An electrochemical mechanisms study: On Steel/IrO₂-Sb₂O₃ electrodes for oxidation of phenol in water

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Abstract

Phenol, a known water pollutant, was electrochemically oxidized on Steel/IrO₂-Sb₂O₃ novel anode. Since the oxidation mechanisms vary based on the anode material, mechanisms study of electro-oxidation of phenol on it was conducted. The phenol oxidation was carried out at 20 mA/cm² constant current density with pH 11.00 Na₂SO₄ medium at room temperature. During 6h of electrolysis, samples were tested for Chemical Oxygen Demand (COD) removal efficiency of anode. The Steel/IrO₂-Sb₂O₃anode showed 76.3% of COD removal efficiency. Both4-nitroso-N, N-dimethylaniline (RNO) and the HCO_3^-/CO_3^2 -radical scavenger tests confirmed the formation and presence of the hydroxyl radicals in the system. Therefore, it was concluded that the hydroxyl radicals which are generated on the anode surface are the main cause for the oxidation mechanism. Moreover, ICE, HPLC and UV-vis absorbance and cyclic voltammetry results confirmed the presence of catechol and benzoquinone as intermediates and the reaction mechanism.

Keywords:

Benzoquinone, Catechol, Oxidation mechanisms, Phenol, Steel/ IrO2-Sb2O3 anode

Introduction

Phenol (C_6H_5OH) is a known hazardous aromatic hydrocarbon which is produced through both natural and anthropogenic processes.¹ In recent, phenolic compounds have been detected in ground and surface water as contaminants.² Moreover, they have a potential to impact on human health and ecology even at low concentration^{1, 3} due to high toxicity, high oxygen demand and low bio degradability. As such, it is important to degrade them in to harmless species. Hence, a great deal of attention has been created on contamination of water by these phenolic compounds.

Several treatment technologies have been researched for recovery or destruction of phenol in water such as photo-catalytic oxidation⁴, biological treatment⁵, chemical oxidation⁶, electrochemical oxidation⁷ and adsorption.⁸ But there are drawbacks in these techniques such chemical oxidation require large amount of reactive chemicals and it caused harmful effects on environment. Even though biological treatment methods are environmental friendly they are inefficient and slow. Also they are impractical for high toxicity conditions and limited in the case of non-biodegradable compounds.⁶ More on the adsorption methods are efficient but it not widely applicable due to higher reproducible cost of absorbents.

Recently, the electrochemical process (EC) has been popular among these treatment techniques.^{9,10} As one of the EC method, electrochemical oxidation is more attractive² due to its environmental compatibility, safety, high efficiency, cost effectiveness, in-situ chemical generation and ease in operation.^{9,11} The efficiency and the selectivity of electrochemical oxidation is mainly depends on electrode materials.^{2,7} Therefore, anode material and its properties are more important.¹⁰ The ideal anode material for the oxidation of organic pollutant must be highly active towards organic oxidation while low activity towards secondary reactions such as oxygen evolution reactions. In addition, both stability in electrolyte medium and the inexpensiveness are needed. Considering above facts, several

anode materials have been studied under various experimental conditions. Such investigated anode materials for phenol/phenolic compounds oxidation include Ti/SnO₂-Sb¹², Ti/RuO₂-TiO₂¹³, boron-doped diamond ¹⁴, Ti/IrO₂, Pb/PbO₂ ¹⁵, Ti/Pt–Ir, Ti/PbO₂, Ti/PdO–Co₃O₄ and Ti/RhO_x–TiO₂ ¹⁶ and graphite ¹⁷. Though, there are similar electrodes on different substrates such as Ti/IrO₂ ^{18, 19}, Ti/ IrO₂-ShO₂-Sb₂O₅ ²⁰, Ti/SnO₂-Sb₂O₃/PbO₂ ²¹, all these electrodes show different oxidation efficiencies and mechanisms which are specific to their surface.

Although the electrochemical oxidation of phenol has been studied and reported, literature on mechanisms involved are limited.²² In addition, these mechanisms may vary based on the anode material as well. More specifically, phenol oxidation mechanisms by different types of anodes still remain to be investigated. Objectives of this paper are to develop and study a novel Steel/IrO₂-Sb₂O₃ anode material for phenol oxidation and investigating the mechanism and reaction pathways of the possible reactions. Authors expect that this work will shed more light on the field of waste-water treatment and understanding the reaction mechanisms of phenol oxidation.

