

Removal of Fluoride from Contaminated Ground Water Using Raw and Modified Bauxite

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Abstract Endemic fluorosis affects millions of people worldwide. Fluorosis arises from the consumption of fluorine (F) contaminated water and was observed also in some parts of Turkey with volcanic rocks and geothermal resources. In the present study the removal of F from drinking water by raw and modified bauxite at the laboratory scale was investigated using a batch mode. Modified bauxite was prepared by using Na and Mg incorporated (B–Na, B–Mg) bauxite and calcination of Mg incorporated bauxite at 500°C (B–Mg-500). The equilibration time for F between bauxite and water was identified to be 3 h. Adsorption of F increased with increasing adsorbent dose. Moreover, F adsorption isotherms fitted well with the Freundlich model. Low F adsorption was obtained onto the raw and incorporated bauxite. In contrast, maximum F adsorption was found for B–Mg-500, with K_f value of 0.247. This observation may be explained by the meaningfully stabilized and elevated number of positively charged sites in B–Mg-500.

Keywords Defluoridation · Modification · Local adsorbents · Batch method · Isotherms

The ground waters in many parts of the world may have very high fluoride (F) concentrations. Fluoride contamination of drinking water and associated fluorosis in human beings is a worldwide problem (Thakre et al. 2010). Latest estimates suggest that about 200 million people are suffering from fluorosis (Gao et al. 2009). Fluoride in water

derives mainly from dissolution of natural minerals such as rocks and soil. Hence, high F concentrations can occur in ground waters, which have long residence times (Lunge et al. 2011). Depending on the nature of sedimentary and volcanic rocks and geothermal resources, F level in ground water varies substantially.

The excessive intake of F may cause dental or skeletal disorder (Gao et al. 2009). Taking such health effects into consideration, the World Health Organisation (WHO 1994) has set 1.5 mg/L as the maximum permissible level of F for drinking water (Jagtap et al. 2011). High levels of F in ground water which may be used as drinking water were found and fluorosis cases were identified in Sarım and Karataş villages in the north-west region of Şanlıurfa, Turkey. Hand pump and tube wells are the major source of water in these rural areas, while a replacement by uncontaminated drinking water sources is not manageable. Therefore, removal of excess F is the only feasible solution, while adsorption is considered as the most suitable technique especially in rural areas. A wide range of adsorbents have been used for F removal such as clay (Agarwal et al. 2003), alumina, metal oxides, chitin-chitosan, cement (Jagtap et al. 2011), activated carbon, bone charcoal, coconut shell carbon, natural zeolites and lime (Gao et al. 2009). However, bauxite is one of the abundantly available mineral in the area under investigation, mainly consisting of alumina, iron, silica and titanium oxides, while its composition varies considerably but exhibits usually an aluminium content ranging between 50 % and 70 % (Dixon and Schulze 2002). Bauxite is claylike and earthy and ranges in color from white to deep brown or red according to the nature and quantity of its components.

Moreover, it was used as an adsorbent for the removal of arsenic (Giles et al. 2011), phosphate (Kamiyango et al.

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2011), several trace contaminants (Mayes et al. 2011) and chromate(VI) (Yuhua et al. 2008). Anionic pollutants can be adsorbed by the positively charged sites of the material. To increase these sites we prepared homoionic bauxite with magnesium (Mg) and sodium (Na). Activation of homoionic bauxite by heating (calcination) additionally increases the stability of cations and hence the number of positively charged sites in its pores (Wang and Reardon 2001). In some earlier studies, adsorption ability of heat activated bauxite for the removal of pollutants such as Cr(VI) and As(III) has been reported. Thermally activated bauxite was studied for F removal from aqueous solutions (Sujana and Anand 2011). However, limited information is available on the comparison of F adsorption efficiency of raw and modified bauxite. Therefore, the aim of the present study was (1) to investigate the removal of F from water by adsorption on the raw bauxite which is locally available, cost-effective, simple and abundant in Turkey and (2) to increase its F removal capacity by the incorporation of Na and Mg also considering calcination processes.

