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Aims and scope

The Journal of Environmental Sciences, an international monthly journal established since 1989 and sponsored by the Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, is devoted to publishing original, peer-reviewed research papers and reviews on main aspects of environmental sciences, such as environmental chemistry, soil chemistry, atmospheric chemistry, environmental biology, ecotoxicology, geochemistry. The aim of the journal is to provide a platform for the latest research advancement.

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A comparative study and evaluation of sulfamethoxazole adsorption onto organo-montmorillonites

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ABSTRACT

Three organo-montmorillonites were prepared using surfactants, and their adsorption behaviors toward sulfamethoxazole (SMX) were investigated. The surfactants used were cetyltrimethyl ammonium bromide (CTMAB), 3-(N,N-dimethylhexadecylammonio) propane sulfonate (HDAPS) and 1,3-bis(hexadecylidimethylammonio)-propane dibromide (BHDAP). The properties of the organo-montmorillonites were characterized by X-ray diffraction, scanning electron microscopy and N2 adsorption–desorption isotherm measurements. Results showed that the interlayer spacing of montmorillonite was increased and the surface area as well as the morphology were changed. Batch adsorption experiments showed that the surfactant loading amount had a great effect on the adsorption of SMX. The adsorption process was pH dependent and the maximum adsorption capacity was obtained at pH 3 for HDAPS-Mt, while CTMAB-Mt and BHDAP-Mt showed a high removal efficiency at pH 3–11. The adsorption capacity increased with the initial SMX concentration and contact time but decreased with increasing solution ionic strength. Kinetic data were best described by the pseudo second-order model. Equilibrium data were best represented by the Langmuir model, and the Freundlich constant (n) indicated a favorable adsorption process. The maximum adsorption capacity of SMX was 235.29 mg/g for CTMAB-Mt, 155.28 mg/g for HDAPS-Mt and 242.72 mg/g for BHDAP-Mt. Thermodynamic parameters were calculated to evaluate the spontaneity and endothermic or exothermic nature. The adsorption mechanism was found to be dominated by electrostatic interaction, while hydrophobic interaction played a secondary role.

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Introduction

In recent years, the presence of pharmaceuticals and personal care products (PPCPs) discharged into the water environment has been recognized as one of the common emerging issues worldwide (Kumar and Xagoraraki, 2010; Richardson et al., 2005). Among the diverse categories of PPCPs, antibiotics used in both human and veterinary medicine draw special attention due to their wide distribution and potential risk to aquatic ecosystems and human health (Kümmerer, 2009; Grung et al., 2008). Sulfamethoxazole (SMX) is one of the most frequently detected antimicrobials in the environment, and shows an ecological risk to progeny (Yu et al., 2011).
Recently there has been growing concern about the elimination of SMX residues from wastewater, and technologies studied include photo-catalytic degradation (Niu et al., 2013; Xu et al., 2012), biodegradation (Huang et al., 2012), electrical mineralization (Lin et al., 2013), oxidation (Ahmed et al., 2012; Hu et al., 2007) and other advanced combination degradation processes (Beltrán et al., 2008; Nasuhoglu et al., 2011). Although chemical treatments, especially advanced oxidation processes, can break down organic molecules into simple compounds, these processes are very expensive and difficult to operate for effective removal of recalcitrant compounds such as antibiotics (Moussavi et al., 2013a). Among the available processes for the treatment of SMX, adsorption is one of the most promising techniques owing to its convenience in the current water treatment processes (Kyzas et al., 2013). Previous studies have revealed pH-dependent sorption of SMX onto various adsorbents, such as activated carbon (Çalışkan and Göktürk, 2010; Delgado et al., 2012), carbon nanotubes (Wu et al., 2012), mesoporous nanocomposite (Qiang et al., 2013), high silica zeolite (Fukahori et al., 2011), and clay minerals (Farias et al., 2011; Gao and Pedersen, 2005). Activated carbon (AC) is a popular adsorbent for removal of organic pollutants, however, the application of activated carbon is limited due to the high cost of treatment and difficult regeneration process (Dawood and Sen, 2012).

Over the past few decades, bentonite clays modified by organic molecules have been widely employed for the removal of organic pollutants from wastewater (Park et al., 2011; Kan et al., 2011), due to their high efficiency and cost-effectiveness. Considering the good performance of organo-clays, further studies are still necessary to investigate their adsorption behavior. However, few of the previous studies (Polubesova et al., 2006) have involved the removal of SMX with the most commonly used material, organo-montmorillonite (organo-Mt). It is well known that the microscopic properties of organo-Mt depend greatly on the selection of the organic modifier (Heinz et al., 2007), and surfactants are often used as modifiers whose properties can be tuned by varying the alkyl chain length or the functional groups. Quaternary ammonium salts are some of the most widely used surfactants, whose performance in the preparation of organo-Mt and removal of organic pollutants have been studied intensively. Recently, two novel classes of surfactants (zwitterionic and gemini surfactants) have been considered as promising candidates for the preparation of organo-Mt owing to their special structure and properties. Zwitterionic surfactants contain both positively and negatively charged head groups (Liu et al., 2012; Christov et al., 2004), while gemini surfactants contain two alkyl chains and two positive groups in the structure (Mahajan et al., 2013).

In this article, we chose one traditional surfactant, cetyltrimethyl ammonium bromide (CTMAB), and two novel surfactants, 3-(N,N-dimethylhexadecylammonio) propane sulfonate (HDAPS) and 1,3-bis(hexadecyldimethylammonio)-propane dibromide (BHDAP) for the preparation of organo-Mts. The purpose of this study is to systematically investigate the performance of the three organo-Mts in removing SMX, as well as the key influencing factors and mechanisms controlling sorption of SMX, including surfactant loading amount, solution pH, ionic strength, contact time, initial SMX concentration and temperature. The experimental results may provide practical help to determine the optimum conditions for environmental applications.

1. Materials and methods

1.1. Montmorillonite and chemicals

Natural Na-montmorillonite was supplied by Zhejiang Institute of Geology and Mineral Resources, Hangzhou, China. The cation exchange capacity (CEC) and basal spacing (d001) were 112 mmol/100 g and 1.19 nm, respectively. The SMX (>99% purity) was purchased from Sigma-Aldrich, Shanghai, China. CTMAB was purchased from Beijing Chemical Reagent Co., Ltd., Beijing, China. HDAPS was supplied by Nanjing Robiot Co., Ltd., Nanjing, China. BHDAP was synthesized according to the procedure reported by Zana et al. (1991). The molecular structures of surfactants and SMX used in this work can be seen from Fig. 1. All agents were of analytical grade and used as received.

1.2. Preparation and characterization of adsorbents

A series of surfactant-modified organo-Mts were prepared as follows: First, 5 g montmorillonite was dispersed in a solution of CTMAB (the amount of CTMAB was equivalent to 0.2–2.5 times CEC). Next, the mixture was continuously agitated for
6 hr at 60°C, then the final sample was separated by centrifugation and washed with deionized water until free of bromide. All products were dried at 80°C for 12 hr and triturated to fine powders passing through a 200-mesh sieve. The resulting organo-Mt was designated as CTMAB-Mt, and CTMAB-Mt-0.2 means that the Raw-Mt was modified by the CTMAB in the amount equivalent to 0.2 times CEC. The other two organo-Mts were prepared and designated similarly.

The interlayer spacing of organo-Mts was measured by X-ray powder diffraction (XRD, Shimadzu XRD-6000, Japan, Cu Kα radiation, 40 kV, 40 mA, Japan), and data were collected for 2θ ranging from 1.3° to 10° with the scan speed of 1°/min. The specific surface area (BET) and pore distribution of the prepared samples were investigated by N₂ adsorption–desorption isotherms using an ASAP 2420 system (Micromeritics, Micromeritics Instrument Corp., USA). The morphology and structure of the material were characterized by a scanning electron microscope (SEM) analysis (FEI Quanta 200F, Portland, USA).

