

# Adsorptive Bromate Removal from Aqueous Solution by Commercial Strongly Basic Resin Impregnated with Hydrated Ferric Oxide (HFO): Kinetics and Equilibrium Studies

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**Supporting Information** 

**ABSTRACT:** Commercial strongly basic resin D201-Cl was impregnated with hydrous ferric oxide (HFO) in FeCl<sub>3</sub>–HCl– NaCl solution for absorptive removal of bromate from aqueous solution. The influences of initial bromate concentration, contact time, initial pH, temperature, and competing anions on the uptake of bromate by HFO-impregnated resin D201-Cl (HFO-201) were investigated by batch adsorption experiments. Experimental results showed that the adsorption process could be described by pseudofirst-order kinetics and be divided into three stages according to the intraparticle diffusion parameter. The maximum adsorption potential of HFO-impregnated resin for bromate was 292.81 mg·



 $g^{-1}$  at 298 K, which is much greater than those reported in previous studies. The experimental data fitted well to the Redlich– Peterson isotherm model ( $R^2 > 0.99$ ). Thermodynamic parameters such as free energy, enthalpy, and entropy demonstrated that bromate adsorption on HFO-201 was spontaneous and exothermic and occurred by physisorption. Meanwhile, HFO-201 maintained greater adsorption capacity for bromate in salt coexisting solution. Results of the present study suggest that the cheap and facile HFO-impregnated resin possesses great potential for bromate removal from drinking water.

# 1. INTRODUCTION

When water containing bromide (Br<sup>-</sup>) is disinfected by ozone, a harmful byproduct, bromate (BrO<sub>3</sub><sup>-</sup>), is formed during the molecular ozone and hydroxyl radical (•OH) reactions.<sup>1</sup> The range of bromate concentrations in drinking water after ozonation is <2–293  $\mu$ g·L<sup>-1</sup>, depending on the bromide concentration, ozone dosage, pH, alkalinity, and dissolved organic carbon in the source water.<sup>2</sup> A large number of studies in the literature have demonstrated that bromate is possibly carcinogenic.<sup>3,4</sup> The International Agency for Research on Cancer (IARC) has classified it as a group B-2 carcinogen (as a possible human carcinogen).<sup>5</sup> So the maximum contaminant level (MCL) for bromate in drinking water has been set as 10  $\mu$ g·L<sup>-1</sup> in many countries including China.

There are two approaches to be used in controlling of bromate contamination in the water supply: inhibition of bromate formation during ozonation by adjusting pH or adding NH<sub>3</sub> or organic hydroxyl radical scavengers<sup>6–8</sup> or removal of bromate after ozonation via adsorption or chemical or biological reduction.<sup>9–11</sup> However, the first approach will bring in extra chemical materials and affect the water supply quality. Risk also exists in that bromide formed from bromate reduction can be oxidized to carcinogenic bromate again.

Therefore, the second approach is more attractive, wherein adsorption due to simplicity in operation. $^{9,12,13}$ 

Various types of adsorbent have been used in the adsorption of bromate. The most common ones are activated carbon,<sup>1</sup> anion-exchange resin,<sup>9</sup> metal hydroxide,<sup>14</sup> clay,<sup>15</sup> and a variety of iron-based adsorption materials such as granular ferric hydroxide<sup>16</sup> and ferric modified materials.<sup>17,18</sup> Recently, hydrated ferric oxide (HFO) has become a preferable adsorbent for removing inorganic pollutants such as arsenate, phosphate, fluoride, and selenite $^{19,20}$  due to its high isoelectric points (8.1) and specific surface area.<sup>21</sup> HFO has surface areas of 350-600 m<sup>2</sup>·g<sup>-1</sup>, which is greater than other iron oxides such as goethite or magnetite  $(<150 \text{ m}^2 \cdot \text{g}^{-1})$ .<sup>22</sup> However, HFO is generally perceived as amorphous and suspended in solution, which are not suitable fixed-bed or other flow systems. To resolve this problem, HFOs are often immobilized within nanoporous supports to form the novel adsorbent. Qiu and his workers immobilized HFO on strong-acid cation-exchange resin, and the resulting composite exhibited high capacity and selectivity to heavy metals such as Pb, Cu, and Cd.<sup>23</sup> Wang et

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al. found that the size of HFO loaded on polystyrene (PS) resins was controlled by the pore structure of the support. PS-HFO with smaller average pore sizes had higher adsorption rates for arsenite sorption due to the formation of smaller HFO nanoparticles.<sup>24</sup> Cumbal and Sengupta compared commercial cation and anion exchangers as host materials for dispersing HFO nanoparticles.<sup>25</sup> The anion easily permeated into the anion exchanger owing to the Donnan membrane effect of the host material. On the contrary, the cation easily permeated into the cation exchanger.

