Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of Colloid and Interface Science 300 (2006) 437–441
JOURNAL OF Colloid and Interface Science
www.elsevier.com/locate/jcis

Note

Removal of bromide and iodide anions from drinking water by silver-activated carbon aerogels

M. Sánchez-Polo [a,b], J. Rivera-Utrilla [a,*], E. Salhi [b], U. von Gunten [b]

[a] *Departamento de Química Inorgánica, Facultad de Ciencias, Campus Fuentenueva s/n, Universidad de Granada, 18071 Granada, Spain*
[b] *Swiss Federal Institute for Aquatic Research and Technology (EAWAG), Ueberlandstrasse 133, CH-8600 Dübendorf, Switzerland*

Received 16 January 2006; accepted 15 March 2006

Available online 11 May 2006

Abstract

The aim of this study is to analyze the use of Ag-doped activated carbon aerogels for bromide and iodide removal from drinking water and to study how the activation of Ag-doped aerogels affects their behavior. It has been observed that the carbonization treatment and activation process of Ag-doped aerogels increased the surface area value (S_{N_2}), whereas the volume of meso- (V_2) and macropores (V_3) decreased slightly. Chemical characterization of the materials revealed that carbonization and especially activation process considerably increased the surface basicity of the sample. Original sample (A) presented acidic surface properties ($pH_{PZC} = 4.5$) with 21% surface oxygen, whereas the sample that underwent activation showed mainly basic surface chemical properties ($pH_{PZC} = 9.5$) with only 6% of surface oxygen. Carbonization and especially, activation process considerable increased the adsorption capacity of bromide and iodide ions. This would mainly be produced by (i) an increase in the microporosity of the sample, which increases Ag-adsorption sites available to halide anions, and (ii) a rise of the basicity of the sample, which produces an increase in attractive electrostatic interactions between the aerogel surface, positively charged at the working pH ($pH_{solution} < pH_{PZC}$), and the corresponding halide. To test the applicability of these aerogels in water treatment, adsorption of bromide and iodide was studied under dynamic conditions using waters from Lake Zurich. Results obtained showed that the carbonization and activation processes increased the adsorptive capacity of the aerogel sample. However, results showed that the adsorption capacity of the aerogel samples studied was considerably lower in water from Lake Zurich. Results showed $X_{0.02}$ (amount adsorbed to initial breakthrough) values of 0.1 and 4.3 mg/g for chloride anion and dissolved organic carbon (DOC), respectively, during bromide adsorption process in water from Lake Zurich. This indicates that the adsorptive capacity reduction observed may be due to (i) blocking of the porosity, caused by adsorption of dissolved organic matter on the aerogel surface, that would impede the access of bromide and iodide ions to Ag-adsorption sites, and (ii) the competition of chloride anions for the same adsorption sites. Bromide- and iodide-saturated columns were regenerated with NH_3 (0.02 M), observing little change in column characteristics. Moreover, the organic polymer precursors were not dissolved and the concentration of surface Ag-adsorption sites is not significantly changed after two adsorption/regeneration cycles. According to these results, Ag-doped activated carbon aerogels could be a very promising agents to remove bromide and iodide from drinking water.

The presence of bromide anions in water resources generates bromate anions during water treatment with oxidant agents [1]. Bromate anions are highly toxic for humans and, according to the World Health Organization (WHO), 25 μg/L is the maximum concentration permitted in drinking water. The presence of iodide anions in drinking water generates iodomethanes (I-THMs), which have a low taste and odor threshold [2,3]. Various alternatives have recently been proposed to remove these halide anions from drinking water, but none of them have proven sufficiently effective for large-scale application [4]. In a previous study, the efficacy of Ag-doped carbon aerogels in removing chloride, bromide, and iodide anions from surface and mineral waters was analyzed [5]. The results obtained indicated a high adsorption capacity (7.32 μmol halide/g aerogel). Analysis of the halide adsorption isotherms showed a greater adsorption capacity (X_m) as the anion radius decreased and its polarizing power increased [5]. Moreover, an increase in the value of X_m was observed, regardless of the anion considered, with a higher Ag concentration on the aerogel surface. Results

* Corresponding author. Fax: +34 958248526.
E-mail address: jrivera@ugr.es (J. Rivera-Utrilla).

0021-9797/$ – see front matter
doi:10.1016/j.jcis.2006.03.037

obtained also showed that the percentage of Ag adsorption sites available to halides anions was very low, indicating that most of the Ag(I) adsorption sites were not accessible for the halide adsorption process, possibly because of the low surface area of the materials used (500 m^2/g). Therefore, to increase the porosity and surface area of these materials, Ag-doped carbon aerogels have been prepared by carbonization and CO_2 physical activation. The aim of this study was to analyze the use of these new materials for bromide and iodide removal from drinking water and to study how the activation of these aerogels affects their behavior.

In order to carry out this study, Ag-doped carbon aerogels (sample A) first underwent a carbonization process (sample A-C) and then an activation treatment (sample A-A). Preparation of Ag-doped carbon aerogels is reported elsewhere [5]. Resorcinol (R) and formaldehyde (F) were dissolved in water (W) containing silver acetate as catalyst (C). The stoichiometric R/F, R/W, and R/C molar ratios were 1/2, 1/8, and 15, respectively. The mixtures were stirred to obtain homogeneous solutions that were cast into glass molds and cured for a certain period of time [6]. Gel rods were then cut into 5-mm pellets and supercritically dried with carbon dioxide to form the corresponding aerogel (A). The carbon aerogel sample (A-C) was obtained by treating sample A at 1173 K in N_2 flow (100 cm^3/min) for 3 h. Activated aerogel sample (A-A) was obtained by heating sample A-C at 1173 K in CO_2 flow (100 cm^3/min) for 1 h. Samples were texturally and chemically characterized by N_2 adsorption at 77 K, CO_2 adsorption at 273 K, mercury porosimetry, determination of pH at point of zero charge, X-ray diffraction, and X-ray photoemission spectroscopy (XPS) [6]. Bromide and chloride were measured by ion chromatography and conductivity detection. The detection limits as determined for bromide and chloride were 3 and 1 μg/L, respectively [5]. Iodide measurements were made using a selective electrode (Orion 96-53 Combination iodide electrode, detection limit 5×10^{-3} mg/L). The dissolved organic carbon (DOC) was determined using Shimadzu TOC-5000A equipment. The analysis of halides aerogel adsorption capacity was carried out (i) under static conditions, by determining the corresponding adsorption isotherms, and (ii) under dynamic conditions, by studying halides breakthrough curves. Halides breakthrough curves were obtained by passing a solution of bromide or iodide (150 μg/L) through columns containing 3 g of the aerogel with a height of 8 cm and an inner diameter of 1 cm. The flow rate was 1.5 ml/min. Samples of the solution were taken at the column outlet until column saturation was reached. A more detailed description of the methodology used to perform these experiments was previously published [5]. In order to determine the applicability of these materials in natural waters containing natural organic matter (NOM), experiments were also conducted with water from Lake Zurich (Switzerland) ([DOC] = 1.4 mg/L, $[HCO_3^-] = 2.6 \times 10^{-3}$ M, $[Cl^-] = 4$ mg/L). Saturated columns were regenerated by passing a 0.02 M NH_3 solution through the column at a flow rate of 1.5 ml/min for 24 h. Subsequently, and to remove the NH_3 adsorbed onto the aerogel surface, the column was washed by passing Milli-Q water for 24 h at a flow rate of 1.5 ml/min.

Table 1
Textural properties of the aerogel samples studied

Sample	S_{N_2} [a] (m^2/g)	V_{mic} [b] (cm^3/g)	V_2 [c] (cm^3/g)	V_3 [d] (cm^3/g)
A	428	0.073	0.35	0.84
A-C	634	0.150	0.28	0.62
A-A	845	0.248	0.18	0.54

[a] Area determined by applying BET equation to N_2 adsorption at 77 K.
[b] Micropore volume determined applying Dubinin–Raduskevich equation to CO_2 adsorption isotherm.
[c] Volume of pores with diameter of 50 to 6.6 nm determined by using mercury porosimetry.
[d] Volume of pores with diameter above 50 nm determined by using mercury porosimetry.

