Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2023.29671

299 (2023) 102–109
July

Aqueous bromate (BrO_3^-) removal using FILTRASORB 400 activated carbon: effect of process variables and modeling

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Received 3 January 2023; Accepted 5 June 2023

ABSTRACT

Aqueous phase bromate (BrO_3^-) treatment using a commercial granular activated carbon (GAC, FILTRASORB 400) indicated that bromate removal is highly influenced by the operational factors such as pH, initial bromate concentration, contact time and the adsorbent dosage. The effect of pH on bromate treatment indicated higher to significant bromate removal at pH ≤ 4, whereas for pH range 5–9 ~ 50% bromate removal was noted. At pH higher than 9, a significant decrease in the bromate removal was noted that was ascribed to changes in the GAC surface speciation. Furthermore, a higher mass-based bromate removal transpired with an increase in the initial bromate concentration that was explained based on higher mass transfer and diffusion. Also, the bromate adsorption experimental data fitted well to the Freundlich adsorption isotherm, indicating a multilayer bromate ions accumulation on the GAC surface. Furthermore, an increasing 'q_e vs. C_e' trend also implied a multilayer bromate ions attachment on the GAC surface. Moreover, the kinetics experiments showed that the pseudo-second-order kinetic model better describes the respective GAC-based bromate removal as compared to pseudo-first-order kinetic model. This indirectly indicated that the removal of bromate using granular activated carbon is a more involved process, with both adsorption and reduction causing the noted bromate removal ($\underline{GAC}\text{-}BrO_3 \leftrightarrow \underline{GAC}\text{-}BrO \leftrightarrow \underline{GAC}\text{-}Br$). It is suggested that initially the adsorbed BrO_3^- ion is reduced to BrO^- (hypobromite) followed by a further reduction of BrO^- to Br^- (bromide) ion. Additionally, as the surface bound bromate ion is reduced to bromide, it would cause further mass transfer of solution phase bromate ion towards the GAC surface, which is also indirectly supported by the aforementioned Freundlich based multilayer bromate removal trend.

Keywords: Bromate (BrO_3^-); Granular activated carbon; FILTRASORB 400; Adsorption; Kinetics

