

THE INFLUENCE OF OXYGEN ON THE EFFICIENCY AND THE MECHANISM OF CARBAMAZEPINE DECOMPOSITION BY MEANS OF THE PHOTOCATALYSIS PROCESS

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Received: 24.07.2015; Revised: 15.09.2015; Accepted: 22.09.2015

Abstract

Advanced oxidation processes are one of the most effective methods in the treatment of aqueous streams contaminated with hardly-biodegradable organic micropollutants including pharmaceutical substances which are classified as biologically active compounds. The study assessed the impact of the presence of oxygen on the efficiency of photocatalytic oxidation of the psychotropic drug – carbamazepine. The oxygen was supplied to the reaction medium as a mixture of gases present in atmospheric air by means of an aeration pump or in pure form using an oxygen concentrator. The HPLC analysis preceded by solid-phase extraction was used to evaluate the effectiveness of the process. It was demonstrated that the presence of oxygen was an essential factor for the proper conduction of photochemical processes. With the increase of the oxygen concentration the increase in the removal rate of tested psychotropic drug was observed. In addition, the study evaluated the possibility of generation of toxic by-products of the oxidation and reduction of carbamazepine using Microtox® biotest. It was found, that the presence of dissolved oxygen intensified the formation of toxic by-products during the carbamazepine decomposition, which result in higher toxicity of the treated aqueous matrix.

Streszczenie

Zaawansowane procesy utleniania należą do jednych z najskuteczniejszych metod oczyszczania strumieni wodnych z trudno biodegradowanych mikrozanieczyszczeń organicznych, w tym również substancji farmaceutycznych zaliczanych do związków aktywnych biologicznie. W pracy oceniono wpływ obecności tlenu na efektywność fotokatalizacyjnego utleniania leku psychotropowego – karbamazepiny. Tlen doprowadzano do środowiska reakcji jako mieszaninę gazów za pomocą pompki napowietrzającej lub formie czystej przy użyciu koncentratora tlenu. Do badania skuteczności procesu zastosowano analizę HPLC poprzedzoną ekstrakcją do fazy stałej. Wykazano, że obecność tlenu jest niezbędnym czynnikiem pozwalającym na prawidłowy przebieg procesów fotochemicznych. Wraz ze wzrostem stężenia tlenu obserwowano wzrost stopnia usunięcia leku psychotropowego. Dodatkowo w ramach pracy oceniono możliwość generowania toksycznych ubocznych produktów utleniania i redukcji karbamazepiny przy użyciu biotestu Microtox®. Stwierdzono, że obecność tlenu rozpuszczonego intensyfikuje powstawanie toksycznych produktów ubocznych w trakcie rozkładu karbamazepiny, skutkujących wzrostem toksyczności oczyszczanej matrycy wodnej.

Keywords: Carbamazepine; Photocatalysis; Oxygen; Microtox® .

1. INTRODUCTION

The presence of hardly-biodegradable organic micropollutants in surface waters, which are the potential source of drinking water, creates the need to develop new methods for their in-depth treatment.

Among anthropogenic micropollutants pharmaceutical compounds are listed. Their cyclic structure impedes their natural biodegradation, hence they become substances of high environmental relevance. One of the most frequently identified pharmaceutical in an aqueous environment is carbamazepine. This

drug is a dibenzodiazepine derivative with a psychotropic activity [1]. Because of a relatively high polar character it has poor sorption properties, what limits the possibility of its removal in water treatment processes [2]. Satisfactory effects of its decomposition can be achieved by the use of advanced oxidation processes, which include also the process of heterogeneous photocatalysis [3]. Nevertheless, not all mechanisms of the oxidation of micropollutants have been exactly identified and the decrease of a compound concentration not always indicates its complete mineralization. Transformation products, which are more resistant to degradation can be formed.

