



Bromate removal from water by granular ferric hydroxide (GFH)

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ABSTRACT

The feasibility of granular ferric hydroxide (GFH) for bromate removal from water has been studied. Batch experiments were performed to study the influence of various experimental parameters such as effect of contact time, initial bromate concentration, temperature, pH and effect of competing anions on bromate removal by GFH. The adsorption kinetics indicates that uptake rate of bromate was rapid at the beginning and 75% adsorption was completed in 5 min and equilibrium was achieved within 20 min. The sorption process was well described by pseudo-second-order kinetics. The maximum adsorption potential of GFH for bromate removal was 16.5 mg g^{-1} at 25°C . The adsorption data fitted well to the Langmuir model. The increase in OH peak and absence of Br–O bonding in FTIR spectra indicate that ion-exchange was the main mechanism during bromate sorption on GFH. The effects of competing anions and solution pHs (3–9) were negligible. Results of the present study suggest that GFH can be effectively utilized for bromate removal from drinking water.

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1. Introduction

Bromate (BrO_3^-) is a disinfection by-product, generally formed by the reaction of ozone and naturally occurring bromide in drinking water, during ozonation process [1,2]. United States Environmental Protection Agency (US EPA) has classified bromate as a possibly carcinogenic substance to humans by the oral route of exposure [3]. In children, serious poisonings have been reported following the ingestion of 60–120 mL of 2% bromate [4]. Other toxic effects of bromate include nausea, vomiting, abdominal pain, anuria and diarrhoea, varying degrees of central nervous system depression, haemolytic anemia and pulmonary edema [5]. In view of the above harmful effects of bromate on human health, US EPA and American Water Works Association (AWWA) have set bromate maximum contaminant level (MCL) in drinking water as $10 \mu\text{g L}^{-1}$ [2]. Thus, an efficient technology is required for bromate removal from drinking water.

There are some chemical and physical methods for the removal of bromate from drinking water such as reduction using zero-valent iron (Fe^0) [6,7], reduction with Fe^{2+} [8,9], and SO_3^{2-} [9], adsorption and reduction by granular activated carbon [10–12], ionic exchange [13,14], filtering by reverse osmosis membrane [15], UV irradiation [16], high-energy electron beam (HEEB) irradiation [17]. The applicability of most of these methods on commercial scale is limited

due to high operational and maintenance costs, secondary pollution and complicated procedure involved in the treatment. Comparatively, adsorption process seems to be the more attractive method for the removal of aquatic pollutants due to simple design and ease of operation [18–20].

It has been observed from previous studies [21] that iron and aluminum oxides play an important role for the removal of anions from aqueous solutions. Technical University of Berlin (Germany) has developed a new adsorbent, granular ferric hydroxide (GFH) [22] which has been successfully applied for removal of arsenic, fluoride and natural organic matters from water [22–24].

In the present work, the potential of GFH has been assessed for bromate removal from water. Equilibrium and kinetic studies were performed to describe the adsorption process. The influence of several operating parameters on the adsorption of bromate, such as effect of contact time, initial bromate concentration, temperature, pH, and competing anions was investigated. Different kinetic models were tested to identify the adsorption mechanism and the results are presented in this communication.

2. Materials and methods

2.1. Granular ferric hydroxide (GFH)

The GFH was obtained from the supplier (GEH Wasserchemie, Germany). GFH is a poorly crystallized $\beta\text{-FeOOH}$, including chloride, which supports the structure of adsorbent [25]. The adsorbent was dried at room temperature for 16 h, as it always has water to

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maintain its crystal structure [25]. It may be converted to goethite, if it is dried further [25]. The grain size ranged from 0.32 mm to 2.0 mm and median adsorbent diameter of 1.16 mm was used in this study. The specific surface area of GFH has been reported to be 250–350 m² g⁻¹ and moisture content of 40–50% [26].

2.2. Adsorbate

Stock solution of bromate (1000 mg L⁻¹) was prepared by dissolving NaBrO₃ (Sigma–Aldrich, USA) in deionized water. A range of dilutions (5–400 mg L⁻¹) were prepared from the stock solution. All chemicals used were of analytical reagent grade. Initial pH was controlled by 0.1 M HCl and 0.1 M NaOH in pH experiments.