Inspired by the excellent adsorption performance of HFO for bromate and the Donnan membrane effect of anion exchanger, we tried to immobilize HFO on commercial strongly basic resin (D201-Cl) to produce HFO-based adsorbents (HFO-201) for bromate removal. Adsorption kinetics and thermodynamics were investigated to reveal the mechanism of bromate adsorption on HFO-201. The effect of initial bromate concentrations, initial pH, temperature, and competing anions on bromate removal were also evaluated.

#### 2. MATERIALS AND METHODS

**2.1. Materials.** D201-Cl was purchased from Dayu Chemical Co. Ltd. (Changsha, China), which is a macroporous, strong-base anion-exchange resin with average diameter of 9.7 nm. Prior to use, it was washed with deionized water and ethanol to remove the impurities and dried under vacuum at 323 K for 24 h. NaBrO<sub>3</sub> (Shanghai Chemical Reagent Co. Ltd. China) was dissolved in ultrapure water as a stock solution for further use. Other chemicals were of analytical grade and provided by Shanghai Chemical.

2.2. HFO-Based Adsorbent Preparation. FeCl<sub>4</sub><sup>-</sup> was an excellent precursor to form HFO, which could be formed in high concentration of mixed solutions HCl and NaCl and selectively exchanged on the macroporous, strong-base anionexchange resin D201-Cl due to the lower hydration energy than Cl<sup>-.26-29</sup> D201-Cl samples were first soaked in FeCl<sub>3</sub>-HCl-NaCl solution (0.3 mol·L<sup>-1</sup> FeCl<sub>3</sub>, 0.2 mol·L<sup>-1</sup> HCl, and 0.4  $mol \cdot L^{-1}$  NaCl) at 278 K with intensive ultrasonic vibration for 2 h. Then the resins were separated through filtration and quickly soaked in NaOH-NaCl solution (1 mol·L<sup>-1</sup> NaOH and 0.6 mol·L<sup>-1</sup> NaCl) at 278 K with intensive ultrasonic vibration for 2 h. The FeCl<sub>4</sub><sup>-</sup> loaded on D201-Cl was resolved to form  $Fe(OH)_3$  under alkaline condition. Finally, the synthesized material was washed with deionized water until the pH was below 8 and dried at 323 K for 12 h and the HFObased adsorbent (HFO-201) was obtained. We stored the HFO-201 in a sealed glass bottle for future use.

**2.3. Batch Adsorption Experiments.** Batch adsorption experiments were performed in 500 mL capped Erlenmeyer flasks with known initial concentrations of bromate solution and amount of HFO-201 shaking on a thermostated rotary shaker (SHZ-82A, Jintan Medical Instrument Factory, Jiangsu, China) at 150 rpm.

A series of batch experiments were conducted to investigate the effect of initial bromate concentration, initial pH, temperature, and competing anions on the bromate adsorption on HFO-201. To study the effect of initial bromate concentration, 0.1 g of HFO-201 was placed in 500 mL of bromate solution with different initial bromate concentration (200, 400, and 600  $\mu$ g·L<sup>-1</sup>) at 298 K to reach equilibrium. At predetermined time intervals, samples were taken for bromate analysis and the adsorption kinetics was determined. The effect of pH was investigated by adjusting the initial pH from 3.0 to 10.0 using 0.1 M H<sub>2</sub>SO<sub>4</sub> or 0.1 M NaOH with the initial bromate concentration of 200  $\mu$ g·L<sup>-1</sup> and adsorbent dosage of 0.2 g·L<sup>-1</sup> at 298 K. The adsorption isotherm was studied by adding 0.05 g of HFO-201 into 250 mL of bromate solution with initial concentration varying between 5 and 150 mg·L<sup>-1</sup> at fixed temperature for 24 h. For the competitive adsorption test, chloride (Cl<sup>-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), and sulfate (SO<sub>4</sub><sup>2-</sup>) with different initial concentrations were employed as the competing anion and introduced into 200  $\mu$ g·L<sup>-1</sup> bromate solution.

