Comparative Experimental Study on an Endocrine Disruptor Degradation by UV/H₂O₂ and UV/H₂O₂/TiO₂ Systems

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Abstract: Bisphenol A (BPA) – an endocrine disruptor, degradation was studied using the following systems: UV/H₂O₂ and UV/H₂O₂/TiO₂. Optimum operating conditions were established for both studied systems and experimental results showed that the two systems could be successfully used for advanced degradation of BPA achieving degradation efficiencies for BPA of 99.99% in optimum working conditions. The two systems were compared and both advantages and disadvantages of each system were identified. Nine degradation intermediates were identified for BPA degradation in UV/H₂O₂/TiO₂ system and a possible degradation pathway was proposed.

Keywords: bisphenol A, transformation products, H₂O₂, photocatalysis

1. Introduction
Bisphenol A (BPA), 2,2-bis(4-hydroxydiphenyl) propane (BPA) is an endocrine disruptor found often in the environment [1]. Its presence is due to its extensive use as raw material in fabrication of plastics based on polycarbonate and epoxy resins. Moreover, according to relatively recent data [2], BPA will become one of the contaminants of concern for aqueous systems in the near future.

It was proved that endocrine disruptors such as BPA are perturbing reproductive function, organisms’ development, neuronal, cardiovascular, metabolic and immunity systems. BPA exposure lead to high levels of anxiety, depression, hyperactivity and behavior problems for children. It was also traced in maternal milk, urine and placenta tissue, which proves the global exposure [3-4].

BPA was found in all environmental media, including water [5-9] and cannot be adequately degraded by conventional wastewater treatment plants processes [10]. In order to surpass this issue there is a need for more performant degradation processes from which advanced oxidation processes (AOPs) were thoroughly studied in the recent period for the degradation of recalcitrant organic pollutants [11, 12].

Quite recent researches proved that BPA oxidation in UV/S₂O₅²⁻ system [13] has better efficiency compared with UV/H₂O₂ system, concluding that SO₄•⁻ has better oxidative performance compared with hydroxyl radicals not only for BPA degradation but also to BPA mineralization.

Other researchers focused on investigation of BPA degradation using Fenton process in the presence of β-cyclodextrin and its derivatives [14] and reported BPA degradation efficiencies higher than 87%. Heterogeneous photo-Fenton with Fe-Y molecular sieve catalyst system was also investigated [15] and the results proved that its performance was higher compared with photolysis, photo-oxidation, heterogeneous and homogeneous photo-Fenton systems.

Electrochemical oxidation [16], ultrasonic degradation [17] and catalytic wet air oxidation coupled with photocatalysis [18] are other approaches that seems to be feasible for BPA degradation.

The most intensive studied AOP was the photocatalysis. Researches focused on both performance assessment of classic photo catalysts such as undoped [19] or doped TiO₂ [1] and ZnO [20] and on

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development of new catalysts. From the latest, nano-composites such as \( \text{TiO}_2/\text{WO}_3/\text{GO} \) [21] and \( \text{ZnFe}_2\text{O}_4/\text{TiO}_2 \) [22] were developed, characterized and proved to be efficient when used for BPA degradation under visible light. Use of FeOOH and Fe\(_2\)O\(_3\) co-grafted TiO\(_2\) photo catalyst [23], solar activation of TiO\(_2\) with graphene [10], BPA degradation induced by dense nano-cavities inside 2D-TiO\(_2\) nanostructures [24] represent other successful approaches that were studied for BPA photocatalytic degradation.

Use of undoped TiO\(_2\) for BPA degradation under UV radiation was subject to authors’ previous work [12, 25] as well as for other researches [1], the obtained results suggesting that TiO\(_2\) assisted photocatalysis can be considered a promising method for BPA degradation.

There is limited information on BPA degradation using UV/H\(_2\)O\(_2\)/TiO\(_2\) system. It has to be mentioned one study that uses UV/H\(_2\)O\(_2\)/Fe-TiO\(_2\) system for BPA degradation [26], which reports complete BPA removal after 120 min.

In this context our study was focused on comparison of BPA degradation efficiencies by UV/H\(_2\)O\(_2\), and UV/H\(_2\)O\(_2\)/TiO\(_2\) systems based on both previous works and recent experimental data and also on elucidation of active species involved in the process and BPA degradation intermediates identification.

2. Materials and methods

2.1. Materials

\( \text{TiO}_2\) photo catalyst and H\(_2\)O\(_2\) were purchased from Merck, BPA 99% purity was obtained from Sigma Aldrich. Ultrapure water was generated by a MilliQ Integral 15 equipment. All reagents used for analytical determinations were HPLC grade.

