Removal of natural organic matter (NOM) from an aqueous solution by NaCl and surfactant-modified clinoptilolite

Mehdi Vosoughi Niri, Amir Hosein Mahvi, Mahmoud Alimohammadi, Mohammad Shirmardi, Hafez Golastanifar, Mohamma Javad Mohammadi, Abolfazl Naeimabadi and Maria Khishdost

ABSTRACT

Zeolitic tuffs are found in different parts of the world. Iranian zeolite is a low-cost material that can be frequently found in nature. Surfactant-modified zeolite (SMZ) can be used for the adsorption of natural organic matter (NOM) from aqueous solutions. The adsorption study was conducted to evaluate the adsorption capacity of SMZ; furthermore, the effects of contact time, initial pH, and the initial adsorbent dose on the adsorption process were investigated in a batch system. The kinetic studies showed that the adsorption of NOM on SMZ was a gradual process. The optimum initial pH values for the adsorption of NOM on SMZ were in the acidic ranges. The batch kinetic experiments showed that the adsorption followed the pseudo-second-order kinetic model with good correlation coefficients. The equilibrium data were well described by the Langmuir isotherm model. The results show that the natural zeolite being modified with NaCl and hexadecyltrimethylammonium bromide as a cationic surfactant was an appropriate adsorbent for the removal of NOM.

Key words | adsorption isotherm, adsorption kinetics, hexadecyltrimethylammonium bromide, natural organic matter, zeolite

INTRODUCTION

Natural organic matter (NOM) is considered a complex matrix of organic compounds present in many water resources, especially surface water (Wang et al. 2006; Zazouli et al. 2007; Brigante et al. 2008). NOM causes a wide variety of problems in drinking water treatment operations. The presence of NOM in water may be carcinogenic as a result of reactions between NOM and disinfectants. The presence of NOM in raw water sources is unfavorable and has long been a problem for water supply systems in industries. In particular, NOM affects the quality of drinking water in several ways. For example, color, taste, and odor are important esthetic drinking water quality problems caused by such compounds (Mahvi et al. 2009; Li et al. 2011; Ben-Sasson et al. 2013). In addition, NOM can bind with synthetic organic pollutants (such as pesticides) and heavy metals and result in their transport through treatment units and the distribution network (Anirudhan & Ramachandran 2007; Mahvi et al. 2009; Imyim & Prapalimungsri 2010). Also, as a consequence of the presence of high concentrations of NOM in raw water, the chlorination of raw water can result in disinfection by-products such as trihalomethanes during the chlorination process (Anirudhan & Ramachandran 2007; Chiang et al. 2009). Therefore, the removal of NOM from drinking water resources is very important.
Different methods have been applied to remove NOM from drinking water including coagulation and flocculation, ion exchange, adsorption by activated carbon, and membrane filtration (Landrum et al. 1984; Cornelissen et al. 2008; Chiang et al. 2009; Zhan et al. 2010a). Among the above-mentioned processes, adsorption is a promising method. Many different adsorbents including activated carbon, resin, carbon nanotube, and chitosan have been used to remove NOM (Newcombe et al. 2002; Wu et al. 2002; Chen & Wu 2004; Anirudhan & Ramachandran 2007; Wang & Zhu 2007; Sun et al. 2012). Natural zeolites are hydrated aluminosilicates with the chemical composition of tetrahedrons of SiO$_4$ and AlO$_4$, and include water molecules, and alkali and alkaline earth metals in their structures (Wang et al. 2006; Zhan et al. 2011b). Surfactant-modified zeolite (SMZ) can be used for the adsorption of NOM from aqueous solutions. Various surfactants can be used for modification of natural zeolites such as cetylpyridinium bromide, hexadecyltrimethylammonium bromide (HDTMA), and cetyltrimethylammonium bromide (Wang et al. 2006; Karadag et al. 2007; Lin et al. 2011a). Natural zeolites can generally exchange cations instead of anions, which make them appropriate for surface modification by cationic surfactants (Anirudhan & Ramachandran 2007; Zazouli et al. 2008). Cationic surfactants comprise positive groups that can readily exchange their group with the exchangeable cations on the external surface of the zeolite, making a monolayer or bilayer surfactant depending on the conditions, which results in an improvement in the adsorption capacity (Wang et al. 2006; Zhan et al. 2011b). Some studies have investigated the evaluation of NOM adsorption capacity of natural and SMZ. Anirudhan’s study showed that surfactant-modified bentonite can be used for the removal of humic acid (HA) from wastewaters (Anirudhan & Ramachandran 2007). HDTMA-modified zeolite was used in Wang et al.’s study on the adsorption of fulvic acid from aqueous solution (Wang et al. 2006). Adsorption of tannic acid from aqueous solution onto SMZ was examined by Lin et al. (2012).

