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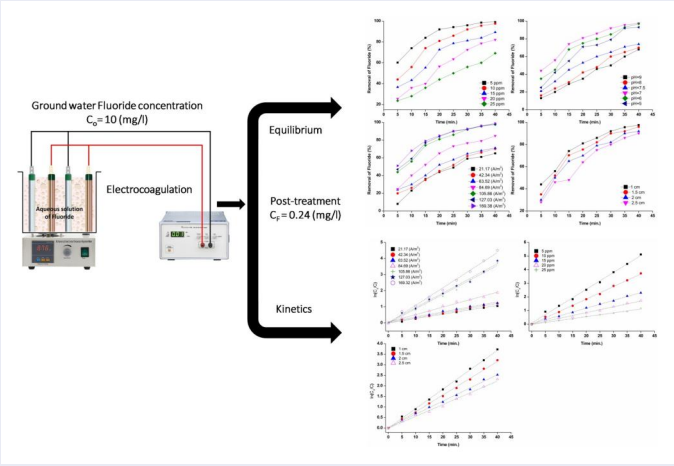
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ABSTRACT

In the current study, aluminum electrodes have been employed in electrocoagulation (EC) to remove fluoride ions from groundwater. The effects of various operating process variables of EC, including pH, salt dosage, stirring speed, inter-electrode distance, and current density have been studied, as well as the operating cost and kinetics of the process. The most favorable values of the EC process parameters have been observed, which are effective for the removal of 97.6% fluoride, such as an initial value of pH 7.0, a current density value of 105.86 A/m^2, an IED of 1 cm, a dose of salt of 0.33 g/L, a rotating speed of 700 RPM, and a time 40 min. The operating cost for the removal of fluoride (97.6% efficiency) from groundwater by EC was found to be 0.27 US$/m^3. The effectiveness of the EC process in the removal of turbidity and TDS from different operating circumstances have also been investigated. First-order kinetics was observed in the kinetic study. The reaction rate constant k increases with CD increase, k decreases with IED increase, and k decreases with initial concentration increase. EDX analysis and FTIR spectra of the sludge confirm the availability of trace amounts of fluoride in the sludge produced. The EC process can effectively reduce the fluoride concentration from synthetic water as well as real groundwater up to below 1.5 mg/L as per WHO recommendations for drinking water.

GRAPHICAL ABSTRACT



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Groundwater; defluoridation; electrocoagulation

Introduction

Groundwater contamination has become a significant problem due to the existing numerous contaminants including fluoride, pesticides, heavy metals, etc. One of the major issues around the world is fluoride (F) contaminated groundwater.[1] Fluoride contamination is a major issue in several regions of India as well as around the world since its excessive presence (>1.5 mg/L) in the groundwater results in fluorosis, which is a serious condition that causes severe damage to the teeth and bones.[2–4]

The World Health Organization recommends 1 mg/L as the tolerable safe limit of fluoride (WHO, 1984).[5] Fluoride ions (F^-), one of these carcinogenic ions when present in groundwater at levels above 1.5 mg/L can cause serious illnesses such as thyroid disease, skeleton fluorosis, dental fluorosis, neurological problems, joint pain, weak bones, cancer, infertility in women, low hemoglobin, and cardiac insufficiency.[4,5] The World Health Organization suggests more than 1.5 mg/L of fluoride should not be present in drinking water.[5]

Natural sources and the effluent of industrial wastewater contaminate groundwater with fluoride ions.[6] Groundwater

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is primarily contaminated by fluoride as a result of oxidative weathering and geochemical processes.[7,8] Fluoride emerges from various natural sources, such as temperature, pH, the presence or absence of complexion or precipitating ions and colloids, the solubility of fluorine-bearing minerals including fluorite (CaF_2), apatite (Ca_5 $[PO_4]_3$(Cl, F, OH), and topaz $Al_2F_2[SiO_4]$), the anion exchange capacity of aquifer materials (i.e., OH^- for F^-), the size and type of geological formations traversed by water, and the contact period the weathering and erosion of fluoride-bearing minerals.[9–11]

According to the literature, numerous techniques are used to remove fluoride from contaminated water, including membrane separation,[12] adsorption,[10,13] electrocoagulation (EC),[1,2,6,11] and combinations of these processes have been suggested by different scientists to reduce the fluoride ions in water sources. EC has been seen as one of the above processes that is more effective at simultaneously removing various water contaminants from contaminated water.[1] Low investment costs, no additional chemical requirements, ease of operation, and most importantly very little sludge generation are some of the major benefits of EC.[1,11,14]

The first step involved in the EC process is flocculation, the second is oxidation–reduction, and the last is bubble flotation.[1] The EC method is based on the principle of a typical electrochemical cell. In the EC process, electrical current is applied to remove flocculate contaminants without adding a coagulant.[2] The advantages of coagulation, flotation, or precipitation, and electrochemistry are combined in the EC process.[1,11] Anodes and cathodes, two pairs of metal sheets used in the EC process, get placed in pairs. When direct current is applied to the electrodes in the EC reactor, wastewater flows between them. Metals, primarily iron (Fe) or aluminum (Al), are typically used to make electrodes because they are readily available, affordable, nontoxic, and effective.[11] The specified effluent quality and polluted wastewater determine the selection of electrode material. Typically, iron is used to treat wastewater, and aluminum to treat drinking water.[1] The process of EC produces metallic hydroxide flocks by electro-dissolving soluble anodes made of iron or aluminum. The anode produces metallic cations as a result of the oxidation process of the aluminum, whereas the cathode often produces H_2.[2] The principal cathodic and anodic reactions for removing fluoride using aluminum electrodes are summarized as follows[1,15,16]:

Anodic reaction:

$$Al \rightarrow Al^{+3} + 3e \quad (1)$$

Cathodic reaction:

$$2H_2O + 2e \rightarrow H_2 + 2OH^- \quad (2)$$

When the potential of the anode is high enough, oxygen evolution also happens as a result of secondary reactions

$$2H_2O \rightarrow O_2 + 4H^+ + 4e \quad (3)$$

When ions of aluminum (Al^{+3}) and OH^- are produced respectively as a consequence of anodic and cathodic reactions. Various monomeric species are created when they react, like $Al(OH)^{+2}$, $Al(OH)_2^+$, $Al(OH)_2^{4+}$, and $Al(OH)_4^-$. Reactions occur in the following order:

$$Al^{+3} + H_2O \rightarrow Al(OH)^{+2} + H^+ \quad (4)$$

$$Al(OH)^{+2} + H_2O \rightarrow Al(OH)_2^+ + H^+ \quad (5)$$

$$Al(OH)_2^+ + H_2O \rightarrow Al(OH)_{3(s)} + H^+ \quad (6)$$

$$Al(OH)_3 + xF^- \rightarrow Al(OH)_{3-x}Fx + xOH^- \quad (7)$$

In the current study, the effects of different parameters on the removal of fluoride, such as initial pH, fluoride initial concentration (C_o), inter-electrode distance; current density, specific electrical energy consumptions, and rotating speed (RPM) are studied.[11] Additionally, the reduction of some significant parameters such as Total dissolved solids (TDS), turbidity, pH, and salinity is also investigated and discussed significantly. Fluoride removal is primarily influenced by their initial concentration. Therefore, the influence of change of initial concentration on fluoride removal efficiency also has been studied.

