ORIGINAL ARTICLE

Fluoride Removal from Aluminium Finishing Wastewater by Hydroxyapatite

Paraschos Melidis

Abstract The hexavalent chromium toxicity forces the aluminium finishing industry to use fluoride-containing chemicals in order to improve aluminium passivation. Disposal of industrial wastewaters containing excess concentration of fluoride to surface and ground waters can cause several health hazards. Effluents containing fluoride need treatment to reduce their concentration to disposable values before being discharged into public sewage. In this study, fluoride-containing wastewater from the aluminium finishing industry was firstly treated by precipitation at pH 12.5, achieving residual fluoride concentrations of 8.69 ± 1.84 mg/L from an initial concentration of 74.5 ± 4.6 mg/L, and then by adsorption of the remaining solution onto hydroxyapatite (HAP), resulting in fluoride effluent concentrations of 4.09 ± 0.16 mg/L. The total fluoride removal efficiency was 94.5 %. The sorption onto HAP data fitted well the Freundlich ($r^2=0.992$) and Langmuir ($r^2=0.994$) models. The adsorption capacity indicator (K_F) was equal to 0.723. The dimensionless constant R_L of 0.62 indicates favorable sorption of fluoride onto HAP. It is concluded that the adsorption step using HAP can be used as a post-treatment to remove fluoride from aluminium finishing industry wastewater.

Keywords Aluminum finishing industry · Wastewater treatment optimization · Fluoride removal · Hydroxyapatite · Precipitation · Absorption

1 Introduction

The increasing interest of construction market on aluminium use has resulted in the production of large quantities of wastewaters generated from the chemical treatment of the aluminium surface. These wastewaters consist of large volumes of rinse water and smaller amounts of spent finishing solutions (Barros et al. 2008; Saunders et al. 1982; EC reference documents 2006). Among several organic and inorganic contaminants, including dissolved aluminium, high levels of fluoride are also present in the case of the non-chromium-containing aluminium passivation method that uses hexafluorotitanate (Chen et al. 2014; Grilli 2010). The treatment of fluoride-containing wastewaters is of high concern and strictly regulated since fluoride discharge into surface water can lead to ground water contamination, with various possible

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adverse effects on human health (Boulétreau et al. 2006). The current methods that are widely applied in removing fluoride from wastewaters are precipitation (Reardon and Wang 2000) and adsorption (Singh et al. 2013; Bhatnagar et al. 2011). Reverse osmosis, molecular sieves and ion exchange can also be used (Castel et al. 2000), although such methods are expensive and applied only in the final polishing of the treated effluent (Bejaoui et al. 2014). The wastewater treatment systems of the aluminium finishing industry conventionally include pH neutralization, precipitation using calcium hydroxide solution, polyelectrolyte addition, gravity clarification, and sludge dewatering processes (Nath and Dutta 2010). However, CaF_2 has the lowest solubility in water among the alkali earth metals (0.0016 g/100 mL). Generally, lime is used as a calcium source that reduces fluoride concentration down to 10–20 mg/L and contributes positively to wastewater alkalinity by increasing effluent pH. The clarified effluent is commonly discharged to domestic wastewater treatment plants or to a regional receiving stream when discharge limits are met. Adsorption is often proposed as a simple, robust, low cost method to decrease the levels of fluoride ions below the discharge limits (Ezzeddine et al. 2014; Tomar et al. 2014). Large number of low cost adsorption materials has been tested, such as calcite (Hamdi and Srasra 2007), activated and amorphous alumina (Kumar et al. 2014), natural materials like clay, zeolite, charcoal, bleaching earth and red mud (Oguz 2007; Wu et al. 2007; Zhou et al. 2004). Among them, activated carbon is the only effective absorbent at pH below 3.0. As an additional treatment step, calcium hydroxyapatite adsorption was examined in this study to remove residual fluoride from aluminium finishing industry wastewaters.

