Research Paper

Attapulgite as Potential Adsorbent for Dissolved Organic Carbon from Oily water†

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Abstract

The adsorption capacity of attapulgite, a natural clay, for the removal of dissolved organic carbon (DOC) from oily water was investigated in a batch system. The aim of this study was to understand the mechanism associated with the removal of DOC by attapulgite. The effectiveness of attapulgite to adsorb DOC was investigated as a function of equilibrium time, initial DOC concentration, solution pH, temperature, and attapulgite concentration. Two particle sizes of attapulgite were used, granular (1 mm) and powder (0.25 mm). In most cases the equilibrium data fit best with the Langmuir isotherm. The maximum monolayer coverage was found to be 31 mg/g for granular and 65 mg/g for powder attapulgite. The separation factor, $R_L$, from the Langmuir isotherm and, $n$, the constant from the Freundlich isotherm indicated favorable adsorption. Changes in the pH of the oily water had no significant influence on the adsorption capacity. The adsorption follows the pseudo-second order model. The governing transport mechanisms in the sorption process appear to be both external mass transfer and intra-particle diffusion. The adsorption process was found exothermic in nature. The Langmuir isotherm model equation was adopted to design a single-stage batch absorber for DOC adsorption onto attapulgite. The study demonstrated that attapulgite can be utilized as a potential alternative low-cost adsorbent for the removal of DOC from oily water.

Keywords: Adsorption, DOC, Equilibrium isotherms, Kinetic models, Thermodynamics

Abbreviations: DOC, dissolved organic carbon; D-R, Dubinin-Radushkevich; FTIR, Fourier transform infrared; SEM, scanning electron microscopy

1. Introduction

Large volumes of water generated during oil and gas production are considered as the largest and most important waste stream on the basis of volume. This water contains a complex mixture of organic and inorganic compounds [1, 2]. The major compounds of produced water include dispersed hydrocarbons, dissolved hydrocarbons, dissolved non-hydrocarbons, dissolved formation minerals, production solids, and dissolved gases [3]. The removal of dissolved oil poses great challenges compared to dispersed oil. The dissolved oil components are polar organic compounds and range between low and medium carbon ranges [4]. Benzene, toluene, ethylbenzene and xylene, organic acids and low molecular weight aromatic compounds are classified as dissolved oil [5]. Dissolved organic carbon (DOC) is used as an indicator of the amount of dissolved organic compounds present in water and operationally can be defined as organic matter that can pass through a 0.45 µm filter [6]. The presence of DOC in aquatic systems poses a threat to the human and aquatic environment [7–9]. Different techniques are applied to eliminate DOC from wastewater such as the application of Al or Fe salts as
coagulants, followed by flocculation and clarification [10], ion exchange, membrane filtration, ozonation and biodegradation [11--14]. Although many techniques are available for the purification of oily water, there is no single technique which is sufficient to eliminate the constituents in oil--water emulsions to comply with the stringent environmental regulations. Each technique works well for the removal of specific constituents. There is a need to apply different combinations of various technologies to achieve the target quality for the treated water. Recently, adsorption is recognized as a major, efficient and cost effective purification technique for the purification of wastewater in the oil and gas industry [15--18]. The advantages of using adsorption are that it does not produce harmful substances, is flexible and simple in design, has low initial cost, is easy to be operated and is not affected by the presence of toxic pollutants [19--21].

