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Degradation of Pharmaceuticals by Advanced Oxidation Technologies in Aqueous Matrices

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Declaration:
Hereby I declare that this doctoral thesis, my original investigation and achievement, submitted for the doctoral degree at Tallinn University of Technology has not been submitted for any academic degree.

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II. **Epold, I.**, Dulova, N., Trapido, M. Degradation of diclofenac in aqueous solution by homogeneous and heterogeneous photolysis. – *Environmental Engineering & Ecological Science*, 2012, 1, 1-8.

III. **Epold, I.**, Trapido, M., Dulova, N. Degradation of levofloxacin in aqueous solutions by Fenton, ferrous ion-activated persulfate and combined Fenton/persulfate systems. – *Chemical Engineering Journal*, 2015, 279, 452-462.

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Trapido, M., Dulova, N., **Epold, I.**, Bolobajev, J. Emerging micropollutants in water/wastewater: growing demand on removal technologies. – *e-Proceedings of the 3rd European Conference on Environmental Applications of Advanced Oxidation Technologies*, Almeria, Spain, October 27-30, 2013, P171-1-P171-3.

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INTRODUCTION

The release of pharmaceuticals into natural matrices including surface water, groundwater, sediments and soil is an important environmental issue due to their potential influence on human health and ecosystems. Most of pharmaceuticals are not fully degraded after application, only partially metabolised and oxidised by processes used in wastewater treatment plants and get into the environment in an unchanged or slightly modified form. In the present study two important groups of pharmaceuticals including non-steroidal anti-inflammatory analgesics (ibuprofen (IBP), diclofenac (DCF)) and antimicrobial drugs (sulfamethoxazole (SMX), levofloxacin (LFX)), both widely consumed all over the world, were investigated. Similarly to other pharmaceuticals, all the studied compounds have been detected in aquatic environments at concentrations ranging from ng/L to µg/L. Therefore, developing effective remediation technology for elimination of pharmaceuticals, including SMX, IBP, DCF, and LFX, from water, wastewater and groundwater is of great scientific and public interest.

The application of radical-based advanced oxidation technologies (AOTs) has shown a great potential to degrade recalcitrant and bio-refractory organic compounds resented in various aqueous matrices. The advantages of AOTs, as water/wastewater/groundwater treatment techniques, include high reaction rates, non-selective oxidation due to hydroxyl radicals ($HO^{\bullet}$) and more selective activity of sulphate radicals ($SO_4^{\bullet-}$), which allow the simultaneous degradation of multiple contaminants and potentially reduce a toxicity of treated aqueous matrix. The $HO^{\bullet}$ can be generated by the combination of ozone and/or hydrogen peroxide with activators such as transition metals, semiconductors, ultraviolet light and ultrasound irradiation. Among $HO^{\bullet}$-AOTs, the Fenton process is a widely studied and used technique for water and wastewater treatment based on the generation of $HO^{\bullet}$ from hydrogen peroxide catalysed by ferrous ions at acidic pH. Persulphate is a relatively new oxidant, which has the potential to overcome some limitations associated with *in situ* activated hydrogen peroxide applications. The main methods used for $SO_4^{\bullet-}$ generation from persulphate are heat, ultraviolet light or ultrasonic activation, transition metal activation, peroxide activation, and alkaline activation. Among different transition metals used in persulphate activation, ferrous iron is the most extensively studied metal for environmental applications. To combine the main benefits of both AOTs, the combined Fenton/persulphate system is proposed in this study for the first time.

Among the aims of the present research was to study and compare the efficacies of different AOTs, including direct ultraviolet photolysis and ozonation, for degradation of selected pharmaceuticals as well as to clarify the influence of treatment conditions and aqueous matrix on pharmaceuticals' degradation efficacy in the studied advanced chemical oxidation techniques in order to optimise treatment conditions and achieve the maximum practicable treatment efficacy. Nowadays, a priority in the EU water policies is considering

the limit concentrations for emerging micropollutants, including pharmaceuticals, in drinking water supplies and in wastewater discharges into receiving water bodies. Therefore, the data obtained within this study could provide valuable knowledge for further implementation in drinking water and wastewater treatment as well as *in situ* groundwater purification by means of $HO^{\bullet}$- and $SO_4^{\bullet-}$-AOTs application.

ABBREVIATIONS

AOP	advanced oxidation process
AOT	advanced oxidation technology
COD	chemical oxygen demand
DCF	diclofenac
EU	European Union
IBP	ibuprofen
HPLC	high performance liquid chromatograph
HPLC-PDA	high performance liquid chromatography combined with a diode array detector
HPLC-MS	high-performance liquid chromatography combined with a mass spectrometer
GC	gas chromatograph
GC-MS	gas chromatography combined with a mass spectrometer
LC-MS	liquid chromatography combined with a mass spectrometer
LFX	levofloxacin
MW	molecular weight
MWW	municipal wastewater
ND	not detected
NPOC	non-purgeable organic carbon
NPX	naproxen
NSAID	nonsteroidal anti-inflammatory drug
PC	pharmaceutical
SMX	sulfamethoxazole
SW	surface water
TP	transformation product
TW	tap water
UV	ultraviolet light
UVC	ultraviolet light C (100-280 nm)
Vis	visible light
WWTP	wastewater treatment plant

1. LITERATURE REVIEW

1.1. Pharmaceuticals in the environment

Pharmaceutical drugs (further referred as pharmaceuticals) are nowadays used to diagnose, cure, or prevent disease [1]. Pharmaceuticals can be classified in various ways, such as by chemical and therapeutic properties, route of administration or biological system affected. Anatomical Therapeutic Chemical classification system elaborated by the World Health Organisation is widely used. This classification system divides pharmaceuticals into different groups according to the organ or system on which they act and their therapeutic, pharmacological and chemical properties [1]. The main groups of pharmaceuticals are represented by antibiotics, analgesics and antipyretics, antidepressants and tranquilisers, antiinflammatory and antirheumatic products, steroids and related hormones, anaesthetics, betablockers, antiepileptics, antineoplastics, blood lipid lowering agents, and x-ray contrast products [2].

