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Bromate removal from water samples using strongly basic anion exchange resin Amberlite IRA-400: kinetics, isotherms and thermodynamic studies

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ABSTRACT

The removal of bromate (BrO_3^-) from aqueous medium by Amberlite IRA-400 anion exchange resin was explored in order to identify the capability of this resin to remove bromate from real water samples. The effects of several physicochemical parameters such as contact time, initial BrO_3^- concentration, initial pH, and temperature were studied. The concentration of BrO_3^- was determined using ultra-performance liquid chromatography–tandem mass spectrometry. The adsorption kinetics and isotherms were well fitted by pseudo-second-order model and Freundlich model, respectively. The adsorption was evaluated thermodynamically and the results showed the endothermic nature of BrO_3^- adsorption as the value of ΔH^o was positive. The negative values of ΔG^o revealed the spontaneity of process. The analytical application of Amberlite IRA-400 for real water sample analysis was studied with very promising results.

Keywords: Water samples; (BrO_3^-); Adsorption; Kinetics; Thermodynamics

1. Introduction

Bromate (BrO_3^-) has been identified in drinking water as a byproduct, originated from the reaction of the ozonation disinfection process [1]. The ozonation disinfection process tends to oxidize bromide (natural constituents of the source water) to BrO_3^- or when chlorinated water is exposed to sunlight [2]. Nevertheless, the ozonation disinfection process has the advantageous of being able to control *Cryptosporidium parvum* zoonotic parasitic protozoan, and its oocysts are refractory to the majority of disinfectant chemicals [3]. Along with BrO_3^-, the environmental protection agency (EPA) has recognized, haloacetic acids, chlorite, and trihalomethanes as substantial disinfection byproducts in drinking water [1]. BrO_3^- is known to be a strong oxidant and is chemically reactive which caused cancer, diarrhea, abdominal pain, nausea, anuria, vomiting, pulmonary edema, hemolytic anemia, and central nervous system depression [4–7]. Based on carcinogenicity, the maximum contaminant level goal for BrO_3^- has set at zero μg L^{-1} level by EPA in drinking water. Nevertheless, the maximum contaminant level has set at 10 μg L^{-1} in drinking water, based on the practical quantification limit [8]. The listing was based on the

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EPA and the World Health Organization has classified BrO_3^- as a Group B2 substance (probable human carcinogen) with adequate information of carcinogenicity in studied animals [9]. Therefore, BrO_3^- removal from the water is an important issue from the last few decades. There are various methods for wastewater treatment including UV irradiation [10], ion exchange [11], reduction and adsorption using granular activated carbon [12,13] and granular ferric hydroxide [14], reduction using zero-valent iron (Fe0), Fe^{3+}, and SO_3 [2,15–17], and filtration by reverse osmosis membrane [18]. All the above methods have their own merits and demerits which have been given in several papers [10–21]. Among all these methods, adsorption and ion exchange are the most effective and attractive techniques due to their low cost, high efficiency, and easy design [22–29].

This paper describes the removal of BrO_3^- using a strongly basic anion exchange resin Amberlite IRA-400 (OH^- form). Numerous operating parameters such as pH, contact time, temperature, and initial BrO_3^- concentration were investigated to find the optimum conditions for the adsorption process. Adsorption, desorption, and regeneration studies of Amberlite IRA-400 resin were studied. The analytical applicability of Amberlite IRA-400 resin was established for the BrO_3^- adsorption from bottled water and municipal water samples. The concentration of BrO_3^- in the water samples was determined by ultra-performance liquid chromatography–tandem mass spectrometry (UPLC–MS/MS) which is a very sensitive, precise, and rapid method [30].