2.2. Experimental set-up

Photo degradation experiments were conducted using a Heraeus type UV reactor equipped with a TQ 150-Z3 medium pressure mercury lamp which emits in the range of 310 – 550 nm, cooling jacket and aeration inlet (Figure 1). The air flow for aeration was kept constant at 50 L h\(^{-1}\) for all experiments. Samples subject to irradiation were mixed during the experiments using a magnetic stirrer.

All experiments were done using synthetic solutions of BPA.

![Figure 1. UV reactor used for BPA degradation](image)

1-UV lamp, 2 – cooling jacket, 3 – feed/sampling point, 4-reactor vessel, 5 – magnetic stirrer
2.3 Analytical methods

BPA concentration and determination of BPA degradation intermediates was performed via liquid chromatography coupled with mass spectrometry (LC-MS) technique. LC-MS analysis was performed using an Agilent LC-MS system (Agilent, Waldbronn, Germany) consisting of: binary pump with degasser, autosampler, column thermostatic compartment and a Triple-Quadrupole mass analyser with electrospray ionization source (ESI). Chromatographic runs were carried out on a Luna 3 µm C18(2) 100 A column (150 x 2.0 mm, 3.0 µm) from Phenomenex which was kept at 35°C. Mobile phase composition was 0.01% acetic acid in H₂O (A) and MeOH (B) in the ratio 38/62 (v/v). BPA and BPA degradation products were eluted in isocratic regime of the mobile phase with a chromatographic runtime of 10 minutes. Mobile phase flow-rate was set to 0.15 mL/min in accordance with column internal diameter and an injection volume of 5 µL was used. MS detection of BPA and its degradation products was achieved in negative polarity using SIM (degradation products) and MRM (BPA) acquisition modes. ESI ionization source parameters were: 300°C drying gas temperature, 8 L/min drying gas flow-rate, 40 psi nebulizer pressure and 5000 V capillary voltage. MRM transition of BPA was 227 → 212 @ 15 V CE (collision energy), 150 V fragmentor and 1 V for the collision cell accelerator voltage.

3. Results and discussions

3.1. BPA degradation in UV/H₂O₂ system

UV/H₂O₂ system represents one of the AOPs commonly used for organic pollutants degradation. The reactive species are represented by •OH radicals generated by the following reaction:

\[ H₂O₂ + hν \rightarrow 2 \cdot OH \]  

In order to determine the influence of H₂O₂ dose upon BPA degradation efficiency, the H₂O₂ concentration was varied according to molar ratios \([\text{H}_2\text{O}_2]/[\text{BPA}]_0 = 1:5 – 1:72\). Pseudo first order rate constants were calculated based on the following equations:

\[ [\text{BPA}] = [\text{BPA}]_0 e^{-kt} \]  

\[ -\ln\frac{[\text{BPA}]}{[\text{BPA}]_0} = kt \]

In the equations 2 and 3 [BPA] is the residual concentration of BPA, \([\text{BPA}]_0\) represents initial concentration of BPA, \(k\) is the pseudo first order rate constant and \(t\) is the time of irradiation.

| [H₂O₂]/[BPA]₀ | [BPA] (mg L⁻¹) | [BPA] (M) | -ln([BPA]/[BPA]₀) | \(k\) (s⁻¹) | BPA degradation efficiency (%) |
|---------------|---------------|-----------|-------------------|-------------|-------------------------------|
| 5             | 0.192         | 8.42 x 10⁻¹ | 4.23              | 2.350 x 10⁻³ | 98.56                         |
| 9             | 0.056         | 2.46 x 10⁻¹ | 5.46              | 3.035 x 10⁻³ | 99.58                         |
| 18            | 0.034         | 1.49 x 10⁻¹ | 5.96              | 3.312 x 10⁻³ | 99.75                         |
| 36            | 0.018         | 7.89 x 10⁻⁴ | 6.60              | 3.665 x 10⁻³ | 99.87                         |
| 54            | 0.024         | 1.05 x 10⁻⁷ | 6.31              | 3.506 x 10⁻³ | 99.82                         |
| 72            | 0.102         | 4.47 x 10⁻⁷ | 4.86              | 2.702 x 10⁻³ | 99.24                         |
BPA degradation efficiency and pseudo first order rate constants increased with H$_2$O$_2$ concentration up to an optimum corresponding to [BPA]$_0$ / [H$_2$O$_2$] molar ratio of 1:36 (Table 1). At highest H$_2$O$_2$ concentrations both the BPA degradation efficiency and pseudo first order rate constants decreased due to the fact that high H$_2$O$_2$ concentration scavenges radicals according to the following reactions [27], making the degradation less performant:

\[
\begin{align*}
H_2O_2 + \cdot OH & \rightarrow HO_2\cdot + H_2O \\
HO_2\cdot + \cdot OH & \rightarrow O_2 + H_2O \\
HO\cdot + \cdot OH & \rightarrow H_2O_2 \\
HO_2\cdot + HO_2\cdot & \rightarrow H_2O_2 + O_2
\end{align*}
\]

(4)  (5)  (6)  (7)

Optimum H$_2$O$_2$ dose assured a BPA degradation efficiency of 99.87% with a pseudo first order rate constant of photolysis of $3.665 \times 10^{-3}$ s$^{-1}$ = 0.2199 min$^{-1}$, results there were consistent with those obtained by other recent researches on BPA degradation in UV/H$_2$O$_2$ system [26, 28].

