Indirect Electrochemical Treatment of Bisphenol A in Water via Electrochemically Generated Fenton's Reagent

B E L G İ N   G Ö Z M E N , [†]
M E H M E T   A .   O T U R A N , [‡]
N İ H A L   O T U R A N , [‡]   A N D
O K T A Y   E R B A T U R * , [†]

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Bisphenol A (BPA) has been treated with electrochemically generated Fenton's reagent in aqueous medium. Hydroxyl radicals that were formed in Fenton's reagent reacted with the organic substrate producing two different isomers of monohydroxylated product and, upon successive hydroxylation, mainly one dihydroxylated product. Further hydroxylation first degraded one of the aromatic rings, and the side chain thus formed was then cleaved off the other aromatic ring. The second aromatic ring was also degraded upon successive hydroxylations. Small saturated and unsaturated aliphatic acids were the last products prior to mineralization. It was found that use of cuprous/cupric ion pair resulted a faster conversion of BPA and faster mineralization when compared using ferrous/ferric ions, but this happened at the expence of excess electrical charge utilized for an equivalent conversion or mineralization. Degradation by using ferrous/ferric ions was more efficient than cuprous/cupric ions case in terms of total mineralization versus charge utilized, and a mineralization of 82% had been achieved by applying 107.8 mF of charge to a 0.7 mM BPA solution of 0.200 dm^3. The rate constant of the monohydroxylation of BPA in the presence of ferrous/ferric ions had been determined as 1.0×10^{10} M^{-1} s^{-1} where BPA and salicylic acid competitively reacted with hydroxyl radicals in aqueous medium with the initial concentrations of Fe^{2+}, BPA, and SA of 1.0, 0.5, and 0.5 mM, respectively. In a similar experiment where the initial concentrations of Cu^{2+}, BPA, and SA were 1.0, 0.5, and 0.5 mM, respectively, the corresponding rate constant was determined to be the same as the rate constant obtained for Fe^{2+} (i.e., 1.0×10^{10} M^{-1} s^{-1}). While the use of Cu^{2+} cannot be advised for processing BPA and similar substrates by using the electro-Fenton technique for both technical and economical reasons, the use of [Fe^{2+}]/[BPA]$_0$ values in the range 3−4 will be sufficient to achieve an efficient mineralization of BPA and similar substrates by the electro-Fenton process in aqueous medium.

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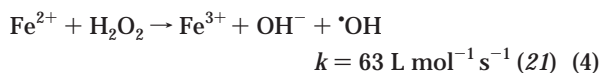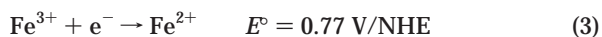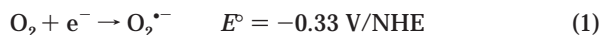[†] Çukurova University.
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Introduction

Phenols are among TBP class chemicals (i.e., they are toxic, bioaccumulative, and persistent in environmental matrixes). Bisphenol A (BPA) is one of these phenols that is frequently encountered in wastewaters and in surface waters. The systematic name of this compound is 2,2-bis-(4-hydroxyphenyl)propane. It is the monomer of certain polymers and finds wide application in polymer industry. In addition to being used as monomers for the production of polycarbonates, epoxide phenol resins, etc., it is also utilized as antioxidant in softeners, fungicides, and similar products (*1, 2*). BPA, like some other alkyl phenols (e.g., nonyl phenol), can act like estrogens, altering cell molecular structure and biochemistry. For example, metabolic activation of BPA leads to DNA binding (*3*). Epoxy resins used for the renovation of water pipes are based on bisphenol A diglycidyl ether or a mixture of BPA and diglycidyl ether. Residues of this compound in water appear to be due to incomplete polymerization (*4*). Matsumoto et al. (*5*) and Matsumoto (*6*) determined BPA in surface waters contaminated with industrial wastewater discharges.

Different processes have been applied for removal of BPA from wastewaters (*7, 8*). Biological treatment processes are not effective enough for degradating compounds such as BPA. On the other hand, the use of conventional oxidative chemicals may create additional pollution due to the discharge of excess chemicals and/or their toxic byproducts. Instead of these conventional chemical techniques, the use of oxidative or reductive electrochemical techniques seems to be more promising (*9−13*). The main advantage in using these electrochemical techniques is that reactive chemicals in bulk quantities are not being used, instead the degradation of the organic toxic substrate is being initiated by electron transfers on the surface of electrodes. In these techniques, electricity as a clean energy source is being used; therefore, the total process does not create additional pollution due to the discharge of various reactive chemicals used in the process or of their toxic byproducts.

Boscoletto et al. (*15*) and Kuramitz and co-workers (*14*) applied direct electrochemical treatment to BPA-containing wastewater. Boscoletto et al. have determined many products (28 total) among which some of the aromatics and quinone types are also resistant to electrochemical oxidation (*15*). Kuramitz and co-workers observed the formation of an electopolymerized film of BPA on carbon electrode, which led to its inactivation (*14*).