2.3. Adsorption studies

The adsorption of bromate on GFH was studied at room temperature (25 ± 2 °C) by batch experiments, except for investigation of temperature effect. Ten millilitre of bromate solution of varying initial concentrations (5–400 mg L⁻¹) in capped glass tubes was shaken with 0.1 g of adsorbent (GFH) for a specified period of contact time in a temperature controlled shaker (Jeio Tech Co., SWB-20 shaking water bath). The pH of the solutions was measured before and after the equilibration and a slight change in pH was observed. The pH of blank bromate solutions (5–400 mg L⁻¹) was observed 6.4–6.8, and after adding the GFH, it was 5.2–5.4. After equilibrium, samples were filtered using 0.25 μm filters (Versapor, Pall Co., USA) and the concentration of the bromate in the residual solution was determined by single-column ion chromatography (Metrohm, 761 compact IC, Switzerland). The latter consisted of a mixture of 3.2 mM sodium carbonate (Na₂CO₃) and 1.0 mM sodium bicarbonate (NaHCO₃) delivered at the flow rate of 0.6 mL min⁻¹. A 813 compact autosampler (Metrohm, Herisau, Switzerland) was assembled with a 50 μL injection loop. The separation column Metrosep A Supp 5, 4.0 mm × 250 mm (Metrohm Herisau, Switzerland) was packed with polyalcohol + polystyrene/methacrylate. Suppressed conductivity detector maintained at 25 ± 0.1 °C. The data acquisition was performed using a 761 compact IC 1.1 program (Metrohm, Herisau, Switzerland).

The amount of bromate adsorbed (q_e in mg g⁻¹) was determined as follows:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where, C_0 and C_e are the initial and equilibrium concentrations of bromate in solution (mg L⁻¹), V is the volume of solution (L), and m is the mass of the adsorbent (g). The adsorption was studied as a function of contact time, initial bromate concentration, temperature, pH, and in presence of competing anions.

2.3.1. Fourier transform infra red (FTIR) studies

FTIR spectra of the GFH samples (original and bromate-sorbed) were obtained using a Nicolet Magna 750 spectrometer with resolution of 4 cm⁻¹. The GFH sample was ground into powder and equilibrated with bromate solution (25 mg L⁻¹ and 50 mg L⁻¹). The FTIR pellet samples were prepared by pressing KBr and bromate-sorbed GFH powder. A pure KBr pellet used as background was subtracted from the FTIR spectra of the bromate-sorbed GFH samples.

3. Results and discussion

3.1. Effect of contact time and initial bromate concentration

In order to understand the sorption mechanism and to know the equilibration time for maximum uptake, the sorption of bromate

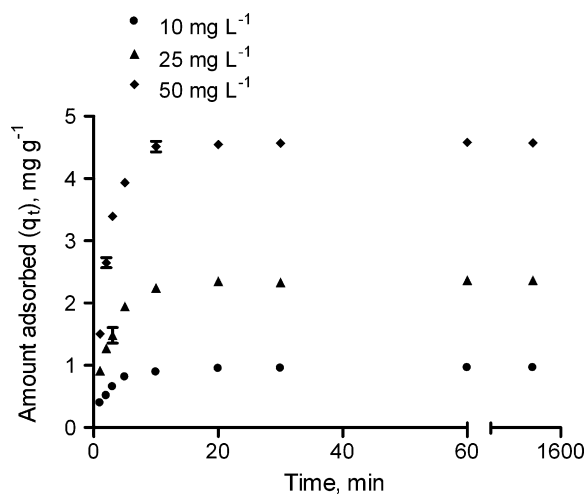


Fig. 1. Effect of contact time and initial concentration on adsorption of bromate on GFH (temperature = 25 °C, GFH concentration = 10 g L⁻¹, pH = 6.0–7.0).

on GFH was studied as a function of contact time with initial bromate concentrations of 10 mg L⁻¹, 25 mg L⁻¹ and 50 mg L⁻¹ and the results are shown in Fig. 1. It was observed that the bromate removal increased with the time. The adsorbent exhibited an initial rapid uptake removing nearly 75% of the dissolved bromate within the first 5 min followed by a slow kinetics to reach a plateau. There was no significant change in amount adsorbed after equilibrating the samples for 60 min and/or 24 h (Fig. 1) therefore, the equilibration period of 60 min was selected for further experiments. The results indicate that bromate shows fast kinetics onto GFH compared to the other conventional adsorbents, such as Granular Activated Carbons (GACs) and Powdered Activated Carbons (PACs), which show longer equilibration time from 4 h to 20 h [8,12,17].

The effect of initial concentration on equilibrium time was also investigated at three different concentrations (10 mg L⁻¹, 25 mg L⁻¹ and 50 mg L⁻¹) and results are also shown in Fig. 1. It was observed that the amount of bromate adsorbed increases with an increase in initial bromate concentration (Fig. 1). The bromate uptake by GFH increases from 0.95 mg g⁻¹ to 4.56 mg g⁻¹ (extent of adsorption ca. 90–96%) when the initial bromate concentration is increased from 10 mg L⁻¹ to 50 mg L⁻¹. This behavior can be explained due to the increase in the driving force of the concentration gradient, as an increase in the initial bromate concentration. Such phenomenon is common in a batch reactor with either constant adsorbent dose and varying initial adsorbate concentration or vice versa [27].

3.2. Kinetic modeling

Kinetic modeling is one of the important characteristics in defining the efficiency of adsorption. Various kinetic models have been proposed by different researchers. Four kinetic models including pseudo-first-order (Supporting information, Section 1), pseudo-second-order, Weber and Morris intraparticle diffusion model and Bangham's pore diffusion model (Supporting information, Section 2) have been applied in the present study to investigate the sorption mechanism of bromate on GFH. The applicable models have been discussed in detail below and modeling parameters are provided in Table 1.

3.2.1. Pseudo-second-order model

The adsorption kinetics was described as pseudo-second-order process [28,29]

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

Table 1
Kinetic parameters for the removal of bromate by GFH and calculated $q_{e(\text{cal})}$ and experimental $q_{e(\text{exp})}$ values for different initial bromate concentrations.

Pseudo-first-order model				
C_0 (mg L ⁻¹)	$q_{e(\text{exp})}$ (mg g ⁻¹)	$k_f \times 10^{-1}$ (min ⁻¹)	$q_{e(\text{cal})}$ (mg g ⁻¹)	R^2
10	0.96	2.60	0.91	0.975
25	2.35	2.69	1.33	0.984
50	4.58	2.14	1.76	0.963
Pseudo-second-order model				
C_0 (mg L ⁻¹)	$q_{e(\text{exp})}$ (mg g ⁻¹)	$k_s \times 10^{-1}$ (g mg ⁻¹ min ⁻¹)	$q_{e(\text{cal})}$ (mg g ⁻¹)	R^2
10	0.96	5.19	1.03	0.998
25	2.35	2.58	2.45	0.999
50	4.58	1.04	4.86	0.998
Bangham's model				
C_0 (mg L ⁻¹)		$k_0 \times 10^{-1}$ (mL (g L ⁻¹) ⁻¹)	α	R^2
10		1.51	0.30	0.847
25		1.57	0.25	0.918
50		0.15	0.27	0.973
Weber and Morris model				
C_0 (mg L ⁻¹)	$k_{id,1}$ (mg g ⁻¹ min ^{-1/2})	R^2	$k_{id,2}$ (mg g ⁻¹ min ^{-1/2})	R^2
10	0.37	0.969	0.03	0.731
25	0.80	0.979	0.05	0.668
50	1.20	0.895	0.17	0.639

where, q_e and q_t are the amount of bromate adsorbed (mg g⁻¹) at equilibrium and at time t and k_s is the rate constant of pseudo-second-order kinetics. The plots between t/q_t versus t were drawn and are shown in Fig. 2(A). The slope and intercept of plot (Fig. 2 (A)) were used to determine the pseudo-second-order rate constants (k_s) and $q_{e(\text{cal})}$ and are compiled in Table 1 alongwith correlation coefficient (R^2) values. The plots were found to be linear with good

correlation coefficients varying from 0.998 to 0.999 and the theoretical $q_{e(\text{cal})}$ fit well to the experimental $q_{e(\text{exp})}$ values at three concentrations studied. This suggests that the present adsorption system can be defined more favorably by the pseudo-second-order kinetic model.

