



Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

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

Removal of diclofenac from water by zeolite-assisted advanced oxidation processes



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ARTICLE INFO

Article history:

Received 4 September 2015

Received in revised form 27 January 2016

Accepted 29 January 2016

Available online 15 February 2016

Keywords:

Diclofenac

FeZSM5

Biodegradability

Toxicity

Catalyst stability

ABSTRACT

The goal of the study was to evaluate the performance of zeolite-assisted advanced oxidation processes for the removal of diclofenac (DCF) in water matrix. Heterogeneous Fenton type catalyst (FeZSM5) was prepared by solid-state ion exchange and characterized by SEM/EDS and ICP/MS analyses. The uniform distribution of iron and atom economy was established. The influence of key operating parameters of applied UV-A/FeZSM5/H₂O₂ process on the activity of zeolite catalyst was investigated using statistical modeling. The results obtained revealed the contribution of adsorption and oxidative degradation to the overall treatment effectiveness, whereas the oxidation became dominant at the end of the treatment. UV-A/FeZSM5/H₂O₂ process applied at optimal conditions determined within the investigated range (pH 4, [H₂O₂] = 50 mM and [Fe]_{FeZSM5} = 2.0 mM) resulted in significant improvement in biodegradability and lower toxicity after 2 h treatment of DCF aqueous solution. The used catalyst showed good stability and retained its catalytic activity in consecutive runs, which was documented by low iron leaching and similar consumption of oxidant in repetitive cycles.

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1. Introduction

Diclofenac (DCF) is one of the most widely available non-steroidal anti-inflammatory drugs, with annual sales of approximately 100 tons. It is estimated that 15% of DCF is excreted unchanged after consumption [1]. Consequently, DCF is detected in influents and effluents of municipal sewage treatment plants and surface waters at $\mu\text{g L}^{-1}$ concentrations, which may cause adverse effects to human health and the environment [2]. DCF showed tendency to bioaccumulation and in combination with other pharmaceuticals, the toxic effect considerably increases [3,4]. During the recent prioritization process DCF is included in the first “watch list” in order to gather monitoring data required for identification of appropriate measures to address the risk posed by priority substances in water [5]. Whilst control at the source is the most desirable and effective measure, the application of appropriate water treatment remains essential. Due to the fact that conventional wastewater treatment systems do not efficiently remove DCF [6], advanced treatment technologies capable of its

complete removal or destruction of its biological activity need to be evaluated and eventually employed.

The technologies based on well-known Fenton reactions may offer a viable solution for the treatment persistent and potentially harmful organic pollutants in water [7–10]. The oxidative mixture of ferrous salt and hydrogen peroxide yields highly reactive transient radical species, such as hydroxyl radicals (HO[•]) [7]. In this work we addressed constraints of Fenton process related to the formation of stable ferric complexes restraining the Fenton catalytic cycle and the separation of homogeneous catalyst after the treatment [7–9]. We applied iron-exchanged zeolite (FeZSM5), as a Fenton type catalyst within UV-A/FeZSM5/H₂O₂ process for the treatment of DCF in water. FeZSM5 is capable to selectively adsorb smaller organic compounds [11–14] and to sustain Fenton catalytic cycle through the surface reactions [11,15,16]. As organic and inorganic ferric complexes can be decomposed under UV-A irradiation [17] surface iron remains available to participate in the Fenton catalytic cycle. At the same time, organic and hydroxyl radicals may be formed upon photolysis of organic and hydroxyl iron complexes, respectively, contributing to the overall process effectiveness. We tested FeZSM5 activity and determined the influence of key operating parameters of applied processes using statistical/empirical approach combining Box–Behnken

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experimental design (BBD) with response surface methodology (RSM). The operating conditions yielding the highest DCF removal and conversion were determined. The effectiveness of UV-A/Fe-ZSM5/H₂O₂ in terms of TOC removal and mineralization, biodegradability and toxicity improvement, and FeZSM5 reuse was assessed.

2. Materials and methods

2.1. Chemicals

Diclofenac sodium salt (C₁₄H₁₀Cl₂NNaO₂, p.a., Sigma–Aldrich) was used as a target pollutant. Methanol (CH₃OH, HPLC grade), and *ortho*-phosphoric acid (o-H₃PO₄, w=85%), both Sigma–Aldrich, were used as HPLC mobile phases. The catalyst was prepared from NH₄ZSM5 zeolite (CVB8014, Zeolyst International, USA), and ferrous sulphate (FeSO₄ × 7H₂O, p.a., Kemika, Croatia). Hydrogen peroxide (H₂O₂, w=30%), sulfuric acid (H₂SO₄, >96%), sodium hydroxide (NaOH, p.a.), sodium chloride (NaCl, p.a.), sodium sulfite (Na₂SO₃, p.a.), potassium thiocyanate (KSCN, p.a.), hydrochloric acid (HCl, 36.5%), and ammonium metavanadate (NH₄VO₃, p.a.) were all purchased from Kemika, Croatia.

2.2. Experimental procedure

The FeZSM5 catalyst was prepared by solid solid-state ion exchange according to the procedure given by Rauscher et al. [18]. The preparation started with the intensive mashing of FeSO₄ × 7 H₂O (0.9 g) and NH₄ZSM5 (5.0 g) in a mortar under ambient conditions, followed by a thermal treatment under aerobic conditions (in the conventional furnace) at 400 °C for 3 h. The final step involved the calcination process at 600 °C for 1 h.