In this work, we have used an indirect electrochemical method for treating BPA in aqueous medium. The technique uses the Fenton reaction (*16*) as the source of hydroxyl radicals in which the Fenton reagent is produced electrochemically and regenerated throughout the process (*17−20*). In cathode compartment, the main reactions toward the formation of hydroxyl radical (•OH) are

$$O_2 + e^- \rightarrow O_2^{\bullet-} \qquad E° = -0.33 \text{ V/NHE} \tag{1}$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad E° = 0.695 \text{ V/NHE} \tag{2}$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad E° = 0.77 \text{ V/NHE} \tag{3}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH$$
$$k = 63 \text{ L mol}^{-1} \text{ s}^{-1} \text{ } (21) \tag{4}$$

whereas in anodic part oxygen evolves due to the decom-

position of water:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad E^\circ = 1.23 \text{ V/NHE} \qquad (5)$$

The possibility of degrading and even mineralizing refractory organic compounds in aqueous medium by using Fenton reagent attracted considerable attention. Many papers have been published relevant to the treatment of such refractory organics by using classical Fenton reagent or by using electro- or photoinduced Fenton processes (20–28).

The aim of this work is to investigate the mechanism and the kinetics of BPA conversion and further degradation of the products under electro-Fenton conditions and also to determine the efficiency of the electrochemically induced Fenton medium to oxidize and finally mineralize BPA in aqueous medium (which has not been done before) and compare the results with those of direct electrochemical oxidation and other methods.

Experimental Section

Mohr salt $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$, $CuSO_4 \cdot 5H_2O$, and Nafion 117 were bought from Aldrich. Graphite felt (RVG 2000) was from Carbone Loraine. Pure oxygen gas (99.99%) has been bought from different companies.

Electrolytic experiments were conducted in a 0.300 dm³ glass reactor. The platinum gauze anode was separated from the cathode part by using Nafion 117 membrane. The carbon felt (3 × 5 cm) was used as the working electrode (cathode). Saturated calomel electrode was used throughout the electrolytic experiments as the reference electrode. Controlled potential electrolysis and coulometric measurements were performed by an EG&G Par model 273A electrochemical system. In a typical electrolytic experiment, following the addition of the appropriate amounts of the organic substrate (BPA) and the metal salt into a 0.01 M HCl aqueous solution, O_2 gas was bubbled through the solution for 20 min and then −0.55 V/SCE constant cathodic potential was applied to the system while O_2 gas bubbling was continued throughout the electrolysis. Predetermined amounts of aliquots were withdrawn from the system at certain time intervals or at certain Coulombic charge passages. Each aliquot of solution that was withdrawn from the system had been injected immediately into HPLC or kept in vials at 0–5 °C. Some of the aliquots were silylated for GC−MS analysis.

High-performance liquid chromatograph (HPLC; a Gilson instrument having double pumps, UV−visible detector, and pressure regulating and mixing units and connected to a data processing unit controlled by Dynamax program) and an HPLC coupled with mass spectrometer (LC−MS; LC Waters made coupled to an MS of Vacuum Generators with a particle beam interface) were used. HPLC analysis were performed on Hypersil C18 columns (4.6 mm × 250 mm and 3.9 mm × 150 mm of 5 μm and 100 A each). Composition of the mobile phases were 52/46/2 methanol/water/glacial acetic acid and 40/60 acetonitrile/water. The UV detector was set at 280 nm, and the flow rate of the mobile phase was 0.5 mL/min. In LC−MS, applications of both chemical ionization with NH_3 and electron ionization (EI) with 42 eV were applied.

Since the qualitative analysis of the oxidation products were so complex, a gas chromatograph coupled with a mass selective detector (HP 5890 GC coupled to HP 5871 MSD) was also used for analyzing the silylated samples by using the standard EI of 70 eV. The GC capillary column of length 30 m with a 50% methyl/50% phenyl siloxane stationary phase was used in GC−MS applications. The initial temperature of the column oven was 40 °C and following a 5 min hold at this temperature had been increased up to 280 °C with a heating rate of 6 °C min^{-1}. Injection and detector port temperatures were 270 and 280 °C, respectively.

In some electro-Fenton applications, a 20-mL aliquot of solution withdrawn from the reactor has been successively extracted (four times) by using 5 mL of diethyl ether at each step. The combined organic phase was concentrated to 1 mL under reduced pressure at ambient temperature. This concentrated solution was treated with 0.8 mL of BSTFA [N,O-bis(trimethylsilyl)trifluoroacetamide] and 0,7 mL of aceto-nitrile. The solution was refluxed in a micro apparatus at 90 °C for 1 h. These silylated solutions were subjected to GC−MS analysis.
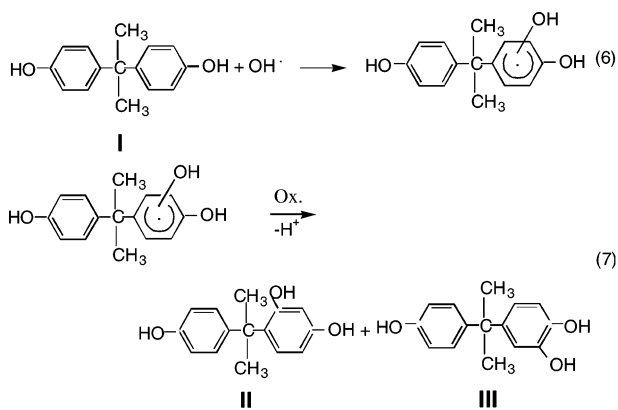
Total organic carbon (TOC) contents of the aqueous aliquots withdrawn from the reactor at certain time intervals were also determined by using a Tekmar Dohrmann Apollo 9000 instrument. In a typical application, an aliquot of 11 mL was withdrawn from the reactor and filtered through glass frit to get rid of carbon contamination from the carbon felt used as electrode in the reactor. The sample was ignited at 700 °C on platinum-based catalyst, and the carbon dioxide formed was swept by pure oxygen as the carrier gas through a nondispersive infrared (NDIR) dedector.

