Industrial wastewater treatment using electrochemical process

D Bhagawan¹, V Chandan¹, K Srilatha¹, G Shankaraiah¹, M Y Rani¹ and V Himabindu¹,²
¹Centre for Environment, IST, JNTUH, Hyderabad, Telangana, 500085, India
E-mail: drvhimabindu@gmail.com

Abstract. Wastewater treatment has become an essential part of industrial operations. A proper treatment is required to discharge this wastewater into water bodies. Pesticide production is one of the major supporting factors to the agriculture field, since India is an agricultural-based economy. The pesticide industry wastewater (PIW) contains chlorinated toxic pollutants. Treatment of such type of wastewater using conventional treatment methods might have their limitations due to the presence of toxic compounds, time consumption and complexity of the treatment process. In the past few years, the electrochemical method (Electrocoagulation (EC)/Electro oxidation (EO)) has been proposed as an effective method to treat many types of industrial effluents. In the present study, the treatment of pesticide processing industrial wastewater has been carried out using electrochemical method and with combination of other advanced methods.

1. Introduction
Water resources are the main sources of water, which are potentially useful. Uses of water include agricultural, household, industrial, recreational and activities [1]. The naturally available water is excessively used and contaminated by the effluents from these activities.

Wastewater treatment is becoming an essential part of industrial manufacturing operations in the production process [2,3]. This is often contaminated with a wide variety of components. A proper treatment is required to discharge this wastewater to water bodies. Otherwise, it can affect the environment and human life. The use of toxic pesticides to manage pest problems has become a common practice around the world. Pesticides have been found in air, food, soil, water and even in breast milk [4-8].

Intermediate manufacturing industrial chloro-pesticides effluent may contain chemicals, which are toxic and carcinogenic. Moreover, chloropesticides wastewater is known to have various pH (either alkaline or acidic, depending on the process used), high temperature, high Chemical Oxygen Demand (COD) and high concentration of suspended solids (SS) [4]. In China, approximately half million people are poisoned by pesticides contamination in each year [5]. Pyrethrins and insecticides commonly used in common bug killers, which can cause potentially poisonous condition if breathed in. These pesticides can cause long term effect problems like cancer, neurological effect and reproductive effects.

The treatment of this wastewater includes the techniques like adsorption, reverse osmosis, nanofiltration, electro-dialysis, membrane distillation, incineration, ozonation/UV radiation, fenton-oxidation, phytoremediation, photo-catalytic degradation and biodegradation [9-11]. However, these...
techniques are neither cost effective, nor eco-friendly, and not be able to treat at low concentration. Each technique provides a different and unique approach and perhaps provides certain advantages over others for a particular situation. However, when large volumes of water containing toxic elements are to be treated, it would be a great advantageous, to have a cost effective method.

In recent years, there is an increasing interest in the development of environmental friendly electrochemical methods to treat toxic organic pollutants in wastewater. Many studies have been especially focused on the use of electrocoagulation (EC) due to the increased environmental restrictions on effluent waste water [1,12,13].

EC is a simple and efficient process, where the production of coagulating agent is managed in situ by means of sacrificial anode. In this case, there is no need for adding chemical coagulants or flocculants to perform the treatment. In the EC process, the destabilization mechanism of contaminants, particles suspension and breaking of emulsions can be summarized into three successive steps [1, 2]. The optimization and efficiency of pesticide industry wastewater (PIW) has been assessed in this study using different physico chemical parameters.

2. Materials and methods

The industrial wastewater sample was collected from the industrial site, Hyderabad, (17.29.43N 78.23.34E) Telangana, India. The physicochemical characterization of wastewater samples was carried using the “Standard Methods for Examination of Water and Wastewater” [1,12].

2.1. Electrochemical treatment of chloro PIW

The electro chemical system was used for the treatment of chloropesticide wastewater, every experiment repeated for 3 time to estimate the accurate treatment efficiency. The optimization studies were performed using various parameters such as reaction time, electrode materials (Fe, SS, Ti and Al) and pH.

The pH was adjusted with a 0.1N/1.0N HCl or 0.1N/1.0N NaOH. Working electrodes were connected to a DC power supply (APLAB regulated DC power supply L6403) unit with to 84V voltage supply capacity. The samples were collected for every 10min time interval to analyze the residual metal content. Further mineralization of PIW was performed with sonication, photo catalytic and carbon filtration processes for a better removal of remaining organic matter from PIW.

This EC effluent was further treated with sonication and photo catalysis processes.

