

A NEW ADSORBENT FOR FLUORIDE REMOVAL: THE UTILIZATION OF SLUDGE WASTE FROM ELECTROCOAGULATION AS ADSORBENT

YILMAZ A.E.^{1,*}
FIL B.A.^{1,2}
BAYAR S.¹
KARCIOĞLU KARAKAŞ Z.¹

¹Atatürk University, Engineering Faculty,
Environmental Engineering Department, Erzurum, Turkey
²Balikesir University, Faculty of Engineering
Department of Environmental Engineering, Balikesir, Turkey

Received: 12/06/2014
Accepted: 09/12/2014
Available online: 28/02/2015

*to whom all correspondence should be addressed:
e-mail: aerdemy@atauni.edu.tr

ABSTRACT

This work investigated the potential of calcined electrocoagulation sludge (CES) within metals hydroxide generated during removal of boron using Al electrode for adsorption of fluoride from aqueous solution. The effects of contact time, pH of the solution (2-10), stirrer speed (50-450 rpm), initial concentration (5-100 mg l⁻¹), adsorbent dose (1-4 mg l⁻¹), solution temperature (293-333 K) and particle size (0.125-1000 µm) on fluoride removal were investigated. All the experiments were carried out by batch mode. It was found that the maximum adsorption takes place within 2 h at pH 6.0. The adsorption removal increased with increase in the adsorbent dose, but decreased with increase in fluoride concentration. It was found that the adsorption removal decreases with increase in temperature, which showed that the adsorption process was exothermic in nature. The decrease in particle size increased fluoride removal efficiency. The maximum adsorption capacity (q_m) increased from 45.5 to 124.6 mg g⁻¹ when the adsorbent dosage was adjusted to 1 instead of 4 g l⁻¹. The Freundlich isotherm and Langmuir isotherm were used to fit the data of equilibrium experiments. The adsorption data fitted well into the linearly transformed Langmuir equation. The efficiency of CES to remove fluoride was found to be 99.99% at pH 6, contact time for 2 h, dose of 4 g l⁻¹, when 25 mg l⁻¹ of fluoride was present in 100 ml of water. Comparison with literature reported values of q_m, it was found that CES was an attractive adsorbent.

Keywords: Fluoride, adsorption, waste utilization, calcined electrocoagulation sludge

1. Introduction

Fluoride is an essential element for both humans and animals depending on its concentration in drinking water. According to the World Health Organization guidelines, the maximum concentration limitation of fluoride is 1.5 mg l⁻¹ for drinking water ((WHO), 1993). Fluoride is beneficial to human when present within permissible limits of 0.5–1.5 mg l⁻¹ for the calcinations of dental enamel and bone formation. Concentrations higher than this not only affects teeth and skeleton but also cause several neurological damages in severe cases (Kagne *et al.*, 2008). Thus, water and wastewater containing high fluoride concentration (> 1.5 mg l⁻¹) must be treated before used or discharged. Various treatment procedures have been reported for the removal of excess fluoride from water e.g. adsorption (Tor *et al.*, 2009), precipitation-micro filtration (Lu and

Liu, 2010), ion-exchange (Solangi *et al.*, 2009), electrocoagulation (Behbahani *et al.*, 2011, Khatibikamal *et al.*, 2010), reverse osmosis (Sehn, 2008) and electrodialysis (Banasiak and Schäfer, 2009). Among the methods, adsorption technique is economical, efficient and produces high-quality water. The efficiency of this technique mainly depends on nature of the adsorbents (Viswanathan *et al.*, 2009).

In present work, calcined electrocoagulation sludge was used to remove fluoride from synthetic aqueous NaF solutions and deionized water. The effect of various factors such as solution pH, the adsorbent dosage, initial fluoride concentration, stirring speed, particle size and temperature on the removal of fluoride have been investigated. The main objective of this study was to investigate the fluoride removal potential of calcined electrocoagulation sludge by batch adsorption studies.

2. Materials and methods

2.1 Materials

All reagents used in the present study were of analytical grade purchased from Merck. A stock solution of fluoride was prepared by dissolving known weight of sodium fluoride in distilled water and desired working fluoride solution was prepared from stock solution by appropriate dilution.

2.2 Adsorbent preparation

The sludge used for the adsorption tests was obtained from electrocoagulation experiments with aluminum electrodes. The electrolyte was a geothermal water containing boron. The residue sludge from electrocoagulation was filtered and then dried at 105 °C for approximately 2 hours. The dried sludge was grinded to powder in a grinder. The dried sludge was calcined at 773 K for 4 h for preparation of the adsorbent used for all experimental results reported in this work. Experiments had shown that leached concentration of boron in solution remain under maximum limit of 1 mg l⁻¹ with dried sludge, framed by the W.H.O.

2.3 Batch adsorption experiments

Batch adsorption experiments were carried out for an adsorption period of 120 min in a 250 mL erlenmeyer flask, filled with 100 ml of water containing desired fluoride concentrations. Flasks in which different amounts of the adsorbent were added were allowed to shake for 120 minute in a shaker. The effect of adsorbent dosage on removal was studied with adsorbent dosage varying from 0.1 to 0.4 g/100 ml while maintaining the fluoride concentrations at 5 and 100 mg l⁻¹. The effect of fluoride concentration on removal was studied at an initial pH of 2.0-10.0 intervals. Effect of pH on the fluoride removal was studied using 0.2 g of adsorbent dosage for the fluoride concentrations of 5 and 100 mg l⁻¹. Control experiments were carried out duplicate to verify the fluoride adsorption on adsorbent surfaces. The amounts of fluoride adsorbed were calculated from the concentrations in solutions before and after adsorption. The amount of fluoride adsorbed (mg g⁻¹), (q_e), onto calcined sludge was calculated from the mass balance equation as follows:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C_0 and C_e are the initial and equilibrium liquid phase concentrations of fluoride solution (mg l⁻¹), respectively; V the volume of fluoride solution (L), and W the mass of calcined electrocoagulation sludge sample used (g).

