



## Role of hydroxyl radical during electrolytic degradation of contaminants

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### ARTICLE INFO

#### Article history:

Received 8 October 2009  
Received in revised form 19 March 2010  
Accepted 10 May 2010  
Available online 16 May 2010

#### Keywords:

Naphthalene  
Competitors  
Scavengers  
Anodic oxidation  
Hydroxyl radical

### ABSTRACT

The role of hydroxyl radical is investigated in electrochemical oxidation of organic contaminants with naphthalene as a model compound. The strategy employed was competitive kinetic for hydroxyl radical between naphthalene and other hydroxyl scavengers if the hydroxyl radical is produced in situ at the anode by the electrolysis of water. Methanol, d3-methanol, acetone and d6-acetone were used as competitors for hydroxyl radical and their molar concentrations were calculated based on their reaction constants with hydroxyl radical. The hydroxyl radical was not responsible for naphthalene loss in these experiments. The first order reaction rate constants in the batch experiments containing only naphthalene, 2 mM of each of acetone and d6-acetone were 0.093, 0.094 and 0.118 h<sup>-1</sup>, respectively. Higher concentrations (4 mM) acetone and d6-acetone did not affect naphthalene degradation. Rate constants using methanol and d6-methanol as competitors for hydroxyl radical in batch degradations test were 0.128 and 0.099 h<sup>-1</sup>, respectively. Based on the naphthalene degradation trends and reaction rate constants, it was concluded that, under the given set of conditions, hydroxyl radical was not responsible for naphthalene degradation during electrolytic degradation tests. This research suggests that the role of hydroxyl radical should be considered very carefully in modeling such indirect electrolytic oxidation processes.

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### 1. Introduction

Electrochemical oxidation is a powerful tool for the treatment and purification of a variety of organics present in the liquid waste. The technique has been successfully used for the treatment of domestic sewage [1], landfill leachate [2], removal of organic pollutants from industrial wastewater [3], purification of phenolic wastewater [4] and treatment of wastewater containing cyanides [5]. Electrolytic degradation of contaminants can occur either by direct oxidation or by indirect oxidation [6]. Indirect oxidation of contaminants occurs by an oxidant produced in situ at any of the electrode surfaces during electrolysis of water, whereas the direct electrochemical oxidation is a result of electron transfer between the electrode surface and the substrate (contaminant). The scheme for these possible pathways is presented in Fig. 1.

Hydroxyl radical is frequently considered as one of the possible reasons contributing to contaminant loss in many of the studies aimed at indirect electrochemical oxidation of contaminant [7–12]. These researchers have hypothesized that hydroxyl radical can be produced by chemical oxidation of water and/or by direct oxidation

of hydroxyl ions.



Amadelli et al. [13] observed the degradation of trans-3,4-dihydroxycinnamic acid at PbO<sub>2</sub> electrodes during electrolysis. By observing variations of the electrode potentials for repeated chronopotentiometric measurements, they concluded that the hydroxyl radical was responsible for the loss of the contaminant. Panniza and Cerisola [3] tested the effect on anode material on the electrochemical degradation of 2-naphthol and, using cyclic voltammetry, attributed the degradation to hydroxyl radicals produced at the anode. Most recently, we tested different mechanisms of contaminant loss during electrolytic oxidation with naphthalene as a model compound [7]. Among many side reactions tested in lab scale 500 ml batch reactors with naphthalene as a model contaminant, direct anodic oxidation of naphthalene was also tested at pH 4 and pH 7. Naphthalene disappearance was attributed to the oxidation either directly at the anode or through the involvement of hydroxyl radicals formed in situ.

Despite numerous studies on the direct electrochemical degradation of chemicals, the role of hydroxyl radical during electrolytic degradation is still not well understood. Researchers have typically assigned the cause of contaminant degradation to the indirect oxidation by in situ formed hydroxyl radical based on the intermediates formed during in situ tests. Generically, the discovery of

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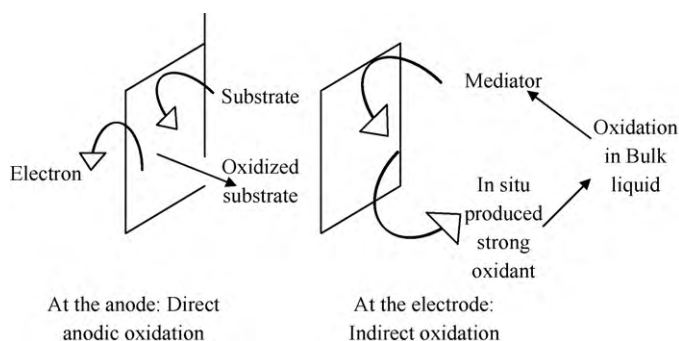


Fig. 1. Hypothetical model showing direct and indirect electrochemical oxidations.

hydroxylated products (e.g., hydroxylated aromatics) is often cited as evidence that the hydroxyl radical is present during a process. In fact, this kind of circumstantial evidence is quite weak as any number of potential oxidation processes can generate hydroxylated products in aqueous solution.

