

Evaluating the effectiveness of a hybrid sorbent resin in removing fluoride from water

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ABSTRACT: In some regions of the world, the concentration of fluoride in groundwater is high. To reduce the amount of fluoride to acceptable drinking water standard, it is highly recommended to treat the water. Fluoride adsorption in aqueous solution by a hybrid resin was studied in this research because of its functional groups likeness with goethite. Kinetic data showed that F adsorption was rapid in the beginning and maximum uptake occurred in within 10 min and equilibrium reached within 100 min. The experimental results showed that fluoride adsorption was influenced by pH of solution and optimum operating pH was in the range of 3 to 5.5. Langmuir model was applicable to the present study and F ions were exchanged with hydroxide ions in nano-scaled structure on the surface of sorbent. This adsorbent with 61 % efficiency is suitable for the regions where F concentration is less than 4 mg/L.

Keywords: Fluoride removal; Functional groups; Hybrid resin; Goethite; Langmuir model

INTRODUCTION

Fluoride is an essential mineral that in permissible guideline level (WHO, 2006) is beneficial to mankind in dental protection and excessive intake led to various disorders and diseases such as crippling skeletal fluorosis, brittle bones, cancer (lung and bladder), infertility in women, brain and hepatit damage and Alzheimer syndrome (Chinoy, 1991; Shivarajashankara *et al.*, 2001; Guo *et al.*, 2003; Jamode *et al.*, 2004; Mahvi *et al.*, 2006a; Dobaradaran *et al.*, 2008a).

Wide varieties of minerals, including fluorspar, rock phosphate, cryolite, apatite, mica and thermal waters especially with high pH have significant level of F. Aluminum smelters that use the F salt cryolite, brick and iron work, coal fired power stations which discharge wastewater with high F concentrations are contributing to entry F to the environment (De la Puente *et al.*, 1997; Abe *et al.*, 2004; Dobaradaran *et al.*, 2009a). Groundwater as drinking water is usually the main source of F intake (Dobaradaran *et al.* 2009b), groundwater with high F concentrations occurs in India, Pakistan, West Africa, Thailand, China, Sri Lanka,

Southern Africa, Iraq, Iran, Sudan, Ethiopia, Uganda, Kenya and the United Republic of Tanzania (WHO, 2006; Abdel-Ghani *et al.*, 2007; Kumar *et al.*, 2009) and because of daily fluoride intake importance, there are many studies about fluoride contents in water and black tea (Mahvi *et al.*, 2006b; Nouri *et al.*, 2006; Dobaradaran *et al.*, 2008b). Precipitation, ion exchange (Hichour *et al.*, 1999), membrane separation (Ndiaye *et al.*, 2005) and adsorption (Abe *et al.*, 2004) are examples of several technologies that have been developed for F removal. Among various techniques, adsorption is a promising technology, in which F is concentrated onto a small adsorbent mass. Sorption media, including bone charcoal, activated alumina and clay are packed in columns and used for a period of time; this material after saturating are renewed or regenerated.

Several researches have been studied and confirmed with a large number of natural materials (Magnesite, natrolite, clinoptilolite, goethite, kaolinite, bentonite, zeolite(s), serpentine, alkaline soil, kaolinitic clay, China clay) for F removal (Bower and Hatcher, 1967; Rao and Viraraghavan, 2002; Fan *et al.*, 2003). Iron and aluminum oxides such as GFH (Kumar *et al.*, 2009), goethite

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(Jinadasa *et al.*, 1993), activated alumina (Hiemstra and Van Riemsdijk, 2000; Ku and Chiou, 2002) and alumina cement granules (Tang *et al.* 2009) play an important role in removal of anions from aqueous solutions.

In the present study, the adsorption potential of innovative hybrid sorbent (Lewatit FO 36) consisting of a combination of a polymeric anion exchange resin and an iron oxide with a goethite (α -FeOOH) structure has been assessed for F removal from water. This research was performed in Tehran University of medical science from September until December 2008.

