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Note

Bromide and iodide removal from waters under dynamic conditions by Ag-doped aerogels

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Abstract

The objective of this study was to analyze the efficiency of Ag-doped aerogels in the removal of bromide and iodide from water. 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 and a mineral water. The results obtained by using these waters showed a high breakthrough volume ($V_{0.02} = 0.4$ L) of the columns, while the height of the mass transfer zone ($H_{MTZ} = 6.8$ cm) was low, regardless of the anion under study. Bromide- and iodide-saturated columns were regenerated with NH_4OH. No change in the column characteristics was observed after two regeneration treatments, regardless of the type of water considered.

Keywords: Ag-doped aerogel; Halides; Adsorption; Dynamic conditions

Aerogels [1,2], first developed at the end of the 1980s, have received considerable attention in the literature because of their chemical and textural properties and simple preparation [3,4]. Metal-doped aerogels can be readily prepared by adding a soluble metal salt to the initial resorcinol/formaldehyde mixture [5–7]. After gelation, the metal salt is trapped within the gel structure and the metal ions can be chelated by functional groups of the polymer matrix. These properties make aerogels highly promising materials in water treatment. The presence of bromide (Br^-) and iodide (I^-) in water resources can result in the formation of undesired inorganic and organic bromine- and/or iodine-containing by-products if an oxidative treatment is applied during drinking water production [8,9].

In previous papers [10,11], the analysis of the adsorption isotherms of chloride, bromide, and iodide on Ag-doped aerogels indicated that a chemisorption process takes place:

$$Ag^+ + Cl^- \rightarrow AgCl, \quad K_{sp} = 2.8 \times 10^{-10}, \tag{1}$$

$$Ag^+ + Br^- \rightarrow AgBr, \quad K_{sp} = 5.2 \times 10^{-13}, \tag{2}$$

$$Ag^+ + I^- \rightarrow AgI, \quad K_{sp} = 8.5 \times 10^{-17}. \tag{3}$$

The solubility products (K_{sp}) of these silver halides range from 2.8×10^{-10} for AgCl to 8.5×10^{-17} for AgI. Consequently, the corresponding halides are retained on the aerogel surface by a chemisorption process. Moreover, Ag3$d_{5/2}$–Ag4d XPS spectrum analysis of halide-saturated Ag-doped aerogel confirmed the mechanism proposed due to the presence of maxima at 362.7 ± 0.2, 362.5 ± 0.2, and 362.0 ± 0.2 eV corresponding to AgCl, AgBr, and AgI, respectively. An increase in the adsorption capacity was also observed, regardless of the anion considered, with an increase in the concentration of Ag(I) on the aerogel surface. Moreover, it was detected that the presence of chloride and dissolved organic carbon (DOC) in the water reduces the adsorption capacity of bromide and iodide in the samples studied [10].

According to the results obtained, Ag-doped carbon aerogels could be a very promising material for removing bromide and iodide from waters. However, important issues have to be elucidated regarding the applicability of this material in water treatment, such as like (i) possible leaching of precursors of the carbon aerogels and (ii) the possible reduction in the concentration of surface Ag after several regeneration treatments. Thus,

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the main objective of this work is to test the applicability of Ag-doped aerogels in water treatment studying the adsorption of bromide and iodide under dynamic conditions using waters from Lake Zurich and a mineral water and analyzing the regeneration of the exhausted aerogels in order to reuse them.