2. Experimental

2.1. Chemicals and materials

Potassium bromate was purchased from BDH chemicals Ltd. (Poole, England) and formic acid was obtained from Panreac (Barcelona, Spain). The standard solutions of potassium bromate of various concentration levels (10–100 μg mL^{-1}) were prepared in Milli-Q water for calibration curves. Amberlite IRA-400 (OH^- form) was purchased from Sigma-Aldrich (USA). Water was purified through a Milli-Q water purification system (Millipore Corporation, Bedford, MA, USA). Other chemicals and reagents were of analytical reagent grade.

2.2. Chromatographic separation

The chromatographic separation of BrO_3^- was conducted using an UPLC technique, equipped with a quaternary pump system (Waters, Milford, MA, USA). The analytical column was used an Acquity BEH C_{18} of dimension 50 × 2.1 mm id and 1.7 μm particle size (Waters, Milford, MA, USA). The best possible separation was accomplished with a mobile phase consisting of 99.9% Milli-Q H_2O with 0.1% of formic acid. The flow rate of mobile phase and sample injection volume was 200 μL min^{-1} and 5 μL, respectively [30].

2.3. Mass spectrometric conditions

The UPLC technique was coupled to a Quattro Premier triple quadrupole mass spectrometer equipped with ESI source. The mass spectrometer instrument was used in negative ionization mode, and data were achieved in MRM form using the deprotonated molecular ion of BrO_3^- as a precursor ion. The ESI source working parameters were as follows: capillary voltage, 3.0 kV; cone voltage, 30 V; desolvation temperature, 350°C; source temperature, 120°C; desolvation gas flow rate, 600 L h^{-1}; and cone gas flow rate, 60 L h^{-1}. Nitrogen (99.99% purity) and high-purity argon (99.99%) were applied as cone and collision gases, respectively. An Oerlikon rotary pump, model SOGEVAC SV40 BI (Paris, France) supplied the primary vacuum to the mass spectrometer. The optimum MS/MS conditions such as dwell times, collision energy voltages, and precursors and products ions related to the selected transitions for BrO_3^- are presented in Table 1. The most abundant product ion was observed to estimate the BrO_3^-, and the second most abundant product ion was observed to confirm the BrO_3^- identification. The data acquisition were achieved by MassLynx V4.1 software (Waters, Milford, MA, USA) [30].

2.4. Batch adsorption studies

Amberlite IRA-400 (OH^- form) was washed with Milli-Q water for five times to remove the stacked impurities from resin surface and dried in oven at 50°C for 2 h. The adsorption of BrO_3^- on Amberlite IRA-400 resin was studied by batch experiments. The adsorption experiments were conducted in 100 mL conical flasks. In a conical flask, 50 mg of Amberlite IRA-400 was loaded with 50 mL BrO_3^- solution of known concentration which was kept in thermostat cum shaking assembly. The solution was shaken continuously at constant temperature for a certain time to get the equilibration time. After equilibration time, Amberlite IRA-400 was filtered off using Whatman filter No. 41. The concentrations of BrO_3^- in the solution phase before and after adsorption were determined by

Table 1
MRM parameters used with the triple quadrupole instrument[a] [30]

		Quantitation		Confirmation	
Analyte	Precursor ion (m/z)	Product ion (m/z)	Collision energy (eV)	Product ion (m/z)	Collision energy (eV)
BrO_3^-	128.85	112.85	22	116	26

[a]Dwell time was 0.1 s.

UPLC–MS/MS. Several parameters such as pH, contact time, initial BrO_3^- concentration, and temperature were altered to optimize the adsorption process.

The amount of adsorbed BrO_3^- at equilibrium, q_e (mg g^{-1}) was computed as follows:

$$q_e = \frac{V(C_o - C_e)}{W} \quad (1)$$

where V is the volume of BrO_3^- solution in litre, C_o, and C_e are the initial and final concentrations (mg L^{-1}) of BrO_3^- in solution, respectively, W is the weight (g) of Amberlite IRA-400.

Kinetics studies were accomplished by varying the bromate concentration (C_o, 500, 700, and 1,000 by μg L^{-1}). Isotherm and thermodynamic studies were evaluated by varying initial concentration of BrO_3^- solution (300–1,000 μg L^{-1}) and temperature (20–55°C).

2.5. Desorption and regeneration studies

For the desorption studies, 50 mL of 500 μg $L^{-1}BrO_3^-$ solution was treated with 50 mg of Amberlte IRA-400 resin in flask at 120 revolution min^{-1} for 1 h. After 1 h, Amberlte IRA-400 resin was filtered off and washed several times with Milli-Q water to remove the excess of bromate. Then, Amberlte IRA-400 resin was treated with 50 mL of 0.01 mol L^{-1} NaOH solution in flask at aforementioned conditions. After 1 h, the solution was filtered and remaining concentration of BrO_3^- in the solution was evaluated by UPLC–MS/MS.

The regeneration studies were also conducted by batch method. Amberlte IRA-400 resin (50 mg) was saturated with 500 μg L^{-1} BrO_3^- solution for 1 h. Subsequently, Amberlte IRA-400 resin was washed several times with Milli-Q water to remove unadsorbed bromate. To regenerate the saturated Amberlite IRA-400 resin, it was treated with 50 mL of 0.01 mol L^{-1} NaOH solution. The same process was repeated for five consecutive cycles.

3. Results and discussion

Amberlite IRA-400, (OH^- form) was used for the removal of BrO_3^- which is a Group B2 substance (probable human carcinogen). The equilibration time for the optimum adsorption of BrO_3^- on Amberlite IRA-400 resin was conducted at different time intervals (5–60 min). It can be seen from Fig. 1(a) that the adsorption was fast at the beginning, and equilibrium was established at 40 min where 84.1% adsorption was found. The different rate of adsorption might be due to the fact that all resin sites were vacant at the starting. So the adsorption of BrO_3^- was high. Later, owing to the decrease in the numbers of adsorption sites as well as BrO_3^- concentration, the BrO_3^- adsorption onto Amberlite IRA-400 became slow [31]. The effect of pH for the adsorption of BrO_3^- using Amberlite IRA-400 resin was studied at pH range 2–7 pH meter (744, Metrohm, Switzerland). The removal of BrO_3^- was increased from 39 to 85% with the increase in pH from 2 to 6.5 (Fig. 1(b)). From the above results, it was concluded that Amberlite IRA-400 resin could be effectively used at the neutral pH and there was no need to adjust the pH. The BrO_3^- adsorption onto Amberlite IRA-400 resin was also studied by varying the BrO_3^- concentration (200–1,000 μg L^{-1}) at pH 6.5 for 40 min. The percentage removal of BrO_3^- was decreased from 89 to 65% as the concentration of BrO_3^- was increased from 200 to 1,000 μg L^{-1}, which was owing to the less availability of adsorption sites at the surface of Amberlite IRA-400 resin for the higher dose of bromate (Fig. 1(c)). The effect of temperature was carried out by varying the temperature from 20 to 55°C at pH 6.5 for 40 min (Fig. 1(d)). It was seen that the adsorption of BrO_3^- was increased from 53.1 to 83.4% with the increase in temperature from 20 to 45°C, which demonstrated the endothermic nature of BrO_3^- adsorption onto Amberlite IRA-400 resin.

3.1. Adsorption kinetics

The pseudo-first-order equation [32] was given as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (2)$$

where k_1 (min^{-1}) is the rate constant for pseudo-first-order, q_e, and q_t are the amounts of BrO_3^- adsorbed at