Mass transport processes may be similar for porous metal oxides and activated carbons [30]. The adsorption of solute from the solution by the adsorbent is driven by four mass transport mechanisms: diffusion at bulk space, film diffusion, intraparticle diffusion and sorption into interior sites. Generally, the first and fourth steps are rapid and thus, not considered as rate-limiting steps, therefore, film and intraparticle diffusion are the major steps controlling the rate of adsorption. The Weber and Morris intraparticle diffusion model and Bangham's pore diffusion model (Supporting information, Section 2) have been further applied to observe the diffusion mechanism.

3.2.2. Weber and Morris intraparticle diffusion model

Kinetic data (Fig. 1) were applied in intraparticle diffusion model proposed by Weber and Morris [31]:

$$q_t = k_{id} t^{1/2} + C \quad (3)$$

where, k_{id} is the intraparticle diffusion rate constant and C is the intercept, related to the thickness of the boundary layer. If the Weber and Morris plot of q_t vs. $t^{1/2}$ gives a straight line, then the sorption process is controlled by intra-particle diffusion only. However, if the data exhibit multi-linear plots, then two or more steps influence the sorption process. The Weber and Morris plots of bromate sorption on GFH are shown in Fig. 2(B). There are two separate zones (Fig. 2(B)): first linear portion (phase I), and second straight line (phase II). In phase I, approximately 65% of bromate was rapidly uptaken by GFH within 3 min. This is attributed to the immediate utilization of the most readily available adsorbing sites on the adsorbent surface. Phase II may be attributed to very slow diffusion of the adsorbate from the surface site into the inner pores. Thus, initial portion of bromate adsorption on GFH may be governed by the initial intraparticle transport of bromate controlled by surface diffusion process and the later part controlled by pore diffusion.

The values of $k_{id,1}$ and $k_{id,2}$ (intraparticle diffusion rate constants for phase I and II, respectively) obtained from the slope of linear plots are listed in Table 1 along with correlation coefficients (R^2). It is evident from k_{id} values (Table 1) that $k_{id,1}$ (value of phase I) is higher compared to $k_{id,2}$ (value of phase II) indicating that initial step (phase I) is rapid followed by a slow step (phase II). The intercept of the line fails to pass through the origin at each concentration and the R^2 values at the two concentrations are also less than 0.999

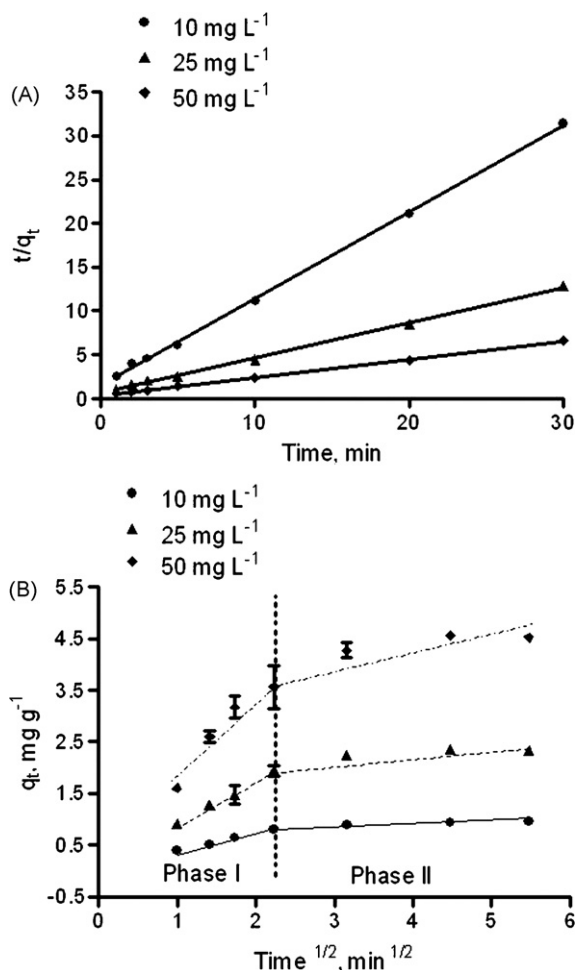


Fig. 2. Kinetic modeling of adsorption of bromate on GFH (A) Pseudo-second-order kinetic plots; (B) Weber and Morris intraparticle diffusion plots.

suggesting that two or more steps are involved in the sorption process. The deviation of straight line in Weber and Morris model may be due to the difference in the rate of mass transfer in initial and final stages of adsorption [32].