Materials & method

Materials

All chemicals including $H_2C_2O_4.2H_2O$ (99%, LOBAL Chemie), HCl (37%, BDH), IrCl₃.3H₂O (Ir - 53-56 %, ACRDS Organics), Sb standard solution (Fisher Scientifics), ethanol (99%, AR, Fisher Scientifics), isopropanol, $K_2Cr_2O_7(99\%)$, Avondale Laboratories), H_2SO_4 (98%, Fisher Scientifics), Ag₂SO₄ (Reagent grade , Fisher Scientifics), phenol (99%, Sigma-Aldrich), Na₂SO₄ anhydrous (AR, 99%, SDFCL), Na₂CO₃ (99%, BDH) , NaOH (97.5%, BDH), RNO (Sigma-Aldrich), KH₂PO₄ (AR, 99.5%, BDH)were of analytical reagent grade. All aqueous solutions were prepared by using deionized (DI) water.

Methods

Electrode preparation

In the pre treatment process, substrate was mechanically treated by using a sand paper with grit of 120 to increase the adhesiveness of the surface followed by a chemical pretreatment process. Chemical pre treatment 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 ~1 cm²). Finally, the substrate was sonicated in distilled water and dried at 100 °C .²³ The anode was developed on pretreated steel support with rare metal oxide coatings using the dip coating process followed by calcinations steps. The coating solution was prepared by mixing 0.56 g of IrCl₃.3H₂O in 4.6 ml ethanol and 0.33 ml Sb (1000 ppm) standard solution in 1.65 ml isopropanol. Then the wet coating surface was air dried in 80 °C airflow to evaporate solvents and calcinated in an oven at 450°C for 10 min. The coating process was repeated until achieving the final coating load of 1mg/cm². Finally, the electrode was post backed at 500 °C in muffle furnace (OT-HTMF-05, Optics technology, Delhi India) for 1 h.²⁴

Electrochemical oxidation of phenol

Electrochemical oxidation of phenol was conducted for 50ml batch contains 40ml of 5.00mM phenol solution and 10 ml of 10g/L Na₂SO₄supporting electrolyte. The electrochemical cell was formed with 1 cm² Steel/IrO₂-Sb₂O₃ anode and 1 cm² stainless steel cathode. During the 6 h of electrolysis, the continuous mixing was carried out by using magnetic stirrer and the distance between two electrodes was set at 1.0 cm. The initial conductivity of solution was recorded as 2760 µS/cm. The initial pH was adjusted to 11 by adding aqueous NaOH drops, because majority of industrial wastewater samples are having pH values close to 11. Further, based on the preliminary studies, Steel/IrO₂-Sb₂O₃ anode gave the highest performance when the pH of the medium is between 9 and 12. The electrochemical measurements were carried out in room temperature, 25°C. Electrolytic analysis apparatus ANA-2 (Tokyo photoelectric Co. Ltd., Japan) was employed as the DC power supply. All the voltage variations

recorded under 20 mA/cm² of consistent current density and initial voltage of the system was set to 4 V. During the electrolysis, 0.5 ml samples were withdrawn at one hour intervals for the determination of COD and the analysis of intermediates. The effect of variation of batch volume to the concentration was negligible.

Analysis and detection of intermediates

The COD test was conducted according to the standard potassium dichromate method.²⁵ The pH and conductivity of each sample was recorded by using a pH meter (Model: Thermo Scientific, Orion 5 star). The intermediates were recognized by high performance liquid chromatograph (HPLC) and UV-vis absorbance spectra.⁴ In HPLC (Shimadzu, Japan) a C18 reversed phase was used to determine intermediates. The samples were injected (8 μ L) and intermediates were monitored at 245 nm wavelength. 1ml/min was the flow rate of the mobile phase (35% methanol and 65% distilled water). In UV analysis, different natures of intermediates were identified by their specific wave lengths.190-1100 nm wide scan spectra of the solutions were acquired by UV-2450(Shimadzu, Japan) spectrophotometer and a quartz cell with 1 cm light path length.

