

Fluoride removal with electro-activated alumina

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Abstract

A new activation technique using alumina was developed for the removal of fluoride from water. This technique is based on an electro-activation by means of an electrical field. The optimum activation parameters (potential and contact time) were determined, and an activation time of about 120 min and a potential of +100 mV/SCE were then selected. The effect of various experimental parameters — ionic strength, pH hardness, and fluoride-alumina concentration ratio (C_{F_0}/C_A) — was determined for the adsorption capacities of the electro-activated alumina. The effect of these parameters on the fluoride adsorption capacities of both electro-activated adsorbent and conventional alumina was essentially the same, except for the ionic strength parameter. Indeed, ionic strength did not have a considerable effect on the performance of the conventional alumina. However, for the electro-activated alumina, an increase in ionic strength induced a slight increase in the fluoride adsorption capacity of the electro-activated adsorbent. The optimum conditions, determined in the batch mode, gave an optimal pH ranging from 3.5 to 5 and a C_{F_0}/C_A ratio of about 4. At a NaCl concentration of 800 mg dm⁻³, the fluoride adsorption capacity of the electro-activated alumina was about 55% better than that of conventional alumina.

Keywords: Adsorbent activation; Electrochemical technique; Fluorine; Alumina

1. Introduction

Electrosorptive techniques have been used to treat various contaminated waters [1–4] and/or to deionize water [5,6]. In a previous work, the authors demonstrated that the electrosorptive technique may be introduced to increase the

adsorption capacity of a bed adsorbent. Under the 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 [3].

The aim of this study is to propose a new activation technique for alumina based on application of an electric field, which ameliorates

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significantly the performance of this adsorbent. In this study we investigate the effectiveness of electro-activated alumina for removing fluoride from water and determine the optimum conditions in the batch mode.

2. Materials and methods

Acid activated alumina (AA) with a particle size of 63–200 μm (purchased from Merck-Paris, France) was soaked overnight in distilled water before the beginning of each experiment. The main characteristics of the activated alumina used as an adsorbent are presented in Table 1.

2.1. Electro-activation apparatus

The electro-activation experiments were realized with an electrochemical cell designed in our laboratory (Fig. 1). This apparatus was equipped with two stainless-steel electrodes utilized as working and auxiliary electrodes. They were introduced into a PVC column (2 cm in diameter and 20 cm long) to produce an electrical field in the AA bed. Previously, the column was filled with a wet AA, and a conductive solution was added until contact with the salt bridge was assured. An electrochemical potential was then maintained constant during a chosen activation time by means of a Tacussel PRT20-2X potentiostat. The electrochemical potential applied was measured by means of saturated calomel electrode (SCE), as reference and working electrodes. The electro-activated alumina was then tested in batch mode and its performance was compared to conventional AA.

2.2. Fluoride kinetic adsorption

The second step consisted in quantifying the adsorption capacity of the adsorbent with and without electrochemical activation. Comparison between electro-activated alumina and conventional AA was achieved by determining their

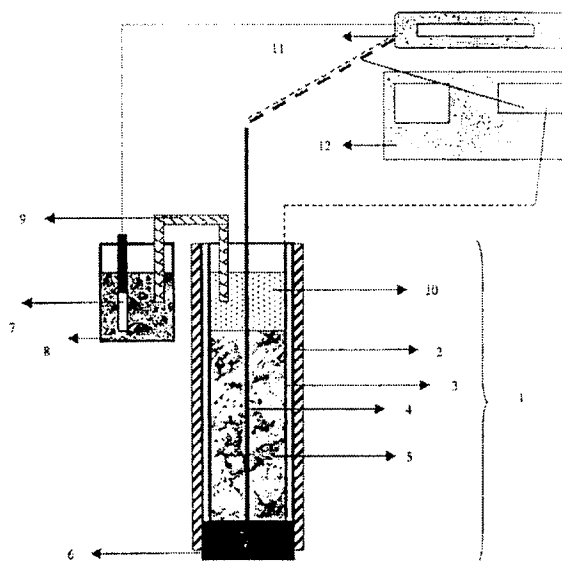


Fig. 1. Electrochemical apparatus utilised for alumina activation. 1 electro-activation cell, 2 PVC column, 3 auxiliary electrode, 4 working electrode, 5 adsorbent: activated alumina, 6 glass wool, 7 reference electrode, 8 KCl 3M, 9 bridge salt, 10 conductive solution, 11 Milivoltmeter, 12 potentiostat.