2.4 Methods of analysis

Following agitation, the adsorbent and adsorbate were separated through filtration and fluoride content of the filtrate solution was spectrophotometrically determined. A high precision, double beam spectrophotometer (Shimadzu UV-160A) was used to measure the absorbance of fluoride solution at

wavelengths between 200 and 800 nm and 570 nm was chosen as the suitable wavelength in this study to measure the fluoride concentration in water (Brownley and Howle, 1960). The equivalent amount of adsorbed fluoride was calculated from the difference in their initial and final concentrations (Greenberg *et al.*, 1992). The pH and temperature were measured by a multimeter (WTW, Multiline).

3. Results and discussion

3.1 Effect of solution pH

The initial pH of solution is one of the important parameters that could obviously affect the extent of fluoride adsorption. Therefore, the adsorption of fluoride on the calcined electrocoagulation sludge was examined at different pH values ranging from 2.0 to 10.0. The effect of pH on the adsorption of fluoride by using calcined electrocoagulation sludge is shown in Figure 1.

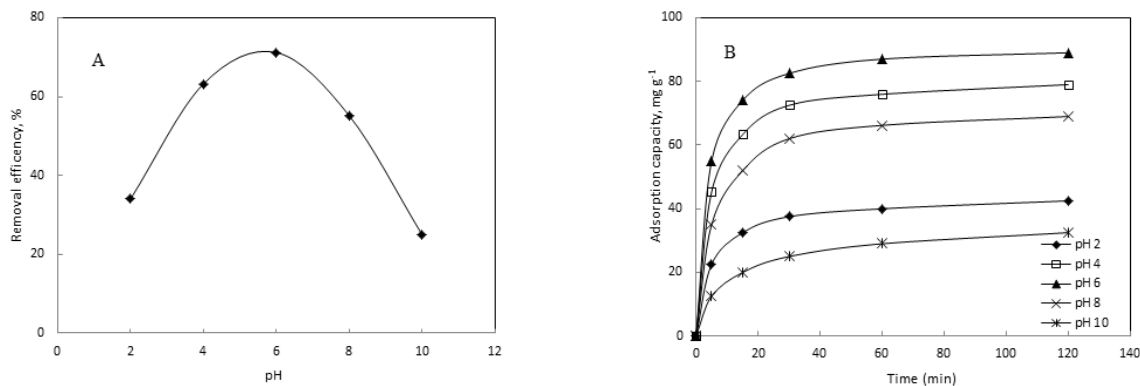
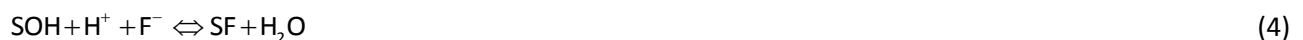


Figure 1. Relationship between (A) the percentage removal of fluoride, (B) the adsorption capacity of fluoride and the time, for various pH (solution temperature=293 K, initial fluoride concentration = 25 mg l⁻¹, amount of adsorbent = 0.2 g, stirring speed = 300 rpm)

The results showed that adsorption was the highest at the pH 6. The adsorption of fluoride increases with increased pH, reaches a maximum of 71.2% at pH 6.0, and then decreases with further increase in pH (Figure 1A). Figure 1B shows changes in the adsorption capacity of fluoride with time for various pH values (2.0, 4.0, 6.0, 8.0 and 10.0). The amount of fluoride adsorbed is strongly decreased in the acidic pH range, may be due to the formation of weak hydrofluoric acid or the change of adsorbent chemical structure. At pH above 6.0, fluoride removal decreases sharply because of stronger competition with hydroxide ions on adsorbent surface. The adsorption mechanism is an interaction between the metal oxides at the surface of the calcined electrocoagulation sludge and fluoride ions which can be explained by the following steps. The specific adsorption of fluoride on adsorbent surface (S) follows the schemas (Tor, 2006):



which combined gives



The obtained result for maximum adsorption is in agreement with fluoride removal studies in literature (Tor, 2006, Mohapatra *et al.*, 2004).

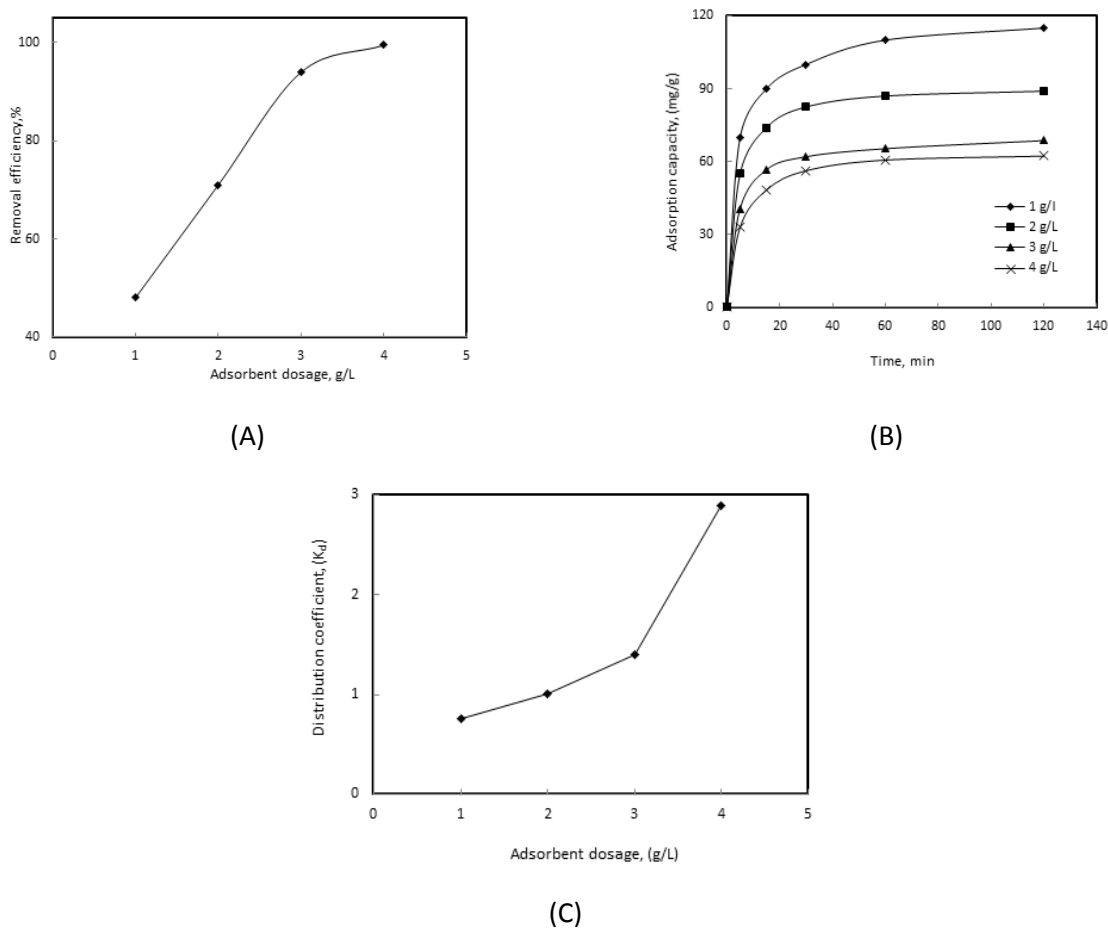


Figure 2. Relationship between (A) the percentage removal of fluoride, (B) the adsorption capacity of fluoride and the time, for various adsorbent dosage, (C) distribution coefficient for various adsorbent dosage (solution temperature: 293 K, initial fluoride concentration: 25 mg l⁻¹, solution pH: 6.0, stirring speed: 300 rpm).

3.2 Effect of adsorbent dosage

The effect of adsorbent dosage on the removal of fluoride from aqueous solution was studied at pH 6.0 and fluoride concentration of 25 mg l⁻¹ for 2 h and the obtained results were shown in Figure 2. It can be seen that the removal efficiency increased with increasing dosage of adsorbent. The highest removal efficiency was obtained at 0.4 g calcined electrocoagulation sludge (99.5%) (see Figure 2A). In Figure 2B, it can be seen that the adsorption capacity of fluoride increases with increasing dosage of adsorbent.

The adsorption capacity of fluoride is the highest when the dosage of adsorbent is 0.4 g/100 mL. The influence of dosage of adsorbent is mainly related to its surface area. It is explained that the more the addition of adsorbent in the solution, the more the availability of active sites for the fluoride binding. A distribution coefficient, K_d , reflects the binding ability of the surface for an element and is dependent on pH of the solution and type of surface of the adsorbent. The distribution coefficient values for fluoride-adsorbed on calcined electrocoagulation sludge at pH 6.0 was calculated using the following equation (Tripathy *et al.*, 2006):

$$K_d = \frac{C_s}{C_w} \quad (5)$$

where C_s is the concentration of fluoride on the solid particles (mg kg^{-1}) and C_w is the equilibrium concentration in solution (mg m^{-3}). Figure 2C shows that the K_d value increases with an increase in adsorbent dose at constant pH that implies the heterogeneous surface of calcined electrocoagulation sludge. Because the surface is not homogeneous, the K_d values at constant pH changed with adsorbent dose (Tripathy *et al.*, 2006).

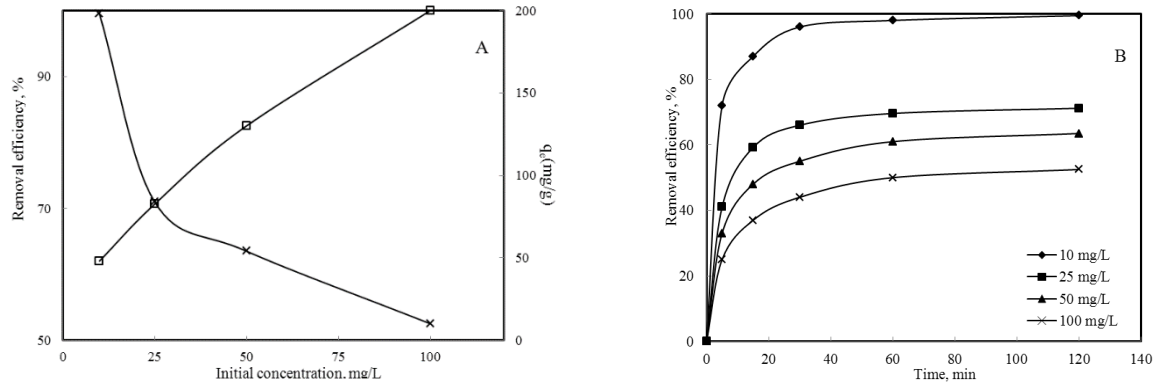


Figure 3. Relationship between (A) the percentage removal of fluoride and equilibrium concentration, (B) the adsorption capacity of fluoride and the time, for various initial fluoride concentration, (solution temperature: 293 K, adsorbent dosage: 2 g l⁻¹, solution pH: 6.0, stirring speed:300 rpm)

3.3 Effect of initial fluoride concentration

The effect of initial fluoride concentration on the removal efficiency was studied at different initial fluoride concentrations by keeping all other parameters constant such as adsorbent dose; 0.4 g/100 mL, solution pH 6.0, stirring speed; 300 rpm and contact time; 2 h. The effect of initial fluoride concentration on the removal efficiency is shown in Figure 3. The highest removal efficiency was obtained at 10 mg l⁻¹ initial concentration (99.5%) (see Figure 3A). It is clear from Figure 3B that the uptake of fluoride ions increases rapidly with time and reaches to saturation in 30 min. It was realized that increase in initial concentration decreased the removal efficiency. It may be because at higher adsorbate concentration, the binding capacity of the adsorbent approaches saturation, resulting in a decrease in overall percent removal. This could be due to the occupation of available surface area by fluoride ion. The results obtained are also consistent with the literature (Swain *et al.*, 2011). Besides, the results revealed that the amount of fluoride ions adsorbed per unit mass of the adsorbent is increased with an increase in concentration. This is due to the availability of higher number of fluoride ions per unit mass of adsorbent (Karthikeyan *et al.*, 2009).

3.4 Effect of particle size

In order to evaluate the effect of particle size on the removal efficiency, the adsorption experiments were conducted in grain size range of 125–1000 μm , calcined electrocoagulation sludge of 0.2 g/100 mL and initial fluoride concentration of 25 mg l⁻¹ at initial pH 6.0. The results were given at Figure 4.

As seen Figure 4A, the increase in grain size decreased removal efficiency. In Figure 4B, it can be seen that the adsorption capacity of fluoride decreases with increasing particle size. It may be because at higher grain size, the binding capacity of the adsorbent approaches minimum level, resulting in a decrease in overall removal efficiency. As grain size increases, particle active surface area is reduced. As a result of reduction in particle active surface area, binding capacity of the adsorbent capacity is reduced. Depending on this result, the increasing grain size leads to decrease in removal efficiency.

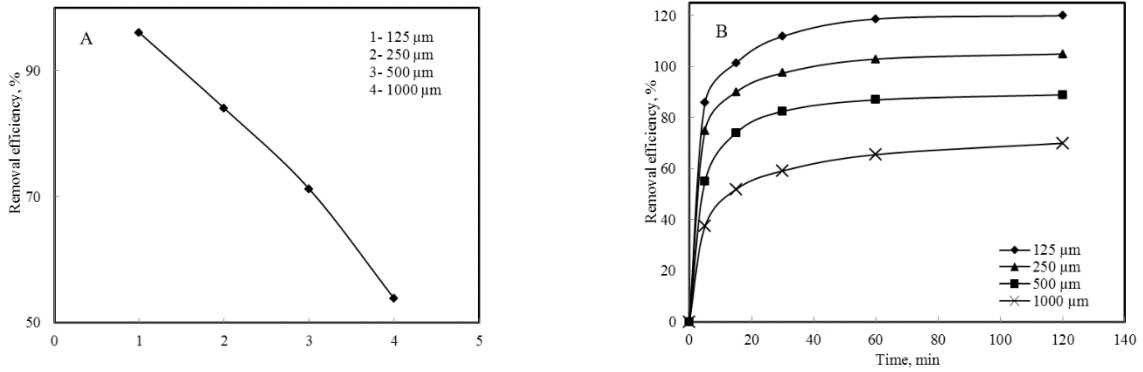


Figure 4. Relationship between (A) the percentage removal of fluoride and time, (B) the adsorption capacity of fluoride and the time, for various particle size, (solution temperature: 293 K, adsorbent dosage: 2 g l⁻¹, solution pH: 6.0, stirring speed: 300 rpm, initial fluoride concentration: 25 mg l⁻¹).

3.5 Effect of stirring speed

Stirring speed has important effects on the removal efficiency at the adsorption process. The influence of stirring speed on the fluoride removal efficiency was investigated by using four stirring speed. Adsorption experiments were carried out at various stirring speed (50, 150, 300 and 450 rpm) by keeping all other experimental conditions constant (adsorbent dosage; 0.2 g/100 mL; initial fluoride concentration; 25 mg l⁻¹, solution pH;6.0, temperature; 293 K). The fluoride removal efficiency is affected in the stirring speed range of 50-450 rpm so it can be concluded that the present adsorption process is stirring speed-dependent. The results were given in Figure 5. As seen Figure 5A, increasing the stirring speed to 300 rpm increased the removal efficiency. Higher stirring speed than 300 rpm decreased the removal efficiency. The sufficient contact between the adsorbent and adsorbate was not achieved at smaller stirring speeds than 300 rpm.

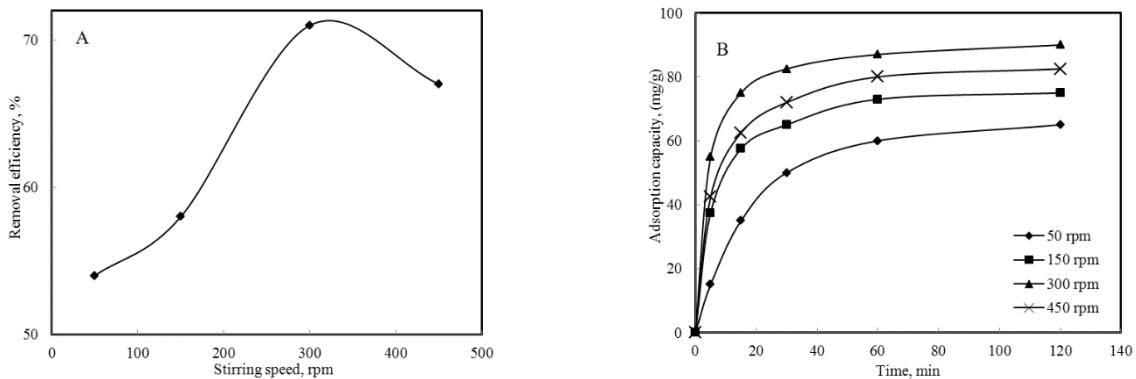


Figure 5. Relationship between (A) the percentage removal of fluoride and time, (B) the adsorption capacity of fluoride and the time, for various stirring speed, (solution temperature: 293 K, adsorbent dosage: 2 g l⁻¹, solution pH: 6.0, initial fluoride concentration: 25 mg l⁻¹)

