ORIGINAL ARTICLE

The effect of electrocoagulation (EC) on total arsenic, arsenite (As^{3+}) and arsenate (As^{5+}) species removal from model groundwater investigating toxicity and sludge characteristic

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Abstract

This study showed that the model groundwater containing As^{3+} and As^{5+} species was successfully treated with electrocoagulation (EC) first time in the literature investigating toxicity reduction, inorganic arsenic species and detailed sludge characterization. The arsenic removal from model groundwater with 1000 μg/l total arsenic containing equal arsenite (As^{3+}) and arsenate (As^{5+}) concentration was examined by the EC treatment optimized with following parameters; current density (5.0, 7.5 and 10.0 mA/cm^2) supporting sodium sulfate electrolyte amount (10, 20 and 30 mM Na$_2$SO$_4$) and initial water pH (3, 6 and 9). In EC treatment, the 99.87% arsenic removal was obtained with 10 mA/cm^2, 10 mM Na$_2$SO$_4$ at pH 3 after 40 min supplying 1.44 μg/l effluent As concentration lower than the WHO limit for drinking water. Through transformation mechanisms of more toxic As^{3+} to less toxic and easily settled As^{5+} according to As speciation analysis, the toxicity of the model groundwater was successfully decreased in parallel with total arsenic, As^{3+} and As^{5+} removal during EC. The precipitated Al(OH)$_3$ and Al$_2$O$_3$ coagulants were the main peaks in the FTIR-ATR spectrum as well as As(III)–O vibration observed between 717 and 721 cm^{-1} peaks and As(V)–O vibration dominated 899 and 972 cm^{-1} peaks were detected in the produced sludge after the EC. The SEM–EDS morphological analysis was demonstrated that the sludge was consisted of mostly amorphous structure aggregated size range of 200 μm–2 mm, relatively uniform cake including O, Al, As, Na, and S.

Keywords Groundwater · Arsenic · Electrocoagulation · Arsenic specification · Toxicity · Sludge characterization

Introduction

Environmental pollution has converted a serious subject across the world, and among the world's top ecological worries, water pollution is a foremost risk to the human life and water ecosystem (Madima et al. 2020). Correspondingly, it is a pressing problem to defend the ecosystem and human from the poisonous effects of heavy metal pollution (Bushra et al. 2014). Management of water supply is a magnificent task in the recent century because of pollution and climate change that are reducing the amount of drinking water. Therefore,

there is a need for enhanced techniques to treat polluted water sources (Madhura et al. 2018).

Arsenic concentrations found in surface and groundwater increase in parallel with to widely use of arsenic-containing pesticides used to raise agricultural productivity. Arsenic (As) is found certainly in soil, in some rock types, and particularly in minerals and ores covering lead and copper. The As dust carried by the wind can arrive the air and water ecosystems as a result of surface run off and infiltration into the groundwater (Tsiepe et al. 2018). The contaminant level of the arsenic in drinking water is 10 μg/l according to WHO guidelines (Viraraghavan et al. 1999). However, the As concentration in groundwater increases with decreasing water level of groundwater due to climate change and excessive usage. As formation in natural waters depends on the geological, hydrogeological, and geochemical properties of the environment, while the anthropogenic sources of As are quite different (Mukherjee et al. 2006). In addition to various industrial activities, the most important factor causing As formation is the usage of pesticides and mining activities.
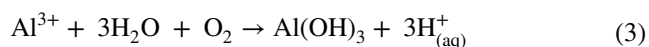
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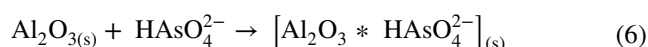
Among the most widely used As-containing pesticides in the world are lead arsenate (Pb$_3$(AsO4)$_2$), calcium arsenate (Ca$_3$(AsO$_4$)$_2$), magnesium arsenate (Mg$_3$(AsO$_4$)$_2$), zinc arsenate (Zn$_3$(AsO$_4$)$_2$), and zinc arsenide. (Zn(AsO$_2$)$_2$) (Zhang et al. 2019). Many researches indicate the importance of As pollution in groundwater and its health effects. As listed as priority water pollutants impact on humans' targeting pancreas, skin, lungs, urinary bladder, kidney, and liver (Jang et al. 2016). Conventional physical and chemical removal techniques (i.e., coagulation and flocculation) may not be effective in As removal alone, but combination of some alternative methods also must be required to obtain efficient removal of toxic heavy metals (Kumar et al. 2019). Membrane filtration, adsorption, ion exchange, electrodialysis, advanced oxidation processes, and phytoremediation can be efficient for As removal, but they have same pros and cons reported in the literature (Jeevanantham et al. 2019).

Electrocoagulation (EC) method, that has high removal efficiency in the treatment of water and wastewater containing arsenic, is preferred since it has lots of advantages comparing to other methods. Ghosh et al. (2019) reported that EC is a unique and robust technical solution for arsenic removal solving the lack of affordable and sustainable technology. The mechanism of removal of heavy metals by EC is generally controlled with aluminum and iron electrodes (metal), which are frequently used in wastewater treatment as electrode material (Govindan et al. 2014a). Even if the aluminum and iron electrodes are used in wastewater treatment, the aluminum electrode is used extensively in electrocoagulation studies because it is very effective and low-cost electrode material (Govindan et al. 2014b). When the electrolytic dissolution of aluminum anode at low pH results in cationic species such as Al^{3+} and Al(OH)$_3$. In accordance with the following reactions, at the appropriate pH values, the aluminum electrode first converts to Al(OH)$_3$ and then polymerizes to (Al(OH)$_3$)$_n$ as an intermediate reactions showing between Eqs. (1) and (4) (Flores et al. 2014).

$$Al \rightarrow Al^{3+} + 3e^- \tag{1}$$

$$3H_2O + 3e^- \rightarrow 1.5H_2 + 3OH^- \tag{2}$$

$$Al^{3+} + 3H_2O + O_2 \rightarrow Al(OH)_3 + 3H^+_{(aq)} \tag{3}$$

$$n\,Al(OH)_3 \rightarrow \left(Al(OH)_3\right)_n \tag{4}$$

Arsenic can be found in the four oxidation states such as arsines and methyl arsines (As^{3-}), elemental arsenic (As^0), arsenite (As^{3+}) and arsenate (As^{5+}), and among these arsenic species, the inorganic formed arsenic (As^{3+} or As^{5+}) is highly toxic and mobile in the environment compared to the organic form (As^{3-}). In specific, arsenite

(As^{3+}) is found to be ten times more toxic than arsenate (As^{5+}). Arsenite (As^{3+}) is one of the most widely available and predominant forms of arsenic in natural groundwater. Typically, As^{5+} is dominant in surface waters, while As^{3+} is found in groundwater. At neutral pH, the predominating species of As^{5+} present negative charge, HAsO$_4^{2-}$, while the species of As^{3+} generally have no charge, HAsO$_{2(aq)}$ and H$_3$AsO$_{3(aq)}$. The Al(OH)$_{3(s)}$ and Al$_2$O$_{3(s)}$ flocs adsorbing HAsO$_4^{2-}$ indicating following reaction given in the Eqs. (5) and (6) (Ghurye and Clifford 2004).

$$Al\,(OH)_{3(s)} + HAsO_4^{2-} \rightarrow \left[Al\,(OH)_3 * HAsO_4^{2-}\right]_{(s)} \tag{5}$$

$$Al_2O_{3(s)} + HAsO_4^{2-} \rightarrow \left[Al_2O_3 * HAsO_4^{2-}\right]_{(s)} \tag{6}$$

Flores et al. (2014) reported 92% total As removal in continuous flow EC system with aluminum electrode 6 mA/cm^2 current density at pH 7.5 and 1.8 cm/sec velocity. Similar to EC process, chemical-oxidation followed by adsorption was reported as more effective method for arsenic removal by Ghurye and Clifford (2004) with the aim of oxidation is to convert As^{3+} to arsenate As^{5+}, and the removal of As^{3+} was found to be faster than the removal of As^{5+}, because As^{3+} is oxidized to As^{5+} simultaneously. The EC mechanism is highly dependent on the chemistry of the aqueous medium, particularly its conductivity. In addition, parameters such as pH, particle size and concentration of chemical components are effective in the electrocoagulation process. Coreño and Nava (2018) studied the removal of hydrated silica, fluoride and arsenic from groundwater by EC using a special design continuous reactor. They reported that the EC was effective in the continuous reactor using aluminum plates applying the current density (4–8 mA/cm^2) and mean velocity (0.057–0.57 cm/s) on the silica (Si), F, and As removal efficiencies. Arsenic removal was performed after As^{3+} was oxidized to arsenate As^{5+} to attain the precipitation of As^{5+}, which is less mobile and is adsorbed more easily by the Al(OH)$_{3(s)}$ and Al$_2$O$_{3(s)}$ flocs in the summarized studies above, but this arsenic species and their toxicities are not detailly examined in EC treatment.

