Degradation of cyanide, aniline and phenol in pre-treated coke oven wastewater by peroxide assisted electro-oxidation process
Hariraj Singh and Brijesh Kumar Mishra

ABSTRACT
The present study explored the feasibility of using graphite electrodes for the electrochemical oxidation of cyanide, thiocyanate, phenol and aniline with hydrogen peroxide. The dosing effects of hydrogen peroxide and current density were examined in the pre-treated coke oven wastewater. It was found that 0.025 M hydrogen peroxide and 13.63 mA/cm² of current density were more favorable for the removal of 100%, 90%, 71% and 40% cyanide, thiocyanate, phenol and aniline respectively. The increased removal of phenol in the coke oven wastewater was attributed to the pre-treatment of wastewater. Initially, 28% phenol was converted to phenolate ion by air stripping process, which increased the removal rate of phenol by the electro-oxidation process as the removal of phenolate is quite easy compared to phenol. The advanced oxidation process degrades the more toxic cyanide into less toxic intermediate cyanate ions (CNO⁻), which further cut down into nontoxic end products such as N₂, HCO₃ and CO₂. The experimental results show that the primary mechanisms in the oxidation of cyanide and phenol are mediated electro-oxidation by hydroxyl radicals and hypochlorite ions. The operating cost under the optimized conditions for the removal of 100% cyanide and 71% phenol was estimated to be 616.95 INR/m³.

Key words | air stripping, coke oven, electrical charge, electrochemical, oxidation capacity

HIGHLIGHTS
- Graphite electrodes with an oxidizing agent (H₂O₂) have completely mineralized the toxic cyanide into non-toxic products.
- Higher cyanide removal rate and less ammonia formation have been observed at initial pH, i.e. 8.9.
- Complete removal of cyanide was obtained in less than 2.0 Ah/m³ of specific electrical charge.
- Post treatment with electro-oxidation process has reached mineralization of phenol of more than 70%.

INTRODUCTION
Coal coking and coal gasification are carbonization processes in which a huge amount of water is used in various stages such quenching of coke and by-product recovery. The wastewater generated from these industries is rich in pollutants such as phenolic compounds, cyanide, thiocyanate, ammonia, suspended solids, polycyclic aromatic hydrocarbons (PAHs), sulfate, biochemical oxygen demand (BOD) and chemical oxygen demand (COD) (Liu et al. 2015; Ozyonar & Karagozoglu 2015), etc. The coke oven industry effluent has the problem of ammonia, phenol, aniline and cyanide pollution, which is more toxic and needs proper treatment with effective processes. Due to high toxicity, phenol and cyanide lead to environmental and regulatory concerns. The phenolic compounds can easily migrate within an aqueous environment and contaminate groundwater because of their high solubility in water. Moreover, phenols are responsible for the depletion of dissolved oxygen and thus degrade the quality of water bodies. The cyanide is more toxic than any other pollutant present in the wastewater. Thereby, coke wastewater needs an effective process to meet the prescribed regulatory standards. Aniline reported in this study is a potential
occupational carcinogenic organic compound, which required more concern because of mobility in surface water, unlike polycyclic aromatic compounds. The aniline in the coke wastewater might be formed due to the presence of phenol and ammonia with metal catalytic activity. The possible mechanism of aniline formation might be the cumene-phenol process (Kahl et al. 2000).

The conventional methods used nowadays generate more activated sludge, which requires further treatment for its disposal; this, in turn, is a time-consuming process. Various authors have studied coke oven wastewater treatment by coagulation (Lai et al. 2007), biological processes (Chatterjee et al. 2012), adsorption (Tyagi et al. 2018) and combining biological processes with ultrafiltration, nanofiltration and reverse osmosis (Jin et al. 2013), and the forward osmosis–nanofiltration (FO–NF) integrated system (Kumar & Pal 2015). However, these methods are either technically complicated or uneconomic, due to difficulties in practical application, so an alternative technique is required. Nowadays, electrochemical oxidation (ECO) is used as an emerging technique to overcome these issues.

The oxidation of wastewater is principally based on the hydroxyl radical (OH) generated on the surface of the electrode, which is a strong oxidizing agent with a standard oxidation potential of 2.8 V (Kausley et al. 2017). Two different possible mechanisms that are occurring in the ECO process, namely direct oxidation on the surface of the electrode and indirect oxidation mediated by the oxidizing radical generated in situ, were used to degrade the organic molecules. Various oxidants such as nascent oxygen, ozone, hydrogen peroxide, free chlorine and free radicals are the effective oxidizing agent in the oxidation process, which play an important role in oxidizing the organic pollutants. At the anode surface, the hydroxyl radicals generated at the surface of the anode act as mediated oxidants, and they are highly reactive and oxidizing for organic pollutants (Raju et al. 2009). These hydroxyl radicals are generated according to the following Equations (1)–(3):

\[
2H_2O \rightarrow 2OH^- + 2H^+ + 2e^- \quad (1)
\]

\[
OH^- \rightarrow OH^+ + e^- \quad (2)
\]

\[
2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad (3)
\]

In the last few years, emerging electrochemical techniques with different assisted combinations have been successfully used for the treatment of various types of wastewaters due to environmental compatibility, current efficiency, cost-effectiveness, easy operation, less retention time, and lower amount of sludge (Ozyonar & Karagozoglu 2013). The electro-oxidation process is an advanced oxidation process to mineralize the organic as well as inorganic compounds without generating any kind of sludge by converting the more toxic compounds into less toxic ones (Poyatos et al. 2010).

