



# Adsorption of Bromate in Aqueous Solution by the Modified Activated Carbon

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## ABSTRACT

The presence of bromate in drinking water has attracted much attention, because it is a carcinogen and mutagenic to humans. 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 analysed by the Langmuir and Freundlich models of adsorption. Kinetic adsorption data were analysed by the pseudo-first-order kinetic model and the pseudo-second-order model respectively. The thermodynamics parameters were also calculated.

## INTRODUCTION

The presence of bromate in drinking water has attracted much attention, because it is a carcinogen and mutagenic to humans (Listiarini et al. 2010, Ding et al. 2010). The kidney is a target for both  $\text{BrO}_3^-$  induced toxicity and cancer, the peritoneum for cancer, testes for lower sperm count and the thyroid for follicular cell cancer (Delker et al. 2006). Bromate is formed from bromide dissolved in water during the ozonation process, hypochlorination or chloramination of water containing bromide (Moslemi et al. 2012). 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 (Butler et al. 2005, Hsu & Singer 2010, Johnson & Singer 2004). 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 (Bouland et al. 2003, Kim et al. 2007, Sánchez et al. 2007). The third approach is using physical and chemical methods to remove bromate after ozonation (Huang & Cheng 2008, Chen et al. 2012).

Activated carbon is an effective adsorbent material widely used in water treatment. Corresponding research into the reduction and removal of various compounds from water are often presented (Gong et al. 2013, Wang et al. 2010, Huang & Cheng 2008). However, they can be catered to a 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 the 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, kinetics and thermodynamics 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 with deionized water. It was dried at 378 K for 12 h, to achieve constant weight, then comminuted and sieved into a uniform size of 200 mesh. Then, the 50 g of the granular activated carbon was soaked stillly with 200mL 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 0.20g of activated carbon and 100 mL of bromate ion solutions with various initial concentrations (5 mg/L, 10 mg/L, 15 mg/L and 20 mg/L). The initial pH (3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0 and 11.0) 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) and 200 rpm. The samples were filtered and the residual concentration of bromate ion was analysed by the ion chromatography.

**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:

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

Where  $C_0$  and  $C_t$  (mg/L) are the initial and equilibrium liquid-phase concentrations of bromate ion respectively.  $V$  (L) is the solution volume and  $m$  (g) is 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 (SD). The value of the SD was calculated by Excel software. All data were analysed 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 a standard deviation of means (mean $\pm$ SD). All statistical significance was noted at  $\alpha=0.05$  unless otherwise noted.

## RESULTS AND DISCUSSION

**Characterization of the modified activated carbon:** Fig. 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<sup>2</sup>/g, the total pore volume is 0.32 cm<sup>3</sup>/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 0.20g of activated carbon and 100 mL of bromate ion solutions with various initial concentrations (5

mg/L, 10 mg/L, 15 mg/L and 20 mg/L). 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. Fig. 2 is the effect of initial bromate ion concentration on the 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 the 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 0.20g 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) 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. Fig. 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 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<sup>-</sup> 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 behaviour. To research on the mechanistic parameters associated with bromate ion adsorption, the results obtained by the adsorption experiments were analysed by Freundlich model (Freundlich 1906) and Langmuir (Langmuir 1918) model.

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

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad \dots(2)$$

Where  $C_e$  is the equilibrium concentration of bromate ions (mg/L),  $q_e$  is the amount of bromate ions adsorbed (mg/g),  $q_m$  is the maximum adsorption capacity of bromate ions (mg/g), and  $K_L$  is the Langmuir adsorption equilibrium constant (L/mg) related to the affinity of the binding sites.

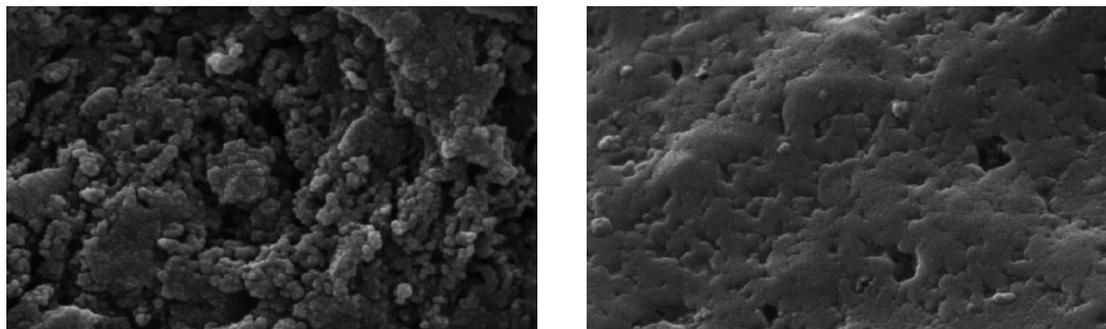


Fig. 1: SEM images of the granular activated carbon (left) and the modified activated carbon (right).