1.3. Adsorption experiments

Batch experiments were carried out to select the optimum conditions for the adsorption of SMX onto the organo-Mts. The amount of SMX adsorbed onto the organo-Mt was calculated by Eq. (1) and removal efficiency, i.e. adsorption (A, %), was calculated by Eq. (2).

\[ q_t = \frac{(C_0 - C_t)}{m} V \]  
\[ A = \frac{(C_0 - C_t)}{C_0} \times 100 \]  

where, \( q_t \) (mg/g) is the amount of SMX adsorbed by organo-Mt; \( C_0 \) (mg/L) and \( C_t \) (mg/L) is the initial and residual concentration of SMX at time \( t \); \( V \) (L) is the volume of the solution, and \( m \) (g) is the mass of the adsorbent used.

To examine the effect of the surfactant loading amount on the adsorption of SMX, a series of organo-Mts (surfactant loading amount of 0.2–2.5 CEC, 0.05 g) were mixed with SMX (100 mg/L, 20 mL) at initial pH 3, and then the mixture was stirred (150 r/min) at 25°C for 6 hr to achieve adsorption equilibrium. The effect of pH on SMX adsorption was studied by adding 0.05 g organo-Mt to 20 mL of SMX solutions with an initial concentration of 100 mg/L. The final mixtures were centrifuged and filtered through 0.45 µm membrane filters, then the concentration of SMX was analyzed using a UV–vis spectrophotometer (Shimadzu UV2550, Kyoto, Japan) at the maximum absorbance wavelength (\( \lambda_{max} = 266 \) nm). A calibration curve for SMX was made in the concentration range of 0–20 mg/L with linear correlation coefficients (\( R^2 > 0.99 \)).

2. Results and discussion

2.1. Characterization of organo-montmorillonites

The XRD patterns of organo-Mts prepared with CTMAB, HDAPS, and BHDAP surfactants for a series of concentrations (0.2–2.5 CEC) are shown in Fig. 2. Compared with Raw-Mt, the organo-Mts have larger basal spacing. The original basal spacing of the Raw-Mt is 1.19 nm, broadened slightly to 1.4 nm for CTMAB-Mt-0.2 and HDAPS-Mt-0.2, while a broad reflection peak appears for BHDAP-Mt-0.2, probably owing to the existence of a mixed structure for BHDAP, such that the orientation of the two alkyl chains in the interlayer space adopts at least two different arrangements (B. Liu et al., 2011). A previous experimental study showed that the lateral-monomolecular arrangement in the organo-clay gave a basal spacing of 1.3–1.5 nm and a spacing of 1.77–1.98 nm for the lateral-bilayer (He et al., 2005). Therefore, a reflection appears at 1.6 and 1.7 nm for CTMAB-Mt-0.4 and HDAPS-Mt-0.2, indicating the transition structure of surfactants from lateral-monomolecular to lateral-bilayer within the clay interlayer, consistent with the results of He et al. (2005). Under the same surfactant loading amount below 1.2 CEC, BHDAP is more capable of expanding the basal spacing than CTMAB and HDAPS. When the surfactant loading is increased, the main reflection peak shifts to smaller angles, and a secondary reflection peak begins to appear at 1.2, 1.0, 0.4 CEC for the above three organo-Mts, respectively. For CTMAB-Mt-0.8 and HDAPS-Mt-0.6, the d spacing reaches 2.1 and 2.2 nm, suggesting a pseudo-trilayer structure in the organo-Mts (Czimerová et al., 2006). At higher surfactant loading levels (1.5–2.5 CEC), the XRD patterns show much sharper basal reflections and higher intensity peaks, which suggests that the surfactant molecules have formed multiple models and more regular arrangement in the interlayers. Compared with the traditional surfactant material CTMAB-Mt, HDAPS-Mt has a larger interlayer spacing at the high surfactant loading level (Zhu et al., 2011), while BHDAP-Mt shows the second peak at smaller surfactant loading amount. These observations of \( d \) spacing changes suggest that the additional chain length and the functional group (–SO₃), as well as amount of surfactant, have a great effect on the arrangement of the intercalating surfactant.

The SEM images of Raw-Mt, CTMBA-Mt, HDAPS-Mt, and BHDAP-Mt are shown in Fig. 3 (∗×20,000). It can be seen that the Raw-Mt shows a large and compacted particle form (Fig. 3a), while there are some obvious changes in the morphology of the mineral surfaces after modification. The introduction of CTMAB leads to smaller particles and a coarse surface; in addition, there are also some tiny lamella curly...
surfaces in the particles (Fig. 3b). Moreover, this phenomenon becomes more obvious for HDAPS-Mt and BHDAP-Mt. The intercalation of surfactant can increase the interlayer spacing of montmorillonite, which may be beneficial for the penetration of SMX molecules into the galleries.

The BET surface area increased from 20.07 (Raw-Mt) to 32.71 (CTMAB-Mt) and 23.90 m²/g (BHDAP-Mt), while it decreased to 14.02 m²/g for (HDAPS-Mt). This reveals that the treatment of montmorillonite with CTMAB and BHDAP can enhance the surface area of Raw-Mt, but HDAPS will decrease...
its surface area. The average pore diameters of three organo-Mts were all enlarged.

2.2. Effect of surfactant loading on SMX adsorption

The effect of surfactant loading on the removal efficiency of SMX is shown in Fig. 4. It is clear that SMX is adsorbed onto the Raw-Mt to a much lower extent (<5%), and similar findings suggest that the SMX molecule does not intercalate into the montmorillonite (Gao and Pedersen, 2005). However, the removal efficiency of SMX is greatly enhanced by the modification by the three surfactants, and the maximum removal efficiency is about 97%, 95% and 65% for CTMAB-Mt, BHDAP-Mt and HDAPS-Mt, respectively. The adsorption of SMX onto CTMAB-Mt increases with increasing amounts of CTMAB, and reaches equilibrium after 1.5 CEC, while HDAPS-Mt and BHDAP-Mt exhibit different adsorption trends, such that optimum adsorption is obtained at 1.2 and 0.6 CEC, respectively. Recalling the XRD data, the d spacing is increased gradually and the second peak (Fig. 2) begins to appear at 1.2, 1.0 and 0.4 CEC respectively. Thus, large d spacing makes the SMX more able to intercalate into the interlayer of organo-Mts, and the maximum adsorption of SMX is obtained at 1.5, 1.2 and 0.6 CEC.

The adsorption of SMX by BHDAP-Mt is much larger than that for CTMAB-Mt and HDAPS-Mt below 0.6 CEC, since a larger interlayer spacing was formed at 0.2 and 0.4 CEC. In addition, considering the limited hydrophobicity of SMX, increased sorption is caused by electrostatic attraction between the two \( \text{N}^+ \) of BHDAP and the negatively charged group of SMX. When the surfactant loading is over 1.2 CEC for HDAPS-Mt and 0.6 CEC for BHDAP-Mt, the removal efficiency is decreased gradually. For the high level surfactant concentrations, the HDAPS and BHDAP will undergo self-assembly in the bulk and at interfaces at low concentrations due to the low Critical Micelle Concentration (CMC) (Tehrani-Bagha et al., 2012). A micellization monolayer or multiple layers (Zhang et al., 2011) are formed in the interlayer spacing or hatch boundaries, with alkyl chains inside the micelle and quaternary ammonium head group point outward (Chen et al., 2011), and these micelles packed in the interlayer will reduce the access of SMX. Adsorption of SMX on BHDAP-Mt is less than that on HDAPS-Mt since the surfactant loading amount is beyond 1.2 CEC, which may be related to the d spacing, with the d spacing of BHDAP-Mt (1.94 and 3.9 nm) smaller than that of HDAPS-Mt (2.1 and 4.3 nm).

In the subsequent batch experiments, 1.2, 1.2, and 0.6 CEC were selected for the preparation of CTMAB-Mt, HDAPS-Mt, and BHDAP-Mt, respectively.

2.3. Effect of pH on SMX adsorption

The pH of the solution is an important parameter controlling the adsorption capacity of ionic organics onto an adsorbent (Vasudevan et al., 2009); it affects not only the surface charge of the adsorbents, but also the ionization of SMX. In this experiment, the effect of pH on adsorption was studied in the range of 1.00–11.00.

