

Chemically modified chitosan polymers for bromate removal

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ABSTRACT

Bromate is a harmful byproduct formed during drinking water disinfection processes. In this work, adsorption of bromate by natural chitosan and its chemically modified polymers has been investigated. Bromate adsorption was found between 22.73 mg/g and 43.48 mg/g. Adsorbents were analysed by Fourier transform infrared-ATR spectroscopy. It is suggested that chemical adsorption is the main bromate adsorption mechanism. By fitting theoretical results to experimental data, it is shown that the Langmuir adsorption model and the second-order kinetic model are more applicable to explain the adsorption process. Furthermore, increased bromate adsorption is found at high temperature and at low pH, while coexisting ions have little influence at low concentrations.

Key words | adsorption isotherms, bromate adsorption, chitosan, pseudo-second-order kinetics model, thermodynamics

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INTRODUCTION

Bromide exists in many drinking water sources. It can be converted to bromate, a harmful byproduct, during drinking water disinfection processes, such as ozonisation and chlorination (Boorman *et al.* 1999). Bromate is considered a potential 2b carcinogen by the international agency for research on cancer (Kurokawa *et al.* 1990). A provisional guideline value of 25 µg/L of drinking water was proposed by the World Health Organization (Siddiqui & Amy 1993; von Gunten & Hoigne 1994). However, in many locations, bromate concentration is found above this level, even up to 75 mg/L (Cotruba *et al.* 2005). As the bromide concentration in many natural drinking water sources is much above that value (Fischbacher *et al.* 2015) and disinfection of drinking water by ozone and chlorine is widely used, research on bromate removal has created great interest. Several methods have been tested to eliminate bromate in drinking water, such as pH depression (Siddiqui & Amy 1993), ammonia addition during the formation of bromate (Ozekin *et al.* 1998), UV irradiation after bromate formation (Siddiqui *et al.* 1994), photocatalysis (Mills *et al.* 1996), as

well as using chemical reducing agents, e.g. sulphite ions and zerovalent iron (Gordon *et al.* 2002). However, these methods are expensive, difficult to handle, and also cause secondary pollution. Meanwhile, adsorption of bromate was studied using granular activated carbon (GAC) (Kirisits *et al.* 2000; Chen *et al.* 2012), granular ferric hydroxide (GFH) (Bhatnagar *et al.* 2009), and mesoporous carbon (Xu *et al.* 2014), where the reported maximum bromate adsorption capacity in a broad range between 24.2 µg/g and 40 mg/g was obtained and the initial bromate concentration was in the range from 10 µg/L to 200 mg/L. However, these adsorbents also have regeneration difficulties and disposal problems. To unlock these problems, it is essential to find a more effective, economical, easy-to-handle, and environmentally friendly alternative for bromate removal.

Chitosan is a deacetylated form of chitin, which contains lots of amino and hydroxyl functional groups. It is cheap, abundant, non-toxic, biodegradable, and antibacterial (Rinaudo 2006). Previous studies have shown that

chitosan and its chemically modified polymers have great adsorption capabilities for macromolecular organic matter, e.g. dyes (Chiou & Li 2002; Annadurai *et al.* 2008; Bhatnagar *et al.* 2009; Zhu *et al.* 2010) and proteins (Guibal *et al.* 1998), as well as for smaller ions (Wu *et al.* 2000; Ngah *et al.* 2011), especially chromium ions (Baroni *et al.* 2008; Aydın & Aksoy 2009) and fluoride (Viswanathan *et al.* 2009). Hence, it is worthwhile to discover whether they can also be used as effective adsorbents for bromate removal.

In the present study, natural chitosan (CTS), cross-linked chitosan (CL-CTS) and β -cyclodextrin-linked chitosan (CD-CTS) are tested for bromate adsorption. Isotherm models and Fourier transform infrared spectroscopy (FTIR) are used for explaining the differences in the adsorption mechanisms. As the effectiveness of adsorption depends on other experimental parameters, analyses of pH, temperature and coexisting ions are also shown.