Table 2
Chemical characterization of Ag-doped carbon aerogels

Sample	pH_{PZC}	Ag(I)$_s$ (%)	N_s (%)	O_s (%)	(–C=O) 532.0 ± 0.2 eV (%)	(–C–O) 533.9 ± 0.2 eV (%)
A	4.5	10	0	21	89	11
A-C	6.8	10	0	14	41	59
A-A	9.5	11	0	6	14	86
A-A-R	9.8	9	4	4	12	88

Table 1 shows the textural properties of the aerogel samples studied. The main characteristics of the samples are their high meso- (V_2) and macroporosity (V_3). Moreover, their pore size distributions showed maxima located at around 32, 36, and 42 nm in diameter for samples A, A-C, and A-A, respectively. It can also be observed that the carbonization and activation treatments increased the surface area value (S_{N_2}) and microporosity volume (V_{mic}), whereas the volumes of meso- (V_2) and macropores (V_3) decreased slightly, which indicates that some of the mesopores and macropores were destroyed during carbonization and activation treatments, developing the microporosity. Results from previous authors agree with those described in Table 1 [6]. Interestingly, the surface area of the activated aerogel sample (A-A) was comparable to that found in commercial activated carbons (Merck) (approximately 1000 m^2/g).

Table 2 presents the surface chemical properties of the different samples studied and those of the sample that underwent two adsorption/regeneration cycles (sample A-A-R). Thus, it can be observed that carbonization and especially activation treatment considerably increased the surface basicity of the sample. The original sample (A) presented acidic surface properties ($pH_{PZC} = 4.5$) with 21% surface oxygen, whereas the sample that underwent activation (A-A) showed mainly basic surface chemical properties ($pH_{PZC} = 9.5$) with only 6% surface oxygen. Moreover, according to results of the O1*s* XPS spectrum deconvolution, sample A-A had a low concentration of oxygenated groups in the form of –C=O groups, confirming the basic character of this sample. Results by previous authors agree with those described in Table 2 [6]. Moreover, none of the X-ray diffraction patterns of the samples showed peaks corresponding to Ag compounds, which could indicate a high dispersion of Ag atoms on the aerogel surface.

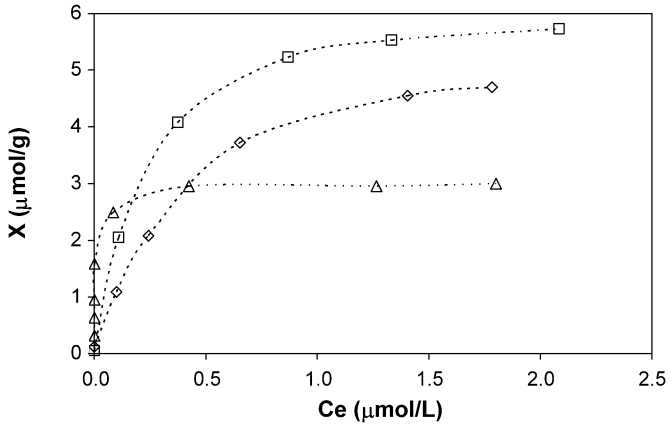

Fig. 1. Adsorption isotherms of the bromide (A) and iodide (B) anions on Ag aerogel samples studied. $T = 25\,^{\circ}\mathrm{C}$, pH = 7. Equilibration time 7 days. (△) A; (◇) A-C; (□) A-A.

Table 3
Results calculated by applying the Langmuir equation to the adsorption isotherms obtained ($T = 25\,^{\circ}\mathrm{C}$, pH 7)

Sample	Halide	X_m (μmol/g)	BX_m (L/g)
A	Br^-	3.01	257
A-C	Br^-	4.68	14.79
A-A	Br^-	5.78	51.54
A	I^-	1.98	156
A-C	I^-	3.71	20.44
A-A	I^-	5.03	38.75