The kinetic study has been done to describe the removal rate of fluoride under various operating conditions, including initial concentration, inter-electrode distance, and current density. Cost estimation of the EC process is essential for economic feasibility studies. The sludge characterization using a Fourier transform infrared spectroscopy (FTIR) and elemental analysis using EDAX are used to investigate the produced sludge composition from the EC process.

This research will be valuable for a clear understanding of how the EC process can be applied to the treatment of drinking water, particularly when building a large-scale plant based on the EC process for drinking water purification to maintain the concentration of various contaminants below permitted limits.

The primary objective of the current work is to determine the optimum values of EC process parameters, kinetic study for analysis of reaction rate constant, and operating costs for fluoride removal efficiency by EC using aluminum electrodes. The main aim of this work is to examine EC's effectiveness for fluorinated groundwater.

Materials and methods

In this study, groundwater samples have been taken from Bhichawa village under Makrana Tehsil of Nagaur District, Rajasthan, India. Bhichawa village groundwater sample's initial fluoride concentration is 10 mg/L at 7.1 pH. Synthetic fluoride containing groundwater with parameters similar to the real groundwater of Bhichawa village was prepared by mixing the right amount of NaF (Fisher Scientific, purity 99%) from tap water. To increase solution conductivity, a supporting electrolyte of NaCl (99% purity, Fisher Scientific) was utilized. For various tests, the initial pH of the test sample water was maintained between pH values of 5 and 9, and it was altered by adding NaOH (1 M) and HCl (1 M). A digital multimeter (Model: PC2700, Make: EUTECH India)

with a pH electrode was used to measure the pH of the liquid mixture. At 25 ± 2 °C, the ambient temperature, all experiments were conducted. FTIR-EDAX analysis was used to determine the sludge's elemental composition (Model: Supra 55 Mono CL4; Make: Carl Zeiss).

Figure 1 demonstrates the experimental setup. For EC process studies, a 2.5 L Perspex glass reactor was used.. The Perspex glass EC reactor with dimensions of length, breadth, and height 13, 13, and 15 cm was used in all tests after being cleaned with diluted HCl throughout each experiment and dried in an oven at 105 °C. About 2 mm thick aluminum (Al) plate electrodes were used for EC having a 59.2 cm^2 total effective area. Four plates were put in the electrochemical reactor for each batch. Table 1 lists specifications of the parameters of EC setup. To maintain a constant current, a source of DC power was attached to the electrodes, and a voltage and current sensor with ranges of 0–20 V and 0–5 A, respectively, were used (Model: L6410S, Make: Aplab India). A digital display magnetic stirrer (Model: 5MLH plus hot plate, by REMI India) was employed to keep the proper mixing with a 4 cm magnetic bar. To determine the impact of different parameters, adjustments were made to the initial concentration of fluoride from 5 to 25 mg/L.[11] The Current density (CD) ranged from 21.1721 to 169.38 A/m^2, the different inter-electrode distance was selected from 1.0 to 2.5 cm, and the magnetic stirrer speed was varied between 500 and 900 RPM. By utilizing the formula mentioned elsewhere, the related Reynolds numbers (N_{Re}) were determined as 0.83×10^4, 1.16×10^4, and 1.5×10^4.[11,17]

Each EC experiment lasted 40 minutes, during which time samples were collected every 5 minutes. The EC cell was frequently sampled for 20 mL to monitor the treatment's progress, and after that, the sludge produced during electrolysis was separated using Whatman filter paper No. 42. For analysis of fluoride of each sample, SPANDS method was used through a spectrophotometer. Table 2 lists the variety of operational parameters that were taken into account for the EC process. A TDS selective electrode was used to measure TDS (Model: CON 2700, Make: EUTECH India). Using a multimeter (Model: PC2700, Make: EUTECH India), conductivity, resistivity, and salinity were all measured simultaneously for each sample. A turbidity meter (Thermo Scientific, EUTECH TN-100) was also used to measure the turbidity of each sample. The experimental error was less than 3% after two replications of each experiment.

The removal efficiency of fluoride has been calculated using the following equation

$$\% = \frac{C_0 - C_t}{C_0} \times 100 \tag{8}$$

where C_0 is the initial fluoride concentration of the sample at time zero (i.e., before conducting EC) and C_t is the fluoride concentration after conducting EC.

Specific Electrical Energy Consmption (SEEC, KW h/(kg Al) for various operating settings was calculated by comparing the experimental weight loss ($M_{loss,\ Experimental}$) of electrodes during the EC process with a theoretical quantity of metal dissolve in solution ($M_{loss,\ Theoretical}$) by Faraday's law and using following Eqs. (9)–(11)[18]]

Table 1. Specifications of the parameters of EC reactor setup.

Parameter	Specification
Volume of EC reactor	13 cm × 13 cm × 15 cm = 2.535 cm^3 = 2.5 L
Total effective electrode area	59.2 cm^2
Electrode thickness	2 mm
Electrode material	Aluminum
Electrode shape	Rectangular
Plate arrangement	Mono-polar in parallel
EC reactor make	Perspex glass
No. of electrodes used	Four
Current range (A)	0–3
Voltage range (V)	0–20

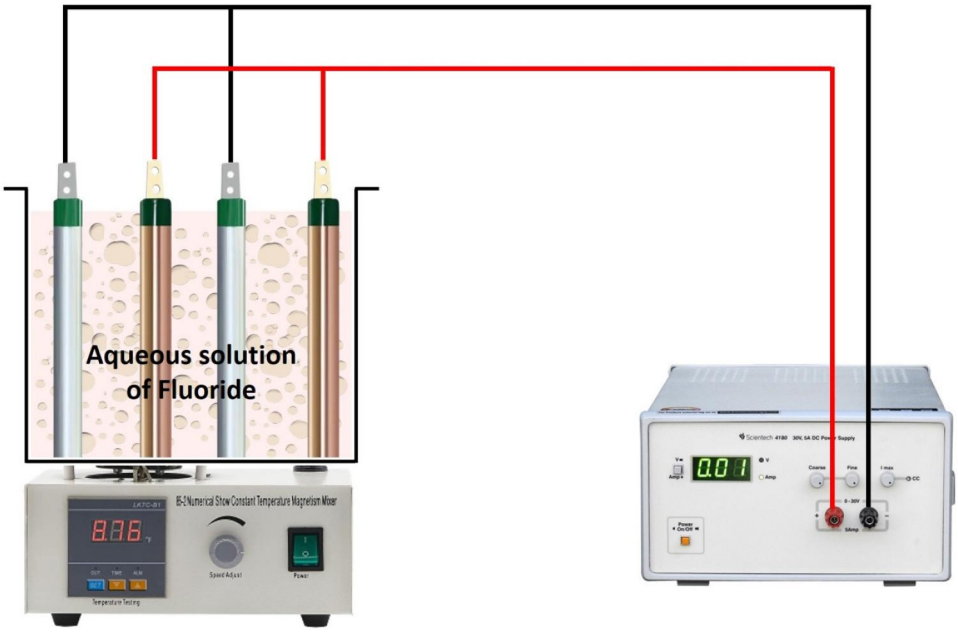


Figure 1. Electrocoagulation (EC) experimental setup schematic diagram.

