Performance Efficiency of Electrocoagulation Adsorption Process of Oxyfluorfen Herbicide from Aqueous Solutions Using Different Anodes

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Abstract

The main purpose of this work was to assess the removal of the herbicide oxyfluorfen and chemical oxygen demand (COD) in aqueous solution using the electrocoagulation process. The results showed that the maximum removal efficiency for oxyfluorfen and COD were (98.5% and 90%), (99.2% and 85%) and (96.1% and 70.5%) at 30 min by using iron (Fe), stainless steel (S.S) and aluminum (Al) as anode respectively, at a current density of 75 mA.cm^{-2} and pH of 5.8. The energy consumption in the electrocoagulation process at optimum conditions (15.9, 16.65 and 14.1 KWh/m^3) using Fe, SS and Al electrodes respectively. The adsorption of oxyfluorfen preferably fitting the Freundlich adsorption isotherm. The adsorption process follows the first order kinetic model with good correlation.

Introduction

In the last decades, the use of agrochemicals has been a common practice in intense agriculture, which has considerably increased pollution problems of surface and ground water [1]. Oxyfluorfen [2-chloro-1-(3-ethoxy-4-nitrophenoxy)-4-(trifluromethyl)-benzene], a member of the herbicide class nitrodiphenyl ether, has a high degree of weed control and great versatility of application [2]. Oxyfluorfen is considered to be highly resistant to degradation in water [3]. And has Potential adverse effects on the ecosystem even if present at very low concentration levels, where the half-life of oxyfluorfen ranged from 72 to 160 days for water [4,5]. Many conventional methods have been successfully applied for the efficient removal of oxyfluorfen from water sources such as adsorption [6], advanced oxidation [7], photo Fenton [8], UV/H$_2$O$_2$ [9], and biological treatment [10]. In recent years novel methods for water purification have been developed including chemical, electrochemical and photochemical processes [11]. In this scenario, the electrocoagulation (EC) is an electrochemical has attracted increasing interest as a promising powerful method for efficiently removing pesticides from water such as Malathion [12], methyl parathion, atrazine and triazophos [13], imidacloprid and chlorpyrifos [14], and 2,4- dichlorophenoxyacetic Acid (2,4-D) [15].

The aim of this study is to conduct an experimental investigation on the removal of a oxyfluorfen and COD from the aqueous solution using the electrocoagulation method. and to investigate the kinetic and adsorption isotherm studies on the removal efficiency.

Experimental

Chemicals

For all electrocoagulation experiments, a commercial formulation of the herbicide oxyfluorfen from Dow AgroSciences, USA, was used. The properties of the oxyfluorfen is given in Table 1. Mineral salts was routinely used for all electrocoagulation experiments. Sodium chloride, potassium chloride, sodium carbonate, sodium fluoride, sodium sulfate, sodium hydroxide, sulfuric acid, potassium dichromate, were of analytical grade and purchased from Merck. Distilled water was used for the preparation of solutions. Standard solutions of potassium dichromate (K$_2$Cr$_2$O$_7$), sulfuric acid (H$_2$SO$_4$) reagent with silver sulfate (Ag$_2$SO$_4$), Mercury sulfate (HgSO$_4$) and sulfuric acid (H$_2$SO$_4$) were prepared to measure the COD. A stock solution of herbicide (1000 mg.L^{-1}) was prepared by dissolving an accurate quantity of the herbicide in distilled water and suitably diluted to the required initial concentrations. Different standard solutions of herbicide with concentration from 50–250 mg.L^{-1} were prepared to measure its removal at different conditions.

Electrolysis and analytical method

The solution volume of 100 mL was used for each experiment as the electrolyte. The pH of the electrolyte was adjusted, if required, with HCl or NaOH (Merck, Darmstadt, Germany) solutions and measured by a pH meter (AC28-TOA electronics Ltd, Japan) at the beginning and during the experiment. After adjusting the initial solution pH to the desired value, the current density was set. Magnetic stirring at 250 rpm provided a homogeneous solution in the batch reactor intervals, samples were taken for analysis. Temperature studies were carried at varying temperature (10-50°C) to determine the type of reaction. The chemical oxygen demand (COD) was analyzed using UV–Vis Spectrophotometer (model UV 1601 is from Shimadzu, Japan).

Experimental device

Electrocoagulation is an electrochemical separation process that uses a direct current between pairs of metal sheets called electrodes. Metal electrodes immersed in solution, coagulant agents that destabilize pollutants [16] (Figure 1).
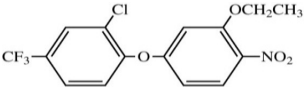
The experiments were carried out in reactor using 100 ml Plexiglas vessel that was fitted cell cover with slots to introduce the electrodes, pH sensor, a thermometer and the electrolytes. Iron, stainless steel and aluminum of surface area (4 cm^2) acted as the anode. The cathode was iron, stainless steel and aluminum sheets of the same size as the anode is placed at an inter-electrode distance of 1 cm.

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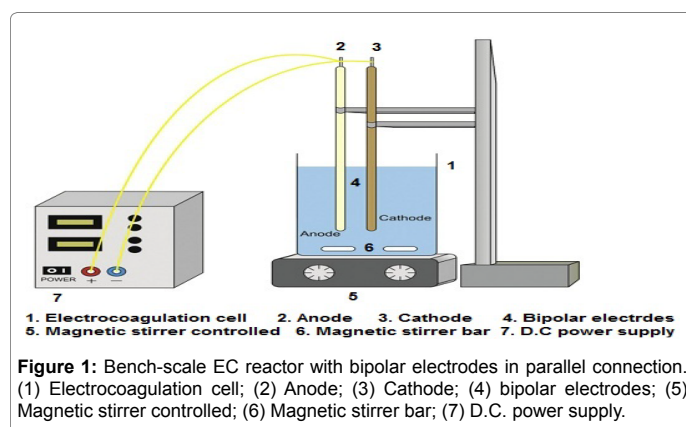
Chemical structure	
Commercial Name	Goal
UV/VIS absorption (max.)	neutral: 275 nm, 320 nm acidic: 273 nm, 320 nm basic: 273 nm, 320 nm
Chemical formula	$C_{15}H_{11}ClF_3NO_4$
Molecular Weight (g/mol)	361.70 g·mol^{-1}
Form	Solid at room temperature(pure compound)
IUPAC Name	2-chloro-1-(3-ethoxy-4-nitrophenoxy)-4-trifluoromethyl)benzene
Solubility in water (state temperature, state purity and pH)	0.116 mg/L (at 25°C, 99.1%)
Hydrolysis half-life	half-life of 3.9 days (20°C, pH 5-9)
Appearance	Yellow to brown
n-octanol/water (log P_{ow})	4.7
Partition coefficient, soil organic carbon/water (K_{oc})	6.831 cm^3.g^{-1}
Vapor pressure	2×10^{-7} mmHg at 25°C

Table 1: Chemical - Physical Properties of oxyfluorfen.

Figure 1: Bench-scale EC reactor with bipolar electrodes in parallel connection. (1) Electrocoagulation cell; (2) Anode; (3) Cathode; (4) bipolar electrodes; (5) Magnetic stirrer controlled; (6) Magnetic stirrer bar; (7) D.C. power supply.

Analysis

The remaining pollutants of oxyfluorfen concentration was measured with the double-beam UV-Vis spectrophotometer at λmax=320 nm. The COD was determined using a closed reflux colorimetric method [17].

The equation used to determine the herbicide adsorption in the treatment experiments was:

$$\%E = [(A_o-A)/A_o] \times 100 \tag{1}$$

Where A_0 and A are absorbance values of herbicides solutions before and after adsorption.

The calculation of COD removal efficiencies after electrocoagulation treatment were performed using the following formula [18].

$$C_R(\%) = [(C_o-C)/C_o] \times 100 \tag{2}$$

Where C_o and C are concentrations of herbicides before and after electrocoagulation.
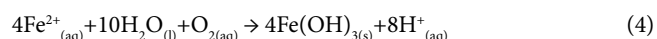
Mechanism of electrocoagulation process

The mechanisms of the removal of herbicides by EC will be explained with two specific examples involving iron and aluminum since these two metals have been extensively used to clarify pollutant

water [19]. Following each run, the electrodes were put in HCl (5% V/V) and rinsed with tap water then distilled water and dried until they are used again. Electrocoagulation of herbicide solution using iron (Fe), stainless steel (S-S) and aluminum (Al) electrodes takes place according to the following mechanisms [20].
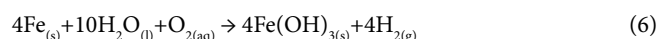
Iron electrodes

Mechanism 1

Anode:

$$4Fe_{(s)} \rightarrow 4Fe^{2+}_{(aq)}+8e^- \tag{3}$$

$$4Fe^{2+}_{(aq)}+10H_2O_{(l)}+O_{2(aq)} \rightarrow 4Fe(OH)_{3(s)}+8H^+_{(aq)} \tag{4}$$

Cathode:

$$8H^+_{(aq)}+8e^- \rightarrow 4H_{2(g)} \tag{5}$$

Overall:

$$4Fe_{(s)}+10H_2O_{(l)}+O_{2(aq)} \rightarrow 4Fe(OH)_{3(s)}+4H_{2(g)} \tag{6}$$

Mechanism 2

Anode:

$$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)}+2e^- \tag{7}$$

$$Fe^{2+}_{(aq)}+2OH^-_{(aq)} \rightarrow Fe(OH)_{2(s)} \tag{8}$$

Cathode :

$$2H_2O_{(l)}+2e^- \rightarrow H_{2(g)}+2OH^-_{(aq)} \tag{9}$$

Overall:

$$Fe_{(s)}+2H_2O_{(l)} \rightarrow Fe(OH)_{2(s)}+H_{2(g)} \tag{10}$$

Aluminum electrodes

Anode: $Al_{(s)} \rightarrow Al^{3+}_{(aq)}+3e^- \tag{11}$

Cathode: $3H_2O_{(l)}+3e^- \rightarrow 3/2H_2+3OH^- \tag{12}$

Overall: $Al_{(s)}+3H_2O_{(l)} \rightarrow Al(OH)_{3(s)} \tag{13}$
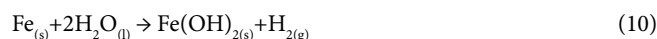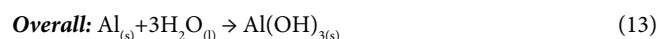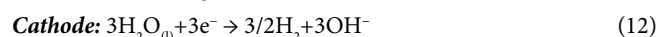
Result and Discussion

The adsorption of oxyfluorfen was examined by EC using Fe, S-S and Al electrodes. The effects of current density, initial pH, type of electrolyte, NaCl concentration, initial herbicides concentration, temperature and Effect of anode materials were investigated on oxyfluorfen and COD removal efficiency. The main parameters discussed from this work are:

Effect of current density (mA.cm^{-2})

The effect of current density on the oxyfluorfen and COD removal efficiency a series of experiments were carried out at time 30 min, pH 5.8, oxyfluorfen 200 mg.L^{-1}, NaCl 1 g.L^{-1}, inter-electrode distance 1 cm and temperature 10°C. Figure 2 show the effect of current densities for oxyfluorfen and COD removal efficiencies increased by increasing the current density up to (95% and 84%), (99% and 85%) and (96% and 70%) at Fe, S-S and Al electrodes respectively. The increase of coagulant and bubbles generation rate lead to the increase number of H$_2$ bubbles and decrease their size with increasing current density resulting in a faster removal of herbicides [21]. The sufficient amount of flocs needed to coagulate the herbicide might be available at optimal current density and further formation of flocs which did not change herbicide and COD removal efficiency [22].
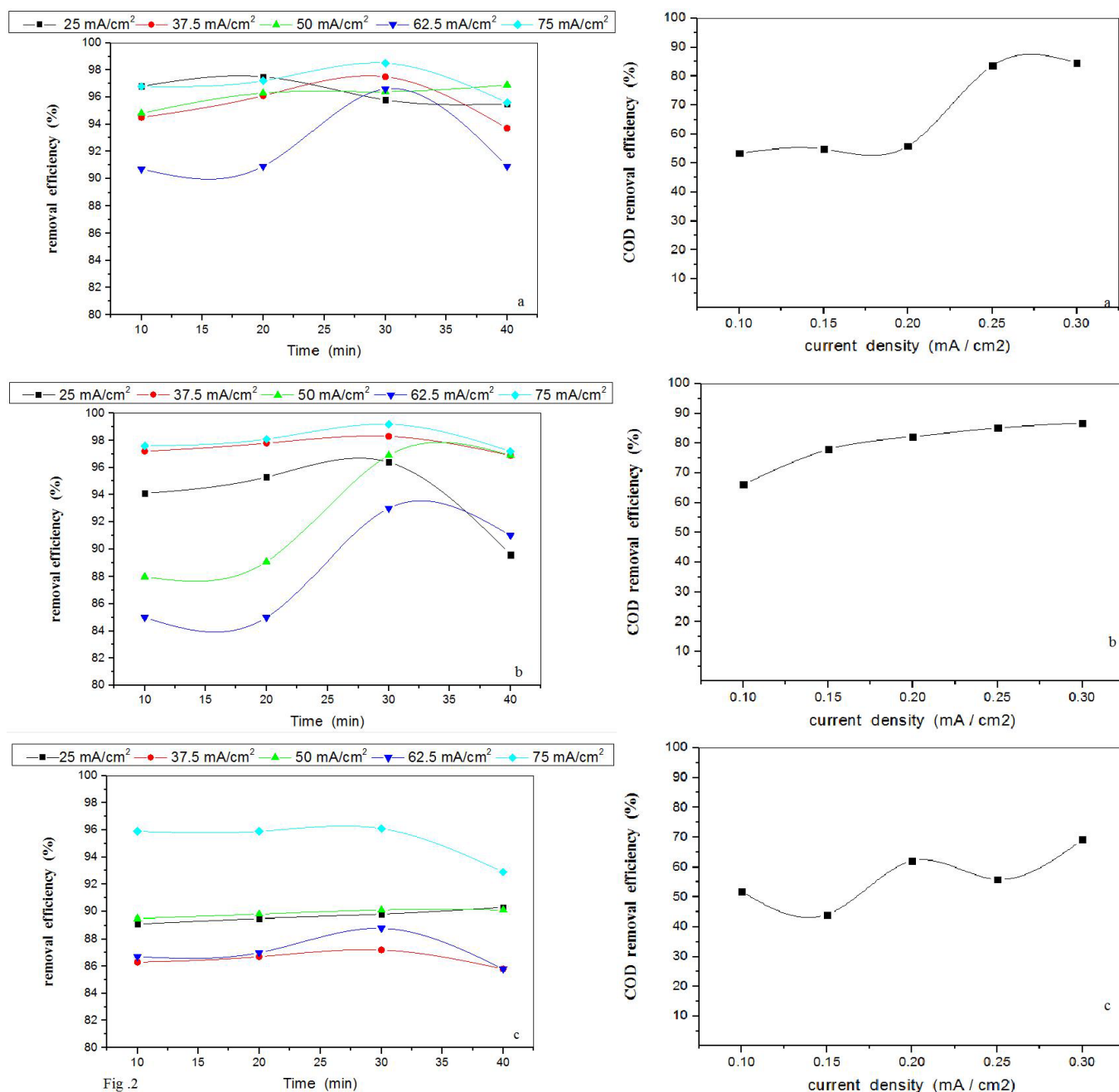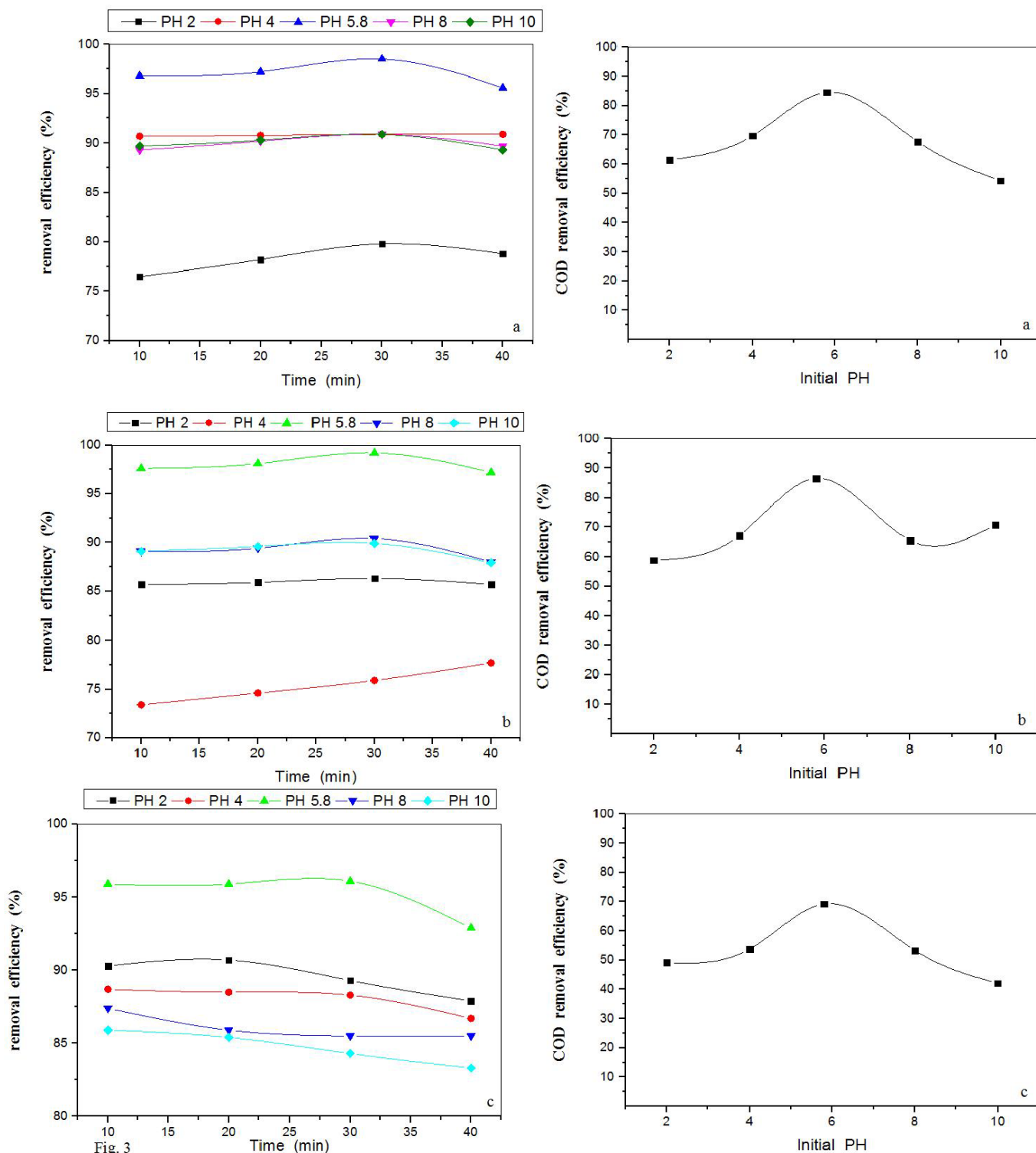
Figure 2: Effect of current density and COD on the removal efficiency of oxyfluorfen using Fe (a) S-S (b) and Al (c) electrodes. Initial concentration of the oxyfluorfen=200 mg/L, [NaCl]=1 g/L, pH=5.8, inter-electrode distance=1 cm, temperature=10°C.

Effect of initial pH

pH is an important operating factor influencing the performance of the electrocoagulation process. A series of experiments was carried out to evaluate this effect, using solutions containing a sample with an initial pH varying in the range (2-10) at time 30 min, oxyfluorfen 200 mg.L^{-1}, current density 75mA.cm^{-2}, NaCl 1 g.L^{-1}, and temperature 10°C. From Figure 3 it can be seen that the removal efficiency of oxyfluorfen was increased by increasing the pH and the maximum removal efficiency was obtained in neutral and slightly alkaline medium.

Effect of type of electrolyte

Figure 4 show the effect of electrolyte type on the removal efficiency of oxyfluorfen and COD at 30 min using different anodes in the presence of different supporting electrolytes including (KCl, Na$_2$CO$_3$, NaF and Na$_2$SO$_4$) at time 30 min. It can be seen from Figure 4 that in the presence of chloride ions for NaCl and KCl electrolytes the removal efficiency of herbicides and COD were high due to formation of hypochlorite (OCl$^-$) and hypochlorous acid (HOCl). But in another electrolytes which not contain chloride ions such as Na$_2$CO$_3$ and Na$_2$SO$_4$, the removal
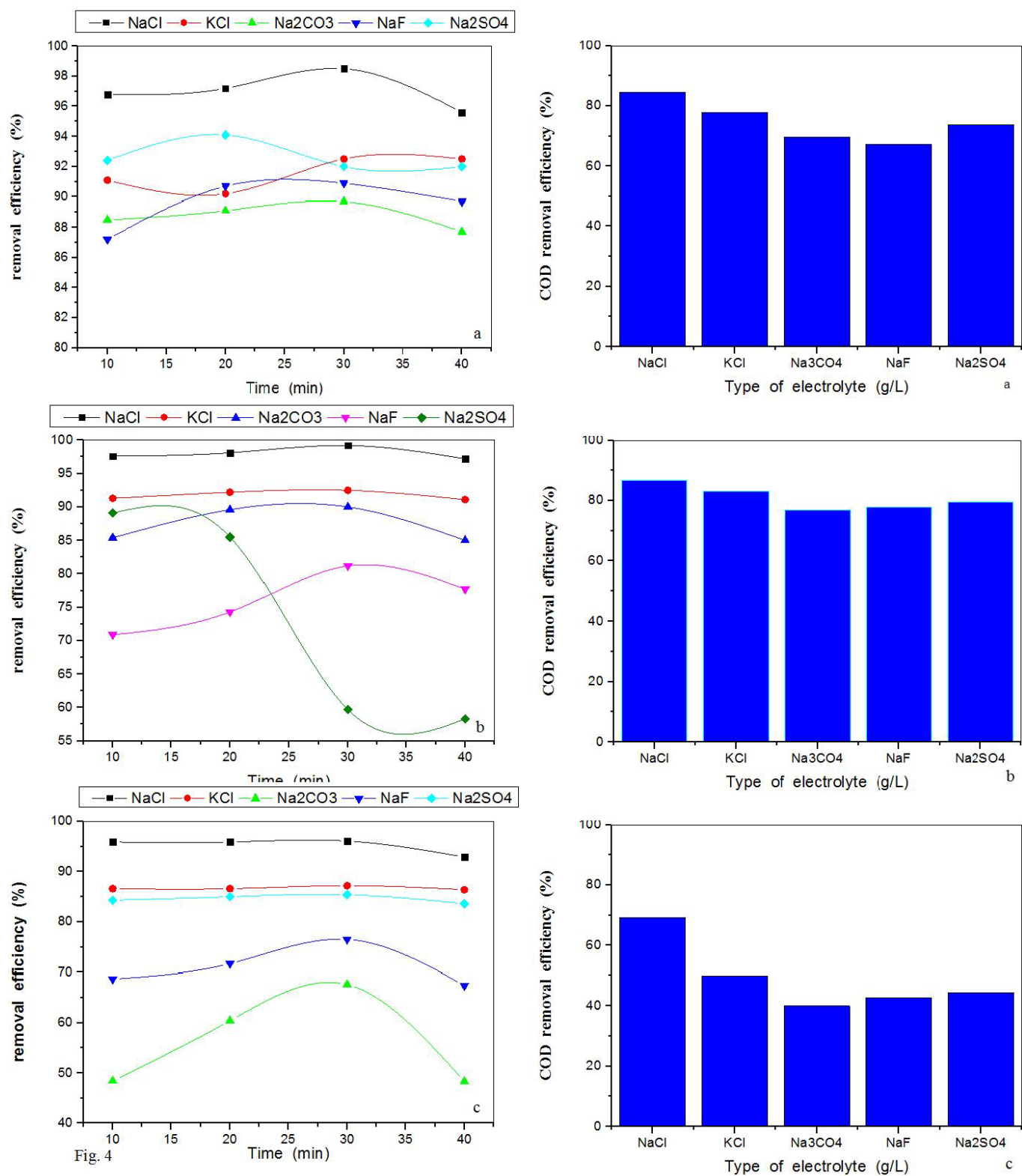
Figure 3: Effect of initial pH and COD on the removal efficiency of oxyfluorfen using Fe (a) S-S (b) and Al (c) electrodes. Initial concentration of the oxyfluorfen=200 mg/L, [NaCl]=1 g/L, current density=75 mA/cm^2, inter-electrode distance=1 cm, temperature=10°C.

efficiency of herbicides and COD dropped. This may be attributed to the formation of an adherent film on the anode surface which poisons the electrode surface [23].

Effect of electrolyte concentration (g.L^{-1})

The conductivity of the water is adjusted to the desired values by adding NaCl [24]. Figure 5 represent the effect of electrolyte

Figure 4: Effect of electrolyte and COD on the removal efficiency of oxyfluorfen using Fe (a) S-S (b) and Al (c) electrodes. Initial concentration of the oxyfluorfen=200 mg/L, [electrolyte]=1 g/L, pH=5.8, current density=75 mA/cm², interelectrode distance=1 cm, temperature=10°C.

concentrations on oxyfluorfen and COD removal efficiencies at time 30 min. pH 5.8, oxyfluorfen 200 mg.L^{-1}, 75 mA.cm^{-2}, inter-electrode distance 1 cm and temperature 10°C. The results obtained from the above figures indicate that 1 g.L^{-1} NaCl was the maximum value
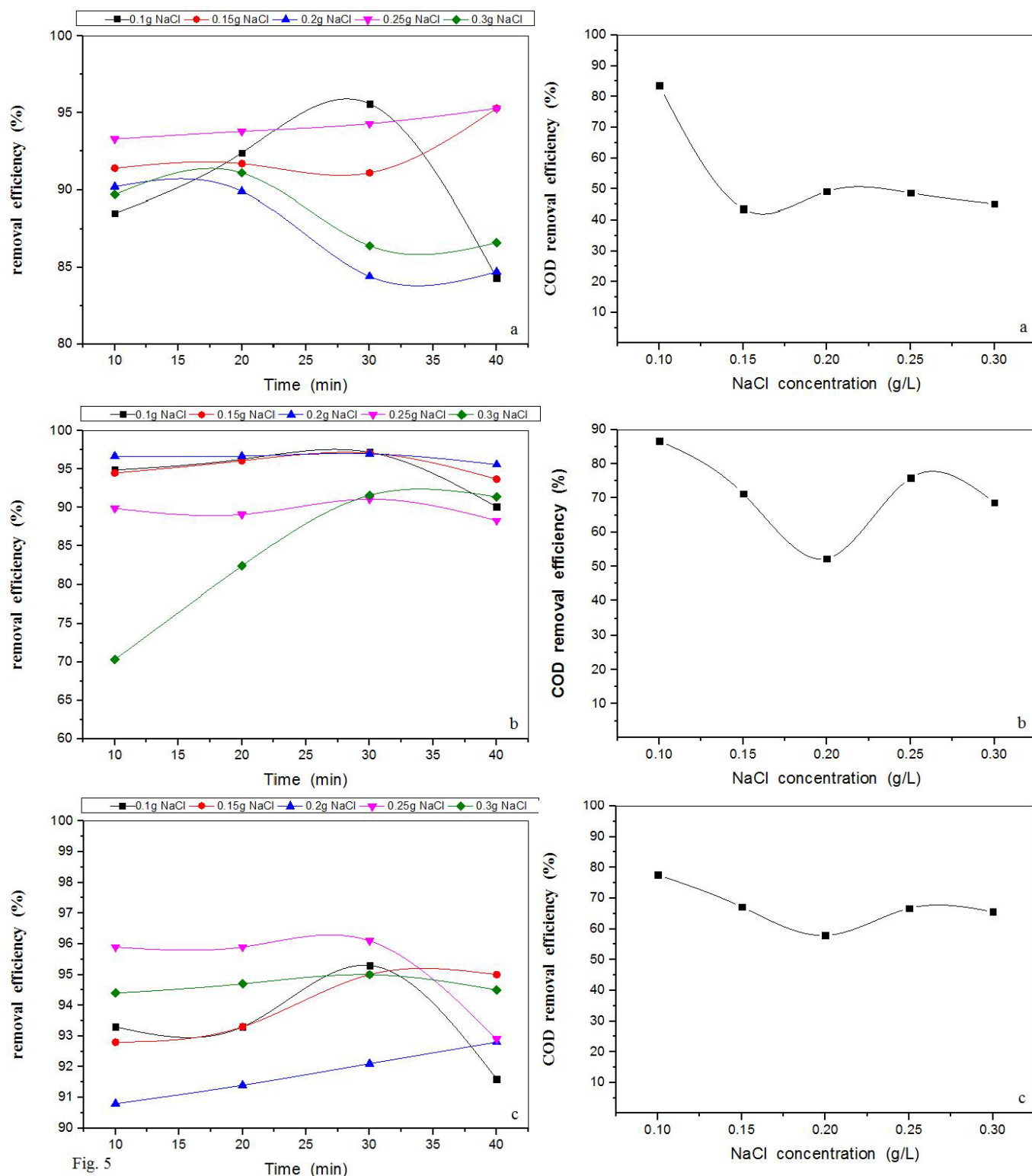
Figure 5: Effect of electrolyte concentration and COD on the removal efficiency of oxyfluorfen using Fe (a) S-S (b) and Al (c) electrodes. Initial concentration of the oxyfluorfen=200 mg/L, pH=5.8, current density=75 mA/cm², interelectrode distance=1 cm, temperature=10°C.

for removal efficiencies. It can be attributed that the increase of the conductivity by the addition of sodium chloride is known to reduce the cell voltage at constant current density due to the decrease of the ohmic resistance of solution [25,26].

Effect of initial oxyfluorfen concentration (mg.L^{-1})

To observe the effect of initial herbicide concentration on oxyfluorfen and COD on the removal efficiencies by EC, experiments were carried out for five different oxyfluorfen concentration (50-250 mg.L^{-1}) for 30 min, pH 5.8, NaCl 1 g.L^{-1}, current density 75 mAcm^{-2}, inter-electrode distance 1 cm and temperature 10°C. Figure 6 show the percentage removal efficiencies of oxyfluorfen and COD for different initial oxyfluorfen concentration. The maximum removal was obtained at herbicide concentration 100 mg L^{-1}. Further increasing of the initial concentration leads to decrease in the herbicides removal efficiency. Because the amount of hydroxyl and metal ions produced on the electrodes was not sufficient to adsorb at high oxyfluorfen concentrations at a constant current density [27].

Effect of temperature (°C)

Figure 7 show the effect of temperature on oxyfluorfen and COD removal efficiencies at 30 min., initial concentration of the oxyfluorfen=200 mg/L, [NaCl]=1 g/L, pH=5.8, Inter-electrode distance=1 cm and temperature=10°C. Increasing temperature has a negative effect on both removal efficiency of herbicides and COD values, where the optimal temperature for oxyfluorfen were 10°C using all electrodes. While at higher temperature value the herbicide and COD removal dropped to low values. It may be concluded that at low temperature the dissolution of anode occurs at a lower rate. When the temperature was over 10°C, the removal efficiency began to decrease. In this case, the volume of colloid $M(OH)_n$ will decrease and pore production on the metal anode well be closed [28].

Effect of anode materials

Effect of different anode materials on the removal efficiency of oxyfluorfen was evaluated using iron, stainless steel and aluminum anodes. Due to the effective adsorption nature, the contaminants in the water will be removed by the adsorption with metal hydroxides produced from the chemical coagulants [29]. A contaminant free ion source allows maximum adsorptive removal of the various dissolved forms of metals that could be present and require treatment. During the electrolysis of anodes like Fe/S-S/Al, respective hydroxides (microflocs) are formed rapidly by anodic dissolution according to reactions (3)-(13). The main advantage in the case of Fe and S-S electrode is that the residual iron if any present in treated water will not cause any health problem like aluminum.

