Removal of haloacetonitrile by adsorption on thiol-functionalized mesoporous composites based on natural rubber and hexagonal mesoporous silica

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ABSTRACT
Haloacetonitriles (HANs) are nitrogenous disinfection by-products (DBPs) that have been reported to have a higher toxicity than the other groups of DBPs. The adsorption process is mostly used to remove HANs in aqueous solutions. Functionalized composite materials tend to be effective adsorbents due to their hydrophobicity and specific adsorptive mechanism. In this study, the removal of dichloroacetonitrile (DCAN) from tap water by adsorption on thiol-functionalized mesoporous composites made from natural rubber (NR) and hexagonal mesoporous silica (HMS-SH) was investigated. Fourier-transform infrared spectroscopy (FTIR) results revealed that the thiol group of NR/HMS was covered with NR molecules. X-ray diffraction (XRD) analysis indicated an expansion of the hexagonal unit cell. Adsorption kinetic and isotherm models were used to determine the adsorption mechanisms and the experiments revealed that NR/HMS-SH had a higher DCAN adsorption capacity than powered activated carbon (PAC). NR/HMS-SH adsorption reached equilibrium after 12 hours and its adsorption kinetics fit well with a pseudo-second-order model. A linear model was found to fit well with the DCAN adsorption isotherm at a low concentration level.

Keywords: Adsorption, Composite material, Haloacetonitrile

1. Introduction
Haloacetonitriles (HANs) are nitrogenous species of disinfection by-products (DBPs), which can be formed by reactions between chlorine, chloramine or bromine disinfectants and natural organic matter (NOM). HANs are of concern because they cause problems in wastewater and tap water. The disinfection of drinking water reduces microbial risks but increases chemical exposure to man. Increasing of human health risks are due to the formation of disinfection by-products (DBPs) in the organic and inorganic precursors. Monochloroacetronitrile (MCAN), dichloroacetonitrile (DCAN), trichloroacetonitrile (TCAN), bromochloroacetonitrile (BCAN), and dibromoacetonitrile (DBAN) are common HANs. Several techniques can remove DBPs from water such as adsorption [1], ozonation [2] and membrane filtration [3]. Among these three processes, however, the adsorption process has been most popular for water treatment because of its low cost and simple application. Although different materials have been used to adsorb DBPs, a suitable one for use with tap water has not been identified. Consequently, a study on the removal HANs from tap water using modified adsorbents can be deemed useful.

Among porous materials, mesoporous silicas provide a number of advantages as adsorbents because of their high surface area and narrow pore size, which improves their adsorption capacity and adsorption selectivity. Moreover, hexagonal mesoporous silica (HMS) is one of many kinds of adsorbents that have been used. In the past, a polymer/silica composite has been studied as a new material that has the advantages of silica and organic polymer. Natural rubber (NR) is an organic material that many have attempted to modify because of its thermal stability and mechanical properties. A NR/HMS composite has been synthesized and characterized as an attractive prospective adsorbent.

Consequently, the objectives of this study are to investigate the adsorption efficiency of a thiol-functionalized mesoporous com-

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posite made from natural rubber and hexagonal mesoporous silica (NR/HMS-SH) in haloacetonitrile (HANs) removal. In this study, dichloroacetonitrile (DCAN) was selected as the representative HAN because it is a chloro-DNB that is highly toxic and has a considerable presence in water. The modification of hexagonal mesoporous silica (HMS) with the thiol group (R-SH) and natural rubber was employed to investigate the effect of surface functional groups on the DCAN adsorption. The adsorption experiments were carried out in batch experiments. The adsorption kinetics and the adsorption isotherm were studied to investigate the adsorption mechanisms. Moreover, the ionic strength and pH of synthesized water was controlled so that it could adequately represent tap water in this study.

2. Materials and Methods

2.1. Preparation of NR/HMS-SH

2.1.1. Materials and reagents

TEOS (AR grade, >99%), MPTMS (AR grade, 95%), and DDA (AR grade, 98%) were purchased from Sigma-Aldrich (Germany), THF (AR grade, 99.5%), C2H5OH (AR grade, 99.9%), and H2SO4 (AR grade, 98%) were purchased from QRëC (New Zealand). The NR (commercial grade) was supplied by the Thai Hua Chumporn Natural Rubber Co., Ltd. (Thailand).

