



Decomposition of diclofenac in sewage from municipal wastewater treatment plant using ionizing radiation

Anna Bojanowska-Czajka

Abstract. The decomposition of diclofenac (DCF) in sewage sludge from municipal wastewater treatment plant was investigated. It was found that adsorption of DCF on sludge is about 40%. Compared to previous studies, where the degradation yield in aqueous solution was 100%, in those experiments at the dose up to 5 kGy, only 50% of initial DCF concentration of 50 mg L⁻¹ was decomposed in sediment and in solution over the sediment. The experiments were carried out using both gamma radiation and electron beam. It has been observed that DCF in the aqueous phase, above the sediment, was decomposed with the same efficiency using both gamma radiation and electron beam. Whereas for DCF in the sediment, a higher degradation efficiency was found when gamma radiation was applied. This is most likely due to the limited penetration depth of the electron beam into the sludge layer. It was shown that the applied peroxide addition (in a stoichiometric amount needed for complete mineralization of 50 mg L⁻¹ DCF) did not cause increase in yield of DCF decomposition.

Keywords: Diclofenac • Degradation efficiency • Electron beam • Gamma rays • Sewage sludge

Introduction

At the present time in Europe, the topic of organic pollutants is regulated by European Union (EU) Directive 2013/39. This document introduces the obligation to monitor the concentrations of selected chemical substances from the observation list in surface waters. The observation list contains substances for which the available information suggests that they may pose a risk to the EU aquatic environment. As a result of the last update in 2015, four substances from the pharmaceutical group were added to the list, of which one was diclofenac (DCF). DCF is one of the most commonly used non-steroidal anti-inflammatory drugs (NSAID), and its average consumption is 0.33 ± 0.29 g/person/year [1]. For relatively large production, a large number of various types of pharmaceuticals containing DCF as an active substance are available on the market without a prescription. It causes high consumption of DCF, which leads to more and more frequent detection of this drug in the environment. DCF was detected in samples from influent, effluent, and receiving streams, in surface waters, in groundwater, and even in drink-

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ing water, at a concentration level from 13 ng L^{-1} to $7.1 \text{ } \mu\text{g L}^{-1}$ [2]. Some ecotoxicological studies have shown that trace amounts of DCF can accumulate in aquatic organisms, which then become toxic to other microorganisms. The available literature data show that in biological treatment processes, 100% efficiency is not achieved. Joss *et al.* [3] found that biological removal varies strongly from compound to compound, with no evident correlation to the chemical structure of the compound. In these conditions, they reported the partial removal of DCF from wastewater at 20–40%. When the membrane bioreactor was applied for wastewater treatment, even after 26 days DCF was still present and the efficiency of decomposition was 0% [4]. Numerous studies are being carried out to find new, more efficient methods of removing these types of pollutants from water and wastewater [5–10], with the use of radiation technology [11–15]. NSAID pharmaceuticals are a relatively large group for which this research has been carried out, including DCF [16–19]. A separate problem is the sewage sludge generated in wastewater treatment plants, which may contain a wide range of harmful, toxic substances, such as heavy metals, polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-p-dioxins and dibenzo-p-furans, polychlorinated biphenyls, di-phthalates, polybrominated diphenyl ethers, and residues of detergents, pharmaceuticals, personal care products, endogenous hormones, synthetic steroids, and much more. The amounts of sludge produced in the EU are very large. The 28 EU Member States generate >10 tons of sewage sludge (dry matter) from municipal wastewater treatment plants annually [20]. Germany, the United Kingdom, Spain, France, and Italy produce >55–65% of the total sewage sludge amount generated [21]. Only around 40% of the sewage sludge produced in Europe is used as fertilizer in agriculture. The use of sludge in agriculture in the EU is currently regulated only by the limits of heavy metals (Cd, Cu, Hg, Ni, Pb, and Zn) listed in Council Directive 86/278/EEC. These documents are now over 30 years old. Several European countries have introduced more stringent requirements compared to the EU directive and have adopted concentration limits for other heavy metals, synthetic organic compounds, and microbial contamination. Poland, like Denmark and Finland, is in the group of countries that allow the use of sewage sludge after its preliminary treatment, for example, chemical treatment, heat treatment, composting, pasteurization, or fermentation. In Austria, Belgium, Germany, and the Netherlands, the use of sewage sludge in forests and green areas is completely prohibited [22]. One of the hygienization methods is the application of electron beam treatment. In this process, a small radiation dose causes deactivation of all microorganisms and their spore forms in sewage sludge [23]. As a part of this research, DCF was selected as a representative of organic pollutants present in sewage sludge. The degradation efficiency of DCF was determined with the applied radiation dose sufficient for complete hygienization.

