Phenol Contaminated Water Treatment on Several Modified Dimensionally Stable Anodes

Pavithra Bhakthi Jayathilaka¹, Kushani Umanga Kumari Hapuhinna¹, Athula Bandara², Nadeeshani Nanayakkara³, Nalaka Deepal Subasinghe¹*

ABSTRACT: Phenolic compounds are some of the most common hazardous organics in wastewater. Removal of these pollutants is important. Physiochemical method such as electrochemical oxidation on dimensionally stable anodes is more convenient in removing such organic pollutants. Therefore, this study focuses on development of three different anodes for phenol contaminated water treatment. The performances of steel/IrO2, steel/IrO2-Sb2O3, and Ti/IrO2-Sb2O3 anodes were tested and compared. Nearly 50, 76, and 84% of chemical oxygen demand removal efficiencies were observed for steel/ IrO₂, steel/IrO₂-Sb₂O₃, and Ti/IrO₂-Sb₂O₃ anodes, respectively. The formation of intermediates was monitored for three anodes and the Ti/IrO2-Sb2O3 anode showed the most promising results. Findings suggest that the developed anode materials can enhance phenol oxidation efficiency and that mixed metal oxide layer has major influence on the anode. Among the selected metal oxide mixtures IrO2-Sb2O3 was the most suitable under given experimental conditions. Water Environ. Res., 89, 687 (2017).

KEYWORDS: phenol, dimensionally stable anodes, IrO₂-Sb₂O₃ anode, wastewater treatment.

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Introduction

Water pollution is one of the major global environmental issues. It has an impact on the world economy, health, and the environment. Therefore, recently great attention has been focused on identifying the water pollutants and their sources and on water treatment techniques.

It has been found that, among the water pollutants, synthetic organic chemicals released to the environment by human activities are some of the most harmful. Phenol is one of such harmful organic chemicals and is discharged mainly by factories such as pharmaceutical, petroleum refineries, dye and pesticide industries, and so forth (Jayathilaka et al., 2014; Li et al., 2009; Zhang et al., 2013). Due to its high toxicity and low biodegradability, standards, rules, and regulations have been established for discharging phenol to the environment. According to World Health Organization (WHO), phenol content should be lower than 0.5 pg L^{-1} for drinking water (Li et al., 2009; Mofizur Rahman et al., 2011). In addition to the prevention of phenol contaminations and taking precautions, many treatment methods have been investigated by researchers. Some of these studies were wet oxidation (Yan et al., 2016; Zapico et al., 2016), biological methods, use of mixed metal catalysts (Wu et al., 2014), photocatalytic (Zhang et al., 2011), and electrochemical oxidation (Zhang et al., 2011; Zhang et al., 2013). Most of these findings reveal that advance oxidation processes (AOPs) are more convenient in organic pollutants removal. Therefore, phenol treatment by AOPs is more popular especially because of the simplicity of method, cost-effectiveness, and environmental friendliness. Advance oxidation of phenol can be done by direct oxidation or indirect oxidation methods. In direct oxidation methods, phenol oxidation into harmless species occurs on dimensionally stable anode (DSA) surfaces such as IrO₂, PbO₂, and boron-doped diamond anodes.

These DSAs are prepared by using metal oxides. Different metal oxides are utilized to enhance catalytic activities and to modify the properties (Wu et al., 2014). New desirable properties are developed through mixing different metal oxides and these improvements are due to many reasons (Wang et al., 2009; Wu et al., 2014) such as the enhancement of surface area, change in chemical states of metal ions, or increase of active sites. More often, DSAs are developed by depositing mixed metal oxides on an inert substrate material such as stainless steel, titanium, carbon, and others. However, their performances are based on the composition of the metal oxide mixture.

¹ National Institute of Fundamental Studies, Kandy, Sri Lanka.

² Department of Chemistry, University of Peradeniya, Sri Lanka.

³ Department of Civil Engineering, Faculty of Engineering, University of Peradeniya, Sri Lanka.

⁴ Postgraduate Institute of Science, University of Peradeniya, Sri Lanka.

