

Electrochemical treatment of industrial wastewater

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Abstract

This paper presents the results of the treatment of phenolic compounds containing wastewater generated from phenol–formaldehyde resin manufacturing, oil refinery and bulk drug manufacturing industries by electrochemical method. Experiments were conducted at a fixed current density of 5.4 A/dm² using Ti/TiO₂–RuO₂–IrO₂ electrode and an undivided reactor. During the various stages of electrolysis, parameters such as COD and TOC concentrations were determined in order to know the feasibility of electrochemical treatment. Adsorbable organic halogens (AOX) were detected at high concentrations during the electrolytic treatment of the effluents. However, it was observed that increasing the electrolysis time bring down the AOX concentration to lower levels. Energy consumption and current efficiency during the electrolysis were calculated and presented. The present study proves the effectiveness of electrochemical treatment for highly concentrated bio-refractory organic pollutants present in the industrial wastewater.

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Keywords: Electrochemical treatment; Industrial effluents; COD; TOC; AOX; Current efficiency

1. Introduction

Water is one of the abundantly available resources in nature and is essential for animal and plant life. Pollution of water bodies is increasing steadily due to industrial proliferation and urbanization. Nowadays, the worldwide production and use of chemical compounds have increased tremendously which find their way into the environment and many of these compounds are biologically non-degradable. Therefore, the major concern is to treat the wastewater before it is discharged into the environment.

Phenol and phenolic compounds are among the most prevalent forms of chemical pollutants in the industrial wastewater. Conway and Ross [1] reported the concentrations of phenolic compounds in various industrial wastewater. Phenolic compounds in the wastewater stream mainly come from oil refineries, coal conversion plants, petrochemicals,

polymeric resins, coal tar distillation, pharmaceuticals, etc. Phenolic compounds inhibit the normal function of microbial population, thereby affecting biological treatment process. Phenolic compounds causes acute toxicity characterized by sweating, cyanosis, lowering of body temperature decreased respiration, loss of reflex activity and death from respiratory failures [2].

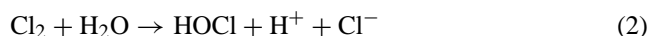
Treatment technologies available for phenolic waste are physical, chemical, biological and electrochemical processes. Several researchers have investigated the use of anaerobic biological processes for the removal of phenolics [3,4]. However, biological processes cannot treat high concentration of phenolics associated with industrial wastewater. Blum et al. [5] reported that high phenol concentration showed 50% initial-rate inhibition with different seed cultures and substrates. The inhibition potential of phenol itself and the presence of other organic and inorganic inhibitors are a major drawback of the process. Electrochemical technology offers ideal tools for addressing environmental problems. The main reagent used here is electron, which is a clean reagent and therefore there is no need for adding extra reagent [6].

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In the electrochemical process, the pollutants are destroyed by either direct or indirect oxidation process. In direct anodic oxidation process, the pollutants are first adsorbed on the anode surface and then destroyed by the anodic electron transfer reaction. In indirect oxidation process, strong oxidants such as hypochlorite/chlorine, ozone, hydrogen peroxide are electrochemically generated. The pollutants are then destroyed in the bulk solution by oxidation reaction of the generated oxidant. All the oxidants are generated in situ and are utilized immediately [7]. The electrochemical generation of hypochlorite/chlorine in a solution containing chloride ions may be given by the following reaction:



The application of indirect electrochemical oxidation mediated by chlorine/hypochlorite was studied for various industrial effluents by several investigators. Szpyrkowicz et al. [8] applied this technique for the treatment of tannery wastewater using Ti/Pt and Ti/Pt/Ir anodes. Similarly, tannery wastewater with initial COD value of 9600 mg/L was treated using graphite anode. At optimum current (34 mA/cm²) density and 120 min of electrolysis, a final COD of 59 mg/L was obtained [9]. Vlyssides and Israilides [10] studied electrochemical degradation of textile dye and finishing wastewater using Ti/Pt anode. At the end of 40 min of electrolysis, there was 92% COD, 92.2% BOD and 94% colour reduction with energy consumption of 44 kWh/kg of COD removal. Szpyrkowicz et al. [11] conducted experiments using seven different electrode materials for the degradation of disperse dyes. The best results were obtained in a chloride rich medium under acidic pH using Ti/Pt–Ir anode. Naumczyk et al. [12] reported the formation of organochlorine compounds during the treatment of textile dyeing wastewater. Electrochemical treatment of landfill leachate showed complete removal of ammonia and 92% of COD removal using Ti/SnO₂–PdO₂–RuO₂ (SPR) anode by operating at 15 A/dm² current density for 240 min of electrolysis with 7500 mg/L additional chloride concentration [13]. Olive oil wastewater treatment using Ti/Pt electrode showed 93% COD and 81.4% TOC removals when operated at 0.26 A/cm² current density and 10 h of electrolysis [14]. Vlyssides et al. [15] reported that maximum COD removal was obtained at pH 9.5 and 4% chloride concentration during the treatment of vinasse (from beet molasses). The initial COD of 72,000 mg/L was reduced to 8000 mg/L under optimum operating conditions. The electrochemical process was also applied to treat phenol and phenolic compounds using different electrode materials such as Ti/IrO₂ [16], Ti/Bi–PbO₂, bismuth doped PbO₂ [17], Ti/Pt [18] and cast iron [19].