In this work, calcium hydroxide precipitation and adsorption onto hydroxyapatite were employed in order to evaluate the fluoride removal efficiency in an aluminium finishing industry wastewater treatment plant. It is noteworthy that this study examines for the first time the effectiveness of the implementation of HAP absorption after $Ca(OH)_2$ precipitation in real fluoride-rich industrial wastewaters.

2 Materials and Methods

2.1 Hydroxyapatite Synthesis

Hydroxyapatite was synthesized according to He and Cao (1996). In brief, 20 g of $Ca(OH)_2$ was mixed with 200 mL of diluted in water H_3PO_4 (1:5) and heated at 85 °C for 6 h. After filtration, the pH was adjusted to 12 using a saturated NaOH solution and boiled for 40 min. The white sediment produced was filtered, washed with deionized water to neutrality and dried at 105 °C.

2.2 Experimental Set-up

The fluoride-containing wastewater was freshly collected from an aluminium finishing industry near Xanthi, Northern Greece (41°8′N, 24°53′E) and consisted of rinse waters and spent finishing solutions. Aluminium and fluoride concentrations of the inffluent ranged between 54.2–98.4 and 66.5–79.5 mg/L, with mean values of 76.3 and 74.2 mg/L, respectively. The influent pH was within 7.10 and 7.48 with a mean value of 7.29, while suspended solids fluctuated between 215 and 345 mg/L, with a mean value of 280 mg/L. Two experimental setups were carried out at pH 10.5 and 12.5 in order to remove fluoride using calcium hydroxide. The fluoride concentration remained after precipitation was reduced during the third experimental set where hydroxyapatite adsorption was implemented.

2.3 Hydroxyapatite Adsorption

The batch equilibration method was employed for process optimization. In details, 1000 mL of the treated (with precipitation) wastewater from experiment II containing ca 12 mg/L fluoride were mixed with different HAP doses (0.4 to 4 g) in glass vials of 2 L and the mixture was subjected to gentle agitation at 20 °C for a time period of 240 min. The solution was then filtered and the residual fluoride was analyzed through an ion selective electrode (ISE, Crison). The amount of fluoride adsorbed onto HAP was estimated by using the formula: $q_e = \frac{(C_o - C_e)V}{m}$, where q_e represents the equilibrium adsorption capacity of fluoride per HAP mass used (mg/g), C_o and C_e represent the initial fluoride concentration and the fluoride concentration at equilibrium, respectively (in mg/L), V is the volume of the treated (with precipitation) wastewater, and m the weight of HAP used (g).

3 Results and Discussion

3.1 Defluoridation Experiments

3.1.1 Fluoride Removal by Precipitation at pH 10.5 and 12.5

During the first experimental period, fluoride ions were removed from wastewater by precipitation. Calcium hydroxide solution was added and monitored through a pH controller until pH being adjusted to the desired pH values (10.5 or 12.5) since pH is an essential factor that affects the degree of fluoride precipitation (Hartinger 1994; Warmadewanthi and Liu 2009; Larsen et al. 1993). By increasing pH through calcium hydroxide addition, calcium concentration is increased and higher amount of CaF_2 is precipitated, according to solubility product (Rabosky and Miller 1974). Under these conditions, dissolved fluoride was combined with calcium cations and calcium fluoride was precipitated. Figure 1 presents the initial and the remaining fluoride concentrations at pH 10.5 and 12.5. At pH 10.5, fluoride concentration had a minimum value of 13.5 mg/L and a maximum value of 16.9 mg/L with a mean of 15.0 mg/L, while the respective values were 4.9, 11.0 and 9.1 mg/L at pH 12.5. The fluoride removal efficiencies were estimated to be 79.7±1.5 and 88.3±2.6 % at pH 10.5 and 12.5, respectively. As it is shown in Fig. 1, the pH increase resulted in improving fluoride removal by 5.9 %. In accordance to our results, Islam and Patel (2007) found 80.6 % fluoride removal during wastewater treatment with quick lime, resulting in a final fluoride concentration of 9.7 mg/L. Similar precipitation efficiencies were determined by Rabosky and Miller (1974), achieving 40 and 92 % fluoride removal at pH 11 and 12, respectively. Finally, fluoride removal of 90 % was achieved from aluminum fluoride manufacturing wastewater by using calcium hydroxide precipitation (Ezzeddine et al. 2014).