3.3. Adsorption isotherms and mechanism of bromate uptake onto GFH

In order to evaluate the adsorption potential of GFH for bromate removal, the equilibrium adsorption of bromate was studied as a function of bromate concentration at room temperature (25 °C) and the adsorption isotherms of bromate are shown in Fig. 3. The equilibrium was not achieved in the lower bromate concentration range ($\mu\text{g L}^{-1}$) (as seen in the inset of Fig. 3), therefore higher concentrations (in mg L^{-1} level) of bromate were chosen to attain equilibrium and to know the maximum adsorption potential of GFH for bromate removal. It is further clear from Fig. 3 that initially isotherm rises sharply indicating that plenty of readily accessible sites are available for adsorption. However, as concentration increased, site saturation of GFH occurred and a plateau is reached indicating that no more sites are available for adsorption. An adsorption capacity of 16.5 mg g^{-1} was observed for bromate on GFH at room temperature (25 °C). GFH shows higher sorption potential for bromate removal compared to other conventional GACs adsorbents ($2\text{--}7 \text{ mg g}^{-1}$) for bromate [12].

To study the mechanism of bromate sorption onto GFH, kinetics and equilibrium studies were undertaken. The concentration of bromate and chloride was monitored simultaneously as a function of time (C_t) during kinetic experiments and the results are shown in Fig. 4(A). The experiments were conducted under identical conditions similar to kinetic study in Section 3.1. The initial bromate concentration was 50 mg L^{-1} (0.39 mmol L^{-1}). Interestingly, chloride concentration has been increased rapidly in the solution (due to its desorption from GFH) within first few minutes of the experiments. Simultaneously, the bromate concentration was decreased in the solution with rapid increase in chloride concentration until 20 min (equilibrium). These results indicate that bromate removal by GFH takes place by ion-exchange mechanism with chloride

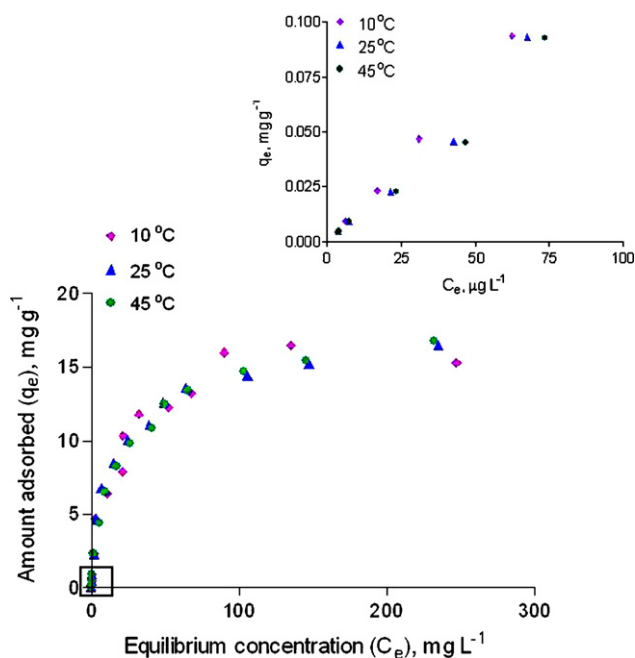


Fig. 3. Sorption isotherms of bromate on GFH (contact time = 60 min, GFH concentration = 10 g L^{-1} , pH = 6.0–7.0). (The figure in inset shows the data points at lower bromate concentration ($\mu\text{g L}^{-1}$) range of the isotherm.