The mechanism of the reaction, that occurs on the catalyst surface during heterogeneous photocatalysis is divided into five stages: the photoexcitation, diffusion, trapping, recombination, and oxidation [4,5]. The photoexcitation occurs when the particles of the TiO₂ catalyst are irradiated with UV light with an energy greater than the band gap energy of the catalyst. In the case of TiO₂ the irradiation energy should be greater or equal to 3.2 eV [6]. As a result, the electron from the low-energy valence band transfer high-energy conduction band and “electron-hole” pairs are generated. In the diffusion stage, the spatial bonding among the TiO₂ surface, water molecules and micropollutants, – which should be decomposed, [7] is formed. The presence of oxygen is indispensable in the stage of trapping. Oxygen molecules (O₂) act as electron acceptors for electrons generated during the formation of strongly oxidizing hydroxyl radicals (OH•) during the reaction between water molecules or hydroxyl ions and photogenerated holes. Due to the reduction of oxygen molecules with electrons, reactive superoxide radical (O₂^{•-}) capable of complete mineralize of a range of organic micropollutants, are formed. There is the opportunity that during the charge transfer to diffused micropollutants the electron-hole pair recombination and trapped carrier recombination occur simultaneously. Those phenomena can take place on the recombination stage of heterogeneous photocatalysis and result in liberation of energy in the form of heat:



The last stage of the photocatalysis process is the oxidation of micropollutants adsorbed on the surface of the catalyst and/or free stage compound dissolved in the water matrix may react directly with free radicals [7].

The effectiveness and mechanism occurring during the process of photocatalytic oxidation of organic compounds are determined by a number of operating parameters of the process, which include the oxy-

genation method of the reaction mixture.

In this paper the influence of the presence of oxygen in different concentration on the efficiency of photocatalytic decomposition of carbamazepine is discussed. The oxygen was supplied to the reaction medium by means of an aeration pump as a mixture of gases present in atmospheric air or in pure form using an oxygen concentrator. To examine the effectiveness of the process chromatographic analysis (HPLC) preceded by solid-phase extraction was used. The Microtox® biotest has been applied as a tool for the determination of oxidation by-products.

2. EXPERIMENTAL

2.1. Research methodology

The subject of the study was simulated solutions prepared on deionized water matrix, to which carbamazepine (Fig. 1) at a constant concentration of 1 mg/dm³ was added. The analytical standard of the pharmaceutical micropollutant was supplied by Sigma-Aldrich (Poland). The solution pH was adjusted to pH 7 using 0.1 mol/dm³ HCl and 0.1 mol/dm³ NaOH solutions.

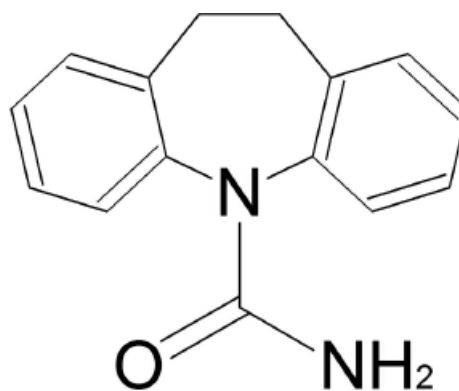


Figure 1.
Structural formula of carbamazepine

The photocatalysis process was carried out in a laboratory batch reactor Heraeus (volume of 700 cm³) equipped with an immersed medium-pressure mercury lamp of power 150 W ($\lambda_{\text{exc}} = 254, 313, 365, 405, 436, 546$ and 578 nm) placed in a cooling jacket made of the special glass Duran 50, which enabled the blockage of radiation of wavelength < 300 nm. The process temperature was equal to $20 \pm 1^{\circ}\text{C}$. The radiation was carried out constantly for 60 minutes. The oxidation process of simulated water solution was

performed with or without oxygen supply. The oxygen was introduced to the reactor by the use of an aeration pump of capacity 4 dm³ of air per minute or a oxygen concentrator TOKYO 5F-WY by Elmar (Poland) of oxygen capacity from 1 to 5 dm³/min (Table 1). The oxygen concentration in non-aerated water solution was equal to 2.52 mg/dm³.

Table 1.
Parameters of oxygen supply methods

Method	Aeration pump	Oxygen concentrator				
		1	2	3	4	5
Air flow [dm ³ /min]	4					
Oxygen concentration [%]	21	93±3				
Oxygen flow supply to the reactor [dm ³ /min]	0.8	0.9	1.9	2.8	3.7	4.7
Oxygen concentration in aerated water solutions [mg/dm ³]	6.3	6.9	7.3	8.2	8.6	9.1

Titanium dioxide (TiO₂) by Evonik Degussa (Germany) in the dose equal to 50 mg/dm³ was used as the photocatalyst. The contact time of the catalyst with treated water before its irradiation was established for 15 minutes during the preliminary stage of the study. This procedure was used in order to enable the adsorption of micropollutants on the particles of the catalyst. The degree of adsorption has a direct influence on the efficiency of the photocatalysis process. The separation of the catalyst from the treated solution was carried out by the use of a filtration set comprised of glass fiber filter (0.45 µm) by Millipore, which was connected to the vacuum pump AGA Labor.