Materials and Methods

Raw (natural) bauxite (BR) used in the present study was a local material procured from Seydişehir aluminium process plant, Eskişehir, Turkey. BR from Eskişehir is still being used in the aluminium production. BR was grounded in Geological Engineering Laboratories in Istanbul Technical University and air-dried and sieved (<2 mm).

To prepare homoionic bauxite with Mg; 10 g of BR was mixed with 100 mL of 1.25 M MgCl₂ solution and the mixture was agitated for 6 h. Subsequently, the mixture was kept in a water bath at 60°C for an hour and then at room temperature for 24 h. The mixture was finally washed twice with distilled water in 1:20 ratio to remove excessive Mg from media. It was centrifuged and aqueous supernatant was removed in each washing step. The mixture was transferred into glass petri dish and dried at 150°C in oven. The dried mass was then grounded to fine powder (2 µm) (Mumcu 2006). Similar procedure was used to obtain homoionic Na bauxite (NaCl solution was used instead of MgCl₂). To activate the homoionic bauxite by heating, dried mass was grounded to fine powder and calcinated at 500°C for 4 h in muffle furnace (Thakre et al. 2010). Modified bauxite identified as:

Incorporated BR with MgCl₂: B–Mg

Incorporated BR with NaCl: B–Na

Incorporated BR with MgCl₂ and calcined: B–Mg-500

Adsorption tests were carried out using a batch mode for the raw, incorporated and calcinated bauxite. Adsorption kinetics, optimum adsorbent dosage and adsorption

isotherms were determined by adsorption tests at natural pH (7.6) and room temperature. Stock F solution (100 mg/L) was prepared by dissolving 0.221 g anhydrous NaF (Merck) in 1 L of deionized water. This was further diluted to get the desired concentration for practical use. Effect of contact time and adsorbent dose studies and adsorption isotherms were carried out on the raw bauxite and modified adsorbents.

A preliminary kinetic experiment was carried out to establish the equilibration time for F adsorption. Tests were conducted in duplicate samples in 50 mL polypropylen test tubes. Test solution of 5 mg/L F was prepared from fresh stock solution, keeping in mind that the maximum concentration of F reported in ground water of most of the F-affected area is around 5 mg/L (Yadav et al. 2006). Raw BR samples (0.2 g) were shaken with 40 mL of F solutions (5 mg/L) on a reciprocating shaker (150 rpm) for 1, 2, 3, 4, 5, 11, 24 h to attain the equilibration time at room temperature and then supernatant was filtered through syringe filters and analyzed for the residual F. All reported results constituted the mean of duplicate measurements. Optimum conditions were selected for further studies. In the equilibrium studies, contact time was regarded 3 h. Samples were shaken with 40 mL of F solutions with variable initial concentrations. All the experiments were executed with controls-with only F in tube (no adsorbents) and blanks-with the same amount of adsorbent in tube (without F). All solution samples were filtered through 0.45 µm syringe filters. Fluoride analyses were performed by Hach mark Fluoride Meter (product code: 2589 99) by TISAB method (Liu et al. 2010).

Adsorption data were analyzed using linearized form of the Freundlich isotherms (Eq.1);

$$\log C_s = \log K_f + (1/n_f) \times \log C_e \quad (1)$$

where K_f and 1/n_f are the empirical Freundlich constants. By plotting log C_s (amount adsorbed to adsorbent, mg/g) versus log C_e (amount of F in solution, mg/L), 1/n_f is calculated as the slope of the curve and the intercept is equal to log K_f (Sparks 1995).

Results and Discussion

The effect of contact time on the extent of adsorption of F on raw bauxite is shown in Fig. 1a. Initially, F adsorption increased with increasing contact time. After 3 h, it approached an almost constant value. The sudden change in the removal rate might be due to the fact that initially all adsorbent sites were vacant and the solute concentration gradient was high, while at later contact times the number of vacant adsorption sites decreased (Yadav et al. 2006). Therefore the equilibration time was set at 3 h and was used in all further experiments of the present study.