In this research, we present results of our systematic approach to evaluate the role of hydroxyl radical during electrolytic degradation of organics. The competitive kinetic approach was used to evaluate the role of hydroxyl radicals in electrolytic experiments. The approach adopted here is similar to Goel et al. [7] except that the batch reactors contained different hydroxyl radical scavengers in addition to naphthalene. The underlying hypothesis for this research is that relatively less naphthalene degradation will occur in batch experiments containing hydroxyl radical competitors than in the batch tests not containing the competitors.

## 2. Materials and methods

### 2.1. Preparation of the reagents

Naphthalene (Fisher Scientific, Fairlawn, NJ) was added to the deionized water and stirred for 12–14 h to prepare a saturated solution of naphthalene. This stock solution was filtered and diluted to the desired concentration (10 mg/l) with deionized water. 1.42 g/l of sodium sulfate (Fisher Scientific, Fair Lawn, NJ), was added as an electrolyte to make a 0.01 M  $\text{SO}_4^{2-}$  solution. All the tests were performed at a pH of  $7 \pm 0.2$ . The pH was adjusted using either 0.1(N)  $\text{H}_2\text{SO}_4$  or 0.25N NaOH.

### 2.2. Electrolytic reactor assembly and electrolysis experiments

The electrode assembly in the present study was identical to the assembly used by Goel et al. [7]. Briefly, the electrode assembly consisted of a stainless steel plate cathode (Type 304, #3 polish, 0.07 cm thickness (Metal Supermarket, Columbia, SC) and a titanium anode with a mixed metal oxide coating (Type EC-600, 0.15 cm. thick, mesh anode (Eltec Systems Corp., Chardon, OH)) held together by nylon screws. The electrodes were 3.18 cm  $\times$  6.35 cm separated by a distance of 1.4 cm. Titanium screws and nuts were used as the current collector on both the anode and the cathode to minimize the reactivity of the current collectors and to reduce the possibility of corrosion. The current collectors on the cathode and anode were connected to copper wires, which were connected directly to a power supply unit (HP Model E3612A, Agilent Technologies, Inc., Englewood, CO). The connection between the copper wires and titanium screws at the cathode and anode were sealed using a fast drying epoxy and coated with a silicon sealant.

The reactor vessels used for these experiments were 500 ml amber-colored bottles. Holes were drilled through the caps to run the wires connected to the electrode assembly. The gap between the copper wires running through the cap was sealed with an epoxy

Table 1  
Different hydroxyl radical competitors and their concentrations.

Species	Rate constant	% of $\cdot\text{OH}^a$	Conc. (mM)
Naphthalene	$5 \times 10^9$ [14]	Varies	0.078
Acetone	$1.1 \times 10^8$ [15]	36%	2
d6-Acetone	$2.5 \times 10^7$ [16]	11%	2
Acetone	$1.1 \times 10^8$	53%	4
d6-Acetone	$2.5 \times 10^7$	21%	4
Methanol	$9.7 \times 10^8$ [17]	38%	0.24
d3-Methanol	$4.3 \times 10^8$ [18]	21%	0.24

<sup>a</sup> Percentage of in situ produced hydroxyl radical (pre-assumed to react with the corresponding chemical species).

sealant. One 1/2 mm hole was drilled on the cap of all the bottles, including the experimental control, to keep the system under atmospheric pressure. Five hundred milliliters of test solution was transferred to separate 500 ml amber-colored bottles. Naphthalene degradation experiments were carried out in the presence of different hydroxyl radical competitors. Table 1 shows the scavengers and their concentration used. The corresponding references for the source of each rate constant in Table 1 are also included in this table. In each set of experiments, a control reactor bottle was also run to take into account the naphthalene loss due to volatilisation. The control reactor bottle contained an electrode assembly but without an active current. The contents of the bottles were stirred continuously using a magnetic stirrer bar and plate. Samples were withdrawn periodically from the bottles by opening the cap. All experiments were conducted as an electric current of 50 mA. With the electrode surface area of 21.7 cm<sup>2</sup>, the corresponding current density was 2.3 mA cm<sup>-2</sup>. The cell voltage was in the range of 3.1–3.3 V.