2.2. Sonochemical reactor

The experimental setup consisted of a 3.3 L ultrasonic bath (Model No. EN-30-US, Enertech Electronics Pvt. Ltd., Bombay, India) with a high-frequency Mosfet based electronic ultrasound generator (figure 1). The ultrasonic bath has two piezo-ceramic transducers merged to the bottom of a stainless-steel tank, with an operating frequency at 33 kHz in continuous or pulse (5s on and 1s off) mode. The ultrasonicator was operated at power outputs 1255 W (power calculated by the calorimetric method) [14].

2.3. Photo chemical reactor set-up

The experiments were performed in a cylindrical photo-reactor with a total volume of 1 L. The reactor was covered in a quartz tube to protect it from direct contact with an aqueous solution flowing through an annulus between the internal surface of the vessel and the outer surface of the quartz tube, placed at the axis of vessel. The reactor (figure 2) was provided with inlets for the supply of the reactants and ports, for determining the temperature and withdrawing the samples. The reactor remained open with a Teflon coated magnetic stirring bar placed in the bottom for homogenization of the solution. The UV irradiation source was a 250 W low pressure mercury vapor lamp (maximum emission at 365 nm) covered with a quartz tube. The lamp was axially centered and was immersed in a wastewater solution. A syringe was used to collect the sample at regular intervals from the sample port of the reactor [15].
2.4. Carbon filtration
The carbon filtration method used a bed of activated carbon to remove contaminants and impurities. A 150 ml sample and 3 g of activated charcoal were added. Charcoal was dispersed in a 150 ml sample and kept in shaking incubator for 30 min.

2.5. Removal percentage calculation
The quantitative reduction of pollutants was measured according to the APHA standard methods [1,12] and the percentage removal was calculated using equation (1).
% Removal = \frac{C_0 - C_t}{C_t} \times 100 \quad (1)

where, $C_0 =$ Initial concentration, $C_t =$ Final concentration.

3. Results and discussion

3.1. Initial physicochemical characterization of PIW

The initial physicochemical characterization of PIW is shown in table 1.

| S. No | Parameter $^1$ | Initial Concentration | CPCB Limits |
|-------|----------------|------------------------|-------------|
| 1     | pH             | <2                     | 6.0-9.0     |
| 2     | Electrical Conductivity [EC] | 85.8ms cm$^{-1}$       | NA          |
| 3     | Chemical Oxygen Demand | 1,60,000mg. l$^{-1}$ | 250mg. l$^{-1}$ |
| 4     | Nitrates       | 92.8mg. l$^{-1}$      | NA          |
| 5     | Sulphates      | 1957mg. l$^{-1}$      | 400mg. l$^{-1}$ |
| 6     | Phosphates     | 243mg. l$^{-1}$       | 5mg. l$^{-1}$ |
| 7     | Total Solids [TS] | 86,000mg. l$^{-1}$ | NA          |
| 8     | Total Dissolved Solids [TDS] | 76,000mg. l$^{-1}$ | NA          |
| 9     | Chlorides      | 36,240mg. l$^{-1}$   | NA          |
| 10    | Total Organic Carbon [TOC] | 50,000mg. l$^{-1}$ | NA          |

Notes: All parameters were expressed in mg l$^{-1}$ except pH, EC. EC expressed in Milli Siemens; NA-Not Applicable.

3.2. Effect of the electrochemical method for the treatment of chloropesticide wastewater

![Figure 3. Effect of electrochemical reaction time on PIW treatment. Experimental conditions: Electrode Material = Fe-Fe & SS-SS, Applied Voltage = 5 V; pH < 2; Area of Electrode = 40 cm$^2$; Volume of Sample = 250 ml; Inter Electrode Distance = 2 cm and Reaction Time = 10, 20, 30 & 40 min.](image)

3.2.1. Effect of the electrochemical reaction time on PIW treatment. The reaction time for PIW treatment has been investigated at different reaction time intervals (10–40 min) with Fe–Fe and SS-SS
electrodes. From figure 3, we observed that the maximum removal percentage of COD, TS, TDS, Cl\(^-\) and TOC were 60%, 25%, 22%, 26% and 29% for the Fe-Fe electrode and with SS-SS electrode as 77%, 52%, 56%, 41% and 40% respectively in 40 min. However, the percentage removal rate has not increased to a considerable range from 30 to 40 min, which might be due to the passivation layer on the electrode material (figure 3). Similar results have also been observed by Bhagawan et al [13] Bazafshan et al [16] and Sepideh et al [17]. Therefore, to avoid excess operational cost, the reaction time has been optimized to 30 min.