The consumption of pharmaceuticals is steadily growing all over the world both in medical care and veterinary sectors. About 4000 pharmaceuticals are manufactured and consumed annually in quantities of up to hundreds of tons. For example antibiotics account ca 200000 tons per year [3]. Pharmaceutical production is a significant source of toxic industrial waste. The pharmaceutical industry wastewaters are usually very heavily polluted and undergo more or less proper treatment before the effluents are discharged to the environment. The pharmaceuticals consumed are usually not totally converted to the metabolites and conjugates in the body and substantial part of them is excreted unchanged from the organism to the hospital, life-stock farms and household wastewater or as non-point source pollution to the soil of pastures. The main sources and mobility pathways of pharmaceuticals and their metabolites are shown in Figure 1. As it is problematical and costly to remove the pharmaceuticals from wastewater, they find their way into water supplies and food web. Improper utilisation of non-consumed pharmaceuticals to sewerage system or to landfill may contribute up to 60-80% of the total pollution load in developing countries [3].

Thus, recent research activities aim to ascertain the pharmaceutical pollution level in the water bodies and bottom sediments, groundwater, soil, etc. and to characterise the impact to living organisms. The detection levels of pharmaceuticals in natural waters are usually in the ng/L range; however, as it is shown below, the concentrations may reach the level of several μg/L and even higher (Table 1).

As the pharmaceuticals' concentrations in natural water are quite low to present any observable acute toxic effects, their long term impacts to living organisms including humans are to a great extent uncertain. Among the known impacts, the development of drug resistant bacterial strains and their proliferation when antibiotics, especially the broad spectrum ones, enter the aquatic medium have been definitely observed [4]. Also the effects of steroids

on the aquatic biota at concentration levels of about 1 ng/L or less have been reported [5-7]. Adverse effects from the presence of pharmaceuticals have been observed for bacteria, invertebrate, aquatic vertebrate, and algae in waters receiving WWTP effluents [8].

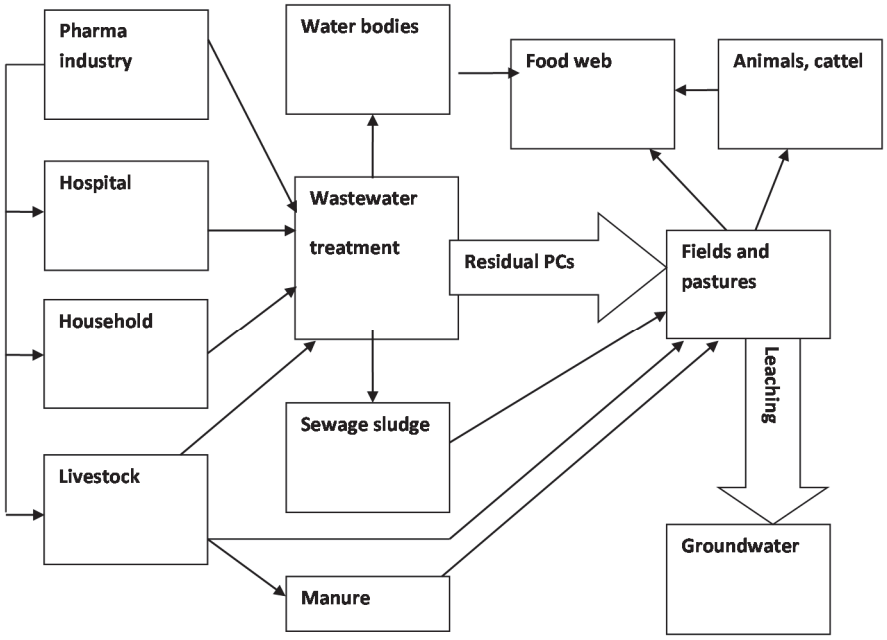

Figure 1. Sources and pathways of pharmaceuticals and their metabolites in the environment (modified from [3]).

As many of pharmaceuticals are characterised by low aqueous solubility and recalcitrance to biodegradation they accumulate in bottom sediments and soil at the levels exceeding the concentrations commonly found in ground- and surface water. Similar to other micropollutants, the pharmaceutical have a tendency to sorb onto WWTPs' sludge. Land application of pharmaceuticals containing manure and WWTPs' sludge (see Figure 1) can lead to groundwater contamination and to exposure to terrestrial organisms [7].

Hospital wastewaters represent another important source of pharmaceuticals where high peak concentrations of various pharmaceuticals have been measured (Table 1).

