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Optimization of fluoride removal using ultrasonically improved electrochemically generated adsorbent: A Taguchi approach

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Ultrasonically improved electrochemically generated adsorbent (UEGA) has been synthesized and used for adsorption of fluoride ions from fluoride laden waste water. UEGA was prepared in two major steps, firstly electrochemically generated adsorbent (EGA) was prepared using electrolytic method followed by ultrasonication treatment. Ultrasonication causes size reduction which leads to increase in surface area viz. active site which helps to enhance attachment of negatively charged fluoride ion on positively changed UEGA from waste water. UEGA was prepared at three different amplitude i.e. 50, 70 and 90% respectively. Taguchi optimization for defluoridation was carried out considering operating parameters such as initial concentration; contact time; adsorbent dose; and temperature. The results obtained demonstrated that adsorption showed different fluoride removal at varying frequency. This study proved that varying percentage amplitude of ultrasonication significantly affects defluoridation efficiency.

Keywords: isotherms, kinetics, defluoridation, electrolyte, ultrasonication

1. INTRODUCTION

Fluoride pollution in drinking water is becoming a global issue. Increased fluoride concentrations (> 1.5 mg/L) in groundwater have already affected more than 25 countries around the world. Fluoride has a maximum tolerance level of 1.5 mg/l in drinking water and 15 mg/l in industrial effluents, according to the WHO and other pollution control agencies. Fluoride reduction from wastewater treatment has become a need for mankind's and the environment's health. Many research articles have been published to date on the removal of fluoride from water sources (Ruthven, 1984). Adsorbent preparation is a two-step process, firstly synthesis of electrochemically generated adsorbent (EGA) using NaCl as an electrolyte in a reactor, as described in a previous study (Jadhao et al., 2019), and secondly ultrasonification to produce UEGA (Barathi et al., 2014). The electrolytic process is regulated by the sacrificial anode's electrochemical dissociation, which results in the formation of coagulant. The electrolytic process includes the steps of (i) anode

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dissociation, (ii) formation and hydroxide ion and hydrogen gas liberation at the cathode, (iii) formation of coagulant as a precipitate. On aluminium electrodes, cathodic and anodic reactions occur as per Eqs. (1) and (2), while coagulant (sludge) production happens as per Eq. (3) (Mouedhen et al., 2008).

$$\text{Anode:} \qquad Al_{(s)} \rightarrow Al^{2+} + 2e^{-} \tag{1}$$

$$\text{Cathode:} \qquad 2H_2O + 2e^{-} \rightarrow H_{2(g)} + 2OH^{-} \tag{2}$$

Fluoride ion precipitation with aluminium hydroxide:

$$Al^{2+} + 2H_2 \rightarrow Al(OH)_{2(s)} + 2H^{+} \tag{3}$$

$$Al(OH)_2 + yF^{-} \leftrightarrow Al(OH)_{2-y}F_y + yOH^{-} \tag{4}$$

When an ultrasonic wave passes through a liquid medium, a high number of micro-bubbles emerge and collapse known as ultrasonic cavitations, resulting in a reduction in surface area and this technique is also known as ultrasonication (Sompech et al., 2012). In this paper, the effect of ultrasonication at various amplitude onto UEGA has been studied and defluoridation has been optimized using MINITAB.

2. EXPERIMENTAL

2.1. Chemical and reagents

Sodium fluoride (NaF) from Fisher Scientific India, sodium hydroxide (NaOH) from Merck Life Sciences, and fluoride buffer pillows (HACH, Germany) were utilised with no further precautions. Distilled water was used to make the sodium fluoride (100 mg/L) and sodium hydroxide solutions.

2.2. Synthesis of UEGA

Electrolytic reactor was charged with electrolytic solutions of NaCl in distilled water. Presence of NaCl increases the conductivity of the solution. The cylindrical flat bottom electrolytic reactor (MOC: plexiglass) has a diameter of 90 mm and a height of 220 mm. It consists of four plate-type aluminium electrodes with lengths, breadth and thickness of 10.5 cm, 2 cm, and 0.2 cm, respectively, and an effective surface area of 125 cm^2. A direct current power supply was used to run this electrolytic process resulting in formation of aluminium hydroxide complex as in Eq. (3). EGAs are currently known as vacuum-dried complexes. The electrodes were washed with NaOH (0.1 M), sand paper to eliminate any passive layers before starting each electrolytic batch method. EGA in distilled water was subjected to ultrasonication at 50%, 70%, and 90% amplitudes, respectively for 30 min with 30 s pulse on and 5 s pulse off followed by separation and drying at 80 °C for 12 h. These will be referred to as $UEGA_{50}$, $UEGA_{70}$, and $UEGA_{90}$, respectively. Further, defluoridation batch adsorption experiments were carried out using $UEGA_{90}$, $UEGA_{70}$ and $UEGA_{50}$ respectively.

