

Adsorption and Regeneration of Fluoride Ion on a High Alumina Content Bauxite

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Adsorption of fluoride ion from aqueous solutions by using different silico-aluminous natural products was studied. Preliminary batch tests indicated how bauxite shows a high removal efficiency. Such optimum efficiency is due to the elevated presence of aluminium hydroxide (gibbsite) and aluminium oxide hydroxide (boehmite).

Both batch and continuous experiments were performed: Freundlich equation well described batch equilibrium data. In continuous-flow column experiments, the effects of inlet fluoride concentration (5–50 mg L⁻¹) and flow rate (up to 2.5 mL min⁻¹) on breakthrough time and adsorption capacity were studied. Column studies showed that the dynamic adsorption capacity depends on the inlet fluoride concentration and the flow rate.

After adsorption of fluorides, saturated bauxite, was regenerated by using two different solutions containing NaOH and H₂SO₄. Column tests indicated a different behaviour of original respect to regenerated bauxite.

Key words: Fluoride, Bauxite, Aluminium hydroxide, Adsorption, Regeneration, Kinetics.

1. Introduction

Fluoride is an essential constituent for humans, although accumulation of fluoride ions in the organic tissues is harmful to the human health. The maximum contaminant level of fluoride in drinking water depends on standards fixed by different countries, while the guideline value, set by the World Health Organization (2011), is 1.5 mg L⁻¹.

An excess of fluoride (>1.5 mg L⁻¹) is harmful to the human health. In fact in children, consistent exposure to fluoride at high levels can discolour and disfigure emerging permanent teeth (dental fluorosis), in adults, the same high fluoride level, appears to increase the risk of bone fracture. What is more, a U.S. National Research Council panel (NCR, 2006) noted that fluorides may also trigger more serious problems (bone cancer and damage to the brain and thyroid gland).

In Europe and also in Italy the maximum level for fluorides in drinking water is at the moment 1.5 mg L⁻¹, but higher level of fluoride in groundwater are detected in various country from Africa, Asia, Europe and USA, so that this can be considered a world-wide problem. Excess of fluoride in drinking water is also evident in Italy, where more than 100 districts of two regions (Lazio and Toscana) exceed the suggested European limit.

Fluoride removal techniques include chemical precipitation, membrane process (reverse osmosis), ion exchange and adsorption (Gogoi S. and Dutta R.K., 2015; and Loganathan et al., 2013; Habuda-Stanic et al. 2014), the latter process being widely accepted and used as general pollution removal technique, because of its ease of operation and low cost.

Fluorides adsorption can be carried out utilizing various adsorbents such as fly ash (Chaturvedi et. al., 1990), gypsum (Thole et al. 2012), clays (Çengeloglu et al., 2002), activated carbon (Mohan et al., 2008), activated alumina (Ghorai and Pant, 2004; Ku and Chiou, 2002; Tripathy and Raichur 2008), metallurgical alumina (Pietrelli, 2005), zeolite (Gómez-Hortigüela et al. 2013), rare earth oxides (Raichur and Basu, 2001) and many natural products like tree bark, groundnut husk, sawdust, rice husk, chitin, etc. (Kamble et al., 2007; Chidambaram et al. 2003). The fluoride adsorption onto an industrial product like activated alumina appears to

be the most interesting operation due to the high surface area and crystalline form of this thermally activated material, in fact activated alumina processes may reduce fluorides content below 1 mg L^{-1} .

Between the products that could be employed as sorbent materials the most economic are the natural mineral products which do not need any expensive modification or activation (Malay and Salim, 2001). For this reason in this paper the performance of different silico-aluminous natural materials are experimented and compared; firstly batch tests were carried out and the results show that a natural bauxite, containing high percentage of aluminium hydroxide, can be considered a good natural adsorptive product even in absence of activation processes.

2. Experimental

2.1 Materials

Sodium fluoride (CAS No. 7681-49-4) with purity >99% was purchased from Merck (Darmstadt, Germany). All other chemicals were analytical grade and used without further purification. Synthetic fluoride solutions were prepared by adding appropriate amounts of sodium fluoride to distilled water.