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1. Introduction

An exponential increase in urbanization and industrial growth worldwide has led to an increase in drinking water pollution due to respective anthropogenic activities. Hence, various techniques have been used in order to treat the respective contaminated water bodies. Bromate (BrO_3^-), is one such contaminant that results from several sources including ozonation-based disinfection of drinking water containing bromide [1]. Bromate is considered a concern as it is carcinogenic and also causes other dysfunctions including the thyroid related diseases [2,3]. Therefore, bromate removal from respective water bodies is required. Accordingly, several approaches have been reported in the literature for aqueous phase bromate removal, including ion exchange [4], adsorption onto organic materials [5], carbon nanotubes [6], and granular activated carbon (GAC)-based adsorption [7], under a varying set of process parameters like pH, initial bromate concentration, adsorbent dose, temperature, contact time, and coexisting anions. Adsorption using activated carbon (AC) is one of the most effectively used techniques for the removal of various pollutants both from the water and air [8–12]. However, based on the reported literature and to the best of our knowledge, bromate removal using a commercial activated carbon under a varying set of process conditions is needed. For example, Qiu and Xiong [7] who studied the use of an activated carbon modified with a cationic surfactant having specific surface area of 392 m^2/g, report about 80% bromate removal. Xu et al. [13] who report the use of an activated carbon sample impregnated with nano zero-valent iron report the lowest bromate removal noted between pH 3 and 5. The authors also report that a positively charged activated carbon surface at lower pH values will initiate higher uptake of anionic bromate resulting in latter's higher removal. In addition to that, a higher dissolution of nano zero-valent iron (from the activated carbon surface) at the respective acidic pH and its subsequent reaction with bromate ion, was also suggested to cause higher bromate reduction to bromide. Thus, both enhanced adsorption and subsequent reduction of bromate were ascribed to a higher overall bromate removal at lower pH values between 3 and 5. However, anions especially nitrate, phosphate, and carbonate at high concentration did affect bromate removal. In another study, Xu et al. [14] who investigated the use of a nano-iron hydroxide impregnated granular activated carbon for bromate removal, report the optimum pH for bromate removal to be between 6 and 8, with acidic pH favored because of increased adsorption of anionic species onto protonated GAC surface sites. Farooq et al. [15] who investigated the bromate removal using powdered activated carbon modified with cationic surfactants noted pH ≤ 6 yielding the highest bromate removal with both ion exchange and electrostatic-adsorption suggested to cause bromate removal. Konsowa [16] also studied aqueous phase bromate species removal using GAC and noted both contact time and temperature having a positive effect with about 95% bromate removal. Furthermore, Liu et al. [17] who investigated the application of coal-based activated carbon treated by several acidic and basic groups, report that the ammonia treated GAC with positive surface sites showed higher bromate removal compared to naked GAC. In fact, the respective trends also showed that the ammonia modified GAC yielded the highest specific surface area that in turn resulted into best bromate removal. Mohamoud et al. [18] using HCl modified GAC also report a near complete bromate removal with both adsorption and reduction reported to be the main bromate removal mechanisms. In another study Siddiqui et al. [19] also report that the surface adsorbed bromate was further reduced to bromide via the surface organic functional groups. This indicates that the removal of bromate using activated carbon is a two-step process involving both adsorption and reduction. Xu et al. [14] also report a similar adsorption–reduction pathway for bromate removal using Fe-GAC. Wang et al. [20] report use of powdered activated carbon produced from several different sources for bromate ion removal, with varying specific surface area values ranging from 688 to 1,270 m^2/g, with the fruit-based activated carbon having the highest pore volume and maximum bromate removal capacity of 99.6 mg/g. Furthermore, the bromate removal was discussed based on intraparticle transfer with adsorption as the major bromate removal mechanism along with reduction (with near 20% bromide formation). Dong et al. [21] who studied bromate removal performance of virgin and silver modified GAC noted the silver modified GAC showing better bromate removal performance specifically at lower pH level. Gu et al. [22] also report both virgin and modified GAC application for bromate with both thermal and hydrogen peroxide treated GAC to yield better bromate treatment as compared to the virgin GAC. In summary, the above literature review indicates that the aqueous phase bromate can be removed under a varying set of conditions and using a variety of both unmodified and modified AC-materials with a careful adjustment of process variables. Accordingly, this paper investigates the aqueous phase bromate removal using a commercial granular activated carbon (i.e., FILTRASORB 400). In this regard, various parameters that significantly influence bromate removal performance such as pH, contact time, initial bromate concentration and GAC dosage, have been investigated. Furthermore, the potential role of both adsorption and reduction during the bromate removal using GAC, has been discussed. Adsorption isotherms as well as kinetic models have also been developed considering their importance for practical applications.

2. Materials and methods

2.1. Materials

All chemical used were of high purity reagent grade quality, including potassium bromate (Fisher, USA), sodium carbonate (BDH, UK), sodium bicarbonate (BDH, UK), hydrochloric acid (BAKER, USA), sodium hydroxide (Fisher, USA), and pH calibration standards (Fisher, USA). The FILTRASORB 400 granular activated carbon/GAC (USA) was used for all bromate adsorption experiments; it has a high specific surface area of 948 m^2/g. High purity water obtained using a CORNING System.

2.2. Adsorption studies

2.2.1. pH effect experiments

The synthetic wastewater for the pH effect and also for all the other experiments as completed in the present study was prepared using a 1,000 mg/L bromate (BrO_3^-) stock solution. The respective bromate stock solution was always kept under cool, capped, and covered condition. Using the bromate stock solution, a 10 mg/L bromate solution was first prepared followed by a blank sample collection (as the benchmark). The remaining 10 mg/L bromate solution was then distributed in several 200 mL capped and covered glass bottles with 2 g/L GAC. The pH of the respective samples was then adjusted using either HCl or NaOH solution. The respective bottles were then kept on a plate shaker (for mixing) for a day followed by sample collection and filtration. The filtrate from each bottle (including the blank) was then tested for bromate, and the difference between the bromate concentration in blank and each individual sample, showed the bromate removed.

2.2.2. Initial concentration effect, adsorption isotherm and kinetics experiments

For the bromate initial concentration effect experiments, initially glass bottles with 0.5 g of activated carbon and 250 mL of bromate solution were arranged at initial pH 6 and room temperature. The bromate concentration was varied between 5 and 100 mg/L. The respective experiments were conducted for 7 d. The bromate removal at equilibrium was determined using:

$$q_e = \left(C_o - C_t\right) \times \left(\frac{V}{m}\right) \tag{1}$$

where C_o is the initial concentration and C_t is the final concentration (mg/L), V is the solution volume, and m is the GAC mass (g). Similarly, for the bromate adsorption isotherm experiments, the respective synthetic wastewater was first prepared, distributed into glass bottles, and after this varying GAC quantities were added to each individual glass bottle (with the first bottle as blank, that is, without GAC). The activated carbon dose was varied from 0.2 to 2 g (0.2, 0.4, 0.8, 1.2, 1.6, and 2 g). The specific amount of GAC was put in contact with 250 mL of 100 mg/L bromate solution at pH 6 with mixing to make sure that equilibrium is obtained. The respective bottles were sealed, covered, and then put on the plate shaker for 7 d after which samples were collected, filtered, and analyzed for bromate, followed by using the respective bromate removal data for data fitting to determine the most appropriate isotherm model. For the kinetics experiments, the initial pH was 6.0. The respective bromate solutions (500 mL) were put in contact with GAC (2 g/L) with samples retrieved at several time intervals for the kinetic modeling.

2.3. Analytical methods

An ion chromatograph (Advanced IC, Metrohm, Switzerland) along with conductivity detector set-up was used to measure the concentration of bromate. The eluent composition was 3.2 mM Na_2CO_3/1 mM $NaHCO_3$ that was prepared using high purity reagent grade sodium carbonate (BDH, UK) and sodium bicarbonate (BDH, UK) chemicals. The IC column used was Metrosep Anion Dual 2 (Metrohm, Switzerland). The column also accompanied a guard column. The used IC is equipped both with a built-in suppressor (to reduce the background conductivity resulting from the eluent) and high sensitivity conductivity detector. Furthermore, Magic IC Methrohm software was used to automize data collection and processing. The IC equipment was also regularly calibrated using appropriate bromate calibration standards. Fig. 1a provides a sample calibration curve for the ion chromatography-based analysis of bromate ion. Furthermore, a standard pH meter with electrode was used for the pH measurements. All analyzers were regularly calibrated using the respective calibration standards.

3. Results and discussion

The findings from various bromate removal studies including the pH and initial bromate concentration effect, adsorption isotherm, and adsorption kinetics, are provided.

3.1. pH effect

Considering the fact that the adsorption process is typically a function of pH, the effect of pH on bromate removal was first investigated, with results shown in Fig. 1b. The reported pH values are final pH values after reaching the equilibrium. Fig. 1b that shows bromate removal efficiency at different pH values clearly indicates higher to significant bromate removal at pH ≤ 4 whereas between pH 5 and 9 approx. 50% bromate removal transpires that is followed by a decreasing bromate removal trend at pH above 9. The previous studies on bromate removal using activated carbon also report an anionic type adsorption

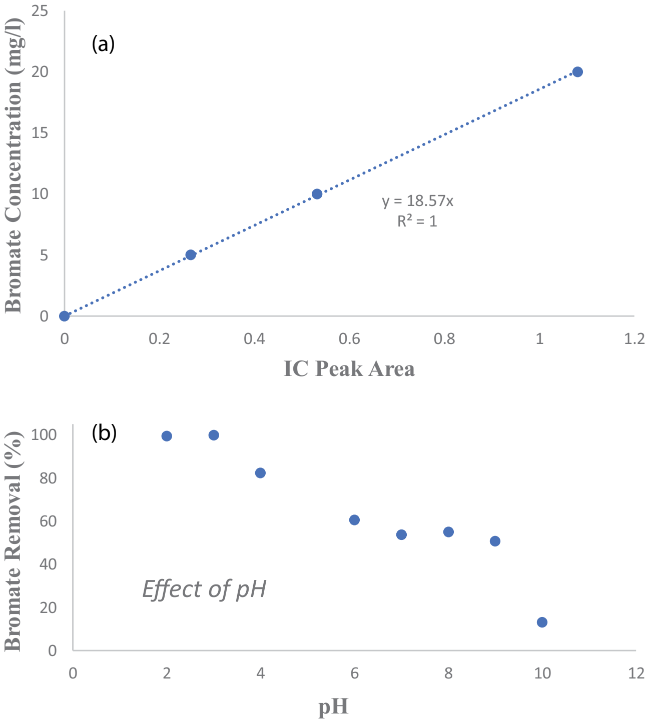

Fig. 1. (a) A sample calibration curve for the ion chromatography-based analysis of bromate ion. (b) Effect of pH on bromate removal efficiency (2 g/L GAC; 10 mg/L bromate; pH final; 24 h).