The main objective of the present study was to investigate cyanide and phenol reduction from coke oven wastewater (CWW) by the ECO process using graphite electrodes in the pre-treated (i.e. air stripping process) coke wastewater. The CCD (Central Composite Design) of the RSM tool, which is used most commonly in wastewater (Sonal et al. 2018) was applied to optimize the pretreatment process. The effects of operating parameters such as initial pH, current density, initial H2O2 concentration and electrolysis time for the ECO processes for reduction efficiencies were studied to determine the optimum operating conditions. The cost of treatment of the ECO process for cyanide and phenol was also investigated and calculated as INR/m3. The effects of the electro-oxidation process on additional pollutants such as aniline and thiocyanate present in the coke oven wastewater were also studied.

**MATERIAL AND METHODS**

**Chemicals and reagents**

All chemicals used in this study were purchased from Merck, were of analytical grade and were utilized without further purification. The amber reagent bottles were used to store the stock solution of phenol, aniline, thiocyanate and cyanide. The glassware used in these studies was supplied by Borosil, India. High density polypropylene plastic storage bottles were also used for collection of coke oven wastewater. An aqueous stock solution of ammonia along with other chemicals was obtained by diluting the stock solution in Milli-Q water.

**Characterization of wastewater**

Optimization of the ECO process was carried out with the help of synthetic wastewater and the efficiency of ECO was also validated with actual CWW. The actual CWW was collected from the coke oven by-product effluent treatment plant of Bokaro district, India. Synthetic wastewater was prepared in the laboratory to simulate the characteristics of actual CWW as per the formulation given by researcher Tyagi et al. 2018, which consists of phenol, cyanide, aniline and trace elements were added. The
physio-chemical characteristics of synthetic wastewater and actual CWW are listed in Table 1.

**Startup of the study**

In the present study, coking wastewater was treated in two stages, namely air stripping and the ECO process, because CWW possesses a high concentration of ammonia and phenol. Air stripping was used as a pretreatment process to reduce the ammonia and phenol concentration load and optimize the operating conditions through the statistical tool for air stripping. The effluent of the pretreatment process was finally treated with the ECO process. The detailed discussion on the treatment processes is described in the following sections.

**Air stripping**

A single stripping column was made with the help of cylindrical plexus glass of 1.50 m height and 6 cm diameter. The cylindrical tube was divided into three segments to allow the packing materials to be filled conveniently. The air flow rate was varied with the help of change in water flow at a fixed air flow rate; that is, 15 L/min, and the removal efficiency of the selected pollutants under different operating conditions (i.e. pH, packing height, and air-water ratio) were studied. The CCD of the RSM tool was applied to optimize the air stripping process and three main operating variables were chosen for the CCD model; that is (A: pH 8.25–11.25, B: height 0.685–0.990 m, B: air-water ratio 250–950) at three levels, i.e. low (−1), central (0), and high (1). According to the design proposed by the software (Design Expert Version 7.0.0), 20 runs were conducted which included several repetitions to get a fair estimate of the experimental error.

**Electrochemical oxidation process**

The effluent coming from the air stripping process has been treated by the ECO process under the optimized conditions of the process. The ECO process with hydrogen peroxide (H₂O₂) oxidising agent was carried out in an electrochemical cell with a working volume of 1 L using graphite electrodes with an anodic surface area of 110 cm² per side submerged in the solution. The experiments were conducted with direct current (DC) using a precision DC power supply of 30 V and 2 A capacity (power supply manufactured by Microtech agencies, Dhanbad) by selecting current values in the range of 250 to 1,750 mA corresponding to a current density from 2.27 to 15.90 mA/cm². Hydroxide peroxide (30%) with different molar concentrations was used to assess the impact of the oxidizing agent in the ECO process.

**Analytical procedure**

The ammonia concentration was measured as per the prescribed titrimetric method (APHA-4500-NH₃-C) (APHA 2017). The phenol concentration was monitored using a UV/VIS spectrophotometer (Model-9100, Labchem, China) as per the prescribed method (APHA-5530-D) (APHA 2017).