Identification of the products of electro-Fenton treatment of BPA was done by making use of the HPLC retention times of the standart samples wherever applicable, and these results were confirmed by LC−MS and GC−MS results. Those that cannot be determined by using HPLC retention times were directly deduced from mass spectra obtained from LC−MS and/or GC−MS applications. The degree of mineralization throughout the electrolytic treatments was determined by measuring the total organic carbon (TOC) contents.

Results and Discussion

Explanations Regarding Terminology. Throughout this paper, the term conversion of BPA will be used for mono-hydroxylation of the aromatic ring, whereas degradation will be used for the destruction of the molecular skeleton of the products (e.g., cleavage of the isopropylidene bridge, destruction of the aromatic rings, and further destruction of the intermediate products up to mineralization stage). Since BPA itself has two hydroxyl groups, one on each aromatic ring, the monohydroxylated product will contain three hydroxyl groups and the dihydroxylated product will contain four hydroxyl groups. Meta-monohydroxylated product and ortho-monohydroxylated product will mean that the incoming hydroxyl group will bind to the meta or ortho positions with respect to the hydroxyl group already present.

Analysis of Products Formed throughout electro-Fenton Treatment of BPA. It has been well-documented that compounds having aromatic rings are attacked by hydroxyl radicals forming an intermediate cyclohexadienyl radical (29–32) and that, in the presence of oxidizing agents such as O_2, Fe^{3+}, or Cu^{2+}, this cyclohexadienyl radical is rapidly oxidized to the hydroxylated derivatives (17, 18, 20). Thus, in the case of BPA the following reactions are expected to take place initially:

	mass/relative abundance of predominant ions										
	1	2	3	4	5	6	7	8	others	M⁺	product id
I	213/100	228/43	119/31	214/29	91/16	135/08	229/08	101/07	65/06, 197/05	228/43	BPA
II	229/100	244/35	230/16	213/13	135/09	91/07	245/06	121/05	69/05, 83/04	244/35	m-hyd BPA[b]
III	229/100	244/44	230/21	119/20	135/12	91/08	213/06	107/05	77/04, 185/04	244/44	o-hyd BPA[c]
IV	86/100	245/81	110/40	135/32	101/20	150/17	77/8	213/7	- -	260/30	dihydbpa[d]

[a] 42 eV EI were applied in MS. [b] 2-(4-Hydroxyphenyl)-2-(2′,4′-dihydroxyphenyl)propane. [c] 2-(4-Hydroxyphenyl)-2-(3′,4′-dihydroxyphenyl)propane. [d] 2-(4-Hydroxyphenyl)-2-(2′,4′,5′-trihydroxyphenyl)propane.

A series of HPLC chromatograms obtained from aliquots of samples withdrawn from the reactor during electro-Fenton treatment of a BPA solution are given in Figure 1.

Since the HPLC column used was nonpolar (reverse phase) and the mobile phase is polar, the most polar products reached the detector first, and then the others were eluted in the order depending on their polarity. BPA eluted last in this application (i.e., the peak labeled with **I** belongs to BPA). The peaks labeled with **II** and **III** correspond to meta- and ortho- (with respect to the hydroxyl group present on the ring) monohydroxylated BPA products, respectively. Peak labeled with **IV** corresponds to the dihydroxylated BPA product:

IV
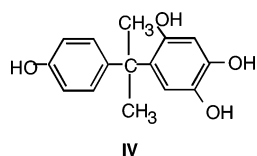
The mass spectral data of these compounds (**I**−**IV**) are summarized in Table 1.