Qualitative analysis of radicals

Hydroxyl radical generation at electrodes was qualitatively investigated with 4-nitroso-N, Ndimethylaniline (RNO).RNO is a good candidate to use in identification of hydroxyl radical due to its selective reaction with OH radicals, electrochemical inertness and the easy color determination.^{22,26} 2×10^{-5} M RNO in 10 g/L Na₂SO₄ solution was electrochemically treated at a constant current density of 20 mA/cm². The color bleaching was monitored through absorbance readings at 440 nm wave length.³

Cyclic voltammetry (CV)

Cyclic voltammograms were obtained by using a potentiostatgalvanostat equipment (Autolab PGSTAT128N). In this study, Steel/IrO₂-Sb₂O₃, stainless steel, and Ag/AgCl electrodes were used as working electrode (WE), counter electrode (CE) and reference electrode (RE), respectively. 40 ml of 5.00 mM phenol solution and pH 11.00, 10 ml of 0.1 M phosphate buffer were involved in CV. Each reading was taken in nitrogen environment to avoid atmospheric oxygen diffusion into the solution.²⁷

Results and discussion

Performance of phenol oxidation by Steel/IrO2-Sb2O3 anode

Chemical oxygen demand (COD)

The mineralization capacity of the Steel/IrO₂-Sb₂O₃ anode was tested during the electrochemical oxidation process of phenol. The initial COD concentration, 282.86 O₂mg/L, was decreased during 6.0 h of electrolysis time as shown in Fig. 1. A COD concentration of 227.90 O₂mg/L was observed after 1 hour of electrolysis, showing a COD removal efficiency of 19.6%. After 2 h, 26.8% COD removal (i.e. 208.19 O₂mg/L of COD concentration) was observed. ACOD removal efficiency of 26.34% (i.e. 188.38 O₂mg/L of COD concentration) was achieved at the end of three hours of electrolysis. COD concentrations at the end of four and five hours of electrolysis were 122.63 O₂mg/L and 82.26 O₂mg/L, respectively. At the end of the 6.0 h of electrolysis period, COD concentration dropped up to 66.60 O₂mg/L. Removal rate at the end of the electrolysis time (6.0 h) was 76.3%.

The resultant COD removal efficiency of 76.3% can be due to the formation of oxidizing agents on the anode surface. Under the experimental conditions used, i.e. in chloride free electrolyte (Na_2SO_4 solution), it was first assumed that the major oxidant contributing to the oxidation would be the hydroxyl radical. In order to investigate if this assumption is valid, further experimental investigations were carried out.

RNO test to validate the assumption

In order to confirm above assumption on generating hydroxyl radicals on Steel/ IrO_2 -Sb₂O₃ anode surface, a RNO test was carried out. RNO solution is yellow in color in absence of hydroxyl radicals. Therefore, initially the highest absorbance reading was recorded at 440 nm wave length. While applying 20 mA/cm²of constant current density to the cell hydroxyl radicals are supposed to generate on Steel/ IrO_2 -Sb₂O₃ anode surface. When these radicals entered into the system RNO color bleach was initiated. Due to the bleach absorbance values were decreased with time. During the first 10 minutes, rapid color bleach was obtained, and a noticeable rapid decrease of absorbance was observed (Fig. 2). The rapid decrease of absorbance during first 10 minutes confirmed the generation of hydroxyl radicals. Therefore, it can be said that the active sites of the Steel/ IrO_2 -Sb₂O₃ anode surface generates the hydroxyl radical.

OH radicals scavenger test to confirmation of presence hydroxyl radicals

After confirming the generation of OH radical in the system, investigations were extended to identify the effect of OH radical in more quantitative manner. In order to accomplish this, Na₂CO₃, a OH radical scavenger, was used as the electrolyte.²⁸ Due to the scavenging effect, increase of Na₂CO₃ concentration decreases the hydroxyl radical up to a considerable level. As a result, COD removal efficiency of the system was low after adding the scavenger. Fig. 3 shows the COD removal efficiency after adding different amount of radical scavengers to the system. When the concentration of Na₂CO₃ was 10 g/L, the COD removal rate was 35.14% after 6 h of reaction time. It was further lowered to 15.29% at a Na₂CO₃ concentration of 20 g/L. These removal efficiencies were considerably low comparing to non-radical scavenger system.

Phenol oxidation pathway and intermediate products identification

Since Steel/IrO₂-Sb₂O₃ anode achieved 76.3% mineralization efficiency, it may yield intermediates due to incomplete oxidation of phenols by OH radicals. The formation and the presence of such intermediates were determined by using the instantaneous current efficiency (ICE) calculations, HPLC, UV- vis spectral analysis and cyclic voltammetry studies.