Electrochemical treatment methods are listed as unique and robust technical solution for arsenic pollution in the groundwater resulted from arsenic-containing pesticides usage in addition to its natural sources. Although the removal of total As and its inorganic species (As^{3+} and As^{5+}) have been studied with different wastewater characteristics in different EC systems, this study obviously states that the effect of EC treatment on these species and their toxicity has not been investigated in the literature yet. This is the first study in the literature investigating the treatment of model groundwater containing As^{3+} and As^{5+}

with EC by using toxicity reduction, inorganic arsenic species, and detailed sludge characterization.

Experiment section

Electrochemical setup

The utilization of total As was investigated for determination of EC treatment efficiency for model groundwater. The EC experimental setup is shown in Fig. 1. EC process was carried out in a reactor with six mono-polar parallel aluminum plate electrodes producing different current density (5.0, 7.5 and 10.0 mA/cm^2) through 400 ml groundwater supported by different Na$_2$SO$_4$ (Merck, Germany) electrolyte concentrations at different initial pH (3, 6, and 9).

The model groundwater was used with total As concentration of 1000 µg/l adding 500 ± 25.00 µg/l As^{3+} from standard stock ICP-MS reference solution (High Purity Standard, USA, Lot number: 1732430, 1000 µg/l As^{3+} in 2% HCl) and 500 ± 25.00 µg/l As^{5+} from standard stock ICP-MS reference solution (High Purity Standard, USA, Lot number: 1709409, 1000 µg/l As^{5+} in 2% HCl). The prepared model groundwater characteristic is given in Table 1.

The reaction kinetic of EC treatment was examined with kinetic models given in Table 2. The reaction constant (k) was determined with linear regression coefficient (R^2) according to following equations given in Table 2. Where C$_0$ and C$_t$ represented As concentrations at the corresponding
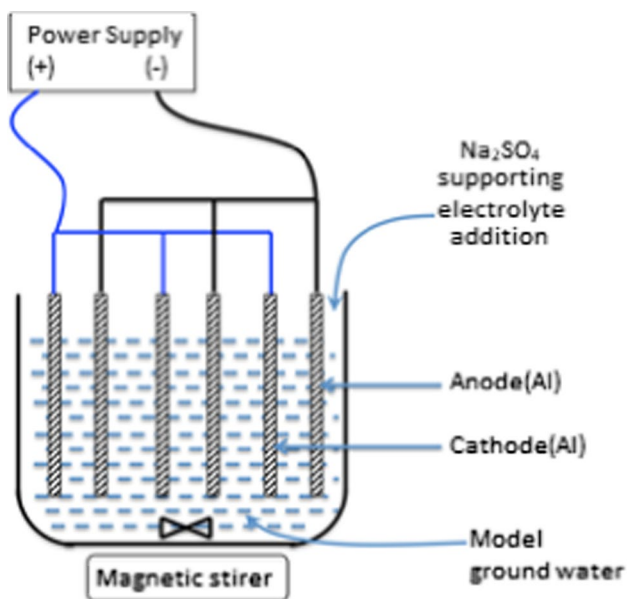
Table 1 The model groundwater characteristic

Parameter	Value
Total Arsenic (µg/l)	1000.00 ± 50.00
Arsenite (As^{3+}) (µg/l)	500 ± 25.00
Arsenate (As^{5+}) (µg/l)	500 ± 25.00
Initial pH	6.01 ± 0.30
Conductivity (µS/cm)	2178.00 ± 35.50

time, $\frac{d[C]}{dt}$ indicated the change of As concentration according to treatment time.

Determination of total arsenic

In order to determine the performance of EC, total arsenic (^{75}As) concentrations both of influent and effluent were analyzed with inductively coupled plasma-mass spectrometer (Agilent 7800 ICP-MS, Serial No:JP17170673, Germany) using autosampler (Agilent SPS 4, Germany) according to EPA 6020A 2007–02. The ICP-MS calibration was made with secondary standard solutions including 0 µg/l, 50 µg/l, 100 µg/l, 250 µg/l, 500 µg/l and 1000 µg/l ^{75}As diluting the primary certificated environmental calibration standard (Agilent, Japan, Lot number: 5183–4688, 10 mg/l ^{75}As in 10% HNO$_3$) with 2% HNO$_3$. For the accurate determination of ^{75}As, the measurements were quantified by internal solution with 200 µg/l ^{72}Ge prepared from ICP-MS internal standard solution (Agilent, Japan, 100 mg/l ^{72}Ge in 10% HNO$_3$) in both no gas mode and helium collision mode. The verification studies were performed with certificated standard material (CRM, NIST, USA, 1640a: Trace Element in Natural Water, 8.075 ± 0.07 µg/l ^{75}As in 10% HNO$_3$). The calibration curves obtained no gas mode (Supplementary Material, Fig. S1) and helium collision mode (Supplementary Material, Fig. S2) were given in the Supplementary Material with detection limit (DL), regression coefficient (R^2) and background concentration (BEC). The ^{75}As concentration was reported using helium collision mode preventing polyatomic interferences such as the presence of ^{40}Ar^{35}Cl$^+$ with $R^2 = 1.000$, DL: 0 µg/l and BEC: 0.015 µg/l.

Arsenic specification as As^{3+} and As^{5+}

As^{3+} and As^{5+} concentrations both of influent and effluent were analyzed with high pressure liquid chromatography-inductively coupled plasma-mass spectrometer (HPLC-ICP-MS). Firstly, the arsenic specification was made by HPLC (Agilent, 1260 Infinity II HPLC, Germany) using manual injection (Agilent 1260 Manuel Injection, Germany), isocratic pump (Agilent 1260 Iso Pump, Germany), and arsenic speciation column (Agilent, G3154-65,001 As speciation

Fig. 1 Experimental setup used in the electrocoagulation (EC) treatment

Table 2 The models of reaction kinetic and their equations

Models	Equations of kinetic models
First order	$-\frac{d[C]}{dt} = k[C], -\frac{d[C]}{[C]} = kdt, ln\frac{[C_0]}{[C_t]} = kt$ (7)
Pseudo-first order	$-\frac{d[C]}{dt} = k[.OH][C], -\frac{d[C]}{[C]} = k[.OH]dt, ln\frac{[C_0]}{[C_t]} = k[.OH]t$ (8)
Second order	$-\frac{d[C]}{dt} = k[.OH][C] = -\frac{d[C]}{[C]^2} = kdt, \frac{1}{C_t} - \frac{1}{C_0} = kt$ (9)

column, Japan) for drinking water. Finally, separated As^{3+} and As^{5+} were detected by ICP-MS (Agilent 7800 ICP-MS, Serial No: JP17170673, Germany).

For As^{3+} and As^{5+} speciation, a mobile phase was prepared with reagents as follows: 1 M NaH_2PO_4 (Merck, Germany), 0.1 M EDTA- 2Na (Merck, Germany), and 1 M NaOH (Merck, Germany), to attain final 2.0 mM NaH_2PO_4/0.2 mM EDTA solution at pH: 6 used as the mobile phase. The mobile phase was introduced at 0.3 ml/min flow rate for one night to condition the column. The flow rate of mobile phase was set to 1.0 ml/min for sample analysis.