A detailed discussion on the positions of hydroxyl groups and the possibility of mass spectra to belong to some other products is as follows:

The following compound also has a molecular mass of 244, and such a structure may be a reasonable candidate instead of the monohydroxylated BPA products having M^+ 244:

V
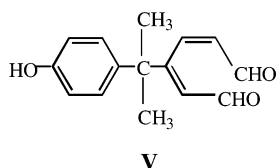
If this is the case, we should expect a strong peak at 215 due to the loss of -CHO, but no such peak appears in the corresponding mass spectrum. The mass spectrum has appropriate m/e peaks, which would be expected from a monohydroxylated BPA product (Table 1), and thus we conclude that peaks labeled with **II** and **III** correspond to the meta- and ortho-monohydroxylated products. The attack of the hydroxyl radical on the aromatic ring normally prefers the π-electron-rich position. Therefore, the major product among the two monohydroxylated products should have the incoming hydroxyl group in ortho position to one of the existing hydroxyl groups because the para position has already been occupied by the isopropylidene bridge connecting the aromatic rings. Thus, peak no **III** should correspond to the ortho (i.e., the abundant mono-hydroxylated product and peak **II** should belong to the meta-hydroxylated derivative of BPA).
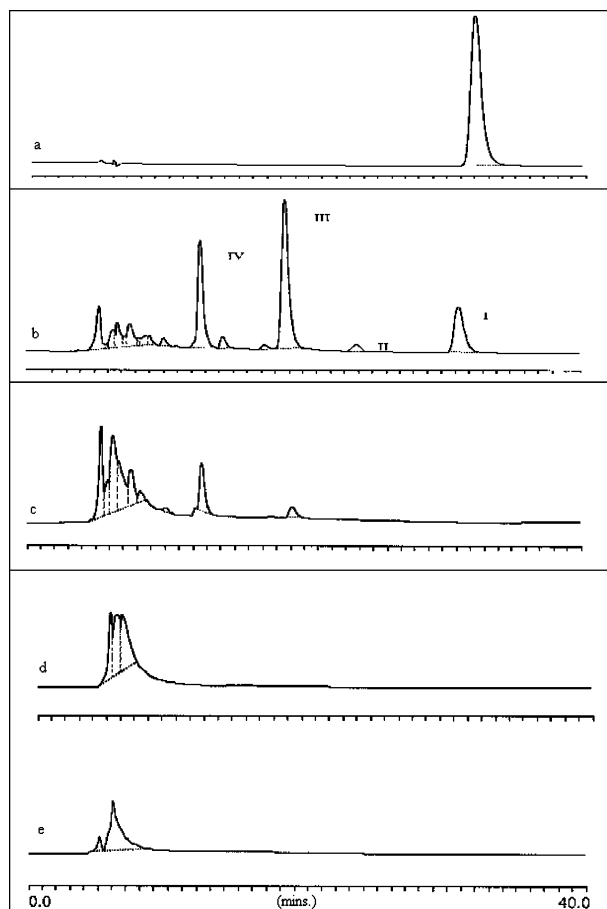
FIGURE 1. Evolution of HPLC chromatograms as a function of electrical charge (C) utilized during electro-Fenton treatment of an aqueous BPA solution: (a) 0 C, (b) 1.036 mF, (c) 2.073 mF, (d) 5.182 mF, and (e) 10.364 mF. $[BPA]_0 = 0.2$ mM, $[Fe^{2+}]/[BPA]_0 = 5.0$, V = 0.125 dm³.

There is also a probable candidate for the M^+ 260 compound in addition to the dihydroxylated derivative of BPA:

VI
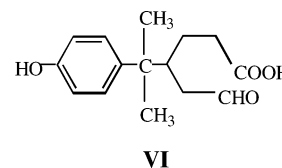
If this is the case, then peaks at 231 and 215 due to the loss of -CHO and -COOH groups should be observed in the corresponding mass spectrum, but none of these peaks can be observed. The peaks in this mass spectrum (Table 1) are also in aggreement with what can be expected from a dihydroxylated BPA structure. The m/e peak at 135 (third
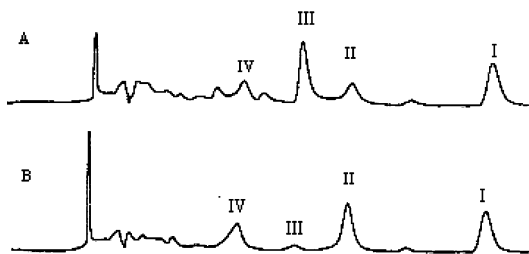
FIGURE 2. HPLC chromatograms obtained following 2.073 mF of charge applied to the 0.200 dm³ BPA solutions. $[BPA]_0 = 0.7$ mM in both solutions and $[Fe^{2+}]/[BPA]_0 = 4.28$ for panel A and $[Cu^{2+}]/[BPA]_0 = 4.28$ for panel B. **I**, BPA; **II**, meta-hydroxylated BPA; **III**, ortho-hydroxylated BPA; **IV**, dihydroxylated BPA.

most abundant) indicates that one of the aromatic rings should only have one hydroxyl group on it (i.e., the major product in this case should certainly have the three hydroxyl groups on the other aromatic ring). The most probable structure might be 2-(4-hydroxyphenyl)-2-(2′,4′,5′-trihydroxyphenyl)propane (**IV**).

The reason for this assumption is that while the 2′ position is para to the existing hydroxyl group and ortho to the isopropylidene group, the 3′ position will be meta to both existing hydroxyl and isopropylidene groups, thus the 2′ position with its relatively high π-electron density will be more amenable to the hydroxyl radical attack. A negligible attack of hydroxyl radical toward 3′ position could be possible, but the three adjacent hydroxyl groups on the aromatic ring would render it highly unstable under the reaction conditions; therefore, no other dihydroxylated BPA product was observed.