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

$$q_e = K_F C_e^{\frac{1}{n}} \quad \dots(3)$$

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 Eq. (3), which are 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 favourable 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):

$$\ln(q_e - q_t) = \ln q_e - k_1 \times t \quad \dots(4)$$

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

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

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \dots(5)$$

Where  $k_2$  is the rate constant of second-order adsorption ( $\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$ ).

According to Eq.(4) and Eq.(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 the adsorption of bromate ion on the modified activated carbon.

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 and thermodynamics parameters:**

Adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing 0.20g 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) and 200 rpm. The effect of temperature is shown in Fig.4.

It was found that the adsorption rate of bromate ion decreased with increasing solution temperature from 293K to 313K. 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).

The thermodynamic parameters of free energy change ( $\Delta G^0$ ), enthalpy change ( $\Delta H^0$ ) and entropy change ( $\Delta S^0$ ) were used to describe thermodynamic behaviour of the adsorption of bromate ions onto the modified activated carbon. These parameters were calculated from the following equations (Duan et al. 2012).

$$\Delta G^0 = -RT \ln K_a \quad \dots(7)$$

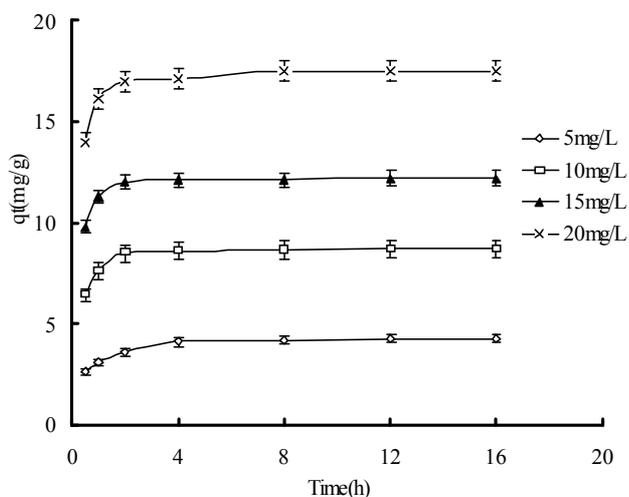


Fig. 2: Effect of pH in solution on removal of bromate ion. Experiment concentration: 0.20g of activated carbon, pH 5.0, 293 K, 200 rpm.

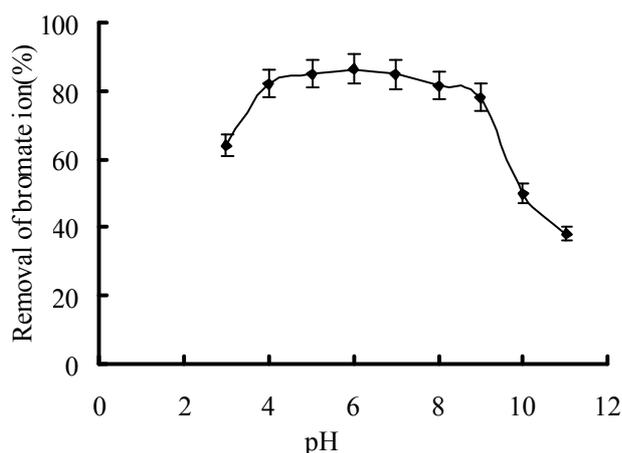


Fig. 3: Effect of pH in solution on removal of bromate ion. Experiment condition: 0.20g of activated carbon, 5 mg/L bromate ion, 293 K, 200 rpm.

$$\ln K_a = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad \dots(8)$$

$$K_a = \frac{q_e}{C_e} \quad \dots(9)$$

Where  $T$  is the solution temperature (K),  $K_a$  is the adsorption equilibrium constant,  $R$  is the gas constant ( $8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ),  $q_e$  is the amount of adsorbate adsorbed per unit mass of adsorbate at equilibrium (mg/g) and  $C_e$  is the equilibrium concentration of the adsorbate (mg/L).