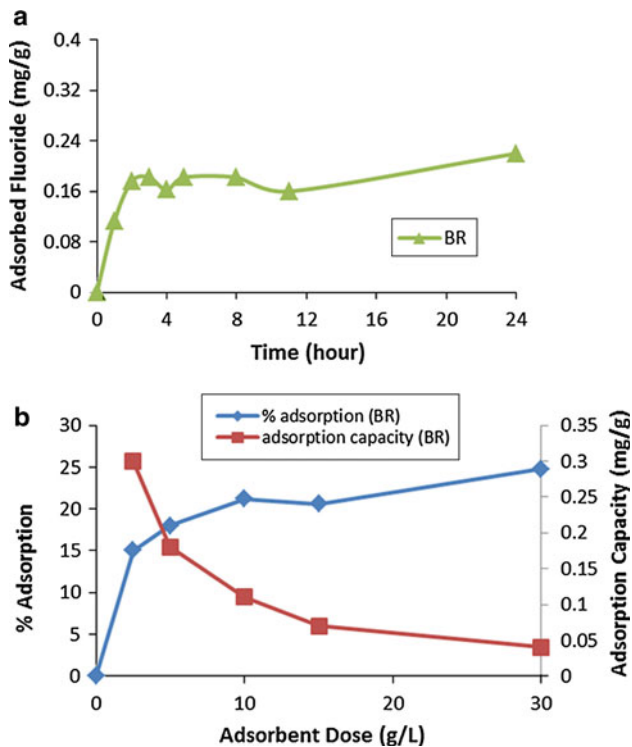


Fig. 1 Effect of contact time (a) and adsorbent dose (b) on the fluoride adsorption rate

The effect of adsorbent dose on F adsorption was studied at room temperature (25°C) and natural pH (7.6) using an initial F concentration of 5 mg/L and a contact time of 3 h. The effect of adsorbent dose on the F adsorption is given in Fig. 1b. It was observed that the amount (mg/g) of F adsorbed was decreased with the increase in dose. The maximum adsorption capacity was found to be 0.30 mg/g for bauxite at a dose of 0.1 g/40 mL (2.5 g/L). It was observed that the percentage of F adsorption increased with the increase in the dosage of the adsorbent and is likely driven by the enhanced availability of active sites (Sundaram et al. 2009). The extent of F removal was 15 % (0.30 mg/g) with 2.5 g/L of adsorbent dose, while it was a little increased to 18 % (0.18 mg/g) with 5.0 g/L of adsorbent. It was noticed that a further increasing of the adsorbent dose did not mean a meaningful change in the percentage of F removal. Hence, the dose of 5 g/L was fixed as optimum dosage for raw bauxite.

According to the Giles classification (Giles et al. 1960), F adsorption isotherm was type C for BR and B–Mg and type L for B–Na and B–Mg-500 (Fig. 2). The C type isotherm implies a constant dispersion while the L type isotherm is typical of an adsorbent with affinity for the adsorbate. Moreover, F adsorption rate and capacity was found highest for B–Mg-500 (Fig. 3). Fluoride adsorption rate of BR, Na and Mg incorporated bauxite ranged between 21 % and 39 %. Fluoride adsorption on B–Mg-

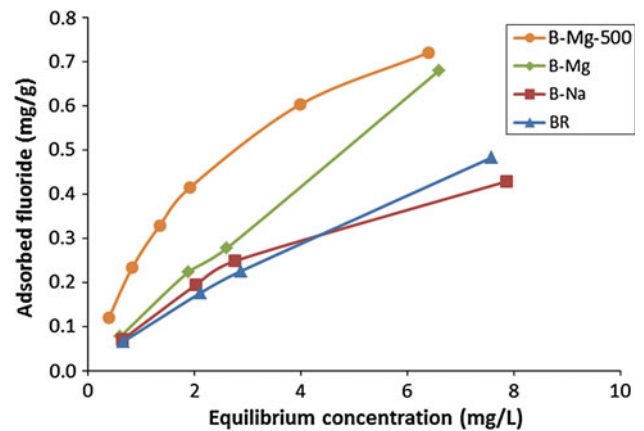


Fig. 2 Adsorption isotherms of raw and modified bauxite

500 was found 60 % and 36 % for 1 and 10 mg/L initial F concentrations, respectively. Incorporation of bauxite with Na did not significantly change the adsorption efficiency of raw bauxite, on the other hand, F adsorption increased a little (6 % for 1 mg/L and 10 % for 10 mg/L initial F concentration) with Mg incorporation treatment. Calcination treatment on the Mg incorporated bauxite influenced its F adsorption capacity substantially. This is especially evident for the low initial F concentrations (<10 mg/L).

