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Electrochemical degradation of Simulated Phenolic Wastewater using Ti/Ni_xO_y-RuO_2-SnO_2-Sb_2O_5 anode

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Abstract

The electrochemical oxidation of simulated phenolic wastewater was studied using Ti/Ni_xO_y-RuO_2-SnO_2-Sb_2O_5 electrode as anode in a single undivided batch electrochemical reactor. The synthesized anode was characterized for morphology and phase detection using SEM and XRD techniques. The effects of significant process parameters like pH, electrolyte concentration and current density on phenol degradation in terms of chemical oxygen demand (COD) removal efficiency were investigated. The electrolysis was carried out at atmospheric temperature and pressure with an initial phenol concentration of 300 mg/L using NaCl as supporting electrolyte. The effect of applied current density on COD decay was found to be more prominent than that of initial pH and electrolyte concentration. The favourable operating conditions for maximum COD removal (73.6%) were found to be initial pH 2, NaCl concentration of 4 g/L and current density of 70 mA/cm^2. It was observed that COD removal efficiency was enhanced in acidic medium with moderate electrolyte concentration and an increase in current density.

Key words: Electrochemical oxidation; phenol; SEM; XRD; COD removal

1. INTRODUCTION

Phenol (C_6H_6O; CAS 108-95-2) belongs to the class of hazardous organic pollutants due to its high toxicity, high oxygen demand exertion (typically, 2.4 kg O_2 per kg phenol), slow biodegradation and bioaccumulation characteristics [1-4]. The industrial sources of phenol and its derivatives include coal conversion, synthetic resins, textiles, pulp and paper, rubber, plastics, paints, perfumes, fertilizers and pesticides, explosives, wood preservatives, general disinfectants, medicinal preparations [1, 5-8].

Electrochemical oxidation (EO) serves as a promising and an environmentally benign advanced oxidation method for abatement of toxic, biorefractory and concentrated organic pollutants, offering ease of operation and control [3]. This technology functions under two mechanisms: direct and indirect electrochemical oxidation [9, 10]. In direct mechanism, direct charge transfer leads to oxidation of pollutants. In indirect oxidation, electrochemically generated strong oxidant at the anode degrades contaminants in the bulk solution. The water dissociation at the anode surface (M) generates hydroxyl radicals M(•OH) as per reaction (Rxn. (1)). In addition, NaCl as supporting electrolyte acts as a mediator generating electroactive chlorine species (Cl_2) according to Rxn. (2) which on subsequent hydrolysis generates HClO and Cl^- as shown in Rxn. (3). HClO and OCl^- are in equilibrium as per Rxn. (4) [11].

$$M + H_2O \rightarrow M(\bullet OH) + H^+ + e^- \tag{1}$$

$$2Cl^- \rightarrow Cl_{2(aq)} + 2e^- \tag{2}$$

$$Cl_{2(aq)} + H_2O \rightarrow HClO + Cl^- + H^+ \tag{3}$$

$$HClO \Leftrightarrow H^+ + OCl^- \tag{4}$$

Dimensionally stable anodes (DSA) represent a class of titanium (Ti) based mixed metal oxide anodes that allow the formation of a superoxide according to Rxn. (5) as their surface (M) and •OH radicals interact strongly with each other [2, 12]. The selective oxidation of organic compounds (R) is then mediated by the redox couple MO/M (Rxn. (6)). Rxn. (7) depicts the oxygen evolution reaction (OER) which is a side reaction occurring from MO decomposition competing with organics oxidation reaction [11].

$$M(\bullet OH) \rightarrow MO + H^+ + e^- \tag{5}$$

$$MO + R \rightarrow M + RO \tag{6}$$

$$MO \rightarrow M + \frac{1}{2}O_2 \tag{7}$$

The electrochemical oxidation of phenol (C_6H_5OH) leads to phenoxy radical reactions induced by electron transfer which further produces cyclic quinonic intermediates like hydroquinone ($C_6H_6O_2$) and benzoquinone ($C_6H_4O_2$) [7, 13]. Fig. 1 shows possible degradation intermediates and products resulting from phenol electrooxidation via partial and complete mineralization. Benzoquinone and hydroquinone act as an active redox couple in equilibrium in aqueous solution. Subsequently, benzoquinone oxidation after ring opening generates various aliphatic carboxylic acids like fumaric acid ($C_4H_4O_4$), oxalic acid ($C_2H_2O_4$), succinic acid ($C_4H_6O_4$) and maleic acid ($C_4H_4O_4$) [7].

