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Kinetic modeling of electrochemical oxidation of phenol on boron-doped diamond anode in the presence of some inorganic species

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ABSTRACT

Phenolic wastewater from many industries contains inorganic species such as cyanide, sulfide, ammonium, thiocyanate, etc. Presence of these inorganic pollutants in phenolic wastewater could hinder the proper understanding of phenol oxidation kinetics when chemical oxygen demand (COD) decay data are used in the kinetic modeling, because these inorganic species exert oxygen demand as phenol. Unlike COD decay data, total organic carbon (TOC) decay data does not have any correlation with such inorganic species, and also available TOC measurements techniques are currently better in terms of automation, accuracy, and reliability compared with COD measurement techniques. In the present study, the kinetics of electrochemical oxidation of phenol on boron-doped diamond anodes in synthetic wastewater containing sulfide, cyanide, and ammonia species in single, binary, tertiary, and quaternary mix matrixes were modeled via employing current limiting modeling (CLM) using TOC in addition to traditional COD decay data. For all the different mix matrixes investigated, comparable trends describing the kinetics of electrochemical oxidation process were obtained for both the COD and the TOC decay models. Statistical diagnostics of the developed COD and TOC decay models parameters revealed that the operating regimes of the oxidation processes were accurately predicted to be limited by mass transfer. These results establish the suitability of using TOC decay for the CLM of phenol oxidation kinetics both in the presence and absence of the inorganic species. Based on these results in relation to the disparity between COD and TOC as parameters for evaluating phenol oxidation kinetics, it was concluded that TOC decay data are more appropriate compared with COD decay data for the CLM of kinetics of electrochemical oxidation of phenol in wastewater containing inorganic species that exert oxygen demand.

Keywords: Phenol; Cyanide; Sulfide and ammonia; Boron-doped diamond electrode; Electrochemical oxidation; COD and TOC decay data; Kinetic modeling; Current limiting modeling

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1. Introduction

Phenol is considered as a high-priority pollutant, because it is harmful to living organisms even at low concentration [1,2]. Phenolic wastewater can be treated using different treatment techniques that include catalytic oxidation, photo-catalytic oxidation, adsorption, biodegradation, and electrochemical oxidation [2–4]. Despite their short comings, electrochemical oxidation techniques have received greater attention due to some distinctive advantages they offer over most of the other aforementioned techniques [1,5–11]. Phenolic wastewater from many industries usually contains some inorganic species such as cyanide (CN^-), sulfide (S^{2-}), and ammonium (NH_4^+) [12–18]. Presence of these inorganic species is expected to influence the kinetics of electrochemical oxidation of phenol. Therefore, oxidation of phenol in aqueous matrixes containing inorganic species such as cyanide, thiocyanate, sulfide, and ammonia has been a subject of investigations [19–21]. Pearl and co-authors [19] have investigated the competitive oxidation of phenol in the presence of sulfide and cyanide ions in binary mix matrixes using photocatalysis with ZnO catalyst. They observed that in both sulfide–phenol and cyanide–phenol binary systems, a strong competition occurred. As a result, the oxidation yield of phenol decreased. A number of studies have been focused on employing enhanced biological processes for the degradation of phenol in the presence of inorganic species [20–22].

The kinetics of electrochemical oxidation of organic pollutant using current limiting modeling (CLM) are traditionally based on chemical oxygen demand (COD) decay data [23–25]. However, presence of oxidizable inorganic species which exert oxygen demand cohabiting organic compound in solution is expected to create a synergetic environment which would no doubt influence the kinetics of the organic compound oxidation. Moreover, under such a scenario, COD cannot be unbiased parameter employable to evaluate the organic pollutant oxidation kinetics considering that both the organic and inorganic species exert oxygen demand. On the other hand, total organic carbon (TOC) is a parameter expected to adequately indicate organic compound oxidation regardless of the cohabiting inorganic species in solution. Additionally, the techniques for TOC measurement are currently better in terms of automation and accuracy, and more reliable and easier than COD measurement techniques. Yet to the best of our knowledge, there have been no published studies that attempted to employ TOC to model the kinetics of electrochemical oxidation of phenol in the presence of inorganic species that exert oxygen demand using the CLM. Hence, the objective of this work was to employ both TOC and COD decay data to investigate the kinetic of electrochemical oxidation of phenol on BDD anodes in synthetic wastewaters containing S^{2-}, CN^-, and NH_4^+ ions in different mix matrixes using CLM.