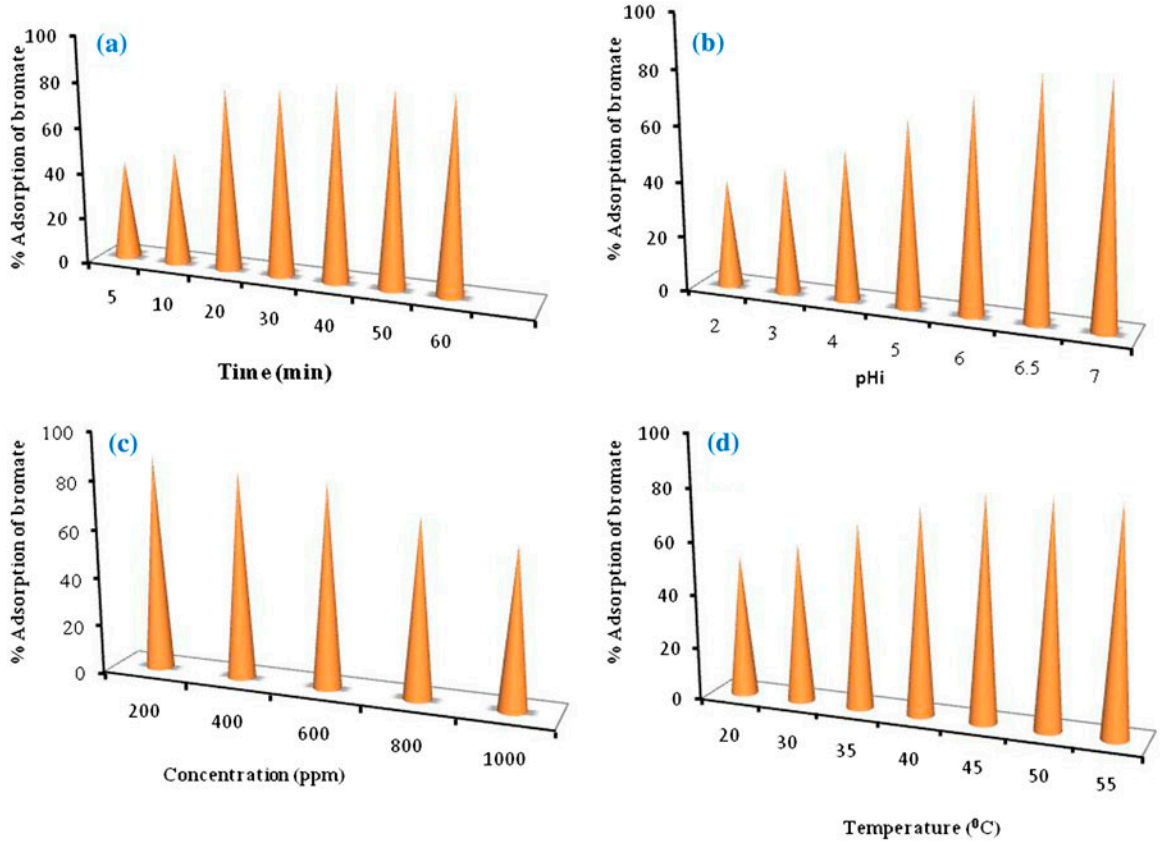

Fig. 1. Percent adsorption of bromate at different (a) time, (b) pH, (c) concentration, and (d) temperature; using Amberlite IRA-400 anion exchange resin.

equilibrium and time t, respectively. The values of k_1 were calculated from the slope of the plot log (qe – qt) vs. t.

The pseudo-second-order kinetic rate equation [33] was given as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

where k_2 is the pseudo-second-order rate constant and its values were determined from the intercepts of the plot t/qt vs. time. The obtained parameters for these two models are shown in Table 2. The values of correlation coefficients (R^2) for pseudo-second-order model were found to be higher than pseudo-first-order model, which showed that pseudo-second-order model was well fitted (Fig. 2(a) and (b)).

3.2. Adsorption isotherms

The Langmuir isotherm [34] model can be expressed as:

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0C_e} \tag{4}$$

where C_e is the equilibrium concentration of BrO_3^-, q_e is the amount of adsorbed BrO_3^-, Q_0 and b are the Langmuir constants and the values of Q_0, and b were obtained from the intercept and slope of linear plots of $1/q_e$ vs. $1/C_e$, respectively (Table 3).

