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Research Article

Kinetic and Equilibrium Studies for the Removal of Bromate by the Modified Activated Carbon

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Abstract: Bromate which was formed bromide dissolved in water during the ozonation process, is carcinogenic and mutagenic to humans. To avoid bromate damage, many countries strictly control its concentration in drinking water. Activated carbon is an effective adsorbent material widely used in water treatment. In order to enhance the adsorption of bromate ion on activated carbon, the modified activated carbon was obtained from granular activated carbon by chemical activation using cationic surfactant as an activator. The adsorption characteristics of bromate ion on the modified activated carbon were investigated through adsorption experiments. The effects of temperature, pH in solution, contact time and initial bromate concentration on bromate adsorption by the modified activated carbon were investigated. The experimental data were analyzed by the Langmuir and Freundlich models of adsorption. Kinetic adsorption data were analyzed by the pseudo-first-order kinetic model and the pseudo-second-order model, respectively.

Keywords: Activated carbon, adsorption, bromate, equilibrium, kinetic

INTRODUCTION

Bromate which was formed bromide dissolved in water during the ozonation process, is carcinogenic and mutagenic to humans (Listiarini *et al*., 2010; Ding *et al*., 2010; Marhaba and Bengranie, 2003). Bromate is formed from bromide dissolved in water during the ozonation process, hypochlorination or chloramination of water containing bromide (Wolf *et al*., 1998). The kidney is a target for both BrO_3^- induced toxicity and cancer, the peritoneum for cancer, testes for lowered sperm count and the thyroid for follicular cell cancer (Moslemi *et al*., 2012). To avoid bromate damage, many countries strictly control its concentration in drinking water. There are three main approaches to reduce the concentration of bromate in water. One approach is to remove the bromate precursors, such as bromide and natural organic matter before ozonation process (Li and Wang, 2011; Huang and Cheng, 2008). The second approach is to control the bromate formation during ozonation through pH control by adding ammonia or hydrogen peroxide and by modifying ozonation operation (Bhatnagar *et al*., 2009). The third approach is using physical and chemical methods to remove bromate after ozonation (Chitrakar *et al*., 2011; Patterson *et al*., 2011; Tsubouchi *et al*., 1981).

Activated carbon is an effective adsorbent material widely used in water treatment. Many works have studied the adsorption by activated carbon adsorption to remove bromate ion from water and have found that it is effective (Chen *et al*., 2012). The bormate ion that is removed by activated carbon has been postulated to be adsorbed, reduced to hypobromite and finally reduced to bromide on the activated carbon surface (Wang *et al*., 2010; Gong *et al*., 2013; Huang and Cheng, 2008). However, they can be catered to specific contaminant by various physical or chemical modification methods.

In this study, the modified activated carbon was obtained from granular activated carbon by chemical activation using cationic surfactant as an activator. Then, it was used for removal of bromate from aqueous solution. The effects of temperature, pH in solution, contact time and initial bromate ion concentration on bromate adsorption by the modified activated carbon were investigated. The adsorption isotherms and kinetics of the model compound over the modified activated carbon were also determined and discussed in detail.

MATERIALS AND METHODS

Preparation of the adsorbents: The granular activated carbon was obtained from East China Pharmaceutical Group Limited Co. Ltd. (China). It was washed by deionized water. It was dried at 378 K for 12 h, to achieve constant weight, then comminuted and sieved

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into a uniform size of 200 mesh. Then, the 50 g of the granular activated carbon was soaked stilly with 200 mL 10 mmol/L of cationic surfactant solution (Cetylpyridinium Chloride, CPC) in 500 mL Erlenmeyer flasks for 48 h at room temperature. Then, it was separated by filtration and washed thoroughly. It was dried at 373 K for 24 h. Then, the modified activated carbon was thus obtained and then stored for later adsorption experiments.

Adsorption experiments: Adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing 0.20 g of activated carbon and 100 mL of bromate ion solutions with various initial concentrations (5, 10, 15 and 20 mg/L, respectively). The initial pH (3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0 and 11.0, respectively) was adjusted with 1 mol/L HCl or 10% NaOH. The flasks were placed in a shaker at a constant temperature (293, 303 and 313 K, respectively) and 200 rpm. The samples were filtered and the residual concentration of bromate ion was analyzed by the ion chromatogrphy.