WWTPs serve as primary barriers against the spread of pharmaceuticals. The elimination is strongly dependent on the pharmaceutical and at conventional WWTPs varies in a wide range of from close to zero to more than 99% [9]. However, WWTPs are currently not designed to eliminate pharmaceuticals. As 80-90% of wastewater generated in developing countries is discharged into surface water bodies without any purification [10] it is a reason for extended levels of pharmaceuticals pollution as can been seen in Table 1.

Table 1. Concentrations of selected pharmaceuticals in natural water, WWTP effluents, hospital effluents and animal manure.

Class	Sub-stance	Concentration	Location	Reference
Antibiotic	Ciprofloxacin (Fluoroquinolones)	2.5-6.5 mg/L	SW, Pakistan	[11]
		28-31 mg/L	WWTP effluent, Pakistan	[12]
		218-236 µg/L	Hospital wastewater, India	[13]
		0.1 mg/kg	Animal manure, China	[14]
		2.61 µg/L	MWW, Western Balkan Region	[15]
		0.03-0.12 µg/L	SW, USA	[16]
		<28-31 mg/L	WWTP, Sweden	[12]
		0.71-16.9 µg/L	Umgeni river, Africa	[17]
		3.6-101 µg/L	Hospital effluent, Sweden	[18]
	Oxytetracycline (Tetracyclines)	19.5±2.9 mg/L	Effluent of oxytetracycline manufacturing plant, China	[19]
		0.64±0.12 mg/L	In the nearby river water	
		3.2 µg/L	MWW and SW in Pakistan	[20]
		183.5 mg/kg	Animal manure, China	[14]
		32.0 µg/L	Overland flow water UK	[21]
		4.49 µg/L	SW, UK	[22]
		0.40 µg/L	Groundwater USA	[21]
	Sulphonamides	4.6 µg/L	MWW and SW in Pakistan	[20]
		0.48 µg/L	SW, Germany,	[23]
		0.41 µg/L	Groundwater, Germany	[21]
		11.60 µg/L	MWW, Western Balkan Region	[15]
		3.68 µg/L	Umgeni river, Africa	[17]
		4.13 µg/L	SW, UK	[22]
		0.24 µg/L	Groundwater Germany	[21]
		0.4-12.8 µg/L	Hospital effluent, Sweden	[18]
NSAID	Diclofenac	8.5 µg/L	Water and wastewater channels of Karachi, Pakistan	[24]
		1.1-15.6 µg/L	Umgeni river, Africa	[17]
		0.48-0.76 µg/L	WWTP, Spain	[25]
		63-785 ng/L	Igarape River, Rio Negro River, Brazil	[26]
		0.06-1.9 µg/L	Hospital effluent, Spain	[27]
	Naproxen	0.66-1.36 µg/L	Karachi, Pakistan	[28, 29]
		1.34-1.36 µg/L	Mallir River, Lyari River, Pakistan	

NSAID, Antipyretics	Ibuprofen	0.98-79 ng/L	SW, Canada	[30]
		ND-1417 ng/L	SW, China	[31]
		5-36.8 ng/L	SW, Costa-Rica	[32]
		ND-8 ng/L	SW, France	[33]
		1-67 ng/L	SW, Greece	[34]
		<15-414 ng/L	SW, Korea	[35]
		5-280 ng/L	SW, Taiwan	[36]
		0.3-100 ng/L	SW, UK	[37]
		0.8-18.9 µg/L	Umgeni river, Africa	[17]
		2.3-10.4 µg/L	WWTP, Spain	[25]
		1.5-151 µg/L	Hospital effluent, Spain	[27]

The information on the pharmaceuticals concentrations in Estonian water bodies and streams has not been published yet. The average total content of five pharmaceuticals representing fluoroquinolones and sulphonamides exceeded 100 µg/kg in sludge samples and 10 µg/kg in the compost of Tallinn and Tartu WWTPs, whereas the highest concentrations were more than 10 times higher [38-39].

Because of increasing amounts of pharmaceuticals entering wastewater, it is important to improve treatment technologies for both wastewater and drinking water sources.

1.2 Advanced chemical oxidation in water and wastewater treatment

Advanced chemical oxidation as a technology in water and wastewater treatment is based on the generation of highly reactive and non-selective radical species, mostly the hydroxyl radical, that is known as one of the most powerful oxidants [40] (see Table 2). Intensive studies on hydroxyl radicals demonstrated their ability to oxidise a wide range of organic compounds at a very high rate with reaction rate constants in order of 10^8-10^{10} L/mol·s [40].

Table 2. Relative oxidation power of some oxidants [40-41].

Oxidizing agent	Potential (V)
h^+ (TiO_2)	+ 3.50
Fluorine	+ 3.03
Hydroxyl radical	+ 2.80
Sulphate radical	+ 2.60
Persulphate anion	+ 2.10
Hydrogen peroxide	+ 1.78
Perhydroxyl radical	+ 1.70
Oxygen (atomic)	+ 2.42
Ozone	+ 2.08
Chlorine	+ 1.36
Chlorine dioxide	+ 1.57
Oxygen (molecular)	+ 1.23
Potassium permanganate	+ 1.68
Hypochlorous acid	+ 1.49

However, some species present in water matrix may terminate the radical chain reaction by reacting with hydroxyl radical. Such species are called hydroxyl radical scavengers as they are able to obstruct the attack of free radicals on the target compound. Thus, hydroxyl radicals are consumed by competitive reactions with carbonate, bicarbonate ions and some organic species. The presence of radical scavengers in water matrix may cut down the total efficacy of advanced oxidation processes (AOPs) in many cases.