^{*} National Institute of Fundamental Studies, Kandy, Sri Lanka; email: deepal@ifs.ac.lk.

In this study, different experiments were conducted to find proper anode materials and the preliminary studies were mainly based on steel/IrO₂ and steel/IrO₂-Sb₂O₃ anode materials. Mainly stainless steel and Ti substrate materials were tested with different coatings. Because IrO₂ has properties such as high electrical conductivity, low over-potential for oxygen evolution reaction (i.e., an O₂ evolution catalyst), and corrosion resistance, it was selected as the noble metal oxide for the novel anode (Lee et al., 2011). When selecting the substrate material, stainless steel was selected due to its corrosion resistance and low cost compared to other substrates (Kholdeeva and Zalomaeva, 2016; Zhang et al., 2010).

Based on preliminary studies, three different anodes were developed by deviating from conventional metal oxides while some differences were made with Sb oxides. The aim of this study was to study and compare performance of those three DSAs: steel/IrO₂, steel/IrO₂-Sb₂O₃, and Ti/IrO₂-Sb₂O₃ anode materials on phenol oxidation, and figure out the best anode material among them.

Methodology

Materials. In this study, H₂SO₄ (98%, Fisher Scientifics), Sb standard solution (Fisher Scientifics), isopropanol, Na₂SO₄ anhydrous (AR, 99%, SDFCL), HCl (37%, BDH), H₂C₂O₄·2H₂O (99%, LOBAL Chemie), ethanol (99%, AR, Fisher Scientifics) and IrCl₃·3H₂O (Ir, 53–56%, ACRDS Organics); analytical grade chemicals were used. All aqueous solutions were prepared with distilled and deionized (DI) water.

Development of Three Kinds of Anodes. In the pretreatment process, substrate was mechanically treated by using sandpaper to increase the adhesiveness of the surface followed by a chemical pretreatment process. Chemical pretreatment was done with 5% (w/w) oxalic acid solution and 37% (w/w) HCl acid prior to the coating process (geometrical area of one electrode was $\sim 1 \times 10^{-4}$ m²). Then, the substrate was sonicated in distilled water and dried at 100 °C (Feng and Johnson, 1991). The anode was developed with rare-metal oxide coatings using the dip coating process followed by calcinations steps.

Electrochemical Degradation of Phenol on Anodes. Laboratory-prepared 5.00×10^{-3} M phenol solution was electrochemically oxidized for 6.0 hours. Ten milliliters of 10.00 g L⁻¹ Na₂SO₄ supporting electrolyte was used. The total treated batch was 50.00 mL. The electrochemical cell was formed with 1 $\times 10^{-4}$ m² selected anode (i.e., steel/IrO₂, steel/IrO₂-Sb₂O₃, Ti/ IrO₂-Sb₂O₃) and 1 $\times 10^{-4}$ m² cathode. The distance between the anode and the cathode was set at 1 $\times 10^{-2}$ m. All measurements were obtained at room temperature: 25 °C, 20 mA cm⁻² of consistent current density and at initial pH of 11.00.

Determination of Chemical Oxygen Demand Removal Percentage. Chemical oxygen demand (COD) values of water samples treated with steel/IrO₂, steel/IrO₂-Sb₂O₃, and Ti/IrO₂-Sb₂O₃ anodes were determined using the standard potassium dichromate method (Cleceri et al., 1998). During the electrolysis, 0.50-mL solution samples were withdrawn at 1 hour intervals for the determination of COD removal percentages. The effect of variation of batch volume to the concentration was considered negligible.

COD removal efficiency =
$$\frac{\left[(\text{COD})_{\text{Initial}} - (\text{COD})_t\right] \times 100}{(\text{COD})_{\text{Initial}}}$$
(1)

Instantaneous Current Efficiency Value Calculation. Instantaneous current efficiencies (ICE) were calculated for each anode for the 6-hour oxidation process by using COD removal data. The calculation was done using the following equation (ICE) (Li et al., 2009):

$$ICE = \frac{\left[(COD)_t - (COD)_{t+\Delta t} \right] \times FV}{8I\Delta t}$$
(2)

where $(\text{COD})_t$ and $(\text{COD})_{t+\Delta t}$ are the initial chemical oxygen demand (g O₂ m⁻³) at time *t* and $t + \Delta t$ (s), respectively. *I* is the applied current (A), *F* is the Faraday constant (C mol⁻¹), and *V* is the volume of the electrolyte (m³).