Attapulgite belongs to the Fuller’s earth group and possesses high sorbent properties thanks to its structure consisting of hydrated magnesium aluminum silicate with a fibrillar structure [22]. Attapulgite is found to exist in huge quantity and high purity in Oman. The estimated amount of attapulgite from two places in Dhofar, southern part of Oman, is around 300 to 400 million tons in the Shuwaymiyah deposit and 200 000 to 1 million tons in the Tawi Attair deposit [23]. Presently, these huge quantities of attapulgite are not mined or utilized. Attapulgite has been considered and utilized as an adsorbent possessing a large specific area and porous structure for the removal of many pollutants due to the fact that it is natural, cheap and available in huge quantities. Many researchers applied attapulgite for the removal of heavy metals [24--29] while others investigated the adsorption of organic compounds [22, 23, 30--33]. Most studies done on the removal of organic compounds focused on the removal of cationic dyes and humic acids from aqueous solutions. There is no study in the literature that reports or investigates the removal of DOC from oily water. In this paper, the applicability of attapulgite as an adsorbent for the removal of DOC from oily water is explored. Adsorption isotherms, thermodynamics and kinetics were performed to determine the adsorption mechanism.

2. Materials and methods

2.1. Experimental materials

The oily water used in this study was collected from an oilfield located in the southern part of Oman, i.e. the outlet of the corrugated plate interceptor unit wherein the oil content varies from 250 to 350 mg/L. Attapulgite used in this study was collected from Dhofar, southern part of Oman. The attapulgite was crushed by a soil grinder into two different sizes, i.e. granular (1 mm) and powder (0.25 mm).

2.2. Analytical methods

Scanning electron microscopy (SEM) was used to study the morphological structure of attapulgite before and after the adsorption of organic compounds. Fourier transform infrared spectroscopy (FTIR, Perkin-Elmer) was used to determine the functional groups of attapulgite. Thermogravimetric analysis was performed by an analyzer (STA 6000, Perkin Elmer) to investigate the thermal degradation characteristics of attapulgite. The attapulgite particle density was measured using the pycnometer method. pH measurements were performed using a Jenway pH meter. The cations present in the oily water and the chemical composition of attapulgite were analyzed by using atomic absorption spectrophotometry while anions were analyzed by using ion chromatography. The analysis for DOC concentration was conducted by using a total organic carbon analyzer.
(TOC-VCPN, Shimadzu). The dissolved oil was performed by gas chromatography–mass spectrometry (Clarus 600, PerkinElmer).

2.3. Adsorption studies
The adsorption batch experiments were conducted by using a known amount of adsorbent (0.5–2.0 g) with 150 mL of oily water with DOC concentrations of 18.5–93.5 mg/L. The mixture was stirred for 120 min at 150 rpm. Adsorption trials were done by varying the initial DOC concentration (18.5–93.5 mg/L), solution pH (4–9), temperature (25–45 °C), and attapulgite doses (0.5–2.0 g). The amount of adsorption at equilibrium \( q_e \) (mg/g) was calculated by the following equation:

\[
q_e = \frac{(C_0 - C_t)}{m} \frac{V}{t} \quad (1)
\]

The DOC removal efficiency was obtained by the following equation:

\[
\% \text{ removal} = \left( \frac{C_0 - C_t}{C_0} \right) \times 100 \quad (2)
\]

where \( C_0 \) is the initial DOC concentration (mg/L), \( C_t \) is the concentration of DOC at any time \( t \) (mg/L), \( V \) is the volume of solution (L) and \( m \) is the mass of attapulgite (g).

2.4. Adsorption Isotherms
In this study, three isotherms models were used namely Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) isotherms models.

2.4.1. Langmuir model
This model is based on the assumption that all adsorption sites are equivalent and the adsorbate forms a monolayer on the outer surface of the adsorbent and thereafter no further adsorption will take place. The linearized form of the Langmuir equation is written as [34]:

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

where \( q_e \) is the amount of DOC adsorbed per gram of adsorbent at equilibrium (mg/g), \( q_m \) is the maximum adsorption capacity (mg/g), \( C_e \) is the equilibrium concentration of DOC in solution (mg/L) and \( K_L \) is the Langmuir constant (L/mg).

The separation factor, \( R_L \), can be obtained from the Langmuir plot as follows [35]:

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

where \( K_L \) is the Langmuir constant and \( C_0 \) is the initial concentration of DOC. \( R_L \) indicates the type of isotherm to be favorable, \( 0 < R_L < 1 \); unfavorable, \( R_L > 1 \); linear, \( R_L = 1 \); and irreversible, \( R_L = 0 \).