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**Table 1** | Characterization of coke oven wastewater used in this study

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Actual CWW</th>
<th>Before treatment</th>
<th>After treatment</th>
<th>Synthetic wastewater</th>
<th>Before treatment</th>
<th>After treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.97</td>
<td>6.75</td>
<td></td>
<td>8.27–8.7</td>
<td>6.66</td>
<td></td>
</tr>
<tr>
<td>Conductivity (mS/cm)</td>
<td>4.167</td>
<td>3.198</td>
<td></td>
<td>3.96–4.67</td>
<td>3.225</td>
<td></td>
</tr>
<tr>
<td>TDS (mg/L)</td>
<td>2,063</td>
<td>1,369</td>
<td></td>
<td>1,998–2,075</td>
<td>1,475</td>
<td></td>
</tr>
<tr>
<td>Chloride Cl⁻ (mg/L)</td>
<td>290–300</td>
<td>42</td>
<td></td>
<td>300 ± 10</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>2,560</td>
<td>358</td>
<td></td>
<td>2,750–2,890</td>
<td>417</td>
<td></td>
</tr>
<tr>
<td>BOD (mg/L)</td>
<td>280.8</td>
<td>32.6</td>
<td></td>
<td>234.5</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>NH₃-N (mg/L)</td>
<td>352</td>
<td>132</td>
<td></td>
<td>380–400</td>
<td>143</td>
<td></td>
</tr>
<tr>
<td>Nitrate (mg/L)</td>
<td>42</td>
<td>18</td>
<td></td>
<td>35 ± 5</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>Phenol (mg/L)</td>
<td>560</td>
<td>165</td>
<td></td>
<td>495 ± 5</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td>Cyanide, CN⁻ (mg/L)</td>
<td>56</td>
<td>BDL</td>
<td></td>
<td>98 ± 2</td>
<td>BDL</td>
<td></td>
</tr>
<tr>
<td>Thiocyanate, SCN⁻ (mg/L)</td>
<td>200</td>
<td>22</td>
<td></td>
<td>200 ± 5</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>Aniline (mg/L)</td>
<td>155 ± 5</td>
<td>69.75</td>
<td></td>
<td>150 ± 5</td>
<td>67.5</td>
<td></td>
</tr>
</tbody>
</table>
The cyanide concentration was measured by the reagent based portable photometer (Model-HI96714; Hanna Instruments) which is designed on the basis of APHA standard method 4500-CN E, while thiocyanate was measured as per APHA standard method 4500-CN M using a UV/VIS spectrophotometer (Model-9100, Labchem, China) separately (APHA 2017). Measurement of pH, conductivity and TDS were carried out with a bench multiparameter meter (Model-HI5521; Hanna Instruments). The aniline was determined by the diazotization-coupling method with N-(1-Naphthyl) ethylenediamine as the coupling agent at 555 nm absorbance (Norwitz & Kellher 1981). The rest of the parameters listed in Table 1 were measured as per standard methods prescribed in APHA; that is, the chloride (method-4500-Cl B), COD (method-5220-C), BOD (method-5210-B) and nitrate (method-4500-NO3 B) respectively (APHA 2017). The percentage reduction of pollutants such as ammonia, phenol cyanide, thiocyanate and aniline were calculated using Equation (4):

\[ R_E = \frac{C_0 - C_t}{C_0} \times 100 \]  

(4)

where \( C_0 \) and \( C_t \) are an initial and residual concentration of pollutants at times 0 and t minutes.

The amount of electrical energy consumed through the electrochemical process was computed by using Equation (5), which is an important economic parameter to optimize the electrochemical treatment.

\[ E = \frac{UIT}{V} \]  

(5)

where \( E \) is the electrical energy consumed (in kWh/m³), \( U \) is the voltage applied (in V), \( I \) is the current (in A), \( T \) is the electrolysis time in hours, and \( V \) is the volumes in liters.

**Oxygen-equivalent chemical oxidation capacity**

In this study, the oxygen-equivalent chemical oxidation capacity (OCC), which is the quantity of oxidant in kg of \( O_2 \) used in the oxidation process to treat the wastewater of 1 m³, was determined. The OCC has provided the information as chemical oxygen demand (COD), which means the oxygen required in kg to oxidize chemically any species of contamination in a wastewater. They are differentiated on the basis of COD, which is used to measure the concentration of organic compounds present in the wastewater and the OCC is proposed to quantify the amount of oxidant that participates in the oxidation process. The OCC calculation was done according to following relations:

\[ 1(\text{kg} \ O_2 \ m^{-3}) = Q \left( \frac{\text{kAh}}{m^3} \right) \frac{1 \text{kmol}^{-1}}{3600 \text{s}} \frac{1 \text{kmol} \ O_2}{96487 \text{kJ} \cdot \text{s}} \frac{32 \text{kg} \ O_2}{4 \text{kmol}^{-1}} \frac{1 \text{kmol} \ O_2}{\text{kmol} \ O_2} = 0.298Q \left( \frac{\text{kAh}}{m^3} \right) \]  

(6)

\[ 1(\text{kg} \ O_2 \ m^{-3}) = \left[ H_2O_2 \right] \left( \frac{\text{kmol} \ H_2O_2}{m^3} \right) \frac{1 \text{kmol} \ H_2O_2}{54 \text{kg} \ H_2O_2} \frac{2 \text{kmol}^{-1}}{1 \text{kmol} \ O_2} \frac{32 \text{kg} \ O_2}{4 \text{kmol}^{-1}} \frac{1 \text{kmol} \ H_2O_2}{\text{kmol} \ H_2O_2} = 0.471[H_2O_2] \left( \frac{\text{kmol} \ H_2O_2}{m^3} \right) \]  

(7)

The above equations are based on stoichiometric calculation, through electrons exchanged in the reduction of the oxidants in the case of \( H_2O_2 \) and also the Faraday number in the case of direct electro-oxidation of graphite electrodes (Cañizares et al. 2007). ‘\( Q \)’ is the specific electrical charge passed during the electrolysis in kiloampere hours per cubic meter (KA h/m³), which depends upon current applied and the amount of \( H_2O_2 \) that was converted in kg/m³ on the basis of molar mass and density calculation of hydrogen peroxide.