behavior [23]. Dong et al. [21] who studied the bromate removal performance of virgin and silver modified GAC noted the silver modified GAC showing better bromate removal performance specifically at lower pH level. It has also been suggested that the anionic bromate interacts more with the positively charged activated carbon surface at acidic pH. For example, Xu et al. [13] who report use of an activated carbon sample impregnated with nano zero-valent iron noted the lowest bromate removal between pH 3 and 5. The authors report that a positively charged activated carbon surface at lower pH values will initiate higher uptake of anionic bromate resulting in latter's higher removal. In addition to that, a higher dissolution of nano zero valent iron (from the AC surface) at the respective acidic pH and its subsequent reaction with bromate ion, was also suggested to cause higher bromate reduction to bromide. Thus, both enhanced adsorption and subsequent reduction of bromate were ascribed to higher overall bromate removal at acidic pH values between 3 and 5. However, anions especially nitrate, phosphate, and carbonate at high concentration did affect bromate removal. In another study, Xu et al. [14] who investigated the use of nano iron hydroxide impregnated granular activated carbon for bromate removal, report the optimum pH for bromate removal between 6 and 8, with acidic pH favored because of increased adsorption of anionic species onto protonated GAC surface sites. Farooq et al. [15] who investigated bromate removal using powdered activated carbon modified with cationic surfactants also noted pH ≤ 6 yielding the highest bromate removal with both ion exchange and electrostatic adsorption suggested to cause bromate removal. A similar pH dependent bromate removal behavior is reported using other materials as well. For example, Naushad et al. [4] who used a specific ion exchange material (De-Acidite FF-IP resin) for bromate treatment also report higher bromate removal within the acidic pH range. Zeino et al. [6] using Fe impregnated carbon nanotubes also noted a better bromate removal efficiency at lower pH values (pH < 5). Nevertheless, the present work reports results at pH 6, which avoids working at very acidic pH values and at the same time is conducive for a higher bromate uptake by the GAC surface, as also noted in the above-mentioned previous works. The noted anionic bromate removal trend can be explained using the changes in the GAC surface speciation vs. pH. Typically, the GAC surface is represented as:

$$\underline{\mathbf{GAC}}\text{-OH}_2^+ \leftrightarrow \underline{\mathbf{GAC}}\text{-OH} + \text{H}^+ \tag{2}$$

$$\underline{\mathbf{GAC}}\text{-OH} \leftrightarrow \underline{\mathbf{GAC}}\text{-O}^- + \text{H}^+ \tag{3}$$

Hence, the high removal of anionic bromate ions at acidic values is because of protonated GAC surface because of high H^+ ions presence close to the solid surface that yields a positive GAC surface charge. This consequently initiates a higher electrostatic attraction between the cationic GAC surface and the anionic bromate species thus causing the bromate ions to be easily transferred to the GAC surface at low pH. However, as the solution pH increases, the surface gradually acquires increasing negative charge resulting in to reduced electrostatic attraction between the GAC surface and bromate ions. Furthermore, the concentration of OH^- ions also increases at high pH values which in turn will also cause a competition between the bromate and OH^- anions for the available sites on the GAC surface; this will eventually cause a reduced bromate adsorption. Bhatnagar and Sillanpää [24] who studied the use of nano Al_2O_3 also report decreased bromate removal at elevated pH. A similar anionic type bromate removal trend is also reported by Al-Ghouti et al. [1] using roasted date pits. Therefore, in summary, the noted pH dependent bromate removal trend (Fig. 1b) transpires essentially because of the changes in the GAC surface charge and speciation as described in reactions 2 and 3.

3.2. Bromate amount effect

After pH, the effect of bromate amount onto its removal was also studied and for that purpose several experiments were conducted at varying initial bromate concentrations at 2 g/L GAC and pH value of 6. Fig. 2 that provides the respective results shows a near complete bromate removal at initial concentrations of 5, 20, and 40 mg/L, while for the 100 mg/L bromate system only 80% bromate removal is noted. This indicates that % removal efficiency of bromate decreases with an increase in the bromate concentration due to diminishing availability of attachment sites at the GAC surface. At higher bromate concentration, the available GAC surface sites become saturated, which in turn results in a lower bromate removal efficiency. Nevertheless, in terms of mass transfer, a higher bromate transfer is still noted with an increase in the bromate concentration. Zeino et al. [6] using Fe impregnated carbon nanotubes also report that the initial bromate concentration had a positive impact on its removal, that is, the higher the bromate concentration the better the mass-based adsorption. This could result due to a higher difference between the bulk aqueous and bulk solid phase bromate concentrations, which will provide an enhanced driving force for the mass transfer of bromate (from the bulk liquid to bulk solid) at higher bromate concentrations. Similarly, Bhatnagar et al. [25] who investigated the use of $Fe(OH)_x$ as an adsorbent noted a positive bromate concentration influence onto its mass transfer across the liquid–solid interface. On the other hand, Konsowa [16] report diffusion as the primary