2.3. Taguchi's design of experiments

Four different factors namely initial fluoride ion concentration, period of contact, adsorbent and temperature respectively have been selected as shown in Table 1.

Table 1. Factors and their levels for the design of experiments

Factors range and levels (coded)	Symbol	Unit	Levels				
			1	2	3	4	5
Adsorbent dose	D	g 40 mL^{-1}	0.1	0.2	0.3	0.4	0.5
Contact time	t	min	60	75	90	105	120
Temperature	T	°C	40	45	50	55	60
Initial concentration	C	mg L^{-1}	5	10	15	20	25

2.4. Experimental procedure

The batch adsorption studies for defluoridation was conducted by addition of UEGA to a 50 mL NaF solution. After 15 minutes of agitation at 500 rpm, the mixture was allowed to rest until equilibrium was attained. All the defluoridation experiments were performed onto $UEGA_{50}$, $UEGA_{70}$, and $UEGA_{90}$ respectively. The fluoride ion concentration in the solution was measured at every equivalent interval of time and denoted as C_t (mg/L). The fluoride ion quantity adsorbed onto UEGA at any time t, is q_t as in Eq. (5). C_t (mg/L) represents the concentration of fluoride ions in the solution at each equivalent interval of time. The quantity of fluoride ions adsorbed onto UEGA at every time t is q_t.

$$q_t = \frac{C_0 - C_t}{W} \cdot V \tag{5}$$

Eq. (6) expresses the capacity of fluoride ions at equilibrium.

$$q_e = \frac{C_0 - C_e}{W} \cdot V \tag{6}$$

3. RESULTS AND DISCUSSION

3.1. Effect of ultrasonication and factors on defluoridation

The fluoride percentage removal was found to be the highest for $UEGA_{90}$ i.e. 92% as compared to $UEGA_{70}$ i.e. 89% and $UEGA_{50}$ i.e.80%. After adsorption onto $UEGA_{90}$ and $UEGA_{70}$, the fluoride content in the solution was found to be below WHO's permitted limits. Because of the high intense waves during ultrasonication it causes mixing forming $UEGA_{90}$ and hence the particle size produced is smaller than $UEGA_{70}$ and $UEGA_{50}$, respectively. As revealed in the SEM micrographs, the size of $UEGA_{90}$ is the least of all in Figure 4. Similar research was reported by Sompech et al. (2012) and Barathi et al. (2014) with another adsorbent.

3.2. Effect of factors on percent fluoride removal

The efficiency of defluoridation by $UEGA_{90}$ has been determined to be the highest of all. Table 2 shows L25 Taguchi design for optimization of adsorbent with percentage fluoride removal and the corresponding S/N ratios (Tomar et al., 2014). This could be attributed to the increased surface area of active sites at high doses, resulting in an increase in effective surface area (Barathi et al., 2014). Almost similar results were reported by the earlier researchers (Ghosh et al., 2019). The % F progressively increased with the increase

of contact time and the maximum removal was observed to be 86.5% at 120 minutes. The results showed that higher S/N ratio was highly influenced at lower temperature (40 °C) and the percentage of fluoride removal was found to be gradually decreasing with the increase of temperature.

Table 2. The L25 Taguchi plan, experiment results and their calculated S/N ratios