The Freundlich equation was used to describe the F adsorption data. The values of the Freundlich adsorption constants are given in Table 1. Fluoride adsorption isotherms for all adsorbents fitted well with Freundlich model ($r > 0.98$). This fact suggests the heterogeneous nature of adsorbents studied. Gupta et al. (2007), Karthikeyan and Elango (2009), Karthikeyan et al. (2009), Mandal and Mayadevi (2009), Sundaram et al. (2009) and Jagtap et al. (2011) also found that the experimental data for F adsorption in various adsorbents fitted well with Freundlich equations. A smaller value of $1/n$ (<1) indicates a weaker bond (physical bonding) between adsorbate and adsorbent (Sujana et al. 2009). It is generally stated that values of n in the range of 2–10, 1–2 and <1 indicate, good, moderate and poor adsorption characteristics (Lavecchia et al. 2012).

Low F adsorption was found on the raw (BR) and incorporated bauxite (B–Na, B–Mg). This fact principally exhibited the weaker bond (physical bonding) between F ions and adsorbents (Thakre et al., 2010) or easy desorption of F from the positive sites (Atasoy and Şahin, 2013). Fluoride adsorption was higher for B–Mg-500, with K_f (Freundlich adsorption coefficient) value of 0.247. Vacant sites in the incorporated bauxite and also the adsorbed, i.e. Mg ions, were probably increased with the calcination treatment at 500°C. Perhaps the apparent gain in F removal capacity with temperature is related to some volatilization or mineralisation of F already present on sorption sites during the heating period (Wang and Reardon 2001).

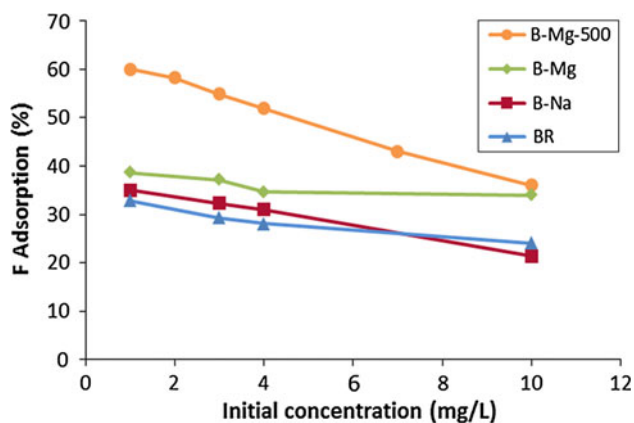


Fig. 3 Fluoride adsorption rate of bauxite for different initial F concentrations

Table 1 Freundlich constants for the fluoride adsorption on raw and modified bauxite

Isotherms	Isotherm constants	BR	B-Na	B-Mg	B-Mg-500
Freundlich isotherm	K_f	0.093	0.106	0.121	0.247
	$1/n$	0.821	0.731	0.911	0.639
	n	1.218	1.368	1.100	1.565
	r^2	0.99	0.98	0.99	0.99

Atasoy and Sahin indicated that F adsorption increased a little on the calcined cement clay at 500°C. Thus, stronger retention between F and sorption sites was achieved with calcination of homoionic clay of the present study. Additionally, transition of F ions may have occurred through the vacant sites and its retention took place on the adsorption sites, such as Al, Fe and Mg incorporated in bauxite.

Taking the ground water F levels into consideration (in average 3 mg/L) in the area under investigation, F removal rates are 29 %, 32 % and 37 % and 55 % for BR, B-Na, B-Mg and B-Mg-500, respectively. Fluoride contamination (≤ 3 mg/L) can be reduced below the acceptable limits of 1.5 mg/L by B-Mg-500. Increased adsorption capacity of B-Mg-500 is related to the increased vacant sites and positively charged sites due to stronger retention of Mg ions on the bauxite by calcination.

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