Table 2. Fluoride removal by EC in a monopolar connection with an aluminum electrode is possible with a variety of operating parameter.

Studied parameter	Variable parameter during the course of experiment	Constant parameter during the course of experiment
Initial pH effect	pH range: 5, 6, 7, 7.5, 8, 9	CD = 105.86 A/m^2; IED = 1 cm; RPM = 700; NaCl = 0.33 g/L; EC time = 40 minutes; C_o = 10 mg/L
Current density effect (A/m^2)	CD range: 21.17, 42.34, 63.52, 84.69, 105.86, 127.03, 169.38 Current (A): 0.5, 1, 1.5, 2, 2.5, 3	IED = 1 cm; RPM = 700; NaCl = 0.33 g/L; EC time = 40 minutes; C_o = 10 mg/L, pH = 7
Inter-electrode distance effect (cm)	IED range: 1, 1.5, 2, 2.5	CD = 105.86 A/m^2; RPM = 700; NaCl = 0.33 g/L; EC time = 40 minutes; C_o= 10 mg/L, pH = 7
Initial concentration effect (mg/L)	Initial concentration range: 5, 10, 15, 20, 25	CD = 105.86 A/m^2; IED = 1 cm; RPM = 700; NaCl = 0.33g/L; EC time = 40 minutes; pH = 7
RPM effect	RPM range: 500, 700, 900	CD = 105.86 A/m^2; IED = 1 cm; NaCl = 0.33g/L; EC time = 40 minutes; C_o = 10 mg/L; pH = 7
NaCl concentration effect (mg/L)	NaCl range: 0.33, 0.5, 0.66, 0.83	CD = 105.86 A/m^2; IED = 1 cm; RPM = 700; EC time = 40 minutes; C_o = 10 mg/L; pH = 7

Error: pH = ±0.215; C_o = ±0.45 (mg/L); CD = ±2.631 (A/m^2); IED = ±0.0525 (cm); RPM = ±21.

$$\Delta M_{loss,\,Theoritical} = \frac{M \times I \times t_E}{n \times F} \tag{9}$$

$$\psi = \frac{\Delta M_{loss,\,Experimental}}{\Delta M_{loss,\,Theoritical}} \times 100 \tag{10}$$

$$\text{SEEC} = \frac{F \times U \times n}{M \times \psi \times 3600} \tag{11}$$

where M denotes the molecular weight of aluminum (g/mol), applied current (A) across the electrode is denoted by I, total EC time (minutes) is denoted by t_E, n is electrons involved in terms of number of moles in dissolution reaction, Faraday constant (F = 96,487 C/mol) is denoted by F, the current efficiency is denoted by Ψ. The following equation uses the Reynolds number (N_{Re}) to represent the system's turbulence[17]

$$N_{Re} = \frac{S_r \times D^2 \times \rho}{\mu} \tag{12}$$

where S_r is the stirrer's rotational speed, the agitating bar (1.57 inch) length is denoted by D, ρ is the solution's density (1.001 g/m^3), and μ is the liquid's viscosity (0.963 cp).

Results and discussions

Influence of pH on fluoride removal efficiency

In the EC process, the pH of the solution is the most decisive parameter for fluoride removal.[1,11,17,18] As per the WHO recommendations, the range of pH of drinking water is 5–9. The previous literature has illustrated that the pH range of 5–9 is the most effective for removing fluoride. According to this fact, the initial pH range of 5–9 has been examined for fluoride removal.[11,17,19] Using an Al/Al combination in a monopolar connection, the initial pH effect on the elimination of fluoride has been illustrated in Figure 2.

The experiments have been conducted at constant CD = 105.86 A/m^2 with different initial pH values (5, 6, 7, 7.5, 8, and 9). It can be viewed from Figure 2 that the fluoride removal was once increased from pH 5–7, and then decreased. As can be observed from the figure, pH 7 resulted in a maximum efficiency of 97.6% for removing fluoride. Figure 2 also demonstrates how fluoride removal effectiveness rises with increasing pH up to 7 after progressively falling beyond that. The lowest reported fluoride elimination effectiveness was 68% at pH 9.

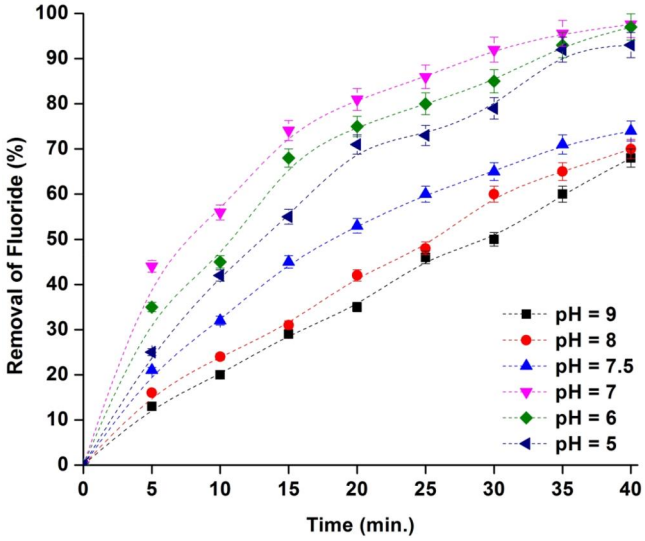


Figure 2. Effect of initial pH on the effectiveness of removing fluoride. 2.5 L of water, 0.33 g/L of sodium chloride, a 1 cm IED, 700 RPM of stirring, and 10 mg/L of C_o. CD: 105.86 a/m^2, monopolar connection.

In accordance with the observation that at the pH range (5–7), raising pH causes a large number of OH^- ions to be produced, there was a change in removal efficiency which had been related to pH. After pH 7, any rise in pH causes OH^- ions to accumulate and stable, insoluble Al $(OH)_3$ flocs to form, which slows the rate at which coagulation occurs.[1,11,18,20] Therefore, a further experiment was carried out at pH 7 for Al electrodes to achieve the highest removal efficiency.