**RESULTS AND DISCUSSION**

**Air stripping process**

In this study, the air stripping process was employed as a pretreatment option to remove the ammonia and a small amount of phenol. Ammonia is a well known pollutant in CWW and is responsible for hindrance of further treatment processes. The air stripping experiments have been optimized through response surface methodology, a mathematical tool through the CCD model. The obtained CCD experimental data were analyzed by two different tests, namely the sequential model sum of squares and model summary statistics, in order to obtain the effective regression models among various models such as linear, interactive, quadratic and cubic. The F-test of the regression models produced very low \( p \)-values (<0.0001), indicating that the model for ammonia has been found to be more highly significant than the phenol model. The value of the regression coefficient (R²) for ammonia response was found to be higher i.e. 0.9938, which indicates good fit of the model, while the phenol response has a value of R² of 0.8845, which indicates slight variation to be fitted. The
value of the adjusted determination coefficient (adjusted 
$R^2 = 0.9881$ and 0.7806) also proved the high significance 
of both ammonia and phenol. The results suggest that the 
model F-value of 176.72 and low probability value ($p$-value 
< 0.001) reveals that the model was significant for the air 
stripping process. The ‘Pred-R-Squared’ of 0.9858 is in 
reasonable agreement with the ‘Adj-R-Squared’ of 0.9881 
for ammonia removal. Similarly, the ‘Pred R-Squared’ of 0.4737 is not as close to the 
$R^2$ for ammonia and phenol removal in its quadratic form, 
high in their working solution (Ozyonar et al. 2012). It has been 
reported in the literature that alkaline pH favors the 
dissociation of phenol into phenolate and hydrogen ions 
(Rivas et al. 1999). The phenolate ions react at $10^7$ times 
faster rate with oxygen than phenol for oxidation reaction 
(Mclurgh 1998). The removal rate of phenol decreased 
with an increase in pH of 10 due to the presence of excessive 
OH$^-$ ions. This decrease is because of the negative impact 
on phenol removal due to its scavenging tendency for 
hydroxyl radicals (OH$^-$). The pretreated effluent generated 
through air stripping was further processed through ECO.

Electrochemical oxidation of cyanide

In this stage, the ECO process was used to treat the pre-trea-
ted (air stripping process) CWW, which was highly loaded 
with phenol, aniline, thiocyanate and cyanide. The pH of 
the coke oven wastewater was alkaline (~9) and all exper-
iments were carried out in this alkaline pH condition 
without pH modification. The ECO experiment was carried 
out with an oxidizing agent of 30% H$_2$O$_2$ having the oxidizing 
potential of 1.77 V by using graphite electrodes. The oxidizing 
agent H$_2$O$_2$ increases the oxidation rate of cyanide, and miner-
alization of organic as well as inorganic compounds present 
in the wastewater takes place (Trejo et al. 2007).

Effect of H$_2$O$_2$ dosing on cyanide degradation and 
ammonia formation

Experiments were conducted with different concentrations 
of H$_2$O$_2$ (i.e. 0.005–0.03 M) at the original pH of the waste-
water at room temperature and atmospheric pressure. The 
results revealed that maximum cyanide reduction was 
100%, which occurred in 150 min of electrolysis time by 
0.025 M H$_2$O$_2$ dosing. The rate of oxidation of cyanide 
ions increases with increasing concentration of H$_2$O$_2$ 
because of an increasing amount of HOO$^-$ in the solution. 
The more toxic cyanide ions present in wastewater were 
first oxidized into less toxic cyanate intermediate products 
under alkaline medium, which further oxidized into pro-
ducts of ammonium and carbonate ions (Sarla et al. 2004). 
The increase in ammonia concentration has validated the 
oxidizing trend of cyanide to ammonia, which is depicted in 
Figure 1. The mineralization of cyanide into bicarbonate 
and ammonia has also been reported (Tran 1992). The pH 
of the wastewater dropped down at a fast rate at a higher 
dose of H$_2$O$_2$ resulting in a low alkaline medium and then 
an acidic one within 120 min of electrochemical process.
The drop in pH led to increased formation of ammonia because the cyanate ions hydrolyzed into ammonium ions, carbonate ions and \( \text{C}_2\text{O}_4^{2-} \) through direct oxidation action according to reactions (20 and 22). In continuance of direct oxidation, the indirect oxidation of cyanide through hydrogen peroxide has also been formulated as per reactions (24 and 25) under low alkaline conditions or a slightly acidic medium. The electrochemically generated hydroxide radicals have also oxidized the more toxic cyanide into less toxic cyanate and then further into \( \text{HCO}_3^- \), \( \text{N}_2 \) and \( \text{H}_2\text{O} \) with a faster rate of oxidation as follows (Valiunien et al. 2013).

