Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2019.24409

165 (2019) 103–110
October

Degradation of pesticide-contaminated wastewater (coragen) using electrocoagulation process with iron electrodes

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Received 3 September 2018; Accepted 14 May 2019

ABSTRACT

The electrocoagulation of coragen-contaminated wastewater for the removal of pollutants was investigated using iron electrodes. The effect of process variables such as initial pH, current density, electrolysis time of the sample and electrode materials in the degradation of coragen was also studied. During various stages of electrolysis, parameters such as COD, chloride and bromide ion concentrations were examined. The maximum removal efficiency i.e., 79% for chemical oxygen demand (COD) was achieved at pH 7 operated at a current density of 7.5 mA/cm^2 with 2.5 mg/L electrolyte (NaCl) concentration and 150 min of electrolysis using iron electrodes. Neutral pH results in the maximum reduction of COD compared to alkaline and acidic pH solution. To be specific, an increase in current density and process time led to increase in COD removal. Moreover, iron electrodes showed maximum removal of COD (79%), chloride (78%) and bromide (77%). The degradation of coragen was further confirmed using FTIR and GC-MS. The experimental results indicate that the electrocoagulation process effectively reduces the COD from coragen-contaminated wastewater.

Keywords: Iron electrode; Coragen; Chlorantraniliprole; Ryanodine; COD; Bromide

1. Introduction

In 21st century, the preservation of both energy and water is the biggest environmental challenge among global nations. To be specific, reduction in water quality has become a crucial problem in developing countries due to high amount of pollution from non-point as well as point sources. Most of the pesticides are non-biodegradable because their molecular structure has stable internal bonds. Pesticides, polluting the natural water, has become a pervasive problem. The wastewater, generated from cleaning activities after batch operation during the syntheses processes in pesticide manufacturing industries pollute the natural sources of water. Such waste water may contain toxic organics and pesticide residues which pose a threat to the quality of surface and groundwater. The wastewater generated in agricultural industries and pesticide formulation or manufacturing plants has been reported to contain pesticide contamination levels as high as 500 mg L^{-1} [1]. Due to the long residence time of these substances in the environment [2], the interest, to examine the pollution that they cause, has grown considerably.

Coragen 20 SC is a new product in India which contains an active substance called chlorantraniliprole and is applied on apples against codling moth (*Cydiapomonella*), apple fruit

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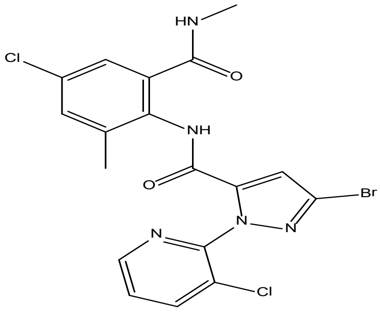
moth (*Argyresthiaconjugella*) and their free leaf living larvae [3]. Anthranilicdiamide insecticide (coragen) mostly affects the ryanodine receptors present in the muscles. Those insecticides (Ryanoids) that target ryanodine receptor plays an important role in the controlled release of calcium ion, a universal intracellular transmitter from intracellular stores [4]. The flow of calcium is regulated by ryanodine receptors, which mediates several metabolic and physiological cellular processes such as neurotransmission, hormonal secretion, muscle excitation and contraction coupling [5]. Coragen contains hydrophobic molecules that bind extensively with biological membranes, especially phosphor lipid bilayers, and causes membrane damage by inducing lipid peroxidation [6–8]. Then, the oxidative stress is induced by free radicals which seek stability through electron pairing with biological macromolecules present in healthy human cells and damage the protein and DNA in addition to lipid peroxidation [9]. Coragen is highly toxic to aquatic organisms and may cause long-term adverse effects in the aquatic environment. The physicochemical properties of coragen are mentioned in Table 1. Recently, electrocoagulation process seems to be an effective and ecofriendly treatment method for drinking water and wastewater treatment [10,11]. Electrocoagulation is a simple and efficient method to remove the flocculants generated by electrooxidation of sacrificial electrodes which are generally made of iron or aluminium. The main advantages of the electrocoagulation process are the usage of meagre amount of chemical reagents, minimal sludge production, low concentration of secondary pollutants and less consumption of electrical energy [12]. On the other hand, electrocoagulation is based on *in situ* formation of coagulant since the sacrificial electrode corrodes due to applied current density, while the simultaneous evolution of hydrogen at cathode allows the removal of pollutants through flotation. One of the main advantages of iron electrodes is its nontoxicity due to which it can be used for drinking water treatment process. When compared with other electrodes like aluminum, stainless steel and copper, iron electrodes cost less in the range of 0.5–0.8 US$/kg. Three interdependent processes are combined to form the electrocoagulation processes namely hydrodynamics, electrochemistry and coagulation. The electrochemical reactions occur at iron electrodes during electrocoagulation process as shown below.

