

# Comparison of Effectiveness of Cl<sub>2</sub>/UV and PDS/Fe Advanced Oxidation Processes in Removing Diclofenac from the Aquatic Environment

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**Abstract** The presence of many anthropogenic substances, including drugs, is a big problem for the environment. Many medicinal substances can have a negative effect on the natural environment. Therefore, methods of removing these substances from the environment are being sought. The so-called advanced oxidation processes can be useful in removing drugs from the aquatic environment. This work compares the effectiveness of two methods, classified as advanced oxidation processes, in removing diclofenac, a popular drug from the group of non-steroidal anti-inflammatory drugs. Two methods were selected for comparison – chlorine/UV method and the second using peroxydisulfate activated with iron(II) ions. Diclofenac was chosen as the model compound because of its relative resistance to oxidation. The results show that the chlorine/UV method is more effective in diclofenac removing (approx. 80% lower diclofenac content after the end of the experiment) compared to PDS/Fe(II) method (it removes approx. 20% of these substance), but it turns out that diclofenac is quite resistant to the effects of both methods of oxidation.

**Keywords:** Diclofenac, AOP, chlorine, PDS, wastewater treatment

## 1. Introduction

Concern for the natural environment continuously takes more and more attention of the research community, due to potential hazards resulting from the presence of various substances. Currently, one of the main problems associated with environmental pollution is the presence of medicaments and their derivatives in the environment [1]. As most of these substances is well-dissolved in the water, they usually bypass the water-treatment procedures and further sediments in the natural water reservoirs, including both surface and underground water. The contaminated water is again used by the humans, thus the problem is more and more important. And as the medicaments are usually active in the trace amounts, even the trace presence of them in the water becomes a very important issues.

The presence of pharmaceuticals are became a global concern as new types of ECs in surface and ground waters (i.e., ground waters, rivers and lakes, hospital effluents, domestic effluents, pharmaceutical industries, and wastewater treatment plants) have been identified and reported due to their extensive uses and enhanced analytical techniques. After being metabolized partially by humans or animals, most of these pharmaceuticals are excreted into wastewater and treated at wastewater treatment plants. The residues of pharmaceuticals and/or PPCPs are, although, generally detected at trace levels ranging from a few nanograms per liter (ng/L) to several microgram per liter (µg/L) in water bodies, their negatively impact on human health and aquatic environment is alarming with long-term exposure [2].

Removal of medicines in sewage treatment plants is conducted mainly by the biological methods, however, according to the results of research [3,4], the effectiveness of these methods is not sufficient. Therefore, it seems necessary to apply other methods of treating sewage. As a consequence, several methods have been proposed recently to solve the problem. For example, high efficiency of AOPs (Advanced Oxidation Process) has been demonstrated - advanced oxidation methods, in removing water pollution [5]. However, some of these methods have several disadvantages. For example, the ozone-based advanced oxidation processes (AOPs) will form bromate ion (a suspected carcinogen) from bromide [6]. And there is a need to treat the off-gas and to strip VOCs [7].

In early 1980s, Advanced Oxidation Processes (AOPs) were first introduced and implemented for drinking water treatment [9], which lately studied and developed in wider aspects by a number of researchers and scientists around the world. Nowadays, these technologies are not only demonstrating for drinking water, a number of Advanced Oxidation Processes (AOPs) have been contributing to increase wastewater biodegradability as well as to remove refractory organic matters, trace organic contaminants (TOxCs) and certain target inorganic pollutants. AOPs have been broadly applied for treatment of different types of wastewaters because the strong oxidants can readily degrade recalcitrant organic pollutants. Earlier, the generation of hydroxyl radicals ( $\bullet\text{OH}$ ), and later on, the extended concept of sulfate radicals ( $\text{SO}_4\bullet^-$ ) as strong oxidants have been applied for the degradation of contaminants.

The aim of this work is comparison of two advanced oxidation methods in case of removing of exemplary drug from water. We chose diclofenac to our research for two reasons. First, it is a very popular drug from the group of non-steroidal anti-inflammatory drugs, and the second, it is relatively resistant to oxidation using method such as ozonation [8]. On the other hand we chose two specific advanced oxidation processes: peroxydisulfate activated by Fe(II) ions, which generate sulfate radicals and chlorine/UV process, in which hydroxyl radicals and chloride radicals ( $\text{Cl}\bullet$ ) were generated.

## **2. Experimental**

### **2.1. Chemicals and reagents**

Diclofenac (sodium 2-[2-(2,6-dichloroanilino)phenyl]acetate) injection ampoules of Sandoz GmbH were purchased from local Pharmacy. Potassium peroxydisulfate (purity >99%) was obtained from Sigma-Aldrich. Chlorine solution was prepared on-site. All other chemicals (i.e. reagents needed to obtaining chlorine solution and for determination of the concentration of chlorine solution) were purchased from Chempur or POCH S.A. Poland.

### **2.2. Experimental procedures**

Solution of diclofenac was oxidized by potassium peroxydisulfate activated in homogenous condition (Fe(II)) and by chlorine activated by UV radiation. pH of solutions was adjusted by adding the solution of sulfuric acid or sodium hydroxide to reach a pH of 5.8. At preselected time intervals of 0, 1, 3, 5, 15, 40 and 60 minutes, an amount of 2.00 ml of the reaction liquid was transferred using Transferpette pipette, from the reactor beaker to the leveled HPLC vials, which contained 50  $\mu\text{l}$  of preloaded methanol as a scavenger of free radicals. Samples were analyzed via HPLC to determine the remaining concentration of Diclofenac and the analysis of each vials were performed in duplicate (twice) and the mean values were taken as results. Additionally, there were performed experiments in which only UV radiation was applied to diclofenac.