In order to calculate the adsorption effectiveness of the adsorption process, the separation factor (R_L) was determined by using the following equation [35]:

$$R_L = \frac{1}{1 + K_L C_o} \tag{5}$$

where K_L is the Langmuir adsorption constant and C_o is the lowest initial concentration of BrO_3. The value of R_L confirms whether the adsorption is linear ($R_L = 1$), unfavorable ($R_L > 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$). In the present study, the values of R_L were greater than zero and less than unity

Table 2
Kinetic parameters obtained for the adsorption of bromate onto Amberlite IRA-400 anion exchange resin

Initial concentration of bromated ($\mu g\,L^{-1}$)	Pseudo-first-order				Pseudo-second-order			
	Slope	Intercept	k_1 (min^{-1})	R^2	Slope	Intercept	k_2 ($g\,mg^{-1}\,min^{-1}$)	R^2
500	−0.0506	2.59	11.65×10^{-2}	0.918	0.0021	0.0129	3.42×10^{-4}	0.992
700	−0.0508	2.74	11.69×10^{-2}	0.920	0.0016	0.0103	2.49×10^{-4}	0.990
1,000	−0.0508	2.91	11.69×10^{-2}	0.930	0.0011	0.0082	1.48×10^{-4}	0.990

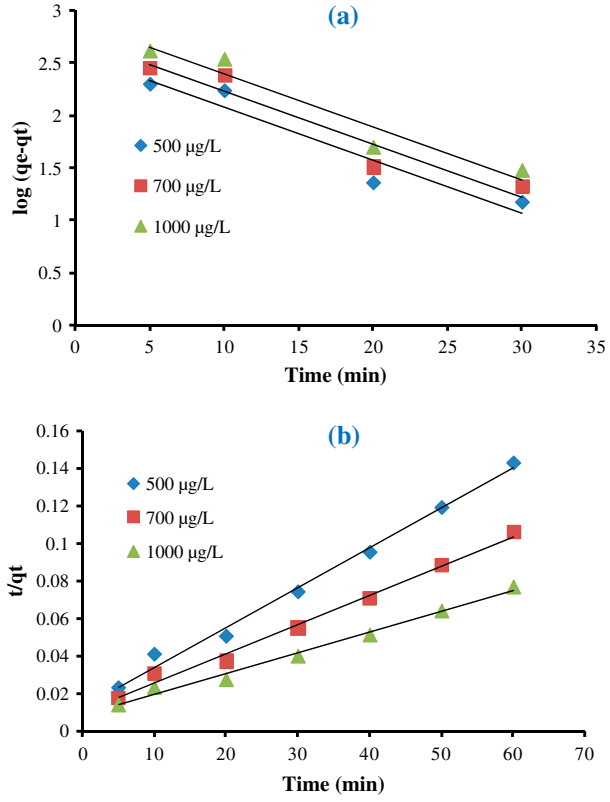

Fig. 2. Plots of kinetic models (a) pseudo-first-order and (b) pseudo-second-order for the adsorption of bromate by Amberlite IRA-400 anion exchange resin.

which designated the favorable adsorption of BrO_3^- onto Amberlite IRA-400 resin.

The Freundlich isotherm is expressed as:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \quad (6)$$

where K_f and n are the Freundlich isotherm constants and their values were obtained from the slope ($1/n$) and intercept (log K_f) the plot of log q_e vs. log C_e, respectively. The value of n is an indication of the feasibility of adsorption. Values of $n > 1$ show favorable nature of adsorption. The value of $n > 1$ for BrO_3^- adsorption onto Amberlite IRA-400 resin indicated the favorable adsorption at different concentrations. The parameters derived by applying these two models (Fig. 3(a) and (b)) are given in Table 3. The Freundlich model showed the better correlation coefficient values ($R^2 > 0.99$), which demonstrated the better applicability of this model.