$$3H_2O + 3e- \leftrightarrow 3/2H_2g + 3OH - aq(cathode) \tag{1}$$

$$Fe + 3aq + OH - aq \leftrightarrow Fe(OH)_3 \tag{2}$$

The metal ions get adsorbed onto iron hydroxide flocs. As the removal of pollutants takes place at the effluent [13], the permissible limits for COD, chloride and bromide industrial effluents discharge are 250 mg/L, 1000 mg/L and 2 mg/L respectively. The main purpose of this study is to investigate the efficiency of electrocoagulation process in the removal of coragen from aqueous environments using iron electrodes. Further, the study also determined the effects of constant parameters such as current density, pH, and electrolysis time when applied on coragen removal efficiency.

Table 1
Physical chemical properties of coragen

Chemical	Properties
Common name	Coragen
Chemical formula	$C_{18}H_{14}BrCl_2N_5O_2$
IUPAC name	5-brom-N-[-4-chloro-2-methyl-6-(methylcarbamoyl)phenyl]-2-(3-chloropyridin-2-yl)pyrazole-3-carboxamide
Molecular weight	485.15 g mol^{-1}
Structure	
Colour	White

2. Materials and methods

2.1. Experimental set-up

In the electrochemical experimental setup, a reaction container of 3.0 L sample holding capacity was used. The iron electrodes (of purity 98%), with each iron electrode measuring 0.6 cm width,12 cm length and 312 cm^2 of total surface area, were used. Monopolar connection was also established for this study. Seven iron rods were connected to a common rod to form the electrodes. The anode and cathode distances were maintained at 2 mm to minimize the ohmic losses. The iron electrode efficiency is shown in Table 2. With the help of DC power supply, different electrical conductivity were achieved manually.

2.2. Analysis

The chemicals used in this study were Sodium chloride (NaCl), Ferrus Ammonium sulphate ($(NH_4)_2SO_4FeSO_46H_2O$), Potassium dichromate ($K_2Cr_2O_7$), Mercuric sulphate ($HgSO_4$), Sodium hydroxide (Na_2SO_4), Potassium chloride (KCl), Silver nitrate ($AgNO_3$), Sulphuric acid (H_2SO_4) and Coragen (of analytical grade). The chemicals were procured from Sigma-Aldrich chemicals Pvt Ltd., India.

2.3. Glassware

All the glassware were washed with standard dish washing detergent, rinsed with tap water and copious amounts of distilled water which were then allowed to dry. After that, the pipettes were rinsed thoroughly using distilled water and checked regularly for proper draining. Volumetric flasks were cleaned as mentioned earlier and used in the preparation of all the solutions.

Table 2
Comparison of different electrode potential for removal of pollutants

Electrode	Pollutants	Optimum pH	EC	% of COD Removal	Reference
Iron	Coragen	7.0	7.5 mA/cm^2	79.0%	This study
Aluminum	Pesticide	6.9	18.5 mA/cm^2	73.1%	Ghalwa et al., 2015 [33]
Aluminum	Leachate	7.0	631 A/m^2	56.0%	FatihIlhan et al., 2008 [34]
Stainless Steel	Emulsion	7.0	8.2 mA/cm^{-1}	72.4%	Olfat A. Fadali et al., 2018 [35]
Stainless Steel	Oil	8.0	0.34 A	40-26%	L. Shamaei et al., 2018 [36]
Fe and Al	Wastewater	7.0	50/100 A/m^2	60.5%	Nadir Dizge et al., 2018 [37]
Copper	Ciprofloxacin	7.0	>58.1 kWh/m^3	70.0%	Mohammad Reza Samarghandi et al., 2018 [38]
Copper	Rice gain water	3.5	89.3 A/m^2	65.0%	Abhinesh Kumar Prajapati et al., 2015 [39]
Copper	Organic wastewater	2.8	14.2 mA/cm^{-2}	78.0%	CarlosBarrera-Díaz et al., 2014 [40]