1.1. Operating regimes during electrochemical oxidation of organic compound

The widely accepted mechanism of electrochemical oxidation process of organic compound on an inactive electrode such as BDD anode in acidic media is based on two steps [8,26,27]. First, hydroxyl radicals are initially produced and adsorbed on the anode as in Eq. (1).

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

For instance, in case of phenol, either the adsorbed radicals oxidize phenol or else convert it to oxygen via oxygen evolution reaction as shown in Eqs. (2) and (3), respectively.

$$\begin{aligned} &C_6H_5OH + 11BDD\,(^{\bullet}OH)_{ads} \\ &\quad \rightarrow 11BDD + 6CO_2 + 17H^+ + 11e^- \end{aligned} \tag{2}$$

$$BDD(^{\bullet}OH_{ads}) \rightarrow BDD + {}^1\!/\!{}_2O_2 + H^+ + e^- \tag{3}$$

Based on the CLM, which depend on the applied current, I_{app} with respect to the limiting current, $I_{\lim}$, two different operating regimes are postulated during the oxidation of organic compounds on inert anodes such as BDD electrode [23–25]. First, under low current ($I_{app} \geq I_{\lim}$) and sufficiently high concentration of the organic compound, electrolysis becomes current controlled, the instantaneous current efficiency (ICE) is high (about 100%) and the COD decreases linearly over time as given in Eq. (4). In the second regime, under high current ($I_{app} > I_{\lim}$) and low organic concentrations, the electrolysis is under mass transport control, and secondary reactions (such as oxygen evolution) commenced, resulting in decreased ICE (i.e. ICE < 100%). In this regime, the COD removal follows an exponential trend and in Eq. (5).

$$COD_t = COD_0\left(1 - \frac{\alpha A k_m}{V_r} t\right) \tag{4}$$

$$COD_t = \alpha COD_0 \exp\left(-\frac{\alpha A k_m}{V_r} t + \frac{1-\alpha}{\alpha}\right) \tag{5}$$

where COD_0 and COD_t represent chemical oxygen demand at time zero and time t in mol O_2 m^{-3}, respectively, V_r is the electrolyte volume in m^3, k_m is the mass transfer coefficient in ms^{-1}, A is the electrode area in m^2, and $\alpha = i_{app}/\ i^0_{\lim}$ where $i^0_{\lim}$ is the initial limiting current density.

2. Materials and methods

2.1. Chemicals reagents

Phenol (C_6H_6O), sodium sulfide ($Na_2S{\cdot}3H_2O$), sulfuric acid (H_2SO_4), sodium hydroxide (NaOH), sodium sulfate (Na_2SO_4), sodium cyanide (NaCN), ammonium sulfate ($(NH_4)_2SO_4$), iron Sulfate ($FeSO_4{\cdot}7H_2O$), potassium dichromate ($K_2Cr_2O_7$), silver sulfate (Ag_2SO_4), and mercury sulfate ($HgSO_4$). All other chemicals used were of high purity (>99%) obtained from either AnalaR or Sigma-Aldrich. Phenolic water containing S^{2-}, CN^-, and NH_4^+ in different mix matrixes in 1,100 mgL^{-1} Na_2SO_4 electrolyte solution was prepared with deionized water produced from a Millipore ultrapure system (conductivity $< 6 \times 10^{-8}$ S cm^{-1} at 25°C).