3.1.2 Fluoride Removal by Adsorption

After the precipitation step with $Ca(OH)_2$ and the removal of significant amount of fluoride (88.36 %), the treated wastewater required polishing in order to meet the discharge limits (8 mg/L). In this study, adsorption onto hydroxyapatite was used as post-treatment and equilibrium studies were carried out to determine maximum fluoride removal conditions.

Figure 2 presents the dependence of residual fluoride concentration on the HAP amount. It is obvious that the required limits (residual fluoride lower than 8 mg/L) were met when HAP
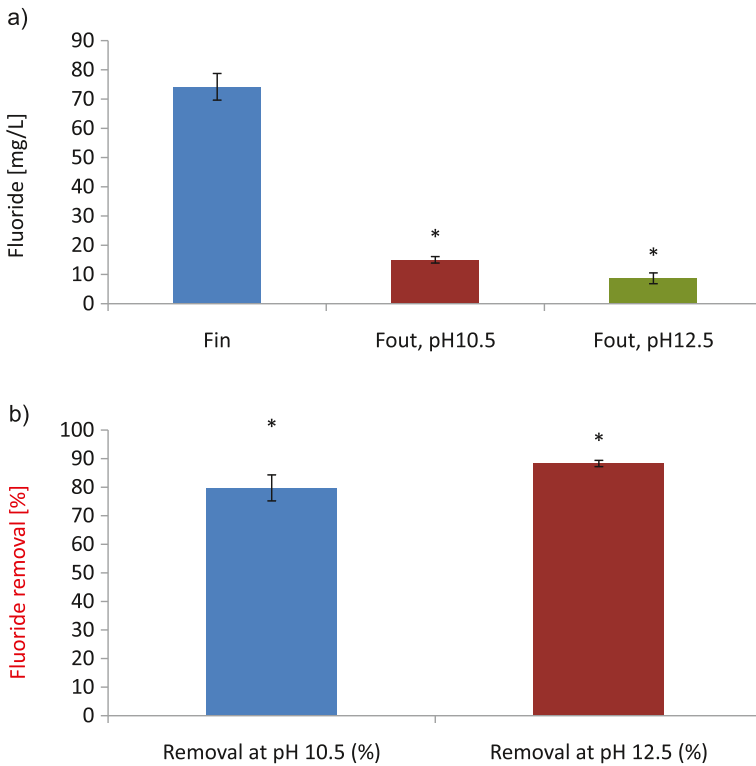
Fig. 1 Fluoride concentrations before and after Ca(OH)$_2$ precipitation at pH 10.5 and 12.5 (**a**) and their respective removal efficiencies (**b**). Asterisk (*) indicates statistically significant differences (ANOVA-Duncan's test for $n=10$)

amount higher than 1.5 g/L was applied. Indeed, the amount of HAP significantly influences the extent of fluoride adsorption (Gao et al. 2009). The lowest residual concentration achieved was 4.09±0.16 mg/L at HAP amount of 4.0 g/L. Adsoption onto HAP enhanced the fluoride removal by 6.2 %, achieving an overall fluoride removal of 94.5 %. Gao et al. (2009) examined various HAP-based adsorbing materials, resulting in removal efficiencies of 88 to 90.9 %, while fluoride removal of 86.3 % was determined by Mourabet et al. (2012) using HAP.

3.2 Adsorption Isotherm Development

The adsorption system is described by an equilibrium isotherm (Fig. 3). The fluoride concentration in equilibrium and the fluoride ion adsorbed on HAP (adsorption equilibrium) were non-linear and the Langmuir and Freundlich equations were used to describe the process. The quantity of fluoride adsorbed on HAP depended on fluoride concentration, solubility and polarity, as well as temperature.