A comparison of maximum monolayer adsorption capacity of BrO_3^- on various adsorbents [14,21,36,37] was carried out and it was found that the maximum monolayer adsorption capacity of Amberlite IRA-400 resin for BrO_3^- was higher than other adsorbents.

3.3. Thermodynamic studies

The thermodynamic parameters, ΔG^o (standard free energy), ΔH^o (enthalpy change), and ΔS^o (entropy change) were evaluated to determine the feasibility and nature of adsorption process. The values of ΔH^o and ΔS^o were calculated from the slopes and intercepts of the plots of $\ln K_c$ vs. $1/T$ (Fig. 4) by using the following equation.

$$\ln K_c = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (7)$$

Table 3
Adsorption isotherm parameters for bromate adsorption onto Amberlite IRA-400 anion exchange resin

Temperature (°C)	Langmuir constants			Freundlich constants			
	Q_m ($mg\,g^{-1}$)	b ($L\,mg^{-1}$)	R^2	$1/n$	n	K_f	R^2
20	1.99	0.57	0.941	0.653	1.53	1.74	0.999
30	1.88	0.82	0.952	0.672	1.49	1.37	0.997
50	1.49	2.99	0.935	0.673	1.48	1.18	0.998

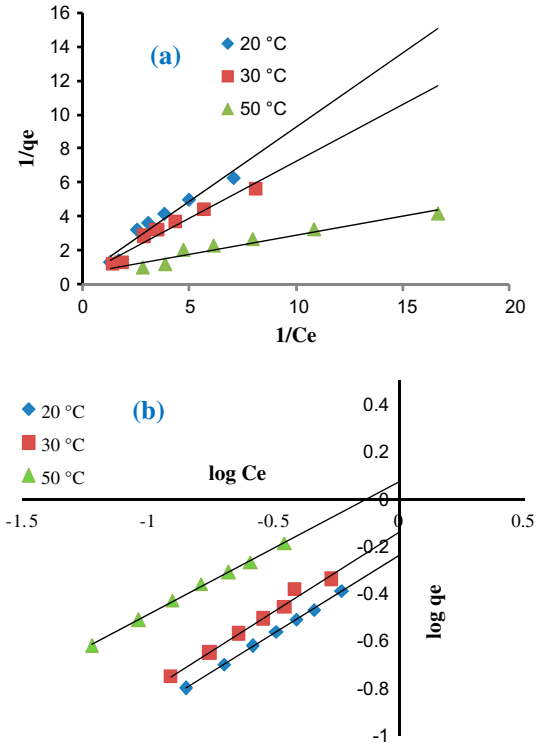

Fig. 3. Plots of isotherm models (a) Langmuir and (b) Freundlich for the adsorption of bromate by Amberlite IRA-400 anion exchange resin.

The ΔG^{o} (free energy change) was calculated from the following relation.

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \quad (8)$$

where R is the gas constant, T (K) is the absolute temperature, and K_c (L mg^{-1}) is the standard thermodynamic equilibrium constant defined by q_e/C_e. The values of ΔG^{o} and ΔH^{o}, ΔS^{o}, for BrO_3^- adsorption onto Amberlite IRA-400 resin are given in Table 4. It is apparent from Table 4 that the values of ΔH^{o} was positive showed the endothermic nature of the adsorption. The positive values of ΔS^{o} reflected an increase in the randomness at the solid/solution

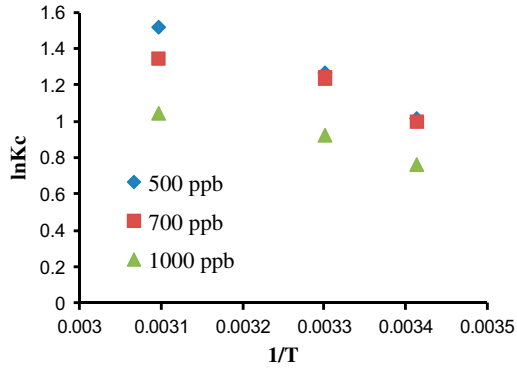

Fig. 4. Van't Hoff plot lnKc vs. $1/T$ for the adsorption of bromate by Amberlite IRA-400.

interface during the adsorption process. The negative values of ΔG^{o} indicated the degree of spontaneity of the adsorption process.