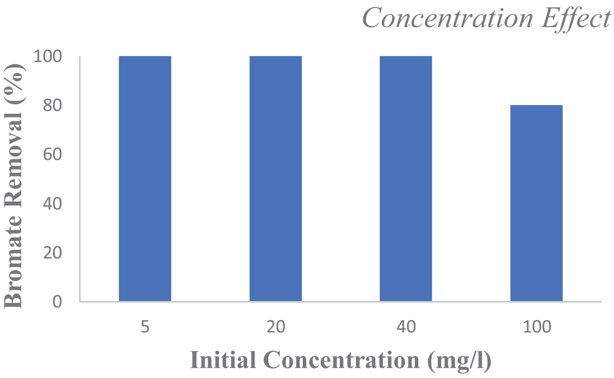

Fig. 2. Effect of initial concentration on bromate removal (initial bromate concentrations varying from 5.0 to 100 mg/L; GAC 2 g/L; pH 6; 7 d).

mechanism affecting bromate removal using GAC. It should also be noted that in Fig. 1b at 10 ppm bromate, we note about 60% bromate removal at 24 h equilibrium time, but in Fig. 2 with 7 d equilibrium time we note near 100% bromate removal, even for 40 ppm bromate. Hence, given more time, the pollutants will be able to diffuse into meso/micropores resulting into higher adsorption. Considering this the adsorption isotherm experiments, as reported in the next section, were then completed at 7 d equilibrium time.

3.3. Adsorption isotherm study

Bromate adsorption isotherm experiments were also conducted and Fig. 3 shows the respective bromate removal results at different GAC dosages. It is observed that the bromate removal efficiency increases from about 11%–60% when the GAC dosage is increased from 0.2 to 1.6 g. However, a further increase in GAC dosage to 2 g shows a slower change. The respective results were first fitted to the Langmuir isotherm:

$$q_e = \frac{q_m \times K_L \times C_e}{1 + K_L \times C_e} \tag{4}$$

where C_e is the equilibrium concentration (mg/L), q_e is the amount of bromate ions adsorbed at equilibrium (mg/g), q_m is the maximum adsorption capacity (mg/g), and K_L is the Langmuir binding sites affinity coefficient (L/mg). The Langmuir linear fit was obtained using Eq. (5):

$$\frac{1}{q_e} = \frac{1}{q_m \times K_l} \times \left(\frac{1}{C_e}\right) + \frac{1}{q_m} \tag{5}$$

Fig. 4 shows the respective Langmuir adsorption isotherm fit with a correlation coefficient of 0.91. The respective model parameters are also given in Table 1 with q_m 23.4 mg/g. The obtained adsorption results were also fitted to Freundlich isotherm:

$$q_e = \left[k_f \left(C_e^{\frac{1}{n}}\right)\right] \tag{6}$$

where k_f is adsorbent capacity measure and n is the Freundlich adsorption affinity constant. For the Freundlich model fit was obtained using Eq. (7):

$$\ln q_e = \ln K_f + \left(\frac{1}{n}\right)\ln C_e \tag{7}$$

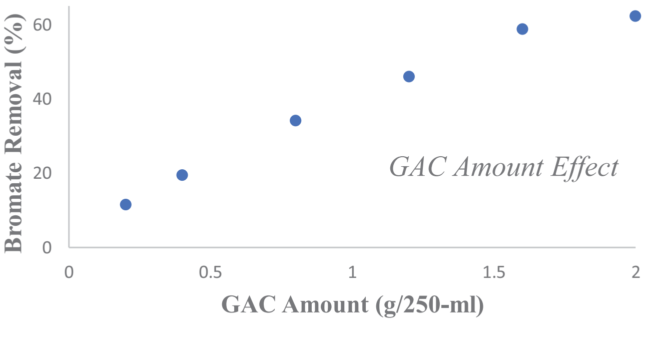

Fig. 3. Effect of GAC amount on bromate removal efficiency (100 mg/L bromate; pH 6; 7 d).