MATERIALS AND METHODS

Preparation of CL-CTS and CD-CTS

CL-CTS and CD-CTS are fabricated using crosslinking methods in order to gain more hydroxyl and amino groups on the polymers' surface by modifying CTS. The employed chemicals are chitosan (84.5–85.5% degree of deacetylation), glutaraldehyde (crosslinking agent, 25 wt%), potassium bromate, β -cyclodextrin (β -CD), sodium bromate (NaBrO_3), sodium chloride (NaCl), sodium nitrate (NaNO_3), sodium bromide (NaBr), and sodium sulphate (Na_2SO_4).

Pretreatment

To prepare CL-CTS, 1 gram of chitosan was dissolved in 100 ml 0.1 mM hydrochloric acid solution. The aqueous solution was treated by ultrasound for 1 h for better dissolution, and then it stayed still for another 1 h.

Chemical crosslinking reaction with glutaraldehyde

The aqueous solution prepared in pretreatment was moved into a 500 ml beaker, heated to 333 K by a hot plate stirrer,

and then 4.8 ml glutaraldehyde solution (25 wt%, 5.3 g) was slowly added into the beaker, while the solution was continuously stirred. The solution was heated to 363 K, and subsequently the temperature was kept at 363 K for 80 min. Afterwards, sodium hydroxide (NaOH) solution (6 mM) was slowly added into the solution until the pH value reached 9, and meanwhile yellow flocs appeared. The liquid was stirred, until reddish sediment was observed in the beaker.

Polymer filtration and drying

The sediment obtained from the step above was filtered, and then washed to neutral pH (=7) by distilled water. Afterwards, the sample was washed by acetone and ethanol, and then the solution was filtrated by a vacuum filter. The filtrate was dried at 318 K for 72 h. In the end, red-brown powder (CL-CTS) was obtained. Note that the preparation of CD-CTS is similar to that of CL-CTS (Chen *et al.* 2009), except that a β -CD solution (200 ml, 25 g/L) was added into the beaker together with the chitosan solution during the second step.

Isothermal adsorption

The first experiment is to establish the isothermal adsorption for different bromate concentrations. An amount of 10 mg of adsorbent was added into 50 ml of solution dosed with a range of bromate concentrations (0.05–50 mg/L). The pH value of the solution was titrated to 6. The solution was shaken in a shaking water bath at 298 K for at least 24 h, which guaranteed the completion of the adsorption based on previous experimental experience. The supernatant of the solution was then filtered by a 0.45 μm filter, and the bromate concentration was analyzed by ion chromatography. The adsorption capacity (Q_e , mg/g) is obtained based on the following equation:

$$Q_e = \frac{(c_0 - c_e)V}{W}, \quad (1)$$

where c_0 (mg/L) is the initial BrO_3^- concentration, c_e (mg/L) is the BrO_3^- concentration at the equilibrium state, V (m^3) is

the volume of solution, and W (g) is the initial weight of the adsorbent.

FTIR spectra

To understand the mechanisms of bromate adsorption, FTIR spectra were performed using a high resolution FTIR system (NEXUS-670, Thermo Nicolet, UK) before and after bromate adsorption. Note that all the samples were pre-treated with potassium bromide.

Adsorption kinetics

In order to probe the relation between adsorption and temperature, isothermal adsorption experiments were performed at four different temperatures. Each time the sample was taken from the supernatant at a fixed time (2–180 min). A fixed bromate solution (100 µg/L, 50 mL) was used for this part of the study.

Competing anions

Other anions present in a water stream, for instance, Cl^- , Br^- , NO_3^- , and SO_4^{2-} , might also be adsorbed, consequently inhibiting bromate adsorption. To examine this issue, CL-CTS is employed to absorb these ions together with the bromate solution with a fixed concentration (50 µg/L, 50 mL). Each time one type of the competing ions was dosed into the solution simultaneously with the adsorbent. The amount of the competing ions is governed by a preset series of molar ratios, i.e. 1:1, 10:1, 100:1, and 500:1. After the experiments, the final concentrations of the competing anions that remained in the solution were analyzed by ion chromatography (Dionex DX-600, ThermoFisher, USA).