The bromate adsorption capacity at equilibrium (or at time, t) and the percentage of removal (%) were calculated by the following equations:

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

$$q_{\rm e} = \frac{(C_0 - C_{\rm e})V}{m} \tag{1b}$$

$$\text{removal/\%} = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

where,  $q_e$  and  $q_t$  ( $\mu g \cdot g^{-1}$ ) are the bromate adsorption capacity of adsorbent at equilibrium and t, respectively.  $C_0$ ,  $C_v$ , and  $C_e$ ( $\mu g \cdot L^{-1}$ ) are the initial, at t, and residual bromate concentrations, respectively, V (L) is the volume of the solution, and m (g) is the mass of the adsorbent.

Reproducibility of the measurements was determined in triplicate, and the average values were used.

**2.4. Analytical Methods.** The samples were filtered with a 0.22 mm membrane filter (LC+PVDF membrane, ANPEL Laboratory Technologies Inc., Shanghai, China). The concentrations of bromate and other anions were analyzed using Dionex ion chromatography (IC; ICS-900, Sunnyvale, CA, USA) consisting of a suppressed conductivity detector. The mobile phase (flow rate, 1 mL·min<sup>-1</sup>) was set with a mixture of 9.4 mM sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) and 1.8 mM sodium bicarbonate (NaHCO<sub>3</sub>). The detection limit of IC for bromate is 0.1  $\mu$ g·L<sup>-1</sup>. The pH was measured by a pH meter (pHS-3C, Shanghai Precision & Scientific Instrument Co., Ltd., China).

The functional groups on HFO-201 were determined using a FTIR 8400S instrument with a standard mid-IR DTGS detector (Shimadzu, Tokyo, Japan). FT-IR spectra were recorded in the range of  $350-4000 \text{ cm}^{-1}$  with a pure KBr pellet used as background. The spectral resolution was 0.5 cm<sup>-1</sup> for the FT-IR spectral regions.

#### 3. RESULT AND DISCUSSION

**3.1. Structure Characterizations of HFO-201.** Fourier transform infrared spectra for the D201-Cl resins before and after their impregnation with HFO are shown in Figure 1. The FT-IR spectra of D201-Cl and HFO-201 showed some similar transmission bands. For example, the transmission bands around 3424 and 3421 cm<sup>-1</sup> for D201-Cl and HFO-201 may be attributed to the O–H stretching vibration. The bands at 1484 and 1483 cm<sup>-1</sup> were associated with the C–H bending vibration of quaternary ammonium groups in the resins.<sup>30</sup> After the modification of D201-Cl, more bands appeared in the FT-IR spectra of HFO-201. The band at 584 cm<sup>-1</sup> can be assigned to the stretching vibration of Fe–O in HFO-201. Gong et al. pointed out that the bands between 700 and 400 cm<sup>-1</sup> are from Fe–O stretching vibration.<sup>31</sup> The FT-IR spectrum of HFO-201 had a weak band at 1125 cm<sup>-1</sup>, which should represent Fe–



Figure 1. FT-IR spectra of (1) D201-Cl and (2) HFO-201.

OH.<sup>32</sup> These results indicated that HFO had been loaded on the D201-Cl resin.

Results of XPS analysis of HFO–D201 are shown in Figure 2. As seen in Figure 2A, there are the elements Fe, O, N, C, and Cl than the more unnecessary elements (such as S and P) in the XPS survey of HFO-201, indicating the prepared sample was of high purity. The peaks at about 710 and 723 eV are ascribed to the positions of Fe 2p (Figure 2B), suggesting the existence of FeOOH in HFO-201 reported in a previous



Figure 2. XPS analysis of HFO-201: (A) overall XPS spectra and (B) individual XPS Fe 2p binding energy region.

study.<sup>33</sup> The characteristics and important properties of HFO-201 compared with D201-Cl are listed in Supporting Information Table S1.