Fig. 1 shows the adsorption isotherms of the bromide and iodide anions for the different samples studied. The results obtained after applying the Langmuir equation to these isotherms are shown in Table 3. It can be seen that the capacity of the aerogels to adsorb halide anions (X_m) was very high (Table 3), higher than that observed in the commercial activated carbons with highest adsorption capacity previously tested ($X_m = 0.25$ μmol/g) [5]. As commented in a previous paper [5], where it was observed that the adsorption capacity of the original aerogel A is proportional to its Ag concentration, the high adsorption capacity of the studied aerogels is due to the presence of Ag(I) on its surface, with the formation of the corresponding halides. The solubility products (K_{SP}) for these compounds range from 5.2×10^{-13} for AgBr to 8.5×10^{-17} for AgI. Consequently, the corresponding halide anions dissolved in water are retained on the aerogel surface as a result of specific Ag(I)–halide interactions [7]:

$$Ag^+ + Br^- \rightarrow AgBr, \quad K_{SP} = 5.2 \times 10^{-13}, \tag{1}$$

$$Ag^+ + I^- \rightarrow AgI, \quad K_{SP} = 8.5 \times 10^{-17}. \tag{2}$$

Results presented in Fig. 1 and Table 3 show that the order of adsorption capacity on Ag-doped carbon aerogel was $Br^- > I^-$. When these results were related to the halides ionic radius (r (Å): $Br^- = 1.95$, $I^- = 2.16$) it was observed that the maximum adsorption capacity (X_m) and the relative affinity (BX_m) increased with a reduction in it. The fact that the adsorption capacity is reduced with an increase in the anion radius may indicate the presence of steric impediments in the chemisorption process of halides onto Ag-doped aerogels. Thus, when the halide radius increases, there is a reduction in the number of accessible adsorption sites, reducing the amount adsorbed.

Results shown in Fig. 1 and Table 3 indicate that the carbonization (sample A-C) and the activation treatments (sample A-A) considerably increased the maximum adsorption capacity for bromide and iodide ions. Thus, the X_m value of sample A-A for bromide and iodide anions was increased by 92 and 154%, respectively, compared to sample A. According to the results in Tables 1 and 2, this would mainly be produced by (i) an increase in the microporosity of the sample, which increases Ag-adsorption sites available to halide anions, and (ii) a rise of the basicity of the sample, which produces an increase in attractive electrostatic interactions between the aerogel surface, positively charged at the working pH ($pH_{solution} < pH_{PZC}$), and the corresponding anion, favoring the attraction of halide anions to Ag(I) adsorption sites. Finally, bromide anions showed the higher adsorption capacity, at any preparation stage (Table 3), because, as discussed in a previous paper, their smaller radius [5] enhances their diffusion toward the interior of the porosity.

From the results presented in Fig. 1 and Table 3, it is interesting to note that the relative affinity (BX_m) of sample A for halide anions is quite high. This fact would confirm that a chemisorption process is taking place between dissolved halide anions and surface silver (Reactions (1) and (2)). In addition, the affinity of the adsorbent for halide anions decreases with the carbonization and activation treatments (Table 3). Thus, the order of BX_m values, regardless of the halide considered, is A > A-A > A-C. These results could indicate that, in addition to the chemisorption process discussed previously, there are other adsorption interactions involved in halides adsorption. Attractive electrostatic interactions between the positively charged carbon surface ($pH_{solution} < pH_{PZC}$) at the working pH (pH 7) and the negatively charged halide anions could be established, favoring the halide adsorption process. This physisorption cooperative effect could explain, in part, the enhancement of the maximum adsorption capacity and the reduction of BX_m values in samples A-C and samples A-A.

The bromide and iodide anion adsorption process was also studied under dynamic conditions using columns filled

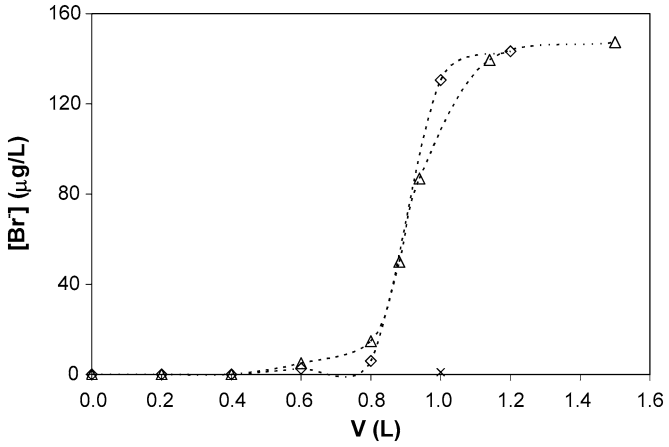

Fig. 2. Breakthrough curve of the column for sample A-A during anion bromide adsorption. $T = 25\,^{\circ}\mathrm{C}$, pH 7, $[\mathrm{Br}^-]_{\mathrm{inlet}} = 150\ \mu\mathrm{g/L}$. (◇) First adsorption/regeneration cycle; (△) second adsorption/regeneration cycle.

