

Removal of pesticides from wastewater by electrochemical methods — A comparative approach

Balakrishnan Ramesh Babu,* Kamal Mohamed Seeni Meera and Perumal Venkatesan

Pollution Control Division
CSIR- Central Electrochemical Research Institute
Karaikudi 630006, India

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ABSTRACT

Three different electrochemical techniques namely, electrooxidation, electrocoagulation and electro-Fenton of pesticide effluent (contains methyl parathion, atrazine and triazophos) were chosen for this study. Experiments were carried out at different pH to determine the optimum pH condition. Chemical oxygen demand (COD) of the effluent reduced at the end of 6 h from 1810 to 431 mg L⁻¹ (pH 6) by electrooxidation, to 210 mg L⁻¹ (pH 10) by electrocoagulation and to 341 mg L⁻¹ (pH 8) by electro-Fenton. The results revealed that a high COD reduction was observed by electrocoagulation at pH 10 (88%), followed by electro-Fenton at pH 8 (81%) and electrooxidation at pH 6 (76%) at a constant current density of 5 A dm⁻². Further we have also determined current efficiency, energy consumption and the cost of degradation.

INTRODUCTION

Various innovative technologies have been proposed for the removal of pesticides namely photocatalytic oxidation, ultrasonic radiation, bioremediation and thermal desorption. They are neither cost effective, nor ecofriendly, nor involving low concentrations. In recent years, there has been an increasing interest in the use of electrochemical methods for the treatment of recalcitrant toxic wastes. Electrochemical methods have been successfully utilized in the purification of olive oil wastewaters, domestic sewage, landfill leachate, tannery wastes, textile wastes. These methods are environmentally friendly and they do not form new toxic wastes. Removal of methyl parathion by about 80% was reported [1]. Removal of pesticide wastewater by three methods was studied individually by electrooxidation process, EOP [2], electrocoagulation process, ECP [3] and electro-Fenton process, EFP [4-7].

Globally pesticides are toxic to non-target receptors including humans and reach them through food chain [8]. Most of the pesticides are non-biodegradable because of their molecular structure with stable internal bonds. Pesticide pollution of natural waters has become a pervasive problem. Wastewaters from pesticide manufacturing industries originate from cleaning activities after batch operation during the synthesis processes. They may contain toxic organics and

pesticide residues which pose a threat to the quality of surface and groundwater. Wastewaters from agricultural industries and pesticide formulation or manufacturing plants were reported to have pesticide contamination levels as high as 500 mg L⁻¹ [9].

The overall impact of a pesticide depends on its behaviour in the environment, its toxicity and the amounts applied [10]. Different pesticides pose different types of risks in varying degrees like cancer and genetic effects [11]. Their residues may persist in soil, aquatic sediment resulting in biomagnifications in the food web. Organophosphate pesticides, with stable structures at atmospheric condition can be harmful to aquatic life even at very low concentrations [12]. For example at about 20 °C and pH 7.4, methyl parathion has a hydrolytic half-life of 108 d and similarly its toxic metabolite, paraoxon, has a half-life of 144 d [13]. The rate of degradation increases with temperature and sunlight intensity. When large concentrations of methyl parathion reach the soil, as in an accidental spill, degradation starts after a few years.

In the recent years, there is an increasing interest in the development of environmentally friendly electrochemical methods to treat toxic organic pollutants in wastewaters [14]. The organic and toxic pollutants present in such wastes, such as phenols which are present in many pesticides, are usually destroyed by anodic oxidation as a result of the production of oxidants such as hydroxyl radicals, ozone, etc [13]. Treatment of

*Corresponding author
Email: akbabu_2001@yahoo.com

concentrated wastewater is often difficult because of microbial toxicity and mass transfer limitations. In this regard, it is advisable to develop technologies that facilitate easier degradation of these biorecalcitrant organic compounds.

The studies of using electrochemical methods for reduction of pesticides are of interest. EOP, EFP and ECP appear to be promising means to solve the environmental problem generated by the discharge of these effluents.

Our current work involves the removal of pesticides from the samples collected from a nearby manufacturing industry by EOPs, EFP and ECP. The removal of pesticides by each of these methods with impact of initial pH was evaluated. The Fourier transform infrared spectroscopy (FTIR) spectral variations during the processes of degradation of methyl parathion, atrazine and triazophos were discussed in this paper.

1. Theory of EOP

The toxic organic contaminants are usually destroyed by oxidants such as Cl_2 , ClO_2 , O_3 , $\bullet\text{OH}$, $\text{O}\bullet$, $\text{ClOH}\bullet$, H_2O_2 etc., that are produced from anodic oxidation during the electrolysis [15].