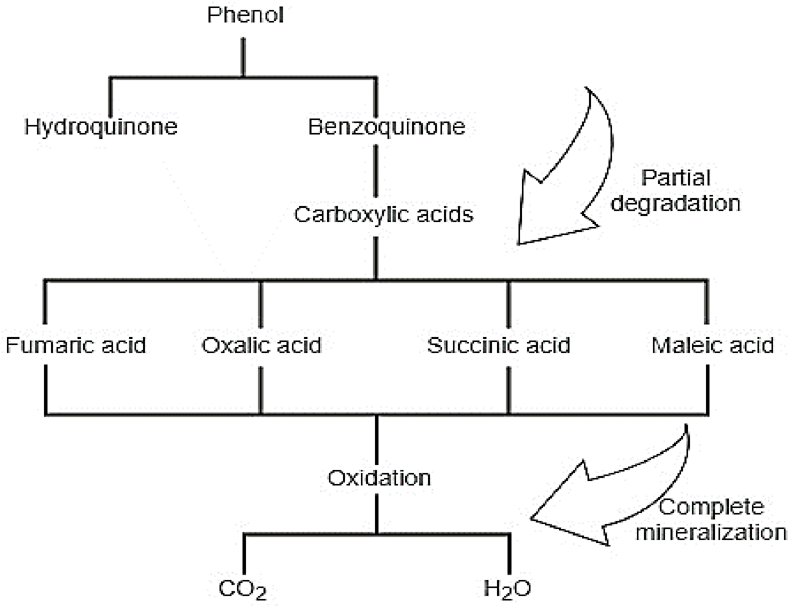

Fig. 1. Possible degradation products/intermediates of phenol electrooxidation

Different mechanisms for phenol electrooxidation by direct and indirect modes have been proposed by various researchers [8]. This conversion of phenol to organic acids represent partial phenol degradation. Total conversion of phenol to CO_2 and H_2O refers to complete mineralization which is practically uneconomical due to high energy cost associated with the process. Organic acids resulting from partial oxidation of phenol may serve as nutrients for subsequent relatively inexpensive biological treatment step [13]. Optimized operating conditions for the electrolysis process can lead to better understanding of the overall degradation mechanism.

2. EXPERIMENTAL STUDIES

2.1 Anode Synthesis

Titanium (Ti) plate with dimensions of (7.5 cm x 5.0 cm x 0.3 cm) used as anode substrate and stainless-steel plate (SS 304) of similar dimensions used as cathode were polished using grit sand paper to remove any surface impurities present. The degreased anode substrate was then subjected to etching in 10% oxalic acid at 90°C for 1 hour followed by thorough washing with water and drying. This was carried out to create micro-pores on the anode surface for proper adherence of catalytic coating. $Ti/Ni_xO_y-RuO_2-SnO_2-Sb_2O_5$ electrode used as working anode was synthesized by thermal decomposition technique [9]. Presence of Ni and Ru has proved to increase catalytic characteristics while presence of Sn and Sb imparts improved conductivity with homogenous film dispersion [14]. During this process, the plate was brushed at ambient temperature with a coating solution containing $NiCl_2.6H_2O$ (0.178 g), $RuCl_3.3H_2O$ (0.169 g), $SbCl_3$ (0.114 g) and $SnCl_4.5H_2O$ (1.05 g) dissolved in a solvent mixture of isopropanol (10 mL) and HCl (1.0 mL). The coat was dried at 85˚C for 5 min and further at 550˚C for 5 min. Likewise, the process was repeated for 10 coats to obtain a catalytic loading of about 2-2.5 mg/cm^2 on the Ti plate. The electrode was then annealed in a muffle furnace at 550˚C for 1 hour and cooled to room temperature.

2.2 Anode Characterization

2.2.1 SEM

The morphology of the freshly synthesized Ti/Ni_xO_y-RuO_2-SnO_2-Sb_2O_5 electrode was analyzed using Scanning electron microscopy (SEM) with SEM, LEO 440 i equipment. As depicted in fig. 2, the mixed metal oxide coating showed a typical surface morphology with a "mud-cracked" appearance imparting high surface area due to microscopic cracks, crevices and pits created by the thermal decomposition fabrication technique [12, 15].