Regeneration

In order to study the regeneration capability of CL-CTS, the isothermal adsorption experiment was repeated in the condition that 10 mg CL-CTS adsorbent was added into 50 mL bromate solution (20 mg/L). After 24 h adsorption, the adsorbent was immediately washed with NaOH solution (50 mM) firstly until no bromate could be detected in the filtrate by ion chromatography, and then washed with HCl

solution (10 mM) until the pH of the filtrate was 7. The adsorption and desorption steps were repeated eight times.

RESULT AND DISCUSSION

Isothermal adsorption

According to the procedure described above, bromate adsorption as a function of equilibrium bromate concentration for all three adsorbents (CTS, CL-CTS, and CD-CTS) can be precisely measured, as shown in Figure 1. Note that from 20 mg/L to 50 mg/L (c_e), all three adsorbents exhibit a very small increase of bromate adsorption, suggesting that bromate adsorption could not be further increased at higher bulk concentrations. It is worth mentioning that the range of the bromate concentration studied in this work is from 50 µg/L to 50 mg/L. Bromate concentrations below the lower boundary can be found in many real cases (Cotrubo *et al.* 2005), which suggests that further study should tackle bromate concentration below 50 µg/L. It is observed that CL-CTS adsorbs the highest amount of bromate regardless of the initial bromate concentrations, whereas natural CTS exhibits the least bromate adsorption.

To further understand the equilibrium adsorption theorem, the classical Langmuir–Freundlich (LF) isotherm is employed to fit our experimental data (Turiel *et al.* 2003), given by Equation (2):

$$Q_e = \frac{Q_{\max} \cdot a \cdot c_e^m}{1 + a \cdot c_e^m}, \quad (2)$$

where Q_e is the amount of BrO_3^- adsorbed by the chitosan (mg/g), Q_{\max} is the maximum amount adsorbed within the monolayer (mg/g), c_e is the final BrO_3^- concentration (mg/L), a is related to the median binding affinity constant K_0 ($=a^{1/m}$), and m is the index of heterogeneity; m is equal to 1 for homogeneous materials, and for heterogeneous materials, it is between 0 and 1. When m is unity, the LF isotherm converts to the Langmuir isotherm, given by:

$$Q_e = \frac{Q_{\max} \cdot a \cdot c_e}{1 + a \cdot c_e}. \quad (3)$$

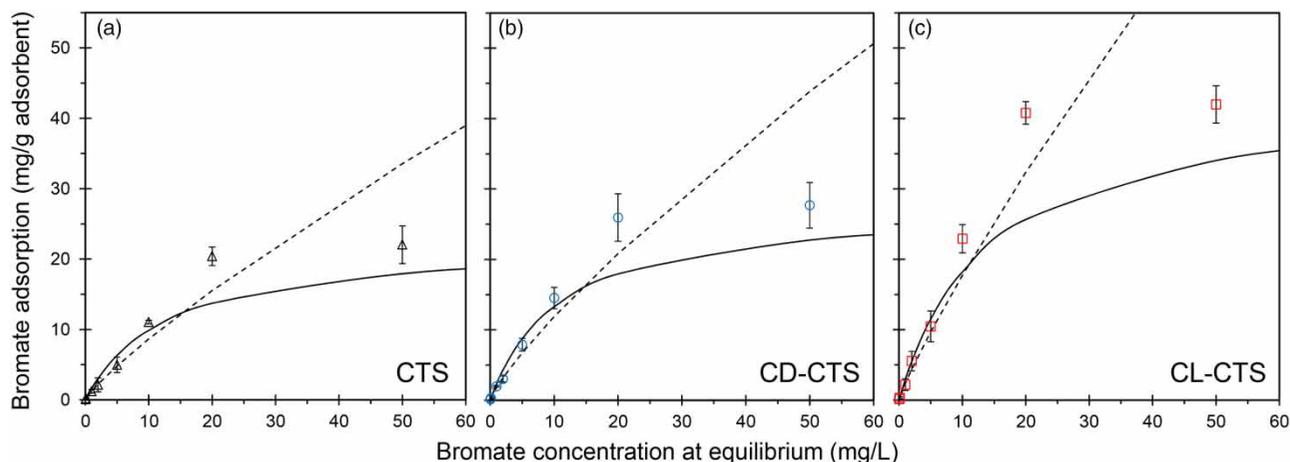


Figure 1 | Experimental and modelling results of the equilibrium adsorption of bromate by (a) CTS, (b) CD-CTS, and (c) CL-CTS as a function of bromate concentration at equilibrium. Symbols are experimental results, solid lines are Langmuir model, and dashed lines are Freundlich model.

When a is a very small number approaching 0, Equation (2) can be transformed to the Freundlich isotherm, as follows:

$$Q_e = a \cdot c_e^m \quad (4)$$

During the fitting procedure by linearizing Equations (3) and (4), the best fitting curve can be obtained when m is equal to 1, which suggests that homogenous adsorption is more applicable to describe the adsorption manner. The correlation coefficients (R^2) of both the Langmuir and Freundlich models are shown in Table 1. Additionally, the maximum adsorption capacity can be derived using the Langmuir approach (Table 1). CL-CTS exhibits the highest adsorption capacity, namely 43.48 mg/g.

FTIR spectra

Figure 2(a) illustrates the characteristics of the molecular structure of CTS, CL-CTS and CD-CTS. Alcohol group peaks are observed at around $1,100 \text{ cm}^{-1}$, and are much

deeper for both CL-CTS and CD-CTS than natural CTS. This phenomenon is due to the increase of alcohol groups (C-OH) contributed by the crosslinking reaction. The chemical reactions of the crosslinking reactions for the formation of CL-CTS and CD-CTS are discussed in previous studies (Zhang *et al.* 2004; Chen *et al.* 2009). During the crosslinking reactions the C=O bond fractures, and the C-O bond forms instead. This phenomenon is found most obviously for CD-CTS, which can be explained by the fact that CD-CTS originally contains more hydroxyl groups (Chen *et al.* 2009). More evidence of the growth of the number of hydroxyl groups (-OH) is that at $3,500 \text{ cm}^{-1}$, the hydroxyl group peaks of CL-CTS and CD-CTS are expanded compared with the natural CTS. At the same time, the peak of the Schiff base (-N=C-) occurs at $1,640 \text{ cm}^{-1}$, which means partially amino groups and aldehyde groups formed the Schiff base by aldimine condensation during the crosslinking reaction (Zhang *et al.* 2004). The rest of the amino groups are converted from primary amino groups to secondary amino groups.

As CL-CTS adsorbs more bromate than CD-CTS, it is interesting to investigate if their molecular structures play a role. By comparison, it is clearly shown that CL-CTS has more amino groups but fewer hydroxyl groups, which underlines that amino groups are more important than hydroxyl groups for bromate adsorption. Note that in the crosslinking reaction, the primary amino groups initially present on CTS are converted to secondary amino groups. This will also benefit bromate adsorption, because the secondary amino groups

Table 1 | Parameters of isothermal adsorption models

Adsorbents	Langmuir			Freundlich		
	Q_{\max} (mg/g)	a (L/mg)	R^2 (%)	a (L/mg)	m	R^2 (%)
CTS	22.52	0.078	99.4	1.25	0.841	86.8
CL-CTS	43.36	0.072	99.9	2.40	0.868	89.3
CD-CTS	29.37	0.092	99.6	1.83	0.812	92.7

