Chemical Engineering Journal 264 (2015) 856–862

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Application of Fenton-like oxidation as pre-treatment for carbamazepine biodegradation

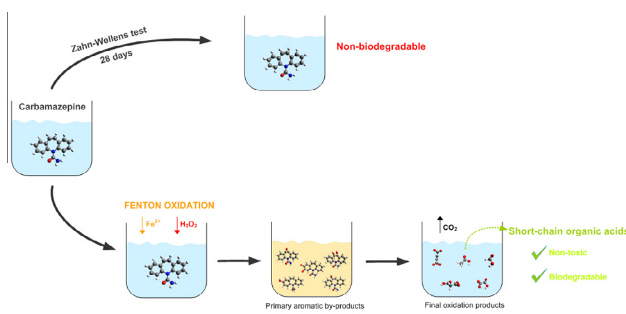
V.M. Monsalvo *, J. Lopez, M. Munoz, Z.M. de Pedro, J.A. Casas, A.F. Mohedano, J.J. Rodriguez

Universidad Autonoma de Madrid, Chemical Engineering Section, Francisco Tomas y Valiente 7, Madrid 28049, Spain

HIGHLIGHTS

- CBZ inhibits the microbial activity being essentially non-biodegradable.
- Fenton oxidation allowed complete conversion of CBZ under mild operating conditions.
- The mineralization efficiency was increased by increasing the temperature.
- Aromatic intermediates were converted into non-toxic short-chain organic acids.
- Fenton oxidation of CBZ enhanced the biodegradability and reduced the toxicity.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 10 September 2014
Received in revised form 28 November 2014
Accepted 29 November 2014
Available online 4 December 2014

Keywords:
Biodegradability
Carbamazepine
Emerging pollutant
Fenton-like oxidation
Respirometry
Toxicity

ABSTRACT

Degradation of carbamazepine (CBZ) upon Fenton-like oxidation has been investigated analyzing the effect of H_2O_2 dose and temperature at a very low catalyst concentration (2 mg L^{-1} of Fe^{3+}). Fenton-like oxidation allowed complete conversion of CBZ, the oxidation rate depending on the amount of H_2O_2 used. The addition of the theoretical stoichiometric amount of H_2O_2 led to the complete conversion of CBZ in 1 h reaction time. The reduction of the H_2O_2 initial concentration down to 10% of the stoichiometric led to a significant increase of that time up to 3 h. The mineralization efficiency of H_2O_2 was considerably increased by increasing the temperature (from 21 to 131 mg TOC/g H_2O_2 at 35 and 50 °C, respectively). Beyond 50 °C no significant effect was observed in the extension of reaction although it proceeded at significantly higher rate. The toxicity and biodegradability of the resulting effluents from Fenton-like oxidation were evaluated by respirometric tests using non-acclimated activated sludge. CBZ strongly inhibits the microbial activity (EC_{50} = 1.8 mg L^{-1}) being essentially non-biodegradable. Fenton-like oxidation of CBZ (10 mg L^{-1}) at 50 °C with the theoretical stoichiometric H_2O_2 amount for complete mineralization (5.6 mg H_2O_2/mg CBZ) allowed obtaining an easily biodegradable effluent.

1. Introduction

There is an increasing concern on the presence of trace organic chemicals, such as pharmaceutically active species, personal care products, endocrine disruptors and pesticides, in water bodies. Approximately 3000 different pharmaceutical ingredients with different specific activity are used in Europe nowadays. Since these compounds commonly undergo transformations in the human body more or less complex combinations of them and their corresponding metabolites are excreted. Among the trace xenobiotics discharged into the aqueous media pharmaceuticals and personal care products are widely represented by a number of compounds largely consumed in modern societies, including drugs (antibiotics,

* Corresponding author at: University Autonoma de Madrid, Seccion Departamental de Ingenieria Quimica, Francisco Tomas y Valiente 7, Madrid 28049, Spain. Tel.: +34 914975615.

E-mail address: victor.monsalvo@uam.es (V.M. Monsalvo).

http://dx.doi.org/10.1016/j.cej.2014.11.141
1385-8947/

tranquillizers, anti-epileptics, etc.), hormones (natural and synthetic), X-ray contrast media, musk fragrances and phytosanitary products among others. These substances can cause different unique impacts on aquatic and terrestrial organisms [1,2]. Moreover, many of them are bioaccumulative since they have been specifically designed to cause biological effects even at trace levels.

Carbamazepine (CBZ), an anticonvulsant and mood-stabilizing drug mainly used for the treatment of epilepsy, bipolar disorder and trigeminal neuralgia, has been found in surface waters. This compound is discharged from private households and from hospitals and eventually reaches municipal wastewater treatment plants (WWTP) [3]. Low removal efficiencies of CBZ (below 10%) are achieved in conventional wastewater treatment plants due to its low biodegradability as well as the poor sorption capacity onto activated sludge [4,5]. Therefore, WWTP effluents are important gateways where carbamazepine can enter the water cycle. Ternes [6] reported the presence of CBZ in 30 WWTP effluents and in 24 of 26 samples from 20 rivers with a 90-percentile of 3.7 and 0.82 $\mu g\ L^{-1}$, respectively. The maximum concentration of carbamazepine in WWTP effluents was 6.3 $\mu g\ L^{-1}$, which was also the maximum concentration detected of all the 32 drugs analyzed in the survey.

