

DOI: <http://doi.org/10.21698/simi.2020.ab14>

OXIDATIVE DEGRADATION OF BISPHENOL A IN AQUEOUS SOLUTION USING BICARBONATE ACTIVATED HYDROGEN PEROXIDE

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Keywords: *Bisphenol A degradation, bicarbonate activated hydrogen peroxide*

Introduction

Due to its widespread use BPA is found in foods, beverages, wastewater and surface waters. The presence of BPA in rivers is due to the drainage of wastewater, the continuous leakage of plastics and resins or the plastic being thrown out directly into the rivers. This leads to numerous harmful effects on the human body that include: effects on the prostate, promotion of cancer cells, metabolic problems, diabetes, effects on the reproductive system and hormonal disruption, BPA being a mimetic of estrogen. As a result of its very high presence and numerous adverse effects, the degradation of bisphenol A from wastewater is considered to be an emergency. In the last year (2020) more than 2000 articles were published on this subject.

Among them, advanced oxidation processes (AOPs) have become very useful in the treatment of wastewater because of their high reactivity and non-specific broad-spectrum efficacy on several organic pollutants. AOPs involve the use of oxidants, such as oxygen, hydrogen peroxide and ozone, to produce extremely oxidizing radicals (hydroxyl, superoxide radical, hydroxy-peroxyl radical and singlet oxygen) to degrade and even completely mineralize organic pollutants like BPA.

The hydrogen peroxide-sodium bicarbonate (BAP) system is characterized by high efficiency because the bicarbonate anion is one of the most abundant freshwater anions and is relatively non-toxic. BPA oxidation occurs due to the attack of the radicals formed in the oxygenated water/sodium bicarbonate system. In the case of using the Co/AO/BIC system, it is assumed that a complex is formed in the first stage between bivalent cobalt and sodium bicarbonate, a complex that binds oxygenated water with radical formation and the BPA to be degraded.

In this paper we used the bicarbonate activated hydrogen peroxide (BAP) system activated either by CoSO₄ or NaNO₂ for BPA degradation.

Materials and methods

The BPA (0.3mM) oxidation was performed with a system consisting of hydrogen peroxide 0.05M, sodium bicarbonate 0.05M and CoSO₄ 4μM or NaNO₂ 50μM (as activators) in a small batch reactor (5mL). Samples of 20 μL were taken over time and analyzed by HPLC (C8 column, 15 x 0.46 cm, 5μm, elution system acetonitrile: 0.1% phosphoric acid in water 50:50 in isocratic mode, 1ml/min flow rate) using a UV-VIS detector at λ=278nm. In these conditions BPA has a retention time at 5.4 min.

Results and conclusions

From the chromatograms recorded in time, it was observed that there was a visible decrease of the peak corresponding to bisphenol A; at the same time, we observed the appearance of other peaks at retention times of 1.3 min and 1.55 min at the beginning of the reaction, and at 2.1 min, 3.6 min and 7.4 min at longer reaction times.

From the areas of peaks associated with BPA we calculated the unreacted substrate concentration and estimated the rate constant for a kinetic of pseudo-first order:

$$\ln\left(\frac{[BPA]_0}{[BPA]_t}\right) = k_t \cdot t$$

as well as degradation efficiency after 30 min:

$$\eta(\%) = \frac{[BPA]_0 - [BPA]_{30 \text{ min}}}{[BPA]_{30 \text{ min}}} \cdot 100$$

The reaction obeys a pseudo-first order kinetics, as it can be seen in figure 1. The presence of small amounts of Co^{2+} and NO_2^- ions lead to an increase of the kinetic constants.

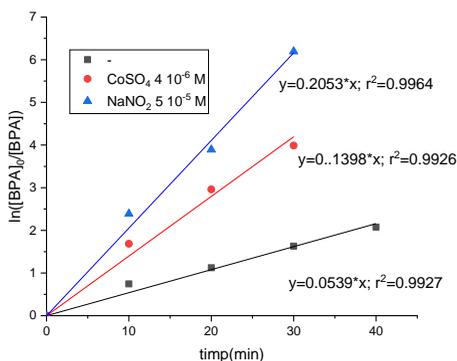


Figure 1. Kinetic curves for BPA oxidation in the presence of Co^{2+} and NO_2^- ($[\text{BPA}]_0=0.3\text{mM}$, $[\text{NaHCO}_3]_0=0.05\text{M}$, $[\text{H}_2\text{O}_2]_0=0.05\text{M}$)

Regarding the degradation efficiency at 30 minutes, we obtained values over 90% both in the presence of nitrite (90.86%) and cobalt (97%); these values seem to be very good, being higher than other values reported in the literature.

Because other organic products were obtained in the reaction, they were quantified via HPLC-MS; the results show a complex mechanism for the degradation of BPA, with a mineralization degree of 77%.