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REMOVAL DICLOFENAC SODIUM FROM AQUEOUS SOLUTION BY ADVANCED OXIDATION PROCESS

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Introduction

Diclofenac sodium (DFC) is one of the best-selling non-steroidal anti-inflammatory drugs. The high level of consumption of this drug (1000 tons/year) leads to high values in municipal waters – 7.1 g/L. In general, anti-inflammatories are characterized by low biodegradability and high persistence in sewage treatment plants, which leads to their bioaccumulation in surface waters, sediments and sludges. Having a complex composition, these pollutants are difficult to remove by conventional or biological methods, and the application of advanced oxidation processes (AOPs) is an effective alternative for their reduction or elimination. It is known that the viability of these methods depends on the source of hydroxyl •OH radical formation. Therefore, the aim of the work is to reduce the concentration of DFC in aqueous solution by AOPs.

Materials and methods

All the experimental samples were analysed for the DFC concentration using Spectrophotometric equipment (model UV-Vis T80+) at wavelength of 276 nm. Chemical oxygen demand (COD) was determined according to the Standard Methods with potassium dichromate. The analysed systems contain sodium diclofenac with an initial concentration of 50 mg/L. The degradation kinetics of diclofenac sodium from aqueous solutions was estimated by the variation of DCF concentration (Ct), determining the reaction rates ($\Delta c/\Delta t$, molL⁻¹s⁻¹), rate constants (kt, s⁻¹). The oxidation/mineralization was monitored by the variation of residual organic compounds (CODt).

Results and conclusions

It was found that upon irradiation with UV-C rays the process proceeds more intensively both for the direct and the induced photolysis of DFC from aqueous solution, thus the rate constant (k) is 4.8·10⁻³ s⁻¹ and the reaction rate ($\Delta c/\Delta t$) of 5.05·10⁻⁷ molL⁻¹s⁻¹. These parameters are higher compared to the rate constant (k) of 2.6·10⁻³ s⁻¹ and the reaction rate ($\Delta c/\Delta t$) of 3.33·10⁻⁷ molL⁻¹s⁻¹ obtained when irradiating the systems with UV-A. This can be explained by the fact that DCF has an absorption maximum at $\lambda < 276$ nm, which falls within the UV-C absorption range. Subjecting the pollutant to direct photolysis, no changes in the initial concentration of the substrate were noted. It was deduced that the energy of UV-A radiation (315–400 nm) is not sufficient to generate transformations of the substrate.

To establish the influence of the nature of the catalyst on the degradation/mineralization kinetics, the following synthetic systems were studied (Table 1). It is observed that the oxidation of 50 mg/L DFC from aqueous solution with Fenton's reagent results in the highest degradation/mineralization, with a rate constant (k) of $2.7 \cdot 10^{-3} \text{ s}^{-1}$ and a reaction rate ($\Delta c/\Delta t$) of $2.1 \cdot 10^{-7} \text{ molL}^{-1}\text{s}^{-1}$.

Table 1. Removal DCF from aqueous; $[\text{DCF}]_0=50 \text{ mg/L}$, UV-C irradiation, $[\text{H}_2\text{O}_2]_0 = 1 \text{ mM}$ and $[\text{Fe}^{2+}]_0 = 0.1 \text{ mM}$, reaction time-600 s, 25°C

Synthetic systems	Degradation, %	Removal COD, %	$k \cdot 10^{-3}, \text{ s}^{-1}$	$\Delta c/\Delta t \cdot 10^{-7}, \text{ molL}^{-1}\text{s}^{-1}$
<i>DFC-UV</i>	5.2	77.9	0.5	0.08
<i>DFC-H₂O₂-UV</i>	58.3	77.1	1.14	1.5
<i>DFC-H₂O₂-Fe²⁺</i>	81.6	80.4	2.7	2.1
<i>DFC-H₂O₂-Fe²⁺-UV</i>	76.2	84.0	2.3	1.9

Diclofenac sodium can be degraded by direct photolysis with UV-C rays, due to the fact that it has an absorption maximum in the UV-C region (276 nm), but the degradation kinetic parameters are lower, because an insufficient concentration hydroxyl $\bullet\text{OH}$ radical (after 10 min of reaction) and increases insignificantly during 60 min. Thus, for complete conversion kinetics, it is necessary to significantly increase the reaction time up to 240 min. In the presence of hydrogen peroxide, the *DFC-H₂O₂-UV* system has much higher degradation/mineralization kinetics because a higher concentration of hydroxyl $\bullet\text{OH}$ radical is formed. Thus, the DCF conversion kinetics occurs with a higher reaction rate ($1.5 \cdot 10^{-7} \text{ molL}^{-1}\text{s}^{-1}$). These results can be attributed to the combined effect of both mechanisms. It can be concluded that the oxidation mechanism in the presence of hydroxyl $\bullet\text{OH}$ radical contributes significantly to the overall DCF degradation kinetics. To accelerate the oxidation process, Fe^{2+} ions were used as a catalyst. Their presence (*DFC-H₂O₂-Fe²⁺* and *DFC-H₂O₂-Fe²⁺-UV*) leads to an almost complete conversion in the first 3 min of reaction, thus both the degradation performance and the degree of oxidation/mineralization are, on average, 80%. These high performances are the result of the formation of aqua ferric ions in large quantities that have a strong catalytic activity in the strongly acidic environment. When interacting with hydrogen peroxide it is formed hydroxyl $\bullet\text{OH}$ radical which oxidize the pollutant to less toxic organic compounds. The oxidation mechanism takes place in 2 stages: in the first 10 min diclofenac is oxidized to intermediate aromatic compounds such as quinone compounds, catechol, phenol, toluene etc. with a much higher rate constant k_1 compared to k_2 for the transformation during 30 min of aromatic compounds into aliphatic intermediate compounds:

