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. Monochloroacetonitrile (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-DBP 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 QRE (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 silicate (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 dissolved in the 99.9% ethanol at 70°C for 8 h and filtered; it was then vacuum dried with ethanol. The pH was checked at around 7 and dried at 80°C overnight.

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 power 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 under evacuation at 25°C. A total of 64 scans over 400-4000/cm at a resolution of 4/cm was averaged for each spectrum.

The particle size of the adsorbent was taken by 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.

2.3. Adsorption Study

Stock solutions of HANs were prepared in deionized water, and a phosphate buffer was used to adjust the pH of the solution to 7 and ionic strength (IS) to 10 mM. The kinetic study was prepared by varying the contact time from 0 to 36 h. DCAN was selected as the model HAN. The initial DCAN concentration was 1 mg/L at pH 7. After that, 0.025 g of the adsorbent and 50 mL of the DCAN solution were mixed in a 125 mL Erlenmeyer flask and covered with aluminium foil. The mixture was stirred at 25°C and the supernatant solution was filtrated through a nylon syringe filter (pore size 0.45 µm). The concentration of DCAN was analyzed by gas chromatography with an electron capture detector (GC/ECD) according to EPA Method 551.1 [6]. The concentrations in the isotherm studies were varied from 0.05 to 2 mg/L in single solutions at pH 7, while the ionic strength, adjusted by a phosphate buffer, remain fixed at 10 mM. The contact time was obtained from the kinetic study. After reaching equilibrium, the mixture was separated using a nylon filter and the solution was analyzed by gas chromatography with an electron capture detector (GC/ECD).

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 2θ in the 2.2°, corresponding to the characteristics 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 between 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.

Fig. 1. XRD pattern of the NR/HMS-SH that was extracted for removing the DDA template.

Fig. 2. FTIR spectra of NR/HMS-SH.

Fig. 3. SEM image of NR/HMS-SH at a magnification (a) x15,000 and (b) x25,000.

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).

$$q_t = q_e (1 - \exp(-k_1 t)) \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

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 ($\text{g/mg} \cdot \text{min}$).

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

$$h = k_2 q_e^2 \quad (3)$$

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

$$\Delta q(\%) = 100 \times \sqrt{\frac{\sum [q_{\text{exp}} - q_{\text{cal}} / q_{\text{exp}}]^2}{N - 1}} \quad (4)$$

where N is the number of data points and q_{exp} and q_{cal} (mg/g) are the experimental and the calculated adsorption capacities. The best fit models should have the lowest Δq (%) 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

Adsorbent	q_e , exp ($\mu\text{g/g}$)	h ($\mu\text{g/g}\cdot\text{min}$)	q_e , cal ($\mu\text{g/g}$)	k_1 (1/min)	k_2 (g/mg·min)	R^2	Δq (%)	Kinetic model
NR/HMS-SH	274	6.13	260	0.0042	-	0.8173	65.23	pseudo-first-order
			268	-	7.51×10^{-5}	0.9969	27.22	pseudo-second-order

Fig. 4. DCAN adsorption kinetics of PAC and NR/HMS-SH at initial concentration 100 $\mu\text{g/L}$, pH 7, IS = 0.01 M. **Fig. 5.** Plot of the intraparticle diffusion model for the adsorption of DCAN on NR/HMS-SH.

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).

$$q_e = K_p C_e \quad (5)$$

$$\frac{1}{q_e} = \frac{1}{K_L q_m C_e} + \frac{1}{q_m} \quad (6)$$

$$q_e = K_F C_e^{1/n} \quad (7)$$

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_e 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

Isotherms		NR/HMS-SH
Langmuir		
q_m (mg/g)		-
K_L (L/mg)		-
R^2		0.6729
q (%)		235.39
Freundlich		
$1/n$		1.6391
K_F (mg/g)		872.3685
R^2		0.7861
$q(\%)$		35.70
Linear		
K_p		102.48
R^2		0.8961

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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References

1. Uyak V, Yavuz S, Toroz I, Ozaydin S, Genceli EA. Disinfection by-products precursors removal by enhanced coagulation and PAC adsorption. *Desalination* 2007;216:334-344.
2. Vaipoulou E, Misiti TM, Pavlostathis SG. Removal and toxicity reduction of naphthenic acids by ozonation and combined ozonation-aerobic biodegradation. *Bioresour. Technol.* 2015; 179:339-347.
3. Uyak V, Koyuncu I, Oktem I, Cakmakci M, Toroz I. Removal of trihalomethanes from drinking water by nanofiltration membranes. *J. Hazard. Mater.* 2008;152:789-794.
4. Nuntang S, Poompradub S, Butnark S, Yokoi T, Tatsumi T, Ngamcharussrivichai C. Organosulfonic acid-functionalized mesoporous composites based on natural rubber and hexagonal mesoporous silica. *Mater. Chem. Phys.* 2014;147:583-593.
5. Tanev PT, Pinnavaia TJ. Mesoporous Silica Molecular Sieves Prepared by Ionic and neutral Surfactant Templating: A Comparison of Physical Properties. *Chem. Mater.* 1996;8: 2068-2079.
6. Hodgeson JW, Cohen AL. Determination of Chlorination Disinfection Byproducts, Chlorinated Solvents and Halogenated Pesticides/herbicides in Drinking Water by Liquid-Liquid Extraction and Gas Chromatography with Electron-capture Detection. Ohio: National Exposure Research Laboratory; 1990.
7. Prarat P, Ngamcharussrivichai C, Khaodhiar S, Punyapalakul P. Adsorption characteristics of haloacetonitriles on functionalized silica-based porous materials in aqueous solution. *J. Hazard. Mater.* 2011;192:1210-1218.