Different materials based on ferric oxide (hematite and ocher), silico-aluminous products (lava, pozzolana) and aluminum hydroxide (bauxite) were used during the preliminary tests. Bauxite was obtained from a sedimentary deposit in Texas (USA), hematite and ocher were from Elba (Livorno, Italy), lava from Stromboli (Messina, Italy) and black pozzolana from Lunghezza (Roma, Italy).

2.2 Methods

The sorption materials were preliminary ground and sieved to obtain powders below 0.5 mm of diameter. After careful washing with deionized water, the materials were dried at $110 \text{ }^\circ\text{C}$ in an electric oven for 3 hours. Then they were cooled in air to room temperature and characterized by standard analytical methods and by X-ray powder diffraction (XRPD).

To assess the ability of each adsorbent to remove fluoride from water, preliminary batch screening tests were conducted. One gram of powdered sample was contacted with 100 mL of 10 mg L^{-1} fluoride solution for 1 h under gentle agitation. After this time, a sample of liquid was taken and the residual fluoride concentration was measured.

A similar procedure was used to perform equilibrium experiments. In these experiments the liquid-to-solid ratio was set at 100 mL g^{-1} and the initial fluoride concentration was varied between 10 and 100 mg L^{-1} (Lavecchia et al., 2012). Then exhausted bauxite was dipped in 0.1 N NaOH solution and left for 12 h, then powders were washed repeatedly with water and then activated with 0.4 N H_2SO_4 solution. Afterwards water washing was carried to rise pH=7 followed by drying in oven for 5 h, this makes activated product ready for the next defluoridation cycle (Ghorai and Pant, 2004).

Column studies were carried out in a glass column with an inner diameter of 1 cm and a length of 20 cm. A glass-wool plug was placed in the bottom of the column to support the adsorbent bed and prevent the outflow of particles. The amount of adsorbent was fixed at 4 g (corresponding to a bed height of 5.5 cm), the inlet fluoride concentration was varied from 5 to 50 mg L^{-1} and the flow rate from 0.5 to $2.5 \text{ cm}^3 \text{ min}^{-1}$. Samples of the outlet solution were collected at definite time intervals and analyzed to determine the fluoride content.

Batch and column experiments were performed at pH 7.0 ± 0.1 and room temperature ($20 \pm 2 \text{ }^\circ\text{C}$). The concentration of fluoride in the aqueous solution was determined according to ASTM D 1179 Standard Method utilizing a potentiometer equipped with an ion-selective electrode (DC219-F, Mettler-Toledo, Novate Milanese, Italy). A series of standard fluoride solutions with concentrations ranging from 0.1 to 10 mg L^{-1} was used to construct the calibration curve.

X-ray powder diffraction (XRPD) analysis was carried out with a diffractometer Bruker model Advance D8, DTA/TGA analyses were performed by using a Stanton Redcroft model 1500 thermobalance.

3. Results and discussion

3.1 Preliminary screening tests

Batch screening tests gave the results presented in Table 1, from which it can be seen that percent removal of fluoride ranged from 3% (ocher) to 63.1% (bauxite). Because of its significantly higher efficiency, bauxite was used in subsequent experiments. Chemical analysis by standard gravimetric methods showed that Al_2O_3 (81.5%), Fe_2O_3 (9.3%) and SiO_2 (8.9%) were the main bauxite constituents. No heavy metals (Pb, Cd, As, Cr) were detected. XRPD analysis revealed the presence of hematite [Fe_2O_3], gibbsite [$\text{Al}(\text{OH})_3$], boehmite [$\text{AlO}(\text{OH})$] and anatase [TiO_2] as the main phases.