It is worth noting that each zeolite has intrinsic properties, and the efficiency with which a particular zeolite absorbs a pollutant may vary. Since the efficiency of Iranian zeolites has not been evaluated for the removal of NOM from aqueous solution, the present study aimed to modify a natural Iranian zeolite with NaCl and HDTMA, and investigate its efficiency as a low-cost and frequent adsorbent for the removal of NOM from water. The effects of operational parameters on the adsorption of NOM were evaluated.

**MATERIALS AND METHODS**

**Raw materials**

The natural zeolite was obtained from Semnan province located in the central region of Iran via Afrazand Co. Ltd. The surface morphology of the natural and surfactant-modified zeolite was analyzed by scanning electron microscopy (SEM) (XL30 Philips Holland). X-ray fluorescence spectroscopy (PW 2404 Philips Holland) was used to analyze the chemical composition of the natural zeolite. The crystallinity phase of the natural and SMZ samples was analyzed using X-ray diffraction (XRD) (Philips-XPERT) techniques. HDTMA was purchased from Merck Company, Germany. Other chemicals used in this study were obtained from Merck Company, Germany. NOM solution samples were real and collected from Tehran Latiyan dam.

**Preparation of adsorbent**

The zeolite tuff was ground and sieved using 0.21–0.3 mm American Standard Test Sieve Series (ASTM) sieves. The milled zeolitic tuff was washed several times to remove inorganic impurities; then, for dissolution of salts, 10 g of the zeolite was completely soaked in 1 L of deionized water for 24 hours. To eliminate organic materials in the zeolite, it was then dried at a temperature above 250 °C in an oven for 24 hours (Koh & Dixon 2001; Torabian et al. 2010).

**Treatment of the natural zeolite with NaCl**

Before the modification of the zeolite surface with the surfactant, in order to make homoionic adsorption sites on the zeolite surface with sodium, 10 g of the zeolite was added to each conical flask containing 100 mL sodium
chloride solution of 2 M concentration. Then the conical flasks were shaken by an incubator shaker (150 rpm; 20 °C) for 24 hours (Torabian et al. 2010). In order to prevent the possible intervention of the chloride anions in the modification of the zeolite, samples were washed several times with distilled water to remove the remaining chloride. The residual chloride in the supernatant of the pre-modified samples was determined by AgNO3 using the argentometry method (Ghiaci et al. 2004). Finally, the samples were dried in an oven at 50 °C for 24 hours (Zhan et al. 2011b).

Treatment of the natural zeolite with surfactant

Zeolite surfactant modification can improve the adsorption capacity. A monolayer is formed when the surfactant concentration is equal to or less than its critical micelle concentration (CMC). The surfactant molecules form a bilayer of surfactant on the surface of the zeolite if the surfactant concentration in a solution exceeds the CMC concentration (CMC). The surfactant molecules form a monolayer when the surfactant concentration is equal to or less than its critical micelle capacity. A monolayer is formed when the surfactant concentration is equal to or less than its critical micelle concentration (CMC) concentrations being lesser, equal, and higher than the CMC of the surfactant, respectively. Cation exchange capacity (CEC) and external cation exchange capacity (ECEC) of the adsorbents were determined according to the procedure of Haggerty & Bowman (1994). For the preparation of the modified zeolite, 10 g of the prepared cationic zeolite was added into 200 mL conical flasks containing 100 mL of different concentrations of HDTMA. Then, the flasks were shaken in an incubator shaker (150 rpm; 20 °C) for 24 hours. The solid was washed with distilled water repeatedly until no Br⁻ was detected by AgNO3 solution, and then it was dried in an oven at 50 °C for 24 hours (Torabian et al. 2010). The zeolites modified with 0.5, 1.8, and 20 mmol/L HDTMA solutions were named SMZ1, SMZ2, and SMZ3, respectively.