The influence of irradiation time on BPA degradation rate was investigated for the optimum H$_2$O$_2$ dose (Figure 2). The increase of irradiation time proved to have a positive effect upon BPA degradation efficiency. Optimum irradiation time was set at 45 minutes, that assures the substrate [BPA]$_0$ = 13.2 mg L$^{-1}$ = 5.79 x $10^{-5}$ M degradation with a 99.99% efficiency. The pseudo first order rate constant was calculated from the slope of the linearized graph according to equation 3 and a value of $k = 0.2204$ min$^{-1}$ was found.

![Figure 2. BPA degradation kinetic in UV/H$_2$O$_2$ system. [BPA]$_0$/[H$_2$O$_2$] = 1:36. [BPA]$_0$ = 13.2 mg L$^{-1}$ = 5.79 x $10^{-5}$ M](image)

### 3.2. BPA degradation in UV/H$_2$O$_2$/TiO$_2$ system

Previously reported researches on UV/TiO$_2$ system application for BPA degradation [12, 25] led the authors to the following optimum parameters: pH = 8, [TiO$_2$] = 200 mg L$^{-1}$, irradiation time 120 minutes, that assures the BPA degradation with an efficiency of 99.93%. Starting from this result and taking into consideration an attempt to study BPA degradation using a combined UV/H$_2$O$_2$/TiO$_2$ system was made. In order to establish the influence of H$_2$O$_2$ concentration, experiments were made using previously established optimum TiO$_2$ dose for an irradiation time of 30 minutes and molar ratios of [BPA]$_0$ / [H$_2$O$_2$] varied within the domain 1:0.5 – 1:5 (Table 2).
Table 2. BPA degradation efficiency in UV/H\textsubscript{2}O\textsubscript{2}/TiO\textsubscript{2} system

| [H\textsubscript{2}O\textsubscript{2}]/[BPA]\textsubscript{0} | [BPA] (mg L\textsuperscript{-1}) | [BPA] (M) | -\ln([BPA]/[BPA]\textsubscript{0}) | k (s\textsuperscript{-1}) | BPA degradation efficiency (%) |
|-----------------|------------------|--------|------------------------|-----------------|-----------------------------|
| 0.5             | 1.470            | 6.44 x 10\textsuperscript{-6} | 2.19        | 1.219 x 10\textsuperscript{-3} | 88.99%                      |
| 1               | 1.375            | 6.03 x 10\textsuperscript{-6} | 2.26        | 1.256 x 10\textsuperscript{-3} | 89.70%                      |
| 3               | 0.489            | 2.14 x 10\textsuperscript{-6} | 3.29        | 1.831 x 10\textsuperscript{-3} | 96.34%                      |
| 5               | 0.139            | 6.09 x 10\textsuperscript{-7} | 4.55        | 2.530 x 10\textsuperscript{-3} | 98.96%                      |

An optimum dose of H\textsubscript{2}O\textsubscript{2} corresponding to the molar ratio [H\textsubscript{2}O\textsubscript{2}]/[BPA]\textsubscript{0} = 1:5 assured the substrate degradation with an efficiency of 98.96% and an irradiation time of only 30 minutes. Prolonging the irradiation time to 60 minutes led to a BPA degradation efficiency of 99.99%.

3.3. Comparison of UV/H\textsubscript{2}O\textsubscript{2} and UV/H\textsubscript{2}O\textsubscript{2}/TiO\textsubscript{2} system

Electrical energy per order of magnitude was used to assess electric energy consumptions for the two studied systems, in accordance with the following equation [29]:

\[
E_{EO} = \frac{P \times t \times 1000}{60 \times V \times \log \left( \frac{[BPA]_0}{[BPA]} \right)}
\]

In equation 8 P is the power of UV lamp (0.15 kW), t represents irradiation time (min), V is treated water volume (0.4 L), [BPA]\textsubscript{0} is the initial BPA concentration and [BPA] is the final BPA concentration.

The main operating parameters of the two studied systems together with their advantages and disadvantages are summarized within the Table 3.