All chemicals (resorcinol, formaldehyde, silver acetate, sodium chloride, sodium bromide, and sodium iodide) were reagent grade or analytical grade when available and were used without further purification. All aqueous solutions were prepared in Milli-Q water. Preparation of metal-doped aerogels was reported elsewhere [12]. Briefly, 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 (25 cm length × 0.5 cm internal diameter) and cured at 60 °C for 72 h and 80 °C for 48 h. The gel rods were then cut into 5-mm pellets and supercritically dried with carbon dioxide to form the corresponding aerogel. This sample will be referred to as A-Ag. The aerogel sample was texturally and chemically characterized using N_2 adsorption at 77 K, mercury porosimetry, determination of the pH of the point of zero charge (pH_{PZC}), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). These techniques have been described in detail elsewhere [13]. Table 1 shows the chemical and textural characterization of the aerogel, which is characterized by elevated meso- (V_2) and macroporosity (V_3). The pH_{PZC} value revealed an elevated surface acidity ($pH_{PZC} = 4.5 \pm 0.1$), and XPS analyses showed a high concentration of surface oxygen (O = 21 ± 1%). The XRD results showed a wide dispersion of the metal on the aerogel surface, with no presence of diffraction peaks (results not shown). The XPS analysis of this sample revealed that the silver on the aerogel surface was in oxidation state +I and that the surface percentage was 10 ± 1%.

Adsorption of bromide and iodide anions was studied under dynamic conditions using A-Ag aerogel columns. A solution of bromide or iodide (150 μg/L) was passed through columns containing 3 g of the aerogel with a height of 8 cm and an inner diameter of 1 cm (column volume = 25 cm^3). The flow rate was 1.5 mL/min. According to the column dimensions, the flow of 1.5 mL/min was chosen to simulate the real conditions on a water treatment plant. Samples of the solution were taken at the column outlet until column saturation was reached. The breakthrough curves and characteristics of the columns were determined from these experiments [14,15]. Solutions were prepared in Milli-Q water in the absence of any buffer (pH 7 ± 0.2). To test the real applicability of the aerogel in the elimination of bromide and iodide from waters, adsorption studies under dynamic conditions were performed, following the procedure described above, in water from Lake Zurich (pH 7.8 ± 0.2, [DOC] = 1.4 ± 0.1 mg/L, [Alkalinity] = 2.6 ± 0.1 mM HCO_3^-) and a mineral water (pH 7.2 ± 0.2, [DOC] = 1.3 ± 0.1, [Alkalinity] = 6.6 ± 0.1 mM HCO_3^-). The initial pH of the solution was not modified during the adsorption process. Saturated columns were regenerated by passing a solution of 0.02 M NH_4OH through them for 24 h at a flow rate of 1.5 mL/min. Then, to remove the NH_4OH adsorbed on the aerogel surface, columns were washed by passing Milli-Q water through them for 24 h at a flow rate of 1.5 mL/min. Bromide and chloride were measured by ion chromatography and conductivity detection [16]. The detection limits determined for bromide and chloride were 3 and 1 μg/L, respectively. Iodide measurements were determined using a selective electrode (Orion 96-53 Combination iodide electrode, detection limit 5 μg/L). The dissolved organic carbon (DOC) was determined using a Shimadzu TOC-5000A equipment.

The adsorption of bromide and iodide anions was studied under dynamic conditions using A-Ag aerogel columns. Fig. 1 depicts, as an example, the breakthrough curves for bromide during one regeneration treatment and the evolution of the bromide concentration during the regeneration process described previously.

The values of column characteristics were determined from the breakthrough curves following the method described in previous papers [12,15]; the results obtained are shown in Table 2. The amount adsorbed at the breakthrough point of the column ($X_{0.02}$) was higher for the bromide than for the iodide anion. However, these values were much lower than those determined in the batch experiment (the maximum adsorption capacities (X_m) for chloride, bromide, and iodide were 7.32, 3.01, and 1.98 μmol/g, respectively) [10]. These findings in-

Table 1
Textural and characterization of the Ag-doped aerogel

Sample	S_{N_2} [a] (m^2/g)	V_2 [b] (cm^3/g)	V_3 [c] (cm^3/g)	pH_{PZC}	Ag (%)	O (%)
A-Ag	428 ± 30	0.35 ± 0.05	0.84 ± 0.05	4.5 ± 0.2	10 ± 1	21 ± 1

[a] Surface area determined by applying BET equation to N_2 adsorption isotherms at 77 K.
[b] Volume of pores with diameter of 50 to 6.6 nm determined by mercury porosimetry.
[c] Volume of pores with diameter above 50 nm determined by mercury porosimetry.