Otherwise, centrifugal force affected on the adsorption process at the higher stirring speeds than 300 rpm. This forces a negative impact on the bonding between adsorbent and adsorbate. Therefore, removal efficiency decreased at the higher stirring speeds than 300 rpm. In Figure 5B, it can be seen that the adsorption capacity of fluoride increases with increasing stirring speed to 300 rpm and the decreases with increasing stirring speed.

3.6 Effect of solution temperature

In order to evaluate the effect of temperature on the removal efficiency, the adsorption experiments were conducted in temperature range of 293–353 K, calcined electrocoagulation sludge of 0.2 g/100 mL and initial fluoride concentration of 25 mg l⁻¹ at initial pH 6.0. The fluoride removal efficiency as a function of temperature shows that adsorption decreases with a rise in the temperature. The results were shown in Figure 6.

As investigated in Figure 6A, it was seen that increase in solution temperature decreased dramatically the removal efficiency. The same tendency was also observed at adsorption capacity as a function contact time. The decrease in adsorption capacity was demonstrated in Figure 6B. The decrease in adsorption capacity of calcined electrocoagulation sludge with temperature may be attributed to decrease in the number of available active surface sites for adsorption on the calcined electrocoagulation sludge. This situation supports the surface heterogeneity of oxide surfaces. The observation shows that the interaction between adsorbate and adsorbent is exothermic in nature. The results obtained were supported by the literature (Das *et al.*, 2003).

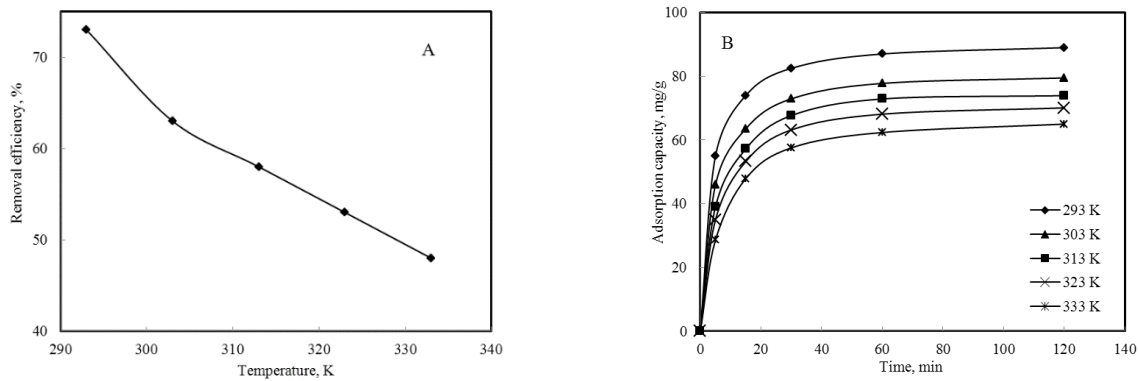


Figure 6. Relationship between (A) the percentage removal of fluoride and time, (B) the adsorption capacity of fluoride and the time, for various solution temperature, (adsorbent dosage: 2 g l⁻¹, solution pH: 6.0, initial fluoride concentration: 25 mg l⁻¹)

3.7 Adsorption isotherms

Equilibrium studies were carried out to determine the optimum conditions for maximum fluoride removal by calcined electrocoagulation sludge. Two general-purpose equilibrium models were used to fit the experimental data: (i) Langmuir and (ii) Freundlich isotherms;

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \quad (6)$$

$$\ln q_e = \ln K_F + \frac{1}{n} C_e \quad (7)$$

where q_m and K_L are the Langmuir constants related to the loading and energy of adsorption, K_F and n are the Freundlich temperature-dependent constants, C_e is the equilibrium concentration (mg l⁻¹), and q_e is the adsorption loading at equilibrium (mg g⁻¹), respectively.

Adsorption isotherms were obtained in terms of Equations (6) and (7) by using experimental adsorption results in these equations. The values q_m , K_L , K_F , R_L and n are summarized in Table 1.

Table 1. Langmuir and Freundlich constants for fluoride adsorption on calcined electrocoagulation sludge

| Adsorption isotherm | 293 K | 303 K | 313 K | 323 K | 333 K |
|---------------------|---------|---------|----------|----------|----------|
| Langmuir | | | | | |
| q_m | 44.248 | 32.575 | 23.311 | 21.053 | 18.248 |
| K_l | 0.279 | 0.178 | 0.133 | 0.123 | 0.110 |
| R^2 | 0.9973 | 0.9951 | 0.9957 | 0.9950 | 0.9947 |
| R_l | 0.125 | 0.183 | 0.231 | 0.245 | 0.267 |
| Freundlich | | | | | |
| K_F | 324.537 | 617.512 | 1443.029 | 1701.005 | 3341.583 |
| n | 1.542 | 1.089 | 0.797 | 0.761 | 0.639 |
| R^2 | 0.9905 | 0.9885 | 0.9901 | 0.9909 | 0.9899 |

It is obtained from R^2 values that the equilibrium data of the system was well explained by the Langmuir model when compared to the Freundlich model. By comparing results listed in Table 1, it is clear that equilibrium data fit Langmuir and Freundlich models. Correlation coefficient of Langmuir model is higher than that of Freundlich, which means that Langmuir sorption isotherm more accurately describe the sorption of fluoride adsorption on the sludge. The fact that the Langmuir isotherm fits the experimental data very well may be due to homogeneous distribution of active sites on the adsorbent surface. Also, as seen in Table 1, the maximum adsorption capacities for fluoride adsorption on the sludge at 293, 303, 313, 323 and 313 K were found to be 44.248, 32.575, 23.311, 21.053 and 18.248 mg g⁻¹, respectively. Maximum adsorption capacities of used adsorbent decreased with the increasing in temperature.