Fig. 5 shows the adsorption behavior of SMX onto the three organo-Mts and Raw-Mt as a function of varying initial pH value. It is evident that the amount of SMX adsorbed onto organo-Mts depends on the solution pH, especially for HDAPS-Mt. The Raw-Mt shows low removal efficiency for SMX over the entire range of pH, and previous studies also indicated that cationic SMX adsorbed by Raw-Mt is caused by cation exchange, while anionic SMX adsorption is negligible (Y.X. Liu et al., 2011). The gradual increase in the amount of SMX adsorbed with pH rising from 1 to 3 (Fig. 5) seems to be dominated by electrostatic and hydrophobic interactions. When the pH is 1 (final pH is 1.1), the SMX molecule mainly exists in the cationic form (\( pK_{a1} = 1.7 \)); hence, the electrostatic repulsion between SMX\(^+\) and the cationic surfactant is unfavorable for the adsorption. Therefore, the increase in removal efficiency for BHDAP-Mt (61.9%), CTMAB-Mt (51.2%) and HDAPS-Mt (18.1%) is mainly ascribed to the hydrophobic interaction. At pH 2 and 3, the amount of SMX adsorbed is

Fig. 4 – Effect of surfactant loading amount on the removal efficiency of SMX. Experimental conditions: initial SMX concentration 100 mg/L; mass of adsorbent 50 mg; volume of SMX solution 20 mL; temperature 25°C; initial pH 3; contact time 5 hr.
increased and reaches optimum values, indicating that both the zwitterionic and anionic form of SMX ($pK_{a1} = 1.7, pK_{a2} = 5.6$) can be adsorbed efficiently, and electrostatic attraction plays a more significant role. Further increasing the pH leads to sharply decreased adsorption onto HDAPS-Mt, owing to the electrostatic repulsion between SMX$^-$ and the $\text{SO}_3^-$ group, while the adsorption of SMX onto CTMAB-Mt and BHDAP-Mt reaches equilibrium. The maximum amount of SMX adsorbed is obtained at initial pH values between 2 and 4 for all adsorbents. To increase the adsorption capacity as much as possible, an initial pH of 3.0 was employed for the rest of the batch adsorption experiments.

### 2.4. Effect of ionic strength

Since the electrostatic interaction is a key factor in the adsorption of SMX, the ions in the solution may exert different effects on the interaction between the SMX and surfactant in the interlayer. When an organo-Mt sample is immersed in aqueous solutions, the ionic strength can affect the double layer thickness of the clay and the electrostatic interaction (Farias et al., 2011).

The influence of ionic strength on SMX adsorption by organo-Mts is shown in Fig. 6. At first glance, the addition of any electrolyte leads to a decrease in removal efficiency of SMX for the three organo-Mts, with the effect being well pronounced for such multivalent cations as Ca$^{2+}$ and Al$^{3+}$ for CTMAB-Mt and BHDAP-Mt. Since these two organo-Mts are prepared with cationic surfactants, the interlayer interfaces of these samples are positively charged, thereby the decreased amount of SMX adsorbed might be explained by virtue of the electrostatic interaction mechanism. In the presence of additional ions, Al$^{3+}$, Ca$^{2+}$, Na$^+$, and Cl$^-$ can screen the charged sites of the adsorbents and the electric double layers of the organo-Mts are compressed, leading to a suppression of the electrostatic interaction (Hu et al., 2013). In the solutions, the hydrolysis of extra cations (e.g., Al$^{3+}$ and Ca$^{2+}$) causes a decrease in the pH, thereby causing a reduction in the

![Fig. 5 - Effect of pH on the removal efficiency of SMX. Experimental conditions: initial SMX concentration 100 mg/L; mass of adsorbent 50 mg; volume of SMX solution 20 mL; initial pH = 1, 2, 3, 4, 5, 7, 9, 10, 11; temperature 25°C; contact time 5 hr.](image)