Fig. 5 shows the respective fitting results with correlation coefficient of 0.93. The respective model parameters are also given in Table 1, along with a slightly better correlation coefficient value as compared to the Langmuir isotherm. Also, in this study (as shown in Table 1) adsorption is relatively good because n value is more than 1, that is, 1.674 [26]. Xu et al. [27] using ordered mesoporous carbon also report bromate adsorption experimental data fitting well to the Freundlich adsorption isotherm. In another study, Xu et al. [28] for ordered mesoporous carbon modified with nano-Fe^o report bromate removal fitting to Langmuir model. Cui et al. [5] who investigated bromate removal using chemically modified corncobs also noted the Freundlich model providing a better fit. Furthermore, Zhang et al. [29] who studied bromate treatment employing a specific layered double hydroxide also report the removal results fitting well to the Freundlich isotherm. Also, as shown in Fig. 6, the values of C_e vs. q_e clearly indicate that q_e increases as the C_e is increased, implying that the bromate ions attach in a multilayer format on the GAC surface, which also supports that the Freundlich isotherm model could better describe bromate adsorption onto GAC (as used in the present study). Considering that the Freundlich isotherm represents a multilayer removal-based trend, the present results also indicate that the removal of bromate using activated carbon is a two-step process involving both adsorption [Eq. (8)] and reduction:

$$\underline{\mathbf{GAC}} - \mathrm{OH} + \mathrm{BrO_3^-} + \mathrm{H^+} \leftrightarrow \underline{\mathbf{GAC}} - \mathrm{BrO_3} + \mathrm{H_2O} \tag{8}$$

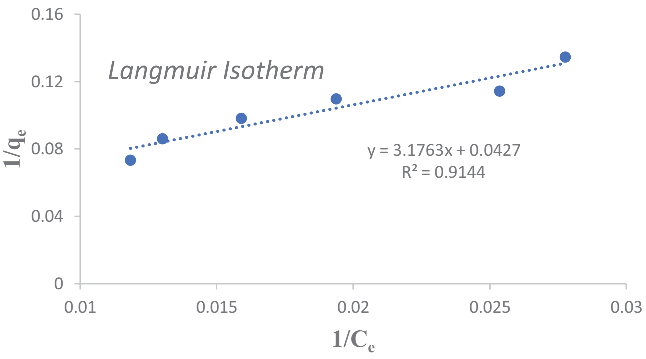

Fig. 4. Adsorption data fitting to Langmuir isotherm for bromate adsorption-based removal by GAC (100 mg/L bromate; pH 6; 7 d).

Table 1
Langmuir and Freundlich isotherm modeling parameters for the adsorption of bromate ion onto granular activated carbon

Langmuir			Freundlich		
q_m (mg/g)	K_L (L/mg)	R^2	k_f (L/g)	n	R^2
23.4	0.013	0.91	0.89	1.67	0.93

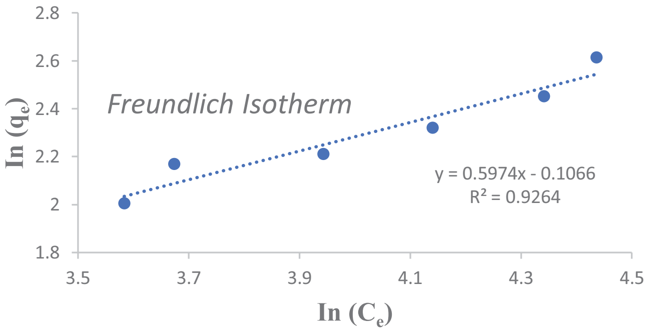

Fig. 5. Adsorption data fitting to Freundlich isotherm for bromate adsorption-based removal by GAC (100 mg/L bromate; pH 6; 7 d).

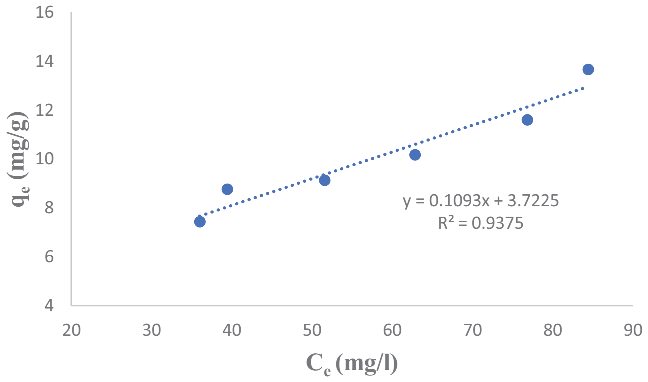

Fig. 6. Adsorption capacity results for bromate adsorption-based removal by GAC (100 mg/L bromate; pH 6; 7 d).