2.4.2. Freundlich model
This model is valid for multilayer adsorption on a heterogeneous adsorbent surface. The linearized form of the Freundlich model can be expressed as [24]:

\[
\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (5)
\]

where \( K_f \) is the Freundlich constant and \( n \) is the empirical parameter related to the intensity of adsorption.
2.4.3. D-R model

This model expresses the adsorption mechanism by a Gaussian energy distribution onto a heterogeneous surface. The linearized form of the D-R model can be expressed as [24]:

$$\ln q_t = \ln q_m - \beta \varepsilon^2$$  \hspace{1cm} (6)

where \(q_m\) (mg/g) is the maximum adsorption capacity, \(\beta\) is a constant related to adsorption energy, and \(\varepsilon\) is the Polanyi potential which is related to the equilibrium concentration as in the following equation:

$$\varepsilon = RT \ln \left(1 + \frac{1}{T^o}\right)$$  \hspace{1cm} (7)

where \(R\) is the gas constant (8.314 J/mol K) and \(T\) is the absolute temperature in K.

2.5. Adsorption kinetics:

In this study, the applicability of pseudo-first order, pseudo-second order, intra-particle diffusion, liquid film diffusion, and double exponential models were investigated for the experimental adsorption data of DOC onto attapulgite.

2.5.1. Pseudo-first order model

This model can be written as [24]:

$$\ln(q_t - q_e) = \ln q_m - k_1 t$$  \hspace{1cm} (8)

where \(k_1\) is the rate constant of the pseudo-first order adsorption (L/min), \(q_t\) and \(q_e\) (mg/g) are the adsorption capacity at time \(t\) and at equilibrium, respectively, and \(t\) (min) is the contact time.

2.5.2. Pseudo-second order model

This model is generally expressed as [34]:

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}$$  \hspace{1cm} (9)

where \(k_2\) is the second-order rate constant of adsorption (g/mg min). \(k_2\) is used to calculate the initial sorption rate \(h\), as follows:

$$h = k_2 q_e^2$$  \hspace{1cm} (10)

2.5.3. Intra-particle diffusion model

This model is usually expressed as [34]:

$$q_t = k_{id} \varepsilon^{0.5}$$  \hspace{1cm} (11)

where \(k_{id}\) is the rate constant of the intra-particle diffusion (mg/g min\(^{0.5}\)) and \(\varepsilon^{0.5}\) (min) is the square root of time.

2.5.4. Liquid film diffusion model

This model can be written as [36]:

$$\ln \left(1 - \frac{q_t}{q_e}\right) = -k_{fd}$$  \hspace{1cm} (12)

where \(\ln(1 - q_t/q_e)\) is the fractional attainment of equilibrium and \(k_{fd}\) is the film diffusion rate constant.

2.5.5. Double-exponential model
This model can be written as [37]:

\[ q_t - q_e = \exp(-k_2 t) - \exp(-k_2 t) \]  \hspace{1cm} (13)

If \( k_1 \gg k_2 \), it means that the rapid process can be assumed to be negligible on the overall kinetics and the linearized form of the equation is:

\[ \ln(q_t - q_e) = -k_2 t \]  \hspace{1cm} (14)

where \( k_1 \) (min\(^{-1}\)) is the diffusion parameter of the rapid step and \( k_2 \) for the slow step.