2.2. Electrochemical reactor and experimental procedure

Electrolyses were undertaken in batch mode using an undivided 2 L capacity reactor made up of internal glass compartment and external Plexiglas material. Synthetic thin-film boron-doped diamond with niobium substrate [CONDIAS, Germany] and graphite material [CONDIAS, Germany], both 10 cm in diameter, served as the working and counter electrode, respectively. Under galvanostatic mode set at a current density of 30 mA/cm^2, different electrolytic experiments of aqueous phenol (100 mgL^{-1}) in single, binary, tertiary, and quaternary mix matrixes with S^{2-}, CN^-, and NH_4^+ (each 200 mgL^{-1}) were carried out all at fixed initial pH of 4.8, and 1,100 mgL^{-1} sodium sulfate electrolyte-based on results of previous studies was reported earlier [28,29]. Constant room temperature of solution during each experiment was maintained by circulating cooling water between the internal glass wall and Plexiglas external wall. Homogenous mixing of solution during each experimental run was ensured by a mechanical stirrer operating at constant speed of 1,200 rpm. Samples drawn at specified time intervals were capped in pre-cleaned 20 mL glass vials, and analyses of COD and TOC followed immediately. All experimental runs as well as sample analyses were carried out in duplicates. More details about the reactor, experimental procedure as well as the instruments calibrations are described elsewhere [28,29].

2.3. COD and TOC analyses

COD was determined with the aid of ECO25 Thermo reactor using closed refluxed titrimetric method according to standard procedure as described by other authors [30,31]. TOC was analyzed using TOC-V_{CSN} analyzer model (Shidmazu, Japan) equipped with an autosampler ASI-V model (Shidmazu, Japan).

2.4. Instantaneous current efficiency

ICE was estimated according to the rate of COD removal using Eq. (6) [8,24,32–35].

$$\mathrm{ICE} = \frac{(\mathrm{COD}_t - \mathrm{COD}_{t+\Delta t})}{8 I_{app} \Delta t} F V_r \tag{6}$$

where COD_t and $COD_{t+\Delta t}$ represent chemical oxygen demand at time t and $t+\Delta t$ in mol O_2 m^{-3}, respectively, F is the Faraday's constant in C mol^{-1}, V_r is the electrolyte volume used in m^3, and i_{app} is applied current in amperes.

3. Results and discussion

Using the data obtained from the experimental part of this study, the kinetics of TOC and COD decay in single matrix (i.e. only phenol in solution) and also in the presence of the inorganic species in different mix matrixes are analyzed and discussed under the subsections below.

3.1. Kinetics modeling of electrochemical oxidation of phenol in the absence of the inorganic species

For the matrix containing only phenol in solution, the kinetics of COD and TOC decay were modeled using the CLM with the help of SIGMAPLOT regression tool. Exponential models were found to be the best-fitted trends ($R^2 > 0.99$) for both the COD and TOC decay data as depicted in Fig. 1(A) and (B), respectively.

Accordingly, the exponential decay of COD and TOC means that mass transfer is controlling the process i.e. the initial values of the COD and TOC are lower compared with that of the amount of the oxidant (i.e. the ·OH radicals) generated at the surface of the BDD electrode anode due to the supply of sufficiently high current. This implies that the change in the concentration of (·OH) due to reaction in Eq. (2) is minimal, and the change in either the COD or TOC with time is a first-order reaction. Hence, under