For the calibration of HPLC-IC-MS, the primary As^{3+} ICP-MS reference solution (High Purity Standard, USA, Lot number:1732430, 1000 μg/l As^{3+} in 2% HCl) was mixed As^{5+} ICP-MS reference solution (High Purity Standard, USA, Lot number:1709409), and the calibration was made with secondary standard solutions including 0, 50, 100 and 200 μg/l As^{3+} and As^{5+} in mobile phase. The calibration curves (Supplementary Material, Fig. S3 and Fig. S4) and chromatogram (Supplementary Material, Fig. S5) obtained in the helium collision mode were given in the Supplementary Material with DL, R^2 and BEC for As^{3+} and As^{5+}. For the sample analysis, 50 μl sample was introduced to HPLC-ICP-MS at ambient temperature with manual injection and the As^{3+} peak was observed 3 min, while a As^{5+} peak was shown in 6 min in the total 10 min run time for each sample.

Toxicity assays

The toxicity tests of treated wastewater samples were analyzed with Microtox Model 500 (Azur Environmental Carlsbad, USA). The lyophilized *Vibrio fischeri* bacteria (NRRL number B-11177, Microtox Acute reagent, Modern Water, USA) with luminescence characteristics were used as test microorganism. The *Vibrio fischeri* bacteria were incubated with reconstitution solution (nontoxic ultra-pure water, Modern Water, USA) and osmatic adjuster solution (22% sodium chloride, Modern Water, USA) at 15 °C during 15 min in glass cells. Four serial dilutions of the sample were prepared with dilution solution (2% sodium chloride, Modern Water, USA), and the samples were tested with the bacteria to obtain lethal concentration required for 50% death of bacteria (LC_{50}). The toxicity reduction was expressed as

relative toxicity index (RTI) with LC_{50} of un-treated and treated wastewater for EC studies expressed as Eq. 10.

$$RTI = \left(\frac{LC_{50} \text{ t} = 0}{LC_{50} \text{ t} = \text{t}}\right) \tag{10}$$

where RTI is the Relative Toxicity Index (dimensionless), LC_{50}t = 0 is the Lethal concentration required for 50% population of bacteria at time 0 (%), and LC_{50}t = t is the Lethal concentration required for 50% population of bacteria at time t (%).

Sludge characterization

The characterization of the resultant sludge samples was carried out by Fourier transform infrared spectrophotometer (FTIR- Shimadzu IRTracer-100) and attenuated total reflectance (ATR-Pike Tech). FTIR-ATR spectroscopy allowed to analyze solid or liquid samples to be measured with minimum volume or weight without making KBr disk requirement easily and fast. The sludge samples were dried at 60 °C for 1 h to remove water moisture. The prepared sludge samples were analyzed with FTIR-ATR with 4 cm^{-1} resolution between 4000 and 700 cm^{-1} wavelengths.

The morphological analysis of the resultant slug samples that was carried out by SEM (SEM, Hitachi TM3030Plus Benchtop) and the chemical composition was determined by energy dispersive spectrum (EDS, Oxford Instruments Swift ED3000) using 20 kVA target voltage, 8.8 mm working distance and 500× magnification without Au coating.

Results

Results of EC treatment

The treatment results of EC methods are summarized in Table 3 with removal efficiency (E, %) the total energy consumption (kWh/m^3), first-order reaction constant (min^{-1}), and their linearity.

Total As removal as μg/l and total energy consumption as kWh/m^3 obtained in the EC treatment are given in Fig. 2 indicating current density (5.0, 7.5 and 10.0 mA/cm^2) effect and Na_2SO_4 supporting electrolyte effect at different initial

Table 3 The treatment results of EC method

	i (mA/cm²)	Na₂SO₄ (mM)	Initial pH	Initial conductivity (µS/cm)	E (%)	Energy Cons. (kWh/m³)	k (min⁻¹)	R²
Electrocoagulation (EC)	5.0	10	6	2353	92.98	35.41	0.0883	0.9301
	7.5	10	6	2194	94.84	50.96	0.0917	0.9485
	10.0	10	6	2173	98.84	64.65	0.1229	0.9924
	10.0	20	6	4420	97.31	69.04	0.1164	0.9736
	10.0	30	6	5374	96.65	66.31	0.0855	0.9606
	10.0	10	3	2373	99.87	15.29	0.1364	0.9945
	10.0	10	9	2406	97.35	28.88	0.1083	0.9837

Fig. 2 Total As removal efficiency and energy consumption of EC (**a**: the current density effect on the total As removal efficiency in EC, **b**: current density effect on energy consumption in EC, **c**: the effect of Na₂SO₄ concentration on total As removal efficiency in EC, **d**: the effect of Na₂SO₄ concentration on energy consumption in EC, **e**: initial pH effect on total As removal efficiency in EC, **f**: the effect of initial pH on energy consumption in EC)
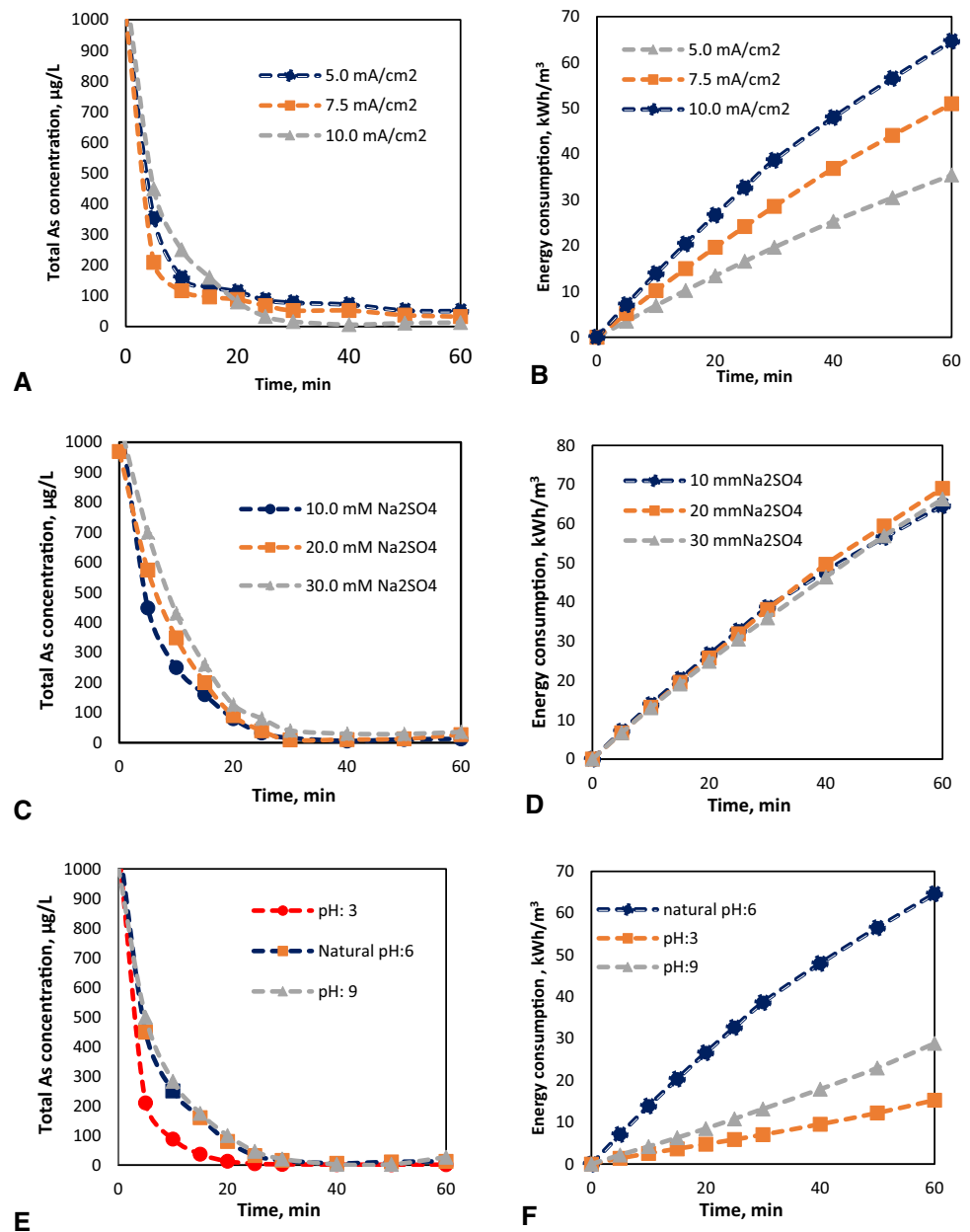
pH (3, 6, and 9). According to Table 2 and Fig. 2, it was determined that the maximum total As removal was 99.87% with 10 mA/cm², 10 mM Na₂SO₄ at pH:3 after 40 min EC treatment. Total As was successfully removed from model groundwater supplying 1.44 µg/l effluent As concentration lower than 10 µg/l, which is maximum contaminant level for the arsenic in drinking according to WHO guidelines.