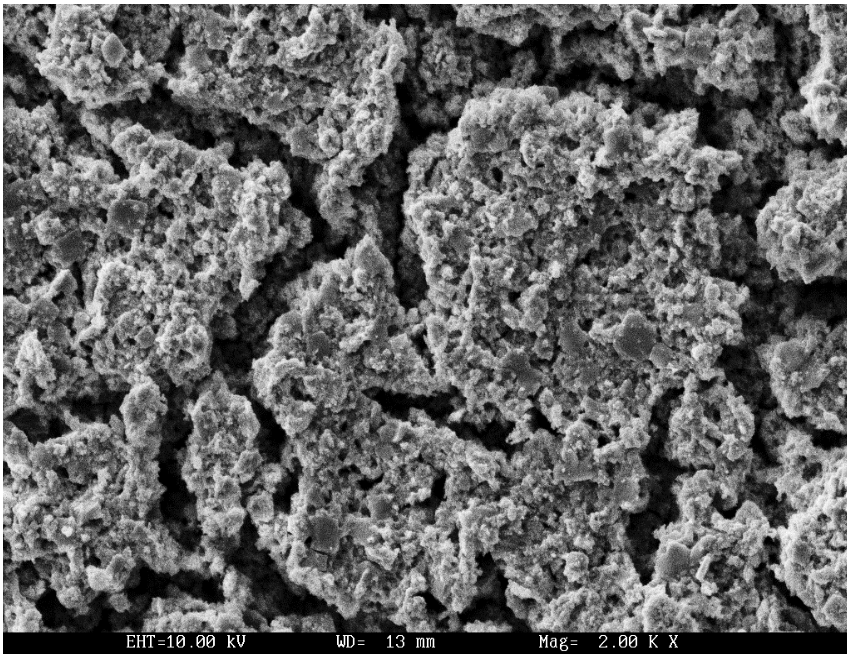

Fig. 2. SEM surface image of synthesized Ti/Ni_xO_y-RuO_2-SnO_2-Sb_2O_5 anode

2.2.2 XRD

The X-ray diffraction (XRD) pattern of synthesized Ti/Ni_xO_y-RuO_2-SnO_2-Sb_2O_5 electrode showed the presence of metal oxide phases of Ru, Sn, Sb and Ni in various oxidation states. The characteristic peaks of metal oxide phases were found to confirm with the JCPDS diffraction peaks [16-19] as shown in table 1.

Table 1. Phases present in the fabricated anode

2θ/°	Phase	JCPDS*
42.1274	NiO	89-7131
50.2165	NiO_2	89-8397
57.658, 65.3211	Ni_2O_3	14-0481
35.3260, 59.468, 73.936	RuO_2	40-1290
52.125, 62.7768	Sb_2O_5	33-0110
26.61, 42.1274, 57.658, 62.7768	SnO_2	41-1445

** Joint Committee on Powder Diffraction Standards*

X-ray diffractogram of the catalytic film coating on the anode shown in fig. 3 was recorded in 10-90° range on a Bruker D8 Advance diffractometer using Cu-Kα radiation (1.5405 Å).