Influence of current densities on fluoride removal efficiency

The electron flow rate depends on current density in EC. Therefore, CD is considered a significant operating parameter.[1,11] Figure 3 shows the variation in fluoride removal percentage for current densities ranging from 21.17 to 169.38 A/m^2 (I = 0.5–3 A). Figure 3 demonstrates that as

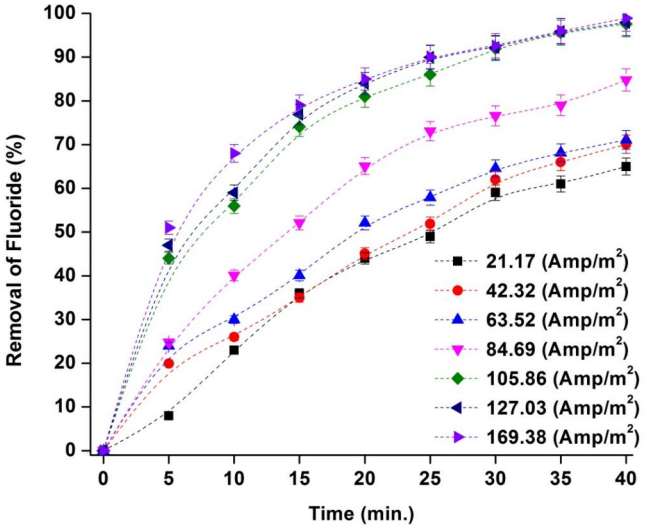


Figure 3. Effect of CD on the rate of fluoride elimination over time. 2.5 L of water, 0.33 g/L of sodium chloride, and a 1 cm IED. Initial pH: 7.0, stirring speed: 700 RPM, C_o: 10 mg/L.

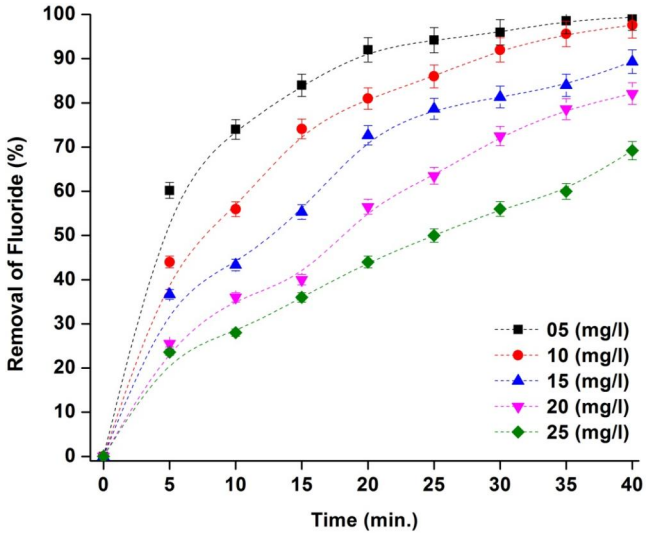


Figure 4. Effect Of the initial concentration of fluoride ions on the rate at which fluoride is removed over time. 2.5 L of water, 0.33 g/L of sodium chloride, 1 cm of IED, 700 RPM of stirring, 105.86 a/m^2, 7.0 starting pH.

current density increased, the rate of fluoride removal also increased. At CD = 21.17 A/m^2, the fluoride ion concentration decreases from 10 to 3.5 mg/L over 40 min of EC. As CD increased from 21.17 to 169.38 A/m^2, the elimination rate of fluoride removal increased from 65% to 98.9%. For the higher CD of 105.86, 127.03, and 169.38 A/m^2, respectively, the higher removal of fluoride of 97.60%, 97.90%, and 98.90% was attained after 40 min.

The anodic process (anode dissolution) and cathodic process (hydrogen synthesis) are both governed by the current density. Generally, as current density rises, anodic oxidation occurs more quickly, encouraging the development of amorphous aluminum hydroxide species near the electrode and in the bulk water.[1,2,11] A fine gelatinous coating is developed on the electrode surface as an effect of this, which often happens close to the anode–water interface Faraday's Law states that the rate at which metal ions are released is directly proportional to the amount of electrode dissolved in the solution. According to Faraday's Law, the sacrificial anode's dissolved ions increase as the current density increases.[19,21] The formation of metallic hydroxide species is enabled by the hydrolysis of the dissolved metal ions due to sufficient current flowing through the water solution. Fluoride ions in the water could thus be allowed to interact with anode-proximal materials to produce complex. As a result, the fluoride removal rate increases with increased current density increases.

Influence of initial concentration on fluoride removal efficiency

The studies used fluoride ion concentrations ranging from 5, 10, 15, 20, and 25 mg/L[11] to examine how the efficiency of fluoride removal in EC is influenced by initial fluoride concentration. Figure 4 illustrates the results of the study. To investigate how effective fluoride removal in EC is affected by initial fluoride concentration, the experiments employed fluoride ion concentrations of 5, 10, 15, 20, and 25 mg/L.[11] Figure 4 illustrates the study results. According to the results, fluoride removal effectiveness reduced as fluoride concentration increased. After 40 min of the EC process, the efficiency of fluoride removal reduced from 99.6% to 73.44% as the initial concentration of fluoride increased from 5 to 25 mg/L. The fluoride elimination efficiency was 97.6%, 89.33%, and 82.1% for concentrations of fluoride 10, 15, and 20 mg/L. The elimination efficiency was 97.6%, 89.33%, and 82.1% for concentrations of fluoride 10, 15, and 20 mg/L. The fact of this is that all initial concentrations produced the same number of aluminum hydroxide complexes at constant CD. Because of this, for a high amount of concentration of fluoride, the flocs generated were not enough to remove a lot of fluoride ions from the solution.[22]

The production of aluminum flocks allows for the maximum absorption of fluoride ions, which increases removal efficiency. As a result, it is evident that under the current operating circumstances, removal efficiency is higher when the starting fluoride concentration is lower.

Influence of inter-electrode distance's (IED) on the effectiveness of fluoride removal

The studies of research literature indicate that IED plays a significant role in the EC process.[1,11] IED has been adjusted between 1 and 2.5 cm to study how it affected the effectiveness of removing fluoride ions from water. Figure 5 shows how the amount of fluoride removed from water varies depending on the IED. Figure 5 reveals that fluoride removal has reduced with an increase in IED. IEDs as short as 1 cm had the highest removal efficiency (97.6%), while IEDs as larger as 2.5 cm was the lowest removal efficiency (90.1%). In other words, the maximum efficiency has been found at the shortest space between electrodes. As distance increases, free electron transit time between electrodes will also increase. Due to this fact, the contact between the

produced flocs and the fluoride ions slows down, which slows down the fluoride removal rate.[23]

Table 3 demonstrates the effects of IED on different parameters related to drinking water quality as conductivity, TDS, salinity, turbidity, and pH. According to Table 2, the TDS rose from 142 to 179 mg/L as the IED grew from 1 to 2.5 cm. Similar results were seen for salinity (125–135 mg/L), conductivity (552–579 µs), and turbidity (0.48–0.79 NTU). Therefore, it can be concluded that during EC, turbidity, salinity, and the percentage of TDS removed have all been decreased, similarly to the fluoride ions. However, pH has reduced from 7.6 to 7.41 as IED increases. It happened as a result of the generation rate of OH^- decreasing with increased IED.