2.2. Analytical methods

The concentration of carbamazepine in the solutions before and after the photocatalysis was determined on the basis of quantitative-quantitative analysis with high performance liquid chromatography HPLC preceded with solid phase extraction SPE. The Supelclean™ ENVI-8 tube phase (C8) was conditioned with methanol and next washed with distilled water of pH 7. After the extraction of water sample of a volume 20 cm³ the column bed was dried for 5 min at vacuum. The analyte was eluted with 3 cm³ of methanol and dried in a nitrogen stream. After dissolution of the sample in 100 cm³ of methanol it was subjected to chromatographic analysis. HPLC by Varian (Warsaw, Poland) equipped with a UV detector (wavelength λ = 220 nm) was used. Hypersil GOLD column by Thermo Scientific of length 25 cm, diameter 4.6 mm and granulation – 5 µm was used as the chromatographic

column. The mobile phase consisted of a mixed water and acetonitrile in the ratio of 85:15 (v/v). The organic solvents of analytical grade used in this study were purchased from the Avantor Performance Materials International Company (Poland).

The separation efficiency and the precision of the applied analytical procedure were determined on the basis of results obtained for five extractions. The extraction yield of carbamazepine in deionized water was 96% and the precision of determination between individual samples did not exceed 2%.

The measurement of the concentration of dissolved oxygen in aqueous samples was performed by the use of a laboratory oxygen meter CO-505 by ELMETRON® (Poland).

The toxicity measurements were carried out according to the Screening Test procedure of MicrotoxOmni system in Microtox analyzer Model 500 by Tigret Ltd. (Poland). The rate of bioluminescence inhibition of *Aliivibrio fischeri* bacteria in reference to the control sample (bacteria exposed to 2% NaCl solution) was measured after 5 minutes of exposure.

3. RESULTS AND DISCUSSION

3.1. Decomposition of carbamazepine

In the first stage of the study the catalyst was contacted for 15 min. with the prepared water solutions. Due to the only adsorption of molecules of the pharmaceutical on the catalyst surface a 12% reduction of its concentration was observed. The low rate of adsorption of micropollutant on catalyst particles indicated that the decomposition of the compound would take place mainly due to the reactions with free hydroxyl radicals and other reactive oxygen species generated in the whole volume of the irradiated water solutions and not only on the catalyst surface.

The process of photocatalysis carried out without the addition of oxygen after 60 minutes of UV irradiation allowed to obtain a removal rate of pharmaceutical below 41% (Fig. 2). Process kinetics calculated with the use of Langmuir-Hinshelwood [8,9] equation as a conjugated function of pharmaceuticals concentration and time, clearly indicated that the decomposition process of carbamazepine was divided into two stages. In the first 30 minutes of UV irradiation the half-life of carbamazepine was 55 minutes and with continued irradiation it doubled and reaches the value of 110 min. The increase of the half-life value may indicate the run out of the source of oxygen molecules, which are acceptors for electrons released

during the generation of OH^\bullet radicals. As a consequence the formation of superoxide radical ($\text{O}_2^{\bullet-}$) which are able to mineralize carbamazepine was inhibited. The introduction of an additional source of oxygen to the system seems to be a good solution to improve the efficiency of pharmaceutical decomposition and it was undertaken in the further part of the study.