EC process is a promising technology for the effective removal of suspended solid, non-biodegradable toxic organic compounds and metal/heavy metals from water like As. Optimum current density was selected with 10 mA/cm² as a results of EC treatment in this study. It was found that the current density more effective than supporting electrolyte and initial pH. The main reason why the current density was the more effective parameter was thought that the current density played an effective role in both the amount Al^{3+} and Al(OH)₃ dissolved from the anode passing current in accordance with Eqs. 1–5 reactions. The current density played a more effective role on As removal than other treatment parameters, since both reactants were produced in the system with increasing current density simultaneously. As it can be seen in Fig. 2, the energy consumption was 35.41 kWh/m³, 50.96 kWh/m³, and 64.65 kWh/m³ for the 5.0, 7.5 and 10 mA/cm², respectively. The high electrical energy consumption with increasing current density was an expected result because higher current density caused to solve more electrode material and remove more pollutant. Can et al. (2014) reported the 99.68% of arsenic removal efficiency at 1.07 mA/cm² current density application resulting 1.23 kWh/m³ energy consumption at the end of 30 min EC treatment with iron (Fe) electrode. They indicated that the current density determined the coagulant dosage rate, the bubble production rate, the size and the growth of flocs. Similarly, Balasubramanian et al. (2009) stated that the arsenate (As^{5+}) removal depends on the directly proportional to the amount of coagulant generated by the applied charge on the Al electrode surface according to Eq. 11.

$$\left(Al(OH)_3\right)_n + AsO_4^{3-} \rightarrow \left[Al(OH)_3 * HAsO_4^{3-}\right]_{(s)} \quad (11)$$

The electrical conductivity of the model water and wastewater may not be sufficient for the formation of a salt bridge in the electrochemical reactor. In such cases, external supporting electrolyte should be added to the EC system. Frequently used supporting electrolytes are NaCl, Na₂SO₄, NaNO₃, KCl, and NaCOOH. In this study, Na₂SO₄ was chosen as the supporting electrolyte, since the permissible concentration in water and wastewater can reach 250–500 mg/l for SO₄$^{2-}$ and it has less harmful effect on human health than CI$^-$ ad NO₃$^-$ anions. While the energy consumption was 64.65 kWh/m³, 69.04 kWh/m³, and 66.31 kWh/m³, the arsenic removal efficiency was 98.84, 97.31 and 96.65% for the 10, 20 and 30 mM Na₂SO₄ addition, respectively. It showed that the supporting electrolyte addition had no significant effect on As removal efficiency and energy consumption. Lakshmanan et al. (2010) obtained 99% As^{5+}, and 80% As^{3+} removal in the batch flow EC reactor with iron electrode as anode and steel electrode as cathode. Similarly, Gomes et al. (2007) attained 99.3% As^{3+} removal in the batch flow EC reactor with aluminum electrodes under the optimum EC conditions with 30 mA/cm² current density at pH 2.4 and 120 min treatment period, while 99.6% As^{3+} removal was obtained with iron electrodes in shorter treatment period with same conditions. Similar to these results, Can et al. (2014) reported that adding supporting electrolyte had no noteworthy effects on the arsenic removal. However, they found that the supporting electrolyte addition decreased energy consumption because amounts of ions in solution increased under constant current density. According to the common view, the real wastewater and groundwater generally have high electrical conductivity, although EC treatment performed using synthetic wastewater to optimize the operating parameters frequently required the supporting electrolyte addition to enhance the electrolytic conductivity. Thus, the supporting electrolyte addition helps in avoiding the formation of oxide layer, declining the ohmic drop, and consequently increasing the power density reducing energy consumption and process cost. However, the recent studies revealed that the opposite effects may occur due to the co-existing ion effect coming with the addition of support electrolyte such as sulfate, nitrate, chloride or main inorganic contaminants of groundwater (i.e., bicarbonate, silicate, phosphate, calcium, and magnesium (Balasubramanian et al. 2009). In this presented study, it would be possible to

Fig. 3 Variation of reaction rate constant with the current density (A), supporting electrolyte concentration (B) and the initial pH (C)
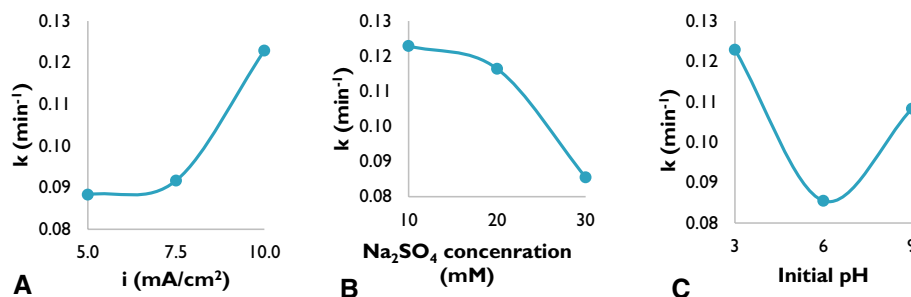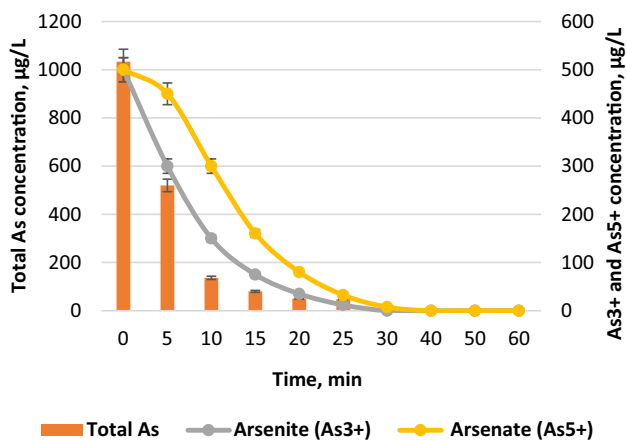
Fig. 4 Variation of As^{3+} and As^{5+} concentrations compering total As during EC treatment

reduce the energy consumption by increasing the amount of supporting electrolyte more than 30 mM, but 10 mM was chosen optimal in order to reduce the amount and cost of the additional chemical requirement and avoiding co-existing ion effect of sulfate.

Groundwater pH is an essential part of EC performance. As a results of pH effects on As removal and energy consumption, the removal efficiency was 99.87, 97.35 and 96.65%, while the energy consumption was 15.29, 66.31 and 28.88 kWh/m³, for the initial pH:3, pH:6, and pH:9, respectively. In acidic condition, As easily settled and removed from model groundwater. Secondly, electrolytic dissolution of aluminum anode at low pH increases the amount of cationic species of Al and this raises the produced coagulant concentration to make more flocs (Sandoval et al. 2021). pH is a major factor that mainly affects the speciation of coagulating agents and arsenic. Kumar and Goel (2010) reported 75% As^{5+} removal at continuous reactor using steel electrode at pH 7.2. During the EC process, pH tends to basic range over time because excessive hydroxide ions production predominates the removal mechanism. Even the arsenic removal efficiency is influenced by pH, oxidation state, and reduction/oxidation potential, it is hard to identify a relationship between pH and arsenic removal due to constant changes in the pH of the treated water during the EC process. However, the oxidation from As^{3+} to As^{5+} is suggested to improve arsenic removal (Zhao et al. 2011). To pre-oxidation of arsenite to arsenate, pH range was reported as 6–9 for iron electrode (Kobya et al. 2011), while the initial pH was indicated acidic pH (3–5) for aluminum electrode (Mohora et al. 2014). As a result, the optimum pH was selected as 3 because the arsenic from model wastewater can be effectively removed by electrocoagulation in acidic conditions. Therefore, continuous monitoring of inorganic arsenic species in groundwater is required in the EC treatment.