Runs	D [g]	t [min]	T [°C]	C [mg/L]	Avg %F^- removal	S/N ratio
1	0.1	60	40	5	84.55	38.54
2	0.1	75	45	10	84.70	38.56
3	0.1	90	50	15	84.60	38.55
4	0.1	105	55	20	84.69	38.56
5	0.1	120	60	25	84.93	38.58
6	0.2	60	45	15	85.07	38.60
7	0.2	75	50	20	85.12	38.60
8	0.2	90	55	25	84.78	38.57
9	0.2	105	60	5	85.00	38.59
10	0.2	120	40	10	85.50	38.64
11	0.3	60	50	25	85.00	38.59
12	0.3	75	55	5	85.00	38.59
13	0.3	90	60	10	85.50	38.64
14	0.3	105	40	15	85.50	38.64
15	0.3	120	45	20	85.50	38.64
16	0.4	60	55	10	85.24	38.61
17	0.4	75	60	15	85.59	38.65
18	0.4	90	40	20	86.00	38.69
19	0.4	105	45	25	85.94	38.68
20	0.4	120	50	5	86.00	38.69
21	0.5	60	60	20	85.69	38.66
22	0.5	75	40	25	85.90	38.68
23	0.5	90	45	5	86.30	38.72
24	0.5	105	50	10	86.32	38.72
25	0.5	120	55	15	86.53	38.74

3.3. Analysis of the S/N ratio

The summary of S/N ratio for four factors i.e. adsorbent dose, contact time, temperature and initial fluoride concentration respectively along with assigned rank have been reported in Figure 1. It was noted that the highest S/N ratio obtained for %F are adsorbent dose at 0.1 g, contact time at 60 min, temperature at 55 °C and initial concentration at 25 mg/L respectively. Therefore the predicted optimal factors for obtaining the highest %F using Taguchi L25 array were found to be D = 0.1 g, t = 60 min, T = 55 °C and C = 25 mg/L and their respective levels were highlighted in Figure 1 for easy understanding. This predicted combination for %F was represented as $D_1 - t_1 - T_4 - C_5$.

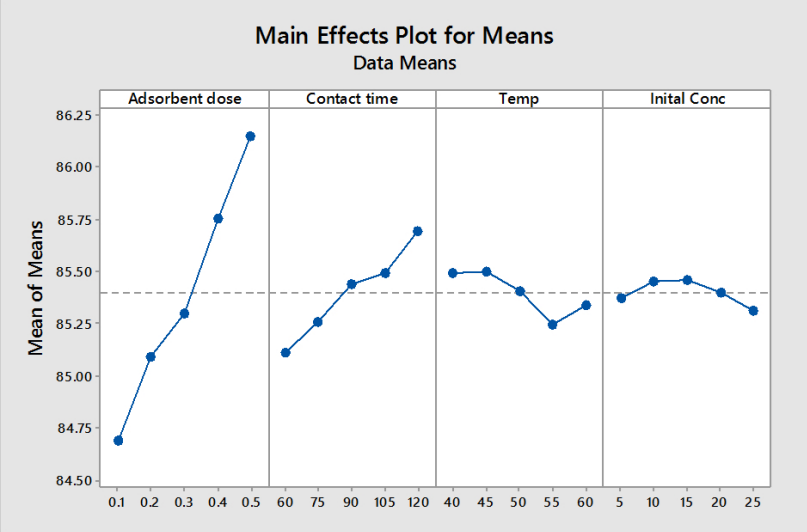


Fig. 1. Effect of factors on %F^- removal

3.4. Analysis of variance

ANOVA shows the contribution of $UEGA_{90}$ for adsorbent dosage, contact time, temperature and initial concentration is 83.37%, 12.78%, 2.91% and 0.97% respectively. The results of ANOVA are consistent with those of S/N ratio analysis showing the contribution of adsorbent dose is maximal.

3.5. Modelling

In the research paper, MINITAB 17 was used to perform linear regression analysis on the dependent factors in order to develop predictive mathematical models for %F as shown below

$$\%F = 84093 + 3569 \times D + 0.00929 \times t - 0.01009 \times T - 0.00344 \times C \tag{7}$$

From Figure 2 it was observed that the residuals fall near the straight line for %F. Figure 3 shows the contour plots explaining the relation between the factor and %F value. From Figure 3a, it was found that a high level of adsorbent dose and contact time leads to high %F value. Figure 3b, 3c shows that high adsorbent dose and relatively low temperature and initial concentration will give high %F.