2.6. Thermodynamic parameters

The feasibility of the adsorption process can be evaluated by thermodynamic parameters such as free energy (\( \Delta G^\circ \)), enthalpy (\( \Delta H^\circ \)), and entropy (\( \Delta S^\circ \)). These parameters can be calculated from the following equations:

\[ \Delta G^\circ = -RT \ln K_d \]  \hspace{1cm} (15)

where:

\[ K_d = \frac{q_e}{C_e} \]  \hspace{1cm} (16)

This equation can be written as:

\[ \ln K_d = \frac{\Delta H^\circ}{R} - \frac{\Delta S^\circ}{RT} \]  \hspace{1cm} (17)

where \( q_e \) (mg/g) is the adsorption capacity at equilibrium, \( C_e \) (mg/L) is the equilibrium concentration of DOC in solution, \( T \) is the temperature in (K), \( K_d \) is the distribution coefficient and \( R \) is the universal gas constant (8.314 J/mol K).

3. Results and discussion

3.1. Characterization of oily water and attapulgite

The main functional groups of the FTIR spectral pattern of attapulgite are structural hydroxyl (OH) groups and Si-O stretching. Similar results were found by different researchers [38–40]. SEM images of granular attapulgite and powder attapulgite before and after adsorption of organic compounds are shown in Fig. 1. SEM analysis reflects the richness of attapulgite fibers in the clay of Dhofar. The fibers may exist as well-separated fibers or might be found as aggregates of clay fibers [41]. This variation in the form of fibers causes variation in the pore spaces ranging between tiny pores between well separated fibers and bigger pores between aggregated fibers [23].

The oily water was analyzed before performing the adsorption experiments. The salinity ranged between 8–9 dS/m and the pH varied from 8.5–9.1. Chloride was the dominant anion present in the oily water. The dissolved organic compounds were found to range from C10 to C30.

The most abundant constituent of attapulgite was SiO\(_2\) (55.7%) followed by Al\(_2\)O\(_3\) (11.5%). Fe, Ca and Mg oxides are present in lower percentages. The particle density for granular and powder attapulgite was 2.42 and 2.28 g/cm\(^3\), respectively.

The thermal decomposition of attapulgite showed four distinct mass losses when subjected to temperature between 30–900 °C. The first step (8.7% loss) occurred at 120 °C and was ascribed to the loss of adsorbed water. The second step occurred at 245 °C and a mass loss of 13% was observed at this step which counts for the hydration water. A third step was observed at 385 °C with a mass loss of 15%. The fourth step was found at 520 °C with a mass loss of 19% indicating the oxidation of some minerals. The major mass loss occurred
between 40 and 520 °C. After 520 °C, there was no significant reduction in weight loss.

3.2. Effect of contact time and adsorption kinetics
The results revealed that the adsorption of DOC was rapid at the initial stages and equilibrium was attained after 120 min, which was independent of the initial DOC concentration.

Different kinetic models were applied to elucidate the mechanism of the adsorption process and to evaluate the performance of the adsorbents. The models were tested at different physico-chemical conditions (Tables 1 and 2). The pseudo-second order kinetic model showed better fit as \( q_e \) calculated from the model \( (q_{e, \text{cal}}) \) was almost matching with \( q_e \) obtained experimentally \( (q_{e, \text{exp}}) \). Therefore, the adsorption of DOC onto attapulgite follows the second-order reaction (Fig. 2).

The results revealed that the sorption rate \( K_2 \) increased with the initial attapulgite dose for both granular and powdered form (Table 1). This can be attributed to the higher availability of active adsorptive sites and consequently higher sorption rates were obtained. The sorption rate \( K_2 \) for the granular and powder attapulgite decreased when the initial DOC concentration was increased from 18.5 to 93.5 mg/L due to the high competition for the active surface sites and consequently lower sorption rates were obtained.

Figure 3 shows the intra-particle diffusion model plots which are commonly used to identify the mechanism involved in the sorption process. The plots confirmed the multi-stages of adsorption as the fitted experimental data are not linear. The adsorption process might be controlled by film diffusion at a fast rate in the beginning followed by a slower intra-particle diffusion rate through pores.