**3.2. Effect of Contact Time and Initial Bromate Concentration.** The adsorption of bromate on HFO-201 was investigated as a function of contact time with different initial bromate concentrations of 200, 400, and 600  $\mu$ g·L<sup>-1</sup>, and the results are displayed in Figure 3. The removal of bromate



**Figure 3.** Effect of contact time and initial bromate concentration on the adsorption of bromate on HFO-201 (adsorbent dosage, 0.2 g·L<sup>-1</sup>; temperature, 298 K; pH, 7.0 ± 0.5).

was divided into two stages: bromate was adsorbed into HFO-201 rapidly at the initial stage, and then the equilibrium was achieved within 200 min. Nevertheless, shorter equilibrium time (10 min) was found in adsorption of bromate by nanocrystalline akaganeite ( $\beta$ -FeOOH)-coated quartz sand (CACQS). This may be attributed to HFO-201 being a porous adsorbent and pore diffusion decreasing the adsorption rate.<sup>34</sup> For the initial bromate concentrations of 200, 400, and 600  $\mu$ g·  $L^{-1}$ , the adsorption capacities of bromate were 1023.02, 2009.23, and 2974.71  $\mu g \cdot g^{-1}$ , respectively. The driving force of mass transfer between the aqueous and solid phases was derived from the concentration gradient.<sup>9</sup> The increasing initial bromate concentration reinforces the driving force to overcome the mass transfer resistance of bromate. Therefore, higher initial bromate concentration is beneficial for the adsorption capacity of resin.

3.3. Effect of Initial pH. The effects of initial solution pH on bromate removal by HFO-201 are shown in Figure 4. The initial pH values ranged from 3.0 to 10.0. As seen from Figure 4, the high adsorption capacity of bromate was observed in the broad pH range (4-9) and the residual bromate concentration  $(C_{\rm e})$  was below or close to MCL (10  $\mu g \cdot L^{-1}$ ). However, the bromate adsorption on HFO-201 was clearly pH-dependent. Acidic pH (<6) was favorable to bromate removal, but the removal obviously dropped in alkaline pH (>9) and acidic pH (<4). At higher pH the surface turned more negative, which enhances repulsion between the sorbent surface and bromate.<sup>18</sup> Meanwhile stronger competition from hydroxyl ions also results in much reduced bromate adsorption on HFO-201.35 The slight drop of equilibrium pH at the alkaline initial pH (Figure 4) also demonstrated the exchange of hydroxyl ions with chloride ions in resins. Contrarily, positively charged sites dominate at lower pH, which enhances the attractive forces between bromate and resins. However, the sharp decrease of



Figure 4. Effect of initial pH on the adsorption of bromate on HFO-201 (adsorbent dosage, 0.2 g·L<sup>-1</sup>; initial bromate concentration, 200  $\mu$ g·L<sup>-1</sup>; temperature, 298 K; contact time, 24 h).

bromate adsorption efficiency below pH 4 should be attributed to the dissolution of HFO.<sup>30</sup>

3.4. Effect of Temperature. The bromate adsorption on HFO-201 was investigated at different temperatures (range of 298-318 K with an interval of 10 K). Figure 5 shows that



Figure 5. Effect of temperature on the adsorption of bromate on HFO-201. Insert: Plots of  $\ln(q_e/C_e)$  vs 1/T (adsorbent dosage, 0.2 g·  $L^{-1}$ ; pH, 7.0 ± 0.5; contact time, 24 h).

temperature does not have a remarkable effect on the adsorption capacity of HFO-201. In general, the adsorption of bromate slightly decreased with the increase of temperature, which suggests that the adsorption process is exothermic. In this study, in-depth information regarding the thermodynamic feasibility of the process was studied from the aspect of energy change. Three basic thermodynamic parameters, standard free energy ( $\Delta G^{\circ}$ ), standard enthalpy ( $\Delta H^{\circ}$ ), and standard entropy  $(\Delta S^{\circ})$ , were calculated using the following equations:

$$\ln\left(\frac{q_{\rm e}}{C_{\rm e}}\right) = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT}$$
(3)