### **2.3. Analytical procedures**

The concentration of Diclofenac was measured by a reverse phase highperformance liquid chromatography (HPLC) system (LC-2040C 3D, Shimadzu, Japan) equipped with a Luna® Omega 3 $\mu\text{m}$  PS C18 100Å column (4.6mm  $\times$  250mm, Phenomenex, California, USA) and a diode array detector (DAD) at wavelength of 192 nm. The mobile phase for the analysis of Diclofenac concentration consists of 15% methanol, 85% water and few droplets of  $\text{H}_2\text{SO}_4$  only for acidic pH. Flow rate was set as 1.0 ml/min and injection value was 20  $\mu\text{L}$ .

## **3. Results and discussion**

The percentage of diclofenac in the tested samples is presented in figure 1.

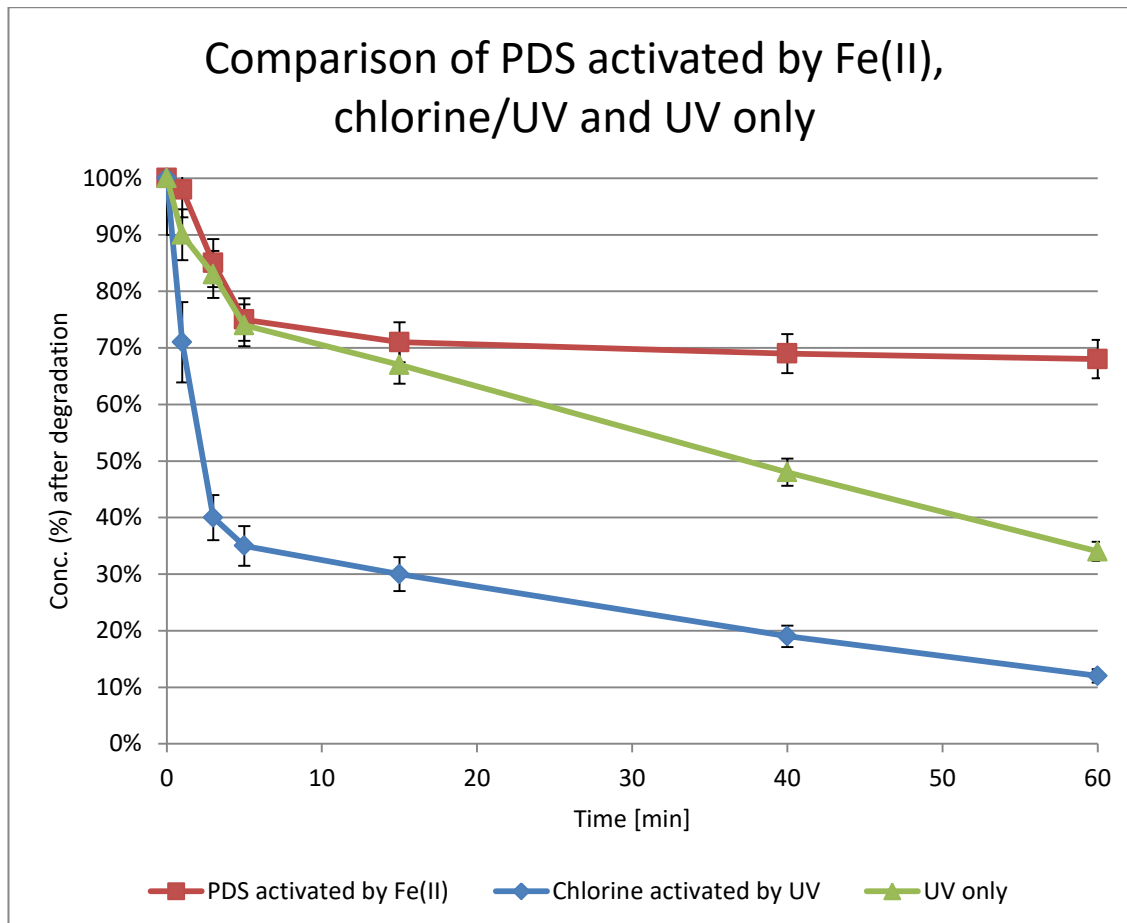


Fig. 1. Percentage of diclofenac in the sample after the appropriate duration of the experiment.

As can be seen from the figure, both methods show the highest activity during the first 10 minutes of the process. It is visible also a significant difference in the degree of diclofenac destruction. Chlorine activated by UV radiation can remove approximately 60% of diclofenac in the first five minutes of experiments, and reach the final level of removal around 90% after 60 minutes of reaction. However, UV radiation can be the main destructive factor. The results for UV only experiments show that it can be observed approximately 70% destruction of diclofenac after 60 minutes of UV lamp work. In case of using PDS/Fe(II) method, only 25% of diclofenac was removed in first 5 minutes of reaction and final removal range is about 30%. It can be observed that there is no significant change of removal range after 15 minutes of experiment. It can suggest that the oxidizing agent has been exhausted.

#### 4. Conclusion

1. Diclofenac confirms its relatively high resistance to oxidizing agents, especially in case of using PDS activated by Fe(II) method.
2. Comparison of these two methods has favourable effect for the chlorine/UV method.
3. Chlorine/UV method showed promising results, which encourage further research.
4. An important issue is the influence of UV radiation on the destruction of diclofenac. Experiments show that UV light is quite effective.

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