Table 1: Results of preliminary screening tests (1 hour contact). FR is the percent fluoride removal

Material	Origin	FR (%)
Bauxite	Texas (USA)	63.1
Hematite	Elba (Italy)	7.3
Lava	Stromboli (Italy)	10.0
Black pozzolana	Lunghezza (Italy)	15.0
Ocher	Elba (Italy)	3.0

3.2 Equilibrium studies

The time needed to reach equilibrium was of the order of 3 h for the original bauxite and independent of the initial fluoride concentration, this results is in accordance with literature (Sujana and Anad, 2011). The equilibrium concentrations in the liquid (c^*) were determined after this time, while the concentrations in the adsorbed phase (q^*) were calculated as:

$$q^* = \frac{V_L}{w} (c_0 - c^*) \quad (1)$$

where V_L is the volume of the aqueous solution, w is the mass of adsorbent and c_0 is the initial fluoride concentration. The data so obtained were well described by the two-parameter Freundlich equation:

$$q^* = K_F (c^*)^{1/n} \quad (2)$$

where K_F is the Freundlich constant and $1/n$ is the heterogeneity factor. K_F represents the amount of solute adsorbed at an equilibrium concentration of unity and thus is a measure of the adsorption capacity of the material, while n reflects the adsorption intensity. It is generally stated that values of n in the range 2–10, 1–2 and <1 indicate, respectively, good, moderate and poor adsorption characteristics.

The Freundlich parameters were obtained from the slope and intercept of the log–log plot yielded $K_F = 0.957 \text{ mg}^{1-1/n} \text{ g}^{-1} \text{ L}^{1/n}$ and $n = 3.18$ (Lavecchia et al., 2012). Saturated bauxite instead showed a different behavior: the time needed to reach equilibrium was of the order of 7 h. Equilibrium data were also well described by Freundlich equation ($K_F = 0.11 \text{ mg}^{1-1/n} \text{ g}^{-1} \text{ L}^{1/n}$ and $n = 1.81$).

3.3 Column studies

At first column experiments were carried out at different inlet fluoride concentrations and flow rates for the original bauxite. The results, expressed as the ratio between outlet and inlet fluoride concentration (c/c_0) versus time, gave typical S-shaped breakthrough curves (Figure 1). As the flow rate (F) increased, the curves became steeper and the breakpoint time decreased. The area above the breakthrough curve (up to $c/c_0 = 1$) provides a measure of the amount of adsorbed fluorides per unit weight of adsorbent, the so-called dynamic adsorption capacity.

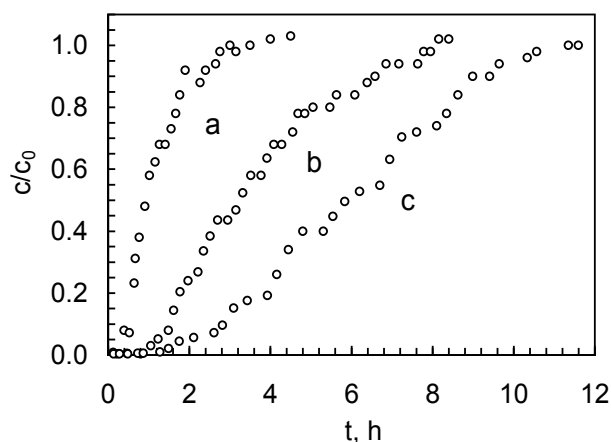


Figure 1: Breakthrough curves for fluoride removal ($C_0 = 25 \text{ g L}^{-1}$) at different flow rates: a = $2.5 \text{ cm}^3 \text{ min}^{-1}$; b = $1 \text{ cm}^3 \text{ min}^{-1}$; c = $0.5 \text{ cm}^3 \text{ min}^{-1}$

Then regenerated bauxite was subjected to column tests by using three different inlet fluoride concentrations ($C_0 = 5, 25, 50 \text{ mg L}^{-1}$) and the maximum flow rate ($2.5 \text{ cm}^3 \text{ min}^{-1}$) utilized in previous tests. Results of breakthrough curves for the original and regenerated bauxite are reported in Figure 2.