The reaction kinetic of electrocoagulation (EC) treatment was examined with reaction kinetic models given in Table 2. The reaction constant was determined with pseudo-first-order reaction kinetic model obtaining high linear regression ($R^2 > 0.93$) shown in Table 3, and the effects of current density, supporting electrolyte concentration and initial pH on pseudo-first-order reaction constant are illustrated in Fig. 3 to determine the effect of these EC parameters on As removal rate.

Singh and Mondal (2017) investigated the effects of initial pH, current density, hydraulic retention time, electrode distance, and supporting electrolyte concentration on the As and fluoride (F) removal considering operating cost of EC. They obtained the 98.51% As and 88.33% F removal under the optimum treatment conditions with 10 A/m² current density, 1 cm inter-electrode distance, 0.71 g/l NaCl concentration at pH:7 with an operating cost of 0.357 USD/m³ treated water. They reported that pseudo-first and second-order kinetic model showed linearity for arsenic and fluoride removal in EC treatment, respectively. They stated that EC treatment was able to reduce the arsenic and fluoride producing sludge confirming arsenic in As^{3+} form, and fluoride in sludge. In Fig. 3a, it was noticed that the reaction rate constant increased with an increase in the applied current density because the rate of coagulant generation from electrode surface obviously increased with applied current density according to Eqs. 1–4. According to Fig. 3b, the supporting electrolyte concentration reduced the rate of arsenic removal with EC treatment. The dissolved ions accompanying in water like supporting electrolyte could have a negative effect on pollutant removal rate, for the reason an additional reaction such as conversion of the sulfate to sulfite or persulphate given as following Eqs. 12–13 (Gayathri et al. 2010) or peroxodisulphate (Govindan et al. 2019).

$$H_2O + \sim \rightarrow H^{\bullet} + OH^{\bullet} \tag{12}$$
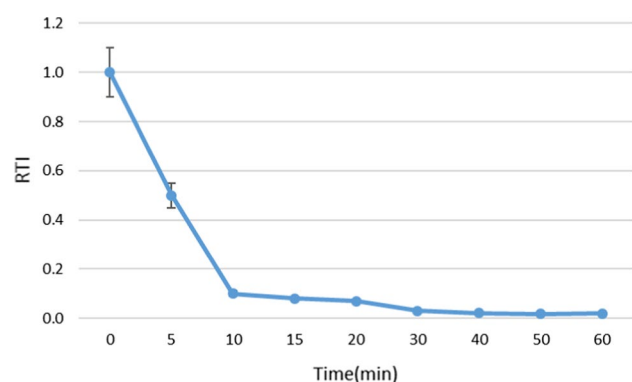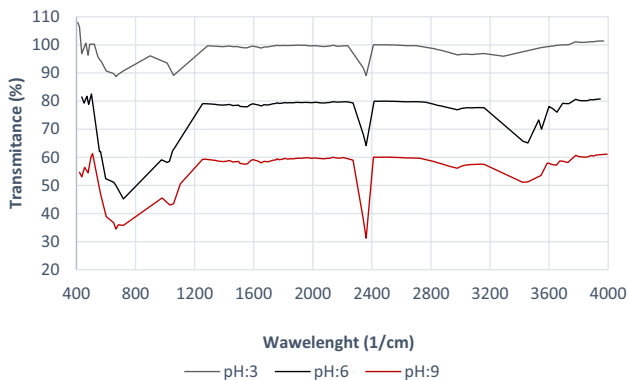

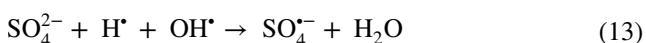**Fig. 5** Toxicity reduction curve during EC treatment
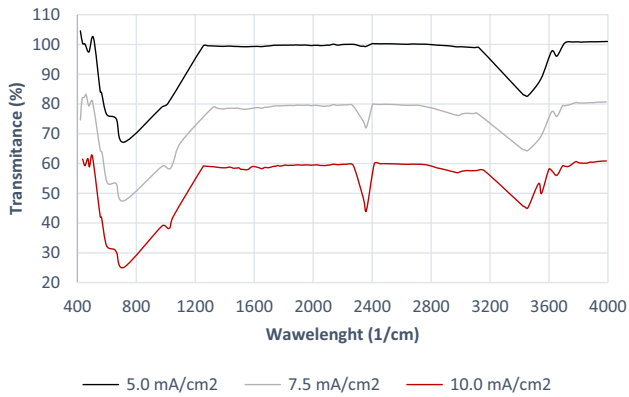
Fig. 6 The effect of current density on produced sludge in EC treatment
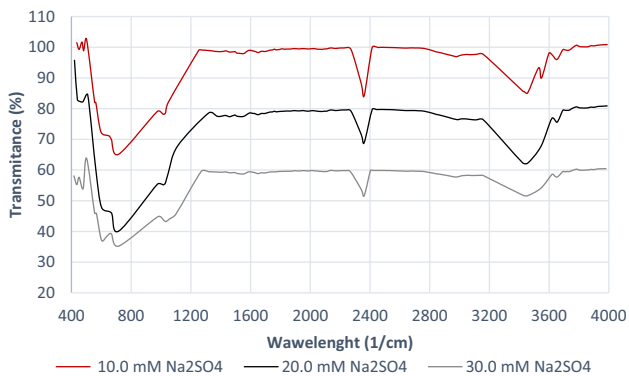
Fig. 7 The effect of supporting electrolyte on produced sludge in EC treatment

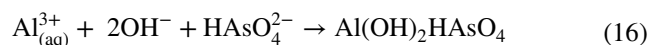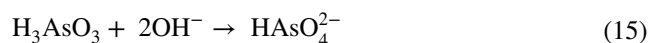**Fig. 8** The effect of initial pH on produced sludge in EC treatment

$$SO_4^{2-} + H^{\bullet} + OH^{\bullet} \rightarrow SO_4^{\bullet-} + H_2O \qquad (13)$$

$$SO_4^{2-} + SO_4^{\bullet-} \rightarrow S_2O_8^{2-} \qquad (14)$$

If these reactions given in Eqs. 12–14 can occur instead of Eqs. 1–4 in the EC treatment, the persulphate can be produced by activating sulfate with formation of hydroxyl radical, and so this decrease in ratio of settleable hydroxo cationic complexes like $[Al(OH)_3 * HAsO_4^{2-}]_{(s)}$ and $[Al_2O_3 * HAsO_4^{2-}]_{(s)}$ given in Eqs. 5–6, which eventually decreases the rate of arsenic removal and in turn the reaction rate constant.

The initial pH of water and wastewater is one of the imperative parameters affecting the performance of EC. A decrease in reaction rate constant when the initial pH was adjusted at 6 in Fig. 3c. This circumstance could be explained by behavior of Al electrodes in EC process in the literature. Reports showed that a decrease in cell voltage could be observed both at acidic (pH:3) and alkaline (pH:9) media, whereas the pH effect is not significant at pH:6 because the other coagulants such as $Al(OH)_2^+$, $Al(OH)^{2+}$, $Al(OH)_3$ and polynuclear hydrolysis products of Al were more effective at both at acidic and alkaline media in addition to $Al(OH)_{3(s)}$ and $Al_2O_{3(s)}$ (Mouedhen et al. 2008). As the initial pH increased from 6 to 9, the OH^- ion concentration was increased due to the adsorption of these ions onto surface of the $Al(OH)_3$ crystals resulting in a decrease in zeta potential and obtaining more effective settling (Koparal et al. 2008).