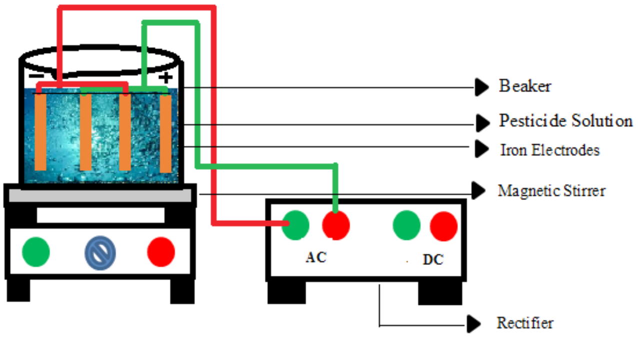


Fig. 1. Electrochemical instrumental setup.

2.4. Coragen stuff

The structure of the coragen used for this study is shown in the Table 1. Pesticide solutions were prepared by pipetting a known amount of coragen into a 1-L Erlenmeyer flask and diluting it with a known amount of distilled water.

2.5. Parameters

According to the standard method (APHA 1995), the wastewater and water were examined. Chemical oxygen demand experiments were carried out by open reflex method. The percentage of pesticide (corage) mineralization was evaluated by measuring COD. Mohr's method was used to analyze the chloride concentration from treated water. Bromide was examined by colorimetric method using spectrophotometer (at 610 nm).

3. Results and discussion

3.1 Effects of initial pH

3.1.1. Effects of initial pH on COD, chloride and bromide removal

Initial pH is a crucial variable in the elimination of pollutants during electrocoagulation process [14–15]. In the current study, the pH values such as 3, 5, 7 and 9 were tested. During the electrocoagulation process, the monomeric ions such as Fe $(OH)_3$ and polymeric hydroxyl complex such as $Fe(H_2O)_6^{3+}$, $Fe(H_2O)_5^{2+}$, $Fe(H_2O)_4(OH)^{2+}$, $Fe(H_2O)_8(OH)_2^{4+}$ and $Fe_2(H_2O)_6(OH)_4^{4+}$ were produced at iron electrodes. The generation of ions and the release of anode and cathode mainly depend upon the pH of the aqueous medium. The metal ions are evaluated at the anode whereas the H_2 gets released at the cathode. Hydrogen (H_2) helps the flocculated matter to float so that it can be removed from the water [16]. To analyze the effects of initial pH on the removal of COD, chloride and bromide, few experiments were conducted by changing the pH from 3 to 9. For these experiments, NaCl concentration of 2.5 mg/L and 1 L of the sample volume of coragen were maintained with applied current density being 2.5 mA/cm^2 at 60 min treatment time. As given in Fig. 2, the results clearly indicate that the COD got removed (57%) at pH 7. Due to neutral conditions, Fe^{2+} ions got immediately converted into ferrous hydroxide which were then quickly oxidized by dissolving oxygen to form irons (III) hydroxide. In acidic and basic pH, the dissolution amount of Fe ions was very less. Due to the acidic conditions, the Fe^{2+} ions got slowly oxidized. In the presence of NaCl, the mineralization of organic pollutants was high [17–19].

In general, NaCl was used to obtain conductivity during the electrocoagulation process. The effect of NaCl concentration in the removal of pesticides is shown in Fig. 3. During the electrolysis process, NaCl got split into Na^+ and Cl^- ions. The Cl^- ions reacted with iron oxide to form ferrous or ferric chloride which remains the strongest degradation compounds in the removal of coragen effluent. Hence, it is an essential feature to analyze the amount of chloride from the treated water. The maximum chloride removal of 39% iron electrode occurred at neutral pH. In neutral pH, the chloride anions were converted in to hypochlorite anions that were oxidized by organic compounds present in the coragen. A number of studies have been conducted on Br removal [20,21]. But only a few reveal that the electrochemical treatment is sufficient to remove Br from wastewater through oxidation though it generates by-products at the end of the process [22]. Hence, nanofiltration can be used to remove Br ions without any

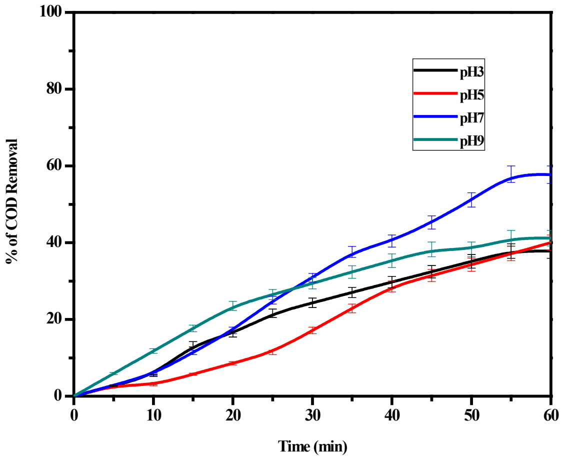


Fig. 2. Effect of initial pH on the removal of COD.

