frost et al. [14] study. The higher mass loss event was observed in this study.

The mass loss 1.897% at 25-150 °C related to the loss of adsorbed water (zeolitic water, which is in channels) according to the following reaction [14].

$$Si_{12}Mg_8O_{30}(OH)_4(H_2O)_4\cdot 8H_2O \rightarrow Si_{12}Mg_8O_{30}(OH)_4(H_2O)_4 + 8H_2O$$

The second mass loss 0.462% at 300–350 °C connected to the loss of hydration of water according to the following reaction.

$$Si_{12}Mg_8O_{30}(OH)_4(H_2O)_4 \rightarrow Si_{12}Mg_8O_{30}(OH)_4(H_2O)_2 + 2H_2O_{12}(OH)_4(H_2O)_2 + 2H_2O$$

The thirth mass loss 5.268% at 480–585 °C connected to the loss of coordination water according to the following reaction.

$$Si_{12}Mg_8O_{30}(OH)_4(H_2O)_2 \rightarrow Si_{12}Mg_8O_{30}(OH)_4 + 2H_2O_6$$

The fourth mass loss 22.46% at 600–822 °C connected to the loss of water through dehydroxylation according to the following reaction.

$$Si_{12}Mg_8O_{30}(OH)_4 \rightarrow 8MgSiO_3 + 4SiO_2 + 2H_2O_3$$

Differential thermogravimetric (dTG) analysis of natural sepiolite and DTMA-sepiolite were illustrated in Fig. 3a and b to observe the modification. The intensity of the differential thermogravimetric (dTG) peaks for DTMA-sepiolite in the temperature region of 25–100 °C was lower than natural sepiolite due to the hydrophobicities of this sample as it can be seen from Fig. 3a and b. The dTG peak between 300 and 400 °C, centered at 365 °C, was observed in DTMA-sepiolite and it confirms the bonding of the surfactant with sepiolite, but this peak is not observed in natural sepiolite.

3.1.6. Zeta potential measurements

The zeta potential graphs for natural sepiolite and DTMA-sepiolite in the presence of naphthalene were depicted in Fig. 4, as a function of suspension pH. As shown in Fig. 4, natural sepiolite has a point of zero charge (pH_{pzc}) at 4.33. The zeta potential is important in the case of DTMA-sepiolite in naphthalene solution and dependent on pH (Fig. 4). The point of zero charge was measured as 4.62 for DTMA-sepiolite in naphthalene solution.

3.2. Adsorption variables

The effects of pH, contact time, adsorption isotherms and thermodynamics were discussed in detail in this part.

3.2.1. Effect of pH

The effect of pH on the removal of naphthalene onto DTMAsepiolite from aqueous solution was illustrated in Fig. 5. As it can be seen from Fig. 5, the maximum naphthalene removal was observed at around neutral pH values. Naphthalene adsorption decreases at pH 1.5, when it is compared with adsorption at neutral pH values. Adsorption increases with the increasing pH value at around 3 and there is almost no further increase in the adsorption up to pH 6 and all experiments were carried out at pH 6.

3.2.2. Effect of contact time

The influence of contact time on the amount of naphthalene adsorbed was investigated at 20 °C as shown in Fig. 6. It can be seen that the amount of adsorption increased with increasing contact time. Maximum adsorption was observed after 75 min, beyond which there was almost no further increase in the adsorption. This was therefore fixed as the equilibrium contact time.



Fig. 2. FTIR spectra of: natural sepiolite (a) and DTMA-sepiolite (b).

3.2.3. Adsorption isotherms

The Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm graphs are illustrated in Figs. 7–9 and their calculated parameters for the adsorption of naphthalene onto DTMA-sepiolite are being listed in Table 1. It is evident from these data that the adsorption of naphthalene onto DTMA-sepiolite is fitted well to all of the isotherm models as indicated by the r^2 values in Table 1.

The adsorption capacity of DTMA-sepiolite increased with increasing in the temperature. The highest value of $q_{\rm max}$ obtained at 20 °C is 1.88×10^{-4} mol g⁻¹ or 24.09 mg g⁻¹ (Table 1) with the $r_{\rm L}^2$ values of 0.975. The $q_{\rm max}$ values of naphthalene adsorbed onto DTMA-sepiolite increased as temperature increased, suggesting that the adsorption of naphthalene may be endothermic. The

Langmuir constant (K_L) for naphthalene adsorbed onto DTMA-sepiolite increased from 2.13 × 10³ to 2.57 × 10³ dm³ mol⁻¹ as the temperature increased from 10 to 20 °C indicating that the affinity of binding sites for naphthalene increased with increasing temperature.