Table 1
Physico-chemical characteristics of activated alumina

Parameter	Value
Moisture, %	0
Density, g cm^{-3}	3.13
Total porosity, %	66
Activation type	Acid
Specific surface, $\text{m}^2 \text{g}^{-1}$	250

fluoride kinetic adsorption under various experimental parameters: ionic strength, pH, hardness and fluoride–alumina concentration ratio ($C_{\text{F}_0}/C_{\text{A}}$) ratio. The apparatus utilised for this purpose consisted of a five-position electromagnetic stirrer equipped with a speed controller which was adjusted to 350 rpm.

The experiments were carried out in a batch mode. A known amount (4 g) of dry adsorbent

was added to a synthetic fluoride solution (volume 0.5 dm^3) until an adsorption equilibrium was reached.

Synthetic sodium fluoride (Prolabo, Paris, France) solutions were prepared with distilled water. During experimentation, in most cases the initial fluoride concentration (C_i) and adsorbent concentration (C_A) were fixed at 10 mg dm^{-3} and 8 g dm^{-3} , respectively. The equilibrium and kinetic curves were drawn by following the evolution of residual fluoride concentration at regular short intervals. The adsorption capacity of the adsorbent (X) was calculated by the following equation, using the residual concentration reached at the equilibrium state (C_e), the initial fluoride concentration and the adsorbent concentration in the reactor.

$$X = (C_i - C_e) / C_A \quad (1)$$

Fluoride concentration was determined by an ionometric method with the PF4L specific fluoride electrode from Tacussel (Lyon, France). To minimize the effect of interfering ions (Al^{3+} , Fe^{3+} , Cu^{2+} , Ca^{2+} , ...), a total ionic strength adjuster buffer (TISAB) (pH = 5.5) was added to the samples.

3. Results and discussion

3.1. Electro-activation

In the first step, the ability of the AA to remove fluoride ions from water was tested with various potentials ranging from +200 to -100 mV/SCE during a fixed activation time of about 60 min. The effect of the potential on the performance of the adsorbent was determined by following the kinetics of the water defluoridation at pH 7 (Fig. 2a). The results indicate that the limiting values of fluoride concentration were reached after 120 min. A contact time of 2 h was thus selected as the equilibrium time for all the following experiments, the residual concentration being constant until 360 min.