Once adsorbed the bound bromate ion would then reduce to bromide. This would cause more mass transfer of solution bound bromate ion towards the GAC surface (as the surface bound bromate converts to bromide), as also indirectly supported by the multilayer Freundlich-based bromate removal trend. This point is further elaborated under the kinetics discussion.

3.4. Kinetics study

Fig. 7 shows the bromate removal kinetics at varying initial bromate concentrations. The results show that the remaining bromate decreases fast between 5 to 30 min, followed by a gradual decrease between 30 to 120 min. The quick bromate removal in first half hour is possible due to an initial higher attachment on the outer surface sites of GAC. Once those outer surface sites are occupied, bromate removal is more gradual due to slower diffusion of bromate towards the remaining sites within the micro pores. The bromate adsorption kinetic mechanism was further investigated using two kinetic models, that is, the pseudo-first-order and the pseudo-second-order models. The linear pseudo-first-order model is described as follows [30]:

$$\log\left(q_e - q_t\right) = \log\left(q_e\right) - \frac{K_1}{2.303} \times t \tag{9}$$

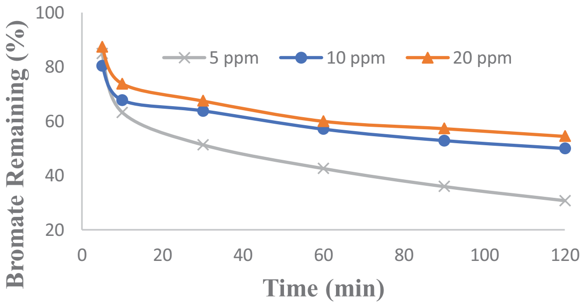

Fig. 7. Kinetics of bromate adsorption on granular activated carbon (GAC 2 g/L; pH 6; bromate 5, 10 and 20 mg/L).

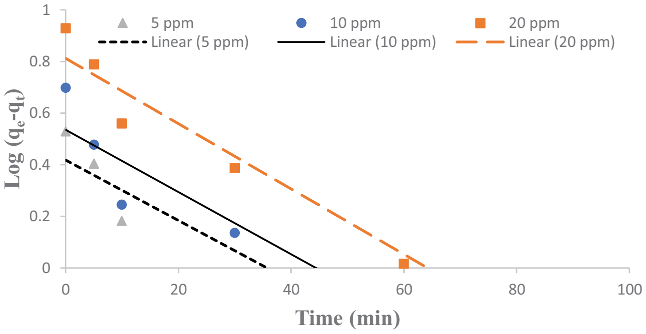

Fig. 8. Pseudo-first-order kinetic modeling outcomes for bromate adsorption.

where q_e (mg/g) is the equilibrium adsorption capacity, q_t (mg/g) is the adsorption capacity at time t (min), and K_1 (min^{-1}) is the pseudo-first-order rate constant. Furthermore, the experimental data was also fitted to the pseudo-second-order kinetic model using the following equation:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} \times t \tag{10}$$

where K_2 (g/(mg·min)) is pseudo-second-order constant rate. Fig. 8 shows the pseudo-first-order kinetic plot for bromate attachment on the granular activated carbon; $\log(q_e - q_t)$ was plotted vs. t (min), and the model parameters K_1 and q_e were calculated from plot and the same are given in Table 2. Also, the pseudo-second-order model fitting is given in Fig. 9 where t/q_t was plotted vs. t (min) and the respective model parameters are given in Table 2. The results reveal that bromate uptake by the GAC is best fitted to the pseudo-second-order kinetic model. This is supported both by the respective correlation coefficient (R^2) value of the pseudo-second-order model (vs. pseudo-first-order model) and also because theoretical q_e (mg/g) values of pseudo-second-order correlate better with those obtained from the experiments (Table 2). Similar was also reported by Qiu and Xiong [7] who studied the use of an activated carbon modified with a cationic surfactant for bromate removal with reaction kinetics following pseudo-second-order trend. Xu et al. [27] using ordered mesoporous carbon also report bromate adsorption kinetics to follow the pseudo-second-order trend. Similarly, Xu et al. [28] using modified ordered mesoporous carbon also

Table 2
Pseudo-first-order and pseudo-second-order kinetic modeling parameters for bromate adsorption onto granular activated carbon