(4) $\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$ 

$$\Delta G^{\circ} = -RT \ln K \tag{5}$$

where  $q_e/C_e$  is the adsorption affinity and is a ratio of  $q_e$  to  $C_{e}$ R is the universal gas constant (8.314  $J \cdot mol^{-1} \cdot K^{-1}$ ), T is Article

related to the Langmuir constant. The values of  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$ were determined from the slope and the intercept of the plots of  $\ln(q_e/C_e)$  versus 1/T (Figure 5). The  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  were -1.5 kJ·mol<sup>-1</sup> and 4.0 J·mol<sup>-1</sup>·K<sup>-1</sup>, respectively. Low  $\Delta H^{\circ}$ (<40.0 kJ·mol<sup>-1</sup>) indicated that the interactions between HFO-201 particle and bromate ion are physical.<sup>18</sup> On the other hand, the negative value of  $\Delta H^{\circ}$  showed that the adsorption reaction is exothermic. As mentioned above, the bromate adsorption on HFO-201 decreased with the increase of temperature. The positive  $\Delta S^{\circ}$  suggested the increased randomness at the solidsolution interface.<sup>9</sup> The  $\Delta G^{\circ}$  calculated with eq 4 was negative and -2.703, -2.743, and -2.784 kJ·mol<sup>-1</sup> at 298, 308, and 318 K, respectively, which demonstrated that the adsorption of bromate onto HFO-D201 is favorable and spontaneous.

3.5. Adsorption Kinetics. Kinetic modeling is one of the important characteristics for evaluating the adsorption process. Based on the equilibrium data obtained at different initial bromate concentrations (200–600  $\mu$ g·L<sup>-1</sup>), the pseudo-firstorder, pseudo-second-order, and Weber and Morris (intraparticle diffusion) kinetics models were used to simulate the bromate adsorption process on HFO-201, and the kinetic parameters of these models are listed in Table 1.

Table 1. Kinetic Parameters for Bromate Adsorption on HFO-201 at Different Initial Bromate Concentrations

$C_0 \; (\mu \mathrm{g} \cdot \mathrm{L}^{-1})$	200	400	600
pseudo-first-order model			
experimental $q_{e}$ ( $\mu g \cdot g^{-1}$ )	1023.02	2009.23	2974.71
calculated $q_{\rm e} \; (\mu {\rm g} \cdot {\rm g}^{-1})$	1063.37	2142.86	2946.58
$k_1  imes 10^{-1} \; (\min^{-1})$	0.155	0.150	0.145
$R^2$	0.9941	0.9960	0.9998
pseudo-second-order model			
experimental $q_{e}$ ( $\mu g \cdot g^{-1}$ )	1023.02	2009.23	2974.71
calculated $q_{\rm e} \; (\mu {\rm g} \cdot {\rm g}^{-1})$	1428.57	3333.33	5000.00
$k_1 \times 10^{-4} \; (\text{g} \cdot \mu \text{g}^{-1} \cdot \text{min}^{-1})$	0.085	0.026	0.021
$R^2$	0.9953	0.9965	0.9974
Weber and Morris model			
$k_{\mathrm{id1}}^{a} (\mu \mathrm{g} \cdot \mathrm{g}^{-1} \cdot \mathrm{min}^{-1})$	76.837	150.606	229.479
$R^2$	0.9951	0.9905	0.9917
Ι	-8.72	-52.68	-50.56
$k_{id2}^{a}$ ( $\mu g \cdot g^{-1} \cdot min^{-1}$ )	29.50	52.01	81.95
$R^2$	0.9779	0.9998	0.9457

 ${}^{a}k_{id1}$  and  $k_{id2}$  are the equilibrium rate constants for the first and the second stages of the adsorption process.

The linearlized pseudo-first-order and pseudo-second-order models were as follows:<sup>32,3'</sup>

$$\ln(q_{\rm e} - q_t) = \ln q_{\rm e} - k_{\rm l}t \tag{6}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$
(7)

where  $q_e$  and  $q_t$  ( $\mu g \cdot g^{-1}$ ) are the amounts adsorbed at equilibrium and at t (min), respectively; and  $k_1$  (min<sup>-1</sup>) and  $k_2$  are the rate constants of pseudo-first-order kinetics and pseudo-second-order kinetics, respectively.

To determine the rate-limiting step in this adsorption process, the intraparticle diffusion model developed by Weber and Morris<sup>38</sup> was used for describing bromate adsorption on HFO-201.