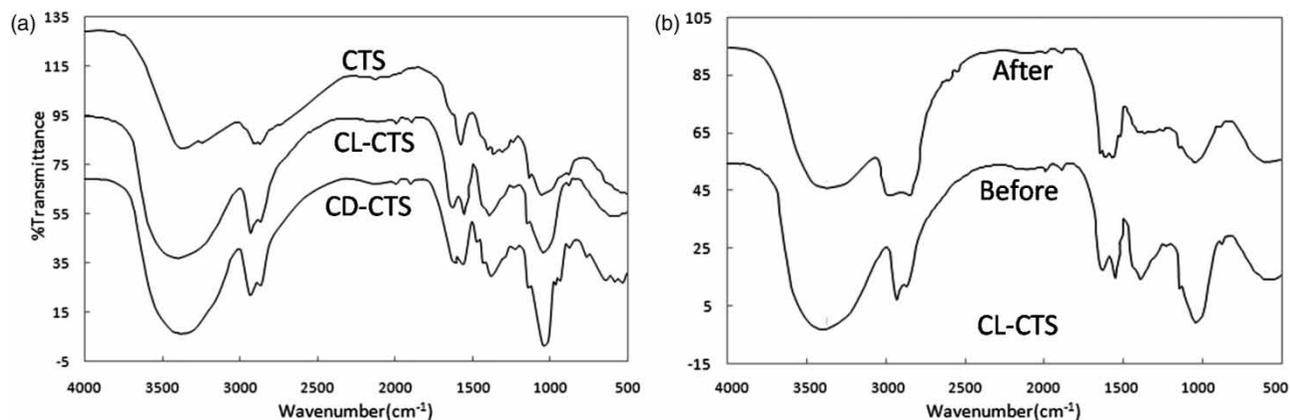
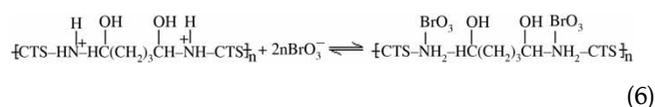
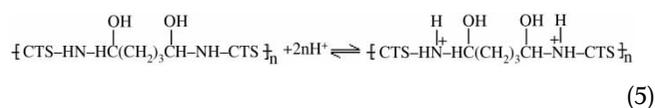


Figure 2 | FTIR spectra of (a) CTS, CL-CTS, and CD-CTS, and (b) of CL-CTS before and after bromate adsorption.

have higher alkalinity than the primary amino groups, and thus would react much more easily with proton ions in the solution to form ammonium ions than the primary amino groups. Given that CL-CTS has the highest secondary amino groups among the three candidates, it achieves the highest bromate adsorption.

The IR spectrum of CL-CTS shows its structure change before and after bromate adsorption (Figure 2(b)). Before bromate adsorption, molecular association happens because of the formed hydrogen bond between nitrogen and hydrogen atoms, which can be witnessed by the peak at 3,300–3,400 cm^{-1} , as shown in Figure 2(b). After bromate adsorption, quaternary ammonium salt is formed, increasing the steric hindrance, thereby decreasing the formation of the hydrogen bond. As a result, the peak shrinks, as shown in Figure 2(b). This change of the shape of the peak indicates that a chemical reaction happens during bromate adsorption. The proposed mechanism of the bromate adsorption process by CL-CTS is given by Equations (5) and (6). During the reaction, most of the secondary amino groups are converted to ammonium ions by combination with protons in the solution, and as a result these protons attract more bromate.



Adsorption kinetics

Since CL-CTS has the highest adsorption capacity, this section focuses on its bromate adsorption kinetics. Adsorption kinetics at four different temperatures were studied by using the pseudo-first-order kinetic model and pseudo-second-order kinetic model (Vasanth Kumar 2006), given as follows:

$$Q_t = Q_e(1 - e^{-K_1 t}) \quad (7)$$

$$Q_t = \frac{K_2 Q_e^2 t}{1 + K_2 Q_e t}, \quad (8)$$

where t (min) is the time, Q_e (mg/g) is the equilibrium adsorption of BrO_3^- , Q_t (mg/g) is the amount of adsorption of BrO_3^- at time t , K_1 (min^{-1}) is the first-order adsorption rate constant, and K_2 (g/mg min) is the second-order adsorption rate constant. The fittings of the theories to the experimental data are shown in Figure 3. The calculated kinetic parameters and correlation coefficients are listed in Table 2. From the correlation coefficients, it is already obvious that the pseudo-first-order model does not explain the experimental data properly, especially at higher temperatures (see Figure 3), whereas the pseudo-second-order model exhibits a perfect correlation, from which it is ascertained that chemical adsorption is involved, and is the rate-limiting step for bromate adsorption (Wang et al. 2007). Both the model and the experimental data suggest that the bromate adsorption rates are in general high and the adsorption equilibrium could be reached within approximately 1 h at all