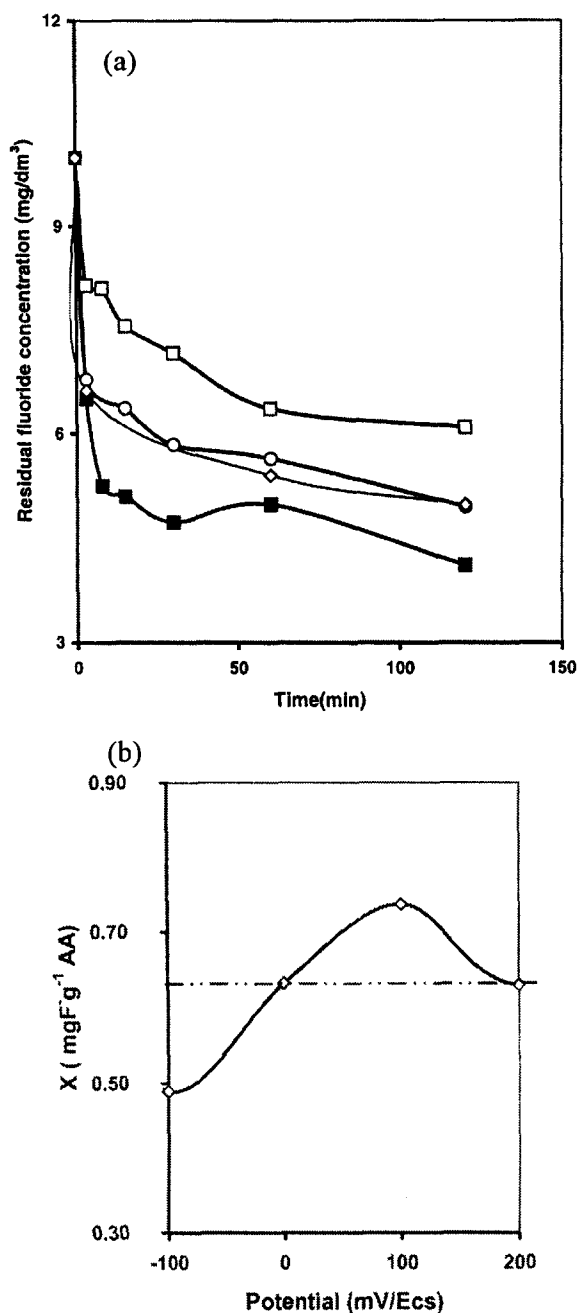


Fig. 2. Effect of the potential on adsorption kinetics and adsorbent capacity. pH = 7, $C_F^- = 10 \text{ mg dm}^{-3}$, $C_A = 8 \text{ g dm}^{-3}$, $T = 25^\circ\text{C}$ and $T_a = 60 \text{ min}$. (a) Kinetic curves at various potentials (\square) $E = -100 \text{ mV/SCE}$, (\circ) $E = 0$ corresponds to conventional AA, (\blacksquare) $E = +100 \text{ mV/SCE}$, (\diamond) $E = +200 \text{ mV/SCE}$. (b) Fluoride adsorption capacity (X) against the activation potential.

These curves made it possible to identify the potential $E = +100$ mV/SCE as an optimum potential which gave the lowest value of residual fluoride concentration. The zero potential represents the conventional A.A, i.e., without electrochemical activation; this makes it easy to compare performance of the electro-activated adsorbent and conventional adsorbent. Calculation of the fluoride adsorption capacity of the adsorbent for various potentials, presented in Fig. 2b, confirms that electrochemical activation may be used to improve adsorbent performance at potentials of about $E = +100$ mV/SCE. Indeed, an increase in the fluoride adsorption capacity of about 20% was obtained by activation at the potential of $E = +100$ mV/SCE. These results are in agreement with those obtained previously in continuous mode using an electrosorption column. In this last case the optimum potential was assumed, by analogy to electrocapillary curves [3], to be the potential of zero charge (PZC) of the fluoride-AA system. On the other hand, the performance of the electro-activated adsorbent at the potential $E = -100$ mV/SCE was less than that of conventional alumina. The decrease in the adsorption capacity as the activation potential decreases from 100 to -100 mV/SCE may be explained by the charge state of the adsorbent.

The effect of the activation time (or contact time in electro-activation) of the adsorbent during electro-activation on the performance of the electro-activated alumina was tested. The kinetic curves obtained by following the variation of the residual fluoride concentration for various activation times indicate that the concentrations were essentially similar with contact times longer than 40 min (Fig. 3a). The fluoride capacity of the electro-activated adsorbent obtained at various activation times, presented in Fig. 3b, confirmed that a limiting value of the adsorption capacity of the adsorbent was reached after 40 min. This activation time was thus selected for all the