The term of "advanced oxidation processes" was first introduced by Glaze et al. [42] who defined it as "the oxidation processes, which generate hydroxyl radicals in sufficient quantity to affect water treatment at ambient temperature and pressure". Later on this technology application was expanded to contaminants removal from soil and polluted air; some other than hydroxyl radical reactive species have been introduced and successfully tested; currently the range of advanced oxidation technologies (AOTs) is not limited by ambient temperature and pressure applications only.

Broad number of chemical oxidation processes is currently qualified under AOT definition: hydrogen peroxide photolysis; photocatalysis; ozonation at elevated pH or combined with UV, hydrogen peroxide, catalysts and activated carbon; the Fenton reaction based processes; ultrasound including processes; microwave; wet air oxidation; persulphate oxidation, etc.

The implementation of AOTs at full-scale has been intensified during recent years and there are more than 500 AOTs installations all over the world [43]. These installations are mainly located in Europe and USA, but the growing market for AOTs commercialisation includes China, Middle East and India. Further implementation of AOTs is partly limited by lack of knowledge on the performance of the selected process on the target group of pollutants and necessity of proper optimisation of the treatment conditions before the installation. The latter enables to reduce the consumption of chemicals and energy and consequently to improve the cost-effectiveness of the selected AOT for the given case.

The main features of AOTs applied in the present research are briefly characterised below.

1.2.1 The Fenton oxidation and related processes

Among the AOTs one very important category involves the Fenton reaction [44] that utilises hydrogen peroxide catalysed by ferrous iron for generation of hydroxyl radicals and other species. The practical application of this reaction also known as the "the classical Fenton reagent", in water, wastewater and soil treatment livened up noticeably during last decade. Moreover, some modifications of the Fenton reagent have been elaborated and successfully introduced. In general, the Fenton and related processes involve complex mechanisms and reaction pathways, and there are several factors influencing these reactions.

The main reaction that results in hydroxyl radicals in the Fenton treatment is electron transfer between hydrogen peroxide and ferrous ion [44]. Iron acts as

the catalyst cycling between Fe^{2+} and Fe^{3+} oxidation states. The reactions occurring consist of several consecutive and simultaneous steps that may be described by following equations [45]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^{\bullet} \quad (1)$$
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \quad (2)$$
$$HO^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \quad (3)$$
$$Fe^{2+} + HO^{\bullet} \rightarrow OH^- + Fe^{3+} \quad (4)$$
$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + H^+ + O_2 \quad (5)$$
$$Fe^{2+} + HO_2^{\bullet} + H^+ \rightarrow Fe^{3+} + H_2O_2 \quad (6)$$
$$HO_2^{\bullet} + H_2O_2 \rightarrow O_2 + H_2O + HO^{\bullet} \quad (7)$$
$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \quad (8)$$
$$HO_2^{\bullet} + HO^{\bullet} \rightarrow H_2O + O_2 \quad (9)$$
$$HO^{\bullet} + HO^{\bullet} \rightarrow H_2O_2 \quad (10)$$

There are more reactions taking place in the reaction mixture; however the overall Fenton reaction can be simplified as [46]:

$$2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O \quad (11)$$

The organics can be completely mineralised by hydroxyl radicals and other reactive species to CO_2, water and inorganic salts if the concentrations of reactants are not limited and the treatment time is long enough [47]. Notably, the complete mineralisation is not usually the target in implementation of the Fenton oxidation.

Several factors are crucial for effective oxidation of pollutants with the Fenton reagent. It is ascertained that the oxidation takes place at pH<5.6 only with the optimum pH value within the range 2.8-3.2 [47-48]. The pollutant to hydrogen peroxide ratio should be carefully optimised to avoid loss of the oxidant by unwanted scavenging reactions between the species in the reaction mixture (eq. 3 and 4). The hydrogen peroxide to iron ratio is important for minimisation of hydroxyl radical scavenging by ferrous iron (eq. 4), reduction of ferric oxyhydroxides formation as well for diminishing of sludge formation in the iron precipitation step [45]. The temperature is also to affect the rate of the Fenton reaction; however, it is accepted that ambient conditions can be safely and effectively used [49].

The intensive research on the application of the Fenton reaction for removal of pollutants from water and wastewater resulted in elaboration of several modifications of the Fenton treatment. They aim to overcome some shortcomings limiting practical application of the Fenton reactions such as sludge generation, the need for pH adjustment, and residual iron in the effluent, etc.

The Fenton reaction initiated by combining H_2O_2 with ferric ions is frequently referred in literature as the “Fenton-like” reaction [48]. In general iron species in oxidation states +II and +III are existing concurrently in the reaction mixture (eq. 1, 2, 4-6). But in practical application it has been observed that initiating with ferric iron usually results in slower initial rate of the reaction

than can be explained of the fact that reaction given in eq. 1 is much faster than that in eq. 2 [45, 50].

Another trend is to utilise solid sources of iron as a catalyst to initiate the Fenton reaction. Indeed, some natural iron minerals as well as iron on supports such as pillared clays, zeolites and silica have shown a catalytic activity. Nevertheless the catalytic activity of heterogeneous catalysts is lower compared to soluble iron salts. Low stability of such catalysts leads to reduction of the catalyst surface, leaching of iron and as well as poisoning that results in deactivation of the catalyst [51, 52].