Kinetic studies of oxyfluorfen

Rate of reaction describes the rates of change in concentration of reactant per unit time [30]. Figure 8 represent the oxyfluorfen removal using EC method of which exhibited pseudo first order with good correlation coefficient 0.9528, 0.9547 and 0.9618 using Fe, S-S and Al electrodes according to following equation:

$$LnA_t / A_o = - Kt \tag{14}$$

Where Ao, At, t and k are the oxyfluorfen absorbance at initial time reaction, oxyfluorfen absorbance after reaction, time of reaction (min) and reaction rate constant (min^{-1}) respectively. The straight lines in plots show a good agreement of experimental data with the kinetic models for different removal rate. The calculated k values from the Figure 8 are 0.023, 0.025 and 0.012 min^{-1} using Fe, S-S and Al electrodes. As indicated from above figures, the efficiency removal rate of oxyfluorfen increase according the order S-S > Fe > Al.

Analyses of adsorption data

Isotherm modeling: In this study, two adsorption isotherms viz., Freundlich and Langmuir models were applied to establish the relationship between the amounts of oxyfluorfen adsorbed onto the Aluminum hydroxides and its equilibrium concentration in the electrolyte containing contaminant ions.

The Langmuir equation: The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface [31]. Based upon these assumptions, Langmuir represented the following equation:

$$1/q_e = 1/q_m + 1/(q_m K_L C_e) \tag{15}$$

where qe (mg.g^{-1}) is amount adsorbed at equilibrium, Ce (mg.L^{-1}) equilibrium concentration, qm is the Langmuir constant representing maximum monolayer adsorption capacity and KL (L.mg^{-1}) is the Langmuir constant related to energy of adsorption. The essential characteristics of the Langmuir isotherm can be expressed as the dimensionless constant R$_L$ [32].

$$R_L = 1/1 + (K_L + C_o) \tag{16}$$

Where C$_o$ is the initial concentration, K$_L$ the constant related to the energy of adsorption (Langmuir Constant). The R$_L$ values between 0 and 1 indicate the favorable adsorption.

Freundlich adsorption isotherm: This is commonly used to describe the adsorption characteristics for the heterogeneous surface [33]. The Freundlich adsorption isotherm typically fits the experimental data over a wide range of concentrations. These data often fit the empirical equation proposed by Freundlich:

$$Log\ q_e = LogK_f + 1/n\ Log\ C_e \tag{17}$$

where kf (mg.g^{-1}) and n (dimensionless) are constants that account for all factors affecting the adsorption process, such as the adsorption capacity and intensity. The Freundlich constants K$_f$ and n are determined from the intercept and slope, respectively, of the linear plot of log q$_e$ versus log C$_e$.

According the equation (15 and 17) the contaminants are usually adsorbed at the surface of the metal hydroxides generated during the electrocoagulation process. Figure 9 and Table 2 represent the Langmuir and Freundlich Isotherms studies of equilibrium.

Operating cost

Operating Cost One of the most important parameters that must be determined to evaluate a method of water treatment is the cost. The operating cost includes material (mainly electrodes) cost, operating cost (mainly electrical energy) In this study, energy and electrode material costs have been taken into account as major cost items [34].

Electrical energy consumption: In an electrochemical process, the most important economical parameter is energy consumption Ec (KWh/m^3) [35]. This parameter is calculated from the following expression:

$$Ec = \frac{V.I.t}{volume.1000} \tag{18}$$

Where V, I, t and Volume stand for average voltage of the EC system (V), electrical current intensity (A), reaction time (h) and treated solution volume (m^3) respectively.
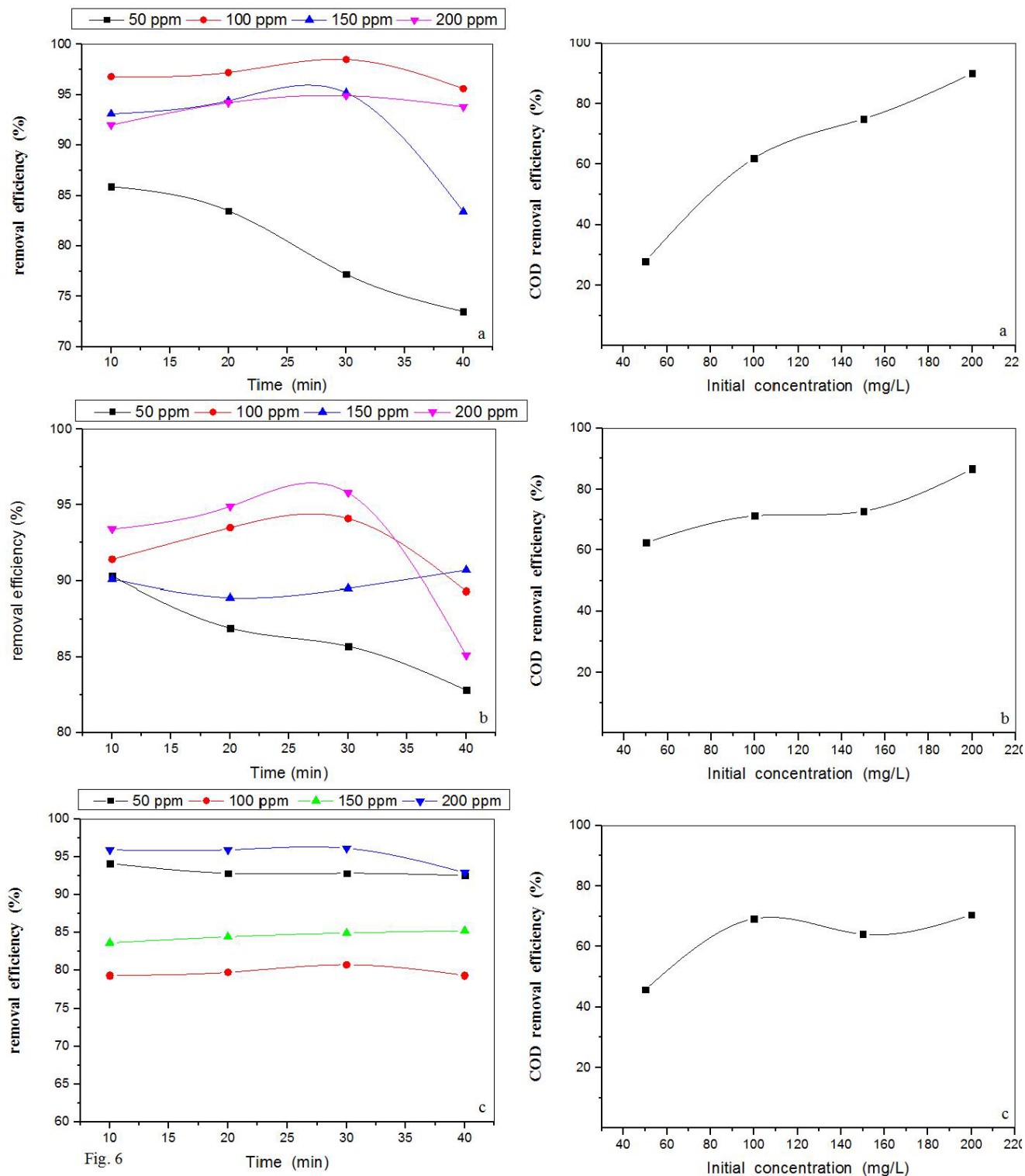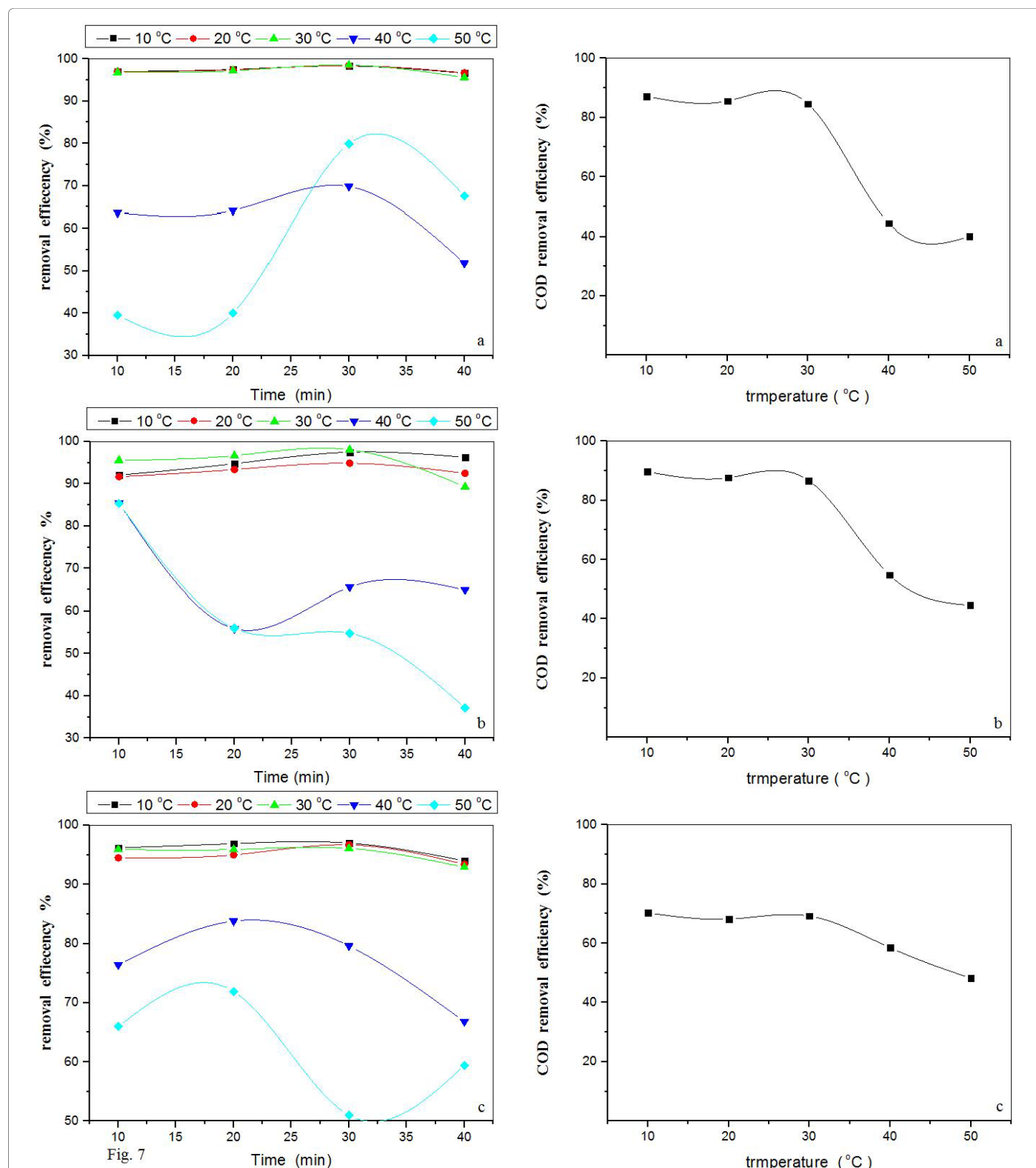
Figure 6: Effect of initial oxyfluorfen concentration and COD on the removal efficiency of oxyfluorfen using Fe (a) S-S (b) and Al (c) electrodes. [NaCl]=1 g/L, pH=5.8, a current density=75 mA/cm², inter-electrode distance=1 cm, temperature=10°C.

According the equation (18), The electrical energy consumption for oxyfluorfen electrocoagulation were (7.95×10^{-3}, 8.325×10^{-3} and 7.05×10^{-3} KWh/m³) using Fe, S-S and Al electrodes respectively according to the equation (18) at current density of 0.3 A and cell voltage (10.6, 11.1 and 9.4 V).

Figure 7: Effect of temperature and COD on the removal efficiency of oxyfluorfen using Fe (a) S-S (b) and Al (c) electrodes. Initial concentration of the oxyfluorfen=200 mg/L, [NaCl]=1 g/L, pH=5.8, a current density=75 mA/cm², interelectrode distance=1 cm.