### 2.3. Analysis method

Naphthalene was quantified using a Varian Model 3380 gas chromatograph equipped with a flame ionization detector, Chrompack capillary column (Select 624 CB  $D_f$  1.8  $\mu\text{m}$ , FS 30 m  $\times$  0.32 mm ID), and an auto-sampler with a 100  $\mu\text{m}$  PDMS coated SPME fiber assembly (Supelco, Bellefonte, PA). The sample adsorption time with the SPME fiber was 10 min in agitate mode and the desorption time was 2 min followed by a 1 min waiting period. The analysis was performed in splitless mode with an injection temperature of 250  $^\circ\text{C}$ , isothermal oven temperature of 180  $^\circ\text{C}$ , and detector temperature of 275  $^\circ\text{C}$ .

## 3. Results and discussion

### 3.1. Theoretical approach

Before the onset of batch experiments, the concentrations of different hydroxyl radical competitors (scavengers) used in this study were pre-calculated based on the model given by Eq. (3):

$$X_i = \frac{[M_i] \times {}^{\text{OH}}R_i}{[M_i] \times {}^{\text{OH}}R_i + [M_{\text{naph}}] \times {}^{\text{OH}}R_{\text{naph}}} \quad (3)$$

where  $X_i$  is the fraction of hydroxyl radical which will react with  $i$ th hydroxyl radical scavenger in the solution,  $M_i$  is the molar concentration of the scavenger present with naphthalene in bulk solution,  ${}^{\text{OH}}R_i$  is the rate constant of this scavenger with hydroxyl radical,  $M_{\text{naph}}$  and  ${}^{\text{OH}}R_{\text{naph}}$  are molar concentration of and rate constant of naphthalene with hydroxyl radical respectively. Eq. (3) is generalized for two chemical species (naphthalene and one hydroxyl radical scavenger) present in the bulk solution and both competing for hydroxyl radical. However, the model can be easily expanded for more than two species. Eq. (3) is suitable to estimate the partitioning of hydroxyl radical based on the competitive kinetics. Similar

approach was used by Naito et al. [19] for evaluating the scavenging effect of Rebamipide and other related compounds on in situ generated hydroxyl radical.

The model described by Eq. (3) requires molar concentrations of each of the chemical species present in the test solution and their respective rate constants with hydroxyl radical. The rate constants of different hydroxyl scavengers used in this study and naphthalene were obtained from the available literature [14–18,20] and are given in Table 1. However, to get an initial estimate of the concentrations of different scavengers to be used in the experiments, each scavenger was assumed to consume a certain percentage of hydroxyl radical. The pre-assigned percentages are also given in Table 1 along with the calculated (using model given by Eq. (3)) concentration of each scavenger. The concentration of naphthalene used in these experiments was same as that used by Goel et al. [7].

In two separate experiments, different concentrations of acetone and d6-acetone were used as hydroxyl radical competitors. In the third batch experiment, methanol and d3-methanol as hydroxyl radical scavenger were used. All these different scavengers have very good affinity for hydroxyl radical, as reflected by their respective rate constants with hydroxyl radicals (Table 1) and would compete with another chemical (naphthalene in this case) separately for hydroxyl radical depending upon their rate constants and their molar ratio with naphthalene. The same concept was used in this research to evaluate the involvement of hydroxyl radical if produced in situ at the anode during the direct electrolysis of water. The motivation behind these experiments originated from our earlier research with direct electrochemical degradation of naphthalene in which case about 40–60% naphthalene degradation was noticed [7]. Furthermore, the naphthalene degradation was independent of the system pH (pH 4 or 7) and applied electric intensity and hence the present experiments were performed at the neutral pH and at a constant current intensity of 5 mA/cm<sup>2</sup> (50 mA).

### 3.2. Competitive reaction with hydroxyl radicals between naphthalene (0.078 mM), acetone (2 mM) and d6-acetone (2 mM)

Fig. 2 shows result of batch degradation experiments with acetone and d6-acetone as hydroxyl competitors. Disappearance in the naphthalene in the blank (black dots) shows the effect of volatilization due to gas bubbles generated at the anode and the cathode. The batch containing only naphthalene solution (no competitor) with active electrode assembly showed about 54% naphthalene degradation, whereas the other two batches containing naphthalene with 2 mM acetone and d6-acetone showed 52 and 62% naphthalene loss, respectively. All batches had same initial naphthalene concentration. From Fig. 2, it is obvious that naphthalene degradation rates are insensitive to the presence of acetone and d6-acetone. These results indicate that the presence of these hydroxyl competitors did not affect the naphthalene degradation. In other words, the naphthalene degradation was possibly not hydroxyl radical mediated.