Table 2. Co	omparison o	f Bromate	Adsorption	on	Different	Adsor	bents
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adsorbent	initial concn $(mg \cdot L^{-1})$	equilib concn $(mg \cdot L^{-1})$	adsorbent dosage $(g \cdot L^{-1})$	$q_{\rm max}~({\rm mg}{\cdot}{\rm g}^{-1})$	ref
CACQS	0.2	0.061	100	0.038	18
GFH	10	0.4	10.0	16.5	16
D201	0.2	<0.01	1.0	105.5	9
HFO-201	0.2	<0.01	0.2	292.81	present study

$$q_t = k_{id} t^{1/2} + I (8)$$

where  $q_t$  is the amount of anion ion retained at  $t (\mu g \cdot g^{-1})$ ,  $k_{id}$  is the intraparticle diffusion rate constant, t is the time (min), and I is the thickness of the boundary layer.

As seen from Table 1, the pseudo-second-order and pseudofirst-order models both simulated well the kinetic data with higher correlation coefficients  $(R^2 > 0.99)$ . However,  $q_e$ calculated from the pseudo-second-order plot was far from the value obtained in the experiment studies. Therefore, the adsorption of bromate on HFO-201 more appropriately followed pseudo-first-order kinetics than that of pseudosecond-order kinetics. The  $q_e$  of HFO-201 for bromate removal increased from 1063.37 to 2974.71  $\mu g \cdot g^{-1}$  when the initial bromate concentration increased from 200 to 600  $\mu$ g·L<sup>-1</sup> with fixed amount of HFO-201, which suggested that HFO-201 had greater adsorption capacity for bromate, but its adsorption capacity did not reach saturation due to a low initial bromate concentration. We chose higher initial bromate concentrations  $(5-150 \text{ mg} \cdot \text{L}^{-1})$  to investigate the maximum bromate adsorption potential on HFO-201. The results showed that maximum adsorption capacity reached 292.82, 283.16, and 266.69 mg $\cdot$ g<sup>-1</sup> at 298, 308, and 318 K, respectively, which was notably greater than those of D201. Compared with D201, HFO-201 displayed a more positive and larger surface area (Table S1, see Supporting Information), resulting in more bromate transferring into the surface of the adsorbent.<sup>39</sup> The maximum adsorption of HFO-201 was also notably greater than other adsorbents reported in previous literature (Table 2).

Figure 6 plots the amounts of bromate adsorbed per unit mass of adsorbent versus  $t^{1/2}$  at different initial bromate



Figure 6. Intraparticle diffusion model plots for bromate adsorption on HFO-201.

concentrations. The multilinear plot suggested that the bromate adsorption on HFO-201 was controlled by two or more diffusion mechanisms.<sup>24,40</sup> As shown as Figure 6, the process of bromate adsorption on HFO-201 was divided into three consecutive steps: bromate diffusion from boundary film to the

surface of resin (film diffusion), bromate diffusion within the pores of the resin (intraparticle diffusion), and bromate adsorption on the interior surface of the resin. The third step is a fast and nonlimiting step. So the adsorption rate can be controlled by the first and/or the second step.<sup>41</sup> The values of  $k_{id1}$  and  $k_{id2}$  (diffusion rate constants for first and second steps, respectively) obtained from the slope of linear plots are listed in Table 1. The values of  $k_{idi}$  all increased with the initial concentration of bromate, which should be attributed to the enhanced effect of the boundary layer.<sup>40</sup> Simultaneously, it was evident that  $k_{id1}$  was higher compared to  $k_{id2}$ , indicating that initial step (film diffusion) was rapidly followed by a slow step (intraparticle diffusion). The relative contributions of initial adsorption and boundary layer diffusion were reflected by the value of intercept I. In this study, the intercept I at each concentration was negative, suggesting that there is a delay of adsorption due to boundary later effect.<sup>42</sup> According to these results, we could conclude that the intraparticle diffusion was not the only rate-limiting step. The adsorption process of bromate on HFO-201 may be a complex process consisting of both surface adsorption and intraparticle diffusion.

In order to further explain the enhanced adsorption mechanism of bromate on HFO-201, the concentration of bromide, bromate, and chloride during the adsorption process were monitored simultaneously and the solution pH was not controlled. As shown as Figure S1 (see Supporting Information), the quick decrease of bromate concentration in solution was accompanied by the rapid increase of chloride concentration while no bromide was detected, indicating that ion-exchange reaction had happened between bromate ions in solution and chloride on HFO-201 instead of reduction. Moreover, similar FT-IR spectra of HFO-201 before and after adsorption (Figure S2, see Supporting Information) also demonstrated that the physical and chemical structure of HFO-201 did not change. So the ion exchange was a major mechanism for bromate removal by HFO-201, in which the existence of HFO raises the positive charge of resin, enhances the entrance of bromate into resin through electrostatic attraction, and then improves the ion exchange between bromate and choride.<sup>39</sup>

**3.6. Adsorption Isotherm.** For a solid–liquid system, the adsorption isotherm is important for describing the distribution of the adsorbate between the liquid and solid phases when the adsorption process reaches an equilibrium state. In this work, various isotherm models including Langmuir, Freundlich, and Redlich–Peterson were used to describe the equilibrium characteristics of bromate adsorption on HFO-201.