Analytical methods: The textural characteristics of activated carbon including surface area, pore volume, pore size distribution were determined using standard N_2-adsorption techniques. The surface physical morphology of activated carbon was observed by a scanning electron microscope.

The amount of adsorbed bromate ion q_t (mg/g) at different time was calculated as follows:

$$q_t = \frac{(C_0 - C_t) \times V}{m} \tag{1}$$

where,

C_0 and C_t (mg/L) = The initial and equilibrium liquid-phase concentrations of bromate ion, respectively

V (L) = The solution volume

m (g) = The mass of adsorbent used

Statistical analyses of data: All experiments were repeated in duplicate and the data of results were expressed as the mean and the Standard Deviation (S.D.). The value of the S.D. was calculated by Excel Software. All data were analyzed by the Langmuir and Freundlich adsorption models to test for the effects of temperature and initial bromate ion concentration. The Kinetic adsorption data were discussed using the pseudo-first-order model, pseudo-second-order model and the intraparticle diffusion model. All error estimates given in the text and error bars in figures were Standard Deviation of means (mean±S.D.). All statistical significance was noted at $\alpha = 0.05$ unless otherwise noted.

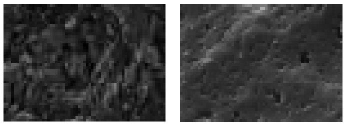

Fig. 1: SEM images of the granular activated carbon (left) and the modified activated carbon (right)

RESULTS AND DISCUSSION

Characterization of the modified activated carbon: Figure 1 is the SEM images of the granular activated carbon and the modified activated carbon. It can be seen from the micrograph that the activated carbon contains porous structures and has a very well structured porosity. Some of the micropores in the modified activated carbon were completely filled with cationic surfactant (Cetylpyridinium Chloride). It showed that the modified activated carbon had coated with cationic surfactant.

The characteristics of the modified activated carbon are obtained from the standard N_2-adsorption techniques. The BET surface area is 392 m^2/g, the total pore volume is 0.32 cm^3/g and the Nominal pore size is 2.45 nm.

Effect of initial bromate ion concentration: Adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing 0.20 g of activated carbon and 100 mL of bromate ion solutions with various initial concentrations (5, 10, 15 and 20 mg/L, respectively). The initial pH 5.0 was adjusted with 1 mol/L HCl. The flasks were placed in a shaker at 293 K and 200 rpm. Figure 2 is the effect of initial bromate ion concentration on removal of bromate ion. As observed in Fig. 2, the increased initial bromate ion concentration caused to the uptake amount of bromate ion onto the resulting sample remarkably increased. This is due to the fact that with increased bromate ion concentration, the driving force for mass transfer also increases. At low concentrations there will be unoccupied active sites on the adsorbent surface.

Effect of pH in solution: Adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing 0.20 g of activated carbon and 100 mL of 5 mg/L bromate ion. The initial pH (3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0 and 11.0, respectively) was adjusted with 1 mol/L HCl or 10% NaOH. The flasks were placed in a shaker for 16 h at 293 K and 200 rpm. Figure 3 shows pH in solution effects on the removal of bromate ion. When the pH in solution was between 4.0 and 9.0, the removal efficiencies of bromate ion were high. It showed that the adsorption of bromate ion on the modified activated carbon was suitable for the pH in solution between 4.0 and 9.0. When pH value was below 4.0 or above 9.0, the removal efficiency of bromate ion decreased markedly. It may have resulted from the electrostatic interactions established between the surfaces of the modified activated carbon and