Mass of loss from anode electrode

The maximum possible mass of Fe and Al electrochemically generated from sacrificial anodes for a particular electrical current was calculated using Faraday's law of electrolysis [36]:
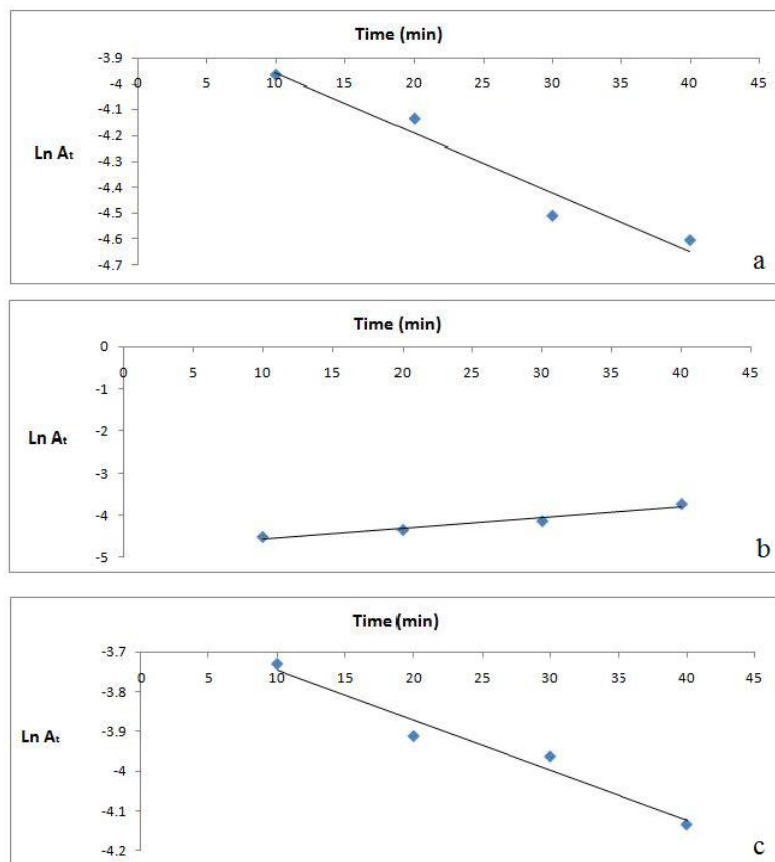
Figure 8: Reaction between LnA_t against the time for oxyfluorfen removal using Fe (a) S-S (b) and Al (c) electrodes. initial concentration of the oxyfluorfen=200 mg/L, [NaCl]=1 g/L, pH=5.8, a current density=75 mA/cm^2, inter-electrode distance=1 cm, temperature=10°C.
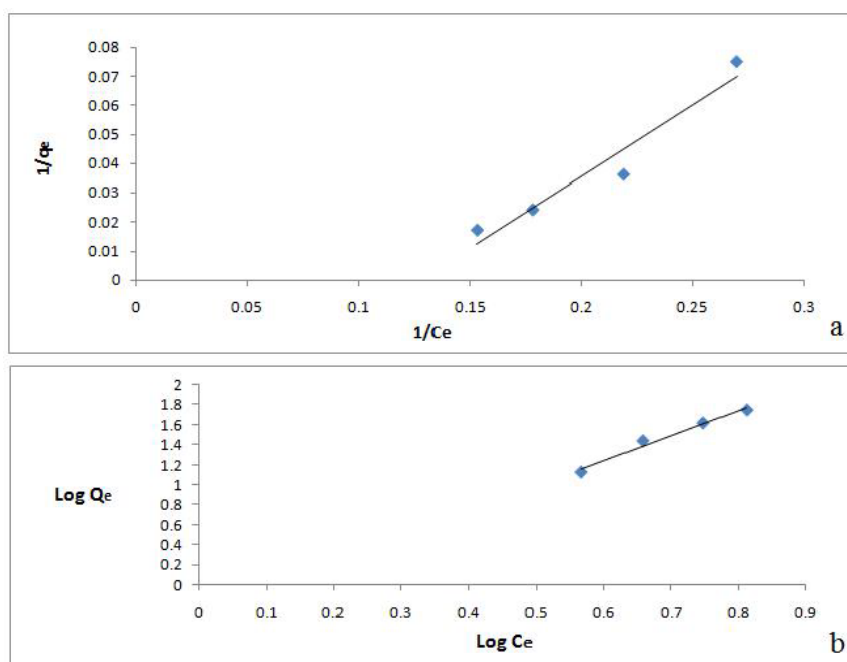

Figure 9: Langmuir adsorption Isotherm, (b) Freundlich adsorption Isotherm.

Langmuir Isotherm				Freundlich Isotherm		
q_m (mg g^{-1})	k_L (L mg^{-1})	R_L	R^2	k_f	n	R^2
16.05	0.127	0.547	0.9378	1.8323	0.39	0.9794

Table 2: Isotherm Parameters for Adsorption of oxyfluorfen onto aluminum at current densities 75 mA/cm^2.

	Fe^{+2} (Kg/m^3)	Fe^{+3} (Kg/m^3)	Al^{+3} (Kg/m^3)
Oxyfluorfen	0.0016	0.001	0.00050

Table 3: Mass of loss from Fe and Al electrode.

$$m = I.A.M.t/V.Z.F \qquad (19)$$

where m is the mass of the anode material dissolved (g), I the current density (A.m^{-2}), A the active electrode area (m^2), M the molar mass of the anode material (g.mol^{-1}), t electrolysis time (s), V volume of the reactor (m^3), z the number of electrons transferred, and F the Faraday's constant (96,485 C mol^{-1}). The cathode dissolution was not considered according to equation (19). The maximum possible mass of Fe and Al electrochemically generated from sacrificial anodes in Table 3 at optimum condition for each process.

Determine the residual concentration of iron in herbicides samples: It appears to be more of a nuisance than a potential health hazard. Iron in water 0.1 mg.L^{-1} for ferrous iron and 0.2 mg.L^{-1} ferric Iron. Water used in industrial processes usually contain less than 0.2 mg.L^{-1} iron [37]. According to following equation Beer-lambert:

$$A = \varepsilon\, b\, C \qquad (20)$$

Where A is absorbance, ε is the molar absorptivity, b is the path length of the sample and C is the concentration of the compound in solution. The concentration measurements of iron (II) was found 0.08 mg.L^{-1} for oxyfluorfen.

Conclusion

1. Oxyfluorfen herbicide and COD removal were (98.5% and 90%) using Fe (99.2% and 85%) using S-S and (96.1% and 70.5%) using Al at 30 min respectively, electrical energy consumption (15.9, 16.65 and 14.1 KWh/m^3) using Fe, S-S and Al electrodes respectively typical operating conditions: current density 75 mA.cm^{-2}, pH 5.8, sodium chloride concentration 1 g.L^{-1}, herbicide concentration 200 mg.L^{-1}, inter-electrode distance 1.0 cm and temperature 10°C using all electrodes.

2. The results were concluded that the electrode material play an important role in electrocoagulation method for treatment of herbicides in aqueous solution.

3. The removal rate of oxyfluorfen followed first order reactions using Fe, S-S and Al electrodes with rate constant 0.025, 0.023 and 0.12 min^{-1} respectively.

4. The oxyfluorfen adsorption was best fitted by the Freundlich adsorption isotherm and the results were in good agreement with the experimental data.

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