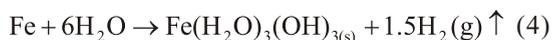
The absorbed hydroxyl radicals then oxidize the organic matter:



Where RO represents the oxidized organic matter that can be further oxidized by the hydroxyl radicals formed from the electrolysis of water.

2. Theory of ECP

ECP is based on the in situ formation of coagulants, as the sacrificial anode corrodes as consequence of the applied current. Simultaneously, there is an evolution of hydrogen at the cathode which allows pollutant removal by floatation or sedimentation. Overall reactions are:

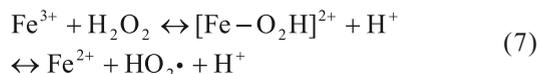


3. Theory of EFP

EF is an advanced EOP based on the electro generation of H_2O_2 [16], $\bullet\text{OH}$ is then produced in the medium by the classical Fenton's reaction between ferrous ion and hydrogen peroxide (Eq. 5):



Regeneration of Fe^{2+} can also be achieved by the oxidation of organics with H_2O_2 or by reaction with hydroperoxyl radical as shown below:

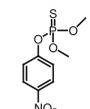
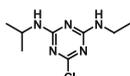
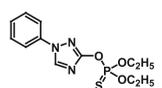


MATERIALS AND METHODS

1. Pesticide Wastewater

The pesticide wastewater used in this experiment was obtained from a nearby pesticide manufacturing plant. It contains mainly methyl-parathion (O,O-Diethyl-O-4-nitro-phenylthiophosphate), atrazine (1-chloro-3-ethylamino-5-isopropylamino-2,4,6-triazine) and triazophos (O,O-diethyl O-1-phenyl-1H-1,2,4-triazol-3-yl phosphorothioate) and their structures are given in Table 1.

Table 1. Structures of pesticides present in the effluent

Name	Structure
Methyl parathion $\text{C}_8\text{H}_{10}\text{NO}_3\text{PS}$	
Atrazine $\text{C}_8\text{H}_{14}\text{ClN}_5$	
Triazophos $\text{C}_{12}\text{H}_{16}\text{N}_3\text{O}_3\text{PS}$	

2. Methods

The pH, total dissolved solids (TDS) and conductivity of the wastewater were measured by using pre-calibrated M/s Elico made meters. FTIR analysis were done using Nexus 670 instrument within the range of 4000 to 400 cm^{-1} by making the samples as disc using KBr. Chemical oxygen demand (COD) was measured by Standard Method by a closed reflux method. The characteristics of the wastewater before treatments are shown in Table 2.

Table 2. Characteristics of pesticide effluent before and after treatment at 5 A dm^{-2} at the end of 6 h

Parameters	Before treatment	After treatment		
		EO	EF	EC
pH	6.84	7.82	8.44	5.78
Conductivity (S m^{-1})	0.284	2.4	1.05	0.524
COD (mg L^{-1})	1810	430 (pH 6)	340 (pH 8)	210 (pH 10)
TDS (mg L^{-1})	1050	7650	5650	1300

3. Electrochemical Methods

Electrochemical cell consists of a 1.5 L glass reac-

tor under batch process. All experiments were conducted with 1 L of the sample as it is and 6 g L⁻¹ of NaCl was added as supporting electrolyte. The electrodes were connected to a digital dc power supply (APlab L-3210). A constant stirring of 300 rpm using magnetic stirrer was ensured during experiment. Electrochemical reaction was performed at room temperature and atmospheric pressure and the duration of electrolysis was 6 h. Samples were drawn at regular intervals to estimate the COD reduction efficiency. All the experiments were performed in triplicate. The set up of electrochemical cell used in EFP is same as in EOP shown in Fig. 1. A constant current density of 5 A dm⁻² was applied in all the three electrode systems for comparison.

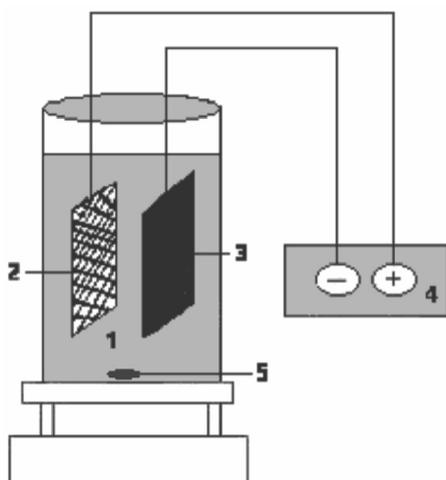


Fig. 1. Experimental set-up: (1) Effluent from pesticide industrial wastewater, (2) anode, (3) Cathode, (4) DC power supply, (5) magnetic stirrer.

4. EOP

Anode and cathode were mixed oxide coated titanium mesh and stainless steel, respectively. The immersed area of anode was 23.7 cm². Experiments were carried out at 5 A dm⁻² and at various pH (6, 8 and 10).