Results of arsenic specification and toxicity analysis in EC treatment

As^{3+} and As^{5+} concentrations both of influent and effluent were analyzed with HPLC-ICP-MS. The results of arsenic specification during EC treatment are summarized in Fig. 4 compering total arsenic removal from model groundwater. Specification studies carried out during the EC process in the optimum treatment conditions showed that As^{3+} was removed from the model groundwater faster than As^{5+}. At the end of 60 min EC treatment, the total concentration of As^{3+} and As^{5+} has fallen below the maximum allowable limit for total As. Similarly, in another study, the adsorption mechanism of As^{5+} was explained based on chemical equilibrium of $H_2AsO_4^{2-}$ species with $HAsO_4^{2-}$ for pH range of 3–7 (Olivera et al. 2018). In the EC treatment process, As^{3+} was precipitated by both active coagulants, and transforming into As^{5+} by the process given in Eqs. 15–16 (Nidheesh and Singh 2017).

$$H_3AsO_3 + 2OH^- \rightarrow HAsO_4^{2-} \qquad (15)$$

$$Al_{(aq)}^{3+} + 2OH^- + HAsO_4^{2-} \rightarrow Al(OH)_2HAsO_4 \qquad (16)$$

Table 4 FTIR-ATR peaks observed in the resultant sludge and their corresponding vibration type and wavenumbers

Oxidation state	Species	Peak wavenumber (cm^{-1})	vibration type	Description
As(III)	$As(OH)_3$	717	As–OH vibration	Symmetry stretch of As–OH
	$AsO(OH_2)^-$	721	As–O vibration	Symmetry stretch of As–O
As(V)	$AsO_3(OH)^{2-}$	899	As–O vibration	Polymeric vibration of As–O
	$AsO_3(OH)^{2-}$	972	As–O vibration	Asymmetric stretch of As–O
Al(III)	$Al(OH)_3$	2272	Al–OH vibration	OH stretching for basic hydroxyl groups from Al–OH
	Al_2O_3	2388	Al–O vibration	O bending for basic oxide groups from Al–O
	$Al(OH)_3$	3456	Al–OH vibration	OH bending for Al–O–H
	H_2O	1015	H–O–H vibration	H_2O bending vibration

The toxicity of arsenic in soil and water depends on the chemical form of this element. Therefore, continuous monitoring of inorganic arsenic species in drinking water is required in addition to total As monitoring. Also, toxicological investigation of As species must be performed to ensure that the more toxic arsenic species remove from water in EC processes. The toxicity of model groundwater containing As was investigated Microtox toxicity test during EC treatment. The toxicity reduction curve indicating relative toxicity index (RTI) is shown in Fig. 5.

The initial toxicity of the model groundwater was reduced by 90% within the first 10 min, and there was no toxic effect at the end of the 60 min total treatment period. Arsenic speciation and mobility can be altered as a result of varying pH, dissolved organic substances, Fe/Al, Mn oxides and (oxy)hydroxides and type of clay minerals in ground water. As^{3+} can be transformed into As^{5+} which is less bioavailable and more toxic in nature due to unstable thermodynamic nature of As under aerobic conditions (Hussain et al. 2021). Rubinos et al. (2014) reported that EC_{50} value of As^{3+} and As^{5+} was 71.4 and 95.5 mg/l, respectively, and they stated that the water content affects the EC_{50} value of As^{3+} and As^{5+}. In another study, EC_{20} values of As^{5+} were reported as 1.86 mg/l at pH:6 and 2.54 mg/l at pH 7 (Fulladosa et al. 2005). When the speciation and toxicity results were evaluated together with the total As removal efficiency, it clearly showed that EC method was an effective and reliable treatment for the arsenic-containing groundwater.

Results of sludge characterization

The characterization of the resultant sludge samples was carried out by FTIR-ATR spectroscopy. Thus, the individual effect of current density, supporting electrolyte, and initial pH on produced sludge was investigated after EC treatment. Their FTIR -ATR spectrums are given in Figs. 6, 7 and 8, respectively.

The variation of current density, supporting electrolyte concentration, and initial pH was not change the basic groups shown in their spectrums, while they altered the amount of these groups. In Fig. 6, the main peak observed at the vibration range between 2272 and 2388 cm^{-1} was increased as the current density raised from 5.0 to 10.0 mA/cm^2 because the peak was resulted as precipitated effective coagulants $Al(OH)_3$ and Al_2O_3 with pollutants. According to Fig. 7, these peaks related effective coagulants were suppressed when the supporting electrolyte concentration increased in parallel with the observed total As removal decrease in the EC treatment. The initial pH altered the precipitated As species according to Fig. 8. The FTIR-ATR peaks observed in the resultant sludge and their corresponding vibration type and wavenumbers are summarized in Table 4.

In the EC process, coagulant is produced in situ by electrochemical degradation of a suitable anode material. EC process consists of following steps; formation of coagulants by electrolytic oxidation of the soluble electrode, destabilization of contaminants and suspended particles and degradation of emulsions, and the destabilized of flocks came together for settling. In the resultant sludge produced after EC treatment, basic hydroxyl groups and their corresponding OH stretching were identified between 3456 and 3626 cm^{-1} peak band for aluminum hydroxide/oxyhydroxides phases. The water bending vibration identified around 1014 and 1030 cm^{-1} peak band (Goldberg and Johnston 2001). As(III)–O vibration at 717 and 721 cm^{-1} peak band and As(V)–O at 899 and 972 cm^{-1} peak band were observed in the FTIR-ATR spectrum (Gomes et al. 2007).

The morphological analysis of the resultant slug samples was carried out by SEM (SEM, Hitachi TM3030Plus Benchtop). The SEM image in Fig. 9 indicated the presence of mostly amorphous structure which had an aggregate size range of 200 μm to 2 mm. The sludge at 500× magnification appeared to be a relatively uniform cake with cracks due to drying. Then, the chemical composition was determined by EDS (EDS, Oxford Instruments Swift ED3000). EDS of the sludge at the optimum conditions for Al electrodes in Fig. 10 showed the presence of As removed from the
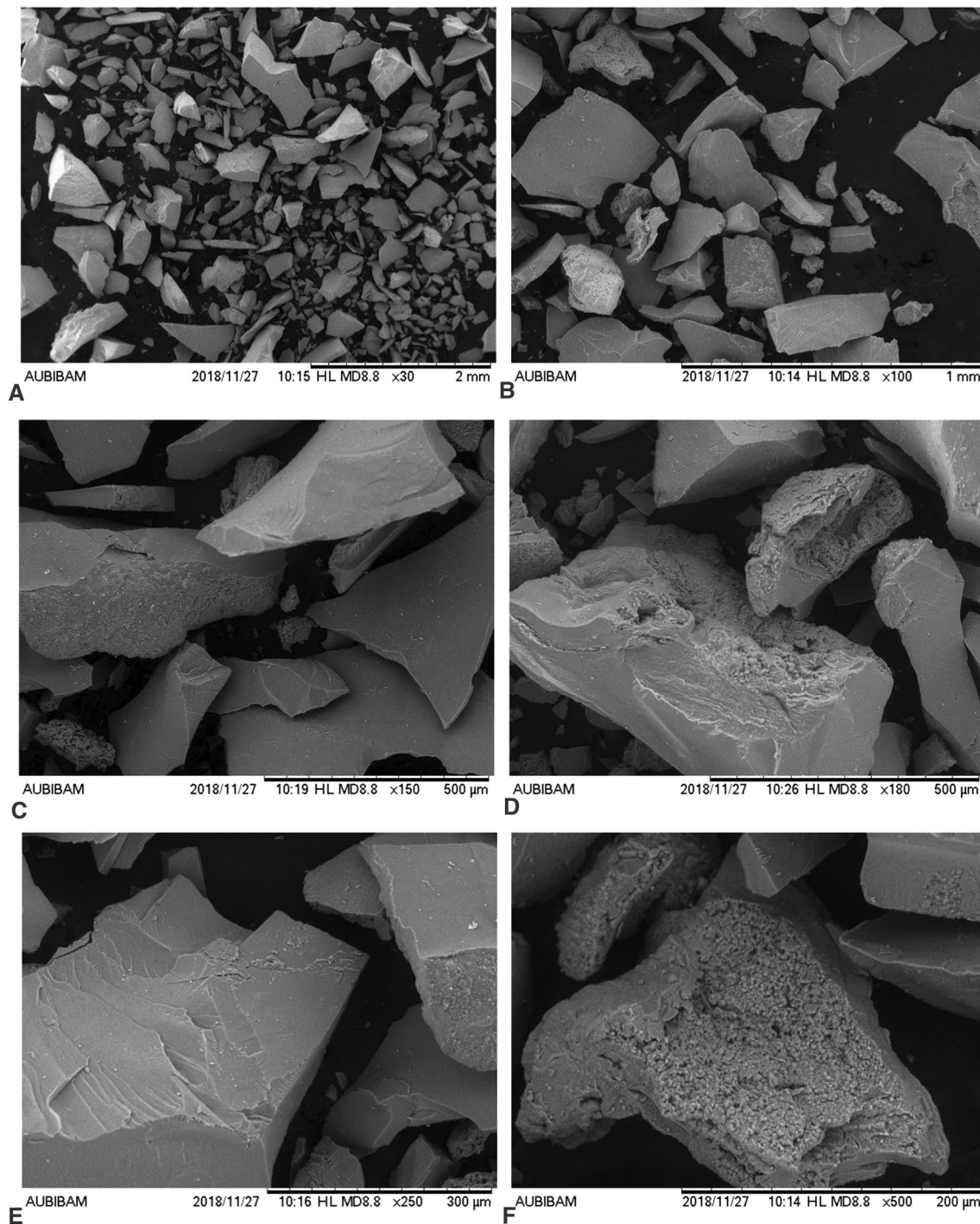
Fig. 9 SEM images of resultant sludge produced in the EC

sample groundwater solution as precipitated. Other elements detected in the sludge are listed in Table 5.