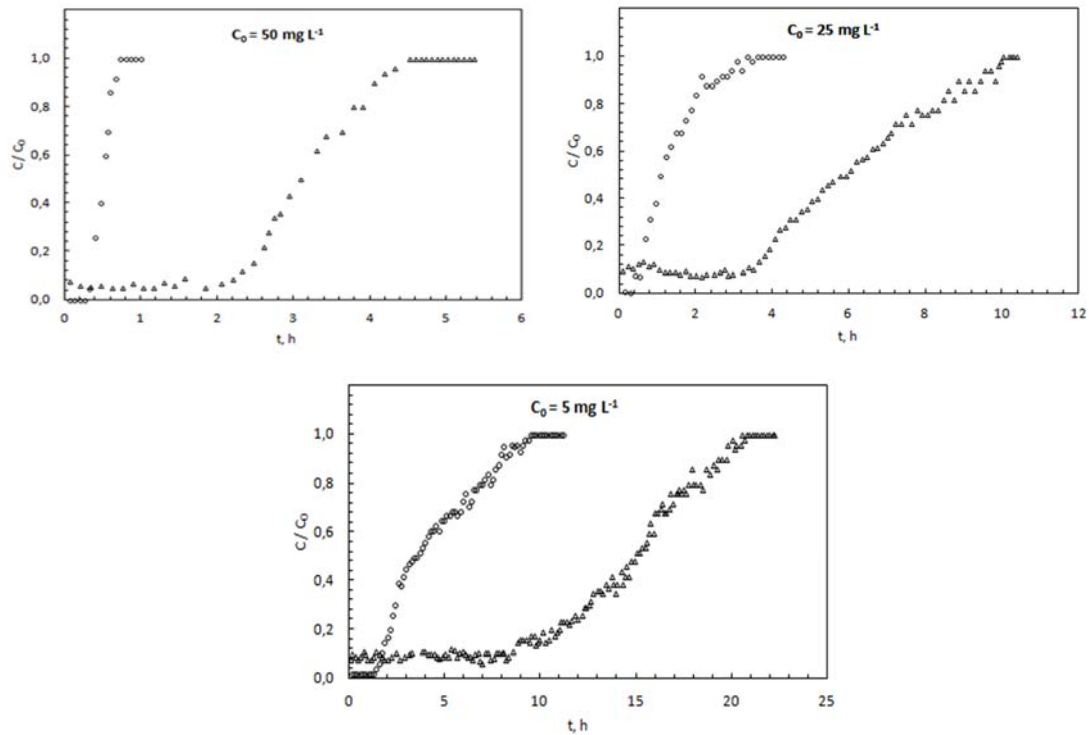


Figure 2: Breakthrough curves for fluoride removal, symbols: \circ original bauxite, Δ saturated bauxite

Breakthrough curves were analyzed by determining the following parameters: the breakthrough time (t_B), i.e., the time corresponding to $c/c_0 = 0.5$; the adsorbent capacity at the breakthrough point (BPC), namely, the specific amount of fluoride adsorbed at $t_{0.5}$ and the adsorbent capacity at the exhaustion point (EPC), namely, the specific amount of fluoride adsorbed at exhaustion. BPC and EPC were calculated as:

$$BPC = \frac{c_0 V_B}{W} \quad ; \quad EPC = \frac{c_0 V_E}{W} \quad (3)$$

where V_B and V_E are the volumes of solution treated at, respectively, the breakthrough point and the exhaustion point. Results of evaluations are presented in Table 2.

Table 2: Characteristic column adsorption parameters calculated from the breakthrough curves

c_0 (mg L^{-1})	F ($\text{cm}^3 \text{ min}^{-1}$)	t_B (h)	BPC (mg g^{-1})	EPC (mg g^{-1})
5	2.5	4.22	0.775	1.250
25	2.5	0.96	1.063	3.125
50	2.5	0.49	0.938	1.375
5	2.5	14.85	1.181	4.668
25	2.5	6.59	4.217	6.125
50	2.5	3.09	4.875	6.175

Examination of the data reveals that the breakthrough time decreased with increasing inlet fluoride concentration both for original or for regenerated bauxite. Regenerated bauxite shows a different behaviour with respect to the original one, namely a lower initial efficiency, but a capacity of adsorption prolonged in time and also a higher adsorbent capacity at the exhaustion point (EPC).

