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Novel technique to regenerate activated alumina bed saturated by fluoride ions

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Abstract

A novel technique to regenerate adsorbent column is presented. The process used is based on the utilization of an electrochemical cell which regenerates several saturated adsorbent bed. This paper presents the regeneration of the activated alumina (AA) bed saturated by fluoride ions. The results obtained in this study demonstrated that desorption of fluoride from activated alumina is a rapid process. Most of the fluoride content desorbed within 6–15 min. The utilization of the electrochemical cell allows a complete desorption of the fluoride under optimum conditions. The reduction of about 90% of the sodium hydroxide amount was attained by the electrochemical process. A study of adsorption–regeneration cycles showed that the electrochemical technique was more efficient than current techniques. A 95%, recovery of the adsorption capacity was realized with the electroregeneration system. In addition, the volume of water used to regenerate the saturated bed was lower than for current regeneration techniques. The washing did not exceed 6% of the treated water volume. The electrodesorption operation was successfully applied for fluoride desorption from saturated activated alumina column by natural water with strong mineralisation. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Activated alumina; Regeneration; Electrodesorption; Column

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1. Introduction

Adsorbent bed regeneration is an important operation which strongly influences the economical performance of adsorption process. Any innovative technique that can reduce the cost of the regeneration operation will contribute to making column bed adsorption more efficient and more attractive.

Electrosorptive techniques have already been used to treat various contaminated waters [1,2] and/or to deionizate water [3,4]. Most of the previous electrosorption studies have been conducted to determine the adsorption capacity of a variety of ions and of neutral organic compounds on metallic electrode [5–12]. In a previous work, the authors demonstrated that the electrosorptive technique may be introduced to increase the adsorption capacity of the adsorbent [1]. Under some chosen electrical potential however, the adsorbent capacity was lower than that obtained without electrical potential. This result may be used to improve the performance of adsorbent bed regeneration.

The aim of this study is to propose a novel electrodesorption cell and test the ability of this system to ameliorate significantly the performance of the desorption operation. This paper investigates the regeneration of the activated alumina bed saturated by fluoride ions. Several regeneration methods of activated alumina column saturated by fluoride ions have been reported in the literature [13–19]. These techniques denoted that, as a cleaning product caustic soda was more efficient than other products such as alumina sulfate, sulfuric acid and aluminate [13–19]. Since chemical desorption with sodium hydroxide does not provide complete restoration of the original fluoride adsorption capacity of activated alumina, electrodesorption techniques can be used for this purpose.

The effect of an electrical field on the mechanism and performance of the regeneration operation was tested with synthetic fluorinated water and with natural water contaminated by fluoride. Various experimental parameters were

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Nomenclature

AA	activated alumina
BV	volume of bed particles (i.e.bed volume) (m^3)
C_B	sodium hydroxide mass percentage (%)
D	volumetric flow rate ($m^3\,m^{-3}\,h^{-1}$)
E	potential (mV)
m_a	fluoride mass initially adsorbed (mg)
m_d	fluoride mass desorbed (mg)
R	regeneration ratio (%)
SCE	saturated calomel electrode
V_c	cleaning agent volume (m^3)

considered including the sodium hydroxide concentration and the volumetric flow rate.

2. Materials and methods

Acid activated alumina with particle-size of 63–200 μm (purchased from Merck Paris, France), was soaked overnight in distilled water before the beginning of each experiment. Both defluoridation of water by means of activated alumina (AA) columns and electroregeneration of the saturated column was achieved in continuous flow mode. Two in house designed cells were used (Fig. 1). The first cell consists of an electrodesorption cell equipped with two stainless steel electrodes used as working and auxiliary electrodes. These electrodes were introduced in a PVC column to produce an electrical field in the AA bed. A potential was maintained constant by means of a Tacussel PRT20-2X potentiostat. The potential applied during each experiment was measured by means of saturated calomel electrode (SCE), as reference and a working electrode. The comparison between performances of electrodesorption cell and current activated column was achieved by means of a second cell of similar dimensions (diameter of 2 cm and length of 20 cm).

Synthetic sodium fluoride and sodium hydroxide (Prolabo, Paris, France) solutions were prepared with distilled water. Solutions were fed by the top of the column and the filtrate was collected at the bottom by means of a peristaltic pump (Watson Marlow 503U with two channels). The experimental temperature was maintained constant at 25°C during the experiments using an MK70 thermostatic control apparatus.

For the continuous regeneration operation of the AA columns (with and without electrochemical system), the fluoride concentration was determined at regular short intervals. For each experiment the final regeneration ratio (*R*) was calculated. This value was later calculated by comparing the fluoride mass desorbed by the novel technique and the fluoride mass initially adsorbed by the AA bed until its saturation as determined by a graphical integration. The regeneration ratio (*R*) was calculated as follows:

$$\boldsymbol{R} = \frac{m_d}{m_a} \times 100 \qquad (1)$$

where m_d and m_a are the desorbed and initially adsorbed masses respectively.