![Fig. 6 - Effect of ionic strength on the adsorption of SMX. Experimental conditions: initial SMX concentration 100 mg/L; mass of adsorbent 50 mg; volume of SMX solution 20 mL; concentration of NaCl, CaCl$_2$ and AlCl$_3$ 0.02, 0.06, and 0.1 mol/L; temperature 25°C; initial pH 3; contact time 5 hr.](image)
pH-dependent adsorption behavior of SMX. There is also a
certain competition between the chloride ions and the SMX−
for the positively charged sites of the surfactant head-groups.
The maximum reduction in the removal efficiency of SMX in
0.1 mol/L AlCl₃ solutions is about 10.5% for CTMAB-Mt and
12.6% for BHDAP-Mt.

On the other hand, the species of electrolyte has an
opposite effect on SMX adsorption by HDAPS-Mt in compar-
ison to the other two organo-Mts. This interesting phenom-
enon may be explained by the following reason: multiply
charged ions (Al₃⁺) are more prone to coordinate with the
anionic head-group of the HDAPS (−SO₃⁻), causing a reduction
in the electrostatic repulsion between −SO₃ and SMX−, so the
decrease in adsorption of SMX on HDAPS-Mt shows the
following order: Na⁺ > Ca²⁺ > Al³⁺. The ionic strength causes
a smaller decrease in the amount of SMX adsorbed onto
HDAPS-Mt (a maximum 2% decrease in NaCl solutions) than
for the other two organo-Mts.

In the case of an additional electrolyte, fewer SMX
molecules will be retained in the interlayer interface because
of the competitive interaction. The presence of anions and/or
cations makes the adsorption process more complicated.
Considering that the tested concentrations of these ions are
much higher than those in natural waters, the inhibition
effect of these co-existing ions on SMX adsorption on
organo-Mt is less important.

3.5. Effect of contact time and kinetics

The effect of contact time on SMX adsorption is shown in
Fig. 7. It can be seen that the amount of adsorption increases
with time and reaches equilibrium after 24, 48, and 120 min
for HDAPS-Mt, CTMAB-Mt and BHDAP-Mt, respectively. The
removal of SMX by HDAPS-Mt is very fast in the initial period
of 6 min, and quickly reaches equilibrium. However, the
adsorption process on CTMAB-Mt and BHDAP-Mt follows a
three-step process (Fig. 7): a rapid initial adsorption followed
by a period of slower sorption, and finally no significant
uptake (Shu et al., 2010). Compared with previous studies
(Akhtar et al., 2011), the sorption rate of organo-Mt for SMX is
more rapid than that of activated carbon (beyond 150 min to
reach equilibrium). To further investigate the effect of time on
SMX adsorption, the experiments were carried out for longer
time intervals (6, 9, 12, 18, 24 hr), and the amount of SMX
adsorbed remained almost the same (data is not shown).

The adsorption kinetics were investigated to achieve a
better understanding of reaction pathways and the SMX
uptake rate. Pseudo first- and second-order kinetic models
(Eqs. (3) and (4), respectively) were used for the analysis of the
adsorption kinetics data (Lian et al., 2009).

\[
\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t
\]

\[
\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t
\]

where, \( K_1 \) (min⁻¹) and \( K_2 \) (g/(mg·min)) are the rate constants
for the pseudo first- and second-order models, respectively.
The initial sorption rate \( h \) (mg/g·min) at \( t \to 0 \) is

\[
h = K_2 q_e^2
\]

The adsorption rate constant \( K_1 \) and predicted \( q_{e,cal} \) are
determined from the plot of \( \log(q_e - q_t) \) versus \( t \). The kinetic
data is given in Table 1. Usually, the linearity of pseudo
first-order adsorption over the whole time range is not good,
and it is often used to describe the initial state of the
adsorption. The calculated value \( q_{e,cal} \) from the first-order
kinetic model is much larger than the experimental one, with
a poor correlation coefficient \( R^2 = 0.2024\)–\(0.3599\), thus the
first-order kinetic model is improper for this system. Howev-
er, the linear plots of \( t/q_t \) versus \( t \) for the pseudo second-order
model show better fitting, with a high correlation coefficient
above 0.999 over the entire range of contact time (Table 1).
Moreover, the theoretical adsorption capacities calculated
from the model are close to experimental values, indicating