3.3. Effect of initial DOC concentration and adsorption isotherms
When the initial DOC concentration increased from 18.5 to 93.47 mg/L, the DOC uptake increased from 2.62 to 8.67 mg/g using granular attapulgite while the increase was more noticeable when powder attapulgite was used, i.e. DOC uptake increased from 4.67 to 18.02 mg/g (Figs. 4 and 5). It was expected that the powder attapulgite would show better uptake since it has a higher surface area and thus, more available adsorptive sites compared to granular attapulgite.

The parameters of the three adsorption isotherm models used are listed in Table 3. The correlation coefficient, \( R^2 \), is used as a tool to test the applicability of the isotherm equation. Although the Freundlich and D-R models showed acceptable linear regression, overall the Langmuir isotherm model was found to have the best fitting for the adsorption of DOC onto attapulgite with \( R^2 = 0.996 \) for powdered attapulgite and 0.89 for granular attapulgite. Thus, the Langmuir isotherm model was chosen to represent the adsorption of DOC onto attapulgite.

The maximum monolayer adsorption from the Langmuir model, \( q_m \), was found to be 31.06 and 65.36 mg/g for granular and powdered attapulgite, respectively.

The \( R_L \) value calculated for the initial DOC concentrations of 10–100 mg/L ranged from 0.899 to 0.471 and from 0.949 to 0.652 for granular and powder attapulgite, respectively. This indicates favorable adsorption as \( R_L \) falls in the category \( 0 < R_L < 1 \).

3.4. Effect of adsorbent (attapulgite) dose
The effect of attapulgite dosage on the adsorption of DOC from oily water was investigated by using three different doses (0.5, 1 and 2 g), 150 mL of oily water with a DOC concentration of 93.5 mg/L, pH 8.9, and 150
rpm stirring speed (Figs. 4 and 5). The results demonstrated that the equilibrium adsorption capacity \( q_e \) decreased with increasing attapulgite dosage. This can be due to the fact that attapulgite would tend to aggregate at an increasing dosage (Figs. 4b and 5b), thus resulting in a lower surface area available for adsorption, which causes an increase in the diffusion path length of DOC [42].

3.5. Effect of initial pH
In order to evaluate the effect of the initial pH on the uptake of DOC, the trials were carried out with an initial DOC concentration of 18.5 mg/L, 0.5 g attapulgite and 150 rpm stirring speed at the pH range of 4–9. The pH of the solution was adjusted by adding either 0.1 M NaOH or 0.1 M HCl. Figure 6 shows that a lower DOC uptake occurred at pH 4 compared with that at pH > 4, which can be explained based on the study by Neaman and Singer [43]. These authors observed that at pH ≥ 9 the fibers of attapulgite (palygorskite) tend to repel each other because the magnitude of the negative charge is high resulting in a high surface area. At pH ≤ 9 the fibers of attapulgite tend to aggregate as the level of the negative surface charge is relatively low and van der Waals attraction predominates over electrostatic repulsion. However, there are several different views reported in the literature on the effect of pH on the adsorption of organic compounds. Narine and Guy [44] reported that the adsorption capacity of bentonite was independent of the pH in the range 4.5 to 8.5. Similar results were found by Bilgiç [45] for the adsorption of organic cations on silicate minerals. On the other hand, other studies [22, 33] reported that higher adsorption rates of humic acids were found at low pH values.

3.6. Effect of temperature and thermodynamics
In order to investigate the effect of temperature on the removal efficiency of DOC, experiments were carried out with a DOC concentration of 97.3 mg/L, 1 g attapulgite, pH 8.9 and stirring speed of 150 rpm over the range 25–45 °C. The uptake of DOC by granular attapulgite decreased from 4.36 (19.6% removal) to 2.94 mg/g (15.1% removal) and by powdered attapulgite from 4.34 (18.3% removal) to 3.26 mg/g (16.8% removal) when the temperature increased from 25 to 45 °C, indicating that the DOC removal was favored at a lower temperature and that the adsorption of DOC onto attapulgite is an exothermic process. Similar results were obtained by another study [46]. The thermodynamic parameters of DOC adsorption onto attapulgite, \( \Delta G^\circ \), \( \Delta H^\circ \), and \( \Delta S^\circ \), are reported in Table 4. The negative value of the enthalpy (\( \Delta H^\circ \)) confirms the exothermic nature of adsorption which is also supported by the decrease in the DOC uptake with the increase in temperature. The positive value of \( \Delta G^\circ \) indicates that the spontaneity is not favored at this temperature range.