\[
\text{CN}^- + 2\text{OH}^* \rightarrow \text{OCN}^- + \text{H}_2\text{O} \\
\text{OCN}^- + 3\text{OH}^* \rightarrow \text{HCO}_3^- + \frac{1}{2}\text{N}_2 + \text{H}_2\text{O}
\]

Effect of pH

The pH of the wastewater during oxidation of cyanide has an important role. The variation of pH with electrolysis time and current density is indicated in Table 2. The results have revealed that the pH of the solution decreases from its initial value with time at all values of current densities. At the end of the process, the pH of the solution was slightly acidic. This indicates that the pH of the solution decreases continuously due to the generation of hydrogen ions (H\(^+\)) in the electrochemical cell. The weak acidic solution, free from cyanide, would have a tendency to oxidize phenol and aniline easily with a high degradation rate (Luo et al. 2016). It has been reported that the breakdown of the intermediate product benzoquinone was high under high acid concentration, resulting in the greater conversion of phenol to CO\(_2\) (Kirk et al. 1985). A number of researchers have reported that the ECO process can be enhanced by the application of external oxidants such as nascent oxygen, ozone, hydrogen peroxide, free chlorine and free radicals (Barrera-Díaz et al. 2014; Daous 2017). The hydroxyl radicals generated at the surface of the anode electrode act as mediated reactive oxidants and enhance the rate of oxidation/degradation of organic compounds (Raju et al. 2009) and the hydrogen ions (H\(^+\)), generated at the anode.
The oxidation of cyanide depends upon the pH of the solution under which ECO is performed, because complete mineralization of cyanide takes place through two different mechanisms. Firstly, conversion of cyanide into CNO\(^{-}\) takes place in alkaline conditions, then the cyanate is mineralized under acidic conditions. Thereby the effect of pH was studied under different pH; that is, 5–10. All experiments were carried out with an initial concentration of cyanide of 100 mg/L and \(\text{H}_2\text{O}_2\) concentration of 0.025 M at 4.54 mA/cm\(^2\) current density, with an initial concentration of cyanide of 100 mg/L and \(\text{H}_2\text{O}_2\) concentration of 0.025 M at 4.54 mA/cm\(^2\) current density. In alkaline conditions, the time required was less into cyanate and hydrolysis of CNO\(^{-}\) into ammonia was slow under such conditions. In acidic conditions, the cyanate remains in HCN gas, which is more toxic and volatile, difficult to oxidize and requires more safety during acidic treatment. The possible oxidation mechanism of cyanide is as follows:

**Direct oxidation:** The decomposition reaction pathways of cyanide mainly depend upon the alkalinity. In a strong alkaline solution, cyanide is first oxidized into cyanate ions (CNO\(^{-}\)) at the anode, which are further oxidized to carbonate or carbon dioxide and nitrogen.

\[
\begin{align*}
2\text{H}_2\text{O} & \rightarrow 2\text{OH}^+ + 2\text{H}^+ + 2e^- \\
\text{OH}^- & \rightarrow \text{OH}^+ + e^- \\
2\text{H}_2\text{O} & \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^- 
\end{align*}
\]

\(\text{CN}^- + 2\text{OH}^- \rightarrow \text{CNO}^- + \text{H}_2\text{O} + 2e^- \) (15)

\(\text{CNO}^- + 2\text{OH}^- \rightarrow \text{CO}_2 + \frac{1}{2}\text{N}_2 + \text{H}_2\text{O} + 2e^- \) (16)

In a neutral and weak alkaline medium, the cyanide ion is oxidized at the anode through which the cyanide radical is formed and \(\text{C}_2\text{N}_2\) is further formed by the coupling of CN radicals, whereas in the neutral solution, ammonium and carbonate ions were produced through hydrolysis of the cyanate ion in the continuance of the process (Pillai & Gupta 2016).

\[
\begin{align*}
2\text{CN}^- & \rightarrow 2\text{CN} \bullet + 2e^- \\
2\text{CN} \bullet & \rightarrow \text{C}_2\text{N}_2 \\
\text{C}_2\text{N}_2 + 2\text{OH}^- & \rightarrow \text{CNO}^- + \text{CN}^- + \text{H}_2\text{O} \\
\text{CNO}^- + 2\text{H}_2\text{O} & \rightarrow \text{NH}_4^+ + \text{CO}_3^{2-} 
\end{align*}
\]

In a weak acidic solution, \(\text{C}_2\text{N}_2\) subsequently hydrolyzed to produce the oxamide \((\text{CONH}_2)_2\), which may be further continuously hydrolyzed to form \(\text{C}_2\text{O}_4^{2-}\) and ammonium ions (Xu et al. 2012).