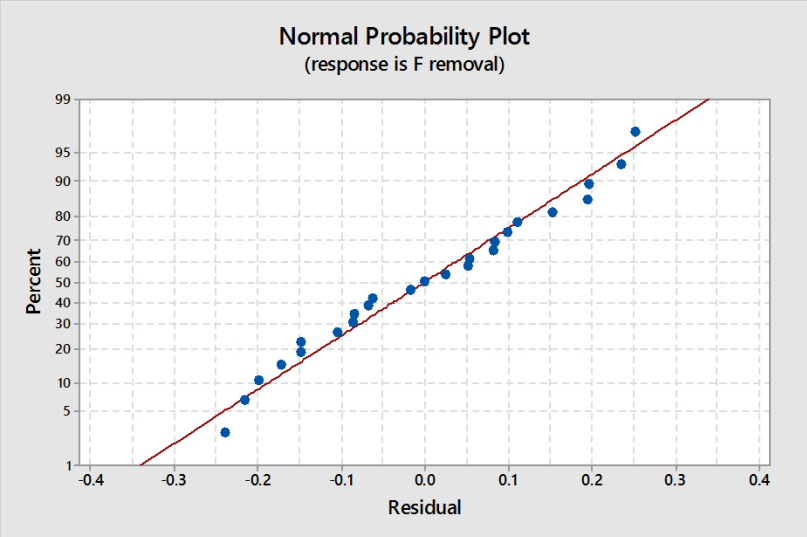
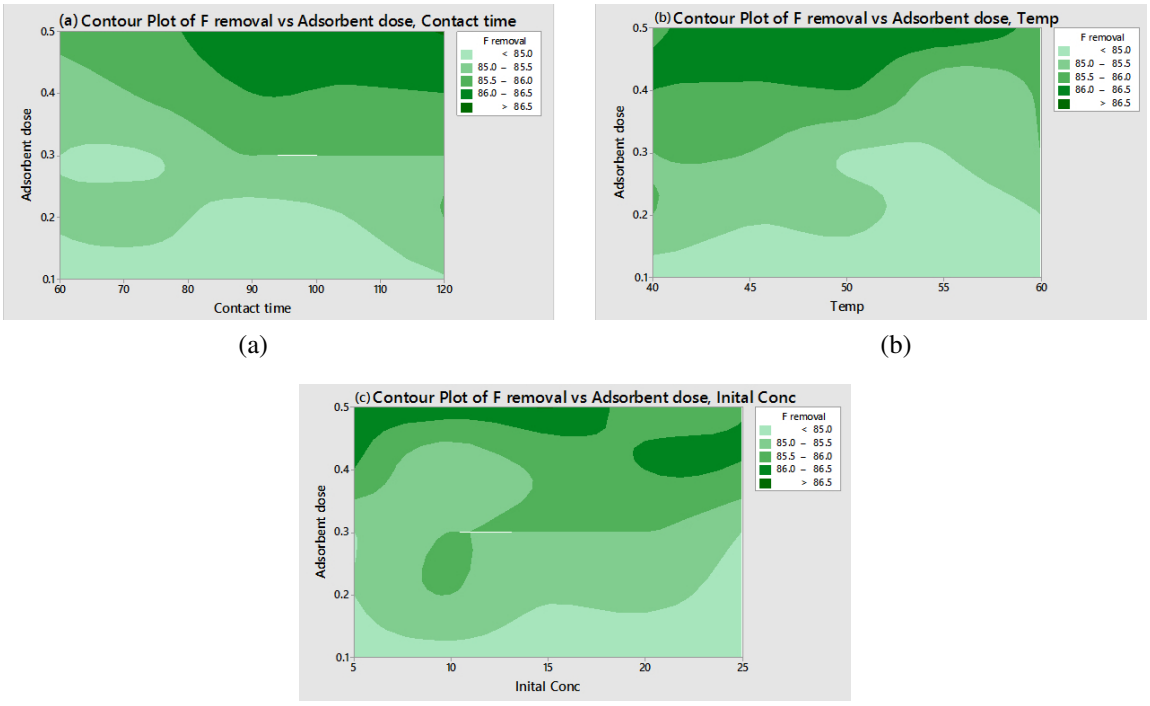


Fig. 2. Residual plots



(a) (b) (c)

Fig. 3. Contour plots for %F: (a) adsorbent dose vs. contact time; (b) adsorbent dose vs. temperature; (c) adsorbent dose vs. initial concentration

3.6. SEM of UEGA

In Figure 4 SEM studies clearly show that the $UEGA_{90}$ after deflurodation has a porous structure with a larger surface area. The particle size of $UEGA_{90}$ was smaller (11–21 micrometers) than that of $UEGA_{70}$