After regeneration of saturated A.A by fluoride ions with NaOH and before a novel cycle adsorption–desorption was performed, two operations were done. The first operation is to wash the bed with distilled water in duration of 2 min at a volumetric flow rate of 48.5 h^{-1} and to decrease the filtrate pH from 12 to about 7. The second operation is to acidificate the bed with 0.2N sulfuric acid to adjust the pH to the initial pH of virgin AA.

The kinetic curves describing the regeneration of AA bed were drawn by following the evolution of the fluoride ion concentrations of the filtrate at short and regular intervals. Fluoride concentration was determined by an ionometric method with a specific fluoride electrode PF4L from Tacussel (Lyon). To minimize the effect of interfering ions (Al^{3+}, Fe^{3+}, Cu^{2+}, Ca^{2+},...), total ionic strength adjuster buffer (TISAB) (pH = 5.5) was added to the samples. Calcium and magnesium measures were achieved by means of a Unicam-Philips SP19 atomic absorption spectrophotometer. Sodium and potassium concentrations were determined using a Perkin Elmer Coleman 59Ca flame photometer and chloride concentration was obtained by a specific chloride electrode using an ionometric method. Bicarbonate (HCO_3^-) concentration was determined by the volumetric method using hydrochloric acid (HCl N/35) [20].

3. Results and discussion

3.1. Influence of potential on the regeneration ratio (R) of the AA bed

Regeneration of the AA by 1% sodium hydroxide solution coupled to the effect of the potential varying from −1200 to +1200 mV/SCE was achieved with the electrochemical cell (Fig. 2). For each potential, the evolution of the fluoride concentration collected at the bottom of the column was determined. Results (Fig. 1) indicate that desorption is a fast operation independent of the experimental conditions. Most of the desorbable fluoride were desorbed within 6–15 min. Determination of the regeneration ratio (*R*) at each potential (Fig. 3) shows that a greater efficiency of the electrodesorption was achieved at the extreme potentials used in both anodic (+1200 mV/SCE) and cathodic (−1200 mV/SCE) zones. With these potentials, regeneration ratio (*R*) greater than 90% were obtained just after 8 min. Under this period, *R* reached a limiting value indicating that the desorption of fluoride was not complete. As indicated in (Fig. 4) where the *R* value evaluated at the end of the electrodesorption experiments is plotted as a function of the potential, three zones for the electrodesorption of fluoride on the saturated activated alumina exist. In the first zone,