Thermodynamic parameters ( $\Delta H^0$ ,  $\Delta S^0$  and  $\Delta G^0$ ) for bromate ion adsorption were evaluated using Eqs. (7)-(9).

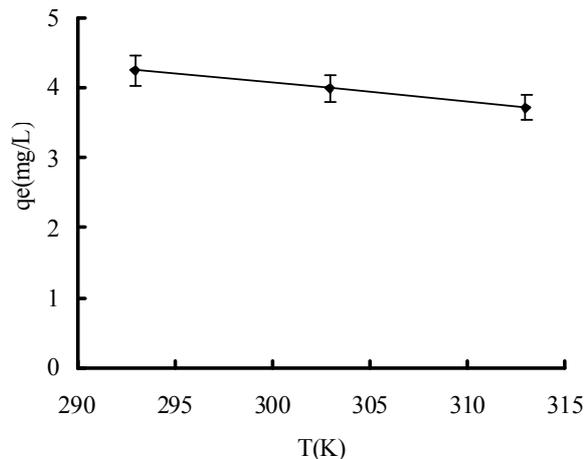


Fig. 4: Effect of temperature on removal of bromate ion. Experimental conditions: 0.20g of activated carbon, 5 mg/L bromate ion, contact time of 16 h, pH 5.0, 200 rpm.

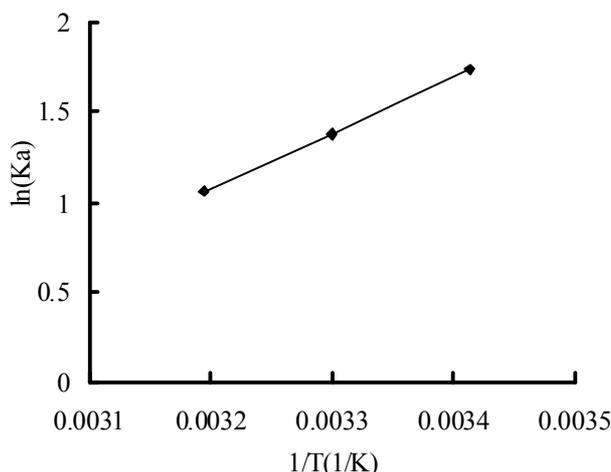


Fig. 5: Enthalpy and entropy determination for adsorption of bromate ion onto the modified activated carbon. Experimental conditions: 0.20g of activated carbon, 5 mg/L bromate ion, contact time of 16 h, pH 5.0, 200 rpm.

The values of  $\Delta H^0$  and  $\Delta S^0$  were determined from the slope and intercept of the plot of versus  $1/T$  (Fig. 5).

The negative value of  $\Delta H^0$  (the value of enthalpy for bromate ion is  $-25.86 \text{ kJ/mol}$ ) indicates that the adsorption of bromate ion onto the modified is an exothermic reaction. Meanwhile, the negative value of  $\Delta S^0$  (the value of entropy for bromate ion is  $-73.88 \text{ J/mol}$ ) reflects the affinity of the modified activated carbon for bromate ion. The calculated value of  $\Delta G^0$  for bromate ion (the value of  $\Delta G^0$  for bromate ion is  $-4.23 \text{ kJ/mol}$ ) at 293 K indicated the adsorption of bromate ion onto the modified activated carbon is spontaneous and thermodynamically favourable.

Table 1: The adsorption isotherm parameters for the adsorption of bromate ion on the modified activated carbon. Experimental conditions: 0.20g of activated carbon, contact time of 16 h, pH5.0, 293 K and 200 rpm.

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

Table 2: The kinetic parameters for the adsorption of bromate ion on the modified activated carbon. Experimental conditions: 0.20g of activated carbon, 5 mg/L bromate ion, pH5.0, 293 K and 200 rpm.

Pseudo-first-order			Pseudo-second-order		
$q_e$ (mg/g)	$k_1$ (min <sup>-1</sup> )	$R^2$	$q_e$ (mg/g)	$k_2$ (g·mg <sup>-1</sup> ·min <sup>-1</sup> )	$R^2$
4.25	0.0513	0.9582	4.24	0.0112	0.9917

### 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 showed that these parameters, such as 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 favourable adsorption. The higher temperature was not suitable for adsorption process. The adsorption of bromate ion onto the modified is an exothermic reaction. Moreover, it is also spontaneous and thermodynamically favourable.

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