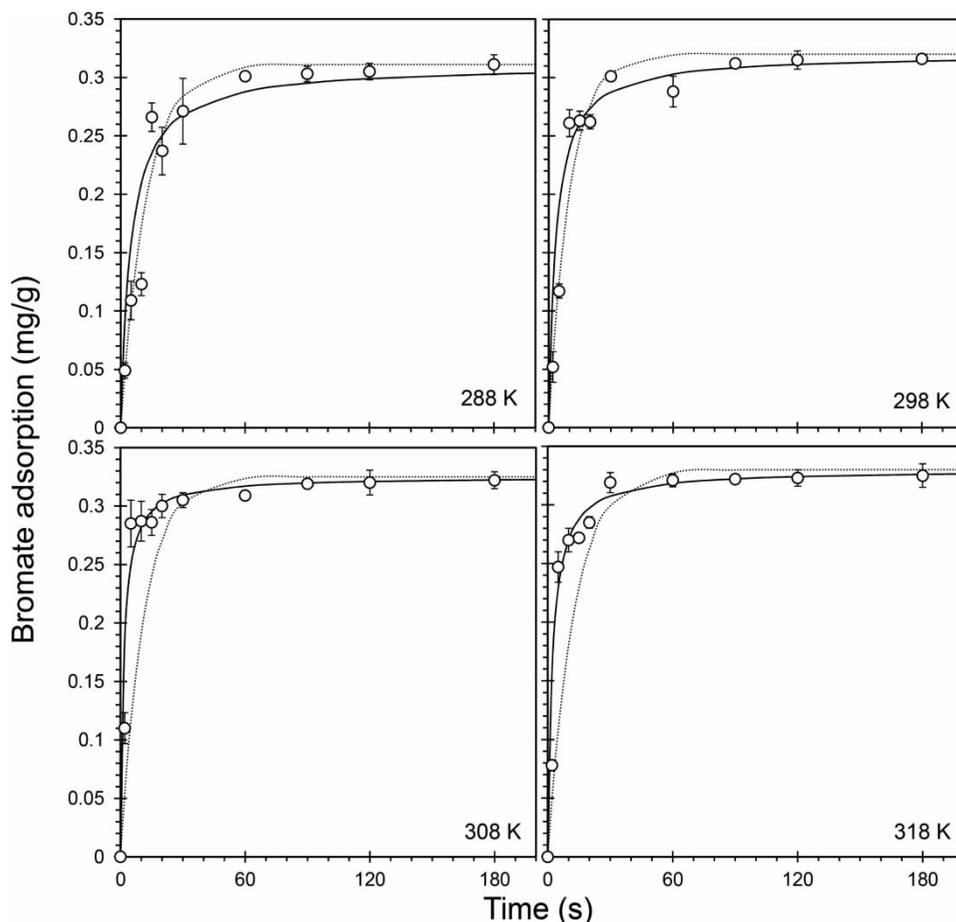


Figure 3 | Adsorption kinetics of bromate on crosslinked chitosan as a function of time for different solution temperatures. Symbols: experimental data. Solid lines: pseudo-second-order kinetics model. Dashed lines: pseudo-first-order kinetics model.