5. ECP

In this process, the mild steel with dimensions of (0.15 x 6 x 7 cm) with an immersed area of 42 cm² was used as anode. Experiments were carried out for 6 h at three different pH conditions as in EO (pH 6-10).

6. EFP

The set up of electrochemical cell used in EF is same as in EO process shown in Fig. 1. In this process H₂O₂ was added to the solution (2 mL initially and continued for every 1 h) to enhance the reactivity, 2 mM of Fe₂SO₄·7H₂O was added initially. Treated samples were withdrawn from the cell at pre-determined time intervals for further analysis, such as COD.

RESULTS AND DISCUSSION

Although all three electrochemical methods have their own advantages and disadvantages, current study targets in understanding the extent of removal of the pesticide waste water. The comparison of these three methods (EOP, ECP and EFP) at identical conditions of pH, current density and time duration helps to identify the conditions at which maximum removal could be achieved.

1. Effect of pH

It has been established that the initial pH of wastewater effluent is an important operating factor influencing the performance of electrochemical process [17]. To examine its effect, the pesticide wastewater was adjusted to the desired pH for each experiment by using 0.1 M NaOH and H₂SO₄ solution.

In the case of EO, the •OH produced reacts with the most organic pollutants present in the wastewater. At the end of 6 h of experimentation, the maximum COD reduction was 76% at a current density of 5 A dm⁻² and pH 6.0. It should be outlined that at acidic pH, chlorine is present in the form of a HOCl that manifests the oxidation process. In case of EC, the maximum COD removal efficiency of 88% was observed at pH 10. This is probably due to the fact that the formation of Fe (aq) ions and their posterior oxidation to Fe³⁺ (aq) causes the precipitation of Fe(OH)₃; this oxidation by oxygen becomes higher at higher pH. In case of EF, the COD removal efficiency was 81% at pH 8. Generally, the optimal pH of the photo-Fenton reaction is in acidic range because the main species, Fe(OH)²(H₂O)₅, is the one with the largest light absorption coefficient and quantum yield for •OH radical production, along with Fe(II) regeneration, in the range 280-370 nm [18]. However, the optimal pH obtained was 8 due to the reactions of organics or its intermediate products that might react with iron species followed by the formation of iron complexes and these could assist the catalytic cycles of iron. Lesser COD removal was observed at other pH conditions for all these methods studied (Fig. 2). The highest COD % at optimum pH condition was observed in the following order: pH 10 (EC) > pH 8 (EF) > pH 6 (EO).

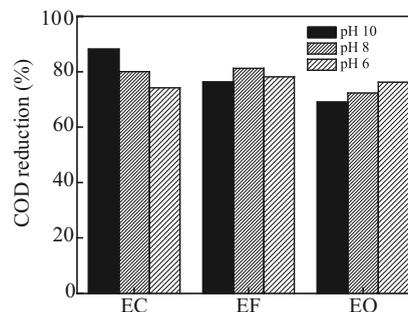


Fig. 2. Comparison of the COD removal efficiency for EO, EC and EF processes in different pH conditions.

2. FTIR Spectral Studies

Figure 3 shows the comparison of the IR spectra of untreated and treated pesticide effluent by EO, EC and EF. From the spectra it is observed that some structural changes might have occurred. Figure 3a shows characteristic peaks of the pesticide effluent. The peaks at 3446 and 3313 cm^{-1} are due to the N-H absorption of atrazine molecule present in the raw wastewater. Peaks found at 3086, 2959 and 2859 cm^{-1} were mainly due to stretching absorption of aromatic and aliphatic C-H groups. Besides, peaks were obtained at 1682, 1636 and 1451 cm^{-1} due to the aromatic C=C and C=N. Presence of peaks at 1451 and 1354 cm^{-1} were due to presence of nitro group and at 870 cm^{-1} due to C-NO₂ group. The other peaks at 1275 and 1037 cm^{-1} were due to P-O-CH₃ and P-O-CH₂CH₃ groups, respectively.

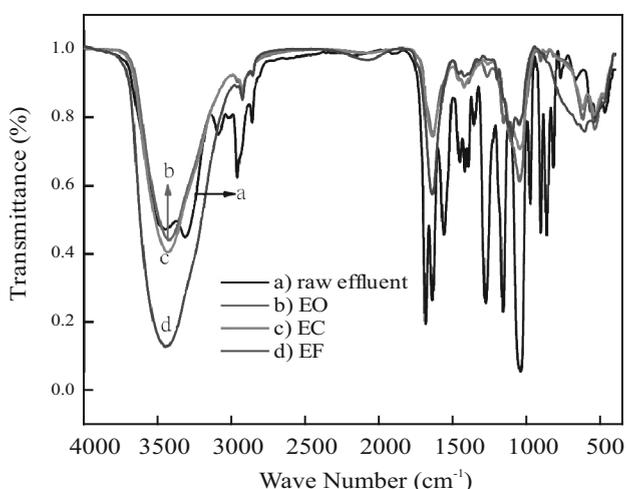


Fig. 3. FT-IR spectra of treated and untreated pesticide effluent samples.