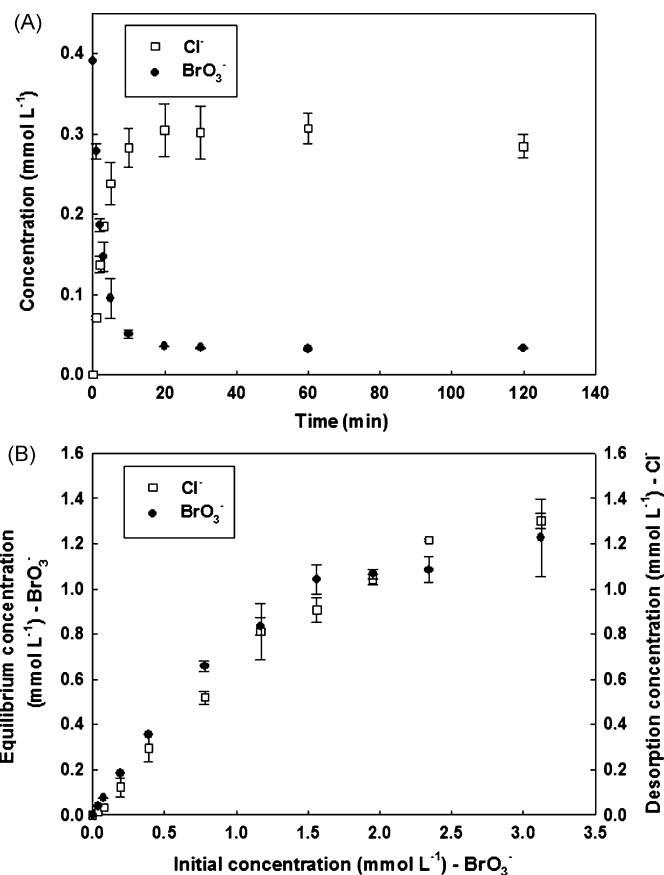
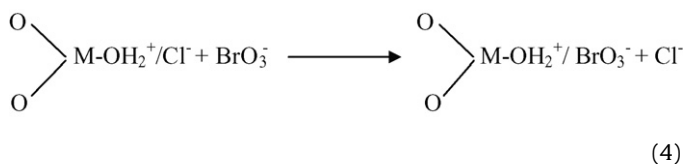


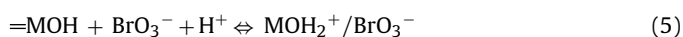
Fig. 4. Experimental results for ion-exchange of bromate with chloride (A) Kinetic studies (B) Equilibrium studies.

(present in GFH to support the structure of adsorbent). Bromate ion was exchanged with chloride with an exchange ratio close to one.

To further confirm this phenomenon, equilibrium experiments were also conducted under identical conditions described previously in this section. The initial bromate concentration was $5\text{--}400 \text{ mg L}^{-1}$ ($0.039\text{--}3.125 \text{ mmol L}^{-1}$). It has been observed that bromate concentration corresponds to desorbing chloride concentration at equilibrium in solution (Fig. 4(B)). Chloride desorption from GFH increased by increasing the initial bromate concentration. These results suggest that ion-exchange mechanism is the main process for the sorption of bromate onto GFH which can be given by ion-exchange reaction as below:



where, M = metal (Fe). The FTIR analysis was also conducted with original GFH (blank) sample and 25 mg L^{-1} and 50 mg L^{-1} of bromate-sorbed GFH samples and the FTIR spectra are shown in Fig. 5. The original GFH (blank) sample exhibited a strong and broad OH peak at 3386 cm^{-1} . The OH intensity significantly increased at 50 mg L^{-1} as more bromate was sorbed on GFH while no Br–O peak was apparent. The increase in OH peak and absence of Br–O bonding indicate that ion-exchange was the main mechanism during bromate sorption on GFH which can be given by Eq. (5):



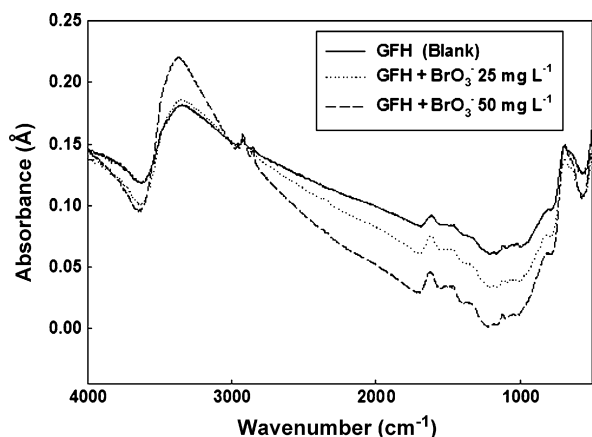


Fig. 5. FTIR spectra of original and bromate-sorbed GFH samples.