Based on COD values, the instantaneous current efficiency (ICE) was calculated as follows³,

$$ICE = \frac{[(COD)_t - (COD)_{t+\Delta t}]FV}{8I\Delta t}$$
(Eq. 01)

Where $(COD)_t$ and $(COD)_{t+\Delta t}$ are the initial chemical oxygen demand (gO_2/m^3) at time t and $t + \Delta t$ (s) respectively. I is the applied current (A), F is the Faraday constant (C/mol) and V is the volume of the electrolyte (m³).

This ICE variation indicates the actual amount of current applied for the necessary reaction compared to the amount of current applied. The change of ICE in each hour of electrolysis for Steel/IrO₂-Sb₂O₃ anode is shown in Fig. 4. It can be seen that, at 20 mA/cm² of consistent current density, ICE is relatively higher at 0-1 h and 3-4 h stages. ICE increment at initial stage of 0-1 h is due to the oxidation of phenol in the system. During this 0-1 h period phenol oxidation with resulting series of intermediates is the principal reaction of the system. Initially at high phenol concentration, hydroxyl radicals react rapidly before starting the oxygen evolution reactions. It might be the formation of catechol or benzoquinone from phenol oxidation. Therefore, ICE shows relatively high value in first hour comparing second and third hours. There is a rapid decrease of ICE values between first and second hours due to oxidation reactions such as aromatic ring opening. Then there is a noticeable increment in ICE during 3-4 h period indicating the oxidation of easily oxidizable products.

Moreover, in HPLC analysis, the primary intermediates; catechol (i.e. at 3.20 min retention time) & benzoquinone (i.e. at 1.65 min retention time) were detected. It was found that the phenol (i.e. at 4.00 min retention time) concentration was decreased with time.

In addition, the intermediates were further monitored by using the UV-vis scan for 200 nm to 400 nm wavelength range. Results are shown in Fig. 5 (a) and (b). The characteristic absorbance wave length for phenol is 270 nm and the peak belongs to the 270 nm was decreased with time. The spectra which were obtained during regular time intervals (1h) were different from the initial one (results not shown here).

The new peaks were appeared after 6 h at 276 nm and 234 nm. Those peaks are associated with catechol and benzoquinone, respectively (Fig. 5 (b)). Hence, the UV-vis spectral findings confirmed that phenol was oxidized into catechol and subsequently catechol was oxidized into benzoquinone on Steel/IrO₂-Sb₂O₃ anode (Eq. 02)

 $Phenol \xrightarrow{HydroxylRadical} Catecol \xrightarrow{HydroxylRadical} Benzoquinone$ (Eq. 02)

Further the above reaction sequence, the oxidation mechanism and the intermediates were confirmed by a cyclic voltammetric behavior as shown in Fig. 6(a).

In Fig. 6 (a) CV, the batch initially contained only phenol molecules. Then the anode was initially at a potential of -2.5 V Vs. Ag/AgCl reference electrode. At this negative potential, only the reduced form of the molecules are present in the solution and further reduction products cannot be expected. Therefore, either no or very little current was observed at -2.5 V. This potential was not enough to cause oxidation of phenol. While electrode potential was slowly swept to anodic direction (or positive direction), single peak was appeared at +0.26 V. If the system contains only phenol molecules, that peak must be related to phenol oxidation. It can be seen from the Fig. 6 (a), as the phenol oxidation peak 1_a (at $E_{pla} = +0.26$ V).

Therefore, appearance of above peak confirmed phenol oxidation into catechol according to following reaction,

$$C_6H_5OH + \dot{OH} \rightarrow C_6H_4(OH)_2 + 1e^- + 1H^+$$
 (Eq. 03)

Then, anodic current was reached up to +0.007 A at 2.5 V potential relative to Ag/AgCl reference electrode. At this point, any phenol molecule which reaches the anode will immediately be converted into its oxidized form, catechol.

Then the potential was swept to the cathodic direction, cathodic current was observed. While scanning, there was a cathodic peak 2_c at E_{p2c} = -0.70 V and it corresponds to reduction of catechol, which is the oxidation product of phenol. This peak position was tally with 99% catechol oxidation peak at -0.36 V which was obtained by cyclic voltammetry analysis of standard 30 μ M catechol (see Fig. 6(b)) under similar experimental conditions.