MATERIALS AND METHODS

Materials

Lewatit FO 36 was purchased from the producer (LANXESS Company, Germany). It is a macroporous, monodispersed, polystyrene-based resin which is doped with a nano-scaled film of iron oxide covering the inner surface of the pores of the polymer bead. Appearance of the adsorbent is brown and mean bead size of the material is 0.35 mm. This adsorbent stability is at pH range of 4-14. A stock F solution was prepared by dissolving 221 mg of NaF (Merck) in 1.0 L of distilled water. The pH of distilled water was in the range of 6.8 to 7.3. The batch method by stirring (390 rpm) was used to study the adsorption of F on Lewatit FO 36 and the effects of contact time and pH were investigated. Standard acid and base solutions (0.1N H₂SO₄ and NaOH solutions) were used for pH

adjustment. The pH of solution was measured using pH meter (metrohm E520). Batch experiment with 1000 mL volume were carried out at room temperature (25 ± 2 °C) by stirring a fixed mass of dry resin and 6 mg/L F solution until equilibrium was reached. After agitation for a specified period of time, solid phase was separated with sedimentation and the concentration of F was determined by UV-vis spectrophotometer (Hatch-Long DR-5000). All experiments were performed in duplicates and the average values were reported. The amount of F adsorbed at time t, q-t, was determined from the mass balance equation:

$$q_t = (C_0 - C_t) V / m$$

RESULTS AND DISCUSSION

Effect of pH

pH is one of the important factors that influences most of adsorption processes. F adsorption was investigated for 6 mg/L F concentration in the pH range of 3 to 9 as shown in Fig. 2. The highest adsorption of 61 % was observed at pH = 5.5. F adsorption was clearly affected by pH of the solution and decreased with increasing pH (Jinadasa *et al.*, 1993; Ayooob *et al.*, 2008; Kumar *et al.*, 2009).

Surface hydroxyl groups in the structure of functional groups are amphoteric and can act as either an acid or base by adsorbing or desorbing H⁺. In high pH presence of OH⁻ ions can interference with F

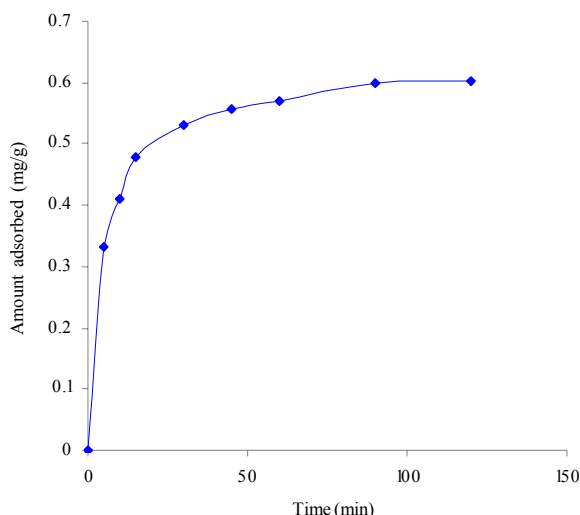


Fig. 1: Effect of contact time on fluoride adsorption on Lewatit FO 36 (F initial concentration = 6 mg/L, Lewatit FO 36 dose = 3 g/L, pH = 5/5, Temp.= 25 °C)

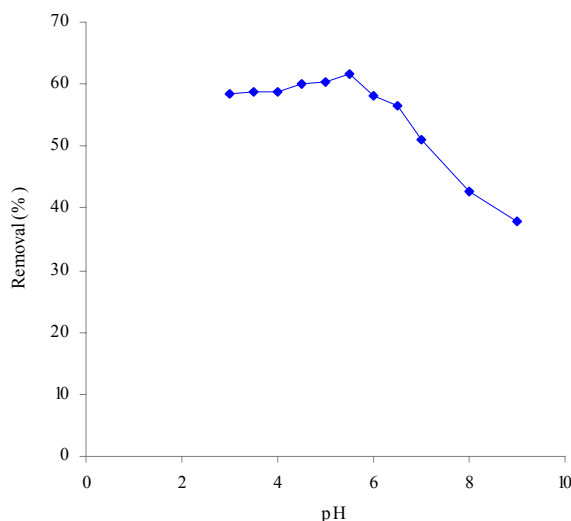


Fig. 2: Effect of pH on fluoride adsorption on Lewatit FO 36 (F initial concentration = 6 mg/L, Lewatit FO 36 dose = 5 g/L, temp = 25 °C, contact time = 120 min)

adsorption because of the same charge and radius of F and hydroxide ions and the competition for the active site by OH⁻ and electrostatic repulsion of F ions by the negatively charged adsorbent surface at high pH (Ayoob *et al.*, 2008; Kumar *et al.*, 2009). (Any FeOOH dissolution did not appear at pH 3).