The degradation of waste was noticed with the aid of IR spectra (Figs. 3b-3d) of pesticide samples after treatment by EOP, ECP and EFP. In Fig. 3b, the characteristic absorption peaks of methyl parathion, atrazine and triazophos were reduced and new peaks were found at 1632 and 1045 cm^{-1} which may be due to the intermediates of organic compounds (EO processed sample). Figure 3c shows the spectra of treated sample by EC (after 6 h). Similar peaks were observed with less intensity due to reduction of organic portion in wastewater during experimentation. EF of treated effluent is represented in Fig. 3d (after 6 h). This reveals that the higher degradation has occurred in EFP.

3. Energy Consumption

To enumerate the efficiency of the processes, energy consumption was calculated. Generally energy consumption was expressed in kWh kg^{-1} COD removal and is given as:

$$\text{Energy Consumption} = \frac{I V t}{\text{vol}(\Delta\text{COD})} \quad (9)$$

From the results of EF, maximum COD reduction of about 81% was obtained with an energy consumption of about 15.2 kWh kg^{-1} COD whereas in the case of EO and EC, the maximum COD reduction was 76 and 88% with an energy consumption of 70.6 and 8.6 kWh kg^{-1} COD, respectively. Energy consumption for the EC is lower than that of EFP but EF has slightly lower % COD removal. All the experimental results indicated that among these three processes, EC is the best due to high % COD removal and moderate energy consumption. COD removal efficiency and energy consumptions are given in Table 3.

Table 3. Selected results obtained for degradation of pesticide effluent using three different processes

Process	Applied Current (A dm^{-2})	Electrolysis Time (h)	COD removal (%)	Energy Consumption kWh g^{-1} COD	Current Efficiency (%)	Energy cost kWh m^{-3}
Electrooxidation	5	6	76	70.6	39	128
Electrocoagulation	5	6	88	8.6	79	16
Electro-Fenton	5	6	81	15.2	140	28

4. Current Efficiency

Current efficiency is an important factor in electrochemical processes that deals with economical aspects of its performance. The current efficiency of EO and EF process can be calculated from COD values using the following relation:

$$\text{Current Efficiency} = \left[\frac{\Delta\text{COD} F \text{Vol}}{8 I t} \right] \quad (10)$$

Where t denotes time in s, F the Faraday constant (96,487 C mol^{-1}), and 8 is the equivalent weight of oxygen (g mol^{-1}). The current efficiency percentage values of selected results are shown in Table 3.

5. Energy Cost

The energy cost (kWh m^{-3}) for removal of pesticides for each process was calculated by applying the following equation:

$$\text{Energy cost} = \left(\frac{V I t}{\text{vol}} \right) \left(\frac{\text{COD}_{in}}{\Delta\text{COD}} \right) \quad (11)$$

Where V = Voltage (in V), I = applied current (in A), t = electrolysis time (in h) and vol = solution volume (in L). Table 3 also summarizes energy costs for the degradation of pesticides in three different electrochemical processes. In EFP, 81% COD reduction efficiency was achieved with an energy cost of 28 kWh m^{-3} at 6 h. The ECP has less energy cost, 16 kWh m^{-3} , and high COD reduction efficiency of 88%. Of these three processes, EO has the highest energy cost (128 kWh m^{-3}) with less reduction efficiency (76%).

CONCLUSIONS

From this work, the following conclusions can be drawn to select a suitable method to reduce pesticides from industrial wastewater among three different approaches (EO, EC and EF) for industrial applications: (1) Results obtained in the EO process at pH 6, shows significant decrease in COD reduction from 1811 to 430 mg L⁻¹. (2) The EF process gives significant removal percentages of COD at all pH. Up to 81% COD reduction was achieved at pH 8 with moderate energy consumption (15 kWh g⁻¹ COD) and also minimum energy cost (28 kWh m⁻³). (3) In case of EC, the maximum COD removal efficiency of 88% was observed at pH 10 with moderate energy consumption of 15 kWh kg⁻¹ and least energy cost 15 kWh m⁻³ and (4) Final products formed in three electrochemical techniques are of same in nature, although the intermediates vary.

Overall ECP shows excellent COD removal efficiency. Hence ECP is recommended for treatment of pesticide industrial effluent in terms of COD reduction, energy consumption and energy cost. The results provide valuable information for practical applications of electrochemical techniques in pesticide industries. The treatment process may be followed by biological process to make it cost-effective and to enhance the performance.

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