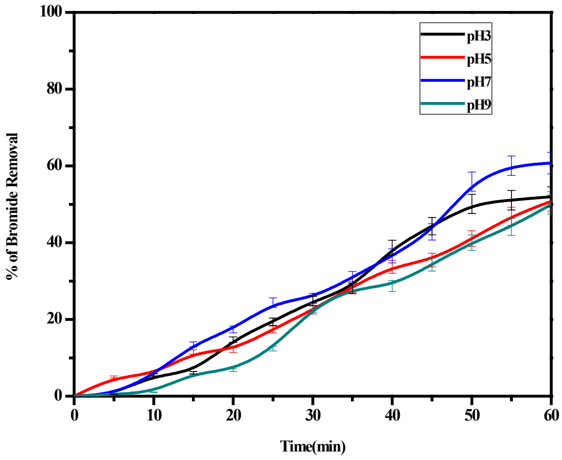


Fig. 4. Effect of initial pH on the removal of bromide.

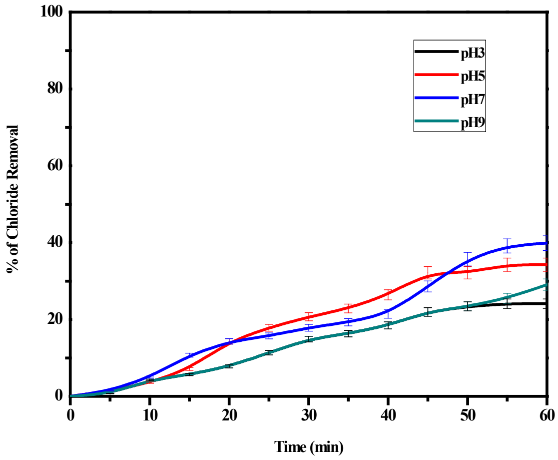


Fig. 3. Effect of initial pH on the removal of chloride.

by-product formation. But it incur high cost which limits its large scale applications [23,24]. Coagulation is considered to be an effective alternative in the removal of Br. The effect of pH in the removal of Br by electrocoagulation was investigated using different pH values such as 3, 5, 7 and 9. Bromide adsorption on electrocoagulation was strongly affected by pH. Bromide removal showed a strong affinity for the surfaces of iron electrode at pH 7 (62%) as shown in Fig. 4. However, an increase in pH decreased the Br adsorption on the iron electrode.

3.2.Effect of current density

3.2.1. Effect of current density on COD, chloride and bromide removal

It has been established that the cell current is one of the important parameters that control the reaction rate during electrochemical processes. The current density, not only determines the coagulant dosage rate, but also the bubble production rate and size [25]. Thus, this parameter creates a significant impact on pollutant removal. The influence of the current density on COD, chloride and bromide removal during the electrocoagulation of coragen at iron electrodes is shown in Figs. 5, 6 and 7. When the current density was increased from 2.5 to 7.5 mA/cm^2, it resulted in the enhancement of oxidation rate [26,27]. After 60 min of electrolysis, the COD, chloride and bromide removal percentage got increased to 79%, 78% and 77% respectively when the current density was maintained at 7.5 mA/cm^2. This behavior indicates that, in these experimental conditions, the oxidation of coragen was completely under mass transport control. The increase in the applied current only favored the secondary reaction of oxygen evolution:

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

It is a well-known fact that the amount of applied current density determines the coagulant production rate and adjusts the rate and size of the bubble production, and hence it affects the growth of floc [28]. The maximum values of COD, chloride and bromide i.e., 79 %, 78% and 77% respectively were removed by electrocoagulation using iron electrode (Figs. 5, 6 and 7). After 60 min of electrocoagulation, the removal efficiencies were almost constant.