3.4. Desorption of BrO_3^- and regeneration of Amberlite IRA-400 resin

Regeneration is one of the most important factors in the applicability of the adsorbents. In the present study, when the Amberlite IRA-400 resin was saturated by BrO_3^- anions, it was regenerated using 0.1 mol L^{-1} NaOH solution. It is clear from Fig. 5 that the adsorption was reduced from 84 to 62.8% and the recovery was reduced from 79 to 61.2% after five sequential cycles, indicated the excellent adsorption stability of Amberlite IRA-400 resin.

3.5. Analytical applications for real water samples

Municipal water samples were obtained in a clear glass bottles (250 mL) from local district supplied by the national company Saline Water Conversion Corporation, Saudi Arabia. Bottled drinking water (non-carbonated) of different brands was obtained from a local super market in Riyadh, Saudi Arabia. The samples were filtered through 0.20 μm PTFE syringe

Table 4
Thermodynamics parameters for bromate adsorption onto Amberlite IRA-400 anion exchange resin

C_o, μg L^{-1}	ΔH°, J mol^{-1}	ΔS°, J mol^{-1} K^{-1}	ΔG°, J mol^{-1}		
			293 K	303 K	323 K
500	12.77	0.052	−5.86	−1.79	−0.49
700	8.31	0.037	−7.00	−2.93	−1.64
1,000	7.11	0.031	−8.21	−4.13	−2.84

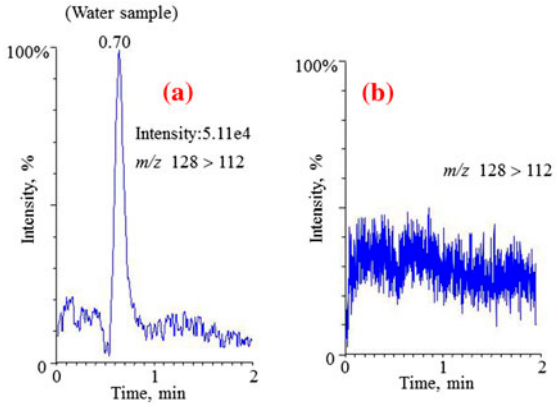

Fig. 5. UPLC–MS chromatograms of bromate in water sample (a) before adsorption and (b) after adsorption.

filter prior to UPLC–MS/MS injection. The BrO_3^- concentration water was labeled (<10 μg L^{-1}) in each bottled by the relevant companies. Each water sample (20 mL) was taken in conical flask and shaken with 0.2 g of Amberlite IRA-400 resin at optimum conditions (pH 6.5, time 40 min and temperature 45˚C) in a thermostated shaker. After equilibration time, the water samples were taken out from the shaker and filtered through 0.22 mm PVDF filter before being injected into UPLC–MS system. It can be seen from Fig. 5 that the BrO_3^- peak was at the retention time of 0.4 min before adsorption which was completely diminished after adsorption.

4. Conclusions

From the above-mentioned experimental results, the following conclusions were found:

(1) Adsorption of BrO_3^- by Amberlite IRA-400 anion exchange resin was fast and the equilibrium established within 40 min.
(2) The maximum monolayer adsorption capacity (Q_m) was 1.9 mg g^{-1} at 20˚C which was higher than other adsorbents studied here.
(3) The adsorption kinetics and isotherms were well fitted by pseudo-second-order model and Freundlich model, respectively.
(4) Amberlite IRA-400 anion exchange resin could be effectively used up to five cycles.

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