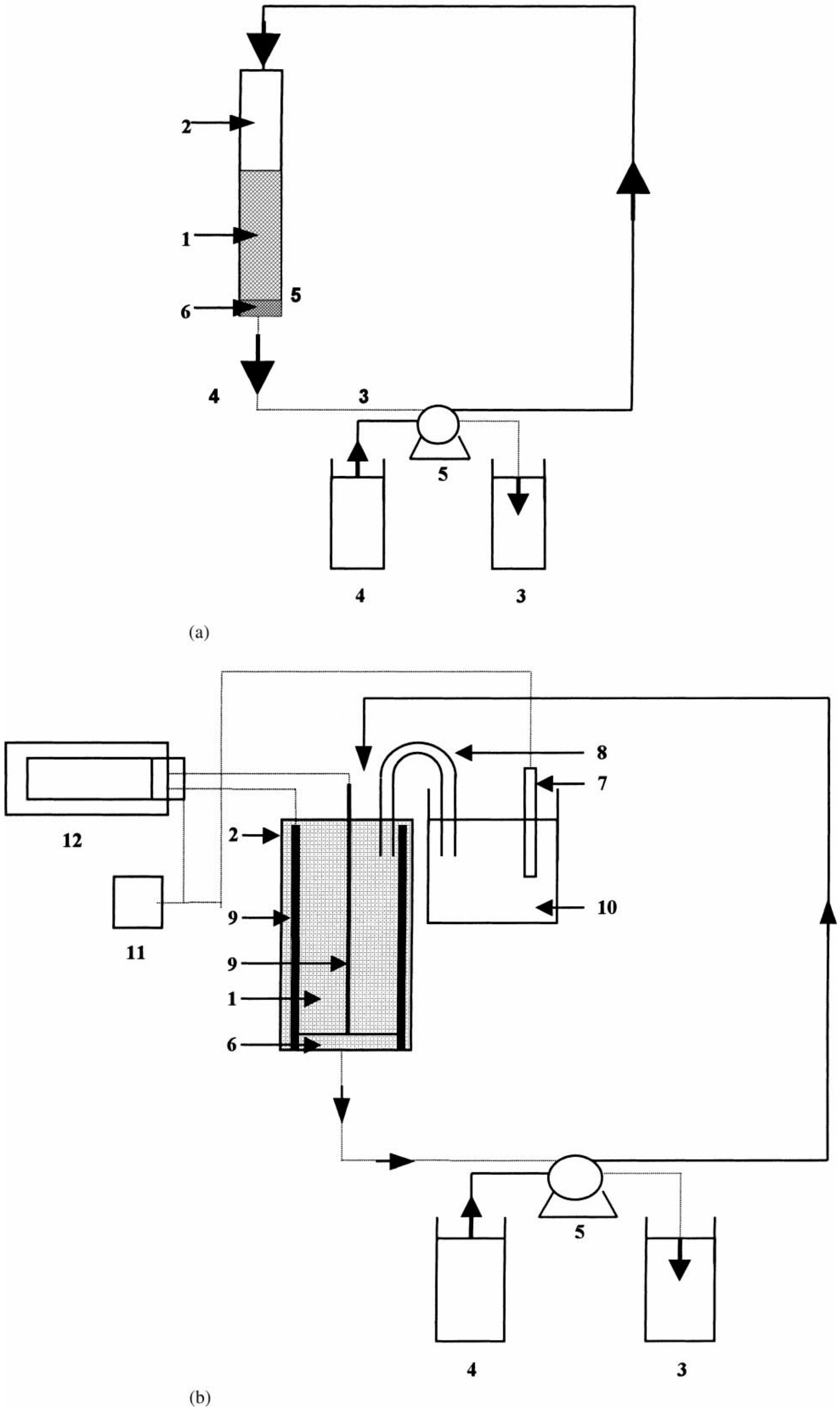

Fig. 1. Schematic experimental systems. (a) current adsorption process; (b) electrodesorption system: (1) activated alumina; (2) column; (3) filtrate tank; (4) feed tank; (5) peristaltic pump; (6) glass wool; (7) reference electrode; (8) bridge; (9) stainless steel electrodes; (10) KCl saturated solution; (11) millivoltmeter; (12) potentiostat.

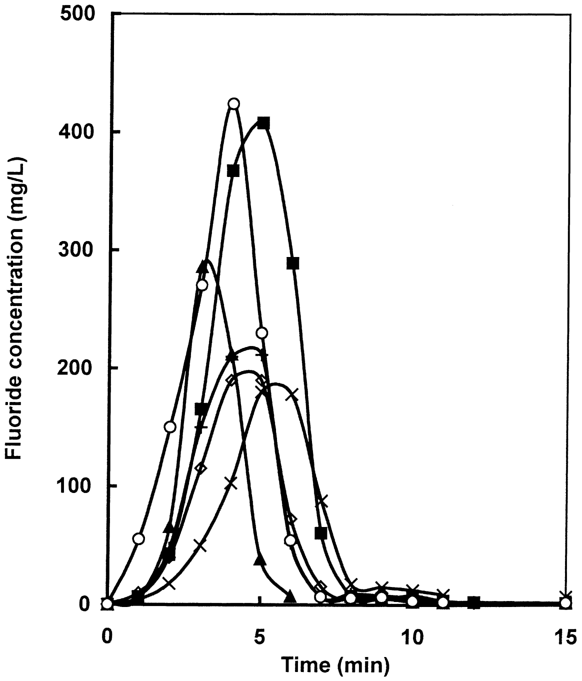

Fig. 2. Evolution of fluoride concentration of the cleaning agent (0.1% NaOH) during the experiments at various potential. $T = 20°\mathrm{C}$; $C_B = 0.1\%$ and $D = 97\,\mathrm{h}^{-1}$: (■) $E = -1200\,\mathrm{mV/SCE}$; (◇) $E = -580\,\mathrm{mV/SCE}$; (▲) $E = 0\,\mathrm{mV/SCE}$; (×) $E = +100\,\mathrm{mV/SCE}$; (+) $E = +580\,\mathrm{mV/SCE}$; (○) $E = +1200\,\mathrm{mV/SCE}$.

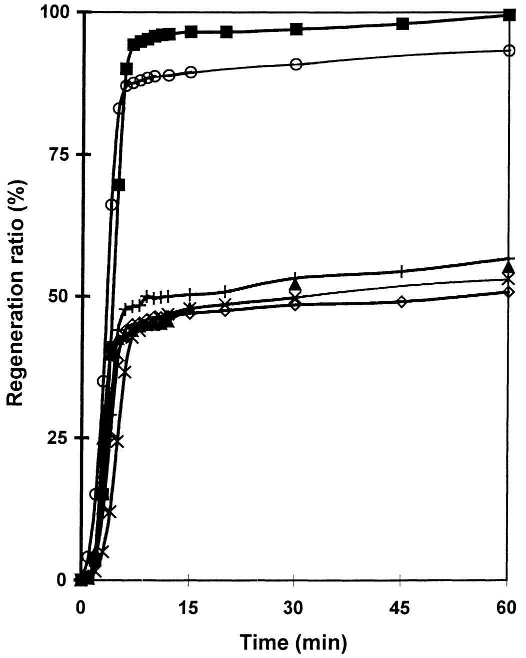

Fig. 3. Influence of the potential on the regeneration ratio (R) during the experiments. $T = 20°\mathrm{C}$; $C_B = 0.1\%$ and $D = 97\,\mathrm{h}^{-1}$: (■) $E = -1200\,\mathrm{mV/SCE}$; (◇) $E = -580\,\mathrm{mV/SCE}$; (▲) $E = 0\,\mathrm{mV/SCE}$; (×) $E = +100\,\mathrm{mV/SCE}$; (+) $E = +580\,\mathrm{mV/SCE}$; (○) $E = +1200\,\mathrm{mV/SCE}$.