Fig. 7 – Effect of contact time on the adsorption of SMX. Experimental conditions: initial SMX concentration 100 mg/L; mass of
adsorbent 50 mg; volume of SMX solution 20 mL; temperature 25°C; initial pH 3.
that the adsorption process is well fitted by the pseudo second-order kinetic reaction. The initial rate \( h \) is 62.27, 25.59, and 11.59 mg/(g·min), demonstrating that SMX is adsorbed more quickly on CTMAB-Mt in the first adsorption stage than the others.

### 2.6. Adsorption capacity and isotherms

The equilibrium adsorption isotherm is of great importance in understanding the adsorption capacity and efficiency. Thus Langmuir and Freundlich isotherm models were applied to fit the experimental data (Li et al., 2010). The Langmuir model is expressed as Eq. (6):

\[
\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}
\]

where, \( q_m \) (mg/g) is the theoretical maximum adsorption capacity; \( K_L \) (L/mg) is the Langmuir equilibrium constant. The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant called the equilibrium parameter, \( R_L \), which is defined by Eq. (7):

\[
R_L = \frac{1}{1 + K_L C_0}.
\]

The nature of the adsorption process is either unfavorable \((R_L > 1)\), linear \((R_L = 1)\), favorable \((0 < R_L < 1)\) or irreversible \((R_L = 0)\).

Langmuir adsorption describes monolayer adsorption and is applicable to homogeneous adsorption processes, and has traditionally been used to assess the performance of different adsorbents. Fig. 8 shows that the amount of SMX adsorbed onto these organo-Mts increases with the initial SMX concentrations. For an initial SMX concentration of 100 mg/L, the calculated \( R_L \) values are in the range of 0.37–0.67 in the present adsorption experiments; this fact reveals that the adsorption processes are favorable. It can be observed in Table 2 that BHDAP-Mt has the largest equilibrium adsorption capacity for SMX (242.72 mg/g), followed by CTMAB-Mt (235.29 mg/g) and HDAPS-Mt (155.28 mg/g) in order. This observation also indicates that montmorillonite modified by a cationic surfactant is more favorable for the adsorption of SMX than by a zwitterionic surfactant. With all correlation coefficients above 0.99, the adsorption of SMX onto the three organo-Mts at pH 3 is well fitted to the Langmuir type isotherm.

The Freundlich isotherm, which is an empirical expression appropriate for heterogeneous surface energy, is written as:

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e
\]

![Fig. 8 – Adsorption isotherms of SMX onto CTMAB-Mt, HDAPS-Mt, and BHDAP-Mt. Experimental conditions: initial SMX concentration 50–500 mg/L; mass of adsorbent 50 mg; volume of SMX solution 50 mL; temperature 25°C; initial pH 3; contact time 24 hr.](image-url)
where, \( K_F \) (L/g) and \( 1/n \) are isotherm constants that indicate the capacity and the intensity of the adsorption, respectively. If the value of \( 1/n \) is equal to unity, the adsorption is linear and considered to be a chemical process, but if the value of \( 1/n \) ranges between 0 and 1, the adsorption is a favorable physical process and non-linear; the more heterogeneous the surface, the closer the \( 1/n \) value is to 0 (Sevim et al., 2011).

The values of \( K_F \) and \( 1/n \) are calculated from the intercept and slope of the plot of \( \log q_e \) versus \( \log C_e \). It can be observed from Table 2 that the constant \( 1/n \) is smaller than 1, indicating a favorable and physical adsorption process. In our study, the values determined for the three adsorbents are 0.54, 0.63, and 0.47, which provide information about the degree of heterogeneity of the interlayer surfaces of these organo-Mts. BHDAP-Mt shows a higher degree of heterogeneity than CTMAB-Mt, followed by HDAPS-Mt.