Effect of contact time

F adsorption as a function of contact time was studied for determining the equilibration time. Effect of contact time on amount of F adsorbed with Lewatit FO 36 is shown in Fig. 1. Maximum uptake was obtained within the first 10 min of contact time that increased rapidly and after that rose slowly in the following 100 min. A further increase in contact time had a negligible effect on the adsorption. In some studies a similar trend was also observed during the adsorption of F onto other metal oxy-hydroxide materials (Tang *et al.*, 2009).

Equilibrium of adsorption

Fruindlich and Langmuir isotherms are useful models for the description of adsorption process by different adsorbents. Equilibrium adsorption of F was conducted at seven different concentrations, ranging from 3 to 6 mg/L at pH=5.5. The Freundlich model(Freundlich 1906) refers to surface heterogeneity of the adsorbent:

$$\text{Log}(q_e) = \text{log } K_f + 1/n \text{ log } C_e$$

Where, K_f and $1/n$ are Freundlich constants, associated with adsorption capacity and adsorption intensity, respectively.

The Freundlich plots between $\text{log } q_e$ and $\text{log } C_e$ are shown in Fig 3.

Langmuir model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate in the plane of the surface.

$$1/q_e = 1/q_m + 1/q_m b C_e$$

Where, q_e is amount adsorbed at equilibrium concentration C_e , q_m and b are the Langmuir constants representing adsorption capacity and Langmuir constant energy of adsorption, respectively. The plots of $1/q_e$ as a function of $1/C_e$ for the adsorption of F are shown in Fig. 3. The monolayer capacity (q_m) has been evaluated from intercept of this plots and Langmuir constant (b) has been evaluated from the slope of graph. The plots were found liner with >0.98 correlation coefficients that showed that Langmuir model was

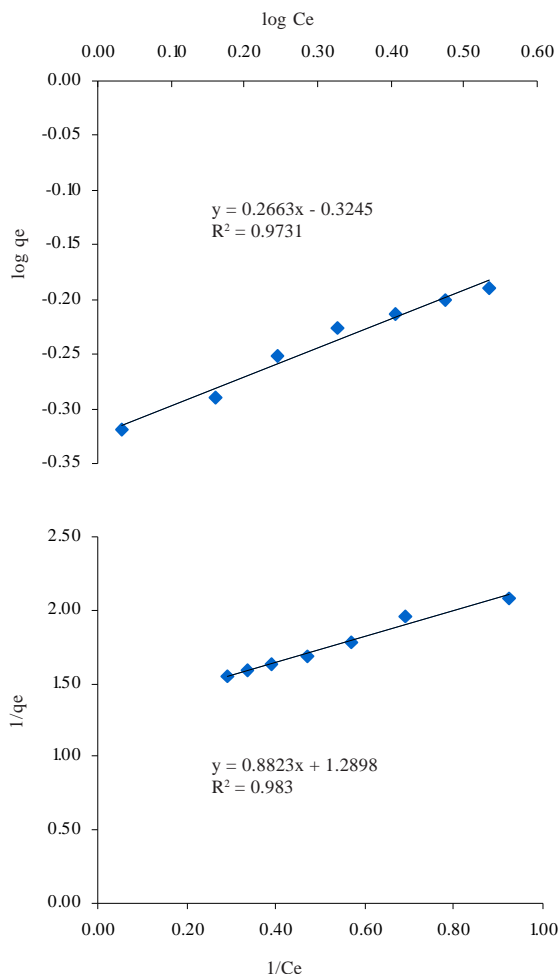


Fig. 3: Isotherms modeling of F adsorption on Lewatit FO36.1)Fruindlich Isotherm 2)Langmuir model

applicable to the present study. This means that the F adsorption is in the form of monolayer coverage on the surface of the adsorbent (Jinadasa *et al.*, 2009). In this study, it has been demonstrated that Lewatit FO 36 can remove fluoride with 61% efficiency where F concentration is less than 4 mg/L. The optimum removal was observed at 3 to 5.5 pH ranges and Langmuir model was applicable for this study.

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