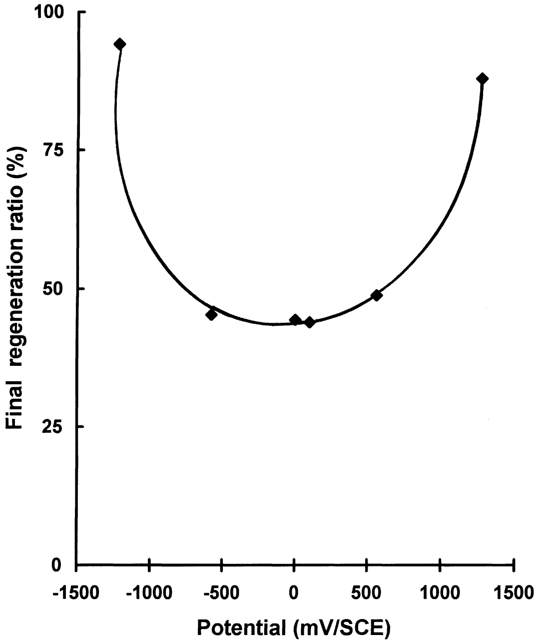

Fig. 4. Regeneration ratio (R) at the end of the experiments at various potentials and with current column. $T = 20°\mathrm{C}$; $C_B = 0.1\%$ and $D = 97\,\mathrm{h}^{-1}$.

with E ranging from -600 to $+600\,\mathrm{mV/SCE}$, the effect of the electrochemical system was practically unable to significantly improve the regeneration of the AA bed. A similar performance was obtained with current regeneration techniques. In this first zone, electrodesorption with sodium hydroxide did not provide complete restoration of the original fluoride adsorption capacity of activated alumina. However, the two outer zones influenced strongly the regeneration efficiency. Greater performances of electrodesorption operation were obtained with the extreme values of cathodic and anodic potentials. At these values, in conformity with Pourbaix diagram [21], water was dissociated into hydrogen and oxygen gases at the potentials of -1200 and $+1200\,\mathrm{mV/SCE}$, respectively.

The electrical field created between the two electrochemical cell metallic electrodes gives greater mobility to hydroxide ions and facilitates the accessibility to active sites located inside the pores. This may explain the improvement of the regeneration of the AA bed by electrochemical cell at the outer zones of both anodic and cathodic regions.

The optimum potential E was found to be the anodic potential $-1200\,\mathrm{mV/SCE}$ which gives practically similar regeneration bed performance at the end of the operation as the cathodic potential $+1200\,\mathrm{mV/SCE}$ but with a lower electrical power.

The pH of the filtrate was increased slightly from pH 7 to a first limiting value of pH 10 reached at the end of the equilibrium reaction [1] between AA bed exchanged hydroxide ions with fluoride anions (Fig. 5) such that

$$\mathrm{AlF} + \mathrm{OH}^- \Leftrightarrow \mathrm{AlOH} + \mathrm{F}^- \tag{2}$$

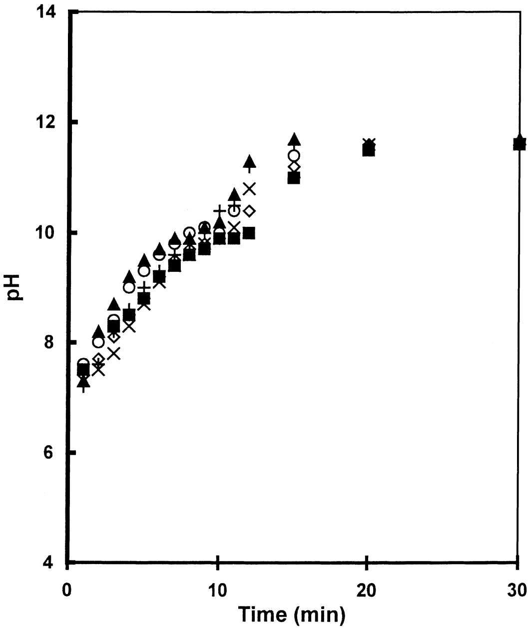

Fig. 5. pH evolution for the outlet cleaning solution during the experiments at various potentials. $T = 20°C$; $C_B = 0.1\%$ and $D = 97\,h^{-1}$: (■) $E = -1200$ mV/SCE; (◇) $E = -580$ mV/SCE; (▲) $E = 0$ mV/SCE; (×) $E = +100$ mV/SCE; (+) $E = +580$ mV/SCE; (○) $E = +1200$ mV/SCE.