Equation (1) describes the empirical Freundlich model, while Eq. (2) describes the commonly used Langmuir model:
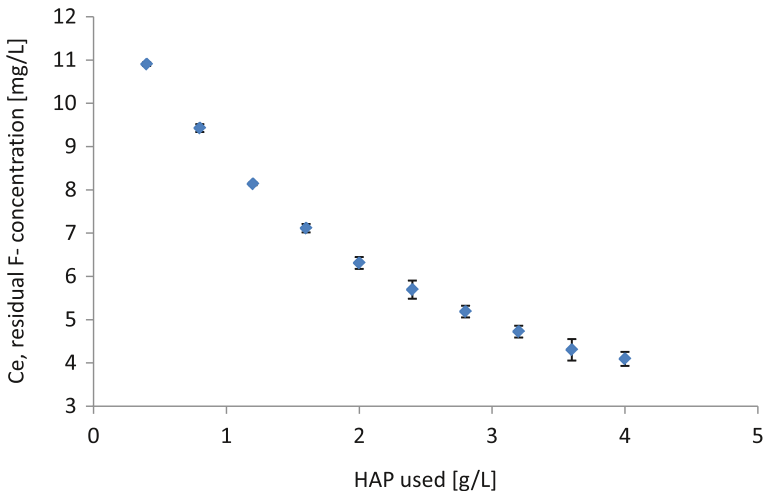
$$q_e = K_F C_e^{\frac{1}{n}} \tag{1}$$

Fig. 2 Effect of HAP amount on fluoride adsorption ($n=10$)

and

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \qquad (2)$$

where: q_e is the equilibrium adsorption capacity (F⁻ adsorbed per mass of adsorbent, mg F⁻ / g HAP); q_m is the maximum fluoride amount adsorbed on HAP (mg/g); K_L is the Langmuir adsorption equilibrium constant (L$_{wastewater}$/mg F⁻); K_F is the empirical Freundlich capacity factor (F⁻ adsorbed per mass of adsorbent, mg F⁻/g HAP); C_e is the equilibrium F⁻ concentration in treated wastewater after adsorption (mg/L); $1/n$ is the empirical Freundlich intensity parameter which indicates the strength of adsorption.

Figure 4a presents the well fitted adsorption isotherm of F⁻ and HAP by the Freundlich isotherm model. The adsorption capacity constant K_F (mg/g) and the adsorption intensity constant n related to surface sorption were determined using the logarithmic form of Eq. (2):
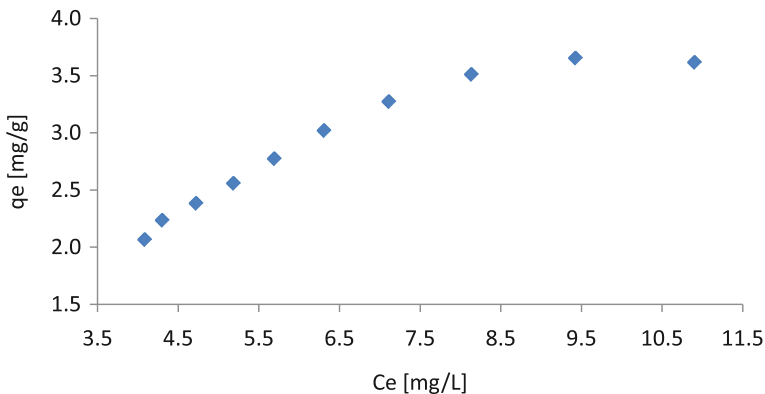