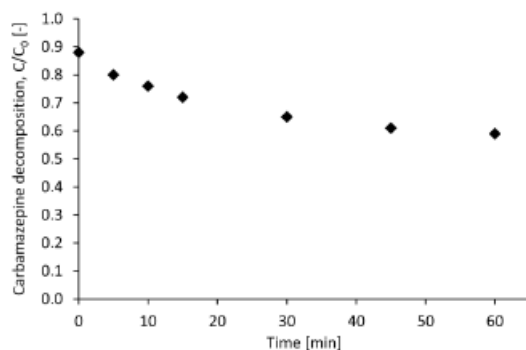


Figure 2.
The decrease of carbamazepine concentration during photocatalysis without aeration

The next part of the study was focused on the evaluation of the impact of the oxygen supplying methods on the decrease of pharmaceutical concentration in the photocatalytic oxidation process. Firstly, the oxygen was introduced into the photocatalytic reactor by the use of an aeration pump or an oxygen concentrator. Both devices worked with at a flow rate of 4 dm³ of gas per minute. The obtained results showed that the effectiveness of the decomposition of tested pharmaceutical compound in the oxygenated process increased continuously with the time of the UV irradiation (Fig. 3). For example, after 10 min of photooxidation assisted by the presence of oxygen supplied by the aeration pump, the rate of degradation of carbamazepine exceeded 31% and after 60 min it reached 68%. The removal rates noted for the process carried out with the oxygen concentrator after 10 and 60 minutes of the process were 45 and 79%. The study of the kinetics also showed that there was a dependence of the half-life on the oxygen concentration. For the oxygen concentration in treated water solution of 6.32 mg/dm³ achieved by the use of the aeration pump, the half-life of carbamazepine was 31 minutes. The higher oxygen concentration of 8.64 mg/dm³, which was the result of the application of an oxygen concentrator, allowed to reduce the half-life to a value below 18 min.

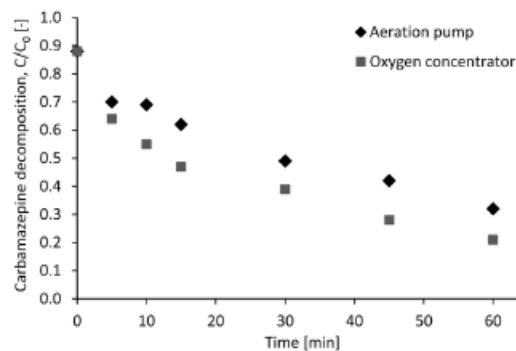
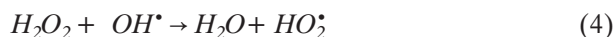


Figure 3.
The influence of aeration method on the decrease of carbamazepine during photocatalysis process (air flow of 4 dm³/min)

The presence of dissolved oxygen in the treated water solutions provide an opportunity to the production of a large number of reactive oxygen forms ($\text{O}_2^{\bullet-}$, HO_2^\bullet), which can act as free radicals able to decompose carbamazepine or force other reactants to form hydroxyl radicals according to the reactions (2) – (7) [7]:



The influence of oxygen concentration in aerated water solutions on the removal efficiency of the psychotropic pharmaceutical compound is shown in Figure 4. The rate of removal of carbamazepine increased with the increase of the oxygen flow supplied to the reactor. The dependence was especially noticeable in the first 30 minutes of the photocatalysis process. The removal rates noted after this time were 52% (flow rate 1 dm³/min), 55% (2 dm³/min), 60% (3 dm³/min), 61% (4 dm³/min) and 66% (5 dm³/min). A similar correlation was also observed in the case of half-life of the pharmaceutical compound. This value decreased with the increase of the concentration of oxygen dissolved in water solutions in the range from 30 minutes for the lowest oxygen flow to less than 13 minutes for the highest applied flow.

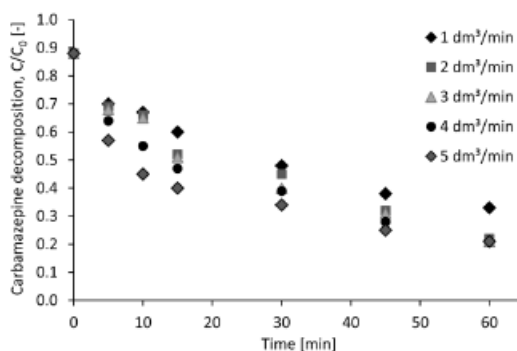


Figure 4.
The decrease of carbamazepine concentration with the increase of air flow by means of the oxygen concentrator

It should be emphasized that the increasing oxygen supply to the reactor does not result in an increase of its concentration in the irradiated water solutions due to the limited solubility of oxygen in the deionized water. In addition, during the photocatalytic oxidation process carried out in an oxygen-free matrix, there is the possibility of recombination of generated hydroxyl radicals according to Equation (8) [10]. This phenomenon results in the decrease of the efficiency of micropollutant oxidation and reduction processes.