Influence of NaCl on SEEC and fluoride removal efficiency

The electrical conductivity of the solution is significant to the EC process's electron transport mechanism and energy efficiency.[11,24] In laboratory experiments of the EC process, water's conductivity is altered by using NaCl.[2,11] Experiments were conducted using NaCl doses of 0.33, 0.71, and 0.83 g/L to see how water conductivity impacts outcomes.[11] Table 4 demonstrates the percentage of fluoride removal at various NaCl dosages together alongside the modifications in turbidity, conductivity, and TDS following 40 min of EC. It was found that while water conductivity increased with an increase in NaCl dosage from 0.33 to 0.83 g/L, fluoride removal efficiency marginally increased from 97.6% to 98.32%. Solution conductivity significantly increased from 927 to 1389 µs with an increase in NaCl dosage. As a result, the voltage needed to supply the necessary CD drastically decreased from 16 to 5 V. SEEC thus dropped from 36.25 to 11.32 (kW h/kg Al). Taking into account the volume of water treated, the overall consumption of energy dropped from 10.93 to 3.39(kW h/m^3). Therefore, an increase in solution conductivity has a significant impact on SEEC.

It was also observed that when the dosage of NaCl was increased, the initial value of TDS rose from 527 to 548 mg/L, and the turbidity rose from 1.5 to 1.73 NTU. After 40 min of the EC process, TDS and turbidity increased from 142 to 154 mg/L and 0.48 to 0.75 NTU, respectively. It should be noted that adding salt to a solution to improve its conductivity reduces SEEC while increasing the concentration of another metal ion in the solution. Lower NaCl dosage is therefore preferred when taking water cleanliness into account. In the current work, we have used a salt dosage of 0.33 g/L.

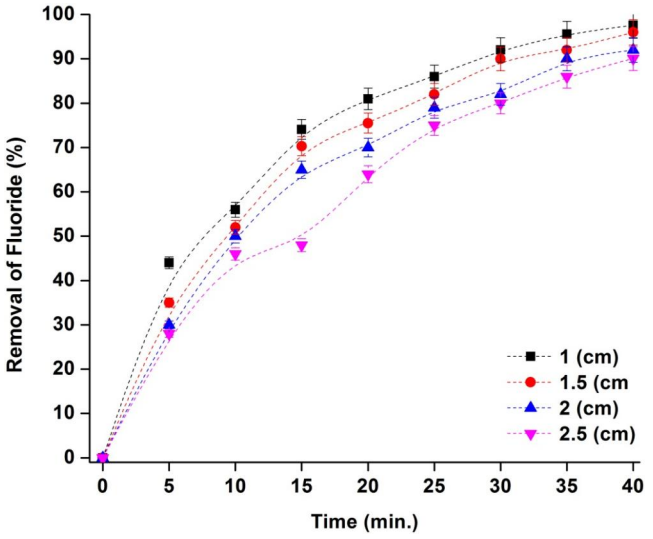


Figure 5. Effect of IED on the rate of fluoride removal over time. Initial pH is 7.0, 2.5 L of water, 0.33 g/L of NaCl, 10 mg/L of C_o, 700 RPM of stirring.

Influence of rotating speed on fluoride removal efficiency

By stirring the solution, the produced flocs and contaminant come into contact during EC. Slower stirring speed leads to poor agitation in the solution and lower interaction between flocs and contaminated species. Slower stirring speed leads to poor agitation in the solution and lower interaction between flocs and contaminated species. However, under conditions of faster stirring speed, both produced flocs and contaminants rotate rapidly without actually making contact, which reduces the removal percentage of contaminants and results in an excess of both pollutants and flocs. Thus, the turbulence or speed of stirring has a significant impact on the effectiveness of the EC process for removal.

Table 3. Experimental results showed values for different parameters before and after EC treatment for 40 min, with varying initial fluoride concentrations and inter-electrode distances.

		TDS (mg/L)		Turbidity (NTU)		Conductivity (µs)		Salinity (mg/L)		pH	
Fixed parameter	Operating parameters	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
Initial fluoride conc. (mg/L)											
IED = 1 cm	5	520	129	1.48	0.39	910	492	530	119	7	7.8
CD = 105.86 A/m^2	10	527	142	1.5	0.48	927	551	546	125	7	7.71
Salt = 0.33 g/L	15	530	158	1.54	0.59	928	609	551	236	7	7.72
RPM = 700	20	542	163	1.56	0.67	970	630	554	225	7	7.74
pH = 7	25	553	170	1.57	0.68	951	680	560	238	7	7.74
Inter electrode distance (cm)											
CD = 105.86 A/m^2	1	527	142	1.5	0.48	927	551	546	125	7	7.6
Salt = 0.33 g/L	1.5	530	150	1.6	0.69	962	566	544	131	7	7.4
RPM = 700	2	534	160	1.65	0.73	955	573	547	133	7	7.39
pH = 7	2.5	536	179	1.67	0.79	959	579	544	135	7	7.41

Error: pH = ±0.215; C_o = ±0.45 (mg/L); CD = ±2.631 (A/m^2); IED = ±0.0525 (cm); RPM = ±21.

Table 4. TDS, turbidity, conductivity, fluoride removal, and SEEC are all impacted by the amount of NaCl used.

Initial NaCl dose (g/L)	TDS (mg/L)		Turbidity (NTU)		Conductivity (μs)		Fluoride Removal (%)	Voltage	SEEC (kW h/kg Al)	Energy Consumption (kW h/m^3)
	Initial	Final	Initial	Final	Initial	Final				
0.33	527	142	1.5	0.48	927	551	97.6	16	36.25	10.93
0.5	536	144	1.6	0.54	1050	868	97.86	10	22.63	6.81
0.66	543	150	1.71	0.67	1076	963	98.07	8	18.11	5.44
0.83	548	154	1.73	0.75	1389	1011	98.32	5	11.32	3.39

Error: pH = ±0.215; C_o = ±0.45 (mg/L); CD = ±2.631 (A/m^2); IED = ±0.0525 (cm); RPM = ±21.
CD = 105.86 A/m^2; IED = 1 cm; starting fluoride concentration = 10 mg/L; RPM = 700; initial pH = 7; EC duration = 40 minutes.