Though the application of indirect electrochemical treatment was successful for wastewater treatment, formation of chlorinated organic compounds were reported [12,16,20,21].

Recently we have also reported the formation of AOX during the electrochemical degradation of resorcinol [22] and cresols [23] and require an activated carbon polishing treatment to remove the chlorinated organic compounds before the discharge of the treated water.

Though a number of papers are available for phenol electrochemical degradation, the application to real industrial wastewater containing phenolic compounds is limited. Hence, we aimed to apply the method for wastewater generated from phenol–formaldehyde resin manufacturing, oil refinery and bulk drug manufacturing industries, which contains phenolic compounds. The use of a titanium electrode coated with noble oxides for wastewater treatments is very popular because of its performance, stability, cost, and lifetime [24]. Recently, we have reported the degradation of resorcinol [22] and cresols [23] using a titanium substrate insoluble anode, which is classified under a dimensionally stable anode. Here we report the studies on the degradation of industrial effluents using the same anode, i.e., Ti/TiO₂–RuO₂–IrO₂. In this paper we report COD and TOC removals, AOX concentration, energy consumption, current efficiency and effectiveness during the electrochemical treatment of industrial effluents.

2. Experimental

A bench-top undivided electrolytic cell was assembled to perform the degradation experiments. The anode and cathode were positioned vertically and parallel to each other. Anode material was a titanium mesh (10 cm × 5 cm) coated with TiO₂–RuO₂–IrO₂ (a mixed triple oxide) supplied by M/s. Titanium equipment and anode manufacturing company limited (TEAM), Chennai, India. The total effective surface area of the anode was 27.7 cm². The cathode material was a graphite carbon (plate type—10 cm × 5 cm) supplied by M/s Carbone Lorraine limited, Chennai, India. The current input was controlled by stabilized dc power supply. These electrodes were dipped in the effluent sample of 0.5 L volume. The reactor was kept in a glass bowl containing water to maintain constant temperature of ~30 °C. The solution was constantly stirred at 200 rpm with a magnetic stirrer in order to maintain uniform concentration of the electrolyte solution.

The characteristics of industrial effluents were determined according to the standard methods [25]. The chemical oxygen demand (COD) values were determined by open reflux, dichromate titration method. The concentration of phenolics in the effluent was determined by 4-amino antipyrine spectrophotometric method using Spekol spectrophotometer (Model VIS 960127). The chloride and sulfate content in the effluent was determined by argentometric and turbidimetric methods, respectively. Total dissolved solids content was determined by evaporation method. The pH of the solution was measured using Elico pH meter model L1120. Total organic carbon (TOC) of the initial and electrolyzed solution was determined using TOC analyzer micro N/C model (Analytika

Jena, Germany). The instrument was operated at 680 °C temperature, 200 µL sample injection with oxygen flow rate of 12 mL/min and 3 min strip time. The concentration of AOX at different time of electrolysis were determined according to DIN EN 1485-IDC procedure, using multi X 2000 model, AOX analyzing system (Analytika Jena, Germany). The three steps involved in AOX measurement are, adsorption of the organochlorine compound onto the activated carbon, mineralization of organically bound halogen (chloride in this case) through combustion and determination of chloride concentration by micro coulometric titration. After carbon adsorption, the inorganic chloride which may be adsorbed on the carbon was removed by washing with nitrate solution before the mineralization as per standard methods [25]. The current efficiency (CE) of the treatment process was calculated based on the relationship between COD removal and applied current introduced by Comminellis and Pulgarin [26]. The energy consumption for the removal of 1 kg of COD was calculated and expressed in kWh.