Adsorption experiments

To compare the efficiencies of NOM removal with different types of modified adsorbents, 100 mL of a constant concentration of NOM was poured into conical flasks, and then a fixed dose (0.08 g/L) of different adsorbents was added to each flask. The solutions were shaken until equilibrium was reached (150 min), during which time there was no significant increase in the rate of adsorption. The % removal of NOM was calculated using Equation (1). The adsorbent with the higher adsorption capacity of NOM was chosen for use in the next experiments. All the adsorption experiments were carried out in a batch system. A stock solution of NOM was prepared by mixing the desired amount of natural raw water containing NOM in distilled water. This solution was diluted to obtain the required solutions. The kinetics of the adsorption were determined by analyzing the adsorption of the NOM at different time intervals. A total organic carbon (TOC) analyzer (TOC-VCSH, Shimadzu, Japan) was used to analyze NOM in the aqueous solutions. The effect of different doses of the adsorbent, which ranged from 0.2 to 1.2 g/L, was examined. The influence of initial pH was studied in various ranges (3–11) at a constant adsorbent dose. NOM adsorption experiments were performed to acquire isotherms at a fixed dose of the adsorbent for the time greater than equilibrium at 25 °C in an incubator shaker (Innova 4340, USA). 0.1 M HCl and NaOH prepared from the analytic grade chemicals were used for the pH adjustment. The % removal of NOM was calculated using the following equation:

\[
% \text{Removal of NOM} = \left(1 - \frac{C_e}{C_0}\right) \times 100
\]

where \(C_0\) and \(C_e\) are the initial and residual concentrations of NOM (mg/L), respectively.

Blank samples were used as controls for each series of experiments. The amount of adsorbed NOM on SMZ was calculated using the following equation:

\[
q_e = \frac{(C_0 - C_e) \times M}{V}
\]

where \(q_e\) is the amount of NOM adsorbed on adsorbate (mg/g) at equilibrium time, \(C_e\) is the equilibrium liquid-phase concentration of NOM (mg/L), \(V\) is the volume of the solution (L), and \(M\) is the weight of the adsorbent used (g).
RESULTS AND DISCUSSION

Characterization of the natural zeolite

The XRD patterns showed that clinoptilolite was the main component of the natural zeolite. The structural parameters of the SMZ were very close to that of the corresponding parent natural zeolite, which showed that the crystalline nature of the zeolites remained intact after chemical treatment with surfactant molecules (Figure 1). The surface of the natural and modified zeolite was observed using an SEM device and the observed results are presented in Figure 2. The crystal structure of the natural zeolite can be clearly seen (Figure 2(a)). However, the crystal structure of the SMZ shows different images (Figure 2(b)). This result indicates that an organic layer formed on the zeolite surface when natural zeolite was modified by the surfactant solution. The chemical composition of the natural zeolite is given in Table 1.

The CEC and ECEC of the natural zeolite were determined to be 1.85 and 0.205 meq/g, respectively.

![Figure 1](https://iwaponline.com/jwh/article-pdf/13/2/394/395059/jwh0130394.pdf)

**Figure 1** | XRD patterns of (a) natural zeolite and (b) SMZ.

![Figure 2](https://iwaponline.com/jwh/article-pdf/13/2/394/395059/jwh0130394.pdf)