3.4. Effect of temperature

In order to understand the effect of temperature on the adsorption of bromate, experiments were also performed at 10 °C and 45 °C and results are shown in Fig. 3. Adsorption capacity of GFH for bromate was found to be 18.0 mg g⁻¹, 16.5 mg g⁻¹ and 16.8 mg g⁻¹ at 10 °C, 25 °C and 45 °C, respectively. The adsorption isotherms at 10 °C, 25 °C and 45 °C reveal that temperature does not show much influence on bromate adsorption by GFH. The adsorption equilibrium data were further analyzed using two isotherm models viz. Freundlich (Supporting information, Section 3) and Langmuir models.

The linear form of Langmuir model [33] can be given as:

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

where, q_e is amount adsorbed at equilibrium concentration C_e , q_m is the Langmuir constant representing maximum monolayer adsorption capacity and b is the Langmuir constant related to energy of adsorption. The Langmuir isotherm and model constants are given in Fig. 6 and Table 2, respectively for the removal of bromate by GFH. Langmuir plots are found linear with good correlation coefficients varying from 0.981 to 0.997. Furthermore, the q_m values calculated from Langmuir isotherm accord well with the experimental q_e values. The results indicate the Langmuir isotherm represents a better fit of experimental data and confirms the applicability of Langmuir model in the present adsorption study. These facts suggest that bromate is adsorbed in the form of monolayer coverage on the surface of the adsorbent.

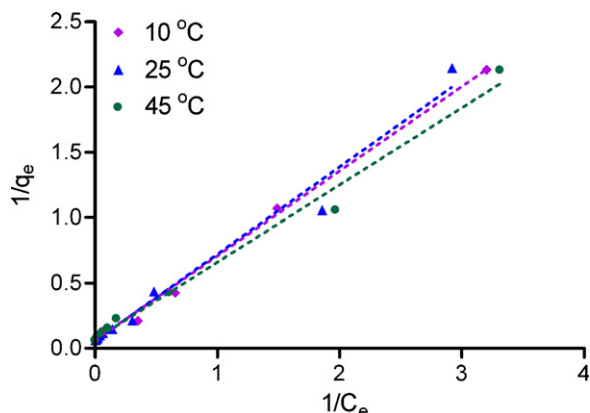


Fig. 6. Langmuir isotherm of bromate adsorption on GFH.

The influence of adsorption isotherm shape has been discussed [34] to examine whether adsorption is favorable in terms of R_L , a dimensionless constant referred to as separation factor or equilibrium parameter. The values of R_L have been discussed using the following equation:

$$R_L = \frac{1}{1 + bC_0} \quad (7)$$

where, b is the Langmuir constant. The values of R_L calculated from Eq. (7), and are given in Table 2. All the R_L values lie between 0 and 1 confirming that shape of the adsorption isotherm is favorable.

3.5. Thermodynamic study

The thermodynamic constants, standard free energy change (ΔG^0), enthalpy change (ΔH^0), and entropy change (ΔS^0) were calculated to evaluate the thermodynamic feasibility of the process and to confirm the nature of the sorption process. The thermodynamic parameters were calculated using the equations (8–10):

$$\Delta G^0 = -RT \ln K \quad (8)$$

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^0}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (9)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (10)$$

where, R is an universal gas constant (8.314 J mol⁻¹ K⁻¹), T is temperature (K), and K is the equilibrium constant, related to the Langmuir constant (b) via Eq. (11) where the value 55.5 corresponds to the molar concentration of the solvent [35,36].

$$K = b \times 55.5 \quad (11)$$

The ΔG^0 value was found -15.91 kJ mol⁻¹ in the present study suggesting the spontaneous nature of the adsorption process. The ΔH^0 value obtained in this study is -8.10 kJ mol⁻¹. In literature [31], when the value of ΔH^0 is lower than 40 kJ mol⁻¹, the type of adsorption can be accepted as a physical process. It would be claimed that the physical adsorption occurs during the bromate adsorption onto GFH. Further, ΔS^0 were 80.58 J mol⁻¹ K⁻¹ which indicates the affinity of the adsorbent for bromate.