Table 5. Effect of stirring rate on TDS, turbidity, conductivity, elimination of fluoride, and pH.

Stirring rate (RPM)	Reynolds number (NRe)	TDS (mg/L)		Turbidity (NTU)		Conductivity (μs)		pH		Fluoride removal (%)
		Initial	Final	Initial	Final	Initial	Final	Initial	Final	
500	0.83×10^4	527	154	1.5	0.69	927	612	7	7.9	85.8
700	1.16×10^4	527	142	1.5	0.48	927	551	7	7.71	97.6
900	1.50×10^4	527	176	1.5	0.79	927	643	7	7.87	89.2

Error: pH = ±0.215; C_o = ±0.45 (mg/L); CD = ±2.631 (A/m^2); IED = ±0.0525 (cm); RPM = ±21.
CD: 105.86 A/m^2, IED: 1 cm, starting fluoride concentration of 10 mg/L, NaCl: 0.33 g/L, and EC duration of 40 minutes.

To determine the best stirring speed, EC experiments using a magnetic stirrer with stirring speeds of 500, 700, and 900 RPM were carried out for 40 min. The calculated corresponding Reynolds numbers (N_{Re}) were 0.83×10^4, 1.16×10^4, and 1.50×10^4. Table 5 demonstrates that at slower stirring speeds, fluoride removal effectiveness is only 85.8% (500 RPM). As stirring speed increases, removal effectiveness grows (700 RPM). However, it is once more demonstrated that removal effectiveness declines at higher stirring speeds, this time to 89.2% (900 RPM). It may be described by the fact that when stirring speed increases, the interaction between fluoride ions and various aluminum hydroxide complexes generated around the electrodes improves, but as RPM increases more, the rate of improvement in contact decreases.[17]

Operating cost calculation

The estimated operating cost of the EC process for groundwater after 40 min is calculated as follows[25,26]:

$$\text{Operatingcost} = \alpha C \text{ energy} + \beta C \text{ electrode} \quad (13)$$

where α is the price of electrical energy, β is the price of the aluminum electrode, C_{energy} is the energy consumption (kW h/m^3), and $C_{electrode}$ is the electrode consumption (kg/m^3) during the EC treatment process. The price of electrical energy and electrode (Al) in the Indian market is 0.0338 US$/kW h and 2.64 US$/kg, respectively.

Energy consumption (E)

For each water treatment, we calculated the energy consumption using the following equation[27–29]:

$$E = \frac{I \times U \times t}{v} \quad (14)$$

where I = current, U = applied voltage, t = EC time, and v = volume of the fluoride water sample. If necessary, the value for E can be calculated in kW hours (kW h) by dividing the answer from Eq. (14) by 1000.

Electrode consumption (w)

For each water treatment, we calculated the electrode consumption using the following equation[27–29]:

$$\text{Electrode Consumption}, w = \frac{I \times t \times M}{n \times F} \quad (15)$$

where M is the atomic mass, F is the Faraday constant 96487.332 (C mol^{-1}), and n ($n = 3$)[30] is the number of electrons exchanged.

The above equation demonstrates that the electrode consumption is directly proportional to the treatment time and current delivered. From Eq. (13), it is found that for the optimal values of various operational parameters, such as pH =7, CD =105.86 A/m^2, IED =1 cm, C_0 = 10 mg/L, and 700 RPM, about 0.27 US$/m^3 is required for the maximum removal 97.6% of fluoride.

Fluoride removal kinetic analysis

Most research suggests that first-order reaction models are more effective in explaining the EC process. The rate equation may be described by a first-order kinetic model, according to Eq. (16)[18,20,21,31]

$$-r_F = \frac{-dC_F}{dt} \quad (16)$$

The rate law for the disappearance rate of fluoride ion

$$-r_F = kC_F \quad (17)$$

where $-r_F$ is the rate law for the removal rate of fluoride ion in mg L^{-1} min^{-1}, t is the EC process time in minutes. When combining Eqs. (16) and (17) and integrating them, the limit $C_F = C_{FO}$ at $t = 0$ gives

$$\ln \frac{C_{FO}}{C_F} = kt \quad (18)$$

where C_F is the fluoride ion concentration after EC time t and k is the specific reaction rate constant for the first-order reaction in min^{-1}.