In this study, the maximum adsorption capacity of DTMA-sepiolite obtained for naphthalene was 24.09 mg g⁻¹ from the Langmuir adsorption isotherm model. It was comparable to data in the literature with Triton X-100 impregnated chitosan hydrogel beads (TCB) (32.39 mg g⁻¹) [22], CTAB impregnated chitosan hydrogel beads (CCB) (31.77 mg g⁻¹) [22], SDS impregnated chitosan hydrogel beads (SCB) (28.66 mg g⁻¹) [22], petroleum coke-derived porous activated carbon (0.0463 mg g⁻¹) [27],



Fig. 3. Differential thermogravimetric (dTG) curves of: natural sepiolite (a) and DTMA-sepiolite (b).

HDTMA-montmorillonite (0.342 mg g⁻¹) [43], BDTDA-montmorillonite (3.888 mg g⁻¹) [43], TPMA-montmorillonite (5.141 mg g⁻¹) [43], HDTMA-kaolinite (21.02 mg g⁻¹) [44], HDTMA-halloysite (28.45 mg g⁻¹) [44] and particulate organic matter (POM) (0.0272 mg g⁻¹) [45]. As it can be seen from above results, the maximum adsorption capacity of DTMA-sepiolite was found to be higher than that of many corresponding adsorbents reported in the literature.

The effect of isotherm shape has been discussed [46] with a view to predict whether an adsorption system is favorable or unfavorable. The essential feature of the Langmuir isotherm can be expressed by means of ' R'_L ', a dimensionless constant referred to as separation factor or equilibrium parameter. R_L is calculated using the following equation.

$$R_{\rm L} = 1/(1 + K_{\rm L}C_{\rm o}) \tag{5}$$

where C_o is the initial naphthalene concentration (mol dm⁻³). The calculated values of R_L as above equation are incorporated in Table 1. As the R_L values lie between 0 and 1, the on-going adsorption process is favorable [46]. In this study, the R_L values for naphthalene

onto DTMA-sepiolite lie between 0.689 and 0.728; therefore, its adsorption is favorable.

The values of K_F derived from the Freundlich model at all temperatures lie at a range of 0.087–0.115 dm³ g⁻¹. The numerical values of *n* at all temperatures change from 1.139 to 1.185 and are greater than unity, indicating that naphthalene is favorably adsorbed by DTMA-sepiolite at all the studied temperatures.

For the D-R isotherm model, the $q_{\rm m}$ values were 1.39×10^{-3} , 1.43×10^{-3} and 1.84×10^{-3} mol g⁻¹ and the β values were 8.39×10^{-3} , 7.76×10^{-3} and 7.77×10^{-3} mol² kJ⁻² at 10, 15 and 20 °C, respectively.

3.2.4. Thermodynamic parameters

In any adsorption process, both energy and entropy considerations must be taken into account in order to determine what the process occurs spontaneously. Values of thermodynamic parameters are the actual indicators for practical application of a process. The amount of naphthalene adsorbed at equilibrium at various temperatures (10, 15 and 20 °C) has been examined to obtain thermodynamic parameters for the adsorption system.



Fig. 4. The zeta potentials of natural sepiolite and DTMA-sepiolite in the presence of naphthalene.



Fig. 5. Effect of pH for the adsorption of naphthalene onto DTMA-sepiolite at 20 $^\circ$ C.

Because K_L is the Langmuir constant and its dependence on the temperature, it can be used to estimate the thermodynamic parameters, such as the change in the Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) associated to the adsorption process and they were determined by using the following equations:

$$\Delta G^{\circ} = -RT \ln K_{\rm L} \tag{6}$$

$$\ln K_{\rm L} = -\Delta G^{\circ}/RT = -\Delta H^{\circ}/RT + \Delta S^{\circ}/R \tag{7}$$



Fig. 6. Effect of contact time for the adsorption of naphthalene onto DTMA-sepiolite at 20 $^\circ\text{C}.$



Fig. 7. Langmuir plots for the adsorption of naphthalene onto DTMA-sepiolite at various temperatures.