One of the novel modifications is the iron-free Fenton-like system where metals with multiple redox states (such as copper, manganese, chromium, cobalt, etc.) are utilised for activating H_2O_2 decomposition in both homogeneous and heterogeneous systems at neutral and even alkaline conditions [48]. Still, ecotoxicity of these metals limits the application of such modification.

However, the effectiveness of the aforementioned modifications for degradation of contaminant is typically inferior to the classical Fenton.

The Fenton reaction rate can be enhanced by UV (λ<400 nm) or even UV-Vis radiation; the system is referred as "photo-Fenton" [49]. Such combination can accelerate the generation of $HO^{\bullet}$ by photolysis of hydrogen peroxide (eq. 12) and additional photo reduction of Fe^{3+} and hydroxylated Fe^{3+} to Fe^{2+} (eqs. 13, 14) [45, 53, 54]:

$$H_2O_2 + h\nu \rightarrow 2HO^{\bullet} \qquad \lambda<310 \text{ nm} \qquad (12)$$

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + HO^{\bullet} + OH^{-} \qquad (13)$$

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2} + HO^{\bullet} \qquad \lambda<580 \text{ nm} \qquad (14)$$

It was found that synergic effect of the different reactions listed above (eqs. 1, 3, 12-14) occurs resulting in a very efficient production of hydroxyl radicals [53]. Consequently, in the photo-Fenton the degradation of contaminants may be accelerated and their mineralisation degree enhanced simultaneously with substantial drop in sludge formation as another benefit.

In combination of the Fenton reaction and the sonification referred as "sono-Fenton" process two main additional reactions are involved:

ultrasonic dissociation of water and oxygen to facilitate the generation of $HO^{\bullet}$ by [55-56]:

$$H_2O +))) \rightarrow H^{\bullet} + HO^{\bullet} \qquad (15)$$

$$O_2 +))) + H_2O \rightarrow 2HO^{\bullet} \qquad (16)$$

and *in situ* generation of H_2O_2:

$$2H^{\bullet} + O_2 \rightarrow H_2O_2 \qquad (17)$$

Consequently, the degradation of contaminants may be enhanced. Still, additional energy required is a major concern in operating the photo-Fenton and sono-Fenton [57].

1.2.2 Ozonation and related processes

Ozone is widely utilised for drinking water (and rarely for wastewater) disinfection and other purposes including removal of micropollutants.

Ozone may react with compounds in two different ways: direct reaction and or indirect reactions via formation of hydroxyl radicals and other reactive species [58]. Direct ozonation of organic pollutants is a selective reaction that typically proceeds with slow or moderate rate with reaction rate constants usually in order of $1\text{-}10^6$ L/mol·s [58].

Inorganic compounds' direct reaction with ozone is faster compare to organics; however, reaction rate constants vary in a wide range of $10^{-3}\text{-}10^{10}$ L/mol·s [58].

There are several ways how the decomposition of ozone leads to generation of $HO^{\bullet}$. Firstly, the ozonation is pH dependent and direct ozonation takes place under acidic conditions (pH<4) only. Indirect ozonation mechanism is prevailing under basic conditions (pH>9) when the reaction between hydroxide ion and ozone initiates the chain of reactions (eqs. 18-22) resulting in formation of hydroxyl radicals [59]:

$$O_3 + OH^- \rightarrow O_2 + HO_2^- \quad (18)$$
$$O_3 + HO_2^- \rightarrow HO_2^{\bullet} + O_3^{\bullet-} \quad (19)$$
$$HO_2^{\bullet} \rightarrow H^+ + O_2^{\bullet-} \quad (20)$$
$$O_2^{\bullet-} + O_3 \rightarrow O_2 + O_3^{\bullet-} \quad (21)$$
$$O_3^{\bullet-} + H^+ \rightarrow HO^{\bullet} + O_2 \quad (22)$$

The hydroxyl radicals are unstable and tend to react with target compounds non-selectively at a very high rate. Consequently, ozonation in the basic medium can be considered as an AOT. At pH between 4 and 9 both ozonation pathways (direct and indirect) are involved.

There are some other ways to promote the decomposition of ozone with the generation of $HO^{\bullet}$. The most common of them are combinations of ozone with hydrogen peroxide (O_3/H_2O_2) and photolytic decomposition of ozone (O_3/UV system) [58, 59].

The formation of hydroxyl radical in O_3/H_2O_2 system can be shortly presented by the following equations (eqs. 23-28) [60]:

$$H_2O_2 + H_2O \leftrightarrow HO_2^- + H_3O^+ \quad (23)$$
$$H_3O^+ \rightarrow H^+ + H_2O \quad (24)$$
$$HO_2^- + O_3 \rightarrow HO^{\bullet} + O_2^{\bullet-} + O_2 \quad (25)$$
$$O_2^{\bullet-} + O_3 \rightarrow O_3^{\bullet-} + O_2 \quad (26)$$
$$O_3^{\bullet-} + H^+ \rightarrow HO_3^{\bullet} \quad (27)$$
$$HO_3^{\bullet} \rightarrow HO^{\bullet} + O_2 \quad (28)$$

Consequently, the net equation is:

$$H_2O_2 + 2O_3 \rightarrow 2HO^{\bullet} + 3O_2 \quad (29)$$

According to eq. 29 two molecules of ozone produce two hydroxyl radicals and the theoretical optimum ratio of H_2O_2 to O_3 is 1 mole to 2 moles. However,

production of $HO^{\bullet}$ radicals is dependent besides the H_2O_2 to O_3 ratio on the pH, ozone concentration, contact time, and presence of other compounds in the aqueous matrix. An excess H_2O_2 is unwanted as it competes with the target compounds for hydroxyl radicals (eqs. 30-31) as follows:

$$HO^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \quad (30)$$

$$HO^{\bullet} + HO_2^{\bullet} \rightarrow H_2O + O_2 \quad (31)$$

Consequently for specific oxidation case the optimum H_2O_2 to O_3 dose ratio has to be determined experimentally.