2.1.2. Synthesis of NR/HMS-SH

The thiol-functionalized mesoporous composite was made of natural rubber and hexagonal mesoporous silica (NR/HMS-SH) according to the condition of NR/HMS-SO3H synthesis [4]. Firstly, 1 g of a natural rubber (NR) sheet was mixed with 30 mL of tetrahydrofuran (THF) at room temperature overnight. The NR sheet was completely dissolved in the THF to obtain a homogeneous solution. Secondly, 7.51 g of dodecylamine (DDA) was added in the solution and stirred. After 0.5 h, 21 g of tetraethoxysilane (TEOS) was added and stirred for another 0.5 h. Next, 106 g of H2O was added and stirred at 40°C for 0.5 h and then 4.96 g of 3-mercaptopropyltrimethoxysilane (MPTMS) was added into the mixture by stirring and then it was left to stand at 40°C for 1 h. The gel was aged at 40°C for 3 days, after which it was precipitated in 100 mL of ethanol. The solid product was vacuum dried at 60°C for 2 h. Finally, the template in the composite was removed with 0.05 M of H2SO4/EtOH that from the concentrated sulfuric acid was distilled off with ethanol. The pH was checked at around 7 and dried at 80°C then vacuum dried with ethanol. The pH was checked at around 7.

2.2. Characterization of NR/HMS-SH

Structural information on the NR/HMS-SH composite was obtained using X-ray powder diffraction (XRD) analysis on X-ray powder of 40 KV and 40 mA. The repeating distance between the pore centers of the hexagonal structure was calculated from the XRD data [5]. A Fourier-transform infrared (FT-IR) spectrometer equipped with a mercury cadmium telluride detector was applied for the identification of NR and the functional groups in the composite. A self-supporting disk (20 mm, 10-20 mg) was placed in the quartz cell attached to a conventional closed circulation system. All the IR spectra were recorded using a scanning electron microscope (SEM). The sample was fixed on an aluminum stub before it was observed by the SEM. The samples on the copper grids were observed without any metal coating.

3. Results and Discussion

3.1. Physiochemical Characteristics of the Synthesized Adsorbents

3.1.1. XRD analysis

Fig. 1 shows the XRD pattern of the NR/HMS-SH composite after the extraction of the template molecules. This material exhibited one diffraction peak at 20 in the 2.2°, corresponding to the characteristic of the hexagonal porous structure.

3.1.2. FTIR spectroscopy

FTIR analysis was used to confirm the presence of NR and the SH functional group in the HMS structure of the NR/HMS-SH composites (Fig. 2). The stretching vibration of the silica framework (Si-O-Si) appeared at ~1000 and 1300/cm. The broad band at around 3500/cm can be assigned to the free silanol group. The band related to the thiol group was observed at around 2550-2620/cm (S-H), but it was a very weak band.

3.1.3. Electron microscopy

The particle size of a NR/HMS-SH composite is shown in Fig. 3. The presence of NR/HMS-SH enhanced the agglomeration of HMS particles. It was observed that NR was homogeneously dispersed throughout the particles of the NR/HMS composite.
3.2. Adsorption Kinetics

The kinetic curve for DCAN adsorption on the porous adsorbent is shown in Fig. 4. A large amount of DCAN was adsorbed over PAC and NR/HMS-SH, but with PAC equilibrium was reached after a short contact time (2 h). For NR/HMS-SH, the amount of adsorbed DCAN reached equilibrium at 12 h.

Kinetic modeling and pseudo-first-order and pseudo-second-order models were employed to investigate the adsorption mechanisms. Pseudo-first-order and pseudo-second-order equations can be defined as shown by Eqs. (1) and (2).

\[
\frac{t}{q_t} = \frac{1}{k_1 q_e} + \frac{t}{q_e}
\]

where \( q_e \) is the amount of adsorbed contaminant at equilibrium (mg/g), \( q_t \) is the amount of adsorbed contaminant at time \( t \) (mg/g), \( k_1 \) is the rate constant of pseudo-first-order adsorption (min\(^{-1}\)), and \( k_2 \) is the rate constant of pseudo-second-order adsorption (g/mg·min).

Based on the pseudo-second-order model, the initial adsorption rate can be determined using Eq. (3).

\[
h = k_2 q_e^2
\]

In order to quantitatively compare the applicability of different kinetic models, a normalized standard deviation \( \Delta q \) (%) was used as shown in Eq. (4).

\[
\Delta q(\%) = 100 \times \sqrt{\frac{\sum (q_{exp} - q_{calc})^2}{N}}
\]

where \( N \) is the number of data points and \( q_{exp} \) and \( q_{calc} \) (mg/g) are the experimental and the calculated adsorption capacities. The best fit models should have the lowest \( \Delta q \) (%) values. The kinetic parameters were calculated and the results are shown in Table 1.
Table 1. Kinetic Parameters of DCAN Adsorption on NR/HMS-SH using Pseudo-first-order and Pseudo-second-order Kinetic Models