Hydroxyl Radical Detection. Because 4-nitroso-N, Ndimethylaniline shows selective reaction with OH⁰ radicals, hydroxyl radical generation at electrodes was investigated with 4-nitroso-N,N-dimethylaniline (RNO) Due to its electrochemical inertness and the easy color determination toward OH⁰ radicals, RNO is used for confirmation of the presence of hydroxyl radicals (Comninellis, 1994; Jayathilaka et al., 2014; Jeong et al., 2006).

The 50-mL batch contained 2×10^{-5} M RNO and 10 mL of 10 g L⁻¹ Na₂SO₄ solution. It was electrochemically treated at a constant current density of 20×10^{-3} A cm⁻². The anode and cathode distance was 1 cm and the cathode was stainless steel. The color bleaching was monitored through absorbance readings at 440 nm wave length by using UV-visible (Shimadzu, UV-2450) spectrophotometer.

Analysis and Detection of Phenol and Intermediates. The intermediate products were identified by high-performance liquid chromatography (HPLC) and UV-vis absorbance spectra. In the HPLC (Shimadzu, Japan), a C18 reversed phase was used to determine intermediates. The samples were injected (8 μ L each) and intermediates were monitored at 245-nm wavelength. The flow rate of the mobile phase was 1 mL/min (35% methanol and 65% distilled water; Jayathilaka et al., 2014). In UV analysis, the different natures of the intermediates were identified by their specific wavelengths. The 190- to 1100-nm-wide scan spectra of the solutions were acquired with a UV-2450 spectrophotometer and a quartz cell with a 1 cm light path length.

Electrochemical Measurements. Cyclic voltammetry (CV) was obtained for the anodes using potentiostat galvanostat equipment (Auto lab PGSTAT128N Metrohm Autolab B.V., Utrecht, Netherlands). Total anodic charge was calculated to compare the electrochemically active areas of each anode. The anodes were studied in 50 mL of 10 g L⁻¹ Na₂SO₄ electrolyte solution. The Ag/AgCl electrode was used as the reference electrode (RE) and Ti electrode was used as the counter electrode. The scanning voltage rate and the scan rate were -2.5 to +2.5 V and 0.05 V s⁻¹ respectively.



Steel/IrO₂ ■ Steel/IrO₂-Sb₂O₃ ■ Ti/IrO₂-Sb₂O₃

Figure 1—COD removal percentage for steel/IrO₂, steel/IrO₂-Sb₂O₃, and Ti/IrO₂-Sb₂O₃ anodes in Na₂SO₄ electrolyte. (Volume per test = 50.00 mL, applied current = 20.00 mA, anode area = 1.00 cm², pH = 11.00, cathode - stainless steel).

Results and Discussion

This section discusses the investigation on electrochemical oxidation of water contaminated with phenol by different DSA anodes: steel/IrO₂, steel/IrO₂-Sb₂O₃, and Ti/IrO₂-Sb₂O₃. Chemical oxygen removal rate and phenol degradation were monitored to compare the effect of anode materials on their performances.

Influence of Anode Metal-Oxide Composition on COD Removal and Phenol Degradation. Chemical Oxygen Demand Removal. Chemical oxygen demand removal percentages were monitored at regular time intervals (1 hour) as it is directly proportional to the variation of phenol concentration. At the end of 6 hours of oxidation, the Ti/IrO₂-Sb₂O₃ anode showed the highest COD removal percentage, while steel/IrO2 resulted the lowest COD removal percentage. It was nearly 53, 76, and 84% for steel/IrO2, steel/IrO2-Sb2O3, and Ti/IrO2-Sb₂O₃ anodes, respectively (Figure 1). These results imply that the IrO₂-Sb₂O₃ metal oxide mixture on Ti substrate has more favorable properties for phenol oxidation than other two combinations. Chemical oxygen demand removal may have occurred by both direct and indirect oxidation. Usually, direct oxidation, which is quite small, produces dimers and polymers that would undergo further oxidation. Tahar and Saval (2009) discussed this issue. They mention that even under the best operating conditions, only 15% of the starting phenol can be removed by direct oxidation. Direct oxidation, if it is significant, would form tarry polymeric material that is deposited on anodes, reducing the oxidation efficiency. No significant tar buildup was observed on the selected anode materials, indicating that direct oxidation was not significant. Anodes will improve rapid indirect oxidation by hydroxyl radical, too. Therefore, 84% COD removal could be due to higher affinity properties of phenol molecules at the Ti/IrO2-Sb₂O₃ electrode.