Table 4
Column parameters determined from bromide and iodide breakthrough curves

Sample	Halide	Cycles adsorption/ regeneration	$V_{0.02}$ (L)	$X_{0.02}$ (μmol/g)	$X_{0.95}$ (μmol/g)	H_{MTZ} (cm)	ϕ	G_{u} (%)
A	Br^-	1	0.30	0.18	0.30	4.77	0.95	60
A-C	Br^-	1	0.52	0.31	0.44	5.08	0.96	70
A-A	Br^-	1	0.80	0.48	0.52	4.88	0.94	92
A-A-R	Br^-	2	0.74	0.44	0.50	5.46	0.92	80
A	I^-	1	0.32	0.14	0.21	5.11	0.97	66
A-C	I^-	1	0.44	0.19	0.32	5.21	0.92	59
A-A	I^-	1	0.61	0.26	0.42	5.16	0.94	61

Note. $V_{0.02}$: Volume of effluent treated to initial breakthrough. $X_{0.02}$: Amount of halide adsorbed to initial breakthrough. H_{MTZ}: Height of mass transfer zone. $X_{0.95}$: Amount of halide adsorbed at 0.95 breakthrough value. ϕ: Fractional capacity within mass transfer zone, $\phi = \frac{\int_{V_{0.02}}^{V_{0.95}} (C_0 - C)\,dV}{C_0(V_{0.95} - V_{0.02})}$, where C_0 is the halide initial concentration, $V_{0.02}$ and $V_{0.95}$ is the volumes of adsorbate solution treated to the 0.02 and 0.95 breakthrough points, respectively, and C is the halide concentration in the effluent at any time. G_{u}: Utility degree, $(X_{0.02}/X_{0.95}) \times 100$.

with aerogel. Fig. 2 shows, as an example, the breakthrough curves of sample A-A for bromide anion during two adsorption/regeneration cycles. Table 4 shows the column parameters determined from bromide and iodide breakthrough curves. It can be observed that, as in the static regime, the amount of bromide anions adsorbed at the breakthrough point of the column ($X_{0.02}$) was higher than that of iodide anions. Nevertheless, these values were much lower than those observed in the static regime (Table 3). These results indicate that during adsorption under dynamic conditions, the problem of anions diffusion of toward the interior of the microporosity of the material was accentuated; thus, a fraction of Ag adsorption sites accessible to halide anions during adsorption in static regime are not accessible in dynamic regime. Results presented in Table 4 show the low height of the mass transfer zone (H_{MTZ}), regardless of the anion considered, whereas the fractional capacity (ϕ) is almost 1. These results indicate the great efficacy of the columns in the removal of iodide and bromide from water, as shown by their degree of utility of 60–90%. Results obtained after applying the above-described aerogel regeneration process showed its high efficacy (Fig. 2, Table 4). The regeneration of columns is due to the replacement of halide anions by ammonia to form a silver–ammonia complex. Ammonia present on the aerogel surface is removed by washing the column with water:

$$\mathrm{AgBr} + x\mathrm{NH_3} \rightleftarrows \mathrm{Ag(NH_3)_x^+} + \mathrm{Br^-}, \quad x \leqslant 4, \tag{3}$$

$$\mathrm{AgBr} + x\mathrm{NH_3} \rightleftarrows \mathrm{Ag(NH_3)_x^+} + \mathrm{I^-}, \quad x \leqslant 4. \tag{4}$$

Table 5
Column parameters determined from bromide breakthrough curves with Lake Zurich water (Switzerland)

Sample	$V_{0.02}$ (L)	$X_{0.02}$ (μmol/g)	$X_{0.95}$ (μmol/g)	H_{MTZ} (cm)	ϕ	G_{u} (%)
A	0.11	0.07	0.17	7.94	0.92	41
A-C	0.22	0.14	0.28	6.58	0.91	50
A-A	0.33	0.21	0.35	6.21	0.94	63