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>( q_e, \text{exp} )</th>
<th>( h )</th>
<th>( q_e, \text{cal} )</th>
<th>( k_1 )</th>
<th>( k_2 )</th>
<th>( R^2 )</th>
<th>( \Delta q (%) )</th>
<th>Kinetic model</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR/HMS-SH</td>
<td>274</td>
<td>6.13</td>
<td>260</td>
<td>0.0042</td>
<td>-</td>
<td>0.8173</td>
<td>0.8524</td>
<td>65.23</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>268</td>
<td>-</td>
<td>7.51\times10^{-5}</td>
<td>0.9969</td>
<td>0.9974</td>
<td>27.22</td>
</tr>
</tbody>
</table>

Fig. 4. DCAN adsorption kinetics of PAC and NR/HMS-SH at initial concentration 100 \( \mu g/L \), pH 7, IS = 0.01 M.

The data fitting curve for NR/HMS-SH is shown in Fig. 5. It displays three regimes; the first regime presents the external mass transfer in the boundary layer and the second presents the diffusion through the pores of the adsorbent. Moreover, the last step presents the DCAN adsorption on the internal site of the adsorbent. It occurred very quickly, so the rate limiting step of the adsorption must have happened during the first or the second step. Both steps together could thus be considered the controlling step.

3.3. Adsorption Isotherms

NR/HMS-SH is a functionalized silica-based material that had a comparable adsorption capacity to PAC. Moreover, the results indicate that increasing the specific surface area of the adsorbent cannot be used as an explanation for DCAN's enhanced adsorption capacities when compared with the results of a previous study, which gave a similar specific surface area for HMS that functionalized with the thiol group without adding the natural rubber (SBET NR/HMS-SH of 880.4 m\(^2\)/g). The results, however, can be used to explain the density of the functional group because NR/HMS-SH provided less density of sulfur than HMS in the previous study [7]. It can be argued that the natural rubber in the adsorbent may have affected the interaction that occurred between the functional group and HMS.

In order to model the adsorption mechanism, linear, Langmuir and Freundlich isotherm models were used to test the experimental adsorption process. The linear, Langmuir and Freundlich equations can be defined as shown in Eqs. (5), (6) and (7).

\[
q_e = K_p C_e
\]  
(5)

\[
\frac{1}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m}
\]  
(6)

\[
q_e = K_f C_e^{1/n}
\]  
(7)

where \( q_e \) is the amount of adsorbate adsorbed at equilibrium (mg/g), \( K_p \) is the linear constant (L/mg), \( q_m \) is the maximum adsorption capacity (mg/g), and \( K_L \) is the Langmuir constant (L/mg). \( K_f \) and \( n \) are constants, \( C_e \) is the equilibrium concentration (mg/L), and \( C \) is the concentration of the adsorbate at equilibrium (mg/L).

The isotherm parameters of DCAN adsorption on NR/HMS-SH are listed in Table 2. Meanwhile, the predicted and experimental data for the equilibrium adsorption of DCAN on NR/HMS-SH are shown in Fig. 6.

Table 2. Isotherm Parameters of the DCAN Adsorption on the NR/HMS-SH Adsorbent

<table>
<thead>
<tr>
<th>Isotherms</th>
<th>NR/HMS-SH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>-</td>
</tr>
<tr>
<td>( q_m ) (mg/g)</td>
<td>-</td>
</tr>
<tr>
<td>( K_L ) (L/mg)</td>
<td>0.6729</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.8961</td>
</tr>
<tr>
<td>Freundlich</td>
<td>235.39</td>
</tr>
<tr>
<td>( 1/n )</td>
<td>1.6391</td>
</tr>
<tr>
<td>( K_f ) (mg/g)</td>
<td>872.3685</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.7861</td>
</tr>
<tr>
<td>( q(%) )</td>
<td>35.70</td>
</tr>
<tr>
<td>Linear</td>
<td>102.48</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.8961</td>
</tr>
</tbody>
</table>
Fig. 6. Comparison of the predicted and experimental data for the equilibrium adsorption of DCAN on the NR/HMS-SH adsorbent.

4. Conclusions

A NR/HMS-SH composite with a high structure order and mesoporosity was successfully prepared. The formation of the NR/HMS-SH composite induced the coalescence of HMS nanoparticles, resulting in enhanced textural porosity and hydrophobicity. DCAN adsorption on the NR/HMS-SH adsorbent followed a pseudo-second order rate kinetic model. A linear model fit well with the DCAN adsorption isotherm at a low concentration level.

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