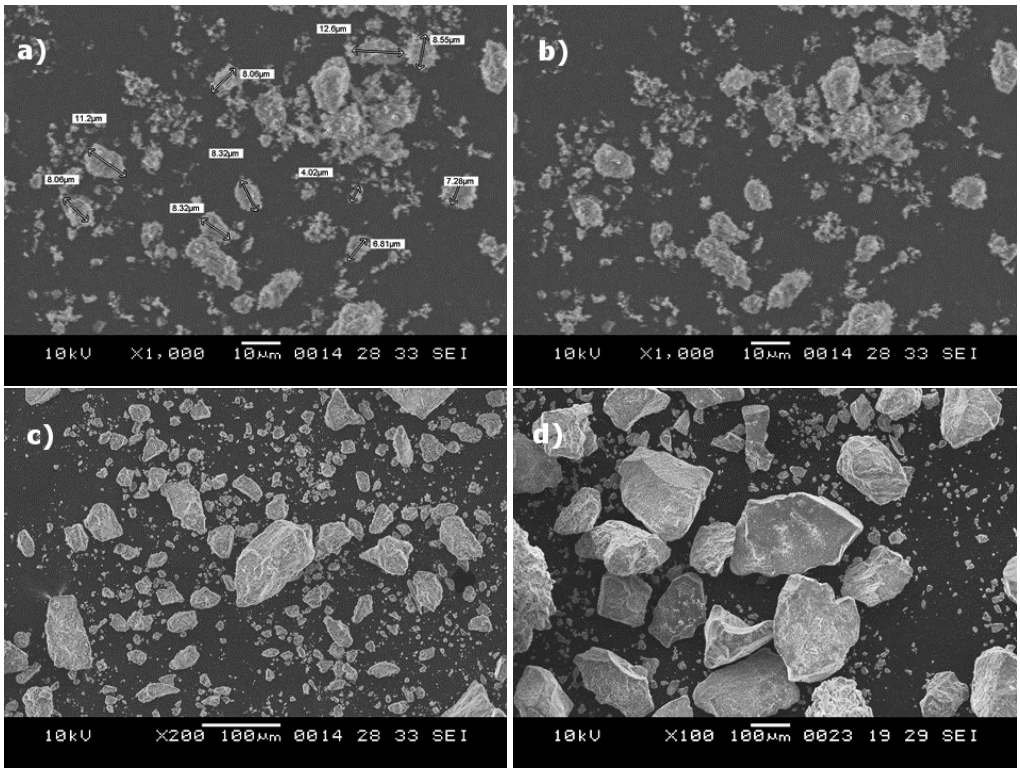


Fig. 4. SEM micrographs of synthesized (a) $UEGA_{90}$, (b) $UEGA_{70}$, (c) $UEGA_{50}$, (d) EGA

and $UEGA_{50}$ (< 200 micrometers in both cases). The effect of reduction in the particle size due to ultrasonication is clearly seen in Figure 4d. The pores function as an active location for fluoride adsorption by aluminium hydroxide complexes.

3.7. FTIR of UEGA

In Figure 5 the peaks of CH, alcohol OH, and NH stretching vibrations are visible at 3845.64 1/cm, 3917 1/cm, and 3961 1/cm. Furthermore, vibrations of 1610 1/cm and 1660 1/cm confirm OH blending