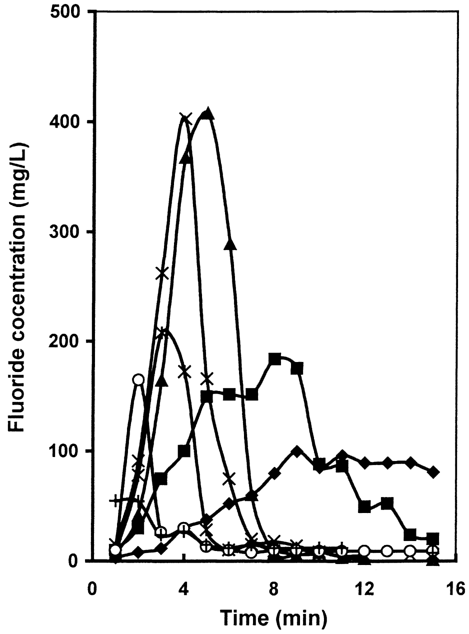

Fig. 6. Evolution of the outlet fluoride concentration at various cleaning agent (NaOH) concentrations during the experiments. $E = -1200$ mV/SCE; $T = 20°C$ and $D = 97\,h^{-1}$: (+) $C_B = 1.0\%$; (○) $C_B = 0.5\%$; (∗) $C_B = 0.2$; (×) $C_B = 0.015\%$; (▲) $C_B = 0.1\%$; (■) $C_B = 0.05\%$; (◆) $C_B = 0.025\%$.

These results confirm that most of the desorbable fluoride are desorbed within 6–15 min. This step was followed by a rapid increase of filtrate pH from 10 to a second limiting value of pH 11 which is practically equal to the initial pH of the feed cleaning solution.

3.2. Influence of NaOH concentration on electrodesorption

The amount of cleaning product necessary to regenerate the adsorption bed capacity is an important parameter in determining the economical performance of the adsorbent column. The determination of the best NaOH concentration was tested between 0.025 and 1% under the optimum potential of −1200 mV/SCE. The filtrate fluoride concentration determined during the experiments (Fig. 6) indicated that the fluoride ions were desorbed more rapidly with an increasing NaOH concentration. The regeneration ratio (R) reached for each NaOH concentration (Fig. 7) indicated that the concentration of 0.1% was most efficient and resulted in a complete desorption of the fluoride. Complete AA column regeneration was achieved during the first 8 min. Regeneration of the saturated AA column without an electrochemical cell (Fig. 8) confirmed that 0.1% NaOH was the optimum concentration. However, in this case the adsorption recovery capacity did not exceed 45%. The optimal NaOH concentration of 0.1% in both cases showed that it is not necessary to use 1% NaOH concentration as reported in the literature [13,14,18,19]. Furthermore, these studies indicated that the regeneration of AA columns did

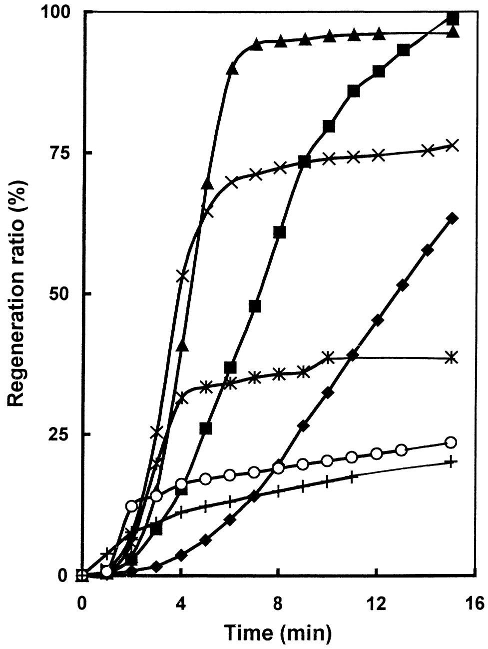

Fig. 7. Influence of the cleaning agent (NaOH) concentration on the regeneration ratio (R) during the experiments. $E = -1200$ mV/SCE; $T = 20°C$ and $D = 97\,h^{-1}$: (+) $C_B = 1.0\%$; (○) $C_B = 0.5\%$; (∗) $C_B = 0.2\%$; (×) $C_B = 0.15\%$; (▲) $C_B = 0.1\%$; (■) $C_B = 0.05\%$; (◆) $C_B = 0.025\%$.

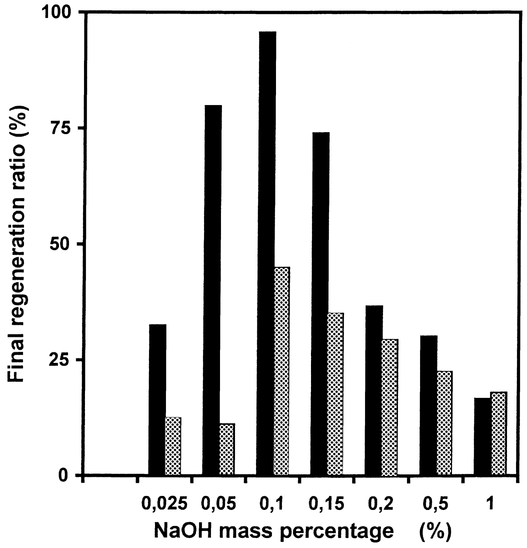

Fig. 8. Regeneration ratio (R) at the end of the experiments at various cleaning agent concentration. $T = 20°\mathrm{C}$ and $D = 97\,\mathrm{h}^{-1}$: (▨) current column and (■) $E = -1200\,\mathrm{mV/SCE}$.

not exceed 71%. It is clear that the electrochemical system used under optimal conditions increases significantly the regeneration operation performance and allows a complete AA bed regeneration with a lower amount of NaOH.