Langmuir and Freundlich models are the most common models to describe the adsorption behaviors. They are twoparameter isotherm models; Langmuir model usually describes the saturated monolayer adsorption, whereas Freundlich isotherm is widely applied in heterogeneous systems.<sup>9</sup> Their equations are given as follows.

Table 3. Adsorption Isotherm Parameters of Bromate on HFO-201

isotherm model	param	298 K	308 K	318 K
Langmuir	calculated $q_{\text{max}}$ (mg·g <sup>-1</sup> )	303.03	285.71	270.27
	b	0.0723	0.0775	0.0736
	$R^2$	0.9772	0.9555	0.9483
Freundlich	$K (\mathrm{mg} \cdot \mathrm{g}^{-1})$	26.8053	25.3571	22.2998
	n	1.8250	1.8157	1.7711
	$R^2$	0.9460	0.9498	0.9430
Redlich–Peterson	$K_{\rm R} \ ({\rm mg} \cdot {\rm g}^{-1})$	22.8	22.5	18.0
	$b_{\mathrm{R}} \left( (\mathrm{mg} \cdot \mathrm{g}^{-1})^m \right)$	0.1351	0.1573	0.1144
	m	0.8474	0.8159	0.8439
	$R^2$	0.9981	0.9942	0.9935

Langmuir:

$$q_{\rm e} = \frac{q_{\rm max}bC_{\rm e}}{1+bC_{\rm e}} \tag{9}$$

Freundlich:

$$q_{\rm e} = K_{\rm f} C_{\rm e}^{1/n} \tag{10}$$

where  $q_e$  ( $\mu g \cdot g^{-1}$ ) is the bromate adsorption capacity at equilibrium concentration  $C_e$ ,  $q_{max}$  represents the maximum adsorption capacity, b is the Langmuir constant, and  $K_f$  ( $\mu g \cdot g^{-1}$ ) and n are Freundlich constants.

The Langmuir equation is sound and well-confirmed for low adsorbate concentration, while the Freundlich model is limited for lower concentration.<sup>43</sup> The Redlich–Peterson (R-P) isotherm model is a hybrid isotherm featuring both Langmuir and Freundlich isotherms, which can be applied either in homogeneous or heterogeneous systems due to its versatility.<sup>44</sup> It can be described as follows:

$$q_{\rm e} = \frac{K_{\rm R}C_{\rm e}}{1 + b_{\rm R}C_{\rm e}^{\ m}} \tag{11}$$

There are three isotherm constants, namely,  $K_{\rm R}$  (mg·g<sup>-1</sup>),  $b_{\rm R}$  ((mg·g<sup>-1</sup>)<sup>*m*</sup>), and *m*. The *m* has a value between zero and one. At m = 0, the R-P equation transforms to Henry's law and at m = 1, transforms to Langmuir equation.

The parameters of isotherm models and their correlation coefficients are given in Table 3, and Figure 7 shows three isotherm models applied to the experimental data at 298 K. We could easily see from Figure 7 that Langmuir, Freundlich, and



Figure 7. Adsorption isotherms of bromate on HFO-201 at 298 K.