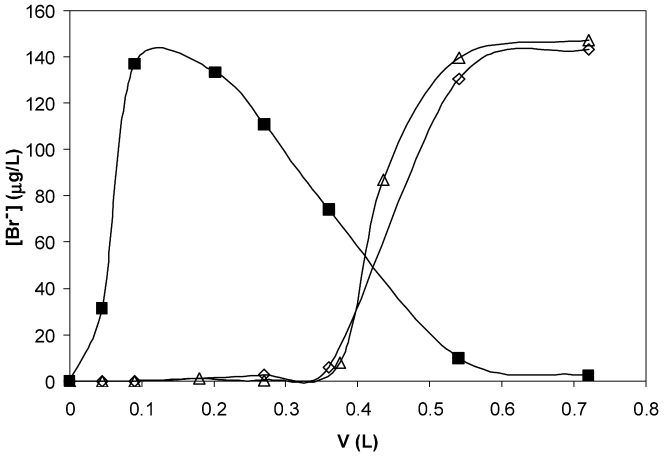

Fig. 1. Breakthrough curves of bromide on A-Ag aerogel. $T = 25$ °C, pH 7, $[Br^-]_{inlet} = 150$ μg/L, flow rate = 1.5 mL/min. (◇) First adsorption process; (△) second adsorption process; (■) regeneration with NH_4OH (0.02 M).

Table 2
Characteristics of the aerogel columns for bromide and iodide adsorption in Milli-Q water

Anion	Regeneration treatments	$V_{0.02}$ (L)	$X_{0.02}$ (μmol/g)	H_{MTZ} (cm)	$X_{0.95}$ (μmol/g)	ϕ	D_u (%)
Br^-	0	0.30	0.18	4.77	0.30	0.95	60
Br^-	1	0.37	0.23	2.94	0.32	0.96	71
Br^-	2	0.35	0.22	3.25	0.34	0.96	65
I^-	0	0.32	0.14	5.11	0.21	0.97	66
I^-	1	0.33	0.15	4.71	0.22	0.97	68
I^-	2	0.30	0.14	6.76	0.21	0.93	66

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 the mass transfer zone: $H_{MTZ} = H[(V_{0.95} - V_{0.02})/(V_{0.02} + (V_{0.09} - V_{0.02})\phi)]$. $X_{0.95}$: Amount of halide adsorbed at the 0.95 breakthrough value. ϕ: Fractional capacity within the mass transfer zone: $\phi = (\int_{V_{0.02}}^{V_{0.90}} (C_i - C)\,dV)/((V_{0.90} - V_{0.02})C_i)$. D_u: Utility degree, $(X_{0.02}/X_{0.95}) \times 100$.

dicate that adsorption under dynamic conditions increases the diffusion problems of anions into the micropores of the material. Consequently, a number of Ag-adsorption sites accessible to the halides in the adsorption process in batch experiments are not accessible under dynamic conditions. Interestingly, the results in Table 2 show that, regardless of the anion considered, the fractional capacity in the mass transfer zone was close to 1. These results indicate the high efficiency of the columns in the removal of iodide and bromide from water, as shown by their utility degree, with values ranging from 60 to 71%.