3.3. Effect of electrolysis time

3.3.1. Effect of electrolysis time on COD, chloride and bromide removal

The efficiency of COD, chloride and Br mineralization depends directly on the concentration of ions produced by the electrodes which in turn depends upon time. When the value of time increases, the concentration of iron ions and their hydroxide floc also increases [29–32]. The study was carried out with different electrolysis times up to 150 min under specific conditions i.e., NaCl concentration of 2.5 mg/L, applied current density 2.5 mA/cm^2 with neutral pH 7. Iron electrodes in Figs. 8, 9 and 10 show the increased mineralization efficiency in first 60 min, reaching over 58%, 42% and 59% respectively. Secondly, the mineralization efficiency increased and reached 60%, 60% and 65% respectively at 150 min of electrolysis.

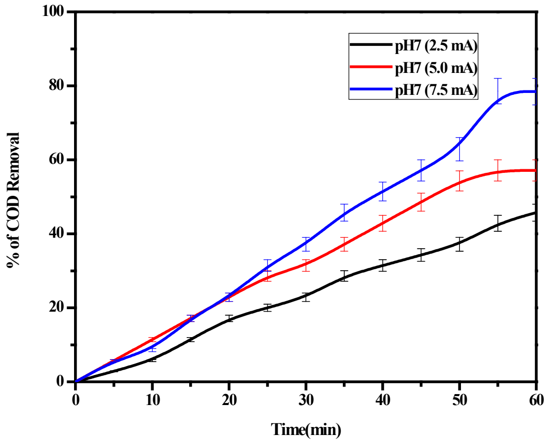


Fig. 5. Effect of current density on the removal of COD.

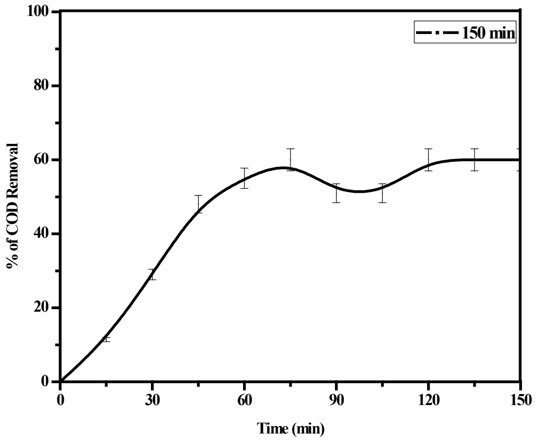


Fig. 8. Effect of treatment time on the removal of COD.

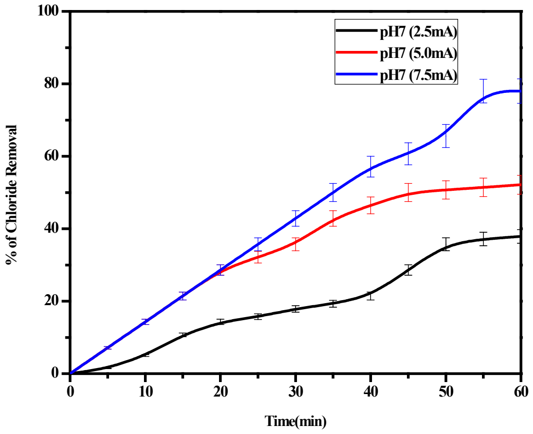


Fig. 6. Effect of current density on the removal of chloride.

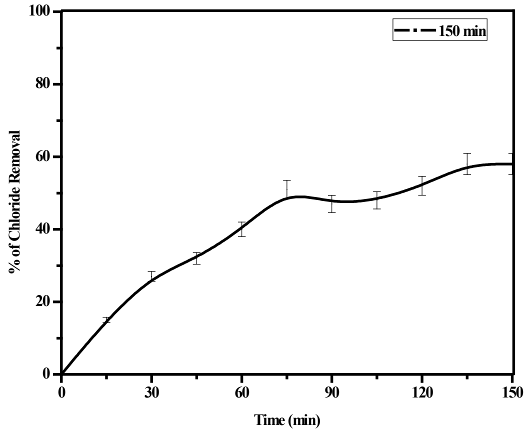


Fig. 9. Effect of treatment time on the removal of chloride.