Co (mg/L)	Pseudo-first-order				Pseudo-second-order			
	R^2	K_1 (min^{-1})	q_e (mg/g)	q_e (mg/g) Exp.	R^2	K_2 (g/mg·min)	q_e (mg/g)	q_e (mg/g) Exp.
5	0.98	0.02695	2.61806	3.24	0.99	0.02535	3.42	3.24
10	0.97	0.02777	3.4298	4.941	0.99	0.0289	5.05	4.94
20	0.98	0.02914	6.48784	8.52	0.99	0.014	8.91	8.52

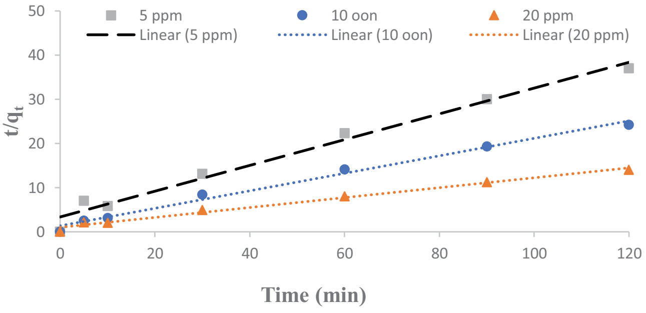

Fig. 9. Pseudo-second-order kinetic modeling outcomes for bromate adsorption.

noted the bromate removal kinetics to be of pseudo-second-order type as also noted by several other investigators for aqueous bromate removal including Cui et al. [5] using chemically modified corncobs, Bhatnagar and Sillanpää [24] using nano-Al_2O_3, Xu et al. [31] employing nano crystalline akageneite coated quartz sand, and Bhatnagar et al. [32] using granular ferric hydroxide. Hence, the pseudo-second-order kinetics can be employed for GAC-based bromate removal. As also mentioned earlier, Siddiqui et al. [19] report the removal of bromate as a two-step process involving both adsorption and reduction ($\underline{\text{GAC}}$-BrO_3 ↔ $\underline{\text{GAC}}$-BrO ↔ $\underline{\text{GAC}}$-Br). In the first place the adsorbed BrO_3^- ion is reduced to BrO^- (hypobromite). This is followed by a further reduction of BrO^- to Br^- (bromide). Konsowa [16] also report a similar mechanism for bromate removal using granular activated carbon. Furthermore, once the surface bromate ion is reduced to bromide, it would cause more mass transfer of solution bound bromate ion towards the GAC surface (as the surface bound bromate converts to bromide), as also indirectly supported by the aforementioned multilayer Freundlich-based bromate removal trend. Furthermore, the above-mentioned pseudo-second-order bromate removal kinetics also indicates a more involved bromate removal process that would include not only the stepwise bromate reduction to bromide, but would also involve mass transfer from the bulk aqueous to bulk GAC surface. In summary, the present results indicate that with a careful adjustment of process conditions, the FILTRASORB 400 GAC can be efficiently used for real life aqueous phase bromate removal applications.

4. Conclusions

Results from the present work show good aqueous phase bromate removal efficiency using a commercial granular activated carbon, that is, FILTRASORB 400. The experimental results indicated that the bromate removal is highly influenced by operational factors such as pH, initial bromate concentration, contact time and the adsorbent dosage. The obtained results were fitted to Langmuir and Freundlich isotherms, and the respective modeling results showed that the bromate removal data fitted well to Freundlich isotherm model indicating a multilayers-based Br-species accumulation onto the GAC surface. It is also suggested that the removal of bromate using activated carbon is a two-step process involving both adsorption and reduction (GAC-BrO_3 ↔ GAC-BrO ↔ GAC-Br). Once the GAC surface bound bromate ion would reduce to bromide, more mass transfer of solution bound bromate ion towards the GAC surface (as the surface bound bromate converts to bromide) would result. This is also indirectly supported by the multilayer Freundlich-based bromate removal trend. Moreover, the kinetics model fitting exercise showed that the pseudo-second-order kinetic model better describes the bromate accumulation onto the GAC surface as compared to pseudo-first-order kinetic model. In summary, the present results for bromate removal show that the FILTRASORB 400 granular activated carbon is very efficient for aqueous bromate treatment, and best bromate removal results can be obtained by optimizing the process parameters as reported in present work.

Acknowledgments

The authors are extremely thankful to the Civil and Environmental Engineering Department at King Fahd University of Petroleum & Minerals (KFUPM) for supporting this work and providing the necessary lab facilities.

Conflicts of interest

The authors declare no conflict of interest.

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