3.2. Determination of water toxicity

On the basis of the results obtained during chromatographic analysis of water samples after the photocatalysis process carried out with and without the supplying of oxygen it has been confirmed that a decrease in the concentration of carbamazepine and thus the decrease of water toxicity can be expected. However, the conducted toxicity test demonstrated an inverse relationship (Fig. 5a, Fig. 5b). The toxicity of water solutions increased with the reaction time elongation. The observed relationship results of the formation of toxic by-products of the decomposition of carbamazepine. The presence of dissolved oxygen not only intensified the oxidation of the parent compound, but also the formation of toxic by-products of its decomposition. This fact proves, that during the proposed conditions of photocatalysis process a complete mineralization of the pharmaceutical does not occur. For example, the inhibition of bioluminescence of water samples after 60 minutes of photocatalysis without oxygenation reached approx. 57% and for oxygenated process (air flow 4 dm³/min) approx. 78% (Fig. 5a). The reference of these values

to the classes of toxicity [11] allows to conclude, that the solutions are classified as toxic and high toxic. Additionally, the bioluminescence inhibition of the solutions after photocatalysis assisted by the presence of oxygen supplied by the aeration pump were surprising. Despite the significantly lower concentrations of oxygen in the reaction mixture more toxic by-products were formed. Therefore, it can be concluded that the presence of nitrogen N₂ and carbon dioxide CO₂ promotes the formation of compounds which are characterized by a higher toxicity than carbamazepine. The results presented in Figure 5b show an increase of the water toxicity with the increased oxygen concentration, irrespective of the duration of the UV irradiation process. Water samples after 15 minutes of photooxidation by the gas flow from 3 to 5 dm³/min can be classified as toxic. After 60 min of UV irradiation the bioluminescence inhibition value exceeded to 75%, which changes the classification of the samples to high toxic.

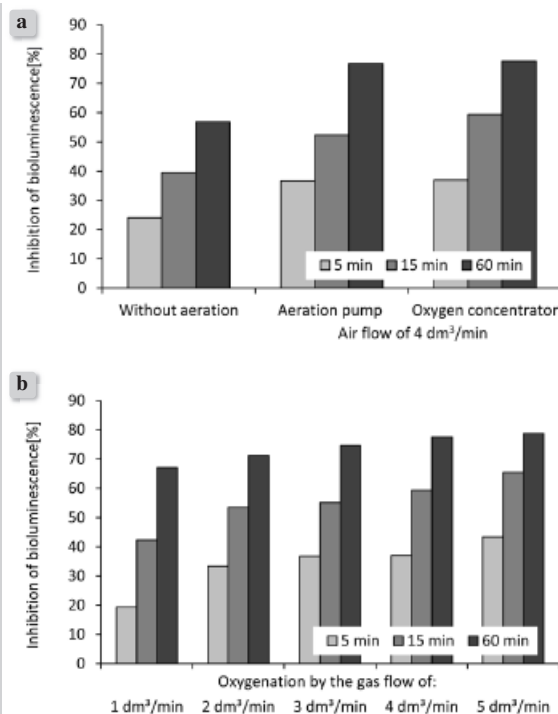


Figure 5.
The influence of the aeration method (a) and the intensity of air flow (b) on the bioluminescence inhibition value of water samples after the photocatalysis process

4. CONCLUSIONS

The conducted research show that the decomposition of carbamazepine takes place by the action of hydroxyl radicals and other reactive oxygen species. The formation of those strongly oxidation species is affected not only by the energy provided by UV radiation, but also by the presence of oxygen dissolved in the water. It has been proved, that the decomposition of carbamazepine increased with the increasing concentration of oxygen in the reaction mixture. On the other hand, high oxygen concentration leads to the formation of more toxic oxidation by-products. This phenomenon has been demonstrated by the results obtained during the toxicological tests. The decomposition of carbamazepine carried out by means of photocatalysis assisted with the addition of oxygen did not allow for complete elimination of the pharmaceutical micropollutant and its degradation of by-products.

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