To explain this different behaviour samples of original and regenerated bauxite were subjected to X-ray diffraction tests (XRPD) and thermal analysis (DTA/TGA). The X-ray diffraction spectra reported in Figure 3 show that the spectra are identical and the same crystallographic phases are present. Thermal analysis highlights that the first weight loss up to 100 °C is due to water evaporation. The weight loss between 300 and 350 °C depends on the gibbsite, while the boehmite loses weight at temperatures between 450 and 570 °C. The contents of boehmite and gibbsite in the sample of the original bauxite were found to be respectively 56.6% and 23.1% while that of bauxite regenerated are 60% and 20.2%: the relationship between the quantities shows no changes inside the material.

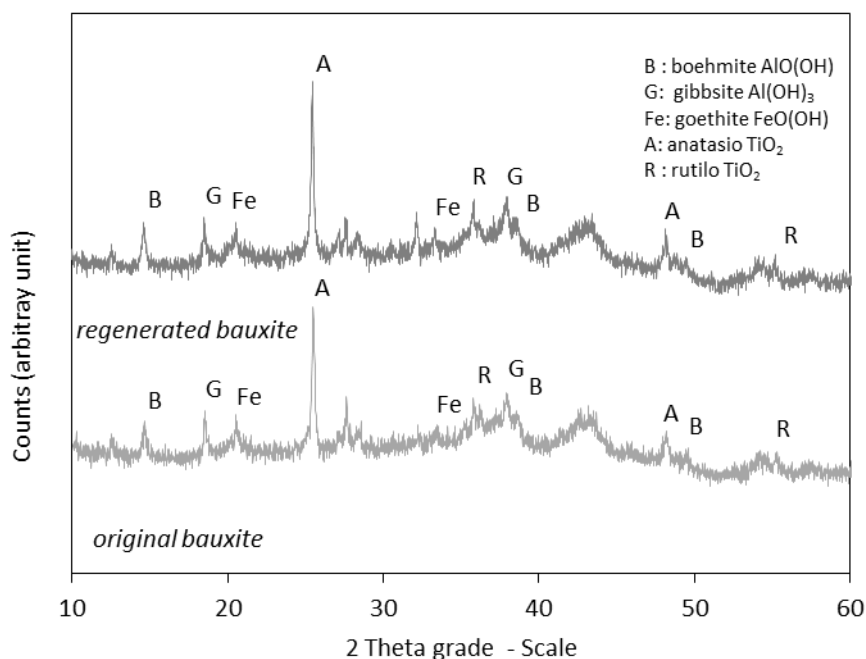


Figure 3: XRPD analyses

The results can be summarized as follows: the original product and the regenerated bauxite present the characteristic peaks of gibbsite and boehmite, which do not disappear after regeneration. This indicates that a portion of “eliminable” fluoride ions are captured by gibbsite and/or boehmite with a prevalent chemical mechanism (namely, replacement of OH⁻ with F⁻). After the regeneration treatment with sodium hydroxide the crystalline structure of gibbsite and boehmite are not destroyed and sulphuric acid activates the adsorption sites present in the matrix: for this reason bauxite longer works.

To confirm this hypothesis final batch tests were carried out, three samples were considered (sample a: original bauxite, sample b: bauxite saturated with fluorides and regenerated, sample c: original bauxite regenerated). One gram of powdered these samples (a,b,c) was contacted with 100 mL of 10 mg L⁻¹ fluoride solution for 24 h under gentle agitation.

All tests were performed in duplicate, and the following results, regarding the removal of the fluoride ion, were obtained: (sample a: 81%, sample b: 94%, sample c: 96%), this means that, at long contact times (24 h), regenerated bauxite offers a greater reduction of fluorides. This result, together with the fact that the bauxite regenerated reaches the equilibrium conditions more slowly (7 h), may explain the different behaviour observed in the column tests.

4. Conclusions

Bauxite constitutes a suitable adsorbent for the removal of fluoride from aqueous solutions. In comparison with other natural materials, bauxite shows better removal capacity; the activity of this natural product is due to the presence of crystalline gibbsite (aluminium hydroxide) and boehmite (aluminium oxide hydroxide).