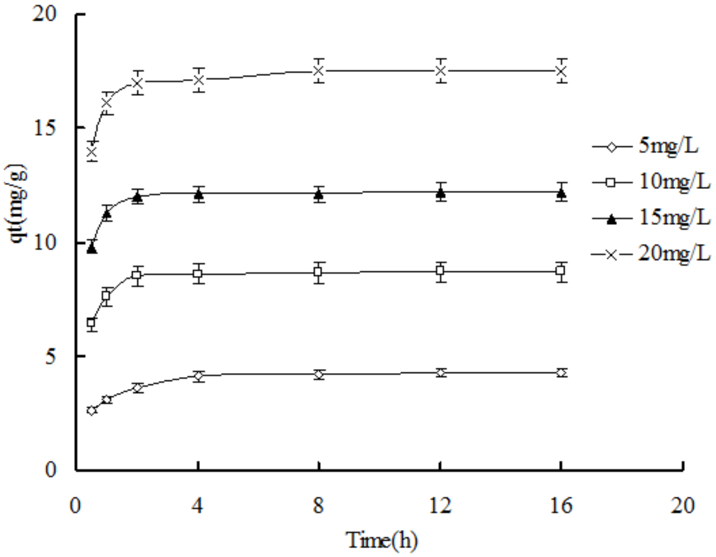

Fig. 2: Effect of pH in solution on removal of bromate ion
Experiment concentration: 0.20 g of activated carbon, pH 5.0, 293 K and 200 rpm

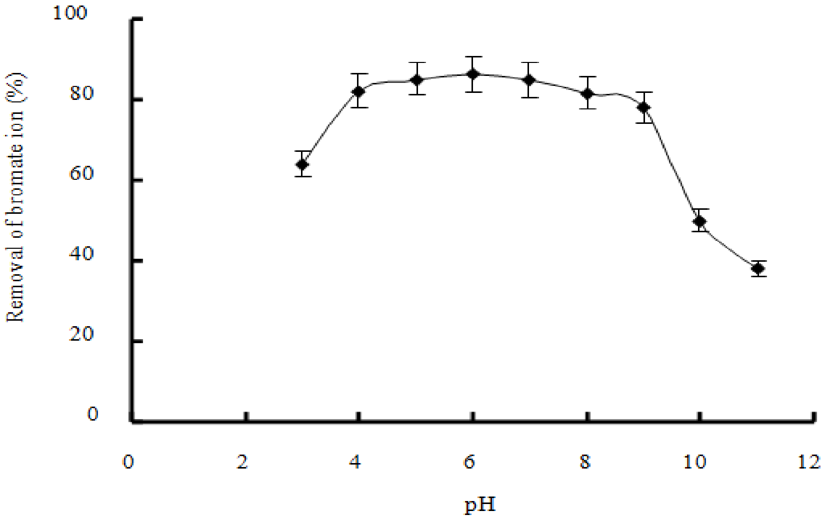

Fig. 3: Effect of pH in solution on removal of bromate ion
Experiment condition: 0.20 g of activated carbon, 5 mg/L bromate ion, 293 K and 200 rpm

bromate ion during the adsorption process. When the pH value was above 9.0, it would reduce the positive charges on the surfaces of modified activated carbon and high concentration of OH^- in solution would affect the adsorption of bromate ion. However, when the pH value was below 4.0, the competitive adsorption of chloride ions would result in a decrease in bromate ion.

Adsorption isotherm: For solid-liquid system, adsorption isotherm is important in description of adsorption behavior. To research on the mechanistic parameters associated with bromate ion adsorption, the results obtained by the adsorption experiments were analyzed by Freundlich (1906) and Langmuir model (Langmuir, 1918).

The Langmuir isotherm equation is represented by the following Eq. (2):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{2}$$

where,

C_e = The equilibrium concentration of bromate ions (mg/L)
q_e = The amount of bromate ions adsorbed (mg/g)
q_m = The maximum adsorption capacity of bromate ions (mg/g)
K_L = The Langmuir adsorption equilibrium constant (L/mg) related to the affinity of the binding sites

Table 1: The adsorption isotherm parameters for the adsorption of bromate ion on the modified activated carbon

Langmuir			Freundlich		
q_m (mg/g)	K_L (L/mg)	R^2	K_f (mg/g)	n	R^2
46.15	0.14	0.9802	9.86	0.38	0.9156

Experimental conditions: 0.20 g of activated carbon, contact time of 16 h, pH 5.0, 293 K and 200 rpm

Table 2: The kinetic parameters for the adsorption of bromate ion on the modified activated carbon

Pseudo-first-order			Pseudo-second-order		
q_e (mg/g)	k_1 (min^{-1})	R^2	q_e (mg/g)	k_2 (g/mg/min)	R^2
4.25	0.0513	0.9582	4.24	0.0112	0.9917

Experimental conditions: 0.20 g of activated carbon, 5 mg/L bromate ion, pH 5.0, 293 K and 200 rpm

The Freundlich isotherm equation is described by the following Eq. (3):

$$q_e = K_F C_e^{\frac{1}{n}} \tag{3}$$

where, K_F and n are the Freundlich adsorption isotherm constants, which are indicators of adsorption capacity and adsorption intensity, respectively.