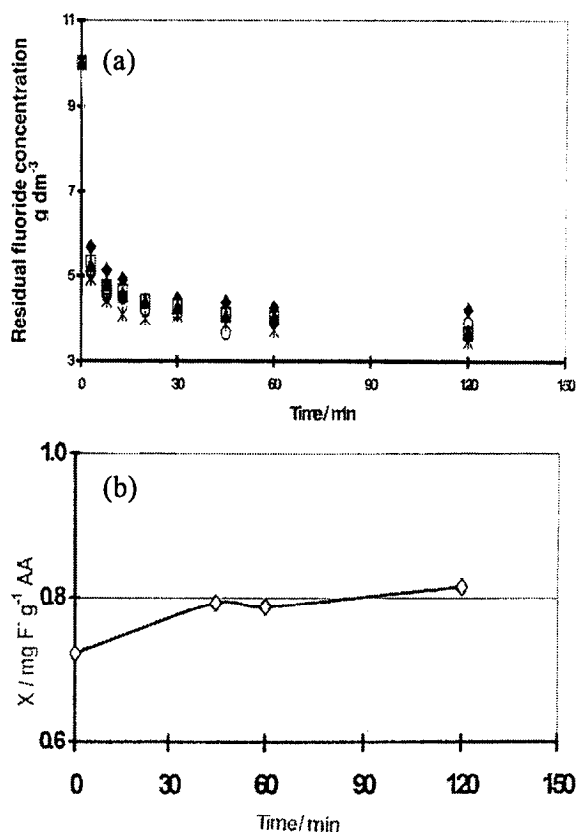


Fig. 3. Effect of activation time on defluoridation kinetics and adsorbent performance. $\text{pH} = 7$, $C_{\text{F}^-} = 10 \text{ mg dm}^{-3}$, $C_{\text{A}} = 8 \text{ g dm}^{-3}$ and $T = 25^\circ\text{C}$. (a) Kinetic curves at various activation times: (\blacklozenge) $T_a = 0$ min (\blacksquare) $T_a = 45$ min, (\blacktriangle) $T_a = 60$ min, (\times) $T_a = 90$ min, ($*$) $T_a = 120$ min. (b) Fluoride adsorption capacity (X) against the activation time.

following experiments, since the fluoride capacity of the electro-activated alumina is constant up to 120 min.

3.2. Effect of experimental parameters on the electro-activated alumina

The influence of various experimental parameters [ionic strength, hardness, pH and fluoride–alumina concentration ratio ($C_{\text{F}^-}/C_{\text{A}}$)] on the performance of the electro-activated alumina was examined.

The effect of the ionic strength of the solution on the adsorbent performance was investigated at pH 7 by using three different NaCl concentrations ranging from 200 to 800 mg dm⁻³. Practically similar defluoridation kinetics were obtained at various NaCl concentrations for the conventional activated alumina, indicating that the ionic strength did not have a considerable effect on the performance of this adsorbent (Fig. 4); a slight decrease was obtained at the higher salt concentration of 800 mg dm⁻³. However, for the electro-activated alumina, an increase in the ionic strength induced a slight increase in the fluoride adsorption capacity of the electro-activated adsorbent. The fluoride adsorption capacity of an electro-activated alumina may be improved by about 20% with a NaCl concentration of 800 mg dm⁻³, as compared with that obtained with fluorinated solutions without the addition of NaCl. These results are of interest for the treatment of strongly mineralized ground water found in the North African Sahara [1]. On the other hand, an increase in salt concentration improved the performance of the adsorbent treated by the electrochemical process. At a NaCl concentration of 800 mg dm⁻³, the fluoride adsorption capacity of the electro-activated alumina was about 55% greater than that of the conventional alumina. The concentration dependence of the adsorption capacity of the electro-activated adsorbent may be explained by the change of the charge state of the electro-activated adsorbent at various salt concentrations.

The effect of the pH of the solution on the adsorbent performance was investigated for pH ranging from 2 to 11. The results, presented in Fig. 5, indicate that the fluoride adsorption capacity of both electro-activated and conventional alumina decreases at pH superior to 4. These results could be explained by the change of the charge state under the various pH. A similar decrease in fluoride adsorption was observed for strongly acid solutions with pH less than 3. These

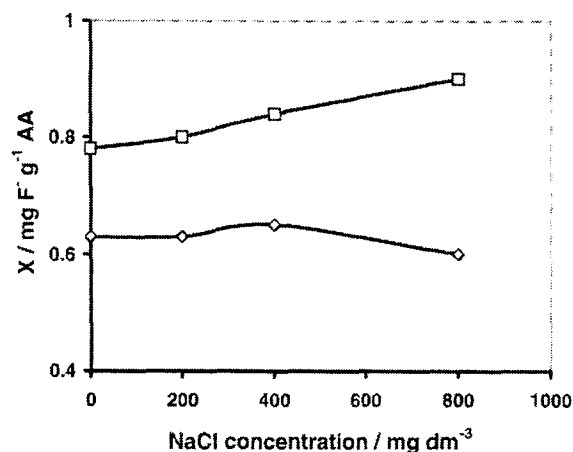


Fig. 4. Effect of the ionic strength on the fluoride adsorption capacity (X). pH = 7, $C_F^- = 10 \text{ mg dm}^{-3}$, $C_A = 8 \text{ g dm}^{-3}$, $T_a = 120 \text{ min}$, $T = 25^\circ\text{C}$. (\square) electro-activated alumina and (\diamond) conventional alumina.