\[
\begin{align*}
\text{C}_2\text{N}_2 + 2\text{H}_2\text{O} & \rightarrow (\text{CONH}_2)_2 \\
\text{C}_2\text{N}_2 + 2\text{H}_2\text{O} & \rightarrow \text{C}_2\text{O}_4^{2-} + 2\text{NH}_4^+ 
\end{align*}
\]

**Indirect oxidation:** In a strong alkaline solution, cyanide is first oxidized into cyanate ions (CNO\(^{-}\)) in the presence of hydrogen peroxide, which is further oxidized into formate ions, or carbon dioxide, as represented in the following reactions (23–25).

\[
\begin{align*}
\text{CN}^- + \text{H}_2\text{O}_2 & \rightarrow \text{CNO}^- + \text{H}_2\text{O} \\
\text{CN}^- + 2\text{H}_2\text{O}_2 & \rightarrow \text{HCOO}^- + \text{NH}_3 \\
\text{CN}^- + 2\text{H}_2\text{O}_2 & \rightarrow \text{CO}_2 + \text{NH}_3 + \text{OH}^- 
\end{align*}
\]

To see the effects of pH on the ammonia formation the detention period for complete removal of cyanide was studied. It has been observed that at low pH (i.e. 5), a 240 minute detention period was required for complete cyanide removal, whereas at alkaline pH (i.e. 10) only 95 minutes’ detention was found to be sufficient for the complete removal of cyanide. The alkaline conditions not only favor the detention period but also cause the low formation of ammonia as the rate of direct conversion of cyanide into CNO ions is greater in strong alkaline conditions rather than in acidic conditions (reactions 15–16). While the rate of formation of \(\text{NH}_4^+\) is more and slowly increases with time at an initial pH of 5 according to reaction (21). At an alkaline pH, cyanide is present as CN ions, which react easily with \(\text{H}_2\text{O}_2\) while in acidic pH, they combine with
hydrogen ions present in HCN gas phase, which are difficult to oxidize (Trejo et al. 2007). The experimental direct oxidation results confirm that the oxidation mechanism of cyanide mainly follows reactions (15) and (16) in the strongly alkaline solution, subsequently, reactions (17) to (20) in the weak alkaline or neutral solution and reactions (21) and (22) in weak acidic conditions.

In alkaline conditions, the Cl\(^-\) ions present in the wastewater are also responsible for high degradation of cyanide. The Cl\(^-\) ions oxidized directly on the anode surface to produce molecular chlorine (reaction 26) and, subsequently, it reacts in the basic solution with OH\(^-\) ions to generate the ClO\(^-\) ion (reaction 27), which is an effective oxidizing agent widely used for cyanide degradation. Then, the hypochlorite reacts with cyanide in alkaline media to yield gas nitrogen, water and chloride and carbonate ions (reaction 28) (Felixnavarro et al. 2011). Thereby, the high degradation rate of cyanide was found to be due to oxidizing agent hydroxide radicals and hypochlorite ions in alkaline conditions.

\[2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^- \quad (26)\]
\[\text{Cl}_2 + 2\text{OH}^- \rightarrow \text{Cl}^- + \text{ClO}^- + \text{H}_2\text{O} \quad (27)\]
\[2\text{CN}^- + 5\text{ClO}^- + 2\text{OH}^- \rightarrow 5\text{Cl}^- + \text{N}_2 + 2\text{CO}_3^{2-} + \text{H}_2\text{O} \quad (28)\]

Effect of current density

The ECO of cyanide in the synthetic CWW was investigated by varying the electrolysis time (i.e. 180 minutes) at different current densities (i.e. 2.27–15.90 mA/cm\(^2\)) at an optimized concentration of H\(_2\)O\(_2\), i.e. 0.025 M without disturbing the initial pH of the wastewater (i.e. 8.9). The results shown in Figure 2 revealed that the increase in current density causes higher removal of cyanide but it also observed that the low current density, 4.54 mA/cm\(^2\) at 150 min of electrolysis time, was found to be also sufficient for 100% removal of cyanide, but this optimized condition was not found to be sufficient for removal of other priority pollutants of CWW (i.e. phenol and aniline). Because of this, 13.63 mA/cm\(^2\) current density and 90 min of electrolysis time were found to be the optimum conditions for 100% removal of cyanide. The possible reason behind such high removal of cyanide is the high concentration of hydroxide radical formation at the anodic surface which oxidizes the cyanide into cyanate along with hydroxide peroxide oxidants. Further electrohydrolysis process plays an important role to mineralize the cyanate into NH\(_3\) and CO\(_2\). Increase in NH\(_3\) concentration, i.e. 41\%, and reduction of pH from 8.9 to 6.67 validated the mineralization process of cyanate. During the experiments, it was also observed that the temperature
of the solution in the electrochemical cell increases with increasing values of current densities and electrolysis time because of in-situ generation and decomposition of H$_2$O$_2$, which decreases the pH of the solution (Kausley et al. 2017), whereas at low current density only significant temperature difference was observed. The temperature of the solution increased up to 46 °C from its initial value of 23.5 °C. The increase in the temperature of wastewater favored the high oxidation of phenolic compounds (Akyurtlu et al. 1998; El-Hamshary et al. 2011) due to which maximum removal of phenol was achieved at higher current density.