Table 5 shows the results obtained after the dynamic regime adsorption study was performed using water from Lake Zurich spiked with bromide anions (150 μg/L). Results obtained showed that, as in Table 4, the carbonization and activation treatments increased the adsorptive capacity of the aerogel sample. However, comparison of Tables 4 and 5 results showed that the adsorption capacity of the aerogel samples studied was considerably lower in water from Lake Zurich. In order to determine the causes of this behavior, the concentrations of chloride anions and DOC were measured simultaneously during the bromide adsorption process (Fig. 3). Results showed $X_{0.02}$ values of 0.1 and 4.3 mg/g for chloride anion and DOC, respectively. According to these findings, dissolved organic matter and chloride anions are adsorbed onto the material surface simultaneously with bromide anions. This indicates that the reduction observed in the adsorption of bromide anions from Lake Zurich water may be due to (i) blocking of the porosity, caused by adsorption of dissolved organic matter on the aerogel surface, which would impede the access of bromide and iodide ions to Ag-adsorption sites and (ii) the competition of chloride anions for the same adsorption sites.

From the standpoint of applicability, important aspects of the use of this material for water treatment are the possible leaching of precursors of the carbon polymer and the possible reduction in the Ag concentration on the surface of the aerogel in the different adsorption/regeneration cycles. To elucidate these aspects, the concentration of dissolved organic carbon (DOC) was followed during the different adsorption/regeneration cycles and XPS analyses of the aerogel sample (A-A) were performed for the different adsorption/regeneration cycles. Results obtained showed that the DOC concentration at the column outlet during the bromide adsorption process was zero, whereas the concentration of surface Ag was 11 and 9% for the original sample (sample A-A) and the sample that underwent two adsorption/regeneration cycles (sample A-A-R), respectively (Table 2). This is within the experimental error of the Ag determination. According to these results, the carbon polymer precursors are not dissolved and the concentration of Ag adsorption sites is not significantly changed after two