Table 2 | Parameters of adsorption kinetics equation at different temperatures

<i>T</i> (K)	<i>Q_e</i> (mg/g)	First-order		Second-order	
		<i>K₁</i> (min ⁻¹)	<i>R₂</i>	<i>K₂</i> (g·mg ⁻¹ ·min ⁻¹)	<i>R₂</i>
288	0.311	0.081	0.722	0.661	0.995
298	0.32	0.099	0.839	0.918	0.996
308	0.325	0.089	0.264	2.03	0.998
318	0.33	0.079	0.259	1.376	0.999

four temperatures. In addition, the increase of the temperature leads to higher bromate adsorption.

Coexisting ions effect

It is inevitable that common ions coexist in the bromate adsorption process, such as Cl⁻, SO₄²⁻, and NO₃⁻, thus

more awareness of their influence on bromate adsorption is desirable. Table 3 exhibits the results of bromate adsorption in the presence of the coexisting ions, where the molar ratios of coexisting ions to bromate were 0, 1, 10, 100, and 500, respectively. Note that '0' refers to the condition in which no other ions are present. To weigh the severity of the coexisting-ion influence, the reduction of adsorption (ROA) is defined by the following equation:

$$ROA = 1 - \frac{\text{adsorption}_i}{\text{adsorption}_0}, \quad (9)$$

where ROA is the reduction of adsorption, subscript *i* denotes any molar ratio, and subscript 0 denotes that there are no coexisting ions present. When the molar ratios of coexisting ions to bromate are lower than 10, ROAs are below 15%. As the molar ratio increases, the effect of the coexisting

Table 3 | Effect of coexisting ions on bromate adsorption by CL-CTS

Molar ratio	Br ⁻		Cl ⁻		NO ₃ ⁻		SO ₄ ²⁻	
	Adsorption (μg/g)	ROA	Adsorption (μg/g)	ROA	Adsorption (μg/g)	ROA	Adsorption (μg/g)	ROA
0	152	–	152	–	152	–	152	–
1	137	0.10	149	0.02	147	0.03	151	0.01
10	129	0.15	143	0.06	137	0.10	147	0.03
100	104	0.32	118	0.22	109	0.28	144	0.05
500	88.2	0.42	105	0.31	95.8	0.37	132	0.13

ions becomes more severe, especially Br⁻ and NO₃⁻. The ROAs could be ranked as: Br⁻ > NO₃⁻ > Cl⁻ > SO₄²⁻.

Regeneration

It is found that bromate adsorption is still 91.5% (34.6 mg/g) compared with the first experiment (37.8 mg/g) after eight times adsorption and desorption steps, which demonstrates a promising regeneration capability.

CONCLUSIONS

Natural and chemically modified chitosan polymers are environmentally friendly materials. In this work, chemically modified chitosan polymers are fabricated using crosslinking methods. The modified chitosan polymers and natural chitosan have been tested for bromate adsorption. Adsorption isotherms show that they have good bromate adsorption properties, especially the crosslinked chitosan, which adsorbs 43.48 mg/g at maximum, much higher than reported for GAC (Kirisits *et al.* 2000) and GFH (Bhatnagar *et al.* 2009). The adsorption data is best described by a Langmuir isotherm with 0.99 consistency. The process kinetics were evaluated by pseudo-first- and pseudo-second-order models. The pseudo-second-order kinetic model exhibited the highest correlation with the data. The FTIR spectrum shows that amino groups play an important role in bromate removal by chemical reactions. Moreover, the influence of the coexisting ions is also investigated. It is shown that at low concentrations, the coexisting ions will not interfere with bromate adsorption significantly. To summarize, bromate removal by modified chitosan polymers is efficient, fast, and spontaneous, has no secondary pollution, and the adsorbent can be easily

regenerated. It deserves further studies, such as optimizing the adsorbent-producing process, upscaling the experimental setup for pilot tests, and investigating the effect of multiple coexisting ions in real water matrices.

ACKNOWLEDGEMENTS

This work was supported by The Innovation Fund Project for Graduate Student of Shanghai (JWCXSL1201), by Shanghai Sailing Program (16YF1403000), and by National Natural Science Foundation of China (21606085).

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First received 7 June 2016; accepted in revised form 16 December 2016. Available online 2 January 2017