**Electrochemical oxidation of phenol**

**Effect of current density**

In order to assess the efficacy of the electrochemical system for the degradation of phenol in CWW, the experiments were conducted at different current densities (2.27–15.90 mA/cm$^2$) at an initial pH value as shown in Figure 3. The result reveals that the increased current density has increased the reduction percentage of phenol and the maximum reduction of 71.48% has occurred at a current density of 13.69 mA/cm$^2$ after 180 min of electrolysis time. Further, an increment in the current density leads to more O$_2$ molecule formation at the anode surface, which decreases the current efficiency by decreasing the active surface area of the anodic surface. The mineralization of phenol in the ECO process is based on a direct as well indirect oxidation mechanism, in which hydroxide radicals generated through electro-activation of hydrogen peroxide (reaction 30), which further oxidized the phenol into the intermediate products and final mineralization take place into CO$_2$ and H$_2$O molecules as per the reaction (31) (Luo et al. 2015).

The possible mechanism of phenol mineralization:

**Electrogernated H$_2$O$_2$:**

\[
O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (29)
\]

**Electro-activation of H$_2$O$_2$:**

\[
H_2O_2 + e^- \rightarrow OH^- + HO• \quad (30)
\]

**Phenol + OH• → Intermediates → CO$_2$ + H$_2$O**

(31)

**Effect of initial concentration of phenol**

To understand the effect of initial concentration of phenol a further investigation was carried out at the optimized conditions. Figure 4 demonstrates that the removal efficiency of...
phenol decreases with increasing initial concentration of phenol. The rate of phenol degradation in the electro-oxidation process depends on the chlorine production (Equation (26)) and hydroxide radical formation (Equation (30)) at the anode surface of the graphite electrode. Higher phenol concentration in wastewater restricted O$_2$ molecule formation at the anode surface and corroded the anode surface, which is one of the prime reasons for the decrease of phenol removal. The reason behind such a reaction has been also reported in literature through which an intermediate of phenoxy radical was produced during anodic oxidation of phenol, therefore, the phenolic oligomer was formed by co-linking the phenoxy radicals and the phenolic oligomer would be adsorbed onto the anode surface and consequently reduces the activity of the anode (Gattrell & Kirk 1990; Chiang et al. 1995). Therefore, the graphite electrode needs a self-cleaning mechanism for smooth operation to be suitable anode material for the electrolysis process at a high current density and higher initial concentration.

### Oxygen-equivalent chemical oxidation capacity

Changes in the concentration of phenol and cyanide from its initial concentration with oxygen-equivalent chemical oxidation capacity (OCC) are shown in Figure 5 for phenol and cyanide at optimized current and hydrogen peroxide concentrations. The parameter OCC was used in literature for a different oxidation process, which explains the oxidant’s capacity produced during the oxidation process in terms of kg O$_2$/m$^3$ of wastewater. The stoichiometry calculation of oxygen-equivalent chemical oxidation capacity (OCC) was determined by the following relation given in the literature (Cañizares et al. 2007).

$$\text{OCC (kg O}_2\text{ m}^{-3}) = 0.298 \times Q (\text{kA h m}^{-3})$$
$$= 0.471 [\text{H}_2\text{O}_2] (\text{kg H}_2\text{O}_2 \text{ m}^{-3})$$

Figure 5 shows the changes in concentration with total OCC; that is, direct electrochemical oxidation by graphite electrodes and indirect oxidation by hydrogen peroxide used in the study. It has been observed that the ECO process is found to be sufficient for complete degradation of the total cyanide present in the coke oven wastewater for which the amount of OCC was less than 2.5 kg O$_2$/m$^3$ under the optimized current density of 4.54 mA/cm$^2$ and H$_2$O$_2$ concentration of 0.025 M. However, the ECO process is unable to degrade the phenol more than 71% until 3 hours of electrolysis period even at higher current density. In the case of phenol, the OCC was calculated under the optimized current density of 13.63 mA/cm$^2$ and 0.025 M of H$_2$O$_2$ concentration.
Electrochemical oxidation treatment cost analysis

For industrial application, the cost of treatment of any process should be minimized to be effective, though the operating variables that affect the cost of operation. In the direct ECO process, applied current, voltage and time of electrolysis are major variables that affect the cost of treatment directly as per Equation (3). Moreover, in the indirect oxidation process, the cost of oxidizing agents, through which faster oxidation rate is achieved, should be included in the total cost of treatment as in Equation (32). The operational cost of ECO treatment for the CWW was calculated on the basis of actual energy consumption and volume of H$_2$O$_2$ utilized for per m$^3$ of wastewater at the optimized condition as per the following equations.

\[
\text{Cost of treatment} = x \times \text{Electrical energy required (kWh/m}^3) + y \times \text{Chemical required (kg)}
\]

\[x = \text{price coefficient of electrical energy in INR/kWh/m}^3 \]
\[y = \text{price coefficient of chemical used in INR/kg} \]