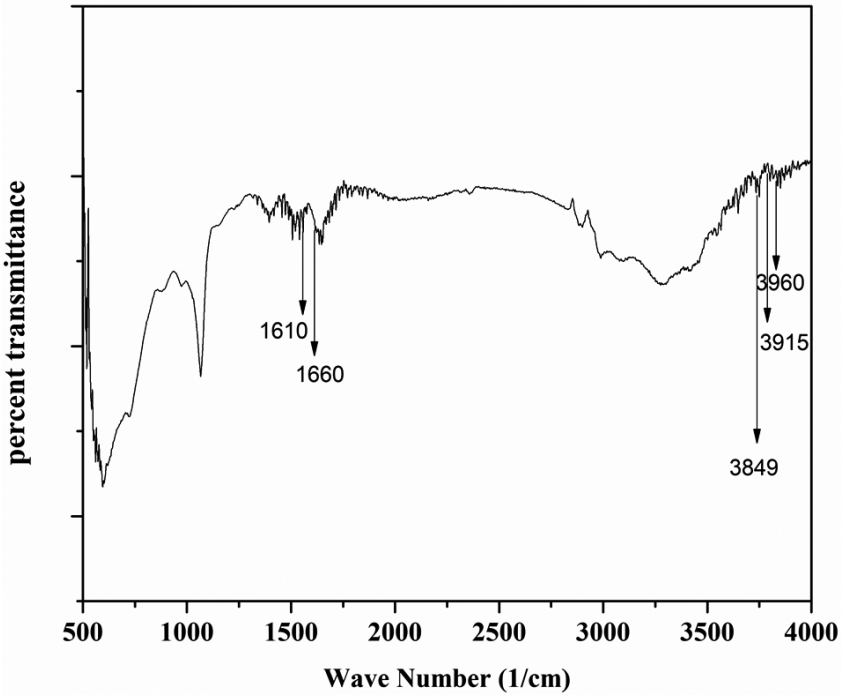


Fig. 5. FTIR spectra of $UEGA_9$

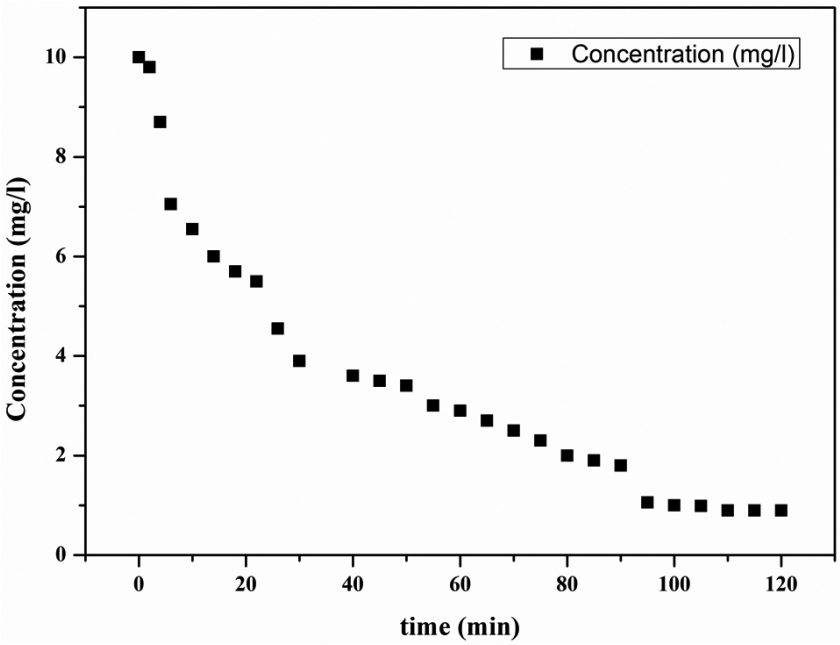


Fig. 6. Fluoride concentration (mg/L) vs. time (min)

stretching. Continuous vibrations in the range of 555 1/cm to 900 1/cm confirm the stretching of aluminium-oxygen (Al-O). Aluminium hydroxides have vibrations in the range of 3000 1/cm to 3500 1/cm, whereas pure aluminium has a wide peak at 3410 1/cm.

4. CONCLUSION

The approach of combining two technologies, ultrasonication and adsorption, has been effectively implemented to improve waste water defluoridation. The defluoridation was found to be maximum onto $UEGA_{90}$ i.e. 92%. After adsorption onto $UEGA_{90}$ and $UEGA_{70}$, the fluoride content in the solution was found to be below WHO's permitted limits. The optimum factors for defluoridation onto $UEGA_{90}$ have been identified as $D_1 - t_1 - T_4 - C_5$: adsorbent dosage of 0.1 g for the contact time of 60 min at temperature 55 °C with the 25 mg/L initial fluoride concentration. As a result, the current study suggests that UEGA could be a feasible alternative adsorbent for defluoridation of polluted water.

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SYMBOLS

D	adsorbent dose, gm
t	contact time, min
T	temperature, °C
$UEGA_{50}$	ultrasonically improved electrochemically generated adsorbent at 50% amplitude
$UEGA_{70}$	ultrasonically improved electrochemically generated adsorbent at 70% amplitude
$UEGA_{90}$	ultrasonically improved electrochemically generated adsorbent at 90% amplitude
C_0	initial fluoride concentration, mg L^{-1}
C_t	fluoride concentration at time t, mg L^{-1}
V	volume of batch experiment, mL
W	weight of adsorbent, g
q_t	quantity of fluoride ions adsorbed onto UEGA at every time t
q_e	quantity of fluoride ions adsorbed onto UEGA at equilibrium

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