3.2.2. Effect of electrode material on PIW treatment. The identification of electrode material is also an important parameter to know the coagulant affinity. The most widely tested materials for their effectiveness are iron (Fe), aluminum (Al), stainless steel (SS) and Titanium (Ti) [12,18,19]. So these materials were used in this study. Figure 4 shows the effect of the electrode material on the PIW treatment. The maximum metal removal has been achieved with Ti-Ti electrodes. Therefore this type of electrodes was considered to be the best choice. The maximum removal percentage of COD, TS, TDS, Cl\(^-\) and TOC was 83%, 67%, 84%, 43% and 43% respectively with Ti-Ti electrodes in the 30 min reaction period (figure 4). This might be due to the effective generation of OH radicals released from the Ti surface. Iron, aluminum electrodes sacrifices and releases coagulants hence release of the OH radicals is comparatively lower that the Ti electrodes. This study suggests that Ti is suitable for removing organic material from industrial wastewater [2,3,12,19].

![Figure 4. Effect of electrode material on PIW treatment. Experimental conditions: Electrode Material = Fe-Fe, Al-Al, SS-SS & Ti-Ti; Applied Voltage = 5 V; pH => 2; Area of Electrode = 40 cm\(^2\); Volume of Sample = 250 ml; Inter Electrode Distance = 2 cm and Reaction Time = 30 min.](image)

3.2.3. Effect of pH on PIW treatment. The present study showed that the removal efficiency was optimal at neutral conditions (figure 5). At pH 7 the maximum removal of COD, TS, TDS, Cl\(^-\) and TOC was 92%, 67%, 84%, 43% and 60% with Ti-Ti electrodes and 88%, 50%, 55%, 41% and 56% with SS-SS respectively. However, this same trend was observed by Li et al [12,18].

The Neutralization of sample needed addition of chemicals, therefore some other advanced methods such as sonication and photo catalysis were considered to avoid this step.
The 4th International Conference on Water Resource and Environment (WRE 2018)
IOP Conf. Series: Earth and Environmental Science 191 (2018) 012022
doi:10.1088/1755-1315/191/1/012022

Figure 5. Effect of pH on PIW treatment. Experimental conditions: Electrode Material = SS-SS & Ti-Ti; Applied Voltage = 5 V; pH =< 2, 5, 7, 9; Area of Electrode = 40 cm$^2$; Volume of Sample = 250 ml; Inter Electrode Distance = 2 cm and Reaction Time = 30 min.

3.3. **Effect of AOP (ultra sonication, photo CATALYSIS) on PIW**
The sonochemical and photochemical degradations were favourable to treat the PIW (figure 6). With the photochemical process, the COD removal increased from 83% to 95% and with the sonochemical process, it has been increased from 83% to 94% (figure 7). This might be due to the effectiveness of photochemical hydroxyl radical, which is more effective than sonochemical process (18, 19).

Figure 6. Effect of AOP (Ultra Sonication, Photo catalysis) on PIW: Condition: Sample ID: EC Ti-Ti treatment effluent (Section 3.2.2); Sonication: Volume of sample = 100 ml, Time intervals = 30, 60, 90, 120, 150 & 180 min; Frequency = 33 KHZ; Photocatalysis: Volume of sample = 500 ml, Time intervals = 30, 60, 90, 120, 150 & 180 min.

3.4. **Comparison study**
The treatment efficiency of EC, sonication and photo catalysis in terms of COD removal for PIW is shown in table 2 and figure 7. It has been observed that, the effective treatment order is for EC Fe-Fe < EC Al- Al < EC SS-SS < EC Ti-Ti < EC SS-SS at pH 7 < EC SS-SS at pH 7 < EC Ti-Ti at pH 7 < EC Ti-Ti – Sonication < EC Ti-Ti – Photocatalysis.
Figure 7. Comparison of the remaining concentrations of COD in mg l⁻¹ after the application of different treatments.

Table 2. Percentage removal for the different treatments.

| Treatment system       | % Removal |
|------------------------|-----------|
| EC Fe-Fe               | 60        |
| EC Al-Al               | 63        |
| EC SS-SS               | 75        |
| EC Ti-Ti               | 83        |
| EC SS-SS at pH-7       | 90        |
| EC Ti-Ti at pH-7       | 91        |
| EC Ti-Ti - Sonication  | 94        |
| EC Ti-Ti - Photocatalysis | 95       |

Treatment – EC of Ti-Ti at original pH followed by photocatalysis achieved the maximum removal of COD and other pollutants (figure 7).