Ozone strongly absorbs ultraviolet light at 253.7 nm. The photolytic decomposition of ozone in aqueous medium leads to *in situ* formation of H_2O_2 [61]:

$$O_3 + H_2O + h\nu \rightarrow H_2O_2 \quad (32)$$

According to [61] decomposition of one mole of ozone leads to one mole of hydrogen peroxide at pH<1.8 only; this ratio increases with the increase of pH.

The following reactions include the heretofore mentioned ozone/hydrogen peroxide reactions (eq. 29) as well as H_2O_2 photolysis. The latter leads to formation of hydroxyl radicals:

$$H_2O_2 + h\nu \rightarrow HO^{\bullet} + HO^{\bullet} \quad (33)$$

The decomposition rate of ozone with UV at 254 nm is about 1000 times higher than of hydrogen peroxide due to higher extinction coefficient of ozone (3300 L/mol·cm [62]) compared with H_2O_2. Therefore the decomposition of ozone is of greater importance than H_2O_2 photolysis and the effect of O_3/UV system is similar to O_3/H_2O_2 process. However, the rate of photolysis of aqueous H_2O_2 increases under basic conditions due to higher molar absorption coefficient of the peroxide anion HO_2^- that is 240 L/mol·cm at 254 nm [62] (the value is only 18.6 L/mol·cm for H_2O_2).

Consequently, in O_3/UV system the pollutants can be degraded by direct ozonation, indirect $HO^{\bullet}$ radical oxidation, and also direct photolysis of the compounds present (whenever they absorb the wavelength used). The relative contribution of these processes depends on UV flux, ozone concentration, the type and concentration of target compound, the pH, and supplementary compounds existing in the reaction matrix [63].

Ozone combination with H_2O_2 and UV light (O_3/H_2O_2/UV) that includes mechanisms involved in O_3/UV and O_3/H_2O_2 systems forms more powerful system with higher rate of $HO^{\bullet}$ generation; the net equation is:

$$2O_3 + H_2O_2 + h\nu \rightarrow 2HO^{\bullet} + 3O_2 \quad (34)$$

The relative contribution of each reaction and mechanism involved in this system is reliant on the pH, the UV radiation flux, concentrations of ozone and hydrogen peroxide, on the target compound and occurrence of radical scavengers. Accordingly, the operation parameters should be carefully optimised for successful application of $O_3/UV/H_2O_2$. Usually the $O_3/UV/H_2O_2$ system improves the degradation of compounds and leads to higher

mineralisation degree [64] but is more costly compared to O_3/UV and O_3/H_2O_2 systems and the ozonation at elevated pH values.

Some more recently developed ways to produce hydroxyl radicals from ozone as ozonation combined with ultrasound (O_3/US system is also called as "sonozone"), catalytic ozonation and combinations of ozone with activated carbon are not considered in the current review.

1.2.3 UV photolysis and related processes

Many substances that absorb UV radiation can through that undergo a decomposition reaction (the pathway known as "direct photolysis"). The molecular structure determines the absorption spectrum of a particular compound as well as the quantum yield for conversion of its excited state to degradation by-products at a given UV wavelength. Consequently, the degradation of compound depends on the flux and spectrum of UV source; the low-pressure UVC lamps generate radiation at a wavelength of 254 nm whereas medium-pressure lamps generate polychromatic radiation [65]. The pH may also affect the degradation of compounds depending on their physico-chemical properties.

The degradation of some compounds could be substantially accelerated when UV photolysis is combined with H_2O_2 in which the latter acts as the primary oxidant. Hydrogen peroxide can be converted to hydroxyl radicals and superoxide anions in the basic medium (eqs. 35-36) [66]:

$$H_2O_2 + OH^- \rightarrow HO_2^- + H_2O \quad (35)$$

$$H_2O_2 + HO_2^- \rightarrow HO^\bullet + O_2^{\bullet-} + H_2O \quad (36)$$

In UV/H_2O_2 system the $HO^\bullet$ is mainly produced as shown in eq. 33 and is able to degrade a variety of organic and inorganic compounds [62, 64, 65, etc.]. As it has been mentioned above the rate of photolysis of aqueous H_2O_2 increases under basic conditions due to higher extinction coefficient of peroxide anion HO_2^- compared to the H_2O_2.