**Figure 2** | SEM images of (a) natural zeolite and (b) SMZ.
Effect of the amount of HDTMA in the zeolitic material

The removal efficiencies of the different types of modified zeolites are shown in Figure 3. According to the figure, the results show that SMZ3 as the zeolite loaded with a surfactant concentration greater than CMC had a higher capacity to adsorb NOM. This result indicates that surface coverage as a bilayer rather than a monolayer has a strongly favorable influence on NOM adsorption onto HDTMA-modified zeolites. Therefore, among the types of adsorbents, SMZ3 was chosen as the best adsorbent and used for the next experiments. The results showed that natural zeolite had an insignificant affinity for NOM in aqueous solutions. This may be due to the strong dipole interaction between natural zeolite and water, which excludes HA from zeolites. Different mechanisms, such as hydrogen bonding, hydrophobic interaction, and partitioning mechanisms, have been suggested to account for NOM adsorption onto SMZ with monolayer coverage (Wang et al. 2006). HA is one of the main components of NOM and contains several kinds of functional groups, such as –COOH and –OH (Hartono et al. 2009). The formation of hydrogen bonds between the N of HDTMA and hydroxyl groups and carboxylic groups of HA may be favorable to HA adsorption onto modified zeolite. Koopal et al.’s study showed the binding of cationic surfactant cetylpyridinium chloride to HA was due to electrostatic and hydrophobic attractions (Koopal et al. 2004). This shows that hydrophobic interaction or electrostatic attraction may be the main mechanism in HA or other NOM adsorption onto cationic SMZ. When a surfactant monolayer forms on modified zeolite, NOM adsorption may be attributed to hydrophobic interaction and hydrogen bonding. NOM components adsorption may be driven by a collaboration of hydrophobic interaction, hydrogen bonding, and electrostatic interaction for modified zeolite with bilayer coverage (Ding & Shang 2010).

Effect of contact time and initial concentration

Figure 4 illustrates the effect of contact time and initial concentration on the adsorption of NOM onto SMZ3. For assessing the effect of contact time and initial concentration of NOM, a fixed dose of SMZ3 at pH = 7 was used for each concentration of NOM. The experiments showed that the amount of adsorbed NOM on the zeolite surface increased gradually; by increasing the contact time, the adsorption rate was initially rapid and then gradually decreased with time until it reached equilibrium beyond which there was no significant increase in the rate of adsorption. Equilibrium was nearly reached after 150 min for five different initial NOM concentrations. Hence, in the present work, 150 min was chosen as the equilibrium time. Figure 4 shows that the amount of adsorbed NOM depends on the initial concentration of NOM in the solution. By increasing the initial concentration of NOM from 4 to 30 mg/L, the amount of adsorbed NOM at the equilibrium time (qe) increased from 4 to 16 mg/g. It was observed that the

<table>
<thead>
<tr>
<th>Component</th>
<th>(w/w) %</th>
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<tbody>
<tr>
<td>SiO₂</td>
<td>69.321</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>10.475</td>
</tr>
<tr>
<td>Na₂O</td>
<td>2.224</td>
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<tr>
<td>MgO</td>
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<tr>
<td>P₂O₅</td>
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<tr>
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</tr>
<tr>
<td>K₂O</td>
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</tr>
<tr>
<td>CaO</td>
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<tr>
<td>TiO₂</td>
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<tr>
<td>Fe₂O₃</td>
<td>0.662</td>
</tr>
<tr>
<td>Sr</td>
<td>0.028</td>
</tr>
<tr>
<td>Zr</td>
<td>11.27</td>
</tr>
<tr>
<td>Loss by ignition</td>
<td>0.017</td>
</tr>
</tbody>
</table>

Table 1 | Chemical composition of the natural zeolite

Figure 3 | Effect of different types of surfactant-modified zeolite on the % removal of NOM (initial concentration = 10 mg/l, pH = 7, and adsorbent dose = 0.8 g/l).
amount of adsorbed NOM increased with the increase in the contact time for all the initial NOM concentrations. These observations show that initial NOM concentration has no effect on required time for equilibrium. During the initial stages, many numbers of vacant sites are accessible on the surface of the adsorbent; therefore, the adsorption rate of NOM is relatively high. The adsorption process becomes less efficient due to the gradual occupancy of these sites. With increasing time, the occupation of the remaining vacant sites becomes more difficult owing to the increased repulsive forces between NOM components on the surface of the adsorbents. These results are consistent with other similar studies (Anirudhan & Ramachandran 2010).