Phenol Degradation and Intermediates Removal by Anodes. Phenol degradation at the end of 6 hours of electrolysis was monitored by using HPLC and UV-vis analysis and compared with initial phenol concentration. In UV-vis spectral analysis,



Figure 2—Phenol removal percentage for steel/IrO₂, steel/IrO₂-Sb₂O₃, and Ti/IrO₂-Sb₂O₃ anodes in Na₂SO₄ electrolyte. (Volume per test = 50.00 mL, applied current = 20.00 mA, anode area = 1.00 cm^2 , pH = 11.00, cathode - stainless steel).

phenol peak appeared at 270 nm. Its peak height was decreased after 6 hours of electrolysis. At the end of 6 hours, the lowest peak height was for the Ti/IrO₂-Sb₂O₃ anode, while the highest peak was observed for steel/IrO₂. It was nearly 60, 85, and 90% reduction for steel/IrO₂, steel/IrO₂-Sb₂O₃, and Ti/IrO₂-Sb₂O₃ anodes, respectively (Figure 2).

Because UV-vis spectral analysis confirmed that the phenol degradation occurred partially on anodes, intermediate analysis was done by using HPLC. It found the presence of catechol (276 nm) and benzoquinone (234 nm) in all three media. Though, the amounts of intermediates present on treated samples varied based on the anode material. The least amount of intermediates was observed for the steel/IrO2 anode, since the lowest phenol degradation efficiency was shown by the steel/IrO2 anode. Under the electrocatalytic conditions with Sb, phenol degradation was rapid for both steel/IrO2-Sb2O3 and steel/IrO2-Sb2O3 anodes. However, without catalytic activity, phenol degradation and intermediate formation were significantly low at steel/IrO2 anode. The byproduct analysis for the Ti/IrO₂-Sb₂O₃ oxidation process revealed that the presence of intermediates in the medium was nearly 30% less than it was found for the steel/ IrO₂-Sb₂O₃ anode. This could be due to the fact that benzene ring breakage is easier at the Ti/IrO2-Sb2O3 than at the steel/ IrO₂-Sb₂O₃. Therefore, the highest amount of intermediates resulted for steel/IrO₂-Sb₂O₃.

Moreover, phenol removal rates for each anode were calculated for further confirmation of results because the main study was based on phenol degradation by the anode material. The rate equation for the phenol removal was developed on the following reaction:

$$C_6H_5OH + \dot{O}H \rightarrow CO_2 + H_2O \tag{3}$$

Rate equation for phenol removal (eq 4) assumes that the hydroxyl radical concentration is constant during the electrolysis:

$$-\frac{d[\text{phenol}]}{dt} = k[\text{phenol}]^a \tag{4}$$

where k is the pseudo-order-rate constant and [phenol] is the concentration of remaining phenol in the electrolysis system at different time periods.

Phenol concentration and intermediates were further monitored using the UV-vis (270 nm). Since a purposely prepared phenol solution was used for the study, it was assumed that phenol is the only source of organic carbon in the system. Therefore, the initial COD value of the system is proportional to the initial phenol concentration.