The phenol–formaldehyde resin manufacturing industry wastewater was collected from M/s. IND-ITAL chemicals, Madavaram, Chennai, India. The effluent of oil refinery was obtained from M/s Madras refineries limited, Manali, Chennai, India. The bulk drug manufacturing industrial wastewater was collected from M/s Curekraft chemicals, Maraimalai Nagar, Chennai, India.

3. Results and discussion

The characteristics of the effluents are furnished in Table 1. Among the effluents, phenol–formaldehyde resin-manufacturing effluent contains higher concentration of phenolics than other effluents. Though phenolic compound concentration was less in bulk drug waste, the COD value was very high because of the presence of other organic pollutants. It is known from the literature and our earlier reports [22,23] that initial pH does not have significant effect in the degradation of organic pollutants by indirect electrochemical oxidation in the range of 3.0–10.0 using Ti/TiO₂–RuO₂–IrO₂ anode. Chiang et al. [13] explained that indirect electrochemical oxidation of organic compounds take place mainly via the electrolytically generated chlorine/hypochlorite. However, the production rate of chlorine/hypochlorite was not

affected by initial pH conditions in the range of 4.0–10.0 during the electrochemical oxidation of landfill leachate using different anodes such as graphite, Ti/PbO₂, Ti/TiO₂–RuO₂, Ti/SnO₂–PdO₂–RuO₂. Vijayaraghavan et al. [9] observed during the treatment of tannery and textile [27] effluents that under fixed current density, the production of chlorine was more or less the same, irrespective of initial pH values (3.5–8.5) using graphite anode. Hence, in the present study, the electrochemical degradation experiments for the effluents were conducted without pH adjustments. Here all the experiments were conducted at a fixed current density of 5.4 A/dm² under galvanostatic (constant current electrolysis) conditions.

3.1. Phenol–formaldehyde resin manufacturing wastewater

The effectiveness of electrochemical method was studied by treating the wastewater from phenolic resin manufacturing unit. The wastewater is mainly generated from the washings of reaction vessel and from the vacuum suction unit where the unreacted phenol and formaldehyde are removed after the formation of resin. The wastewater thus generated had pH value of 6.15 and high concentration of phenol and formaldehyde. The wastewater may also contain sulfate, since sulfuric acid is used for the neutralization process. Since the effluent contains sufficient conductivity and chloride concentration, the experiment was initially conducted without addition of chloride. From our earlier studies [22,23], an optimum amount of 2500 mg/L of chloride has to be maintained for effective degradation of cresols and resorcinol. Hence, the same experiment was also carried out by adding 2000 mg/L of chloride to compare the degradation efficiency. Fig. 1 reveals that the treatment efficiency in terms of COD removal was comparatively high in the chloride added effluent. The reason may be due to the increased oxidation of other pollutants (such as formaldehyde and other additives) in the presence of high chloride concentration. Because, under constant current electrolysis, the chloride when it is present in high concentration may produce adequate amount of hypochlorite/chlorine for the fast indirect oxidation. The COD removal was 61.8% for the effluent as such and 82.4% for chloride added effluent after 24 Ah/L charge input with energy consumption of 161.2 and 102.1 kWh/kg of COD removal, respectively. The

Table 1
Characteristics of industrial wastewater

Parameter	Industrial wastewater		
	Phenol formaldehyde resin manufacturing	Oil refinery	Bulk drug manufacturing
pH	6.15	9.2	10.7
Conductivity (µS/cm)	3320	1733	12840
Total dissolved solids (mg/L)	2740	1333	9320
Chloride (mg/L)	524	112	3119
Sulfate (mg/L)	970	212	440
Phenolics (as phenol) (mg/L)	374	141	54
COD (mg/L)	1084	602	8877

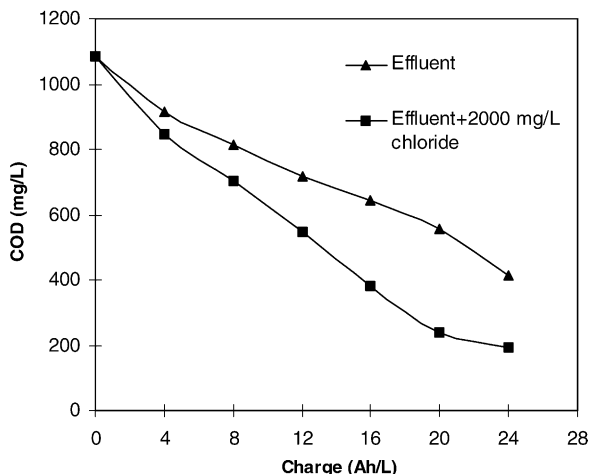


Fig. 1. COD removal during the electrochemical treatment of phenol-formaldehyde resin manufacturing industry wastewater.