According to EDS result giving in Table 5 and EDS spectrum for resultant sludge in Fig. 10, the results performed to examine the elemental constituents of sludge provided direct evidence that O, Al, As, Na, and S found in the waste sludge. After the EC treatment, other elements detected in sludge come from wastewater ingredients and supporting electrolyte solution (Tsiepe et al. 2018). The elements detected in the sludge were C corresponding to the carbon band used for sample fixation on the stab surface in the SEM process. From operating cost point of view, Al electrode was clearly reported more economic material type than Fe electrode in the literature (Kobya
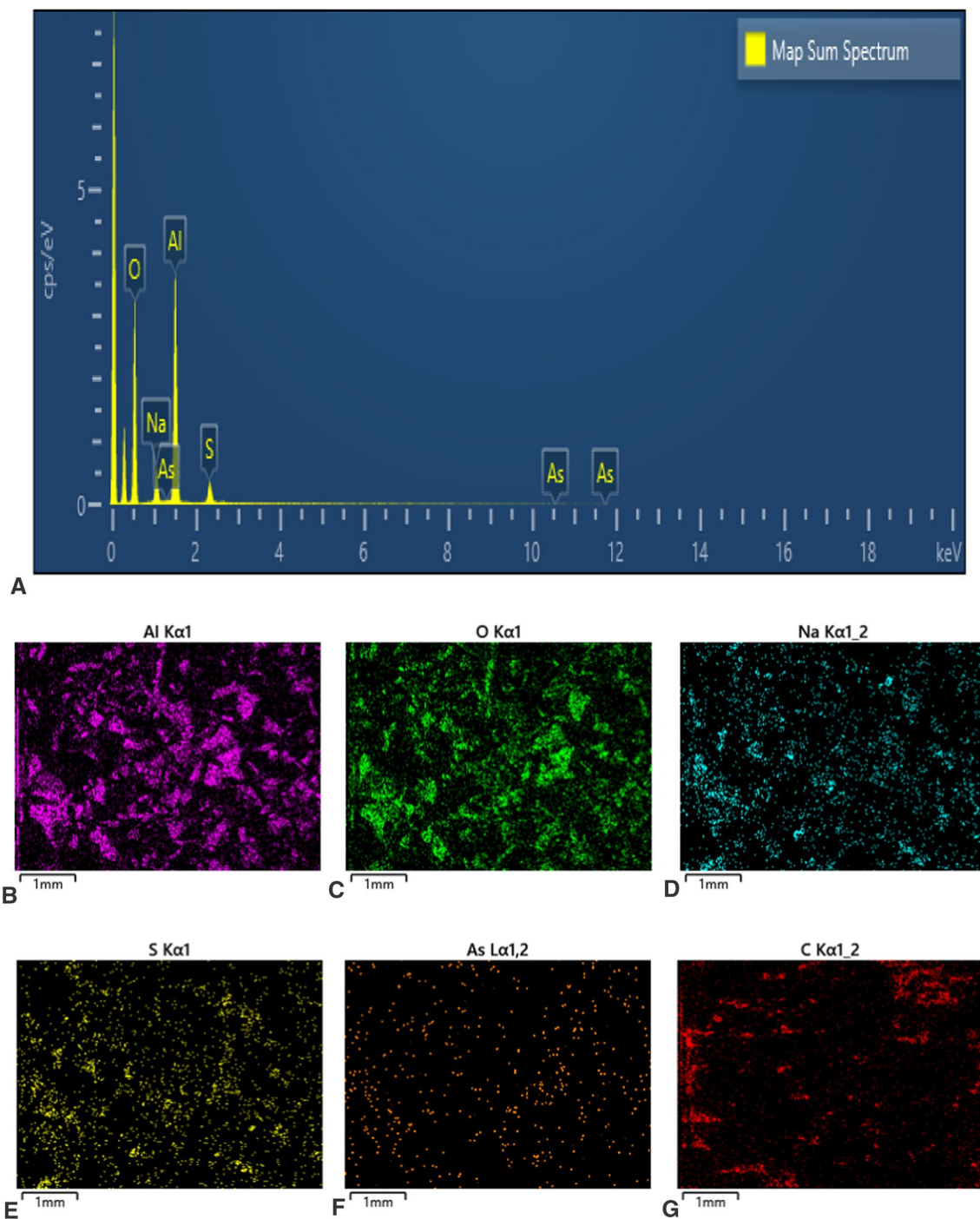
Fig. 10 EDS spectrum of sludge (**a**) and its chemical decomposition **b**: Al, c: O, d: Na, e: S, f: As, g:C

et al. 2011). Thakur and Mondal (2016) stated EDS results performed on the Al flocs, after the elimination of As and F from groundwater by EC, in which they obtained As and F and Al in their sludge with a higher percentage of O and Al. Castaneda et al. (2019) showed the chemical composition of the flocs determined by SEM–EDS and XRF-EDS analyses of the sludge produced with EC treatment

of ground water. In the SEM–EDS results, the amount of Si in a comparatively high percentage indicates Al_2SiO_5 complexes, while the As was not detected because of the low concentration existing in the flocs. Conversely, they reported that XRF-EDS studies of the sludge confirmed the existence of As in the dry flocs. Similar sludge characterization must be carried out since the properties of

Table 5 EDS results of sludge sample

Element	Line type	Weight percentage (%)
C	K series	31.66
O	K series	47.14
Al	K series	15.95
S	K series	1.82
Na	K series	3.33
As	L series	0.09
Total		100

the sludge formed after treatment would determine the disposal or sludge treatment methods and their cost.

Conclusion

In this study, treatment of the model groundwater was carried out with EC method in a parallel plate reactor with aluminum electrodes operating batch flow condition. The total arsenic, arsenite (As^{3+}) and arsenate (As^{5+}), and toxicity analysis were performed for the model groundwater containing arsenic. In EC treatment, the total As was successfully removed from model groundwater supplying allowable effluent As concentration. The reaction kinetic of EC was determined with pseudo-first-order reaction kinetic model obtaining high linear regression varying the effects of current density, supporting electrolyte concentration, and initial pH of groundwater. In the EC treatment process, As^{3+} was removed from the model groundwater faster than As^{5+}, precipitated by both active coagulants and transforming into As^{5+}. The initial toxicity of the model groundwater was reduced by 90% within the first 10 min, and there was no toxic effect at the end of the 60 min total treatment period thank to rapid transformation of As^{3+} to As^{5+}. The precipitated $Al(OH)_3$ and Al_2O_3 coagulants were the main peaks in the FTIR-ATR spectrum as well as As(III)–O vibration observed between 717 and 721 cm^{-1} peaks and As(V)–O vibration dominated 899 and 972 cm^{-1} peaks were detected in the produced sludge after the EC. The SEM–EDS morphological analysis was demonstrated that the sludge consisted of mostly amorphous structure aggregated size range of 200 μm to 2 mm, relatively uniform cake including O, Al, As, Na, and S. When the speciation and toxicity results were evaluated together with the total As removal efficiency, this work clearly say that EC method was an effective and reliable treatment for the arsenic-containing groundwater.