Quite high concentrations of H_2O_2 are necessary for effective degradation of contaminants in UV/H_2O_2 system because of low extinction coefficient of hydrogen peroxide. Upsurge of initial H_2O_2 concentration accelerates the oxidation up to a certain point, at which H_2O_2 starts to impede the degradation of compounds. At increased concentrations the hydrogen peroxide is acting as a free radical scavenger (eq. 37) and less reactive hydroperoxyl radicals are produced (eq. 38) [64]:

$$HO^\bullet + H_2O_2 \rightarrow H_2O + HO_2^\bullet \quad (37)$$

$$HO^\bullet + HO_2^- \rightarrow HO_2^\bullet + OH^- \quad (38)$$

Similar to other AOPs the efficacy of UV/H_2O_2 system for removal of organic compounds is strongly dependent on the experimental conditions including, besides the pH and H_2O_2 concentration, the UV radiation wavelength and flux, and presence of coexisting compounds in water matrix. The radical scavengers, for example bicarbonates and carbonates, may substantially decelerate the

degradation of target compounds in UV/H_2O_2 system. However, the degradation rate of some compounds by direct UV irradiation and UV/H_2O_2 system in surface water or wastewater proved a little bit higher than in distilled water due to the presence of natural organic matter that is able initiate the production of $HO^{\bullet}$ [65].

1.2.4 Activated persulphate oxidation

The persulphate ion ($S_2O_8^{2-}$) is a strong oxidant of peroxygen family (Table 2) used in various industrial processes due to its high reactivity. It was ascertained that under proper reaction conditions persulphate (mainly in the most soluble form of sodium persulphate) can generate free sulphate radicals ($SO_4^{\bullet-}$; Table 2) [41]. The interest in environmental applications of persulphate for the remediation of contaminated sites has risen during the last decade only [67]. The generation of sulphate radical ($SO_4^{\bullet-}$) and other reactive species takes place with considerable rate when the persulphate ion is activated; elevated temperature, UV-radiation, high pH, addition of H_2O_2 or transition metals can be used for activation [68, 69]:

$$S_2O_8^{2-} + \text{activator} \rightarrow SO_4^{\bullet-} + (SO_4^{\bullet-} \text{ or } SO_4^{2-}) \quad (39)$$

Several advantages of activated persulphate oxidation over $HO^{\bullet}$-AOTs could be mentioned. Sulphate radicals are more stable and more selective compared to hydroxyl radicals for oxidizing constituents with unsaturated bond and aromatic compounds. Addition of persulphate does not evoke the exothermic reaction as it appears in the Fenton treatment; however, the decomposition of contaminants takes place with high rate [67].

Persulphate reactivity proved to be high at acidic pH (<3) as well as at pH higher than 10. Accordingly, persulphate could be activated by adjustment of system pH to >10; sodium hydroxide has been suggested as the best choice of such base catalyst [68].

Optimisation of persulphate activation is very important for successful degradation of a target contaminant. The thermal decomposition (i.e., thermal activation) of persulphate is strongly pH-dependent; at pH<2 persulphate was found to decompose thermally without sulphate radical formation. Scavenging reactions also hasten at higher temperature. The optimal activation temperature proved dependent on the pH and the target compound [70, 71].

Ferrous iron (usually as ferrous sulphate or ferrous chloride) is the most common metal activator as it is inexpensive and readily available. The reaction may be presented as [67]:

$$S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^{\bullet-} + SO_4^{2-} + Fe^{3+} \quad (40)$$

During iron activation of persulphate, the metal is involved in both radical generation (eq. 40) and radical scavenging [67]:

$$SO_4^{\bullet-} + Fe^{2+} \rightarrow SO_4^{2-} + Fe^{3+} \quad (41)$$

Accordingly, the iron dose should be carefully optimised to avoid excess scavenging. Usually the application of Fe^{2+} concentration of 100-250 mg/L is effective for activation of persulphate; surplus of iron leads to additional scavenging. The application of chelated iron catalysts for persulphate activation has been successfully tested as a novel possibility for maintaining metal activity for persulphate activation at neutral or alkaline conditions [69].

The hydrogen peroxide activation of persulphate is known as peroxide activation. More efforts are required to clarify the mechanism of such activation due to its complexity. Proposed activation mechanisms include the hydroxyl radical generation from H_2O_2 as well as the heat from the exothermic H_2O_2 reactions [67, 72]. Hydrogen peroxide and persulphate may also have some synergistic features. For example, hydroxyl radicals may initiate persulphate radical formation and vice versa. Moreover, combination of $HO^{\bullet}$ and $SO_4^{\bullet-}$ may lead to a multi-radical attack resulting in more effective degradation of recalcitrant contaminants [67].

The research onto environmental application of activated persulphate has intensified lately and it seems to be a promising technology not only for *in situ* soil remediation [73-75] but also for degradation of contaminants in groundwater. As persulphate and activators also interact with water matrix constituents the optimisation of the treatment conditions is a key for successful application of activated persulphate oxidation in practice.

1.3 Studied pharmaceuticals

As there is a great variety of pharmaceuticals on the market it was not easy to select the pharmaceuticals for the present study. The abundance in water and wastewater samples, lack of the literature data on their degradation by AOTs, low removal efficacy in conventional wastewater treatment according to the literature were among the criteria used for the selection. Our choice was four pharmaceuticals representing antibiotics (SMX and LFX) and nonsteroidal anti-inflammatory drugs (NSAID) (IBP and DCF). Notably, DCF is proposed for the first watch list by Directive 2013/39/EU [76]. The main data on studied pharmaceuticals is given in Table 3.

Table 3. Studied pharmaceuticals [1].