Recently, different advanced oxidation processes (AOPs) have been evaluated to remove CBZ from wastewater [7]. Among the AOPs, Fenton oxidation combines some interesting features, like high performance, simplicity of design and both low cost and low toxicity of the reagents used. This process is based on the generation of hydroxyl radicals from hydrogen peroxide decomposition catalyzed by iron salts in acidic medium. Fenton and photo-Fenton processes are among the AOPs most widely studied for CBZ breakdown [8–11]. The potential application of heterogeneous Fenton oxidation for CBZ removal has been explored using nano-magnetite as catalyst. Sun et al. [12] used a modified Fenton process with ferric-nitrilotriacetate complexes to prevent iron precipitation. Additionally, it has been proved that the estrogenic activity of CBZ and its degradation by-products can be effectively neutralized by Fenton oxidation and ferro-sonication, its combination with ultrasonication [13].

The ability of AOPs to reduce the toxicity and improve the biodegradability of recalcitrant compounds has been previously explored [14–16]. The main goal of those studies was to transform the persistent organic compounds into easily biodegradable intermediates, which would be then removed upon biological treatment. In many cases, these chemical oxidation pre-treatments can significantly reduce the toxicity of the starting pollutants but in some others, depending on the operating conditions, the resulting by-products can still be structurally similar to the original toxic and/or non-biodegradable compounds [17–19]. Thus, the effect of a preliminary chemical oxidation step can eventually be insignificant or even negative for further biological treatability of the effluent because of the formation of more toxic and/or less-biodegradable by-products. In the case of CBZ, it is known that when it is only partially mineralized it can be transformed into acride, a highly toxic by-product, under sunlight exposure [20]. Thereby, effective removal techniques need to be developed both in terms of yield and selectivity, while reducing the toxicity and enhancing the biodegradability of the resulting effluents so that can be effectively treated by conventional activated sludge systems.

The objective of the current study is learning on the potential application of Fenton-like (H_2O_2/Fe^{3+}) oxidation and its eventual combination with biological treatment (conventional activated sludge) for the abatement of CBZ. For this purpose, the effect of the H_2O_2 concentration and temperature will be analyzed as the main operating conditions in the Fenton-like oxidation step working always at very low iron concentration (2 $mg\ L^{-1}$). The toxicity and biodegradability of the resulting effluents will be evaluated through respirometric tests.

2. Materials and methods

2.1. Fenton-like experiments

Fenton-like oxidation was carried out in stoppered glass batch flasks shaken in a constant-temperature bath at an equivalent stirring velocity around 200 rpm for 3 h. The reaction volume was 50 mL and the initial pH was adjusted to 3 with nitric acid, which is the well-known optimum for this process [21]. The starting concentration of CBZ was 10 $mg\ L^{-1}$ in all the experiments. This is much higher than the trace concentrations commonly found in water bodies and wastewaters but allows better detection of the reaction by-products. The H_2O_2 concentration was tested within 10–100% of the theoretical stoichiometric amount for the complete mineralization of CBZ (5.6 mg H_2O_2/mg CBZ) a fairly low concentration of catalyst (2 $mg\ L^{-1}$ Fe^{3+}) was always used in order to prevent an uncontrolled generation of radicals and warrant an efficient consumption of H_2O_2 [22]. This reagent was added at the start of each experiment from 33% aqueous solution. The same for Fe^{3+}, which was fed as $Fe(NO_3)_3{\cdot}9H_2O_2$ 1.5 $g\ L^{-1}$ aqueous solution. The effect of temperature was analyzed within the 35–65 °C range. Each experiment was carried out by triplicate being the standard deviation less than 5% in all cases. Blanks with CBZ in absence of H_2O_2 and Fe^{3+} were also performed at all the temperatures tested.

2.2. Biodegradability tests

The Zahn-Wellens test for the evaluation of inherent biodegradability was carried out according to the OECD guidelines [23]. In this test, a mixture containing the target substance and a certain amount of activated sludge in aqueous medium is agitated and aerated at 20–25 °C under diffuse light for 28 d. The ratio between the carbon content of the sample and the dry-weight of the inoculum must range between 1 and 4. Ethylene glycol was used as reference compound to check the degradation activity of the inoculum, which was removed up to 80% in 5 d. Samples were taken periodically for measuring the concentration of the target compound. In addition, the ready biodegradability of the Fenton-like effluents was evaluated in terms of the TOC reduction after 24 h. The biodegradability was tested in parallel in three different bottles to guarantee reproducibility.

2.3. Toxicity assessment

The toxicity of CBZ over the respiratory activity of a mixed liquor was evaluated following the procedure described by Polo et al. [24]. The toxicity assessment of the effluents from Fenton-like oxidation of CBZ was performed according to the method proposed by Ricco et al. [25], based on the OECD respiration inhibition test for activated sludge [26]. This method determines the inhibition from the ratio between the specific oxygen uptake rate value (SOUR) obtained with a reference substrate (sodium acetate) and the one for that substrate mixed with different concentrations of CBZ. EC_{50} is taken as the concentration of CBZ causing a 50% reduction of the reference SOUR. Experiments were carried out at 30 °C using a biomass concentration of 350 mg volatile suspended solids (VSS) L^{-1}.

2.4. Analytical methods

The progress of Fenton-like oxidation was followed periodically by withdrawing and analyzing liquid samples from the reactor.