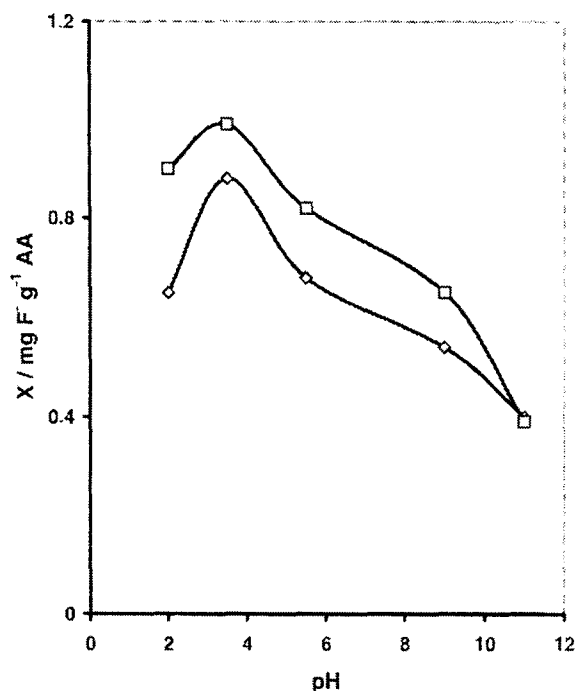


Fig. 5. Effect of the pH on the fluoride adsorption capacity (X). pH = 7, $C_F^- = 10 \text{ mg dm}^{-3}$, $C_A = 8 \text{ g dm}^{-3}$, $T_a = 120 \text{ min}$, $T = 25^\circ\text{C}$. (\square) electro-activated alumina and (\diamond) conventional alumina.

results could be attributed to the formation at high acidity of an adsorbed negatively charged layer by means of HF and HF_2^- which would decrease the adsorbent capacities by electrostatic repulsion of fluoride. The performance of the electro-activated alumina was better than that obtained with conventional alumina for the range of pH utilized. It should be noted that an optimum pH region ranging from 3.5 to 4.5 was determined for fluoride removal by adsorption on both electro-activated and conventional alumina. An optimum pH 4 was utilised for all the following experiments.

The effect of the hardness of the water on the performance of the adsorbent submitted to electrochemical activation was measured by adding calcium carbonate (CaCO_3) salt which conferred hardness in the range of 0 to 400 mg dm^{-3} of CaCO_3 to the synthetic fluorinated water.

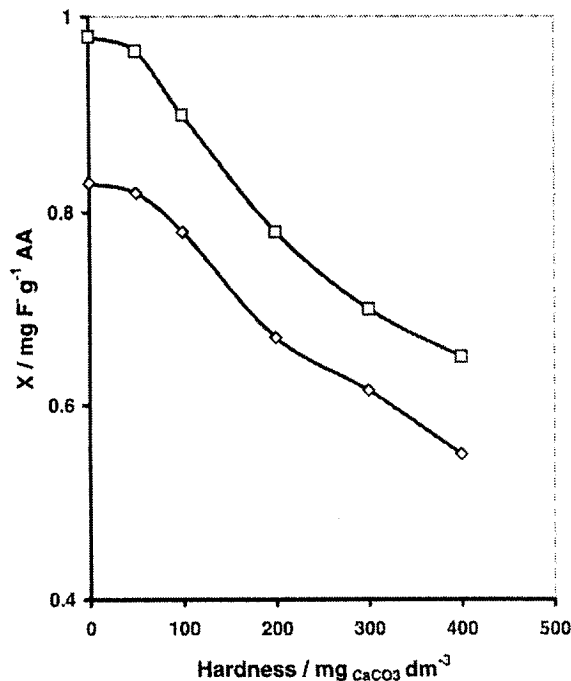


Fig. 6. Effect of hardness on the fluoride adsorption capacity (X). $\text{pH} = 4$, $C_{\text{F}^-} = 10 \text{ mg dm}^{-3}$, $C_{\text{A}} = 8 \text{ g dm}^{-3}$, $T_{\text{a}} = 120 \text{ min}$, $T = 25^\circ\text{C}$. (\square) electro-activated alumina and (\diamond) conventional alumina.