Hence, eq 4 could be expressed as follows:

$$-\frac{d[\text{phenol}]}{dt} = k[\text{phenol}]^a \tag{5}$$

For first-order-rate equation: (When a = 1)

$$\ln \left[\text{phenol}\right]_t = -k_{\text{app}}t + \ln \left[\text{phenol}\right]_0 \tag{6}$$

For second-order-rate equation: (When a = 2)

$$\frac{1}{[\text{phenol}]_t} - \frac{1}{[\text{phenol}]_0} = k_{\text{app}}t \tag{7}$$

where *a* is the order of the rate, $[phenol]_0$ is the initial phenol concentration value of the system, $[phenol]_t$ is the phenol concentration value of the system at time, *k* is the real rate constant, and k_{app} is the global apparent rate constant for phenol removal, respectively.

Based on eqs 6 and 7, the following kinetic model plots were drawn for pseudo-first-order (Figure 3a) and pseudo-second-order (Figure 3b).

When initial phenol concentration was integrated with this concept, it resulted a straight line with slope k_{app} . Regression coefficient (R^2) can be calculated by using the results of phenol removal of each anode (Table 1 and Table 2).

According to Table 1, the pseudo-second-order model results higher regression coefficients (R^2) than the pseudo-first-order model. These results tally with the previous studies on phenol removal of organic molecules by anodes (Samet et al., 2010). Hence, the data in Table 1 clearly indicate that the pseudosecond-order model gives better prediction than the pseudo-firstorder model.

Moreover, it is known that when gas evolution occurs at the electrode surface, mass transport can be significantly increased due to formation and detachment of bubbles. An increase of k_{app} values results by a decrease in this diffusion-layer thickness. Thin diffusion layer causes efficient phenol degradation. Therefore, when k_{app} value is high, it implies that there is efficient phenol degradation. According to Table 2, k_{app} value of the steel/IrO₂-Sb₂O₃ anode is higher than the steel/IrO₂ anode and the highest k_{app} value was for the Ti/IrO₂-Sb₂O₃ anode. This higher k_{app} value implies that the mass transfer rate and oxygen evolution capacity of the Ti/IrO₂-Sb₂O₃ anode surface is high, compared to both steel/IrO₂-Sb₂O₃ and steel/IrO₂ anodes.

These results were confirmed by the observations of experimental study on instantaneous current efficiencies (ICE) calculations and hydroxyl radical generation measurements.

Comparison of Instantaneous Current Efficiencies and Hydroxyl Radical Generation Capacity of Three Different DSA Anodes. *Instantaneous Current Efficiencies*. Instantaneous current efficiencies give an idea about the effective current used for phenol oxidation out of the supplied total amount of current to the system. According to the results of Figure 4, the Ti/IrO₂-Sb₂O₃ anode has the highest ICE and steel/IrO₂ has the lowest value. It was nearly 0.3, and 0.2 for Ti/IrO₂-Sb₂O₃ and steel/IrO₂, anodes, respectively. Therefore, Ti/IrO₂-Sb₂O₃ shows highest efficient phenol degradation.

Both ICE and COD removal percentage studies revealed similar effects on anode materials' metal oxide mixture. That is, the IrO₂-Sb₂O₃ metal oxide mixture on Ti substrate is more suitable for the phenol oxidation process and this may be due to the improvement of strengthened properties of layers and corrosion resistance compared to steel/IrO₂ and steel/IrO₂-Sb₂O₃.

Because the oxygen evolution was always observed at the anodes, the electrolysis occurred under mass transport control. This is in agreement with the trend of ICE calculated from eq 2. As shown in Figure 4, ICE was always below 100% or 1. Therefore, more organic molecules may accompany the Ti/IrO₂-Sb₂O₃ anode than steel/IrO₂-Sb₂O₃ and steel/IrO₂ anodes.