Effect of pH

Figure 5(a) shows that the NOM removal efficiency increases with decreasing pH. A low pH was best for NOM adsorption onto SMZ3, and we used pH 5 for isotherm experiments in the following stages. According to the literature, electrostatic interaction may be the significant mechanism for NOM adsorption onto SMZ, in addition to hydrophobic interaction and hydrogen bonding (Zhan et al. 2010b). HA, fulvic acid, and tannic acid are the principal components of NOM; they are anionic hydrophobic macromolecules and have weakly acidic functional groups. At lower pH, most of the weakly acidic functional groups in HA and fulvic acid are
uncharged and are therefore more susceptible to adsorption by SMZ (Zhan et al. 2011c). NOM components are weak organic acids, and their ionization is strongly dependent on solution pH. At low solution pH, NOM molecules are almost completely ionized at the adsorption of NOM onto SMZ at lower solution pH. NOM molecules are almost completely ionized at higher solution pH. The increase of solution pH from 3 to 11 leads to decrease of hydrogen bonding between NOM and SMZ but increases electrostatic attraction between NOM and SMZ. At higher solution pH, completely ionized NOM molecules cannot supply hydroxyl hydrogen atoms to the nitrogen atom of the HDTMA bilayer of SMZ to form hydrogen bonding (Karadag et al. 2007; Lin et al. 2011a). In addition, the increase of the solution pH leads to the increase of competition between the hydroxyl ion and the ionized NOM molecules for the same positively charged adsorption sites on the surface of SMZ3, which causes a decreased NOM adsorption capacity (Wang & Zhu 2007; Zhan et al. 2011b). Furthermore, it is noticeable that the NOM molecular size may increase from a spherical structure form at lower pH to a linear structure form at higher pH, which also indicates that the adsorption of NOM is reduced at higher pH values (Wang & Zhu 2007; Monash & Pugazhenthi 2010). Similar trends of pH effect were observed for the adsorption of fulvic acid and HA on SMZ (Wang et al. 2006; Anirudhan & Ramachandran 2007). However, Lin’s study showed that the tannic acid adsorption capacity for SMZ was relatively high at solution pH of 4.0–7.0, and decreased with increasing solution pH from 7.0 to 8.5 (Lin et al. 2011b).

Effect of adsorbent dose

Figure 5(b) presents the effect of adsorbent dose on NOM removal at different initial concentrations of NOM. The experiments showed that with increasing the amount of adsorbent dose from 0.2 to 1.2 g/L, % removal of NOM increased for all NOM concentrations. However, qe for different NOM concentrations decreased with increasing the adsorbent dose. For example, according to Figure 5(b), qe (mg/g) for the initial NOM concentration of 4 mg/L decreased from 10 to 4.1 mg/g, and for the initial concentration of 30 mg/L decreased from 55 to 19 mg/g when the adsorbent dose was increased from 0.2 to 1.2 g/L. It is easily understood that the number of available adsorption sites is increased by increasing the adsorbent dose, which results in the increased percentage of NOM removal. On the other hand, the experiments showed that qe decreased when the adsorbent dose was increased, which is due to unsaturated sites on the adsorbent during the adsorption process (Wang & Peng 2010; Lin et al. 2011b).

Adsorption kinetics

The pseudo-first-order of Lagergren is one of the most widely used equations for the sorption of solute from a liquid solution (Ho & McKay 1999). The differential pseudo-first-order equation is expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$

(3)

where $q_t$ and $q_e$ are the amount of the NOM adsorbed (mg/g) at time $t$ and at equilibrium time, respectively, and $k_1$ is the rate constant of adsorption (1/min). The integration of Equation (3) with the initial conditions, $q_t = 0$ at $t = 0$ and $q_t = q_e$ at $t = t_e$ leads to the following:

$$\log(q_e - q_t) = \log q_e - (k_1/2.303)t$$

(4)

Figure 6(a) shows the plots of linear form of pseudo-first-order kinetics for all concentrations of NOM. The intercept and slope of the plots were used to determine the values of $q_e$ and the pseudo-first-order rate constant ($k_1$), respectively (Hartono et al. 2009). The calculated rate constant, experimental and calculated ($q_e$), and corresponding correlation coefficient values are presented in Table 2. It was also observed that correlation coefficients ($r^2$) were relatively low for all NOM concentrations. The calculated $q_e$ values for the pseudo-first-order kinetics do not agree with experimental values very well (Table 2). These results show no suitability of the pseudo-first-order
model in foretelling the kinetics of NOM adsorption onto the SMZ3.

Ho's pseudo-second-order model, the differential equation, is expressed as follows (Ho & McKay 1999; Harno et al. 2009):

\[
\frac{dq_t}{dt} = k_2(q_e - q_t)^2
\]

(5)

where \(k_2\) is the equilibrium rate constant calculated for the pseudo-second-order adsorption model (g/mg/min).