The essential feature of the Langmuir isotherm can be expressed by means of dimensionless constant separation factor or equilibrium parameter, R_l , which is calculated using the following equation (Doğan and Alkan, 2003):

$$R_l = \frac{1}{1 + K_l C_0} \quad (8)$$

R_l values lie between 0 and 1 indicating the on-going adsorption process is favorable for the dye using different adsorbents. According to the value of R_l the isotherm shape may be interpreted as follows:

| Value of R_l | Type of adsorption |
|----------------|--------------------|
| $R_l > 1.0$ | Unfavourable |
| $R_l = 1.0$ | Linear |
| $1 > R_l > 0$ | Favourable |
| $R_l = 0$ | Irreversible |

The results given in Table 1 show that the adsorption of fluoride on calcined the sludge from electrocoagulation is favorable. The q_m value obtained in this study is greater than those of reported and the results were compared in Table 2 (Viswanathan *et al.*, 2009, Meenakshi *et al.*, 2008, Ramdani *et al.*, 2010, Meenakshi and Viswanathan, 2007, Chen *et al.*, 2011, Islam *et al.*, 2011, Sairam Sundaram *et al.*, 2009, Ma *et al.*, 2007, Chang *et al.*, 2006).

3.8 Adsorption Kinetics

The adsorption kinetics of fluoride on the calcinated electrocoagulation sludge was defined by using three different kinetic models, which are pseudo-first order, pseudo-second order and intraparticle diffusion

models. The pseudo-first-order rate constant (k_1) and theoretical equilibrium adsorption capacities (Q_e) calculated from linear plot of $\ln(Q_e - Q_t)$ versus t , are shown in Table 3.

Table 2. The comparison of the Langmuir capacity constant of different adsorbents for fluoride removal

| Adsorbent | q_m , (mg g ⁻¹) | K_L , (l mg ⁻¹) | Reference |
|---|-------------------------------|-------------------------------|--|
| Carboxylated cross-linked chitosan beads | 11.110 | 0.035 | (Viswanathan <i>et al.</i> , 2009) |
| activated kaolinities | 0.782 | 0.133 | (Meenakshi <i>et al.</i> , 2008) |
| natural clay | 1.324 | 2.445 | (Ramdani <i>et al.</i> , 2010) |
| chelating resin (Ceralite IRA 400) | 1.658 | 16.863 | (Meenakshi and Viswanathan, 2007) |
| Al/Fe dispersed in porous granular ceramics | 1.788 | 0.313 | (Chen <i>et al.</i> , 2011) |
| polycinnamamide thorium (IV) ph | 4.749 | 0.540 | (Islam <i>et al.</i> , 2011) |
| nano-hydroxyapatite/chitin (n-HApCh) composite | 8.410 | 0.079 | (Sairam Sundaram <i>et al.</i> , 2009) |
| magnetic-chitosan particle | 22.490 | 0.0338 | (Ma <i>et al.</i> , 2007) |
| SiO ₂ /Fe ₃ O ₄ adopting sol-gel | 38.000 | 0.010 | (Chang <i>et al.</i> , 2006) |
| Calcinated electrocoagulation sludge | 44.248 | 0.279 | (In this study) |

Table 3. Comparison of the pseudo first-order and second-order and intraparticle diffusion adsorption kinetics constants at different temperatures

| Adsorption kinetics | 293 K | 303 K | 313 K | 323 K | 333 K |
|---|---------|--------|---------|---------|---------|
| Pseudo first-order | | | | | |
| q_e , mg.g ⁻¹ | 49.117 | 42.165 | 54.445 | 53.469 | 53.689 |
| k_1 , min ⁻¹ | 0.0993 | 0,0908 | 0.1086 | 0.1012 | 0.1023 |
| R^2 | 0.9899 | 0.9845 | 0.9880 | 0.9891 | 0.9877 |
| Pseudo second-order | | | | | |
| $q_{e,cal}$, mg.g ⁻¹ | 91.043 | 86.957 | 80.645 | 75.188 | 71.942 |
| k_2 , g.mg ⁻¹ .min ⁻¹ | 0.00317 | 0.0038 | 0.00262 | 0.00214 | 0.00184 |
| R^2 | 0.9999 | 0.9999 | 0.9997 | 0.9996 | 1 |
| Intraparticle diffusion | | | | | |
| k_d , mg g ⁻¹ .min ^{-1/2} | 8.4552 | 7.3349 | 8.4921 | 8.8017 | 8.9285 |
| C | 37.692 | 40.255 | 24.703 | 15.674 | 10.219 |
| R^2 | 0.9461 | 0.9618 | 0.9676 | 0.9631 | 0.9564 |
| $q_{e,exp}$, mg.g ⁻¹ | 87.657 | 82.126 | 72.087 | 65.343 | 59.897 |