The results obtained after the aerogel regeneration process described previously indicate its high efficiency (Table 2), with a recovery of about 100% of the adsorptive capacity of the aerogel. In fact, the characteristics of the column remained practically constant after two regeneration treatments, both for bromide and for iodide. The regeneration of the Ag aerogel beds is based on replacement of the halide ions with ammonia to form a silver–ammonia complex (reactions (4) and (5)), which presents a positive charge and, during the halide adsorption, can form the corresponding silver–ammonia complex halide. This means that after one regeneration treatment, the sites are no longer Ag^+ sites, but they definitely turn out to be $Ag(NH_3)_x^+$ sites. Then, the ionic exchange process will play an important role in both bromide and iodide adsorption processes:

$$AgBr + xNH_3 \rightleftarrows Ag(NH_3)_x^+ + Br^-, \quad x \leqslant 4, \tag{4}$$

$$AgI + xNH_3 \rightleftarrows Ag(NH_3)_x^+ + I^-, \quad x \leqslant 4. \tag{5}$$

An important issue regarding the applicability of this material in water treatment is the possible leaching of precursors of the organic polymer and the possible reduction of the concentration of Ag surface atoms after the regeneration treatments. To elucidate these aspects, the concentration of dissolved organic carbon was determined during the adsorption/regeneration processes, and XPS analyses of the aerogel samples were performed after the different regeneration treatments. Results obtained showed that the concentration of dissolved organic carbon at the column outlet was zero, whereas the concentrations of surface Ag was 8 and 10% for the sample subjected to two regeneration treatments and for the original sample, respectively. This is within the experimental error of the Ag determination. According to these results, the organic

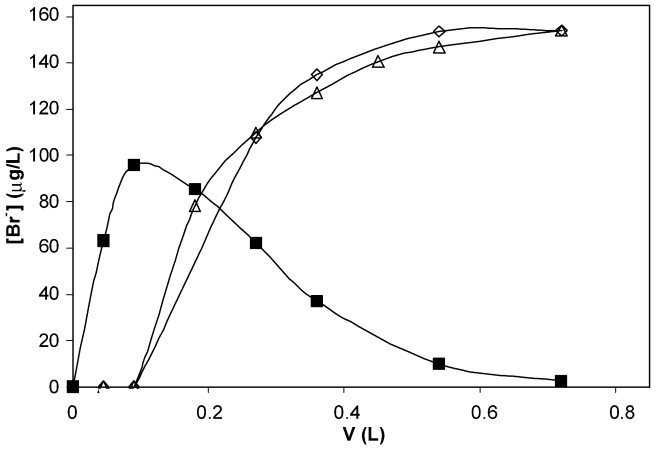

Fig. 2. Breakthrough curves of bromide in Lake Zurich water on A-Ag aerogel. $T = 22\,°C$, pH 7, $[Br^-]_{inlet} = 150$ μg/L, flow rate = 1.5 mL/min. (◇) First adsorption process; (△) second adsorption process; (■) regeneration with NH_4OH (0.02 M, pH 8).

polymer precursors are not released at a high concentration (>0.1 mg/L) and the concentration of surface Ag adsorption sites is not significantly changed after two regeneration treatments.

To determine the applicability of using the Ag-doped aerogel for removal of bromide and iodide from waters, adsorption studies with A-Ag column were performed in water from Lake Zurich, and in a mineral water. Lake Zurich water was spiked with bromide (150 μg/L) and iodide (150 μg/L), whereas the mineral water already contained bromide (20 μg/L) and iodide (40 μg/L).

Fig. 2, as an example, depicts breakthrough curves for column experiments with Lake Zurich water for bromide. Results derived from the breakthrough curves of the different columns are presented in Table 3.

Comparison of the results in Tables 2 and 3 shows that the efficiency of the aerogel in removing bromide and iodide was considerably diminished in both Lake Zurich water and the mineral water, with a more marked reduction of around 80% in the mineral water compared with one of around 60% in Lake Zurich water. The greater reduction in the adsorptive capacity of the columns using the mineral water may be due to both the low concentration of halides and the complex matrix of this water ($[Cl^-] = 10$ mg/L, $[Br^-] = 20$ μg/L, $[I^-] = 40$ μg/L,

Table 3
Characteristics of the column experiments for bromide and iodide adsorption for the different drinking waters