3.7. Design of single-stage batch absorber from isotherm data
The adsorption isotherms obtained in this work can be utilized to design an efficient single batch adsorption system [47]. The main design objective is to find the amount of adsorbent, \( m \) (g), required to reduce the initial DOC concentration of \( C_0 \) to \( C_l \) (mg/L) for a certain solution volume, \( V \) (L). When attapulgite is added to the system the DOC concentration on the surface of the solid changes from \( q_0 \) = 0 to \( q_l \). The mass balance for the sorption system under equilibrium is given by:

\[
V(C_0 - C_l) = m(q_l - q_0) = mw
\]

(18)

The Langmuir isotherm model was found to have the best fit for the equilibrium data and thus it was used to predict the design of single batch system according to the method developed by McKay et al. [47]. Equation
(18) can be rewritten after substituting $q_e$ from the Langmuir model:

\[
\frac{C}{C_e} = \frac{q_e}{q_m} = \frac{1}{K_f + \frac{C_m}{C}}
\]

(19)

Figure 7 shows a sequence of plots derived from Eq. (19). Figure 7 represents the amount of attapulgite ($m$) required to achieve the target DOC removal efficiency (85, 75, 65, and 55%).

4. Conclusion

The present study showed that attapulgite can be utilized as a potential alternative low-cost adsorbent for the removal of DOC from oily water. The DOC uptake was found to increase with the increase in initial DOC concentration and contact time, while it decreased with the increase of temperature and adsorbent dose. Compared to granular attapulgite, powder attapulgite showed a better DOC uptake when the initial DOC concentration increased. Changes in pH of oily water had some influence on the adsorption capacities. The equilibrium data were well-fitted by the Langmuir isotherm equation, which confirmed the monolayer sorption capacity of DOC onto attapulgite. The adsorption process appeared a pseudo-second order kinetic. The kinetic experiments showed that the adsorption of DOC onto attapulgite can be summarized into two steps: a fast rate external mass transfer of the DOC molecules to the external surface of the attapulgite through film diffusion, and a low rate intra-particle diffusion of DOC molecules into attapulgite particles through pores. The thermodynamic analysis showed that the process is exothermic.

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Symbols used

- $C_e$: residue DOC concentration at equilibrium (mg/L)
- $C_f$: final concentration of DOC (mg/L)
- $C_o$: initial concentration of DOC (mg/L)
- $\Delta G^\circ$: Gibbs free energy (kJ/mol)
- $\Delta H^\circ$: change in Enthalpy (kJ/mol)
- $k_1$: pseudo-first-order rate constant, (min$^{-1}$)
- $k_2$: pseudo-second-order rate constant (g/mg min)
- $K_d$: distribution coefficient (-)
- $K_f$: Freundlich constant related to adsorption capacity (mg/g)
- $k_{fd}$: the film diffusion rate constant (-)
- $k_{id}$: intra-particle diffusion rate constant (mg/g min$^{0.5}$)
The Langmuir constant (L/mg)
n empirical parameter related to the intensity of adsorption (-)
$q_e$ amount of DOC adsorbed at equilibrium (mg/g)
$q_m$ maximum adsorption capacity (mg/g)
$q_t$ adsorption capacity at time $t$ (mg/g)
$\Delta S^\circ$ change in entropy (J/mol K)
$R^2$ linear regression coefficient (-)
$R_L$ separation factor (-)
t time (min)
$t^{0.5}$ the square root of time (min$^{0.5}$)