Equation (5) can be arranged to obtain linear form as follows:

\[
t/q_e = 1/(k_2q_e^2) + 1/q_et
\]

(6)

\[
h = k_2q_e^2
\]

(7)

where \(h\) is the initial sorption rate and can be obtained from the intercept. The pseudo-second-order kinetic analysis reveals that the value of the initial adsorption rates, \(h\), increases with increase in the initial NOM concentration (Table 2). The lower the concentration of NOM in the solution, the lower the probability of collisions between the adsorbate and active site on the surface of the adsorbent.

The \(q_e\) is obtained from the slope of the plot of \(t/q_t\) against \(t\) (Figure 6(b)), \(k_2\) can be calculated from the value of the initial sorption rate. The calculated \(q_e\) values agree with the experimental data very well (Table 3). The correlation coefficients \(r^2\) for the pseudo-second-order kinetic model are higher than 0.99 for all concentrations. These

Table 2 | Pseudo-first- and pseudo-second-order adsorption rate constants and the calculated and experimental \(q_e\) for the adsorption of NOM onto SMZ3

<table>
<thead>
<tr>
<th>Kinetic models Concentration (mg/L)</th>
<th>Experimental (q_{e,exp}) (mg/g)</th>
<th>Pseudo-first-order</th>
<th>(k_1) (1/min)</th>
<th>(q_{e,cal}) (mg/g)</th>
<th>(r^2)</th>
<th>Pseudo-second-order</th>
<th>(k_2) (g/mg/min)</th>
<th>(q_{e,cal}) (mg/g)</th>
<th>(r^2)</th>
<th>(h) (mg/g/min)</th>
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<tr>
<td>4</td>
<td>3.8</td>
<td>0.012</td>
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<td>0.90</td>
<td></td>
<td>0.013</td>
<td>3.33</td>
<td>0.993</td>
<td>0.14</td>
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<tr>
<td>8</td>
<td>5.8</td>
<td>0.015</td>
<td>5</td>
<td>0.98</td>
<td></td>
<td>0.006</td>
<td>6.64</td>
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<td>0.26</td>
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<tr>
<td>15</td>
<td>11</td>
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<td>7.34</td>
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<td></td>
<td>0.0048</td>
<td>11.57</td>
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<td>20</td>
<td>13</td>
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<td></td>
<td>0.0041</td>
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<td>0.997</td>
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<td>30</td>
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<td>0.0048</td>
<td>16.58</td>
<td>0.994</td>
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Table 3 | The isotherms parameters and correlation coefficients for NOM adsorption onto SMZ3

<table>
<thead>
<tr>
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<th>Langmuir</th>
<th>Freundlich</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>(q_m) (mg/g)</td>
<td>(K_L) (L/mg)</td>
</tr>
<tr>
<td>25</td>
<td>147.23</td>
<td>0.383</td>
</tr>
</tbody>
</table>

Figure 6 | (a) Pseudo-first-order and (b) pseudo-second-order kinetics for NOM adsorption onto SMZ3 (adsorbent dose = 0.8 g/L and pH = 7).
indicate that the adsorption of NOM from solution onto SMZ3 obeys the pseudo-second-order kinetic model.

**Adsorption isotherm**

In this study, experimental data were analyzed by the Langmuir and Freundlich isotherm models. The linearized form of the Langmuir equation is given as follows:

\[ \frac{1}{q_e} = \frac{1}{q_m K_l C_e} + \left(\frac{1}{q_m}\right) \]  \hspace{2cm} (8)