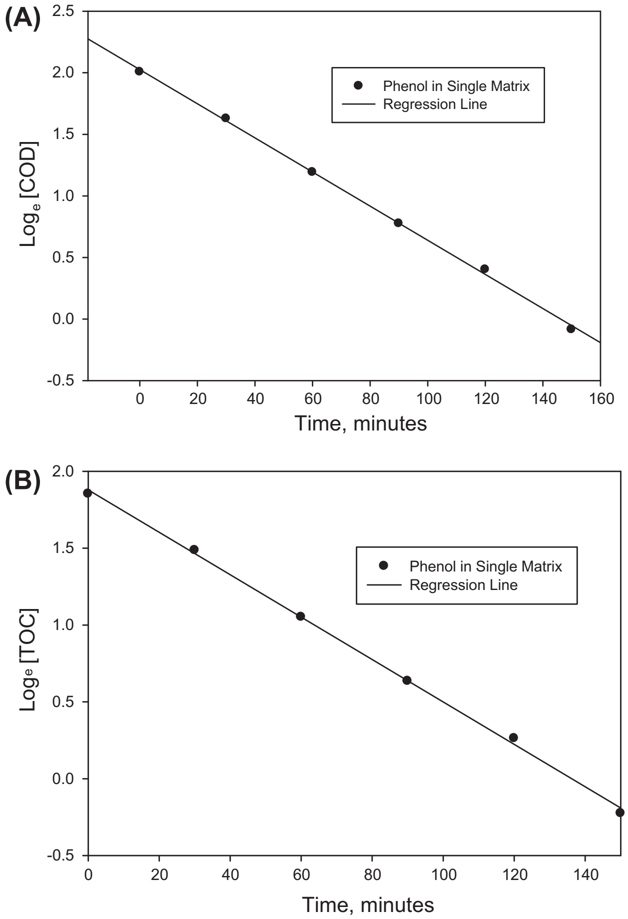

Fig. 1. Decay profiles for single phenol matrix (A) COD and (B) TOC.

steady-state conditions, the rate of disappearance or decay of either COD or TOC of the solution is proportional to the rate of mass transfer of species in solution from the bulk of solution to the electrode surface which can be expressed as follows:

$$\frac{\mathrm{d}[C_0]}{\mathrm{d}t} = -k_{app}[C] = -\frac{A}{V_r}k_m[C] \tag{7}$$

Integrating the left part of Eq. (7) yields

$$\ln\left[\frac{C_t}{C_0}\right] = -k_{app}t \tag{8}$$

where k_{pp} is the apparent observed pseudo-first-order rate constant, t is the electrolysis time, C_0 and C_t are initial COD or TOC and at any time, t, respectively, V_r is the electrolyte volume used, A is the electrode surface area, and k_m is the mass transfer coefficient in $\mathrm{ms^{-1}}$.

Using the right-hand side of Eq. (7), the experimental mass transfer coefficients for the COD and TOC decay were estimated using Eq. (9). It is obvious that mass transfer coefficient is directly proportional to the apparent decay constant.

$$k_m = \frac{V_r}{A}k_{app} \tag{9}$$

For both the TOC and COD decay data, values of k_m were calculated from Eqs. (5) and (9) designated as $k_{m\text{-model}}$ and $k_{m\text{-exp}}$, respectively. In either of the two cases (i.e. for COD or TOC), good regression coefficient (R^2) as well as an insignificant standard error of estimate (SEE) for the $k_{m\text{-}model}$ when compared with the corresponding $k_{m\text{-}exp}$, can adequately indicate the quality of the parameter in describing the electrochemical oxidation kinetics (Table 1).

Moreover, the values of CLM parameters (i.e. α-value and ICE) as presented in Section 1.1 were used to identify the operating regimes (either as mass transport controlled or current controlled). Hence, these two parameters were invoked as a further check for the verification of the established mass transfer limitation of the oxidation process, which is the case if α-value is greater than unity and ICE is less than 100% [23–25]. Table 1 presents the kinetic parameters calculated using Eqs. (5) and (9) as well as the parameters statistical diagnostics. In the absence of the inorganic species, considering that the calculated α-value for COD and TOC models in Table 1 are 1.196 and 1.219 (both >1), and the ICE was estimated as 19.1% as depicted in Fig. 2 suggests that the applied current was in the range greater than the limiting current for phenol oxidation. This further corroborates the fact the electrochemical oxidation of phenol in single

Table 1
COD and TOC removal kinetics parameters for the single phenol matrix

Nature of matrix		k_{app} $\mathrm{min^{-1}}$	$k_{m\text{-exp}}$ cm/min	$k_{m\text{-model}}$ cm/min	α	R^2	STD error of estimate	p-value
Single phenol	COD	0.014	0.3578	0.2996	1.196	0.9942	0.2106	<0.0001
	TOC	0.014	0.3553	0.2921	1.219	0.9924	0.2085	<0.0001

