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Studies on the kinetics of carbamazepine degradation in aqueous matrix in the course of modified Fenton's reactions

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ABSTRACT

The present article describes a study into the kinetics of carbamazepine degradation under influence of the standard Fenton's reagent, light-enhanced Fenton's reagent, as well as modified Fenton's systems in which iron(II) ion is replaced by Cu(I), Cu(II), Ni(II), Mn(II), Cr(III) and V(V) ions. In the course of the study it was established that V(V) ion modified Fenton's reagent was equally effective in relation to carbamazepine as the standard reagent. Parameters of both standard and modified Fenton's reagents were optimized. It was observed that an increased concentration of inorganic ions and acidic pH levels precipitated the decomposition of carbamazepine.

1. Introduction

Dynamic expansion of pharmaceutical markets along with elevated drug consumption are principal reasons behind the increasing pollution of water environments with pharmaceutics and products of their partial decomposition. These substances penetrate into water environments mostly by way of municipal waste, and as biological agents, they pose serious harm to water organisms and to humans [1]. For this reason, one of the overriding goals of environmental chemistry has become to analyze the life cycle of biologically active pharmaceutical substances existent in untreated and treated sewage, as well as in surface water (e.g. rivers, streams, lakes), groundwater, and drinking water [2].

Presence of drugs in surface water is a result of various factors, the most influential among them being: amounts in which the drugs are taken, frequentness and periodicity of their use, forms of their excretion (i.e. as metabolites or in an unchanged form), and effectiveness of their neutralization during sewage treatment. Small as the individual quantities of drugs that enter water environments may be, the sheer constancy of the process leads to their considerable accumulation, followed by increased concentration in water milieus. Pharmaceutical substances prevalent in water ecosystems may be harmful to indigenous water organisms, and – in an indirect way – to humans. Worse still, the negative effects can be non-immediate, cumulating slowly and imperceptibly over a time span of many years to a moment when they become severe threat to human health, especially considering the fact that lifetimes of many drugs in the natural environment reach up to ca. one year, and there are substances which sustain much longer [3]. One of the compounds frequently found in various sections of water ecosystems is carbamazepine (5H-dibenzo[b,f]azepine-5-carboxamide), a drug belonging to the derivatives of dibenzazepine (Fig. 1) which, apart from its common application in the treatment of epilepsy, is administered in neuropathic pains and multiple sclerosis. Carbamazepine exhibits mood-stabilizing properties, and is often used in the therapy of manic episodes and bipolar affective disorders [4,5]. It is characterized by strong lipophilicity; also, ca. 70–80% of the drug bonds with proteins. In the liver, carbamazepine is oxidized, deaminated, hydroxylated and partly esterificated with glucuronic acid. Its main route of excretion is urine, and the metabolites include pharmacologically inert trans-10,11-dihydro-10,11-dihydroxy carbamazepine and pharmacologically active carbamazepine-10,11 epoxide. The biological half-life of the drug is relatively long, and it depends on the duration of the treatment period. In particular, the elimination half-life from the human organism corresponds to the treatment time, amounting to 24–45 h when a single dose is administered, and 15–24 h in long-term therapies [6]. Due to the fact that carbamazepine is so widely used, it belongs to drugs which are most frequently detected in environmental samples, considering the whole gamut of pharmaceutical substances present in the environment. Its mean concentration in municipal waste reaches 2.1 $\mu g\,L^{-1}$ [7]; moreover, it can be found in surface or even drinking water [7,8].

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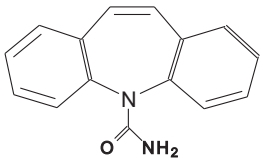

Fig. 1. Carbamazepine structure.

Numerous experiments have confirmed that the compound is highly resistant to photodegradation and biodegradation in conventional sewage treatment plants. Specifically, its photodecomposition lasts between 50 and 100 days [9,10], and the ensuing photoproducts impinge on the natural environment event to a greater extent than the original compound. For that matter, one of the most frequently encountered products of this photodecomposition is acridine, often present in municipal waste [9,11].

In recent years, much attention has been devoted to research on advanced oxidation processes (AOPs). These processes are characterized by great efficiency in the cases of contaminants with high degree of chemical stability and low susceptibility to biological degradation [12,13]. Many organic compounds present in water and sewage in the course of AOP undergo complete mineralization to carbon dioxide and water, or, alternatively, in the course of incomplete oxidation processes, are subjected to decomposition into much simpler molecules such as e.g. alcohols, aldehydes, or biodegradable carboxylic acids.