energy consumption was also less when treating the effluent with additional chloride, because of decrease in cell voltage. Fig. 2 showed the formation of AOX and the removal of TOC as function of charge for chloride added effluent. A maximum AOX concentration of 87 mg/L was observed at 4 Ah/L charge input and this level was reduced to 40 mg/L at the end of 24 Ah/L charge passed.

3.2. Oil refinery wastewater

The concentration of chloride in the oil refinery wastewater was 112 mg/L. Hence, an additional 2400 mg/L of chloride was added for the electrochemical treatment. The results obtained during the treatment are presented in Fig. 3. The initial COD value of 602 mg/L was reduced to 152 mg/L with an energy consumption of 235.3 kWh/kg after 20 Ah/L of charge input. The AOX concentration was maximum (42 mg/L) at 8 Ah/L and decreased to 14 mg/L at the end of electrolysis.

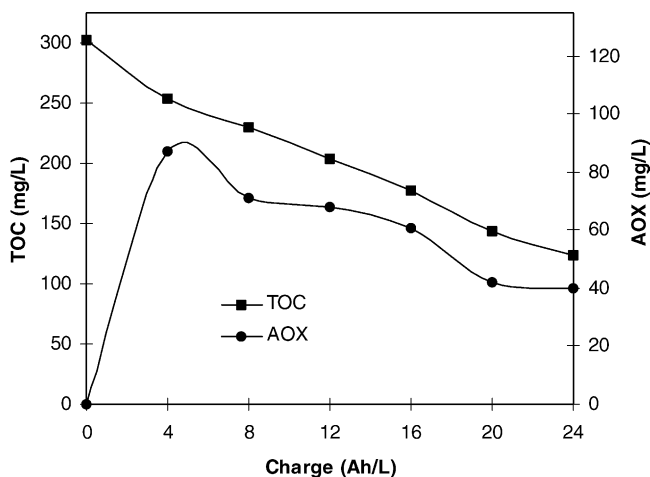


Fig. 2. TOC removal and AOX concentration during the electrochemical treatment of phenol-formaldehyde resin manufacturing industry wastewater with addition of chloride.

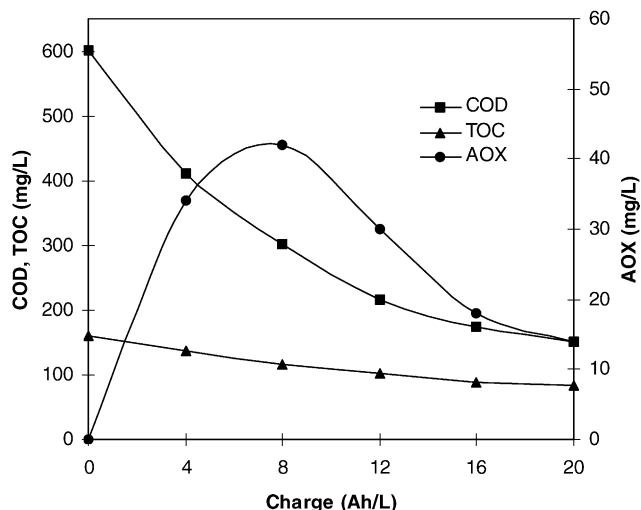


Fig. 3. Results of electrochemical treatment of oil refinery wastewater.

The amount of AOX formed is much lower when compared to that of AOX formed during the electrochemical treatment of pure phenolic compounds [22,23]. The pH of the solution gradually decreased from 9.2 to 7.3 and finally stabilized around 8.3. The COD/TOC ratio was gradually reduced from 3.7 to 1.8 with a final TOC value of 83 mg/L (48% removal). The result clearly reveals that electrochemical treatment with addition of chloride is effective for refinery wastewater.