Based on the model presented by Eq. (3) and the rate constants and concentrations of acetone and d6-acetone present in the bulk solution in the respective batch, about 36 and 11% (Table 1) of total

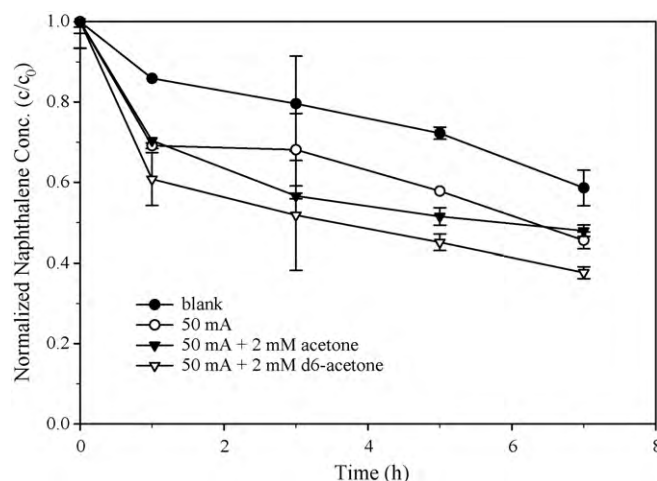


Fig. 2. Electrolytic naphthalene degradation in presence of 2 mM of each of acetone and d6-acetone, respectively.

in situ produced hydroxyl radical should have reacted with acetone and d6-acetone, respectively. This implies that, batch containing acetone with naphthalene should show least naphthalene degradation and the maximum naphthalene degradation should occur in the batch which had only naphthalene solution with no hydroxyl competitor. The naphthalene disappearance first order rate constants for batches containing naphthalene alone, naphthalene plus each of acetone and d6-acetone were calculated to be 0.093, 0.094 and 0.118 h<sup>-1</sup> (Table 2), respectively, which also confirms that the naphthalene disappearance was fast in the batch which contained naphthalene with acetone and does not follow our initial hypothesis about hydroxyl radical competition.

### 3.3. Competitive reaction with hydroxyl radicals between naphthalene and higher concentrations of acetone and d6-acetone

In the first set, the presence of acetone and d6-acetone at 2 mM concentrations did not affect the naphthalene degradation. In the second set of experiment, higher concentrations (4 mM) of acetone and d6-acetone were employed.

Fig. 3 shows naphthalene degradation profiles under different tested conditions at higher concentrations of acetone and d6-acetone. The trend of the curves corresponding to different experimental conditions looks similar to the ones when 2 mM concentration of each of acetone and d6-acetone were used as hydroxyl radical competitors with naphthalene. In this case, the respective rate constants for batches run at 50 mA current and containing naphthalene alone, naphthalene plus 4 mM acetone and naphthalene plus 4 mM d6-acetone were calculated to be 0.093, 0.094 and 0.112 h<sup>-1</sup> (Table 2), respectively, which again disproves our earlier assumption about consumption of hydroxyl radical by these competitors (acetone and d6-acetone) and eventually resulting in less naphthalene degradation in the batches where

Table 2  
First order rate constants of naphthalene with hydroxyl radical under different conditions.

Condition	Naphthalene concentration (mM)	Hydroxyl radical competitor	Rate constant (h <sup>-1</sup> )
Blank	0.078	None	0.072
50 mA	0.078	None	0.093
50 mA	0.078	2 mM acetone	0.094
50 mA	0.078	4 mM acetone	0.094
50 mA	0.078	2 mM d6-acetone	0.118
50 mA	0.078	4 mM d6-acetone	0.112
50 mA	0.078	0.24 mM methanol	0.128
50 mA	0.078	0.24 mM d3-methanol	0.099