Fig. 8. Freundlich plots for the adsorption of naphthalene onto DTMA-sepiolite at various temperatures.

The plot of ln K_L as a function of 1/*T* (Fig. 10) yields a straight line from which ΔH° and ΔS° were calculated from the slope and intercept, respectively.



Fig. 9. D-R plots for the adsorption of naphthalene onto DTMA-sepiolite at various temperatures.

Table 1

Isotherm constants for the adsorption of naphthalene onto DTMA-sepiolite at various temperatures.

	<i>T</i> (°C)		
	10	15	20
Langmuir			
$q_{\rm max} ({\rm mol}{\rm g}^{-1})$	1.52×10^{-4}	$1.75 imes 10^{-4}$	$1.88 imes 10^{-4}$
$K_{\rm L} ({\rm dm^3 mol^{-1}})$	$2.13 imes 10^{3}$	$2.32 imes 10^3$	$2.57 imes 10^3$
r_1^2	0.976	0.995	0.975
RL	0.728	0.711	0.689
Freundlich			
n	1.139	1.185	1.153
$K_{\rm F} ({\rm dm^3}{\rm g}^{-1})$	0.087	0.078	0.115
$r_{\rm F}^2$	0.975	0.991	0.982
Dubinin–Radushkevi	ch (D–R)		
$q_{\rm m}~({ m mol}~{ m g}^{-1})$	$1.39 imes 10^{-3}$	$1.43 imes 10^{-3}$	$1.84 imes 10^{-3}$
β (mol ² kJ ⁻²)	$8.39 imes 10^{-3}$	$7.76 imes 10^{-3}$	$7.77 imes 10^{-3}$
$r_{\rm D-R}^2$	0.973	0.993	0.980



Fig. 10. Plot of ln K_L versus 1/T for the estimation of thermodynamic parameters for the adsorption of naphthalene onto DTMA-sepiolite.

The overall free energy changes during the adsorption process were -18.04 kJ mol⁻¹ at 10 °C, -18.56 kJ mol⁻¹ at 15 °C and

-19.13 kJ mol⁻¹ at 20 °C, which were all negative, corresponding to a spontaneous process of naphthalene adsorption and that the system does not gain energy from an external source.

The low positive value of the enthalpy change $(+7.161 \text{ kJ mol}^{-1})$ indicates that the adsorption is physical in nature involving weak forces of attraction and is also endothermic. The positive entropy change (ΔS°) value $(+88.10 \text{ J mol}^{-1} \text{ K}^{-1})$ corresponds to an increase in the degree of freedom of the adsorbed species [47].

4. Conclusions

In this study, natural sepiolite was firstly modified by using a surfactant, dodecyltrimethylammonium (DTMA) bromide, to obtain DTMA-sepiolite. The BET, XRD, elemental analysis, FT-IR, thermal analysis and zeta potential measurement methods were used for the characterization of adsorbents. Since the pores of natural sepiolite are coverage with modification, the BET surface area decreases. The XRD results revealed that DTMA⁺ cations attached to the edges of sepiolite. TGA and dTG results confirm to the modification of sepiolite with DTMA-Br. The functional groups of natural sepiolite and DTMA-sepiolite were determined by using FT-IR spectrophotometer. The adsorption dynamics of naphthalene onto DTMA-sepiolite were then investigated. The experimental data were fitted well to the Langmuir, Freundlich and D-R adsorption isotherm models. The maximum adsorption capacity for the removal of naphthalene obtained from Langmuir adsorption isotherm model was found to be as $1.88 \times 10^{-4} \text{ mol g}^{-1}$ or 24.09 mg g⁻¹ at pH 6 and 20 °C.

The enthalpy change (ΔH° = +7.161 kJ mol⁻¹) for the adsorption process indicated that the weak physical forces occurred between naphthalene molecules and DTMA-sepiolite. The ΔG° values were negative at all studied temperatures, therefore the adsorption was spontaneous. The positive value of ΔS° suggests an increase randomness at the solid/solution interface through the adsorption of naphthalene onto DTMA-sepiolite. It may be concluded that DTMA-sepiolite acts a respective adsorbent for the removal of hydrophobic organic contaminants in aqueous solutions.

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