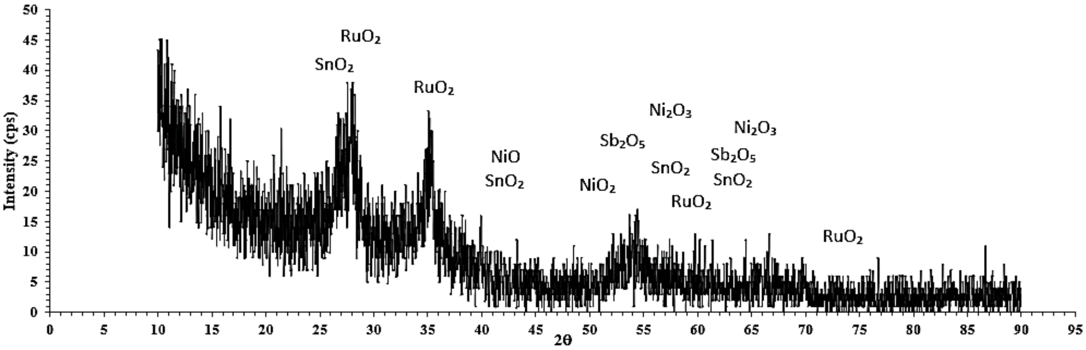

Fig. 3. XRD pattern of synthesized Ti/Ni_xO_y-RuO_2-SnO_2-Sb_2O_5 anode

2.3 Phenol Electrolysis

Phenol and NaCl were procured from CDH (AR, assay 99.5%). Simulated phenolic wastewater containing 300 mg/L of phenol was prepared using tap water. Electrochemical oxidation of phenol was conducted at atmospheric temperature and pressure in an undivided batch reactor placed on a magnetic stirrer with around 230 rpm to ensure constant stirring condition. The anode and cathode plates were placed 1 cm apart into the reaction mixture of 1 L. The current was applied by a DC power source, Aplab India. Process parameters like initial pH, electrolyte concentration and current density were varied during the experiment. All experiments were carried out for 1 hour and samples were drawn every 15 minutes for COD analysis. COD was measured by closed reflux titrimetric method as per APHA standard 5220 C using Hach DRB 200 COD reactor. The COD removal (%) is calculated as per Eq.(1):

$$COD\ removal\left(\%\right)=100\left(1-\left(\frac{COD}{COD_o}\right)\right) \tag{1}$$

where COD is the experimental COD in mg/L at electrolysis time, *t* and COD_o is the corresponding initial value before treatment.

3. RESULTS AND DISCUSSION

3.1 Effect of initial pH on COD removal

Initial pH of the reaction mixture is a vital parameter in indirect elecrtrochemical oxidation as it directly affects the generation of electroactive oxidizing species [4, 11, 18, 20]. The effect of initial pH on phenol degradation in terms of COD removal was assessed by selecting initial pH values in acidic (pH 2), neutral (pH 7) and alkaline (pH 11) ranges. pH was adjusted using concentrated H_2SO_4 and NaOH solutions for acidic and alkaline conditions respectively. During pH variation, other process parameters like NaCl electrolyte concentration and current density were kept constant at 4 g/L and 45 mA/cm^2 respectively. As shown in fig. 4, at the end of 60 min, the COD removal for selected pH values was achieved as: pH 2 (56.0%) > pH 7(41.8%) > pH 11(32.0%). It is clearly evident from the results that $Cl_{2(aq)}$ (until pH 3.0) and HClO (pH 3.0 – 8.0) generated as dominant electroactive oxidizing species in acidic medium have more pronounced effect on phenol electrooxidation efficiency than ClO^- produced at pH>8.0. This is due to the higher standard oxidation potential of $Cl_{2(aq)}$ ($E°(Cl_{2(aq)}/Cl^-) = 1.36$ vs. SHE) and HClO ($E°(HClO/Cl^-) = 1.49$ vs. SHE) compared to ClO^- ($E°(ClO^-/Cl^-) = 0.89$ vs. SHE) [11]. It is also reported that low pH favors phenol elimination and inhibits the extent of oxygen evolution reaction which is an undesirable side reaction consuming a fraction of the power supplied [13, 14, 18].