Electrical power cost was calculated at the average rate of 6.5 INR per kWh, corresponding to the rate of industrial power supply in India, whereas the cost of hydrogen peroxide was calculated at the rate of 40 INR per kg. The total treatment operating cost was found to be 616.95 INR/m$^3$ for a percentage reduction of 100%, 89.69%, 71.48% and 40.98% for cyanide, thiocyanate, phenol and aniline respectively. The cost of treatment might be varied for a particular pollutant depending on its nature, solubility, initial concentration and oxidation mechanism. The present study suggests that the oxidation of cyanide consumed less electrical energy and a low amount of oxidizing agent. So, the cost of wastewater containing cyanide may have reduced significantly. The cyanide reduction in this study is the best example for an individual pollutant. The complete oxidation of cyanide in this study has been observed within 150 min of detention time at even low current density; that is, 4.54 mA/cm$^2$ for which the cost of treatment has been found to be 172.55 INR/m$^3$, which is comparably less than the total cost calculated at the optimized conditions for all pollutants.
Specific electrical charges

The characterization study of CWW shows that aniline, cyanide, phenol and thiocyanate are present at the high initial concentrations listed in Table 1. Thereby, the percentage reduction of most common pollutants present in the coke oven wastewater; that is, aniline, cyanide, phenol and thiocyanate with the specific electrical charge passed during the electrolysis of synthetic wastewater containing the initial concentrations, have also been investigated, respectively. Figure 6(a) and 6(b) show that the least specific electrical charge is sufficient for almost complete mineralization of cyanide even at low current and least electrolysis time, but more abrupt results have been seen in the case of thiocyanate at low current due to the formation and degrading equilibrium mechanism of oxidation of thiocyanate as per

![Graph showing variations in the percentage reduction with a specific electrical charge passed in graphite electrode at different current densities.](https://iwaponline.com/wst/article-pdf/78/10/2214/516672/wst078102214.pdf)

Figure 6 | Variations in the percentage reduction with a specific electrical charge passed in graphite electrode (a) low current density (4.54 mA/cm²); (b) optimized current density (13.63 mA/cm²); (c) high current density (15.91 mA/cm²). Operating condition: pH, 8.9; H₂O₂ concentration, 0.025 M; temperature, 23.5 °C; aniline concentration, 150 mg/L; cyanide initial concentration, 100 mg/L; phenol initial concentration, 350 mg/L and thiocyanate initial concentration, 200 mg/L.
reactions (33–35).

\[
SCN^- + 2OH^- \rightarrow OSCN^- + H_2O \quad (33)
\]

\[
OSCN^- + SCN^- + H_2O \rightarrow (SCN)_2 + 2OH^- \quad (34)
\]

\[
(\text{SCN})_2 + 4/3H_2O \rightarrow 5/3\text{SCN}^- + 1/3\text{SO}_2^2^- \\
+ 1/3\text{CN}^- + 8/3H^+ \quad (35)
\]

However, aniline and phenol cause a high specific electrical charge for the electrolysis cell because the specific electrical charges required for complete treatment are not directly proportional to the initial concentration of pollutants in the wastewater, but the intermediates formed during the electrolysis process also play a role between the contaminants in the wastewater, but the intermediates formed during the oxidation of phenol and aniline through hydroxyl radicals are almost the same as those reported previously for the direct oxidation. It has been reported in the literature that the oxidation of aniline deals with the sequential generation of phenol, hydroquinone, benzenetriol, maleic acid, oxalic acid and the CO₂ final end product, depending on the technology used to generate hydroxyl radicals (Anotai et al. 2006). The degradation of aniline was found continuously as the specific electrical charge increased under higher current density and the residual phenol concentration increased in the solution as shown in Figure 6(c), which means aniline degrades into phenol at a faster rate in comparison to phenol degradation. The phenol present in the solution further required more hydroxide radicals for oxidation, for which more H₂O₂ is added, which causes a drop in the pH of the wastewater and creates a more acidic medium, promoting the breakdown of benzoquinone (Kirk et al. 1985), which causes a greater conversion of phenol to CO₂.

**CONCLUSION**

The ECO process assisted with H₂O₂ by using graphite electrodes can be applied successfully for complete reduction of cyanide and partial reduction of thiocyanate, phenol and aniline from coke oven wastewater. The removal efficiency and electrolysis time were found to be directly proportional to current requirements, and cyanide (100% removal) was found to be most favorable whereas aniline (58% removal) was found to be the most reluctant pollutant in terms of current requirements. The higher removal of phenol i.e. 71%, was attributed to the pre-treatment of wastewater; that is, the air stripping process. Initially, 28% of phenol was converted into phenolate ions by the air stripping process, which increases the removal rate of phenol by the electro-oxidation process as removal of phenolate is quite easy compared to phenol. The presence of chloride ions in the wastewater enhanced the rate of oxidation and increased the mineralization of pollutants. The oxidants generated by the electrode itself reduce the dose of externally fed oxidant; that is, H₂O₂. Thus, it can be concluded that the electrochemical oxidation process (EOP) can be applied successfully for industrial effluent rich with cyanide and phenol concentrations with low-cost graphite electrodes and lower oxidant requirement.

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