Anion	Water sample	Regeneration treatments	$V_{0.02}$ (L)	$X_{0.02}$ (μmol/g)	H_{MTZ} (cm)	$X_{0.95}$ (μmol/g)	ϕ	G_u (%)
Br^-	Zurich	0	0.11	0.07	7.94	0.17	0.92	41
Br^-	Zurich	1	0.10	0.06	8.89	0.19	0.87	31
Br^-	Mineral	0	0.21	0.02	8.21	0.08	0.96	25
Br^-	Mineral	1	0.32	0.03	6.84	0.09	0.96	33
I^-	Zurich	0	0.14	0.05	7.68	0.09	0.96	56
I^-	Zurich	1	0.11	0.04	8.93	0.10	0.94	40
I^-	Mineral	0	0.41	0.04	6.81	0.07	0.95	57
I^-	Mineral	1	0.32	0.03	6.61	0.08	0.87	38

[DOC] = 1 mg/L), which considerably hampered the adsorption of each halide anion by establishing competitive adsorption among these species. Thus, in order to address this issue, the concentrations of DOC and chloride anions in the mineral water were evaluated during the adsorption experiments. Results obtained showed adsorption at the breakthrough point ($X_{0.02}$) of 2.0 and 0.2 mg/g of DOC and Cl^-, respectively. These findings indicate that the adsorption of at least bromide, iodide, chloride, and organic carbon takes place simultaneously during the treatment of mineral water. Therefore it is noteworthy that the utility degree of these columns to remove Br^- or I^- from natural waters (Table 3) is lower than those for the columns used with Milli-Q water (Table 2). However, the regeneration process applied was effective in real waters, with highly similar values of column characteristics in the experiments performed after two regeneration treatments (Table 3).

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References

[1] R.W. Pekala, J. Mater. Sci. 24 (1989) 3221.
[2] R.W. Pekala, C.T. Alviso, J.D. Lemey, J. Non-Cryst. Solids 125 (1990) 37.
[3] L. Wencui, G. Reichenauer, J. Frick, Carbon 40 (2002) 2955.
[4] H. Rotter, V. Landau, M. Carrera, D. Goldfarb, M. Herskowitz, Appl. Catal. B Environ. 47 (2004) 111.
[5] C. Moreno-Castilla, F.J. Maldonado-Hódar, Carbon 43 (2005) 455.
[6] C. Moreno-Castilla, F.J. Maldonado-Hódar, J. Rivera-Utrilla, E. Rodríguez-Castellón, Appl. Catal. A Gen. 183 (1999) 345.
[7] W. Dingcai, F. Rnowen, S.M. Dresselhaus, G. Dresselhaus, Carbon 44 (2005) 675.
[8] U. von Gunten, Water Res. 37 (2003) 1469.
[9] H. Bürgi, T. Schaffner, J.P. Seiler, Thyroid 11 (2001) 449.
[10] M. Sánchez-Polo, J. Rivera-Utrilla, E. Salhi, U. von Gunten, Water Res. (2006), in press.
[11] M. Sánchez-Polo, J. Rivera-Utrilla, E. Salhi, U. von Gunten, J. Colloid Interface Sci. 300 (2006) 437.
[12] F.J. Maldonado-Hódar, M.A. Ferro-García, J. Rivera-Utrilla, C. Moreno-Castilla, Carbon 37 (1999) 1199.
[13] J. Rivera-Utrilla, M. Sánchez-Polo, Appl. Catal. B Environ. 39 (2002) 319.
[14] J.S. Zogorski, S.D. Faust, in: N.P. Cheremisinoff, F. Ellerbush (Eds.), Carbon Adsorption Handbook, Ann Arbor Science, Ann Arbor, MI, 1974, pp. 753–779.
[15] M.A. Álvarez-Merino, V. López-Ramón, C. Moreno-Castilla, J. Colloid Interface Sci. 288 (2005) 335.
[16] E. Salhi, U. von Gunten, Water Res. 33 (1999) 3239.