Freundlich equation well describes batch equilibrium data, in column test a different behavior of the original and saturated bauxite was noticed. Saturated bauxite, after adsorption of fluorides, can be completely regenerated utilizing separately solutions containing NaOH and H₂SO₄. Regenerated bauxite can be reutilized for a new cycle of fluoride removal, because the used regenerating acid solution does not destroy the

crystalline phases of the bauxite. Sodium hydroxide favours the replacement of OH⁻ with F⁻, while sulphuric acid activates the adsorption sites inside the matrix.

References

1. Çengeloglu Y., Kir E., Ersöz M., 2002, Removal of fluoride from aqueous solution by using red mud, *Sep. Purif. Technol.*, 28, 81–86.
2. Chaturvedi A.K., Yadava K., Pathak K.C., Singh V.N., 1990, Defluoridation of water by adsorption on fly ash, *Water Air Soil Pollut.* 49, 51–61.
3. Chidambaram C., Ramanathan A.L. Vasudevan S., 2003, Fluoride removal studies in water using natural materials, *Water SA*, 29, 339–343.
4. Ghorai S., K.K. Pant, 2004, Equilibrium, kinetics and breakthrough for adsorption of fluoride on activated alumina, 2004, *Sep. Purif. Technol.*, 42, 265-271.
5. Gogoi S., Dutta R. K., 2015; Mechanism of fluoride removal by phosphoric acid- enhanced limestone: equilibrium and kinetics of fluoride sorption, *Desalination and Water Treatment*, 1-14, doi: 10.1080/19443994.2015.1010592.
6. Gómez-Hortigüela L., Pérez-Pariente J., García R., Chebude, Y., Díaz, I. 2013, Natural zeolites from Ethiopia for elimination of fluoride from drinking water, *Sep. Purif. Technol.*, 120, 224–229.
7. Habuda-Stanic M., Ravancic M. E., Flanagan A., 2014, A review on Adsorption of fluoride from aqueous solution, *Materials*, 7, 6317-6366.
8. Kamble, S.P.; Jagtap, S.; Labhsetwar, N.K.; Thakare, D.; Godfrey, S.; Devotta, S.; Rayalu, S.S., 2007, Defluoridation of drinking water using chitin, chitosan and lanthanum modified chitosan, *Chem. Eng. J.*, 129, 173–180.
9. Ku, Y.; Chiou H.M., 2002, The adsorption of fluoride ion from aqueous solution by activated bauxite, *Water, Air and Soil Pollution*, 133, 349-360.
10. Lavecchia R., Medici F., Piga L., Rinaldi G., Zuurro a., 2012, Fluoride removal from water by adsorption on a high alumina content bauxite, *Chemical Engineering Transaction*, 26, 225-230.
11. Loganathan P., Vigneswaran, Kandasamy J., Naidu R., 2013, Defluoridation of drinking water using adsorption processes, *J. of Hazard. Mater.*, 248, 1-19.
12. Malay, K.D., Salim, A.J., 2011, Comparative study of batch adsorption of fluoride using commercial and natural adsorbent, *Res. J. Chem. Sci.*, 1, 68–75.
13. Mohan D., Singh K.P., Singh V.K., 2008, Wastewater treatment using low cost activated carbons derived from agricultural byproducts. A case study. *J. Hazard. Mater.*, 152, 1045–1053.
14. NRC (National Research Council), 2006, Fluoride in Drinking Water: A Scientific Review of EPA's Standards. The National Academies Press, Washington, DC, USA.
15. Pietrelli L., Fluoride wastewater treatment by adsorption onto metallurgical grade alumina, 2005, *Annali di Chimica*, 95, 303-312.
16. Raichur A.M., Basu M.J., 2001, Adsorption of fluoride onto mixed rare earth oxides, *Sep. Purif. Tech.* 24, 121–127.
17. Sujana M.G., Anad S., 2011, Fluoride removal studies from contaminated water using bauxite, *Desalination*, 267, 222-227.
18. Thole B., Mtalo F., Masamba W., 2012, Groundwater defluoridation with raw bauxite, gypsum, magnesite and their composites, *Clean-Soil, Air, Water*, 40(11), 1222-1228.
19. Tripathy S.S.; Raichur A.M., 2008, Abatement of fluoride from water using manganese dioxide-coated activated alumina. *J. Hazard. Mater.*, 153, 1043–1051.