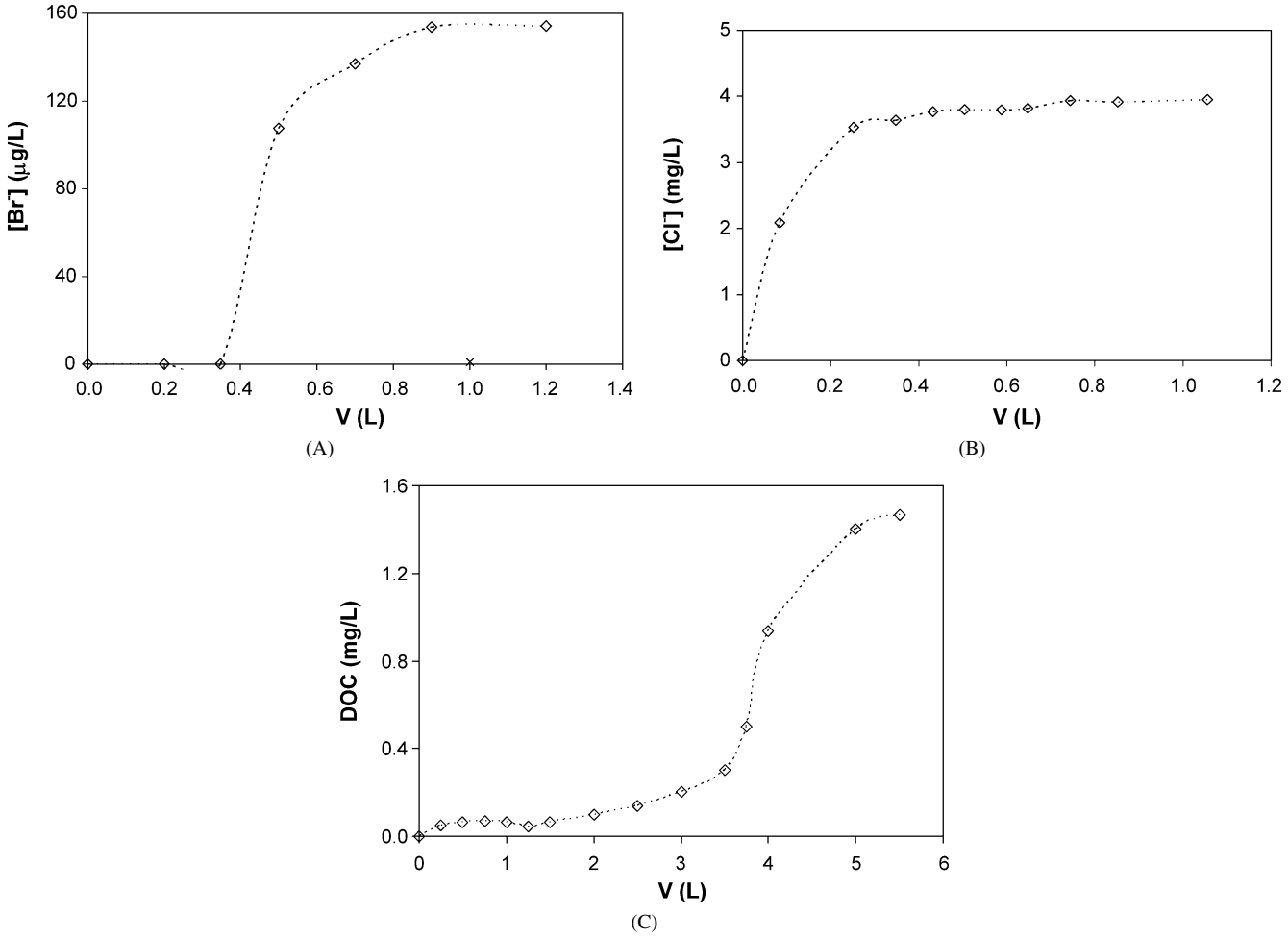

Fig. 3. Breakthrough curves of bromide (A) and chloride (B) anions and dissolved organic carbon (C) on sample A-A with Lake Zurich water. pH 7, $T = 25\,^{\circ}\mathrm{C}$, $[Br^-]_0 = 150$ μg/L, $[Cl^-]_0 = 4$ mg/L, $[DOC]_0 = 1.4$ mg/L.

adsorption/regeneration cycles. However, results presented in Table 2 indicate that NH_3 treatment increased the surface nitrogen content of the sample, thereby increasing its basicity ($pH_{PZC} = 9.8$). As commented above, this will increase the halide adsorptive capacity due to an increase in attractive electrostatic interactions between the surface of the material and the halide ions present in solution.

It can be concluded from these findings that carbonization and activation of the aerogel considerably increased its capacity to adsorb bromide and iodide anions from water because of a larger concentration of Ag-adsorption sites and an increase in the basicity of the carbon surface. According to these results, Ag-doped activated carbon aerogels could be a very promising material to remove bromide and iodide from drinking water. Moreover, (i) presence on the surface of Ag, a highly effective bactericide [8], will stop bacterial mass growth and (ii) the high adsorption capacity of dissolved organic carbon gives this material added value as an adsorbent in water treatment.

Acknowledgments

The authors are grateful for the financial support provided by MCT-DGI and FEDER (Project CTQ2004-07783-C02-01).

References

[1] U. von Gunten, Water Res. 37 (2003) 1469.
[2] J.J. Rock, J. Water Treatment Examination 23 (1974) 234.
[3] Y. Bichel, U. von Gunten, Environ. Sci. Technol. 33 (1999) 4040.
[4] J.S. Hoskins, T. Karanfil, Environ. Sci. Technol. 36 (2002) 784.
[5] M. Sánchez-Polo, J. Rivera-Utrilla, U. von Gunten, L. Salhi, submitted for publication.
[6] C. Moreno-Castilla, F.J. Maldonado-Hódar, Carbon 43 (2005) 455.
[7] R.C. Weast (Ed.), Handbook of Chemistry and Physics, 59th ed., CRC Press, Boca Raton, FL, 1979.
[8] B.R. Kim, J.E. Anderson, S.A. Mueller, W.A. Gaines, A.M. Kendall, Water Res. 36 (2002) 4433.