Although the values of correlation coefficient is very good, $Q_{e,cal}$ determined from the model is not in a good agreement with the experimental values of $Q_{e,exp}$. Therefore it could be said that the fluoride adsorption on the calcinated electrocoagulation sludge does not follow the pseudo-first-order kinetic model. The graph of t/Q_t versus t for the linear pseudo-second-order model was plotted, and the second order rate constant k_2 and maximum adsorption capacity Q_e were calculated from the intercept and slope of this graph, respectively (Table 3). The correlation coefficient value is satisfactory (1.00), and the equilibrium adsorption capacity $Q_{e,cal}$ (91.043 mg g⁻¹) determined by using the second order model is almost as same as with the experimentally defined equilibrium adsorption capacity $Q_{e,exp}$ (87.657 mg g⁻¹). The intraparticle rate constant (k_{id}) and c parameters obtained from the plots of Q_t versus $t^{1/2}$ for the intraparticle diffusion model are given in Table 3. The value of c obtained from intraparticle diffusion model is not zero and the correlation coefficient is not satisfactory (0.9461), indicating that the intraparticle diffusion may not be the controlling factor in determining the kinetics of the process. Consequently, the kinetic data indicates that the fluoride adsorption on calcinated electrocoagulation sludge obeys the pseudo second order kinetic model ($R^2 = 0.9999$) more than intraparticle diffusion model and pseudo-first order kinetic model ($R^2 = 0.9845$), which suggests a

chemisorption process in this experiment. Pseudo-second order model is favorable for the adsorption of fluoride on the calcined electrocoagulation sludge.

3.9 Leaching of boron from adsorbent

Suitability of the sludge as an adsorbent for removal of pollutant not only depends on the adsorption capacity but also on the leached boron concentration to solution during adsorption (Yilmaz *et al.*, 2011). Table 4 shows the concentration of boron at different experimental conditions.

As seen Table 4, boron concentration leached to solution was increased with increasing adsorbent dosage. Leached boron concentration increases with increasing acidity and alkalinity. However, the effect temperature on leaching level of boron was at a negligible level. The leached boron concentration doesn't exceed the critical concentration limit (1.0 mg l^{-1}). Therefore, the sludge can be used as an effective adsorbent for removal of fluoride from aqueous solutions close to pH 6.0 and low adsorbent dosage.

Table 4. Boron concentration leached to solution at different experimental conditions

| Experimental parameters (25 mg l ⁻¹ fluoride concentration, pH 6.0, 293 K) | | | | | |
|--|------------------|------------------|------------------|------------------|---------|
| | 0.10 g adsorbent | 0.20 g adsorbent | 0.30 g adsorbent | 0.40 g adsorbent | |
| Boron mg l ⁻¹ | 0.23 | 0.39 | 0.63 | 0.95 | |
| Experimental parameters(25 mg l ⁻¹ fluoride concentration, 0.20 g adsorbent, 293 K) | | | | | |
| | pH 2.0 | pH 4.0 | pH 6.0 | pH 8.0 | pH 10.0 |
| Boron mg l ⁻¹ | 0.87 | 0.57 | 0.39 | 0.64 | 0.93 |
| Experimental parameters(25 mg l ⁻¹ fluoride concentration, 0.20 g adsorbent, pH 6.0,) | | | | | |
| | 293 K | 303 K | 313 K | 323 K | 333 K |
| Boron mg.l ⁻¹ | 0.39 | 0.40 | 0.39 | 0.41 | 0.41 |

4. Conclusions

A comparative study is performed to evaluate the fluoride removal by calcined electrocoagulation sludge. Based on the experimental data, the following conclusions can be drawn:

1- The results showed that adsorption was the highest at the pH 6. Equilibrium adsorption capacity (q_e) (mg g^{-1}) increases from 42.5 to 89 mg g^{-1} when the initial pH is adjusted to 2.0 instead of 6.0. Equilibrium adsorption capacity (q_e) (mg g^{-1}) decreases from 89 to 32.5 mg g^{-1} when the initial pH is adjusted to 6.0 instead of 10.0.

2- The equilibrium time for fluoride removal was determined to be 30 min.

3- The adsorption capacity of fluoride increases with increasing dosage of adsorbent. Equilibrium adsorption capacity (q_e) (mg g^{-1}) increased from 45.5 to 124.6 mg g^{-1} when adsorbent dosage was increased from 0.1 to 0.4 g/100 mL.

4- The increase in initial concentration decreased the removal efficiency.

5- The decrease in particle size increased the removal efficiency because at higher grain size, the binding capacity of the adsorbent approaches minimum level, resulting in a decrease in overall removal efficiency.

6- The highest adsorption capacity was achieved at 300 rpm. Above and below values of this stirring speed were caused to decreased adsorption removal efficiency.

7- The surface sites become less active with increase in the temperature, as a result of which the fluoride removal efficiency decreases.

8- The adsorption process was fitted well with Langmuir isotherm models.

9- Kinetic study results indicated that the adsorption process followed a pseudo-second-order kinetic model.

10- The leached boron concentration was well below the discharge limit (1 mg l^{-1}) in pH intervals from 2.0 to 10.0, adsorbent dosage intervals from 0.1 to 0.4 g/100 mL and solution temperatures intervals from 293 to 333 K.

From this study, it can be concluded that calcined electrocoagulation sludge could be a promising alternative sorbent for fluoride removal. The utilization of calcined electrocoagulation sludge is a significant application because it has been produced from an electrochemical treatment process so this waste represents unused resources and also present serious disposal problems. The results obtained from the present study demonstrated that calcined electrocoagulation sludge can be used as a no cost, highly effective and easy available adsorbent for removal of fluoride from aqueous solutions.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

AEY carried out the experiments under the guidance of BAF, SB and ZKK. AEY, BAF, SB and ZKK compiled the experimental data in journal format. All authors read and approved the final manuscript.