### 2.7. Thermodynamic studies

In the practical use of an adsorption method, both energy and entropy values must be taken into consideration to determine what processes will occur spontaneously. To investigate the thermodynamics of SMX adsorption onto CTMAB-Mt, HDAPS-Mt and BHDAP-Mt, the adsorption of SMX was studied at various solution temperatures between 15 and 55°C. As can be seen from Fig. 9, the adsorption of SMX onto HDAPS-Mt appears to be temperature-sensitive; the SMX adsorption percentage decreases from 72.5% to 44.9% with the increase of temperature from 15 to 55°C, while for CTMAB-Mt and BHDAP-Mt, the adsorption of SMX only decreases or increases slightly with increasing temperature. The decrease of SMX adsorption with increasing temperature may be related to the desorption of adsorbed SMX.

Thermodynamic parameters are analyzed using Gibb’s free energy (\( \Delta G^° \)), enthalpy change (\( \Delta H^° \)) and entropy change (\( \Delta S^° \)), which are determined by the following equations (Moussavi et al., 2013):

\[
\ln \left( \frac{q_e}{C_e} \right) = \frac{\Delta G^°}{RT} = -\frac{\Delta H^°}{RT} + \frac{\Delta S^°}{R}
\]

\[
\Delta G^° = \Delta H^° - T\Delta S^°.
\]

The calculated values of adsorption free energies, enthalpies, and entropies of SMX onto organo-Mts are presented in Table 3. It can be seen that values of \( \Delta G^° \) are negative for CTMAB-Mt in the range of \(-2.30\) to \(-3.90\) kJ/mol and \(-3.84\) to \(-7.93\) kJ/mol for BHDAP-Mt, which means that the adsorption of SMX onto CTMAB-Mt and BHDAP-Mt is physical and spontaneous. As for HDAPS-Mt, small positive values of \( \Delta G^° \) are observed when the temperature is above 15°C, indicating the non-spontaneous nature of SMX adsorption onto HDAPS-Mt at these temperatures, and the system gains...
energy from its surroundings (Lin et al., 2011). In addition, the positive values of ΔH° suggest that the adsorption of SMX onto BHDAP-Mt is endothermic, while exothermic processes are found for CTMAB-Mt and HDAPS-Mt. The negative value of ΔS° suggests decreasing randomness at the solid solution interface during the adsorption of SMX onto CTMAB-Mt and HDAPS-Mt, while the positive value of ΔS° indicates higher affinity of BHDAP-Mt toward SMX compared with CTMAB-Mt and HDAPS-Mt.

3. Conclusions

The studied organo-Mts can be used as effective adsorbents for the removal of sulfamethoxazole. SMX adsorption shows a maximum at initial pH of 3 due to electrostatic interaction. Kinetic studies reveal that organo-Mts can remove SMX quickly, within 60 min, and the adsorption processes follow a pseudo second-order model. The Langmuir isotherm model gives better fittings with experimental data and shows that the maximum adsorption capacity follows the order: BHDAP-Mt > CTMAB-Mt > HDAPS-Mt. The amount of SMX adsorbed onto organo-Mts is found to decrease with increasing ionic strength. Temperature shows a small influence on the adsorption of SMX onto CTMAB-Mt and BHDAP-Mt, but has a negative impact on HDAPS-Mt: the calculated Gibbs free energy (ΔG°) for SMX adsorption was found to be −3.50, 0.75, and −4.87 kJ/mol for CTMAB-Mt, HDAPS-Mt and BHDAP-Mt, respectively. The enthalpy change (ΔH°) indicates that the adsorption processes are exothermic for CTMAB-Mt and HDAPS-Mt, and endothermic for BHDAP-Mt. The work provides new insights for developing adsorbents to remove SMX.

**References**


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**Table 3 – The thermodynamic information of SMX adsorption onto CTMAB-Mt, HDAPS-Mt and BHDAP-Mt.**

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Temperature (°C)</th>
<th>Kd (mL/g)</th>
<th>ΔG° (kJ/mol)</th>
<th>ΔH° (kJ/mol)</th>
<th>ΔS° (J/(K·mol))</th>
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<td>−7.93</td>
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