RNO Test: Hydroxyl Radical Generation. Because all the experiments were conducted under a chloride free-environment, electrochemically generated hydroxyl radicals are considered as the major oxidant. They have the ability to oxidize harmful organic pollutants in urban water to harmless species. Hydroxyl radicals are generated on anode surface by following oxidation reaction (Comninellis, 1994; Torres et al., 2003).

$$2H_2O \rightarrow 2\dot{O}H + 2H^+ + 2e^- \tag{8}$$

Because the composition of anode surface material affects hydroxyl radical generation capacity, the rate of hydroxyl radical generation will be one of the best parameters to compare electrochemical activity of the anodes. Then free radical production during the electrolysis was observed by using RNO for different three anodes. According to Figure 5, there is rapid decrease of absorbance during first 10 minutes for three anodes, Ti/IrO₂-Sb₂O₃, steel/IrO2-Sb2O3, and steel/IrO2. It proves that the generation of hydroxyl radicals is rapid at the beginning of electrolysis. Then the rates decrease with time for all anodes. This may be due to the physical and chemical changes of anode surface. However, hydroxyl radical production rate of Ti/IrO2-Sb2O3 was higher than steel/IrO2-Sb2O3 and steel/IrO2 anodes. These resulting hydroxyl radicals have nonselective oxidizing ability. They could attack aromatic rings and increase aromatic ring breaking. It confirms that adding catalyst can enhance the anode properties while proving the validity of COD and ICE calculation results.

Influence of Anode Metal-Oxide Composition on Electrochemically Active Area of Anodes. *Voltammetric Behavior of Three Anodes*. Anodes with higher electrochemically active area perform well in oxidation of urban water





Figure 3—(a) Pseudo-first-order kinetic models for different anodes. (b) Pseudo-second-order kinetic models for different anodes (i.e., steel/IrO₂, steel/IrO₂-Sb₂O₃, and Ti/IrO₂-Sb₂O₃).

pollutants. If the electrochemically active area is larger, they show higher anodic charge values. Therefore, getting an idea on anodic charge is important while developing proper anode for urban water treatment. These anodic charge values can be obtained through cyclic voltammetric studies. Cyclic voltammetric studies on different anodes were conducted in similar experimental conditions as in Figure 6. The anodes, steel/IrO₂, steel/IrO₂-Sb₂O₃, Ti, and Ti/IrO₂-Sb₂O₃ under study were used as the working electrode (WE). The Ti electrode was used as the counter-electrode (CE). The Ag/AgCl electrode was used as the reference electrode (RE). Scan rate was selected as 0.05 V s⁻¹. Range of voltage scan was from -2.5 V to 2.5 V. Na₂SO₄ (10 g

Electrode	Steel/IrO ₂	$Steel/IrO_2-Sb_2O_3$	$Ti/IrO_2-Sb_2O_3$
First-order (R ²)	0.394	0.862	0.900
Second-order (R ²)	0.870	0.908	0.999

Table 1—Regression coefficient (R^2) for phenol removal of steel/IrO₂, steel/IrO₂-Sb₂O₃, and Ti/IrO₂-Sb₂O₃ anodes.

 L^{-1}) was used as the electrolyte. Physical surface area of the electrodes was maintained at 1×10^{-4} m² in all the cases. The distance between the anode and the cathode was maintained as 1×10^{-2} m. The following manner was the result of the study:

Anodic charge: steel < steel $/IrO_2$ < Ti < steel / $IrO_2\text{-}Sb_2O_3$ < $Ti/IrO_2\text{-}Sb_2O_3$

The anodic charge of steel anode showed lower value compared to the Steel/IrO₂ anode. That might be due to the absence of IrO₂ on the anode surface. Anodic charge was increased with surface modifications. In addition, when the anode is prepared on Ti substrate, it showed higher anodic charge value compared to steel substrate. Therefore, the Ti/IrO₂-Sb₂O₃ anode was selected as the best one among three anodes.

Operational Cost for the Selected Ti/IrO_2 -Sb₂O₃ Anode. Electricity cost, chemical reagents cost, sludge disposal cost, labor cost, maintenance cost, and cost for equipment are the main operational costs of a wastewater treatment process. But among them, cost of electrode material and consumed electrical energy are the most important parameters influencing the usage of electrochemical process. Therefore, operational cost of an electrochemical oxidation can be calculated by eq 9:

Operational cost = $(C_{\text{energy}} \times \text{electricity price for 1 kWh})$ + $(C_{\text{electrode}} \times \text{average material cost for 1 kg})$ (9)

The average cost of titanium rod and anode materials is around 4.40 US $\$ kg⁻¹ and the electricity price is 0.04 US $\$ kWh⁻¹.