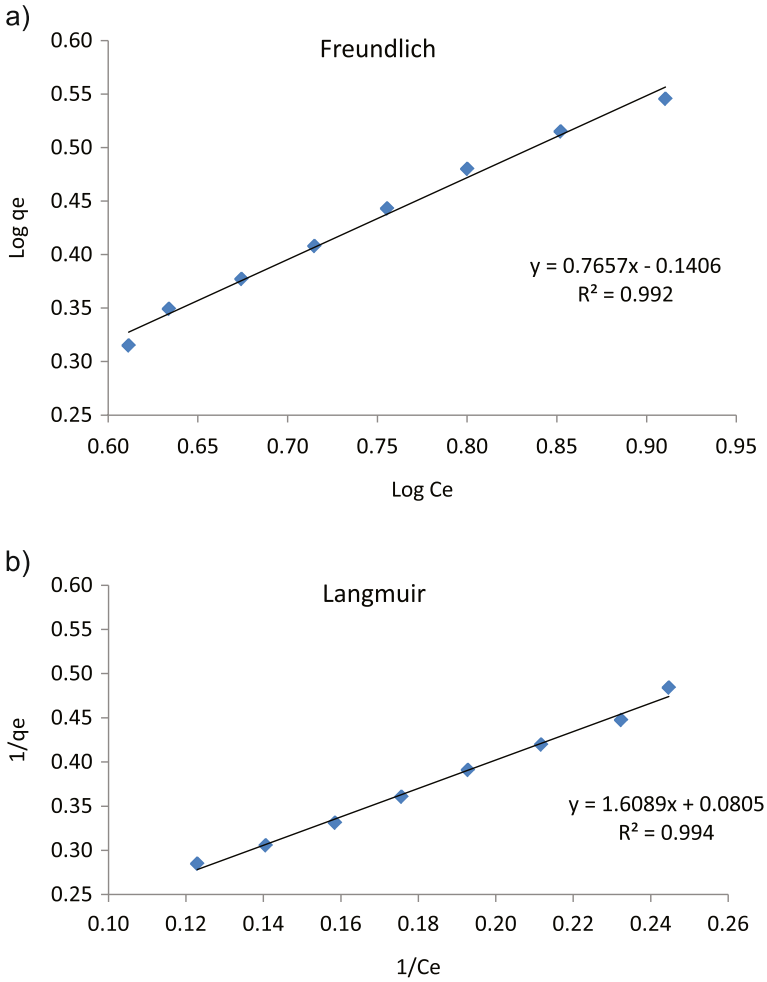**Fig. 3** Isotherm construction using the non-linear method

Fig. 4 Freundlich (**a**) and Langmuir (**b**) adsorption isotherms of F⁻ on HAP

$$\log(q_e) = logK_F + \left(\frac{1}{n}\right)logC_e \qquad (3)$$

by plotting the log(q_e) versus the log(C_e), where the slope and the intercept of this linear plot express these constants.

These were found to be equal to 0.723 and 1.31, respectively (Table 1). Interestingly, much higher constant values (1.45 and 5, respectively) have been determined by Mourabet et al. (2012). In this study, the heterogeneity parameter ($1/n$) of 0.77, which depended on the nature and strength of the adsorption process, indicated a normal distribution of the energy sites; here $1/n$ denoted that 77 % of the active sites where adsorption took place had equal energy and the sorption process was favorable. The adsorption capacity indicator K_F shows the ratio of the amount of F⁻ on the HAP surface to the amount of F⁻ in the solution and had a value of 0.723, which was indicative of effective fluoride sorption onto HAP. K_F values within 0–1 have been reported to correspond to favorable adsorption conditions (Liang et al. 2011). The

experimental equilibrium data fitted well to the Freundlich equation since the determination coefficient was $r^2=0.992$.

The quantitative description of a monolayer fluoride formation on the outer surface of the HAP was evaluated by the use of the Langmuir model, assuming that a fixed number of approachable places in the HAP surface were available, where most of them had the same energy and no displacement of fluoride occurred at HAP surface. At the equilibrium state, the fluoride adsorption rate was equal to the fluoride desorption rate from the surface of the HAP. The Langmuir constants were determined by plotting $1/C_e$ vs $1/q_e$ using the equation:

$$\frac{1}{q_e} = \left(\frac{1}{q_m}b\right)\left(\frac{1}{C_e}\right) + \frac{1}{q_m} \tag{4}$$

and were calculated from the slope and the intercept of the linear plot (Fig. 4b). The constant q_m (maximum amount of the adsorbent), which linked directly to the adsorbed fluoride from the solution, was equal to 12.4 mg/g (Table 1). Furthermore, the binding energy constant K_L was equal to 0.05 L/mg. Mourabet et al. (2012) estimated these constants as equal to 3.12 mg/g and 0.34 L/mg, respectively. The experimental data revealed that the Langmuir adsorption isotherm for fluoride adsorption onto HAP was characterized by a high $r^2=0.994$.