Materials and methods

Chemicals

All chemicals applied were of the highest purity grade available and were used as received. DCF (2-(2-(2,6-dichlorophenylamino) phenyl)acetic acid) was purchased from Sigma Aldrich, Poland. Acetonitrile (used as eluent in high-performance liquid chromatography, HPLC) was purchased from J. T. Baker (USA) and hydrogen peroxide from Stanlab Sp. J. (Poland). Stock solution of DCF was prepared in deionized water Milli-Q (Millipore).

Irradiation conditions

Sewage sludge spiked with DCF to 50 mg L^{-1} was irradiated both with gamma and electron beam (EB). Gamma parameters: Co^{60} source Gamma Chamber with a dose rate of 2.5 kGy/h . The samples were irradiated in sealed 50-mL conical glass flasks. Dosimetry was carried out with the Fricke solution. The EB parameters were irradiation was carried out with an electron accelerator Elektronika (Russia) of beam energy 10 MeV, beam power 15 kW, and in the following operating conditions: pulse duration $4 \text{ } \mu\text{s}$, break between the pulses 2.5 ms, and dose delivered by pulse – 200 Gy. The dose rate was estimated at 20 kGy/s . Irradiated solutions were placed into polyethylene bags forming a layer of liquid on the conveyor (3–4 mm thick). DCF decomposition monitoring was carried out mainly with the use of HPLC analysis, according to our previous study [16].

Extraction procedure

Extraction procedure steps:

1. Sewage sludge spiked with DCF to 50 mg L^{-1} ;
2. 25 mL of the sample prepared in this way was centrifuged (4500 rpm), the supernatant solution was decanted, filtered, and subjected to chromatographic analysis;
3. In the next stage, methanol was added to the centrifuged sediment to a volume of 25 mL. The sample prepared in this way was placed in an ultrasonic bath for 15 min;
4. After this step, the precipitate was centrifuged again (4500 rpm), and the methanol extract of the precipitate was taken, filtered, and submitted to chromatographic analysis.

Results and discussion

Distribution of DCF in the sludge and solution over the sludge

In the current regulations, it is important to develop analytical methods that will allow to determine the level of selected organic pollutants in sewage sludge at relatively low concentration and high accuracy.

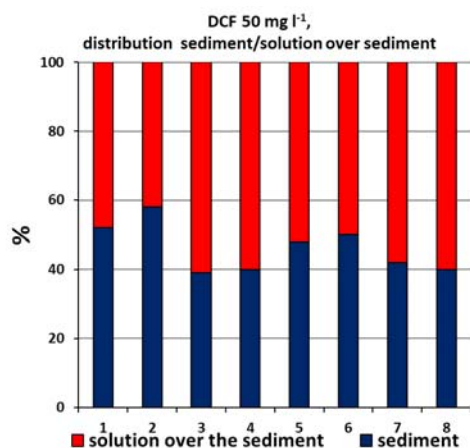


Fig. 1. Distribution ratio for 50 mg L⁻¹ DCF in sewage sludge.

According to various estimates, sample preparation usually takes about 70–90% of the time spent on analysis. Therefore, a great deal of effort is focused on developing reliable procedures characterized by the simplicity of both operations and equipment involved in the process. Of the extraction methods, classical techniques are still relatively most commonly used: Soxhlet extraction and ultrasound extraction [24]. Most often the sewage sludge is freeze-dried or centrifuged before the extraction stage in order to remove as much water as possible. Then extraction is carried out and the analytes are transferred to the organic phase. In the first stage, a procedure for extraction of DCF from the sewage sludge was developed to enable its chromatographic determination. The initial DCF concentration was 50 mg L⁻¹. The concentration was selected in such a way as to be able to compare the obtained results with the results of earlier studies, which concerned the degradation of DCF in water under the influence of gamma radiation [16]. The data obtained for a series of eight repetitions allowed to assume that from an initial DCF concentration of 50 mg L⁻¹, about 45% is adsorbed on the sediment (Fig. 1). These values were used in further studies on the DCF degradation in the sewage sludge using radiation technology both gamma and electron beam. DCF concentration in both phases, sediments and solution over sediment, was carried out according to the previously developed analytical method [16].