4. Conclusion
This study concluded that the titanium electrodes are found to be most efficient, when compared to SS-SS, Fe-Fe, Al-Al electrodes for PIW treatment. The maximum removal of pollutants is observed at a reaction time of 30min with initial pH 7 in the EC process. This study concluded that the photocatalysis followed by EC Ti-Ti is efficient and effective for the removal of pollutants from PIW because the COD removal was 95%.

References
[1] Jotin R and Ibrahim S 2012 Halimoon, Electro coagulation for removal of chemical oxygen demand in sanitary landfill leachate Int. J. Environ. Sci. 3 921-30
[2] Christoph S, Boris S and Konrad W 2017 Chloride contamination of electrochemically grown zinc oxide thick films J. Appl. Electrochem. 47 223-8
[3] Bhagawan D, Saritha P, Shankaraiah G, Vurimindi H and Vidyavathi S 2014 Treatment of the petroleum refinery wastewater using combined electrochemical methods Desalin. Water Treat. doi: 10.1080/19443994.2014.987175

[4] Sadeghi S, Reza Alavi M and Arami M 2013 Improvement of electrocoagulation process on hexavalent chromium removal with the use of polyaluminum chloride as coagulant Desalin. Water Treat. 52 1-12

[5] Gilden R C, Huffling K and Sattler B 2010 Pesticides and health risks J Obstet. Gynecol. Neonatal Nurs. 39 103-10

[6] Duan J and Gregory J 2003 Coagulation by hydrolysing metal salts J. Colloid Interface Sci. 100-102 475-502.

[7] Singh S, Srivastava V C and Mall I D 2013 Multi-step optimization and residue disposal study for electrochemical treatment of textile wastewater using aluminium electrode Int. J. Chem Reactor Engg. 11 1-16,47

[8] Thella K, Verma B, Srivastava V C and Srivastava K K 2008 Electrocoagulation study for the removal of arsenic and chromium from aqueous solution J. Environ. Sci. Health Part A 43 554-62

[9] Song Z, Williams C J and Edyvean R G J 2004 Treatment of tannery wastewater by chemical coagulation Desalination 164 249-59

[10] Crittenden J, Trussell R, Hand D, Howe K and Tchobanoglous G 2005 Water Treatment Principles and Design Edi. 2 (New Jersey: John Wiley and Sons)

[11] Bhausaheb L, Pangarkar, Samir K D and Prashant V T 2014 Pesticide wastewater pollution and treatment methods: review Chem. Sci. Rev. Lett. 3 374-80

[12] Bhagawan D, Saritha P, Chaitanya N, Ravi S, Yamuna R M, Vurimindi H and Vidyavathi S 2017 Industrial solid waste landfill leachate treatment using electrocoagulation and biological methods Desalin. Water Treat. 68 137-42

[13] Bhagawan D, Saritha P, Tulasi Ram P, Srinivasulu D, Shankaraiah G, Yamuna R M, Himabindu V and Vidyavathi S 2014 Effect of operational parameters on heavy metal removal by electrocoagulation Environ. Sci. Pollut. Res. 21 14166-73

[14] Bhagawan D, Saritha P, Shankaraiah G, Elander M and Himabindu V 2016 Remediation of contaminated ground water using sonication: Case study of an industrial area of Hyderabad; India Int. J. Chem. Chem. Engg. 5 143-59

[15] Nalini V L, Saritha P, Rambabu N, Himabindu V and Anjaneyulu Y 2010 Sonochemical degradation of 2chloro-5methyl phenol assisted by TiO2 and H2O2 J. Hazard. Mater. 174 151-5

[16] Bazafrshan E, Mahvim A H, Nasseri S, Mesdaghnin A R, Vaeesi F and Nazmara S H 2006 Removal of cadmium from industrial effluents by electrocoagulation process using iron electrodes Iran. J. Environ. Health. Sci. Eng. 3 261-6

[17] Sadeghi S, Reza A M M and Arami M 2014 Improvement of electrocoagulation process on hexavalent chromium removal with the use of polyaluminum chloride as coagulant Desalin. Water Treat. 52 4818-29

[18] Li X, Song J, Guo J, Wang Z and Feng Q 2011 Landfill leachate treatment using electrocoagulation Procedia Environ. Sci. 10 1159-64

[19] Zhi D, Qin J L, Zhou Z and Yang S X 2017 Removal of tetracycline by electrochemical oxidation using a Ti/SnO2–Sb anode: characterization, kinetics, and degradation pathway J. Appl. Electrochem. 47 1313-22