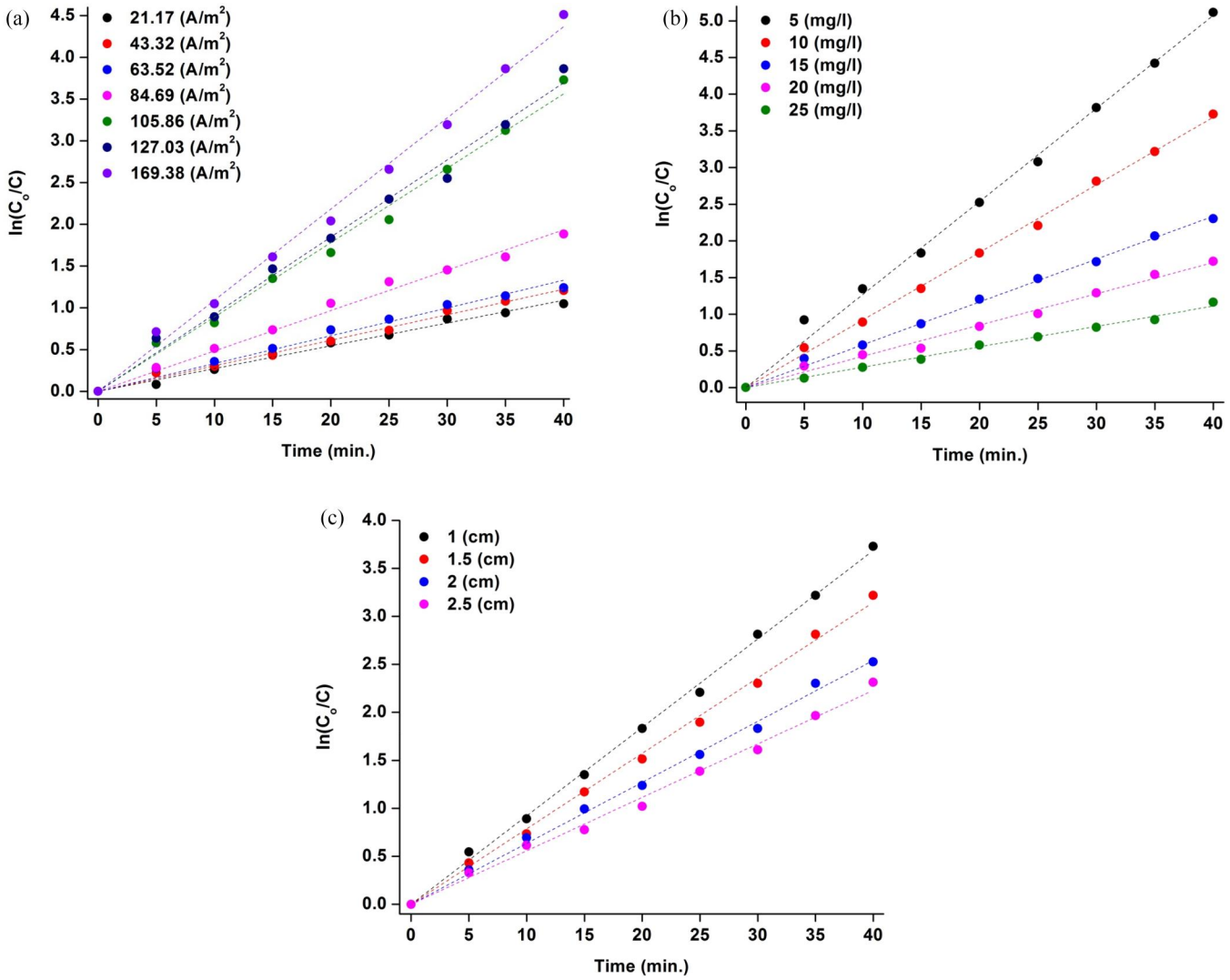


Figure 6. (a) $\ln(C/C_o)$ vs. time for different current density. (b) $\ln(C/C_o)$ vs. time for different initial fluoride concentration. (c) $\ln(C/C_o)$ vs. time for different inter-electrode distance.

The plot of $\ln(C_{Fo}/C_F)$ as a function of time t is linear with a slope of k, so the removal kinetic model has been observed in the first-order. Figure 6a–6c demonstrates the plot of $\ln(C_{Fo}/C_F)$ as a function of time is liner with slope k for EC process parameters (current density, initial fluoride concentration, and distance between electrode IED). Table 6 represents the related values of the determination coefficient R^2 and the specific rate constant k.

The eliminating fluoride ion with related R^2 values has best described by first-order kinetics, as seen in Figure 6a–6c, for various current densities, initial fluoride concentration, and inter-electrode distance is all highly close to unity. The result of the kinetic investigation revealed that when CD ascended from 21.17 to 169.38 A/m^2, more aluminum hydroxide flocs were produced at higher CD, and the rate constant k increased from 0.02738 to 0.10943 min^{-1}. As a consequence of the result, k indicates that the fluoride ion removal rate is proportional to the current density. The removal rate decreases with an increase in IED. Table 6 reveals that the rate constant k decreases from 0.09214 to 0.05587 min^{-1}, for the reason that due to less inter-facial contact of the produced aluminum flocs from the electrode with the fluoride ion over more distances. The rate constant k decreased from 0.12385 to 0.02818 min^{-1} as the initial concentration of fluoride increased from 5 to 25 mg/L. The reason behind this is the high concentration of fluoride ions present compared to less quantity of available flocs in that part of the EC reactor.

Characterization of generated sludge

After the EC process, a white precipitate developed at the bottom of the EC bath. After filtering using filter paper (Whatman filter paper No. 42 India), the precipitate was removed and dried in a hot air oven for 3–4 hours. To characterize the by-product formed by the EC bath, it was ground into a fine powder and prepared for EDAX and FTIR characterization. The EDAX analysis's spectrum is illustrated in Figure 7. Figure 7 shows it clearly, the presence of fluoride in the sludge provides evidence that fluoride ions, along with Al and a small amount of Ca, were captured in the sludge. The FTIR spectrum is shown in Figure 8, with peaks at 1800 and 1750 cm^{-1} that are most likely due to O–H stretching. O–H bending and Al–O bond stretching is both shown by the peaks at 1500 and 1250 cm^{-1}, respectively. Fluoride is linked to

Table 6. Calculated values of the first-order rate constant (k) and the related R^2 values for various CD, starting pH, initial concentration, and IED at monopolar connection at stirring speed of 700 RPM, salt dosage of 0.33 g/L, and 40 minutes of EC process at constant volume of sample water of 2.5 L.

Constant parameters	Operating parameters	Rate constant k (min^{-1})	R^2	Finding
pH 7; C_o 10 mg/L; IED 1 cm	Current density (A/m^2)			
	21.17	0.02738	0.99008	The reaction rate constant k is increased by CD increase, thereby removal rate increases
	42.32	0.03011	0.99236	
	63.52	0.03095	0.98659	
	84.69	0.04655	0.99186	
	105.86	0.08978	0.99117	
	127.03	0.09095	0.98981	
	169.38	0.10943	0.99464	
pH 7; CD 105.86 A/m^2; IED 1 cm	C_o (mg/L)			
	5	0.12385	0.99579	k is inversely proportional to the IED. Therefore, removal rate decreases
	10	0.09214	0.99797	
	15	0.05703	0.99727	
	20	0.04262	0.98991	
	25	0.02818	0.99381	
pH 7; CD 105.86 A/m^2; C_o 10 mg/L	IED (cm)			
	1	0.09214	0.99797	The reaction rate constant k decreases with the C_o increase. Hence, removal rate decreases
	1.5	0.07962	0.99728	
	2	0.06262	0.99641	
	2.5	0.05587	0.99291	

Error: pH = ±0.215; C_o = ±0.45 (mg/L); CD = ±2.631 (A/m^2); IED = ±0.0525 (cm); RPM = ±21.

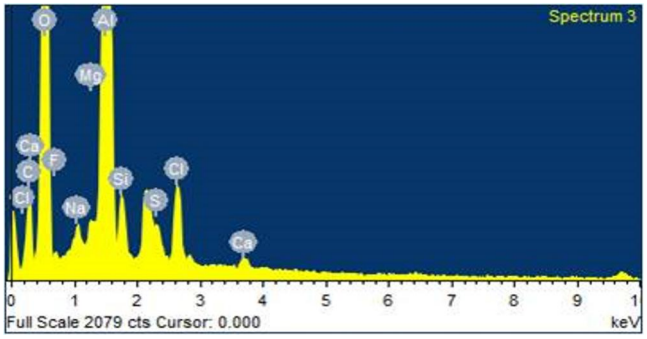


Figure 7. EDX image for produced sludge from EC reactor.

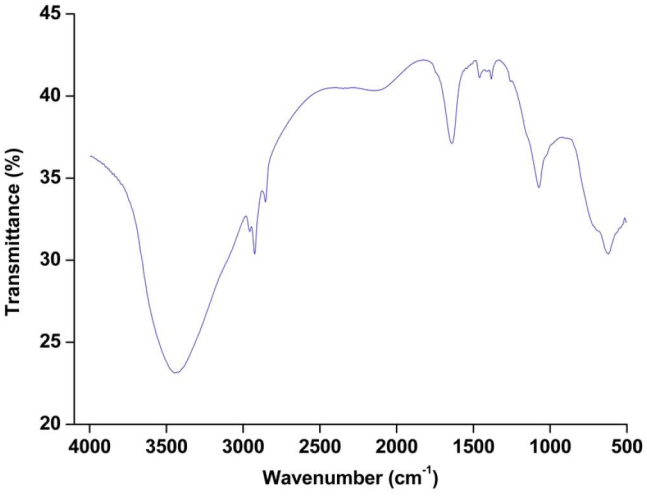


Figure 8. FTIR analysis for produced sludge from EC reactor.

aluminum hydroxide complexes according to the FTIR and EDAX study of sludge.