DCF decomposition in sewage sludge

So far the studies carried out with initial DCF concentrations in the range of 20–50 mg L⁻¹ in aqueous solutions have shown that the decomposition using ionizing radiation takes place both by reaction with hydroxyl radical (OH) and hydrated electron (e_{aq}⁻) [17, 25]. The reaction with the [•]OH radical occurs much faster, in the range of 9.0 [14] to 9.29 × 10⁹ M⁻¹ s⁻¹ [25], than the reaction with hydrated electron (1.53). Toxicity changes using the Microtox bioindication test with an increase in the dose of ionizing radiation were also examined [17, 25]. Our previous works have shown that for an aerated

aqueous solution with initial DCF concentration of 50 mg L⁻¹, the total DCF degradation was observed at a dose of 4 kGy [16]. For the degradation process carried out for natural matrices, the presence of other so-called free radical scavengers, which compete with the substances for which the degradation process is carried out, may have a significant impact. They are primarily nitrates, carbonates, chlorides, or humic compounds. Their presence most often negatively affects the efficiency of the radiolytic decomposition of selected organic pollutants, although there are known cases in which a positive effect of the presence of these compounds has been observed [26]. Previous studies have shown that in the case of an aqueous DCF solution with an initial concentration of 50 mg L⁻¹, the presence of scavengers, that is, nitrates, carbonates, and humic acid at concentrations from 50 mg L⁻¹ to 100 mg L⁻¹ practically does not affect the efficiency of DCF decomposition in water [16]. On the other hand, Zhuan showed that for a DCF with an initial concentration of 30 mg L⁻¹, the gamma-ray yield at dose 0.8 kGy decreases from 80.8% to 62.9% in the presence of 30 mg L⁻¹ humic acid [27]. As the main reason for the decrease in decomposition efficiency, the authors mention the reactions of humic acid with hydroxyl radical. In our study, sludge spiked with DCF up to 50 mg L⁻¹ irradiated both the gamma and electron beam. Using the extraction procedure, degradation efficiency of DCF in the solution over the sediment and in the sediment was determined. The obtained results are presented in Fig. 2.

Compared to previous experimental data on DCF decomposition in water in the presence of scavengers [16, 27], the efficiency of DCF decomposition

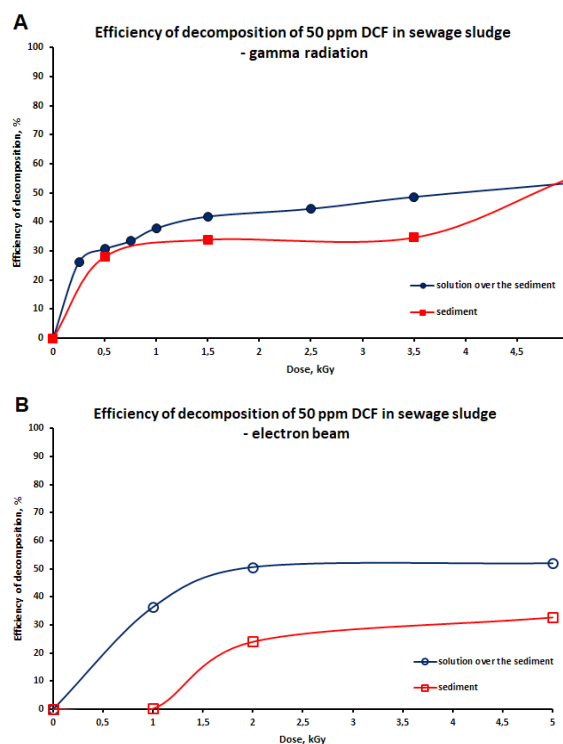
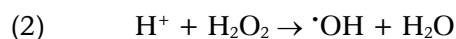
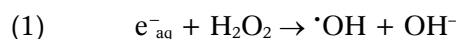


Fig. 2 Efficiency of decomposition of 50 mg L⁻¹ DCF in sewage sludge under the influence of ionizing radiation: (A) gamma radiation and (B) electron beam.

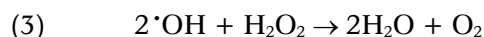
in sewage sludge is much lower. When gamma radiation is used for doses below 5 kGy, the decomposition efficiency in the sediment is slightly lower than in the solution over the sediment. Both for the sediment and for solution over the sediment the maximum efficiency achieved for 5 kGy was only 50%. Significantly greater differences were observed in the case of electron beam application; for each of the applied doses the DCF decomposition efficiency in the sediment was lower than in the solution over the sediment. The maximum efficiency value obtained for a dose of 5 kGy was 30%. The results obtained may indicate that in the case of sludge, the thickness of the irradiated sludge layer is very important; perhaps centrifugation of the sludge before irradiation would allow for a higher degree of DCF decomposition in the sludge itself.