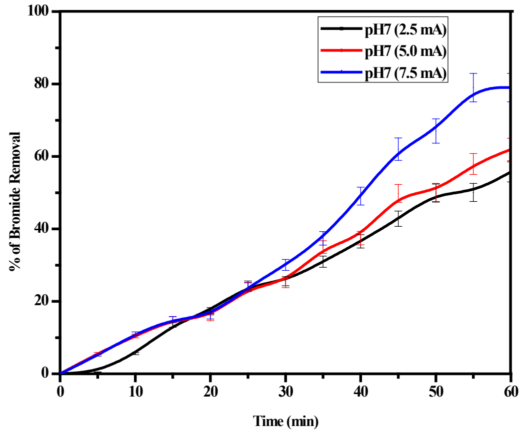


Fig. 7. Effect of current density on the removal of bromide.

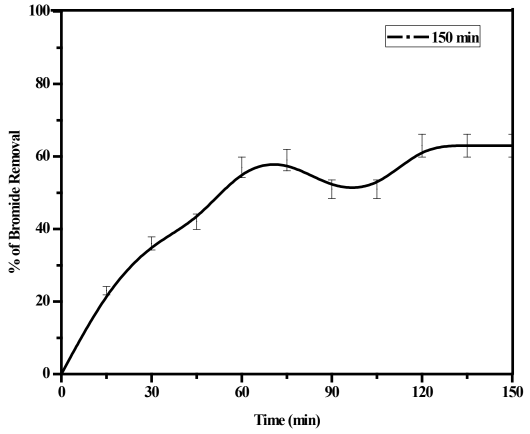


Fig. 10. Effect of treatment time on the removal of bromide.

3.4. FTIR analysis

To investigate the changes in the functional group during electro-oxidation, the samples were monitored using FT-IR spectroscopy (Bruker ALPHA FTIR). Fig. 11 shows the IR spectra of the coragen before and after electrocoagulation at room temperature. Before treatment,1639.234 peaks were found due to stretching absorption of alien and carbonyl(general) C=O groups whereas 1537.57 peaks were found due to the formation of aromatics groups. In the peaks, 1301.07

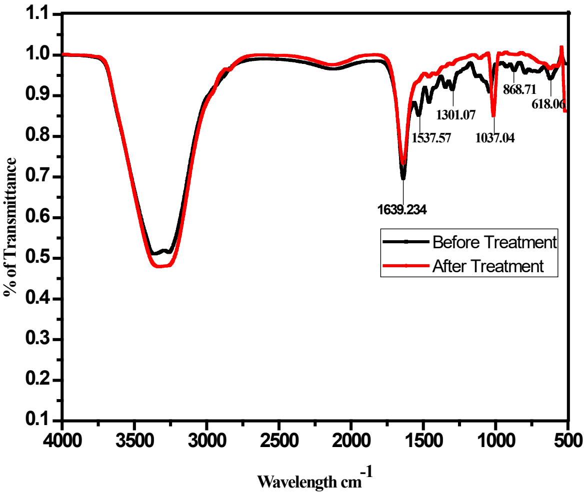


Fig. 11. FTIR image for coragen before and after electrocoagulation process.

and 1037.0 peaks represent the formation of C-H alkyl halides group. 868.71, 618.06 peaks were found due to the formation of C-H oop′ aromatic groups. After electrocoagulation, 1537.57, 1301.07, 868.71 and 618.06 peaks got completely disappeared.1639.234 peaks indicated alien and carbonyl C=O group whereas the other two peaks 1037.04 and 625.05 indicated =C-H bend alkene groups respectively.

3.5. GC-MS analysis

The treated coragen sample was tested by liquid-liquid extraction method. 500 ml of electrolyzed coragen sample was transferred into a separating funnel and distilled with the same amount of diethyl ether and n-hexane (1:1). With the help of gas chromatography-mass spectrometry (GC-MS), the coragen residue was restructured with 1.0 ml of methanol. Through GC-MS (Perkin Elmer-Clarus 600, Germany), with MS capillary column (60× 250 μm), the intermediate analysis was carried out. In this analysis, constant flow rate of helium at1 ml min^{-1} was used as carrier gas. The temperature of the ion source was 200°C. Initial oven temperature was maintained at 50°C for 5 min and the range of scan mode was m/z from 40 to 480 Da. The injection volume was 5 μl. Under these operating conditions, the retention time for standard coragen was 17.40 min. After 60 min, the electrolysis samples were analyzed for intermediates.