3.3. *Influence of the volumetric flow rate on the regeneration performance*

The main purpose of the study of the influence of the volumetric flow rate on the regeneration performance was to obtain the optimum retention time for ion exchange between fluoride and hydroxide ions. Experiments were performed under optimal conditions, i.e. $E = -1200\,\mathrm{mV/SCE}$ and 0.1% sodium hydroxide with volumetric flow rate ranging from 24.25 to 194 h^{-1}. The filtrate fluoride concentration determined during the experiments (Fig. 9) indicated that most of the fluoride ions were desorbed more rapidly with an increase of the volumetric flow rate. The regeneration ratio (R) obtained during the experiments plotted against the bed volume (BV) (Fig. 10) shows that the volumetric flow rates ranging between 50 and $100\,\mathrm{h}^{-1}$ provides a complete regeneration of the AA bed. The volumetric flow rate of $97\,\mathrm{h}^{-1}$ is considered as optimal since it requires the lowest water volume for the bed regeneration. Indeed, at a volumetric flow rate of $48\,\mathrm{h}^{-1}$, the water volume used for regeneration was twice greater than the water volume of 10–12 BV required under optimal conditions. Outside this volumetric flow rate range, the regeneration performance dropped drastically to a value of 60%. At volumetric flow rates greater than $100\,\mathrm{h}^{-1}$, the relative short retention time required did not allow an efficient ion exchange between fluoride and hydroxide ions. At lower volumetric flow rates, however a less facility for hydroxide ions to access saturated sites of the AA may occur.

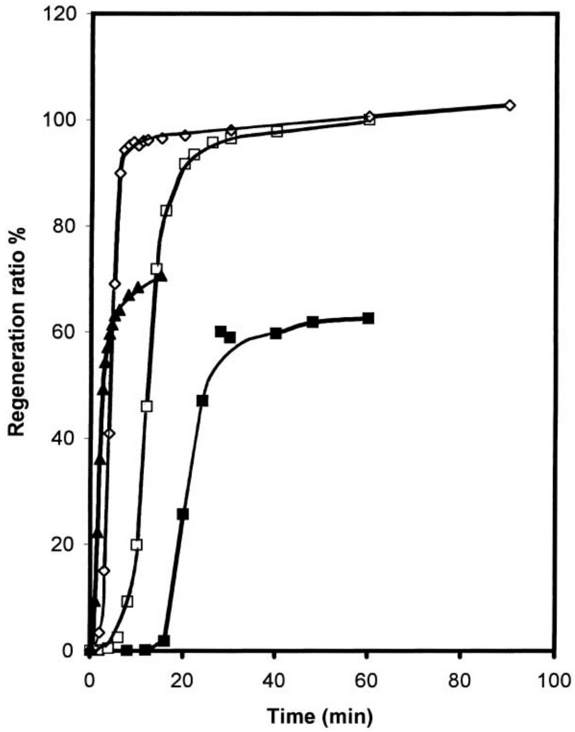

Fig. 9. Influence of the volumetric flow rate on the outlet fluoride concentration. $E = -1200\,\mathrm{mV/SCE}$; $C_B = 0.1\%$ and $T = 20°\mathrm{C}$: (■) $D = 24.25\,\mathrm{h}^{-1}$; (□) $D = 48.5\,\mathrm{h}^{-1}$; (◇) $D = 97\,\mathrm{h}^{-1}$; (▲) $D = 194\,\mathrm{h}^{-1}$.

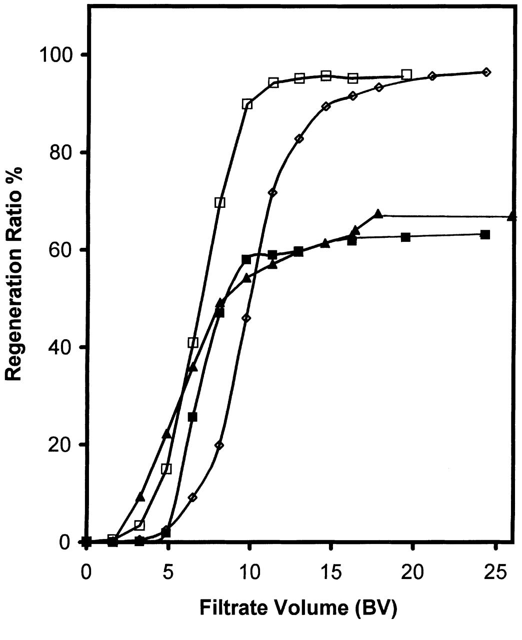

Fig. 10. Regeneration ratio (R) against filtrate volume (BV) at various volumetric flow rates. $E = -1200\,\mathrm{mV/SCE}$; $C_B = 0.1\%$ and $T = 20°C$: (■) $D = 24.25\,\mathrm{h}^{-1}$; (□) $D = 48.5\,\mathrm{h}^{-1}$; (◇) s$D = 97\,\mathrm{h}^{-1}$; (▲) $D = 194\,\mathrm{h}^{-1}$.