3.6. Effect of pH and competing anions on bromate sorption onto GFH

The sorption of bromate ($C_0 = 50$ mg L⁻¹) on GFH was investigated at different pH from 3 to 12 (Fig. 7). High removal efficiency (ca. 95%) of bromate was observed between pH 3–9. A significant decrease was observed in bromate removal rates at pH 10–12. This

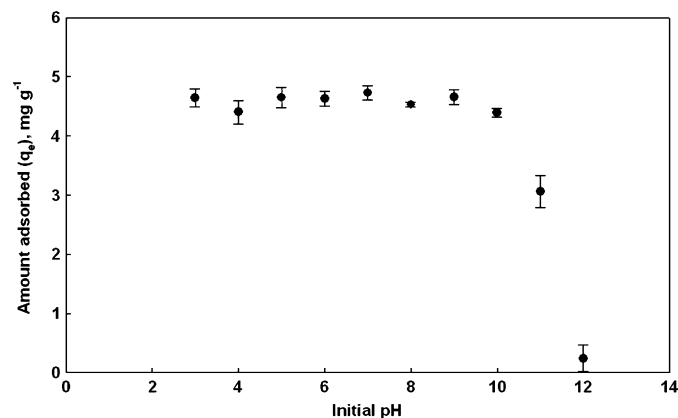


Fig. 7. Effect of pH on bromate adsorption on GFH ($C_0 = 50$ mg L⁻¹, temperature = 25 °C, contact time = 60 min, GFH concentration = 10 g L⁻¹).

Table 2
Langmuir and Freundlich constants and separation factor for the adsorption of bromate on GFH at different temperatures.

Langmuir constants				
Temperature (°C)	q_m (mg g ⁻¹)	b (L mol ⁻¹)	$R_L \times 10^{-2}$	R^2
10	17.86	11.85	2.34	0.997
25	16.95	11.08	2.87	0.981
45	15.63	11.61	2.69	0.989
Freundlich constants				
Temperature (°C)	K (mg g ⁻¹)(L mg ⁻¹) ^{1/n}	$1/n$	R^2	
10	1.20	0.53	0.914	
25	1.21	0.52	0.912	
45	1.18	0.51	0.948	

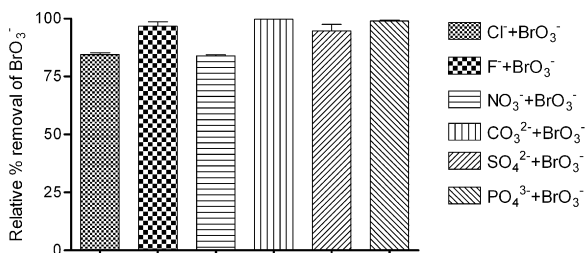


Fig. 8. Effect of competing anions on bromate adsorption on GFH.

may be due to the competition for the active sites by OH⁻ ions and the electrostatic repulsion of bromate ions by the negatively charged GFH surface at high pH. The optimum bromate removal was observed at pH ranges of 4.0–8.0 suggesting that the GFH can be successfully utilized in drinking water processes.

Drinking water and surface water contains several anions. Therefore, it is important to study the effect of competing anions which are generally present in the groundwater. The removal of bromate in presence of competing anions like chloride (Cl⁻), fluoride (F⁻), nitrate (NO₃⁻), carbonate (CO₃²⁻), sulphate (SO₄²⁻), and phosphate (PO₄³⁻) was investigated with the initial concentrations of 100 mg L⁻¹ of competing anions with an initial bromate concentration of 100 mg L⁻¹ at room temperature (25 °C). Effect of competing anions on bromate removal is shown in Fig. 8. It is clear from the figure that the competing anions did not show great influence on bromate sorption. Little influence on bromate sorption was observed in case of chloride and nitrate, which are outer-spherically sorbing anions.

4. Conclusions

Results of the present study demonstrate the potential use of granular ferric hydroxide (GFH) for bromate removal from aqueous solutions. The adsorption capacity of GFH for bromate was 16.5 mg g⁻¹ at 25 °C. The adsorption isotherm was fitted well to Langmuir model. The increase in OH peak and absence of Br–O bonding in FTIR spectra indicate that ion-exchange was the main mechanism during bromate sorption on GFH. Kinetic results indicate that the sorption process can be defined more favorably by the pseudo-second-order kinetic model under the selected concentration range. The bromate sorption was found to be a two step process: first step may be attributed to the transport of bromate by surface diffusion and the second step is controlled by pore diffusion. Bromate removal was unaffected over a wide pH range (3–9) and competing anions did not show much influence on bromate sorption. Experimental data can be further used to guide and optimize pilot scale experiments that can enable the commercial exploitation of GFH for bromate removal from drinking water.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2009.04.123.

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