All methods of advanced oxidation are reliant on generation of highly reactive free radicals, especially hydroxyl radicals (•HO) [14]. It happens that in AOPs the (•HO) radicals are oftentimes provided by the Fenton's reaction. Fenton's reagent exhibits strong oxidative properties in relation to some compounds precisely due to the triggered formation of (•HO) radicals [15,16]. However, in order to boost the performance, efficiency and cost-effectiveness of the reaction, further improvements of Fenton's reagent are sought after. The classic Fenton's reaction, despite its already high efficiency, has certain limitations related to the stability of the solution's pH. Essentially, the acidic character of the solution has to be maintained to ensure that iron(III) hydroxide does not precipitate. Many researchers have been introducing various improvements to the Fenton's reaction, mostly using various sources of iron ions, or other transition metals ions [17–20] alongside additional sources of energy. Accordingly, one can distinguish UV radiation enhanced Fenton's reaction (photo-Fenton), ultrasound aided Fenton's reaction (sono-Fenton), both UV radiation and ultrasound supported Fenton's reaction (sono-photo-Fenton), Fenton's reaction improved by the presence of photocatalyst (UV/TiO_2 + Fenton's reaction), the sono-photocatalytic Fenton's reaction (US + UV/TiO_2 + Fenton's reaction), as well as the electro-Fenton's reactions. All of these have been used for the purpose of efficient removal of harmful substances [21–24].

The experiments described within the scope of the present article aimed at investigating the kinetics of carbamazepine decomposition under the influence of transition metal – hydrogen peroxide type Fenton's reagent, and comparing the results to those obtained by means of the classic and photocatalytic Fenton's reactions.

2. Experimental part

2.1. Reagents

Carbamazepine used in the research was produced by Sigma–Aldrich, USA. Its stock solution with the concentration of 10^{-2} mol L^{-1} was prepared in a 50 mL laboratory flask by dissolving an appropriate weighted amount of the compound in 10 mL of ethanol, and filling up the flask to the full measure with double distilled water. Working solutions of desired concentrations were obtained individually by appropriately diluting the model solution with double distilled water.

Inorganic salts: hydrated iron(II) sulfate, hydrated copper(II) sulfate, copper(I) chloride, hydrated manganese(II) sulfate, hydrated chromium(III) sulfate, hydrated nickel(II) nitrate, ammonium metavanadate were purchased from POCh (Poland). Model solutions of Fe(II), Cu(I), Cu(II), Mn(II), Cr(III) and Ni(II) ions with concentrations of 10^{-2} mol L^{-1} each were obtained by dissolving in double distilled water appropriate weighted amounts of the reagents with the addition of 2 mL 3 mol L^{-1} of sulfuric acid. Individual working solutions were prepared by appropriately diluting the stock solutions. In the case of ammonium metavanadate, the model solution with the concentration of 10^{-2} mol L^{-1} was prepared by dissolving its appropriate weighted amount in 0.1 mol L^{-1} solution of sulfuric acid.

Hydrogen peroxide (CHEMPUR, Poland) in the concentration of 10^{-1} mol L^{-1} was prepared on a daily basis by suitably diluting its 30% solution in MilliQ water.

Samples of raw and treated sewage were taken from the local wastewater treatment plant on 16th March 2013. The samples were adjusted to pH 2 with hydrochloric acid and stored in refrigerator at 0 °C.

2.2. Equipment

Evaluation of the kinetics was carried out observing the changes in absorbance of the carbamazepine solutions by Hitachi U-2800A spectrophotometer.

In the irradiation experiments 16 AU standard UV lamp (Cobrabid, Poland) was used; it was fitted with radiators emitting 256 nm and 366 nm radiation. Considering that the goal of the research was to analyze the course of photodegradation of carbamazepine in the natural environment, the experimental solutions were irradiated with λ = 366 nm UVA radiation.

To determine qualitative compositions of the post-reaction mixtures, a chromatographic system consisting of: a 3D detector Spectra System UV 3000, a low-gradient pump P2000 (Therma Separation, USA), 15 cm long ODS-2 column (SUPELCO INC), and 20 μL Rheodyne injection valve was put into use. ChromQuest Chromatography Data System software version for Windows NT was used for the acquisition and storage of data.

2.3. Experimental procedure

2.3.1. Analysis of the standard and photocatalytic reactions between Fenton's reagent and carbamazepine

A 10 mL volumetric flask was filled in turn with proper measured volumes of Fe(II) and H_2O_2 solution with the concentration of 5×10^{-5} mol L^{-1}, 1 mL of carbamazepine solution (CBZ) with the concentration of 5×10^{-4} mol L^{-1}, and MilliQ water to the full measure. The reaction was observed over a time span of 120 min, during which the absorbance of the solution was periodically recorded, with the first measurement taken after 5 min. Solutions of reagents with identical composition to the scrutinized sample but not containing carbamazepine were used as blanks.

In assessment of the photocatalytic Fenton's reaction, the reaction solution was set up in the same manner as above. Next, the mixture was placed in a crystallizing dish and exposed to 366 nm wavelength radiation. Absorbance was measured every 10 min, the first measurement taken 5 min after the reagents were blended.

2.3.2. Effectiveness of modified Fenton's reagents

The following modified Fenton's systems were taken into consideration: V(V)-H_2O_2, Cu(I)-H_2O_2, Cu(II)-H_2O_2, Ni(II)-H_2O_2,