The separation factor R_L, which was calculated by the Langmuir constant K_L and the initial concentration C_o, was used to predict the affinity between the fluoride in the solution and the HAP. The dimensionless constant R_L is expressed by the equation:

$$R_L = \frac{1}{1 + K_L C_o} \tag{5}$$

and indicates that the Langmuir isotherm is linear if $R_L=1$, reversible if $R_L=0$, unfavorable if $R_L>1$ and favorable if $0<R_L<1$. The fluoride adsorption onto HAP appeared to be favorable because R_L was equal to 0.62 and fulfilled the necessity $0<R_L<1$. In contrast, lower R_L values (0.07–0.22, depending on the initial fluoride concentration examined) were reported by Mourabet et al. (2012).

3.3 Cost Evaluation

At the present time, the most common commercial adsorbents for fluoride removal from aqueous solutions are activated charcoal (809 €/tn) and activated alumina (981 €/tn). In comparison to these commercially available adsorbents, the total cost of calcium hydroxide (142 €/tn) and HAP synthesized from calcium hydroxide and phosphoric acid (485 €/tn), is much lower. Although fluoride removal has been extensively studied in aqueous solutions, only a few reports exist in the international literature about the cost of fluoride removal, focusing mainly on drinking water treatment. Elazhar et al. (2009) calculated the operating cost to 0.212 €/m³ for fluoride removal from 2.32 to 1 mg/L using nanofiltration. Lahnid et al. (2008) estimated the operating cost during electrodialysis of drinking water to 0.154 €/m³. In this study, real wastewater from aluminium finishing industry was treated by calcium

Table 1 Langmuir and Freundlich adsorption constants for fluoride adsorption onto hydroxyapatite

Langmuir		Freundlich	
q_m (mg/g)	12.42	K_F (mg/g)	0.723
K_L (L/mg)	0.050	n	1.31
r^2	0.994	r^2	0.992

hydroxide at pH 12.5 under a cost of 0.166 €/m^3 in order to decrease fluoride concentration from 74.2 to 9.1 mg/L. The cost of the second treatment step, i.e., adsorption onto HAP as described in the current study to further reduce fluoride concentration to 4 mg/L, was estimated to be 0.89 €/m^3.

4 Conclusion

Fluoride-containing wastewater from the aluminium finishing industry was firstly treated by precipitation using calcium hydroxide at different pH values, and then by adsorption onto hydroxyapatite because of its high efficiency and easy handling. The highest fluoride removal by precipitation was obtained at pH 12.5, achieving residual fluoride concentrations in the remaining solution from 4.9 to 11.0 mg/L (removal efficiency of 88.3 %) with a mean value of 8.7 mg/L. The examination of fluoride adsorption onto hydroxyapatite demonstrated that fluoride was strongly adsorbed on hydroxyapatite surface and its equilibrium was almost accomplished within 4 h, achieving residual fluoride concentration of 4.1 mg/L and an overall removal efficiency of 94.5 %. The sorption data fitted well into the Freundlich and Langmuir models, showing a maximum adsorption capacity of 12.4 mg/g. The adsorption capacity indicator (K_F) was equal to 0.723, indicating favorable fluoride sorption onto hydroxyapatite. Moreover, the dimensionless constant R_L indicated that fluoride adsorption onto hydroxyapatite was favorable since it fulfills the necessity $0 < R_L < 1$ ($R_L = 0.62$). Therefore, the additional adsorption step using hydroxyapatite can be used as post-treatment to remove fluoride from aluminium finishing industry wastewaters.

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