A product with M^+ 276 has also been detected. Molecular mass of 276 corresponds to trihydroxylated derivative of BPA, but a close look at the mass spectrum indicates the presence of ketone carbonyls and -CH₂ groups in the structure of the corresponding compound. The mass spectrum also has peaks with masses of 79, 91, and 135, which indicates that one of the aromatic rings and the linking isopropylidene bridge are preserved. Thus, one can conclude that one of the aromatic rings of BPA is opened by the attack of hydroxyl radicals, but the exact structure of the compound cannot be precised by investigating the corresponding mass spectrum only.

The absence of three hydroxylated derivatives of BPA (compound having five hydroxyl groups on the aromatic rings) indicates that such products either react very fast with a fourth hydroxyl group and degradation of the aromatic ring occurs or that attack of the third hydroxyl group on the aromatic ring already destabilizes the system under the reactive conditions and results in degradation of the aromatic ring.

Three small peaks in the total ionization chromatogram with M^+ 232 (probable) are observed. There are many candidates for these M^+ 232 peaks in which one of the aromatic rings is opened and having hydroxyl, aldehyde, and/or carboxyl groups on the open chain part of the structure, but it is not possible to specify which is which. A group of small overlapping peaks eluting in the first group in HPLC analysis with very short retention times are the most polar products including those still having one aromatic ring and some aliphatic acids. Compounds such as catechol, hydroquinone, benzoquinone, resorcinol, 4-hydroxymandelic acid, 4-hydroxybenzoic acid, 2-butenedionic acid, 4-oxobutenoic acid, acetic acid, and formic acid which are determined via HPLC and/or GC−MS are the ones in this overlapping region in the HPLC chromatogram. Complexes of these polar compounds with Fe^{2+} are also eluted fast and appear in this overlapping region in the HPLC chromatogram.

Table 2 summarizes the products that were identified in electro-Fenton-treated BPA solution. The presence of hydroquinone (or 1,4-dihydroxybenzene) might be an indica-
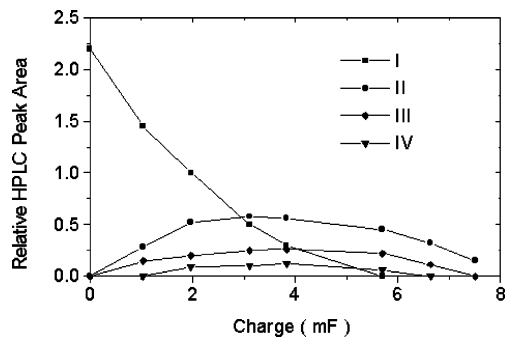

FIGURE 3. Concentration change of BPA and its hydroxylated products as a function of charge during an electro-Fenton treatment. $[BPA]_0 = 0.7$ mM, $[Fe^{2+}]/[BPA] = 4.28$, $V = 0.200$ dm³. **I**, BPA; **II**, meta-hydroxylated BPA; **III**, ortho-hydroxylated BPA; **IV**, dihydroxylated BPA.
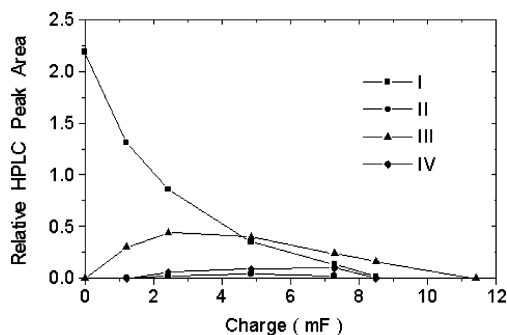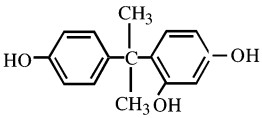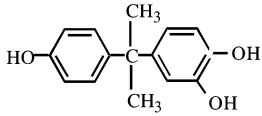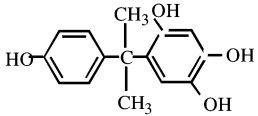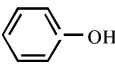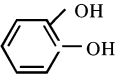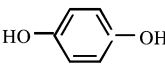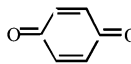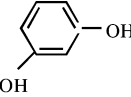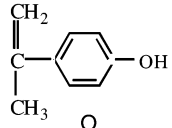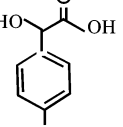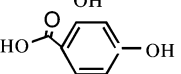

FIGURE 4. Concentration change of BPA and its hydroxylated products as a function of charge during an electro-Fenton treatment. $[BPA]_0 = 0.7$ mM, $[Cu^{2+}]/[BPA] = 4.28$, $V = 0.200$ dm³. **I**, BPA; **II**, meta-hydroxylated BPA; **III**, ortho-hydroxylated BPA; **IV**, dihydroxylated BPA.

tion of the attack of hydroxyl radical to the ipso position of the aromatic ring. The presence of other dihydroxybenzenes and the compounds 4-hydroxymandelic acid and 4-hydroxybenzoic acid point to the fact that isopropylidene bridge linking the aromatic units is also under attack by hydroxyl radicals.