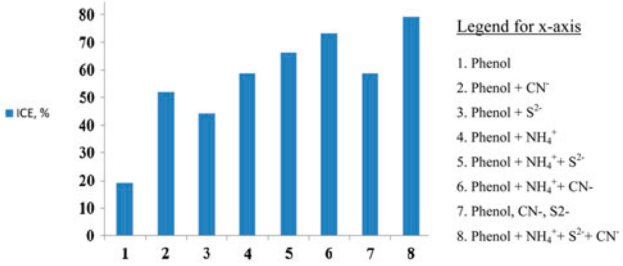

Fig. 2. ICE for the different mix matrixes calculated using Eq. (6).

matrix in this study was limited by mass transfer as we reported elsewhere [28]. Also, from Table 1, the $R^2 > 0.99$, p-values < 0.0001 (for both COD and TOC models at 5% significant level), and SEE are 0.2106 and 0.2085, respectively. Additionally, there is also an acceptable agreement between $k_{m\text{-model}}$ and $k_{m\text{-exp}}$ for both models. These clearly indicate that these two models describe well the experimental results. Considering that there is no any species in solution that could interfere with the value of either the COD or TOC during the phenol oxidation process, any of these two parameters (i.e. COD or TOC) can equally serve as an attribute of phenol oxidation. Conclusively, based on these results analyses, accurate and acceptable description of the phenol electrochemical oxidation kinetics in the absence of the inorganic species can be obtained via using both the COD and TOC decay data without any significant difference.

3.2. *Kinetic modeling of electrochemical oxidation of phenol in the presence of the inorganic species*

It was hypothesized that the kinetics oxidation of phenol would be significantly influenced as result of the presence of oxidizable inorganic species that exert

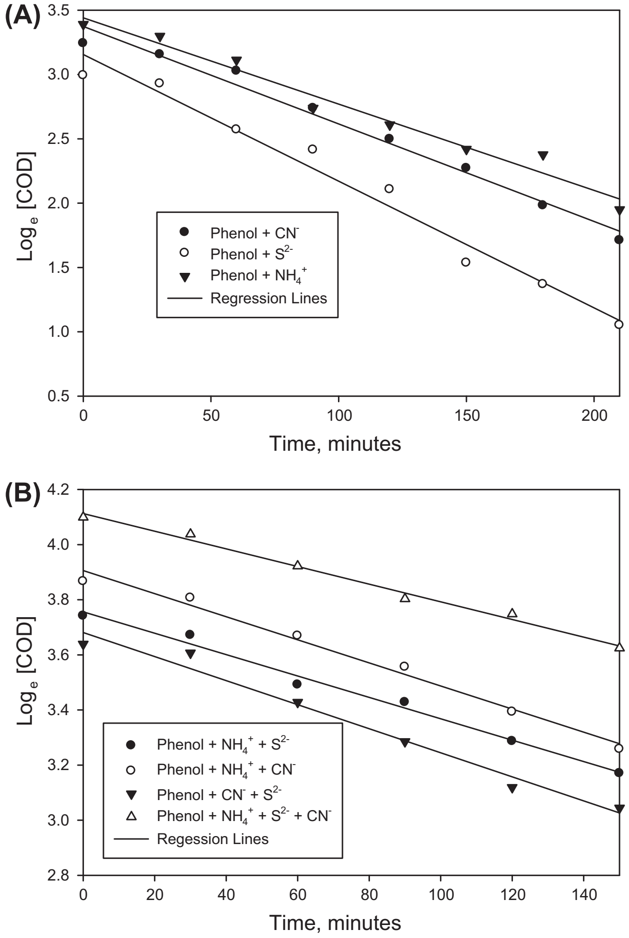

Fig. 3. COD decay profiles for (A) binary matrixes (B) ternary and quaternary matrixes.