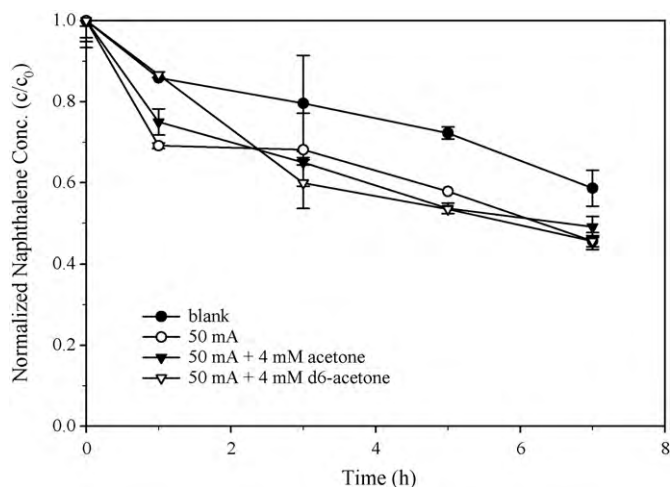


Fig. 3. Electrolytic naphthalene degradation in presence of 4 mM of each of acetone and d6-acetone, respectively.

these competitors were present with naphthalene at 50 mA current. These results suggest the absence of hydroxyl radical in these experiments.

#### 3.4. Competitive reaction with hydroxyl radicals between naphthalene, methanol (0.24 mM) and d3-methanol (0.24 mM)

In our last attempt, we used methanol and d3-methanol, which have higher rate constants for hydroxyl radical than acetone and d6-acetone. Fig. 4 shows results of these experiments. In calculating the concentrations of methanol and d3-methanol, it was assumed that about 38 and 21% of the hydroxyl radical produced (if any) in situ will be consumed by methanol and d3-methanol, respectively, which means that the naphthalene in batches containing methanol and d3-methanol, will undergo approximately 38 and 21% less degradation, respectively. In all these calculations, it is assumed that 100% of in situ produced hydroxyl radical was consumed by the chemical species present in the solution. The respective first order rate constants for naphthalene disappearance were 0.093, 0.128 and 0.099  $\text{h}^{-1}$  (Table 2), respectively, for no competitor containing batch, batch containing methanol and d3-methanol. These rate constants are in close proximity to those obtained for acetone and d6-acetone at different concentrations and demonstrates that, in the present experiment scenario using

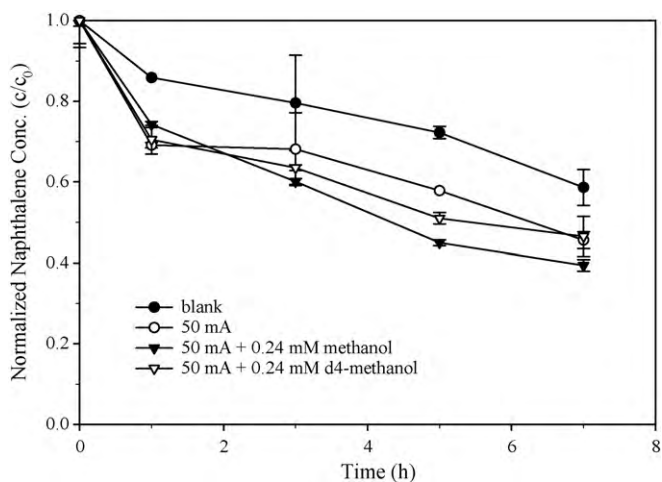


Fig. 4. Electrolytic naphthalene degradation in presence of 0.24 mM of each of methanol and d3-methanol, respectively.

the specified electrodes, naphthalene degradation was not due to hydroxyl radical.

#### 4. Conclusions

Indirect electrochemical degradation of contaminants is possible at the anode with a suitable electrode assembly. However, the mechanisms behind indirect degradation should be considered very carefully especially when in situ produced hydroxyl radical at the anode is held responsible in these reactions. This research presents a concise but very useful methodology for evaluating the role of hydroxyl radical in indirect electrolytic degradation.

The experiments of electrolytic naphthalene degradation in the presence of different hydroxyl radical competitors strongly indicate the absence of hydroxyl radical using the given set of electrodes. Present experimental results suggest that the naphthalene loss occurred as a result of direct electron transfer at the anode as indicated by the hypothetical scenario (direct oxidation) in Fig. 1. The findings are very important especially when hydroxyl radical is considered to be an important species causing indirect oxidation in electrochemical oxidation. The approach adopted in this research can also be used in determining the percentage of hydroxyl radical going to a particular chemical species in the hydroxyl radical mediated oxidation reactions, for example Fenton's type. In fact this approach can successfully be applied in modeling hydroxyl radical mediated advanced oxidation processes.

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