References

- Banasiak L.J. and Schäfer A. (2009), Removal of boron, fluoride and nitrate by electrodialysis in the presence of organic matter *Journal of Membrane Science*, **334**, 101-109.
- Behbahani M., Moghaddam M.R.A. and Arami M. (2011), Techno-economical evaluation of fluoride removal by electrocoagulation process: Optimization through response surface methodology, *Desalination*, **271**, 209-218.
- Brownley F.I. and Howle C.W. (1960), Spectrophotometric Determination of Fluoride in Water, *Analytical Chemistry*, **32**, 1330-1332.
- Chang C.-F., Lin P.-H. and Höll W. (2006), Aluminum-type superparamagnetic adsorbents: Synthesis and application on fluoride removal, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **280**, 194-202.
- Chen N., Zhang Z., Feng C., Zhu D., Yang Y. and Sugiura N. (2011), Preparation and characterization of porous granular ceramic containing dispersed aluminum and iron oxides as adsorbents for fluoride removal from aqueous solution, *Journal of hazardous materials*, **186**, 863-868.
- Das D.P., Das J. and Parida K. (2003), Physicochemical characterization and adsorption behavior of calcined Zn/Al hydrotalcite-like compound (HTlc) towards removal of fluoride from aqueous solution, *Journal of colloid and interface science*, **261**, 213-220.
- Doğan M. and Alkan M. (2003), Removal of methyl violet from aqueous solution by perlite, *Journal of colloid and interface science*, **267**, 32-41.
- Greenberg A.E., Clesceri L.S. and Eaton A.D. (1992), 'Standard Methods for the Examination of Water and Wastewater'. Washington, DC, APHA, AWWA & WEF.
- Islam M., Mishra P.C. and Patel R. (2011), Fluoride adsorption from aqueous solution by a hybrid thorium phosphate composite, *Chemical Engineering Journal*, **166**, 978-985.

- Kagne S., Jagtap S., Dhawade P., Kamble S.P., Devotta S. and Rayalu S.S. (2008), Hydrated cement: A promising adsorbent for the removal of fluoride from aqueous solution, *Journal of hazardous materials*, **154**, 88-95.
- Karthikeyan M., Satheesh Kumar K.K. and Elango K.P. (2009), Conducting polymer/alumina composites as viable adsorbents for the removal of fluoride ions from aqueous solution, *Journal of Fluorine Chemistry*, **130**, 894-901.
- Khatibikamal V., Torabian A., Janpoor F. and Hoshyaripour G. (2010), Fluoride removal from industrial wastewater using electrocoagulation and its adsorption kinetics, *Journal of hazardous materials*, **179**, 276-280.
- Lu N.C. and Liu J.C. (2010), Removal of phosphate and fluoride from wastewater by a hybrid precipitation–microfiltration process, *Separation and Purification Technology*, **74**, 329-335.
- Ma W., Ya F.-Q., Han M. and Wang R. (2007), Characteristics of equilibrium, kinetics studies for adsorption of fluoride on magnetic-chitosan particle, *Journal of hazardous materials*, **143**, 296-302.
- Meenakshi S. and Viswanathan N. (2007), Identification of selective ion-exchange resin for fluoride sorption, *Journal of colloid and interface science*, **308**, 438-450.
- Meenakshi S., Sundaram C.S. and Sukumar R. (2008), Enhanced fluoride sorption by mechanochemically activated kaolinites, *Journal of hazardous materials*, **153**, 164-172.
- Mohapatra D., Mishra D., Mishra S.P., Chaudhury G.R. and Das R.P. (2004), Use of oxide minerals to abate fluoride from water, *Journal of colloid and interface science*, **275**, 355-359.
- Ramdani A., Taleb S., Benghalem A. and Ghaffour N., (2010), Removal of excess fluoride ions from Saharan brackish water by adsorption on natural materials, *Desalination*, **250**, 408-413.
- Sairam Sundaram C., Viswanathan N. and Meenakshi S. (2009), Fluoride sorption by nano-hydroxyapatite/chitin composite, *Journal of hazardous materials*, **172**, 147-151.
- Sehn P. (2008), Fluoride removal with extra low energy reverse osmosis membranes: three years of large scale field experience in Finland, *Desalination*, **223**, 73-84.
- Solangi I.B., Memon S. and Bhangar M.I. (2009), Removal of fluoride from aqueous environment by modified Amberlite resin, *Journal of hazardous materials*, **171**, 815-819.
- Swain S.K., Patnaik T., Singh V.K., Jha U., Patel R.K. and Dey R.K. (2011), Kinetics, equilibrium and thermodynamic aspects of removal of fluoride from drinking water using meso-structured zirconium phosphate, *Chemical Engineering Journal*, **171**, 1218-1226.
- Tor A., (2006), Removal of fluoride from an aqueous solution by using montmorillonite, *Desalination*, **201**, 267-276.
- Tor A., Danaoglu N., Arslan G. and Cengeloglu Y. (2009), Removal of fluoride from water by using granular red mud: Batch and column studies, *Journal of hazardous materials*, **164**, 271-278.
- Tripathy S.S., Bersillon J.-L. and Gopal K. (2006), Removal of fluoride from drinking water by adsorption onto alum-impregnated activated alumina, *Separation and Purification Technology*, **50**, 310-317.
- Viswanathan N., Sundaram C.S. and Meenakshi S. (2009), Sorption behaviour of fluoride on carboxylated cross-linked chitosan beads, *Colloids and Surfaces B: Biointerfaces*, **68**, 48-54.
- W.H.O. (1993) 'Guidelines for drinking water quality', *World Health Organization*, pp. 45–46. Geneva.
- Yilmaz A.E., Boncukcuoğlu R., Kocakerim M. and Karakaş İ.H. (2011), Waste utilization: The removal of textile dye (Bomplex Red CR-L) from aqueous solution on sludge waste from electrocoagulation as adsorbent, *Desalination*, **277**, 156-163.