Table 3. Comparison between BPA degradation by UV/H\textsubscript{2}O\textsubscript{2} and UV/H\textsubscript{2}O\textsubscript{2}/TiO\textsubscript{2} systems

|                         | UV/H\textsubscript{2}O\textsubscript{2} | UV/H\textsubscript{2}O\textsubscript{2}/TiO\textsubscript{2} |
|-------------------------|--------------------------------------|--------------------------------------------------|
| Optimum parameters     | [BA]/[H\textsubscript{2}O\textsubscript{2}] = 1:36 | [BA]/[H\textsubscript{2}O\textsubscript{2}] = 1:5 |
| Irisration time        | 45 minutes                           | 60 minutes                                      |
| BPA degradation efficiency | 99.99%                              | 99.99%                                          |
| Electrical energy per order, kWh m\textsuperscript{-3} | 64.77                                  | 94.35                                          |

Main advantages
- Higher BPA degradation rate
- No need of further processes for catalyst removal
- Shorter duration
- Less electricity required
- Possibility to use solar radiation
- Possibility to recover and reuse the catalyst within further treatment cycles

Main disadvantages
- Higher operational costs due to H\textsubscript{2}O\textsubscript{2} consumption
- Need of additional step for catalyst removal
- More electricity required

3.4. Identification of degradation intermediates in UV/H\textsubscript{2}O\textsubscript{2}/TiO\textsubscript{2} system

The nine BPA degradation intermediates identified during the study are presented in Table 4.
Table 4. BPA degradation intermediates by UV/H₂O₂/TiO₂ system, identified using LC-MS

| Structure name and number | Retention time (min) | Molecular weight | Chemical structure |
|--------------------------|----------------------|------------------|--------------------|
| Bisphenol A (BPA)        | 8.24                 | 228              | ![Bisphenol A](image1) |
| 4-[2-(4-hydroxyphenyl)propan-2-yl] benzene-1,2-diol (1) | 5.43 | 244 | ![Intermediate 1](image2) |
| 3-(hydroxyethyl)-4-[2-(4-hydroxyphenyl)propan-2-yl] benzene-1,2-diol (2) | 2.66 | 274 | ![Intermediate 2](image3) |
| 4-(2-hydroxypropan-2-yl)benzene-1,2-diol (3) | 3.17 | 168 | ![Intermediate 3](image4) |
| 4-(prop-1-en-2-yl) benzene-1,2-diol (4) | 3.16 | 150 | ![Intermediate 4](image5) |
| 4-(2-hydroxypropan-2yl) phenol (5) | 3.20 | 152 | ![Intermediate 5](image6) |
| 4-(prop-1-en-2yl) phenol (6) | 3.54 | 134 | ![Intermediate 6](image7) |
| (4-hydroxyphenyl) ethanone (7) | 3.65 | 136 | ![Intermediate 7](image8) |
| 4-hydroxybenzoic acid (8) | 2.95 | 138 | ![Intermediate 8](image9) |
| 4-(1-hydroxyethyl) phenol (9) | 3.15 | 138 | ![Intermediate 9](image10) |

Based on the nine degradation intermediates identified within this study a possible degradation pathway for BPA was proposed. Experimental results were corroborated with the results reported by other research studies on BPA degradation [14, 20, 21, 28, 30, 31].

Two main pathways for BPA degradation were proposed (Figure 3). The first one is represented by hydroxylation of phenolic ring, followed by scission of bond between isopropylidene group and aromatic ring. The pathway was also reported by other researchers which studied BPA degradation [21, 30]. The second proposed route is represented by hydroxyl radicals attack on BPA’s phenyl group and were also reported in other studies on identification of BPA degradation mechanism [14, 20, 21, 28, 31]. Apart from degradation by-products identified within above-mentioned studies, 4-(1-hydroxyethyl) phenol (transformation product labelled 9) was also identified in our study. The degradation by-products can be further degraded in order to achieve complete mineralization.
Figure 3. Proposed degradation pathway for BPA in UV/H$_2$O$_2$/TiO$_2$ system

4. Conclusions

BPA degradation was studied using UV/H$_2$O$_2$ and UV/H$_2$O$_2$/TiO$_2$ systems. Optimum parameters were found to be for UV/H$_2$O$_2$ system: [BA]/[H$_2$O$_2$] = 1:36; Irradiation time = 45 minutes and for UV/H$_2$O$_2$/TiO$_2$ system: [BA]/[H$_2$O$_2$] = 1:5; [TiO$_2$] = 200 mg/L; Irradiation time = 60 minutes. Both system assured BPA degradation with efficiency of 99.99% and the main advantages and disadvantages of each system were presented.

Nine degradation intermediates were identified for UV/H$_2$O$_2$/TiO$_2$ system using LC-MS technique and a possible degradation route was proposed.

Experimental results proved that BPA advanced degradation using advanced oxidation processes such as UV/H$_2$O$_2$ and UV/H$_2$O$_2$/TiO$_2$ systems could be successfully achieved in optimum working conditions.

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