Using GC-MS spectroscopy (Perkin Elmer-Clarus 600 Germany), the evolution of coragen intermediate chemical compounds were analyzed. Fig. 12 shows the GC-MS image of coragen after 150 min of electrocoagulation at pH 7. Table 3 clearly shows the list of intermediate chemical compounds that are present after electrocoagulation process. The GC-MS results reveal that the coragen mineralization has taken place from higher molecular compounds to lower molecular compounds like (Borofalan 209.0, 4, 6-dichloro-5-fluoro-2-methylpyridine (181.0), Dichlorotrifluoroethane (152.0) and 2-nitroethanol (91.0).

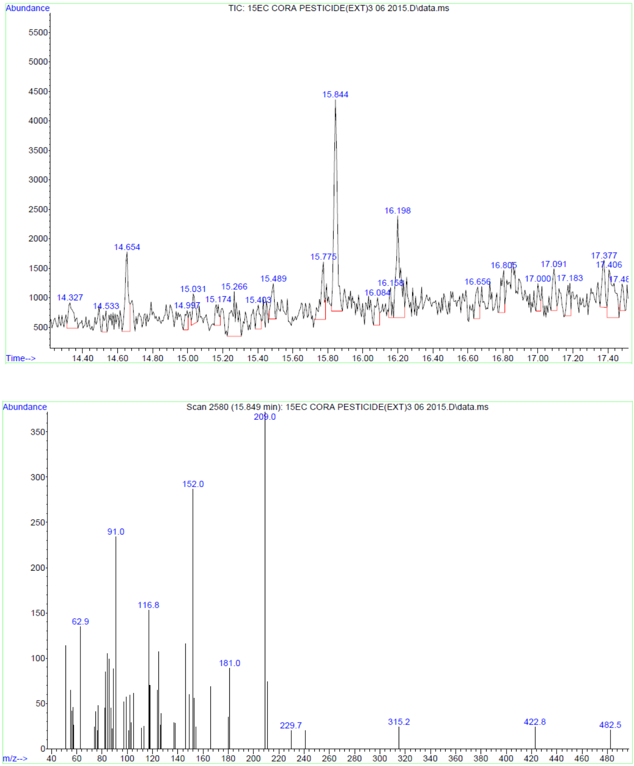


Fig. 12. GCMS analysis for coragen.

Table 3
List of intermediate compound present in coragen degradation using electrocoagulation process by iron electrodes

S. No	Compound	Molecular Weight
1	3-bromo-1-(3-chloro-2-pyridyl)-1h-pyrazole-5-carboxylic acid ($C_9H_5BrClN_3O_2$)	406.11
2	2,6-Dichloro-4-methyl-1-pyridyl(2-1-betaquin azolin-11-one ($C1_5H_9Cl_2N$)	274.144
3	5-bromo-n-methyl-1h- pyrazole-3-carboxylic amide (C_{12} H_{16} Br N_5O)	326.2
4	5-Bromo-N-methyl-1H-pyrazole-3-carboxamide	204.03
5	3- Bromo benzyl chloride nitril($C_9H_{10}ClNO$)	183.64

3.12. Economic analysis

For a sample capacity of 1,000 m^3 wastewater per day, the approximate cost analysis for a large scale plant includes direct and indirect cost items like electrode materials (Fe electrodes), pesticide transportation, disposal costs, maintenance of major instruments like electro coagulators and rectifiers, and labour cost. The total cost analysis for an effective large plant is given in Table 4.

Table 4
The approximate cost analysis for a large scale plant is shown below

Cash flow	Purpose	Amount ($)
Electro coagulation tank (year)	Sample collection	500
Rectifier	Power supply	10,000
Electricity (per hour)	DC power supply	0.06
Labor costs (per hour)	Analysis purpose	2.3
Fe electrode (per kg)	Electrode	0.3
Chemicals (m^3)	Coagulation	0.025

4. Conclusion

The study results for the degradation of coragen-contaminated pesticide wastewater, through electrocoagulation using iron electrodes, seem to be one of the efficient methods as per the results achieved in FTIR and GCMS analyses. Here, pH plays a vital role in electrocoagulation process and to be specific, pH 7 achieved the maximum mineralization of COD, Cl_2 and Br after electrocoagulation. The mineralization rate got increased when increasing the current density and treatment time. With the absence of functional groups in FTIR analysis results, after electrocoagulation of coragen, it can be clearly understood that the minimization occurred in an effective manner. In addition, the GC-MS results also imply that the mineralization of coragen from higher molecular compounds to lower molecular compounds has been achieved. To conclude, the techno economic studies reveal that electrocoagulation using iron electrodes is one of the feasible methods for large scale applications.

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