However, formation of polymeric layer or change of Steel/IrO₂-Sb₂O₃ anode performance was not observed during the process. Specially, the anode layer was stable and actively involved in phenol oxidation even at very negative (i.e.-2.5 V) and very positive (+ 2.5 V) potentials. Therefore, during the cyclic voltammetry measurements, electrode passivation was not observed at high negative and positive potentials.

The second scan in positive direction was done for the same solution without cleaning the anode surface. Then, one anodic peak was appeared at E $_{p2a}$, at -0.32 V. It was related to oxidation of catechol into benzoquinone. Catechol reduction into benzoquinone must be a reversible reaction involving two- electrons. Theoretical potential difference between anodic and cathodic peaks can be calculated as $|E_{pa} - E_{pc}|$. If the difference is close to 30 mV, that reaction is theoretically defined as a two-electron reversible reaction.²⁹ In this study, the difference between the anodic and cathodic peak potentials, $|E_{p2a}- E_{p2c}|$ was 38 mV and it is close to the theoretical value of 30 mV. Therefore, it confirms the reversibility of the peak 2_a and 2_c and it might be due to the presence of catechol in the system. This catechol reduced into benzoquinone through two-electron reversible reaction as following,

 $C_6H_4(0H)_2 \leftrightarrow C_6H_4O_2 + 2e^- + 2H^+$ (Eq. 04)

Moreover, phenol oxidation products were adsorbed to the anode surface and resulting a decrease in the peak l_a current.

According to the above investigations on intermediates products, the following reaction pathway was resulted for the electrochemical oxidation of phenol on Steel/IrO₂-Sb₂O₃ novel anode. No polymer formation was observed on the anode surface and no significant amount of metal was dissolved into the solution (Fig. 7.).

Conclusions

Investigations on bleaching of RNO proved the generation of \dot{OH} radical on Steel/IrO₂-Sb₂O₃ anode surface. Studies based on \dot{OH} radical scavengers showed a sharp decrease in mineralization efficiency, concluding the involvement of \dot{OH} radical in the oxidation process compared to the other possible mechanisms.

ICE, UV-vis and HPLC studies showed that the oxidation of phenol into catechol as the major intermediate of the reaction. Further, catechol was found to be oxidized into benzoquinone. In conclusion, reaction mechanism pathway of oxidation of phenol on Steel/IrO₂-Sb₂O₃ anode was followed below oxidation sequence,

$$C_6H_5OH + OH \rightarrow C_6H_4(OH)_2 + 1e^- + 1H^+ \leftrightarrow C_6H_4O_2 + 2e^- + 2H^+$$
 (Eq. (05))

This work enhances the overall understanding on the mechanisms of oxidation of phenol in water on Steel/IrO₂-Sb₂O₃ anode.

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Figure captions

Fig. 1. Variations of COD removal percentage with electrolysis time for Steel/IrO₂ - Sb_2O_3 anode

Fig. 2.Electrochemical bleaching of 2×10^{-5} M RNO in 10 g/L Na₂SO₄ solution as a function of treatment time (Current density = 20 mA/cm², anode area = 1 cm², batch volume=50 ml) Fig. 3.COD removal percentage comparison with radical scavenger conditions -Steel/IrO₂ - Sb₂O₃ anode

Fig. 4 Variation of ICE with every 1 h of electrolysis - on Steel/IrO2- Sb2O3 anode

Fig. 5. (a)UV- vis absorption spectra of 5.00 mM phenol solution before electrolysis and (b) after 6 h of electrolysis on Steel/IrO₂-Sb₂O₃

Fig. 6.(a)CVs in pH 11.0 0.1 M phosphate buffer 30 μ M phenol: (-) first scan and (...) fifth scan, $v = 50 \text{ mVs}^{-1}$ (b) Standards CV of 30 μ M catechol in pH 11.0 0.1 M phosphate buffer, scan, $v = 50 \text{ mVs}^{-1}$

Fig. 7 Proposed reaction pathway of electrochemical oxidation of phenol on Steel/IrO₂-Sb₂O₃ anode



Fig.1.



Fig.2.



Fig.3.



Fig.4.



Fig. 5.



Fig. 6.

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