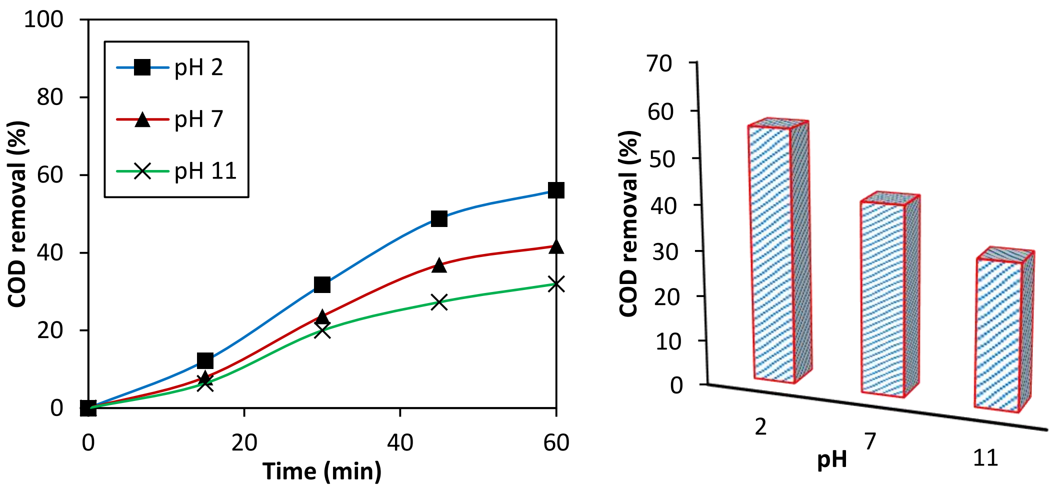

Fig. 4. COD removal with electrolysis time at different pH values

An increase in the pH from 2.0 to 2.7, 7.0 to 7.9 and 11.0 to 11.4 was observed at the end of electrolysis for experimental runs at pH 2, 7 and 11 respectively as depicted in fig. 5. Such pH rise may be due to water dissociation reaction occurring at the cathode forming H_2 gas and OH^- ions [2, 11]. pH 2 was then chosen to continue the studies for electrolyte concentration and current density effects on COD decay.

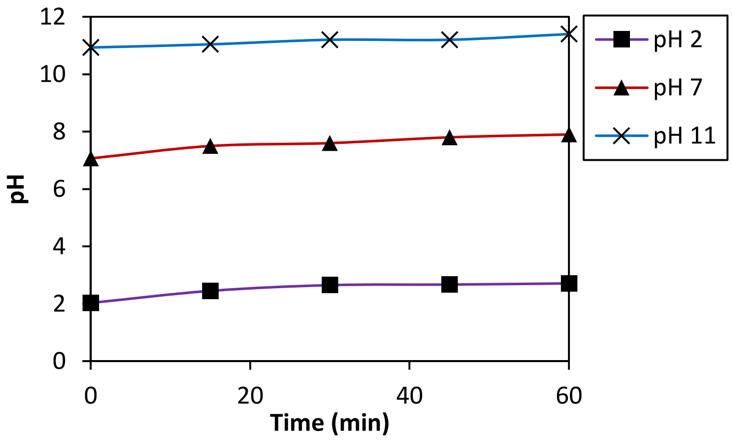

Fig. 5. pH evolution over time during electrolysis at different pH values

3.2 Effect of supporting electrolyte concentration on COD removal

The effect of supporting electrolyte concentration on COD removal over time was studied at selected NaCl concentrations of 0, 2, 4 and 6 g/L. The operation was conducted using 1 L simulated phenolic wastewater containing 300 mg/L phenol at pH 2 by applying 45 mA/cm^2. As can be observed in fig. 6, at the end of 60 min electrolysis, the COD removal for selected electrolyte concentrations was achieved as: 0 g/L (25%) < 2 g/L (42.4%) < 4 g/L (56%) < 6 g/L (63.9%). As reported and also evident from the present experimental results, low NaCl concentrations tend to generate less amount of electroactive oxidizing species and offer reduced solution conductivity thus resulting in lower COD removal efficiencies [11]. On the other hand, higher electrolyte concentrations tend to reach basic pH quickly thus promoting the generation of ClO^- species. Consequent oxidation of these ClO^- species further result in the production of ClO_2^-, ClO_3^- and ClO_4^- species which are essentially weaker oxidizing agents leading to decreased COD removal efficiency [11]. Higher chloride-based electrolyte concentrations are also known to generate chloroorganic compounds during the treatment process [21]. It is also observed that moderate electrolyte concentrations facilitate enhanced mass transfer and decreased energy consumption [4]. Thus, electrolyte concentration of 4 g/L and pH 2 were further selected for current density studies.