Effect of Different Metal Ions on the Efficiency of BPA Conversion. Since Fe^{3+} or other replacement metal ions are reduced to lower oxidation state continually throughout the electrochemical treatment, they act as catalysts in the electro-Fenton system. In this work, cuprous and cupric ions were also used instead of ferrous or ferric ions during electro-Fenton type treatment of BPA.

The HPLC chromatograms of two aliquots of samples withdrawn from two electro-Fenton treatments of BPA, one with Fe^{2+} and the other with Cu^{2+}, are given in Figure 2. When Cu^{2+} was used at a $[Cu^{2+}]/[BPA]_0 = 4.28$, meta-monohydroxylated product (**II**) dominated over the ortho-monohydroxylated product (**III**,) which was contrary to the case with Fe^{2+}. In some other work (*18*) with another phenolic substrate, it was observed that product **II** was increased when Cu^{2+} was used, although the abundant product was still the ortho-monohydroxylated derivative. To clarify this phenomenon, a series of electro-Fenton treatments of aqueous BPA solutions by using different $[Cu^{2+}]/[BPA]_0$ values were carried out (whose kinetic results were given in the next paragraphs of this paper), and it was determined that, with a $[Cu^{2+}]/[BPA]_0$ value of 1.42, ortho-monohydroxylated product formed almost exclusively but that when this ratio was increased, meta-monohydroxylated product also appeared and became the abundant mono-hydroxylated derivative at a value of 4.28 and when this ratio reach about 7, ortho-monohydroxylated product was the abundant product again.

TABLE 2. Identified BPA Conversion and Degradation Products

compound	chemical structure	methods
m-monohydroxylated BPA		LC-MS
o-monohydroxylated BPA		LC-MS
dihydroxylated BPA		LC-MS
phenol		GC-MS
catechol		HPLC and GC-MS
hydroquinone		HPLC and GC-MS
benzoquinone		HPLC and GC-MS
resorcinol		HPLC and GC-MS
4-isopropenylphenol		GC-MS
4-hydroxy mandelic acid		GC-MS
4-hydroxy benzoic acid		GC-MS
butendionic acid	HOOC-CH=CH-COOH	GC-MS
4-oxobutenoic acid	HOOC-CH=CH-C-H	GC-MS
acetic acid	CH_3COOH	HPLC and GC-MS
formic acid	HCOOH	HPLC

On the other hand, when a similar series of electro-Fenton treatments had been applied by using different $[Fe^{2+}]/[BPA]_0$ values, ortho-monohydroxylated product was the dominant product at all ratios.

Concentration change profiles of BPA ($[BPA]_0 = 0.7$ mM and $[Fe^{2+}]/[BPA]_0 = 4.28$) and its monohydroxylated and dihydroxylated derivatives throughout an electro-Fenton treatment by using Fe^{2+} are given in Figure 3 in terms of the HPLC peak areas of the corresponding compounds versus the charge applied to the system.

As can be seen, while BPA concentration is going down, the concentration of the monohydroxylated ortho derivative increases faster than that of meta derivative. While the BPA itself disappeared when about 5.7 mF of charge has been consumed, the concentration of meta-monohydroxylated derivative (**II**) reached its maximum value when a total charge of 3.6 mF has been applied and diminished when a total of 7.3 mF of charge has been consumed. On the other hand, the concentration of the ortho-monohydroxylated derivative (**III**) reached a maximum value and then diminished when
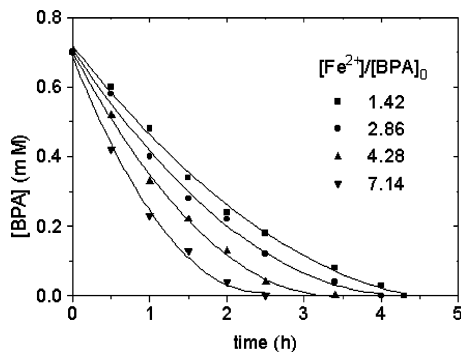
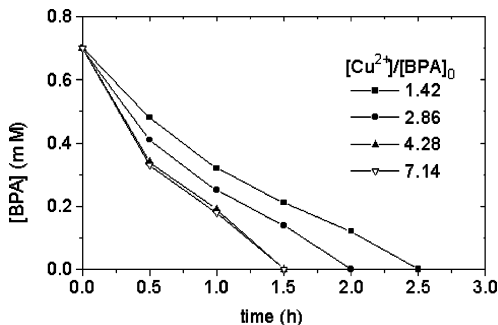FIGURE 5. Decrease of [BPA] with respect to time using different $[Fe^{2+}]/[BPA]_0$ ratios. $[BPA]_0 = 0.7$ mM, $V = 0.200$ dm³.