All experiments were performed with the DCF water solutions (c₀=0.1 mM) in a water-jacketed (V=0.08 L and T=25.0 ± 0.2 °C) glass batch photoreactor. UV-A₃₆₅ lamp (P₀=3.04 × 10⁻⁷ Einstein s⁻¹) was placed vertically in the middle (L=1 cm), while mixing was provided by magnetic stirrer (550 rpm). After the addition of FeZSM5 and pH adjustment, H₂O₂ was added and UV-A lamp was immediately switched on, where applicable. The duration of experiments set by BBD was 15 min. During kinetic experiments, samples were taken at 0, 2, 5, 10, 15, 30, 45, 60, 75, 90, 105 and 120 min. Aliquots were filtered using Chromafil XTRA RC (25 mm, 0.45 μm, Macherey Nagel) and analyzed immediately. Desorption tests were performed by mixing used catalysts in DI water (pH 7.00 ± 0.05) for 15 min.

2.3. Analyses

DCF removal was monitored by HPLC, Series 10, Shimadzu, equipped with UV-DAD, SPD-M10A_{VP}, Shimadzu, using EC 250/4.6 120-5C18 column, Macherey–Nagel, and mobile phase CH₃OH/phosphate buffer operating at 1.0 mL min⁻¹ flow. The organic content was monitored by Total Organic Carbon analyzer, TOC-V_{CPN}, Shimadzu. Chemical oxygen demand (COD) and biochemical oxygen demand (BOD₅) were determined by colorimetric methods using HACH DR2800 spectrophotometer, and LCK reagent kits, Hach-Lange. The toxicity on *Vibrio fischeri* was examined using BioFix Lumi-10 Toxicity Analyzer, Macherey–Nagel, according to ISO 11348-3. UV/vis spectrophotometer (Lambda EZ 201, PerkinElmer) was used for quantification of ferric iron by thiocyanate colorimetric method [19] and H₂O₂ by metavanadate method [20]. NH₄ZSM5 and FeZSM5 were characterized by Inductively Coupled Plasma Mass Spectrometer (ICP-MS), Elan[®] DRC-e, PerkinElmer, and Scanning Electron Microscope (SEM), JSM7001 TTLS, JEOL. The point of zero charge, pHP_{CZ} of NH₄ZSM5 and FeZSM5 was determined using method described by Kragovic et al. [21].

2.4. Calculations

BBD and RSM were employed to investigate the influence of process parameters: pH, [H₂O₂] and [Fe]_{FeZSM5}, represented by independent variables: (X₁), (X₂) and (X₃), respectively, on the effectiveness of dark/and UV-A/FeZSM5/H₂O₂ process and catalyst stability. The chosen responses were: TOC removal, DCF removal, DCF conversion, leaching of iron ions, and oxidant consumption represented by dependent variables; Y₁, Y₂, Y₃, Y₄ and Y₅ respectively. The combined influence of studied parameters on process performance is presented by RSM model [22]:

$$Y_i = \beta_0 + \beta_1 X_1 + \beta_{11} X_1^2 + \beta_2 X_2 + \beta_{22} X_2^2 + \beta_3 X_3 + \beta_{33} X_3^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 \quad (1)$$

The values of independent variables are summarized in Table 1 and Table S1 (Supplementary material). BBD matrices, obtained results and values of chosen responses are given in Table 2 and Table S2 (Supplementary material), for UV-A/and dark/FeZSM5/H₂O₂, respectively. The fitting of RSM models was evaluated by coefficient of determination (R²) and the analysis of variance (ANOVA), using STATISTICA 10.0, StatSoft; Design-Expert 8.0, StatEase; and Mathematica 9.0, Wolfram Research.

3. Results and discussion

3.1. Zeolite catalyst characterization

NH₄ZSM5 and FeZSM5 zeolites were characterized by SEM and ICP-MS analyses to obtain insights into their morphologies and composition. As can be seen from Fig. 1, the shape and size of particles are similar at both SEM images, indicating that the zeolite morphology was preserved upon applied solid-state ion exchange. On the right image, light spots on the zeolite surface can be observed presumably pertaining to iron species. The results of EDX mapping analysis presented in Fig. 2 revealed that the iron species are well distributed through the zeolite surface in spite of few agglomerated structures. The full constitutional map of FeZSM5 zeolites is provided in Fig. S1 (Supplementary material).

ICP-MS analysis revealed that the iron is present in trace amounts in non-exchanged zeolite (0.34 mg g⁻¹). In previous study we demonstrated that NH₄ZSM5/H₂O₂ system did not yield oxidative degradation of targeted pollutants [11]. Such results indicate that iron in NH₄ZSM5 is present either (i) in insufficient amount or (ii) in inactive form to catalyze H₂O₂ decomposition throughout Fenton reaction. The iron content in FeZSM5 zeolite amounts 3.76 × 10⁻² g g⁻¹, which closely corresponds to the theoretically calculated value 3.72 × 10⁻² g g⁻¹. Iron distribution and content indicate the potential of FeZSM5 to be used as heterogeneous Fenton type catalyst.

3.2. Dark/FeZSM5/H₂O₂ process

Preliminary tests were performed in pH range 3–7, [H₂O₂] from 1 to 50 mM, and [Fe]_{FeZSM5} from 0.2 to 2 mM (Table S1, Supplementary material). At pH 7, we did not record any changes

Table 1
Experimental range and levels of independent variables for UV-A/FeZSM5/H₂O₂ process.

Process parameter	Coded value	Levels		
		-1	0	1
pH	X ₁	4	5.5	7
[H ₂ O ₂] (mM)	X ₂	1	25.5	50
[Fe] _{FeZSM5} (mM)	X ₃	0.2	1.1	2.0

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