DCF decomposition in sewage sludge in the presence of H₂O₂

To improve the efficiency of DCF decomposition in the sewage sludge using ionizing radiation, the addition of hydrogen peroxide was used. It is well known that hydrogen peroxide reacts with hydrogen atom H ($k(20^\circ\text{C}) = 2.4 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$) and with the solvated electron e_{aq}^- ($k(20^\circ\text{C}) = 1.5 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$), producing an additional portion of hydroxyl radicals [28], according to the following reaction:



However, the excess hydrogen peroxide in the solution can also act as a typical hydroxyl radical scavenger; the reaction takes place according to the rate k constant (20°C) = $3.1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ as



It is very difficult to correctly determine the optimal amount of hydrogen peroxide needed to improve the efficiency of the radiolytic process, because it requires taking into account the numerous reactions of the generated radicals with intermediate products. In the gamma-radiation study, an addition of 840 μM hydrogen peroxide was applied. The initial DCF concentration was the same at 50 mg L^{-1} . It is a stoichiometric amount of hydrogen peroxide necessary to oxidize such an amount of DCF. Additionally, experiments were also performed in which the amount of added hydrogen peroxide was half of the stoichiometric amount and twice as much as the stoichiometric amount, which were 420 μM and 1.68 mM, respectively. In every case for DCF deposited in the solution over the sediment, no improvement in DCF decomposition efficiency was observed compared to irradiation without hydrogen peroxide support (Fig. 3).

On the other hand, in the case of DCF deposited in the sediment, no DCF decomposition was observed in any case, but only for a dose of 5 kGy in the presence of 1.68 mM H₂O₂, 10% decomposi-

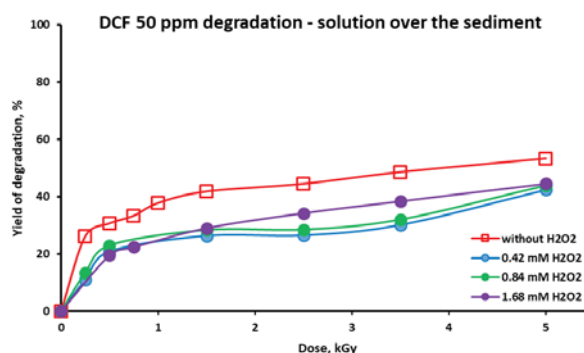


Fig. 3. Degradation of 50 mg/L DCF in sewage sludge (solution over the sediment) in the presence of H₂O₂ addition, \square – without H₂O₂, \bullet – 0.42 mM H₂O₂, \blacktriangle – 0.84 mM H₂O₂, \blacklozenge – 1.68 mM H₂O₂.

tion in relation to the initial amount was observed. Additionally, based on the obtained results, it can be concluded that the applied addition of hydrogen peroxide in quantities from 0.42 μM to 1.68 mM supports DCF adsorption on the sewage sludge, preventing its decomposition under the influence of gamma radiation.

Conclusions

The use of sludge in agriculture in the EU is currently regulated only by limits for heavy metals (Cd, Cu, Hg, Ni, Pb, and Zn) listed in Council Directive 86/278/EEC. Several European countries have introduced more stringent requirements compared to the EU Directive and have adopted limits for concentrations of other heavy metals, synthetic organic compounds, and microbiological contamination. Therefore, for assumption of similar activities in Poland, degradation research of DCF, as a representative of organic pollutants that may be present in this type of sludge, was carried out using electron beam and gamma radiation. In accordance with the theoretical assumptions of radiation processes, it was assumed that similar results were obtained in the case of using ionizing radiation from both gamma sources and electron accelerators. In the case of gamma irradiation, for doses below 5 kGy, the degradation efficiency in the sludge is slightly lower than in the aqueous phase; for both the sludge and the water above sludge, the maximum efficiency that could be obtained for a dose of 5 kGy was 50%. Hygienization of sludge using an electron beam coming from the accelerator already at a dose of 5 kGy allows for a satisfactory degree of hygienization [23]. However, this dose is insufficient to complete degradation of DCF present in the sewage sludge at a level of 50 mg L^{-1} . The degradation efficiency of this pollutant for electron beam is about 30% for the sludge phase and 50% for the water phase. The addition of H₂O₂, used in the case of the gamma source research, does not lead to an increase in the degradation efficiency of DCF. On the basis of the experiments carried out, it should be expected that in the case of sludge hygienization, the use of electron beam partial degradation of pharmaceuti-

cals present in the sewage sludge will be possible. Due to the high content of aqueous phase in the sludge, the mechanism of the process will be related to the mentioned water radiolysis.

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