Greek letter
$\beta$ constant related to adsorption energy (-)
$\varepsilon$ Polanyi potential (kJ$^2$/mol$^2$)

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Figure 1. SEM images of attapulgite, (a) and (b) are for granular attapulgite before and after adsorption respectively, (c) and (d) are for powdered attapulgite before and after adsorption, respectively
Figure 2. Pseudo-second order kinetic model for DOC adsorption at different DOC concentration on (a) granular attapulgite and (b) powder attapulgite
Figure 3. Intra-particle diffusion model for different initial DOC concentrations, (a) granular attapulgite and (b) powder attapulgite
Figure 4 (a) Adsorption capacity with time at different granular attapulgite dosages and (b) Effect of initial granular attapulgite dosage on DOC uptake (initial DOC concentration of 93.5 mg/L, pH: 8.9, stirring speed: 150 rpm, volume of solution: 150 mL)
Figure 5 (a) Adsorption capacity with time at different powder attapulgite dosages and (b) Effect of initial powder attapulgite dosage on DOC uptake (initial DOC concentration of 93.5 mg/L, pH: 8.9, stirring speed: 150 rpm, volume of solution: 150 mL)
Figure 6 Effect of initial solution pH on DOC uptake (initial DOC concentration of 18.5 mg/L, attapulgite dosage: 0.5, stirring speed: 150 rpm, volume of solution: 150 mL)
Figure 7 Attapulgite mass ($m$) versus volume of solution ($L$), (a) granular attapulgite and (b) powder attapulgite
Table 1 Pseudo-first and second order kinetic parameters for adsorption of DOC on attapulgite

<table>
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<th>Type</th>
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<th>( K_1 ) (min(^{-1}))</th>
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Table 2 Intra-particle diffusion and liquid film diffusion and double exponential model for adsorption of DOC on attapulgite

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<th>Double exponential model</th>
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### Table 3 Langmuir, Freundlich and Dubinin-Radushkevich isotherm constants

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<td>$K_L$ (L/mg)</td>
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<tr>
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<tr>
<td>$R^2$</td>
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<td>0.996</td>
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<tr>
<td>Equation</td>
<td>$q_e = \frac{0.347778 c_e}{1 + 0.011198 c_e}$</td>
<td>$q_e = \frac{0.347778 c_e}{1 + 0.005332 c_e}$</td>
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|                  |          |        |
| **Freundlich**   |          |        |
| $K_f$            | 0.8705   | 0.2660 |
| $n$              | 1.7056   | 0.8472 |
| $R^2$            | 0.74     | 0.98   |
| Equation         | $q_e = 0.8705 c_e^{0.8472}$ | $q_e = 0.2660 c_e^{0.8472}$ |

|                  |          |        |
| **Dubinin-Radushkevich** |          |        |
| $q_m$ (mg/g)      | 9.42     | 14.52  |
| $\beta$          | 0.0135   | 0.0135 |
| $R^2$            | 0.99     | 0.85   |
| Equation         | $q_e = 9.42 e^{-0.0135 c_e}$ | $q_e = 14.52 e^{-0.0135 c_e}$ |

### Table 4 Thermodynamic parameters for adsorption of DOC onto attapulgite at different temperature

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<th>Attapulgite type</th>
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<th>$\Delta G^0$ (kJ/mol)</th>
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Figure 1
Figure 2

(a) 

(b)
Figure 3
Figure 4

(a) Graph showing $q_t$ (mg/g) vs. time $t$ (min) for different doses of attapulgite (0.5 g, 1.0 g, 2.0 g).

(b) Graph showing DOC Removal (%) and $q_e$ vs. attapulgite dose (g).
(a) Figure 5
Figure 6

DOC uptake (mg/g) vs. Initial solution pH

- Powder attapulgite
- Granular attapulgite
Figure 7