Comparison of present results and earlier research on fluoride reduction

Current density per unit volume of groundwater has been selected as the criterion to compare with data from literature because the density of the amount of produced flocs per unit volume of solution is the determining factor for any contaminant removal. According to Table 7, the current concentration (CD/L) value reported in the current work is minimum than that of the published earlier works by the researchers. In the present work, the working volume of the EC bath is lower with maximum removal efficiency (97.6%) compared to previous authors. This finding suggests that a larger reactor working volume of water is more effective for fluoride removal from groundwater using the EC process.

First-order kinetics was observed in the kinetic study. The reaction rate constant k increases with CD increase, k decreases with IED increase, and k decreases with initial concentration increase. Therefore, optimum process parameters of CD, IED, and initial concentration are significant for the maximum removal of fluoride from groundwater by EC.

The real groundwater collected from the village of Bhichawa study

The effectiveness of the EC technique was also assessed for the removal of fluoride from an actual groundwater sample of the village of Bhichawa under Makrana tehsil of Nagaur district, Rajasthan, India. Table 8 provides an illustration of the natural groundwater characteristics that were collected

Table 7. Comparison of present results and earlier research on fluoride reduction.

pH	EC time (minutes)	C_o (mg/L)	IED (cm)	CD (A/m^2)	Working vol (L)	CD/L water ($A/m^2.L$)	Kinetics *k*	Operating cost (US$/$m^3$)	Removal %	Reference
7	40	10	1	105.86	2.5	42.34	1st order	0.27	97.6	Present Study
7	32	10	1	129.31	3	43.1	1st order	N.A.	97.2	[11]
7	25	25	3	167	2	83.50	1st order	1.48-1.27	94.5	[31]
8	40	10	0.5	625	3	208.33	N.A.	0.38	90	[32]
7	95	12	1	10	1.4	7.14	Pseudo 1st & 2nd order	0.357	88.33	[1]
8	30	10	0.5	625	3	208.33	N.A.	0.38	90	[2]
7	95	12	1	10	1.4	7.14	N.A.	0.343	88.3	[33]
6	25	10	0.5	20	0.5	40	N.A.	0.379	98	[24]
6–8	55	10	0.5	1250	3.66	341.5	N.A.	N.A.	Under limit	[21]
9.14	30	8.63	0.5	50	2	25	N.A.	0.531	84.86	[34]

Table 8. Initial characteristics of real ground water and the removal percentage of them.

Parameters	Initial value (before treatment)	Final value (after treatment)	Removal %	WHO standards for drinking water[5]
pH	7 ± 0.07	7.6 ± 0.1	–	6.5 to 8.5.
Fluoride (mg/L)	10 ± 0.1	0.19 ± 0.002	98.1 ± 1.0	1.5 mg/L
TDS (mg/L)	540 ± 0.8	130 ± 1.3	76 ± 0.8	300 mg/L
Turbidity (NTU)	1.6 ± 0.9	0.19 ± 0.002	88.1 ± 0.9	5 NTU
Conductivity (μS/cm)	1077 ± 0.7	310 ± 3.1	71.2 ± 0.7	400 μS/cm
Chloride (mg/L)	429 ± 0.8	85.5 ± 0.9	80 ± 0.8	250 mg/L
Calcium (mg/L)	20.1 ± 0.9	1.84 ± 0.02	90.8 ± 0.9	75 mg/L
Magnesium (mg/L)	43.16 ± 0.9	2.75 ± 0.03	93.6 ± 0.9	50 mg/L
Sulfur (mg/L)	66.25 ± 0.8	12 ± 0.1	81.9 ± 0.8	250 mg/L
Sodium (mg/L)	284 ± 0.8	54 ± 0.5	80.98 ± 0.8	200 mg/L

from the village of Bhichawa. The optimum EC conditions (CD = 105.86 A/m^2; IED = 1 cm; RPM = 700; EC time = 40 minutes) have been efficiently applied in natural groundwater after the successful EC treatment of synthetic groundwater and the efficient outcomes have been found. As shown in Table 8, the EC process effectively reduced the fluoride (as measured by its removal efficiency of 98.1%) and other water quality parameters from natural groundwater, such as TDS, calcium, magnesium, sodium, and chloride, to levels that were within the WHO's drinking water criteria.

Conclusion

Fluoride and other contaminants like TDS, turbidity, and conductivity are successfully removed from the groundwater in Bhichawa village utilizing the EC procedure and an aluminum electrode in the current study. The suggested EC process operating parameters have reduced the fluoride concentration from 10 to 0.24 mg/L in groundwater with 97.6% efficiency, below the WHO-permitted level of 1.5 mg/L. The optimum parameters found for the removal of fluoride with 97.6% efficiency are as initial pH level 7, current density 105.86 A/m^2, inter-electrode distance 1 cm, and a speed of stirring 700 RPM. For the EC process, to remove 97.6% of fluoride, the running cost was US$ 0.27 per cubic meter. Therefore, the EC process could be viewed as a treatment that successfully eliminates fluoride, turbidity, TDS, and any associated contaminants as WHO palatable water guidelines. The kinetic study reveals first-order kinetics, with R^2 coefficient values that are very close to unity for different current densities, beginning concentrations, and inter-electrode distances. The reaction rate constant *k* is increased by CD increase because more aluminum hydroxide flocs have formed at higher CD. The removal rate decreases with increasing IED, as the value of the rate constant *k* was found to decrease with increasing IED. The rate constant *k* decreased when the initial concentration of fluoride was increased from 5 to 25 mg/L, indicating a lower rate of fluoride removal. As a consequence, the kinetic study shows that the optimum process parameters like CD, IED, and initial concentration are significant for the maximum removal of fluoride from groundwater by EC. EDAX and FTIR analysis of the sludge produced by the EC bath verify the presence of fluoride. The current concentration calculated (CD/L) and the working volume of the EC bath are lower with maximum removal efficiency (97.6%) compared to previous literature. The EC technology efficiently reduced the fluoride concentration (fluoride removal efficiency 98.1%) from real groundwater according to WHO drinking water guidelines. Consequently, such findings suggest that a large reactor working volume of water is more effective for removing fluoride from groundwater using an EC process.

Disclosure statement

The authors certify that none of their known financial conflicts of interest or close personal ties might have appeared to have influenced the research presented in this study.

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