Redlich–Peterson isotherm models described the adsorption process well. The applicability of these isotherm equations was compared using the correlation coefficient,  $R^2$ , values. As shown in Table 3, the Redlich–Peterson model described the bromate adsorption on HFO-201 better ( $R^2 > 0.99$ ) than the Langmuir and Freundlich model at all temperatures. Meanwhile, the values of *m* were not close to unity, which indicates the

model. **3.7. Competing Anions on Bromate Adsorption onto HFO-201.** Drinking water usually contains more than one anion. So it is necessary to study the effect of coexisting anions on the removal of bromate by HFO resin from drinking water. In this study, inorganic anions including chloride (Cl<sup>-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), and sulfate (SO<sub>4</sub><sup>2-</sup>) were chosen as competing anions due to their widespread existance in drinking water. The effects of different inorganic anions (50, 150, and 250 mg·L<sup>-1</sup>) on HFO-201 for an initial bromate concentration of 200  $\mu$ g·L<sup>-1</sup> removal at pH 7 ± 0.5 are illustrated in Figure 8. We could

isotherms are approaching the Freundlich but not the Langmuir



**Figure 8.** Effect of competing anions on bromate adsorption on HFO-201 (adsorbent dosage, 0.2 g·L<sup>-1</sup>; initial concentration, 200  $\mu$ g·L<sup>-1</sup>; temperature, 298 K; pH, 7.0 ± 0.5; contact time, 24 h).

clearly see that all competing anions had a negative effect on the bromate removal to different degrees. The percentage of bromate removal by HFO-201 in the absence of these competing anions was about 100%, which declined to 73.83%, 38.36%, and 59.95% respectively when Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup> were in the presence of 50 mg·L<sup>-1</sup>. With the increase of the concentration of the coexisting anion, the removal rate of bromate further decreased, indicating that the higher concentrations of NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and Cl<sup>-</sup> inhibited the bromate removal by HFO-201. The negative influence may be due to the fact that these anions compete with bromate through occupying the binding sites on the adsorbents and thereby decreasing the bromate removal. As shown in Figure 8, the impact of different anions followed this order:  $NO_3^- > SO_4^{2-} > CI^-$ . Jia et al. pointed out that this difference in behavior may be attributed to the dissociation between anion and adsorbent.<sup>34</sup>

**3.8. Regeneration and Recycling.** After achieving the adsorption equilibrium, the HFO-201 saturated with bromate was regenerated by NaCl and NaOH/NaCl solution (0.1 M NaOH, 0.6 M NaCl), respectively. Meanwhile the recyclability of HFO-201 for bromate adsorption was investigated by repeating the adsorption/desorption process for five times, and the results were presented in Figure 9. Compared with NaCl



**Figure 9.** Bromate adsorption efficiency of HFO-201 regenerated by two regeneration solutions during five successive cycles (adsorbent dosage, 0.2 g·L<sup>-1</sup>; temperature, 298 K; initial bromate concentration, 200  $\mu$ g·L<sup>-1</sup>; contact time, 24 h).

solution, the adsorption efficiency of HFO- 201 regenerated by NaOH/NaCl solution recovered better with the increase of adsorption/desorption times, which should attribute to the negative charge of HFO in alkaline conditions resulting in the advantage of bromate stripping.<sup>39</sup> Simultaneously, the adsorption efficiency of HFO-201 for bromate was no significant loss after five successive cycles. The perfect renewable characteristics of HFO-201 exhibit its advantage for bromate removal from drinking water, especially for trace levels of bromate.

### 4. CONCLUSIONS

In the present study, commercial strong-base anion resin (D201) impregnated with hydrated ferric oxide (HFO) was proven to be a highly efficient adsorbent for the removal of bromate from aqueous solution. The resulting adsorbent HFO-201 exhibited a high adsorption capacity of bromate within a broad pH range (4-9), and the residual bromate concentration was below or close to MCL (10  $\mu$ g·L<sup>-1</sup>). The maximum capacity of HFO-201 for bromate was 292.82 mg·g<sup>-1</sup> at 298 K. The kinetic data fitted well by a pseudo-first-order model and intraparticle diffusion kinetics model demonstrated that the adsorption process of bromate on HFO-201 may be complex and consist of both surface adsorption and intraparticle diffusion. Equilibrium between bromate and HFO-201 was explained by the Redlich-Peterson adsorption isotherm. The thermodynamics study confirmed the adsorption process was exothermic and spontaneous. The effect of competing anions on bromate removal followed the order  $NO_3^- > SO_4^{2-} > Cl^-$ .

## ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jced.5b00947.

Variation of bromate and chloride concentration during bromate adsorption on HFO-201 (Figure S1), FT-IR spectra of HFO-201 before and after adsorption (Figure S2), and characterization of the resin (D201) before and after being impregnated with hydrated ferric oxide (HFO) (Table S1) (PDF)

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#### Notes

The authors declare no competing financial interest.

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