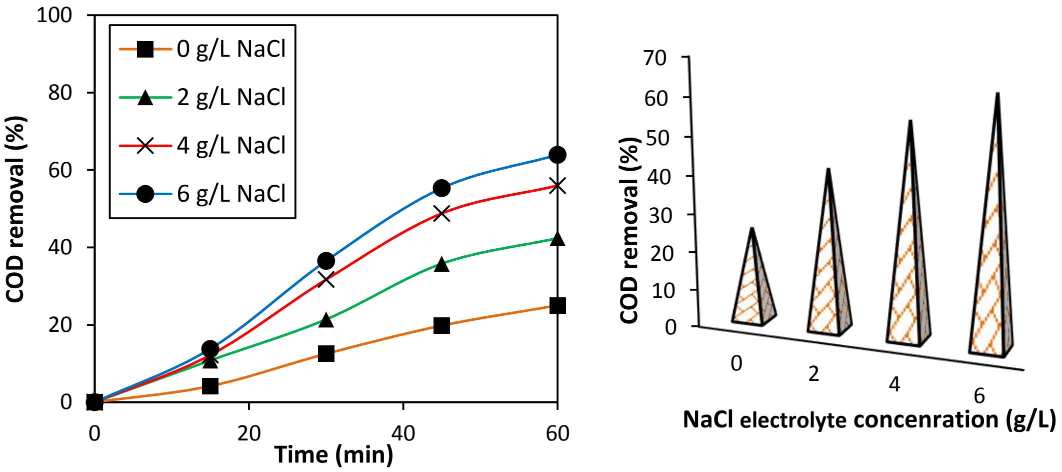

Fig. 6. COD removal with electrolysis time at different NaCl concentrations

3.3 Effect of applied current density on COD removal

The applied current density directly links with the driving force in charge transport and generation of electroactive oxidizing species [11]. The effect of current density on COD removal was assessed at selected values of 20, 45 and 70 mA/cm^2. The results shown in fig. 7 indicate that the rise in current density enhances the COD decay. At the end of 60 min, the COD removal for selected current density application was achieved as: 20 mA/cm^2 (31.4%) < 45 mA/cm^2 (56%) < 75 mA/cm^2 (73.6%). It has been reported that increased current density also leads to rapid phenol conversion to organic acids, the phenomenon typically referred to as ‘electrochemical cold combustion’ [13].

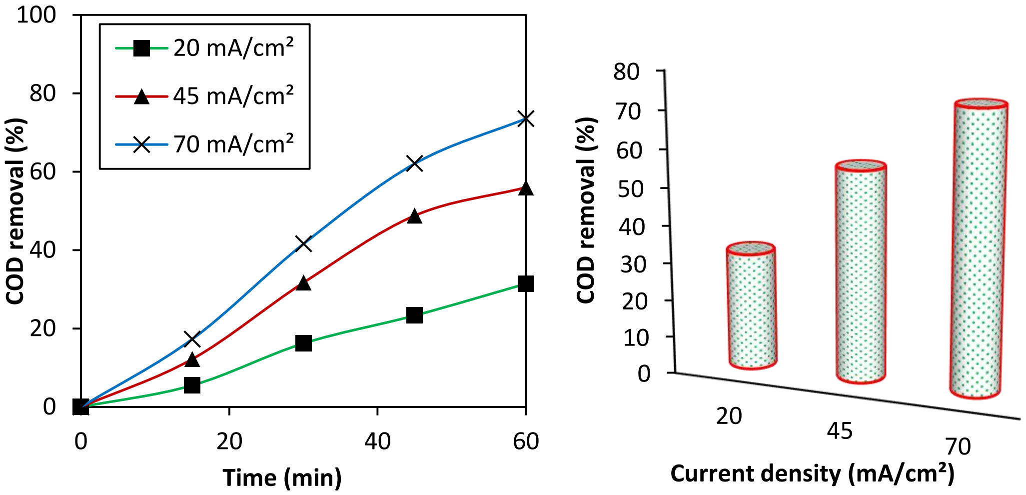

Fig. 7. COD removal with electrolysis time at different current density values

4. CONCLUSIONS

An attempt was made to treat simulated phenol containing wastewater by indirect electrochemical oxidation using Ti/Ni_xO_y-RuO_2-SnO_2-Sb_2O_5 anode in presence of NaCl as supporting electrolyte. Type of electrode, nature and concentration of supporting electrolyte, initial pH and current density have a prominent effect on the pollutant degradation rate, mechanism of degradation, overall cost and efficiency associated with the electrochemical process. Initial pH, electrolyte concentration and current density were selected as important process parameters for the process studies. The extent of phenol elimination in terms of COD removal was observed to be strongly influenced by an increase in current density, pH in acidic range and moderate NaCl electrolyte concentration. The favorable operating conditions for maximum COD abatement (73.6%) achieved were: pH 2.0, 4 g/L NaCl and 70 mA/cm^2. Acidic pH favors generation of $Cl_{2(aq)}$ (until pH 3.0) and HClO (pH 3.0 – 8.0) which are relatively strong oxidizing species than ClO^- (pH>8.0) imparting higher COD removal efficiency and suppressing undesirable oxygen evolution side reaction. Moderate NaCl concentrations result in higher COD decay, enhanced mass transfer, reduced energy cost and reduced chloroorganic compound generation. Increase in current density leads to faster and efficient COD removal. Selected anode for phenol decomposition may lead to partial oxidation of phenol generating aliphatic organic acids which may serve as a pretreatment step for subsequent inexpensive conventional biological treatment.

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