The volume of acidified (H_2SO_4) water used to regenerate the saturated bed represented only 8.5 BV, a value lower than that required by current regeneration techniques.

3.4. Study of adsorption–electrodesorption cycles

The activated alumina behavior over a number of adsorption–electrodesorption cycles was studied. The principal purpose of these experiments was to determine the efficiency of the electrodesorption technique by measuring the regeneration ratio (R) of A.A bed during a number of adsorption–electrodesorption cycles. In a first step, three adsorption–electrodesorption cycles were performed with a synthetic NaF (10 mg/l) solution. The experiments were conducted under the following optimal conditions determined previously.

- Potential $E = -1200\,\text{mV/SCE}$.
- Cleaning product (NaOH) used at $C_B = 0.1\%$, $D = 97\,\text{h}^{-1}$ and $V_c = 13\,\text{BV}$.
- Distilled water (1.5 BV) to wash the regenerated bed at $D = 48.5\,\text{h}^{-1}$.
- Acidification of AA by sulfuric acid 0.2N (6.5 BV) at $D = 24.25\,\text{h}^{-1}$.

The volumetric flow rate used during the adsorption experiments was similar as the optimum value ($D = 97.7\,\text{h}^{-1}$) determined during the regeneration study. The results obtained during three cycles of adsorption–electroregeneration are reported in Table 1. Complete regeneration of AA bed was obtained by the electrosorption cell after each of the three cycles of adsorption–electrodesorption without any loss in AA capacity. In addition, little water and chemical products were consumed for the complete regeneration of the AA bed.

The interesting results obtained with synthetic water, prompted to test the efficiency of the electrosorption system for the defluoridation of groundwater. The groundwater of the south–east of the Sahara region (Debila city, Algeria) is naturally contaminated with fluoride ions and was used to conduct four cycles of adsorption–electrodesorption. The characteristics of this natural water, presented in Table 2, show its strong mineralisation mainly due to chloride, sulfate, calcium and sodium ions. The first cycle was performed under the optimal conditions previously determined with the synthetic fluorinated water. Taking into account the characteristics of the Sahara water, the concentration of the NaOH washing solution was doubled during the last three cycles and experimental conditions were modified to improve the efficiency of the regeneration operation. The optimum conditions determined for the Sahara water were as follows.

Table 2
Physico-chemical characteristics of debila water

Parameters	Average value
F^- (mg/l)	3
HCO_3^- (mg/l)	80
SO_4^- (mg/l)	570
Cl^- (mg/l)	1100
Na^+ (mg/l)	450
K^+ (mg/l)	40
Ca^{2+} (mg/l)	245
Mg^{2+} (mg/l)	120
pH	7,8
Conductivity (μS/cm)	4070

- Potential $E = -1200\,\text{mV/SCE}$.
- Cleaning agent product NaOH 0.1% with $D = 110\,\text{h}^{-1}$ and volume used of 30 BV.
- Distilled water(2 BV) to wash the regenerated bed at $D = 60\ \text{h}^{-1}$.
- Acidification of AA by sulfuric acid 0.2N (7.5 BV) at $D = 28.25\,\text{h}^{-1}$.

The results as obtained, presented in Table 3, indicate that the activated alumina had a lower adsorption capacity with the Sahara natural water than with the synthetic water. This result may be attributed to a competition between fluoride and other anions (SO_4^{2-}, HCO_3^- and Cl^-) present in the Sahara water. It is important to note that the AA was regenerated to 95% of its initial adsorption potential after four cycles. The volume of water used to regenerate the saturated bed was lower than that of current regeneration techniques and did not exceed 6% of the volume of treated water. The cleaning agents quantities utilized to regenerate AA bed were also lower than those reported previously [13–19].

Table 1
Results obtained during adsorption–regeneration cycles of synthetic water

Number of cycles	1	2	3
Activated alumina capacity ($g\,F^-/kg\,AA$)	2.02	2	2
Treated water quantity (BV)	242.5	242.5	244.5
Pure NaOH amount consumed (kg/kg AA)	12.4	12.4	12.4
Pure H_2SO_4 amount consumed (kg/kg AA)	60.5	60.5	60.5
Total water volume consumed for the regeneration (BV)	21	21	21
Percentage of water consumed/water treated (%)	8.7	8.7	8.6

Table 3
Results obtained during adsorption–regeneration cycles of groundwater treatment

Cycle number	1	2	3	4
Activated alumina ($g\,F^-/kg\,AA$)	1.76	1.43	1.57	1.68
Volume of treated water (BV)	792	643	704	754
Pure NaOH amount consumed (kg/kg AA)	14.3	28.6	28.6	28.6
Pure H_2SO_4 quantity consumed (kg/kg AA)	70.5	23.8	70.5	70.5
Total water volume consumed for the regeneration (BV)	25	34.5	39.5	39.5
Percentage of water consumed/ water treated (%)	3.2	5.4	5.6	5.2

4. Conclusion

An electrosorption system was successfully used to regenerate a saturated activated alumina column. Complete regeneration was reached after three cycles under optimal experimental conditions when the adsorbent was saturated with synthetic fluorinated water. It was observed that 90% less cleaning agent (NaOH) was used as compared to current regeneration techniques. Activated alumina saturated by a natural fluorinated water that was strongly mineralized was also regenerated by means of the electrosorption system. In this case, four cycles of adsorption-regeneration with the electroregeneration cell provided a greater efficiency in comparison with current techniques. A 95% recovery of the adsorption capacity was realized with the electrosorption system. Furthermore, the volume of water required to regenerate the saturated bed was only 6% of the treated water volume, a much lower value than with current regeneration techniques. This work is presently being pursued in the laboratory with a study on the electroregeneration of a saturated AA column at pilot scale.