FIGURE 6. Decrease of [BPA] with respect to time using different $[Cu^{2+}]/[BPA]_0$ ratios. $[BPA]_0 = 0.7$ mM, $V = 0.200$ dm³.

3.1 and 8.3 mF of charges were consumed, respectively. The concentration of the dihydroxylated derivative of BPA reached its maximum value when 4.1 mF has been applied and then diminished when a total of about 7.3 mF of charge has been consumed.

The concentration change profiles in Figure 4 are very similar to the profiles in Figure 3 except the situation is reverse for the ortho- and meta-monohydroxylated derivatives. The ortho-monohydroxylated derivative, BPA itself, and the meta-monohydroxylated derivative disappear around when 7.3, 8.3, and 11.4 mF of charges are consumed, respectively.

A comparison of the efficiency of BPA conversions with respect to time using different metal ions with different $[M^{n+}]/[BPA]_0$ are given in Figures 5 and 6.

As can be seen, copper ions are the most effective ones in converting BPA to the hydroxylated products as far as rate is concerned. Similar observations were made during degradation of some other aromatic compounds (33, 34). Cuprous ions not only react with hydrogen peroxide to yield hydroxyl radicals (eq 9) but also react with oxygen in acidic medium to produce hydrogen peroxide (eq 8) (i.e., an additional contribution to hydrogen peroxide production takes place during electrolytic treatment) (33, 34):

$$2Cu^+ + O_2 + 2H^+ \rightarrow 2Cu^{2+} + H_2O_2 \qquad (8)$$

$$Cu^+ + H_2O_2 + H^+ \rightarrow Cu^{2+} + {}^\bullet OH + H_2O \qquad (9)$$
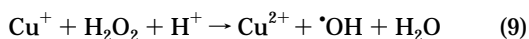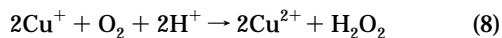
It has been stated that copper ions form complex intermediates with organic structures having oxygen functional groups in the Fenton medium, which could react faster than the bare organic forms (18).

When the [BPA] data presented in Figures 5 and 6 are plotted as a function of charge utilized, one can notice that faster conversion of BPA is obtained by using Cu^{2+} instead of Fe^{2+} at the expence of excess charge utilized. Only at one condition ($[M^{n+}]/[BPA]_0 = 1.42$) are similar conversion rates of BPA obtained by utilizing similar total charges for both

Cu^{2+} and Fe^{2+}. When the ratio $[Cu^{2+}]/[BPA]_0$ is increased, the total charge needed to convert BPA increases (e.g., when this ratio is 7.14, almost 9.3 mF is needed to convert BPA completely). On the other hand, when Fe^{2+} is used, the total charge needed to convert all BPA decreases with the increase of $[Fe^{2+}]/[BPA]_0$ values (e.g., 3.1 mF of charge is sufficient to convert all BPA when this ratio is 7.14). This is only one-third of the electricity consumed when an equivalent amount of Cu^{2+} is used to convert the same amount of BPA!

Rate Constants for Mono Hydroxylations of BPA. The data presented in this paper has shown that the value of the ratio $[M^{n+}]/[BPA]_0$ is crucial both for the mechanism and the kinetics of hydroxylation of BPA by hydroxyl radicals. The rate of mono hydroxylation of BPA by hydroxyl radicals in the electro-Fenton process changes as the value of $[M^{n+}]/[BPA]_0$ changes. We have carried out a comparative kinetic study of monohydroxylation between BPA and salicylic acid (SA) in a solution where the initial concentrations are 0.5 mM for both BPA and SA and 1.0 mM for the metal ion. Data are produced for the first 0.52 mF utilized in order to render dihydroxylation negligible. SA has been chosen for competition toward hydroxyl radicals because the rate constant was well-established $(2.2 \times 10^{10}$ M⁻¹ s⁻¹) (33). Concentration decreases of both BPA and SA were followed in the initial stages of the process (upto a maximum consumption of 0.52 mF), and samplings were done at 0, 0.052, 0.10, 0.20, 0.31, 0.41, and 0.52 mF of charges consumed. Assuming that at this stage of the process there were no side reactions of both BPA and SA, the rates of these mono hydroxylation reactions were given by

$$-d[BPA]/dt = k_{BPA}[OH^\bullet][BPA] \qquad (10)$$

$$-d[SA]/dt = k_{SA}[OH^\bullet][SA] \qquad (11)$$

which can be integrated and combined to give:

$$\ln([BPA]_0/[BPA]_t) = (k_{BPA}/k_{SA}) \times \ln[SA]_0/[SA]_t \quad (12)$$

where the subscripts 0 and t indicate concentrations at time 0 and t, respectively. A plot of $\ln([BPA]_0/[BPA]_t)$ versus $\ln[SA]_0/[SA]_t$ thus yields the rate constant ratio and, therefore, k_{BPA}.

The rate constants of mono hydroxylation of BPA were determined to be the same $(1.0 \times 10^{10}$ M⁻¹ s⁻¹) when Fe^{2+}(1 mM) and Cu^{2+}(1 mM) were employed as catalysts.