Langmuir and Freundlich isotherms were fitted to the experimental data from Fig. 2. The corresponding constants were calculated according to Eq. (2) and (3), which were listed in Table 1.

The results indicated that the Langmuir isotherm fitted better than the Freundlich isotherm for the adsorption of bromate ion on the modified activated carbon. The adsorption process is heterogeneity of the adsorbents and favorable adsorption. The maximum adsorption capacity obtained from the Langmuir isotherm is 46.15 mg/g.

Adsorption kinetics: In order to investigate the mechanism of bromate ions sorption, two models were used in this study.

The linear pseudo-first-order kinetic model of Lagergren is given as follows (Thinakaran *et al*., 2008):

$$\ln(q_e - q_t) = \ln q_e - k_1 \times t \tag{4}$$

where, q_e and q_t are the amounts of bromate ions absorbed onto the adsorbent (mg/g) at equilibrium and at t respectively. k_1 is the rate constant of first-order adsorption (min^{-1}).

The pseudo-second-order kinetic model developed by Ho and McKay (1998) is based on the experimental information of solid-phase sorption. The linear pseudo-second-order model can be expressed as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

where, k_2 is the rate constant of second-order adsorption (g/mg/min).

According to Eq. (4) and (5), the kinetic parameters of pseudo-first-order kinetic model and pseudo-second-order kinetic model for adsorption of bromate ion on the modified activated carbon were calculated. The experiment data came from Fig. 2. Table 2 is the kinetic parameters for adsorption of bromate ion on the modified activated carbon.

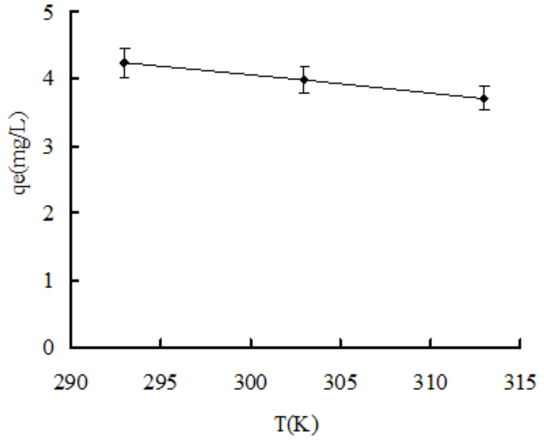

Fig. 4: Effect of temperature on removal of bromate ion Experimental conditions: 0.20 g of activated carbon, 5 mg/L bromate ion, contact time of 16 h, pH 5.0 and 200 rpm

From Table 2, it can be confirmed that the adsorption of bromate ion onto the modified activated carbon better fits to pseudo-second order kinetic model. It implies that the predominant process is chemisorption, which involves a sharing of electrons between the adsorbate and the surface of the adsorbent.

Effect of temperature: Adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing 0.20 g of activated carbon and 100 mL of 5 mg/L bromate ion solutions. The initial pH 5.0 was adjusted with 1 mol/L HCl. The flasks were placed in a shaker for 16 h at a constant temperature (293, 303 and 313 K, respectively) and 200 rpm. The effect of temperature was shown in Fig. 4. It was found that the adsorption rate of bromate ion decreased with increasing solution temperature from 293 to 313 K. It indicated that higher temperature was not suitable for adsorption process. High temperature might lead to the breaking of existing intermolecular bonding between bromate ion and the modified activated carbon, which is an important contribution to the adsorption process (Li *et al*., 2013).

CONCLUSION

In order to enhance the adsorption of bromate ion on activated carbon, the modified activated carbon was obtained from granular activated carbon by chemical activation using cationic surfactant as an activator. The adsorption characteristics of bromate ion on the modified activated carbon were investigated through adsorption experiments. The experimental results were showed that temperature, pH in solution, contact time and initial bromate ion concentration had an important effect on the adsorption process of bromate ion on the modified activated carbon. The Langmuir isotherm fitted better than the Freundlich isotherm for the adsorption of bromate ion on the modified activated carbon. The adsorption process is heterogeneity of the adsorbents and favorable adsorption. The higher temperature was not suitable for adsorption process.

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