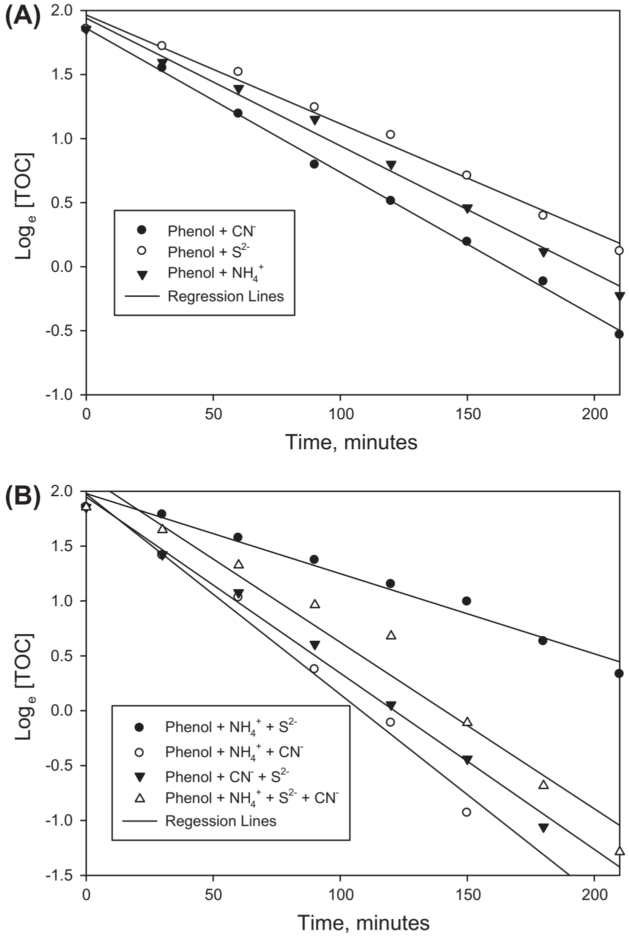

Fig. 4. TOC decay profiles for (A) binary matrixes and (B) ternary and quaternary matrixes.

Table 2
COD removal kinetics parameters for the different mix matrixes

Nature of matrix	Component (s)	k_{app} min^{-1}	$k_{m\text{-exp}}$ cm/min	$k_{m\text{-model}}$ cm/min	α	R^2	STD error of estimate	p-value
Binary	Phenol + CN^-	0.0067	0.1701	0.1141	1.4897	0.9691	1.4374	<0.0001
	Phenol + S^{2-}	0.0085	0.2157	0.1410	1.5247	0.9632	1.3666	<0.0001
	Phenol + NH_4^+	0.0064	0.1624	0.1180	1.3798	0.9813	1.2154	<0.0001
Ternary	Phenol, NH_4^+, S^{2-}	0.004	0.1015	0.0829	1.233	0.9843	1.1801	<0.0001
	Phenol, NH_4^+, CN^-	0.0041	0.1040	0.0797	1.3041	0.9852	1.2297	<0.0001
	Phenol, CN^-, S^{2-}	0.0044	0.1117	0.0825	1.3532	0.9812	1.1636	<0.0001
Quaternary	Phenol, NH_4^+, S^{2-}, CN^-	0.0034	0.0863	0.070	1.238	0.9895	0.9878	<0.0001

oxygen demand due to reasons highlighted earlier. In such circumstances, it is expected that using COD as a parameter for describing kinetics of phenol oxidation during electrochemical to be erroneous. Similarly, in the presence of S^{2-}, CN^-, and NH_4^+ species in difference mix matrixes, the kinetics of phenol oxidation were investigated using both the COD and TOC decay data based on approach presented for phenol in single matrix (Section 3.1). The results for all the different mix matrixes investigated as plotted in Figs. 3 and 4 show that the best-fitted models for both TOC and COD were also consistently exponential in nature.