The fluoride capacity of both electro-activated alumina and conventional alumina continuously decreases with increasing hardness (Fig. 6). The decrease in the removal of fluoride presumably resulted from the competition between fluoride ions and CO_3^{2-} and/or HCO_3^- ions formed after the dissociation of CaCO_3 . Similar effects were found in the removal of fluoride by electro-sorption techniques [3]. On the other hand, CO_3^{2-} and/or HCO_3^- ions may considerably reduce the porosity, which does not facilitate diffusion of fluoride into the adsorbent particles and therefore contributes to a reduction of fluoride adsorption capacity of the adsorbent. This property was positively used during defluoridation by calcite particle CaCO_3 . Indeed, an increase in the porosity of CaCO_3 facilitates the diffusion of F^- ions into and of CO_3^{2-} ions out of the particles [7,8].

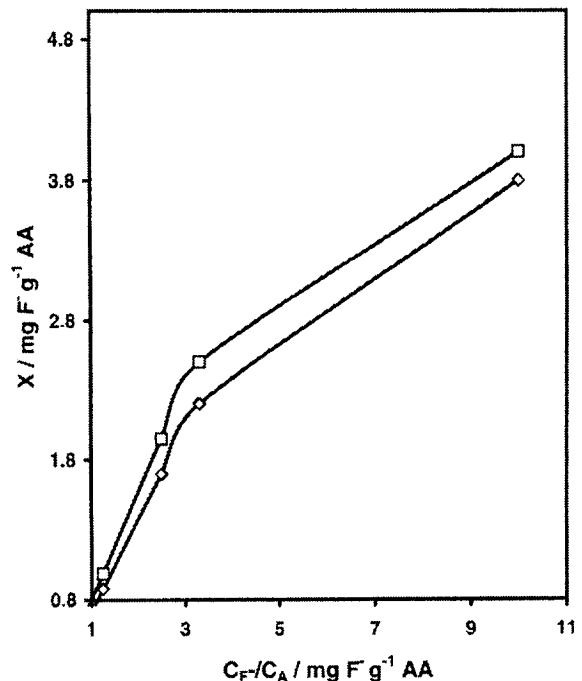


Fig. 7. Effect concentration ratio ($C_{\text{F}^0}/C_{\text{A}}$) on the fluoride adsorption capacity (X). $\text{pH} = 4$, $T_{\text{a}} = 120 \text{ min}$, $T = 25^\circ\text{C}$. (\square) electro-activated alumina and (\diamond) conventional alumina.

The influence of the concentration ratio (C_{F_0}/C_A) on the performance of the fluoride adsorption technique, presented in Fig. 7, shows an important increase in the fluoride adsorption capacity for the two adsorbents when the C_{F_0}/C_A ratio is increased up to 3 mg F⁻/g AA. Below this value, the performance of both adsorbents increased slightly. It is important to note that the higher the C_{F_0}/C_A ratio, the lower are the kinetics. These two parameters, i.e., adsorption capacity and kinetic reaction, then have to be balanced in order to choose an adequate value for the concentration ratio R . In our case, a ratio of about $R=4$ mg F⁻/g AA may be considered suitable for fluoride removal for both adsorbents.

4. Conclusions

This study demonstrates the interest of using electro-activation as a technique for improving the fluoride adsorption capacity of alumina. Indeed, this technique exhibited more efficiency than the conventional activation technique in all cases. Optimal conditions of the electro-activation operation were determined: an activation time of about 2 h and a potential of +100 mV/SCE. The effect of the experimental parameters on the fluoride adsorption capacities of both electro-activated adsorbent and conventional alumina was essentially the same, except for the ionic strength parameter. Indeed, ionic strength did not have a considerable effect on the performance of the conventional alumina. However, for the electro-activated alumina, an increase in the ionic strength induced an increase in fluoride adsorption capacity of the electro-activated adsorbent. Indeed, at a NaCl concentration of 800 mg dm⁻³, the fluoride adsorption capacity of the electro-activated alumina was about 55% greater than that of the conventional alumina. This result may be useful in the

treatment of ground waters of the North African Sahara, which present a strong mineralization and are contaminated by fluoride. Moreover, this study is pursued by determining the relation between the adsorption capacity and the charge state of the electroactivated adsorbent by means of the streaming potential technique.

5. Symbols

C_A	—	Adsorbent concentration, g dm ⁻³
C_e	—	Fluoride concentration at equilibrium state, mg dm ⁻³
C_i	—	Initial fluoride concentration, mg dm ⁻³
T_a	—	Activation time, s
T	—	Temperature, °C
X	—	Fluoride adsorption capacity, mg F ⁻ /g AA

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