The fact that the two rate constants almost have identical values implies that complexes of BPA with copper or iron ions do not respond differently to the hydroxyl radicals throughout monohydroxylation reactions. The probable explanation for the faster reaction rates obtained when copper ions are used might be the additional contribution to hydrogen peroxide production due to the reaction of cuprous ions with oxygen (refer to eq 8), which will supply a higher hydroxyl radical concentration when compared with the corresponding system with ferrous/ferric ions.

Mineralization of the BPA Solutions. Mineralization of the BPA solutions during electro-Fenton treatment are followed by measuring the total organic carbon (TOC) contents of the solutions. Figure 8 summarizes the percent relative decrease of TOC values versus utilized charge for solutions having different $[M^{n+}]/[BPA]_0$ ratios.

As can be seen, the most effective mineralization is obtained for with a ratio of $[Fe^{2+}]/[BPA]_0 = 4.28$ (82% mineralization) following utilization of 107.8 mF, although the ratio of 2.86 also gives a close performance. The system with $[Cu^{2+}]/[BPA]_0 = 2.86$ yields about 70% mineralization by utilizing the same amount of charge. Cu^{2+} when used at various $[Cu^{2+}]/[BPA]_0$ values has been found to yield faster mineralization rates than the corresponding cases with Fe^{2+},
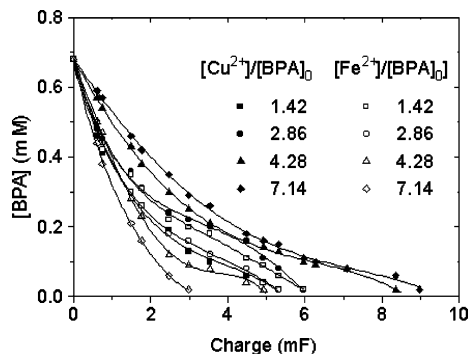
FIGURE 7. Decrease of [BPA] as a function of charge during electro-Fenton treatment by using different $[M^{n+}]/[BPA]_0$ ratios. $[BPA]_0 = 0.7$ mM, $V = 0.200$ dm^3.
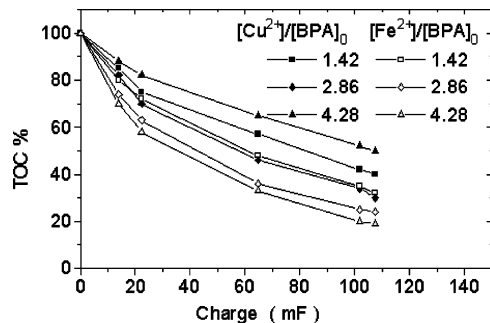

FIGURE 8. Decrease of TOC value as a function of charge utilized during the electro-Fenton treatment of BPA aqueous solution. $[BPA]_0 = 0.7$ mM, $V = 0.200$ dm^3.

but this occurred at the expence of an excess of electrical charge for equivalent mineralization.

One other interesting observation regarding the mineralization of the substrate by using different $[Cu^{2+}]/[BPA]_0$ ratios is that there exists an optimum value below or above which the extent of mineralization of the substrate decreases. No such behavior is observed with Fe^{2+}, at least in the range of $[Fe^{2+}]/[BPA]_0$ values used in this study. Therefore, one can conclude that using Cu^{2+} in the mineralization of BPA and/or similar substrates might be risky; it would not be possible to optimize the ratio of concentration of the metal ion to the organic substrate.

Comparison of the Results with Those of Direct Electrochemical Oxidation. It was concluded that electro-Fenton treatment was effective in degrading and mineralizing refractory organic compounds such as BPA in aqueous medium. The method is certainly advantageous over the alternative electrochemical method of direct oxidation. Boscolotto et al. applied direct electrochemical treatment to convert BPA in alkaline aqueous solution in the presence of 2.8% NaCl (15). Extensive chlorination of BPA took place, and 27 chlorinated products were observed. Other disadvantages observed in this direct electrochemical oxidation were the formation of severe filming of electrode surface and phase separation near the anode surface due to local pH drop in this region. In our work, despite the presence of chloride ions in the solution (acidification is done with HCl solution), no chlorinated BPA products are observed and a high degree of mineralization is achieved. Since the treatment chemicals (hydrogen peroxide and mainly hydroxyl radicals) are produced in in-situ electrochemical application, no hazardous chemicals will be transported to the application point. Controlled electrolysis will not produce excess hydrogen peroxide; therefore, no hazardous excess chemicals will be discharged with the treated water. Since the electrolytic process continually reduces the oxidized metal ion to the lower oxidation state ($Fe^{3+} \rightarrow Fe^{2+}$), a catalytic amount of the metal salt in solution will be sufficient for an effective application.

While the use of Cu^{2+} will not be advised for processing BPA and similar substrates by using the electro-Fenton technique for both technical and economical reasons stated above, it is shown that $[Fe^{2+}]/[BPA]_0$ values in the range of $3-4$ will be sufficient to achieve an efficient mineralization of BPA and similar substrates by electro-Fenton application in aqueous medium.

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