Meanwhile, Tables 2 and 3 present the kinetic parameters for the COD and TOC decay models, respectively. For both the COD and TOC models the k_{app} and $k_{m\text{-exp}}$ were found to be generally lower for the different matrixes compared with that of the single matrix (Table 1). It is apparent that the changes in the kinetic parameters as provided in Tables 2 and 3 suggest that the presence of the inorganic species in different matrixes influenced the kinetics of phenol oxidation at varying degree. Moreover, there was acceptable agreements of the COD models decay patterns with the experimental data based on the $k_{m\text{-model}}$ and $k_{m\text{-exp}}$, SEE (0.987–1.1374), R^2 (0.9691–0.9895), and p-values (<0.0001) were far less than 0.05 as given in Table 2. On the other hand, the TOC decay models were generally, in better agreements with the experimental data (R^2 = 0.9757–0.99880) compared with that of the COD. Furthermore, the SEE of the COD (Table 3) was more than threefold compared with that of TOC, indicating that the TOC is a better estimator of the experimental data. Nevertheless, in both cases, the agreement between $k_{m\text{-model}}$ and $k_{m\text{-exp}}$ in the case of the single matrix was better than that of the different mix matrixes.

Interestingly, for both the COD and TOC models' parameters, all the estimated α-values are greater than unity, while all the ICEs values are lesser than 100% (44.38–79.26) for the different mix matrixes (Fig. 2). Based on the delineated operating regimes of the CLM, this implies that the phenol oxidation process in the presence of the inorganic species is also under the mass transport limitation as in their absence. Currently, literature reviewed shows that TOC has not been reported to be used for modeling phenol oxidation kinetics using the CLM. However, the result presented herein clearly showed that TOC decay data accurately predicted the kinetics of electrochemical oxidation of aqueous phenol either in the absence or presence of oxygen demanding inorganic species. Similarly, statistical diagnostics indicated that the COD decay data effectively predicted the phenol oxidation kinetics both in the absence and presence of the

Table 3
TOC removal kinetics parameters for the different mix matrixes

Matrix	Component (s)	k_{app} min^{-1}	$k_{m\text{-exp}}$ cm/min	$k_{m\text{-model}}$ cm/min	α	R^2	STD error of estimate	p-value
Binary	Phenol + CN^-	0.0112	0.2842	0.2501	1.1409	0.9988	0.0761	<0.0001
	Phenol + S^{2-}	0.0076	0.1928	0.1383	1.3941	0.9925	0.2554	<0.0001
	Phenol + NH_4^+	0.0089	0.2258	0.1862	1.2187	0.9922	0.1879	<0.0001
Ternary	Phenol, NH_4^+, S^{2-}	0.0065	0.16497	0.1125	1.4568	0.9757	0.3084	<0.0001
	Phenol, NH_4^+, CN^-	0.0161	0.40863	0.321	1.2251	0.9911	0.2317	<0.0001
	Phenol, CN^-, S^{2-}	0.0144	0.36548	0.3341	1.1388	0.9964	0.1404	<0.0001
Quaternary	Phenol, NH_4, S^{2-}, CN^-	0.0111	0.28173	0.1988	1.4201	0.9756	0.3791	<0.0001

inorganic species. However, employing COD decay in the presence of the inorganic species exerting oxygen demand is bound to be erroneous due to the fact that the COD decay data are a combined attribute of oxidation of phenol as well as the inorganic species.

4. Conclusions

In the present study, the kinetics of electrochemical oxidation of phenol in synthetic wastewaters containing sulfide (S^{2-}), cyanide (CN^-), and ammonia (NH_4^+) species in single, binary, tertiary, and quaternary mix matrixes on BDD anodes using CLM. Considering that TOC is expected to adequately indicate organic compound oxidation regardless of the cohabiting inorganic species in solution, the TOC decay were also employed in the CLM modeling in addition to traditional COD decay data. For the different mix matrixes investigated, results showed that both TOC and COD decay data are consistently exponential in nature. All the developed TOC and COD kinetic models predicted well the experimental data based on the models statistical diagnostics. For all the different mix matrixes, the CLM α-values are greater than unity, while the ICEs values were less than 100%, accurately predicting that the oxidation processes were limited by mass transfer. These results establish the suitability of using TOC decay for CLM of phenol oxidation kinetics both in the presence and absence of the inorganic species. Based on these results in relation to the disparity between COD and TOC as parameters for evaluating phenol oxidation kinetics, it was concluded that, TOC data are more appropriate compared with COD data for kinetic study of electrochemical oxidations of phenol in wastewater containing inorganic species that exert oxygen demand.

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