3.3. Bulk drug manufacturing industry wastewater

Among the various sections of pharmaceutical industry, the bulk drug production unit generates a large volume of effluent with high concentrations of salt and organic pollutants. The waste generated was more complex and biologically inert. Hence, it was decided to apply the electrochemical treatment method to phenol based bulk drug unit

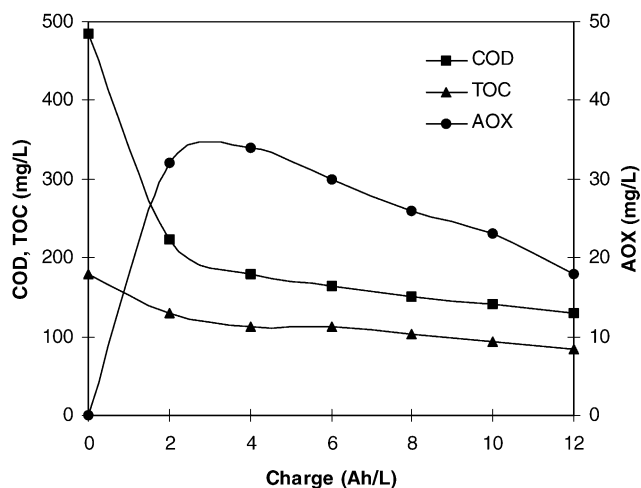


Fig. 4. Results of electrochemical degradation of *o*-acetylsalicylic acid.

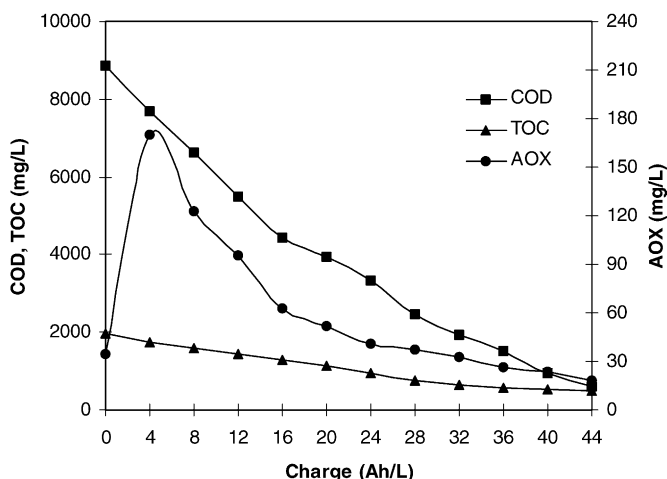


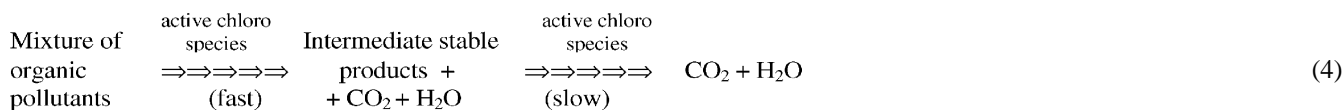
Fig. 5. Results of electrochemical treatment of bulk drug manufacturing industry wastewater.

wastewater. Initially, a preliminary study was conducted to degrade Aspirin (*o*-acetylsalicylic acid) drug, which is a common drug (salicylic acid analogues), manufactured in most of the bulk drug units. The following conditions were maintained for the study: initial pH 9.0; chloride, 2500 mg/L; *o*-acetylsalicylic acid, 300 mg/L; current density, 5.4 A/dm². The results obtained during the treatment are furnished in Fig. 4. The removal of COD was rapid up to 4 Ah/L of charge input, followed by slow removal of COD at increasing charge. The COD and TOC removals were 73.1 and 53.3%, respectively after the passage of 12 Ah/L charge.

The major compounds manufactured in the typical industry are 2,4-dichloro phenyl hydrochloride, quinopyramine salts, 4-chloro 2-amino phenol and dibenzyl oxy benzoyl chloride. It was clear from the characteristics that the effluent has high concentration of COD, total dissolved solids and chloride. Hence, the experiments were conducted without addition of chloride and without any dilution of the effluent. The results obtained during the treatment are presented in Fig. 5. The initial COD value of 8877 mg/L was reduced to 602 mg/L at the end of 44 Ah/L charge. During the initial periods of electrolysis, the current efficiency was high (above 90%) up to 16 Ah/L charge input. After that, the current efficiency gradually decreased to 63.0% at the end of 44 Ah/L charge input, which indicated the slow rate of removal of COD. The current efficiency obtained was very high for bulk drug manufacturing process effluent when compared to that of phenol–formaldehyde resin manufacturing and refinery wastewater studied. A gradual decrease in the cell voltage from 3.5 to 2.9 V was also observed during the electrolysis. The decrease in COD/TOC ratio from 4.5 to 1.3 during the course of electrolysis indicated the formation of stable compounds, beyond which the removal of TOC was less. Similar observations were reported while treating flavour industry wastewater [21]. These observations suggest the following sequence for the process:

Table 2
Summary of the electrochemical treatment of industrial effluents

Industrial wastewater	Charge passed (Ah/L)	Initial COD (mg/L)	Final COD (mg/L)	Kinetics Rate constant k' (min ⁻¹)	r^2	Current efficiency (%)	Cell voltage (V)	Energy consumption	
								KWh/kg of COD	KWh/m ³ of effluent
Phenol-formaldehyde resin manufacture	24	1084	191	1.5×10^{-3}	0.98	12.5	4.0–3.6	102.1	91.2
Oil refinery	20	602	152	1.6×10^{-3}	0.97	7.5	5.4–5.2	253.3	105.8
Bulk drug manufacture	44	8877	602	1.1×10^{-3}	0.95	63.0	3.5–2.9	17.0	140.7



Here the rate of reaction is very fast during the initial periods of treatment and followed by slow removal of pollutants. It was significant that the formation of AOX was maximum at 4 Ah/L and then gradually decreased to lower levels as the charge input was increased. The raw effluent itself contains 35 mg/L of AOX. However, the concentration of AOX increased to 170 mg/L at 4 Ah/L and then it was reduced to 18 mg/L after the passage of 44 Ah/L charge. The energy consumption was 17 kWh/kg of COD removal at the end of the treatment. The energy requirement was less because of high TDS and conductivity, which reduced the cell voltage. The present study clearly demonstrated that the wastewater from the bulk drug unit of pharmaceutical industry could be treated efficiently.

3.4. Kinetics of reaction

In the indirect electrochemical oxidation process, the COD removal rate is proportional to the concentration of the organic compound (pollutant) and to the chlorine/hypochlorite concentration because the indirect oxidation is mediated by chlorine/hypochlorite. Therefore, the kinetics for COD removal is

$$-\frac{d}{dt}[\text{COD}] = k[\text{COD}][\text{Cl}_2] \quad (5)$$

Electrochemical treatment involves the application of an electrical current to the effluent, to convert chloride to chlorine and hypochlorite. The chlorine and hypochlorite will oxidize the organic compound and then get reduced to a chloride ion. The process is then repeated in a catalytic fashion. Therefore, the concentration of chlorine/hypochlorite during the electrolysis is assumed to be a constant and so Eq. (5) can be written as a pseudo first-order kinetic equation:

$$-\frac{d}{dt}[\text{COD}] = k'[\text{COD}] \quad (6)$$

The log plots of the COD concentration curves show the plot of the rate expression:

$$\ln \frac{[\text{COD}]_t}{[\text{COD}]_0} = -k't \quad \text{or} \quad \ln \frac{C_t}{C_0} = -k't \quad (7)$$

The slope of the plot of $\log C_t/C_0$ versus time gives the value of rate constant k' , min^{-1} . Here, C_0 is the initial COD of the effluents in milligrams per litre, and C_t is the COD value at time t . Table 2 provides the rate constant (k') and respective r^2 values for COD removal.

4. Conclusion

Electrochemical method was employed in the present study to investigate the effectiveness of treatment of industrial

effluents containing phenolic compounds. Among the three effluents examined here, bulk drug-manufacturing unit of the pharmaceutical industry showed much higher current efficiency on the removal of COD than the other effluents. However, phenol–formaldehyde resin manufacturing industrial wastewater requires addition of chloride, in order to reduce the energy consumption and to increase COD removal. The treatment of oil refinery wastewater consumed much electrical energy and showed less current efficiency by this method. The results of the study revealed that this method could be applied to the wastewater containing high concentrations of organic pollutants to make this method as practical. Further, scale up of the reactor to larger volume and re-circulation or continuous flow operation should decrease the running cost of the proposed treatment method less costly. Although all the effluents showed a significant increase in the AOX concentration during the initial periods of treatment, extended electrolysis led to decrease in the concentration. Hence, at the end of the electrochemical treatment, it is recommended that the treated water be given an activated carbon polishing treatment to remove chlorinated organic compounds before the discharge.

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