References

[1] L. Adour, Improvement of fluoride adsorption capacity of the activated alumina by electrical field, Master Thesis, Ecole Polytechnique Algiers, 1996.

[2] A.A. Djakov, V.Yu. Rostovtsev, T.N. Perekhozheva, E.I. Zlokazova, N.N. Oshkanov, V.G. Morozov, V.A. Makhov, Electrosorptive technique to deactivate poorly mineralized liquid radioactive waste from NPP, in: Proceedings of the ASME/JSME International Conference on Nuclear Engineering, New Orleans 5 (1996) 5–7.

[3] J.C. Farmer, D.V. Fix, G.V. Mack, R.W. Pekala, J.F. Poco, Capacitive deionization of NH_4ClO_4 solutions with carbon aerogel electrodes, J. Appl. Electrochem. 26 (10) (1996) 1007–1018.

[4] J.C. Farmer, D.V. Fix, G.V. Mack, R.W. Pekala, J.F. Poco, Capacitive deionization with carbon aerogel: carbonate, sulfate and phosphate, Int. SAMPE Tech. Conf. 27 (1995) 294–304.

[5] H.A. Gasteiger, N.M. Markovic, P.N. Ross, Bromide adsorption on Pt(111): adsorption isotherm and electrosorption valency deduced from RRD Pt(111) E measurements, Langmuir 12 (6) (1996) 1414–1418.

[6] N.M. Markovic, C.A. Lucas, H.A. Gasteiger, P.N. Ross, Bromide adsorption on Pt(100): rotating ring-Pt(100) disk electrode and surface X-ray scattering measurements, Surface Sci. 365 (2) (1996) 229–240.

[7] A.G. Anastopoulos, Electrosorption of neutral organic compounds from solvents of high dielectric constant. Triphenylphosphine oxide as a probe molecule, Electochim. Acta 41 (16) (1996) 2537–2544.

[8] J. Clavillier, J.M. Orts, R. Gomez, J.M. Feliu, A. Aldaz, Comparison of electrosorption at activated polycrystalline and Pt(531) kinked platinum electrodes: surface voltammetry and charge displacement on potentiostatic CO adsorption, J. Electroanal. Chem. 404 (2) (1996) 281–289.

[9] S. Zichao, J. Lipkowski, Chloride adsorption at the Au(111) electrode surface, J. Electroanal. Chem. 403 (1-2) (1996) 225–239.

[10] P.A. Rikvold, M. Gamboa-Aldeco, J. Zhang, M. Han, Q. Wang, H.L. Richards, A. Wieckowski, Computational lattice–gas modeling of the electrosorption of small molecules and ions, Surface Sci. 335 (1-3) (1995) 389–400.

[11] J.M. Orts, R. Gomez, J.M. Feliu, A. Aldaz, J. Clavillier, Potentiostatic charge displacement by exchanging adsorbed species on Pt(111) electrodes–acidic electrolytes with specific anion adsorption, Electrochim. Acta 39 (11-12) (1994) 1519–1524.

[12] D. Yang, J. Lipkowski, Adsorption of isoquinoline at the Au(111)-solution interface, Langmuir 10 (8) (1994) 2647–2653.

[13] E.A. Savinelli, A.P. et Black, Defluoridation of water with activated alumina, J. AWWA 50 (30) (1958) 33–44.

[14] P. Mazounie, P. et Mouchet, Procédés d'élimination du fluor dans les eaux alimentaires, Rev. Fr. Sci. Eau 3 (1984) 29–51.

[15] A. Diéye, C. Mar, M. Rumeau, Les procédés de défluoruration des eaux de boisson, Trib. Eau 47 (568) (1984) 27–34.

[16] J.P. Barbier, P. Mazounie, Methods of reducing high fluoride content in drinking water. Fluoride removal methods—filtration through activated alumina: a recommended technique, Water Supply 2 (1984) 3–4.

[17] J.P. Sibony, Perspectives pour l'application de l'alumine activée en traitement d'eau potable, TSM. Eau 3 (1983) 109–114.

[18] P. Belle, C. et Jersalé, Elimination des fluorures par adsorption échange d'ions sur alumine activée, TSM. Eau 2 (1984) 87–93.

[19] J.C. Dernancourt, La défluoruration des eaux potables, TSM. Eau 3 (1980) 135–139.

[20] J. Rodier, L'analyse de l'eau, 7th Edition, Dunod, Paris 1984.

[21] M. Pourbaix, Atlas d'équilibre électrochimiques à 25°C, Ed. Gauthiers-Villars, Paris 1963.