where \( C_e \) (mg/L) is the equilibrium concentration of NOM in the solution, \( q_e \) (mg/g) is the amount of NOM adsorbed onto SMZ3 at equilibrium, \( q_m \) (mg/g) is the maximum adsorption capacity, and \( K_l \) (L/mg) is the Langmuir constant related to the sorption energy. The plot of \( 1/q_e \) versus \( 1/C_e \) gives a straight line (Figure 7(a)), and the slope and intercept of this line correspond to \( q_m \) and \( K_l \), respectively (Fytianos et al. 2000; Shirmardi et al. 2013; Vosoughi Niri et al. 2014). The calculated correlation coefficient \( r^2 \) and the Langmuir constant are presented in Table 3. From the table, it is evident that the maximum NOM sorption capacity of SMZ3 \( (q_m) \) and the \( r^2 \) value are 147 mg/g and 0.97 at 25 °C, respectively. The \( r^2 \) of the Langmuir isotherm was greater than that of the Freundlich isotherm for the adsorption of NOM. This implies that the Langmuir model better depicts the adsorption of NOM onto SMZ3 than the Freundlich model. Some investigations of NOM adsorption using several adsorbents have been conducted. For example, Ferro-Garcia et al. (1998) reported that the adsorption capacity of HA on a commercially available activated carbon was 6.9 mg/g. Daifullah et al. (2004) prepared activated carbon from rice husks by chemical activation using phosphoric acid and determined that the adsorption capacity was 45 mg/g based on a Langmuir isotherm. Table 1 summarizes the results of some experiments using different kinds of zeolites for removal of NOM. According to data provided in Table 1, SMZ has been shown to be an efficient adsorbent for the elimination of NOM. As shown in Table 1, the zeolite examined in this work has a greater capacity for eliminating NOM, compared to those of previously tested adsorbents. Considering its high adsorption capacity, as well as its profound availability and ease of accessibility in nature, it can be concluded that SMZ is an efficient and economic adsorbent for removing NOM, one of the most prevalent contaminants in most surface water. These characteristics, along with the simplicity of operation, introduce adsorption onto SMZ as a suitable technology for treating NOM-contaminated waters, particularly for rural and small communities.

The essential attributes of the dimensionless separation factor \( (R_L) \) can be written as follows:

\[ R_L = \frac{1}{1 + C_0 K_l} \]  \hspace{2cm} (9)

where \( K_l \) (L/mg) is the Langmuir constant and \( C_0 \) (mg/L) is the initial concentration of NOM. The \( R_L \) values between 0 and 1 indicate favorable adsorption. The adsorption
process is irreversible when \( R_L \) is 0, linear when \( R_L \) is 1, and unfavorable when \( R_L \) is greater than 1. By calculating the \( R_L \) values for the examined adsorption system, values were found to be 0.44 – 0.64 for NOM concentrations ranging from 4 to 60 mg/L at 25 °C (Table 3). Accordingly, these values show that the adsorption process is favorable.

Freundlich is another isotherm model for adsorption on an amorphous surface. It assumes the heterogeneity of surface and the exponential distribution of active sites and their energies (Fytianos et al. 2000; Shirmardi et al. 2015). The linearized form of the Freundlich isotherm is presented as the following equation:

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

(10)

where \( C_e \) (mg/L) is the equilibrium concentration of the adsorbate, \( q_e \) (mg/g) is the amount of NOM adsorbed per the mass unit of the adsorbent, and \( k_f \) (mg/g) and \( n \) are the Freundlich constants where \( n \) is an indicator to determine the adsorption process favorability, and \( k_f \) is the adsorption capacity of the adsorbent. These constants can be determined from the linear plot of \( \log q_e \) versus \( \log C_e \) (Figure 7(b)). \( k_f \) can be explained as the adsorption or distribution coefficient and represents the quantity of NOM adsorbed onto SMZ3 for a unit equilibrium concentration. The magnitude of the exponent, \( 1/n \), gives an indication of the favorability of the adsorption. Values of \( n > 1 \) represent a favorable adsorption condition (Haggerty & Bowman 1994; Shirmardi et al. 2012). Values of \( k_f \) and \( n \) are calculated from the intercept and slope of the plot, respectively, and listed in Table 4. The results suggest that SMZ3 adsorbs NOM favorably. However, the values of the correlation coefficients \( (r^2) \) indicate that the Langmuir isotherm is the best-fitted graph for the adsorption of NOM on SMZ3.

### CONCLUSIONS

The results show that SMZ can be used as a low-cost adsorbent for the adsorption of NOM from aqueous solution, especially in areas where there are many zeolite mines. The adsorption of NOM by SMZ was enhanced at acidic pH levels. For SMZ3, the NOM adsorption process developed reasonably well with the pseudo-second-order kinetic model. Results from this study indicate that HDTMA-modified natural zeolite is a favorable adsorbent for the removal of NOM from aqueous solutions. The equilibrium data fitted well with the Langmuir isotherm. The maximum adsorption capacity of SMZ3 with cationic surfactant for NOM was 147 mg/g at 25 °C and pH 5.

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