Declarations

References

Balasubramanian N, Kojima T, Srinivasakannan C (2009) Arsenic removal through electrocoagulation: kinetic and statistical modeling. Chem Eng J 155(1–2):76–82

Bushra R, Shahadat M, Khan MA, Adnan R, Rafatullah M (2014) Optimization of polyaniline supported Ti (IV) arsenophosphate composite cation exchanger-based ion-selective membrane electrode for the determination of lead. Ind & Engin Chem Res 53(50):19387–19391

Can BZ, Boncukcuoglu R, Yilmaz AE, Fil BA (2014) Effect of some operational parameters on the arsenic removal by

electrocoagulation using iron electrodes. J Environ Health Sci Eng 12(1):1–10

Castaneda LF, Coreno O, Nava JL (2019) Arsenic and hydrated silica removal from groundwater by electrocoagulation using an up-flow reactor in a serpentine array. J Environ Chem Engin 7(5):103353–103360

Coreño RMO, Nava JL (2018) Removal of hydrated silica, fluoride and arsenic from groundwater by electrocoagulation using a continuous reactor with a twelve-cell stack. Chem 211:149–155

Flores OJ, Nava JL, Carreño G (2014) Arsenic removal from groundwater by electrocoagulation process in a filter-press-type FM01-LC reactor. Inter J Electrochem Sci 9(11):6658–6667

Fulladosa E, Murat JC, Martínez M, Villaescusa I (2005) Patterns of metals and arsenic poisoning in Vibrio fischeri bacteria. Chem 60(1):43–48

Gayathri P, Praveena R, Dorathi J, Palanivelu K (2010) Sonochemical degradation of textile dyes in aqueous solution using sulphate radicals activated by immobilized cobalt ion. Ultra Sonochem 17(3):566–571

Ghosh S, Debsarkar A, Dutta A (2019) Technology alternatives for decontamination of arsenic-rich groundwater—a critical review. Environ Technol and Innova 13:277–303

Ghurye G, Clifford D (2004) As (III) oxidation using chemical and solid-phase oxidants. J Am Water Works Assoc 96(1):84–96

Goldberg S, Johnston CT (2001) Mechanisms of arsenic adsorption on amorphous oxides evaluated using macroscopic measurements, vibrational spectroscopy, and surface complexation modeling. J Coll Interface Sci 234(1):204–216

Gomes JA, Daida P, Kesmez M, Weir M, Moreno H, Parga JR, Cocke DL (2007) Arsenic removal by electrocoagulation using combined Al–Fe electrode system and characterization of products. J of Hazard Mater 139(2):220–231

Govindan K, Raja M, Noel M, James MEJ (2014a) Degradation of pentachlorophenol by hydroxyl radicals and sulfate radicals using electrochemical activation of peroxomonosulfate, peroxodisulfate and hydrogen peroxide. J Hazard Mater 272:42–51

Govindan K, Oren Y, Noel M (2014b) Effect of dye molecules and electrode material on the settling behavior of flocs in an electrocoagulation induced settling tank reactor (EISTR). Sep Purif Technol 133:396–406

Govindan K, Suresh AK, Sakthivel T, Murugesan K, Mohan R, Gunasekaran V, Jang A (2019) Effect of peroxomonosulfate, peroxodisulfate and hydrogen peroxide on graphene oxide photocatalytic performances in methyl orange dye degradation. Chem 237:124479

Hussain MM, Wang J, Bibi I, Shahid M, Niazi NK, Iqbal J, Rinklebe J (2021) Arsenic speciation and biotransformation pathways in the aquatic ecosystem: the significance of algae. J Hazard Mater 403:124027

Jang YC, Somanna Y, Kim H (2016) Source, distribution, toxicity and remediation of arsenic in the environment–a review. Int J Appl Environ Sci 11(2):559–581

Jeevanantham S, Hemavathy SA, RV, Kumar RV, Yaashikaa PR, Yuvaraj D, (2019) Removal of toxic pollutants from water environment by phytoremediation: a survey on application and future prospects. Environ Technol Innova 13:264–276

Kobya M, Gebologlu U, Ulu F, Oncel S, Demirbas E (2011) Removal of arsenic from drinking water by the electrocoagulation using Fe and Al electrodes. Electrochem Acta 56:5060–5070

Koparal AS, Yildiz YŞ, Keskinler B, Demircioğlu N (2008) Effect of initial pH on the removal of humic substances from wastewater by electrocoagulation. Sep Pur Technol 59(2):175–182

Kumar NS, Goel S (2010) Factors influencing arsenic and nitrate removal from drinking water in a continuous flow electrocoagulation (EC) process. J Hazard Mater 173(1):528–533

Kumar M, Raot S, Isloor AM, Ibrahim GS, Ismail N, Ismail AF, Asiri AM (2019) Use of cellulose acetate/polyphenylsulfone derivatives to fabricate ultrafiltration hollow fiber membranes for the removal of arsenic from drinking water. Int J Bio Macromol 129(1):715–727

Lakshmanan D, Clifford D, Samanta G (2010) Comparative study of arsenic removal by iron using electrocoagulation and chemical coagulation. Water Res 44(19):5641–5652

Madhura L, Kanchi S, Sabela MI, Singh S, Bisetty K (2018) Membrane technology for water purification. Environ Chem Letters 16(2):343–365

Madima N, Mishr SB, Inamuddin I, Mishra AK (2020) Carbon-based nanomaterials for remediation of organic and inorganic pollutants from wastewater. A Rev Environ Chem Lett 18(4):1169–1191

Mohora E, Rončević S, Agbaba J, Tubić M, Mitić A, Klašnja M, Dalmacija B (2014) Removal of arsenic from groundwater rich in natural organic matter (NOM) by continuous electrocoagulation/flocculation (ECF). Sep Purif Technol 136:150–156

Mouedhen G, Feki M, Wery MDP, Ayedi HF (2008) Behavior of aluminum electrodes in electrocoagulation process. J Hazard Mater 150(1):124–135

Mukherjee A, Sengupta MK, Hossain MA, Ahamed S, Das B, Nayak B, Chakraborti D (2006) Arsenic contamination in groundwater: a global perspective with emphasis on the Asian scenario. J Health Pop and Nut 388:142–163

Nidheesh PV, Singh TA (2017) Arsenic removal by electrocoagulation process: recent trends and removal mechanism. Chem 181:418–432

Olivera S, Chaitra K, Venkatesh K, Muralidhara HB, Asiri AM, Ahamed MI (2018) Cerium dioxide and composites for the removal of toxic metal ions. Environ Chem Lett 16(4):1233–1246

Rubinos DA, Calvo V, Iglesias L, Barral MT (2014) Acute toxicity of arsenic to Aliivibrio fischeri (Microtox® bioassay) as influenced by potential competitive–protective agents. Environ Sci Pol Res 21(14):8631–8644

Sandoval MA, Fuentes R, Thiam A, Salazar R (2021) Arsenic and fluoride removal by electrocoagulation process: a general review. Sci Tot Environ 753:142108

Singh TL, Mondal P (2017) Simultaneous arsenic and fluoride removal from synthetic and real groundwater by electrocoagulation process: parametric and cost evaluation. J Environ Manage 190:102–112

Thakur LS, Mondal P (2016) Techno-economic evaluation of simultaneous arsenic and fluoride removal from synthetic groundwater by electrocoagulation process: optimization through response surface methodology. Desal Water Treat 57(59):28847–28863

Tsiepe JT, Mamba BB, Abd-El-Aziz AS, Mishra AK (2018) Fe_3O_4–β-cyclodextrin–Chitosan bionanocomposite for arsenic removal from aqueous solution. J Inorg Organometal Poly Mat 28(2):467–480

Viraraghavan T, Subramanian KS, Aruldoss JA (1999) Arsenic in drinking water—problems and solutions. Water Sci Technol 40(2):69–76

Zhang Y, Xu B, Guo Z, Han J, Li H, Jin L, Xiong Y (2019) Human health risk assessment of groundwater arsenic contamination in Jinghui irrigation district, China. J Environ Manage 237:163–169

Zhao X, Zhang B, Liu H, Qu J (2011) Simultaneous removal of arsenite and fluoride via an integrated electro-oxidation and electrocoagulation process. Chem 83:726–729