Therefore, operational cost for treating 1 m³ of phenol contaminated water is 12 kWh \times 0.04 US\$ kWh⁻¹ + 0.005 kg \times 4.40 US\$ kg⁻¹ = 0.50 US\$.

Where C_{energy} is the energy consumption per cubic meter of phenol contaminated water (kWh m⁻³) and $C_{\text{electrode}}$ is the amount of electrode material consumed during the treatment of 1 m³ of phenol contaminated water (kg m⁻³).

Operational cost was calculated based on local (Sri Lankan) prices and the result showed that operational cost for treatment of 1 m³ of water was 0.50 US\$. Because high energy consumption is the main drawback of electrochemical technol-

Table 2—Global apparent rate constant (k_{app}) for phenol removal of steel/IrO₂, steel/IrO₂-Sb₂O₃, and Ti/IrO₂-Sb₂O₃ anodes.

Electrode	Steel/IrO2	2 Steel/IrO2-Sb2O	$_3$ Ti/lrO ₂ -Sb ₂ O ₃
$k_{app} imes 10^4$ (L/(mg min))	0.114	0.380	0.858



Figure 4—Instantaneous current efficiency values of steel/IrO₂, steel/IrO₂-Sb₂O₃, and Ti/IrO₂-Sb₂O₃ anodes in Na₂SO₄ electrolyte. (Volume per test = 50.00 mL, applied current = 20.00 mA, anode area = 1.00 cm², pH = 11.00, cathode - stainless steel).

ogy, the optimized anode material will provide solution by reducing the energy consumption.

Conclusions

This study was conducted to compare the performances of steel/IrO₂, steel/IrO₂-Sb₂O₃, and Ti/IrO₂-Sb₂O₃ anodes for phenol degradation, under given experimental conditions. During the 6 hours of oxidation, all anodes were capable of more than 50% of COD removal. The above findings reveal that developed anode materials can enhance phenol oxidation efficiency and the mixed metal oxide layer has main influence on it.



Figure 5—Hydroxyl radical generation on steel/IrO₂, steel/IrO₂-Sb₂O₃, and Ti/IrO₂-Sb₂O₃ anodes in Na₂SO₄ electrolyte. (Volume per test = 50.00 mL, applied current = 20.00 mA, anode area = 1.00 cm^2 , pH = 11.00, cathode - stainless steel).

Table 3—Anodic charge variation of differentanode materials.

Anode material	Anodic charge/mC	
Steel	0.151	
Steel/IrO ₂	0.175	
Ti	0.180	
Steel/IrO ₂ -Sb ₂ O ₃	0.189	
Ti/IrO ₂ -Sb ₂ O ₃	0.207	

The study concluded that phenol could be more efficiently degraded at the Ti/IrO_2 -Sb₂O₃ anode than with the steel/IrO₂ and steel/IrO₂-Sb₂O₃ anodes. Because the least phenol degradation efficiency and COD removal (53%) were observed at the steel/IrO₂ anode, the least amount of intermediates was also found for the steel/IrO₂ anode.

Under the electrocatalytic conditions with Sb, hydroxyl radical generation on anode surface and phenol degradation were rapid for both steel/IrO₂-Sb₂O₃ and steel/IrO₂-Sb₂O₃ anodes. However, without catalytic activity, phenol degradation and formation of intermediates were significantly lower at the steel/IrO₂ anode. Because the ring breakage is easier at Ti/IrO₂-Sb₂O₃ than at steel/IrO₂-Sb₂O₃, higher COD removal (84%) resulted for Ti/IrO₂-Sb₂O₃ than steel/IrO₂-Sb₂O₃ (i.e., COD removal 76%). Therefore, among the selected metal-oxide mixtures, IrO₂-Sb₂O₃ was the most suitable and it gives satisfactory results under given experimental conditions. The operational cost for treatment of 1 m³ of phenol-contaminated water using this optimized anode is about 0.50 US\$. Low operational cost makes this an economically viable solution for treating wastewater.



Figure 6—Cyclic voltammetric comparison for anode materials electrochemically active areas.

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