Pharmaceutical	Systematic (IUPAC) name	Trade names	CAS nr.	ATC code	Formula	Mol. mass g/mol	Application
Ibuprofen (IBP)	(*RS*)-2-(4-(2-methylpropyl)-phenyl)propa-noic acid	Advil, Brufen, Ibumax, Ibuprofen, Ibustar, etc	15687-27-1	C01EB16 G02CC01 M01AE01 M02AA13	$C_{13}H_{18}O_2$	206.3	Nonsteroidal anti-inflammatory drug (NSAID), for reliven pain, helping with fever and reducing inflammation,
Sulfamethoxazole (SMX)	4-Amino-*N*-(5-methylisoxazol-3-yl)-benzene-sulfonamide	Bactrim, Septrim, Septra, Biseptol	723-46-6	J01EC01 QJ01EQ11	$C_{10}H_{11}N_3O_3S$	253.3	Sulphonamide bacteriostatic antibiotic, commonly to treat urinary tract infection,
Diclofenac (DCF)	2-(2-(2,6-dichlorophenyl-amino)phenyl)-acetic acid	Diclofenac, Aclonac, Cataflam, Voltaren, etc.	15307-86-5	D11AX18 M01AB05 M02AA15 S01BC03	$C_{14}H_{11}Cl_2NO_2$	296.1	Nonsteroidal anti-inflammatory drug (NSAID), to reduce inflammation and as an analgesic reducing pain in certain conditions.
Levofloxacin (LFX)	(*S*)-9-fluoro-2,3-dihydro-3-methyl-10-(4-methylpiperazin-1-yl)-7-oxo-7*H*-pyrido[*1,2,3-de*]-1,4-benzoxazine-6-carboxylic acid	Levaquin, Tavanic, Quixin, etc.	100986-85-4	J01MA12 S01AE05	$C_{18}H_{20}FN_3O_4$	361.4	Broad spectrum antibiotic of the fluoroquinolone drug class. It is active towards most strains of bacterial pathogens responsible for respiratory, urinary tract, gastrointestinal, and abdominal infections.

SMX is most often used as part of a synergistic combination with trimethoprim in a 5:1 ratio

1.3.1 Treatability of selected pharmaceuticals by conventional biotreatment and advanced chemical oxidation

Selected pharmaceuticals have been detected in 96-100% WWTPs both influent and effluent samples [9, 77]; moreover the highest concentrations in the effluent extended to 0.5 mg/L for DCF, 0.99 mg/L for IBP [6] exceeding by two orders of magnitude predicted no effect concentrations (PNECs) given in [9]. The literature data on the pharmaceuticals removal in conventional WWTPs vary dependent of the drug and the source from close to 0 up to almost 100%. According to [78, 79] the removal of IBP in conventional WWTPs is about 50% while [7, 9, 77] state that it is in the range 69-91%. SMX removal is reported in the range from 33-35% [7, 78, 79] to 74-89% [9, 77]. Similarly, the removal of NPX varies from 0 [79] to 43-90% [8, 77]. According to different sources DCF removal altered from the lowest 9-23% [37, 78, 80] to the highest 81% [27, 77]. The removal efficacy for LFX after activated sludge treatment was 42% [81].

It is not surprising that removal efficacies of pharmaceuticals in WWPTs differ substantially as they are strongly dependent of the activated sludge parameters, hydraulic retention time and other treatment conditions, water matrix, etc., and the compound. However, the existing data enable to conclude that substantial part of pharmaceuticals exits secondary wastewater treatment unchanged and therefore conventional wastewater treatment is not a safe primary barrier against the spread of pharmaceuticals.

The ozonation of pharmaceutical is one of the most studied technologies for their removal that includes also some full-scale cases. Ozone was found quite effective for the degradation of various pharmaceuticals [82, 83]. However, the removal efficacy is compound and case specific as well as strongly dependent on the admixtures present in the water matrix.

Full-scale application of ozonation as tertiary treatment in WWTP resulted in >70% overall removal yield for 31 studied pharmaceuticals; 98-99% removal was observed for SMX and DCF but only 79% for IBP [84]. Similar results were reported by [85, 86] for SMX and DCF after secondary effluent ozonation; whereas during different observations IBP removal was in range of 0-65%.

UV and hydrogen peroxide photolysis may be also used for degradation of pharmaceuticals. The studies indicated that the success of oxidation is strongly dependent on the UV-radiation source (whether low-pressure or medium-pressure UV lamps are used), UV flux and the oxidation time as well as on pH and the water matrix, and the pharmaceutical (spectral and/or physical structures) [65]. The results of different studies are contradictory. For example, the photolysis of DCF was reported to result in degradation efficacy from 5-27% [87, 88] to 100% [89] whereas low-pressure UV lamps were used in both cases. Similar results have been stated for SMX (degradation efficiency 15-99%) [87, 88, 90], NPX (0-50%) [91], and IBP (0-28%) [92] (low-pressure UV radiation sources were implemented in all studies). Medium-pressure UV-lamps were somewhat more effective for the degradation of pharmaceuticals [65, 93], but the main advantage of low-pressure UV-radiation sources in

water/wastewater treatment applications is the simultaneous disinfection along with the oxidation of the pollutants.

The UV/H_2O_2 process improved the degradation and mineralisation rate of some pharmaceuticals; however, proper optimisation of the treatment conditions is the key for successful implementation of hydrogen peroxide photolysis in practice [65, 79, 87, 88-93].

It was ascertained that pharmaceuticals oxidation by-products are similar for ozonation and UV/H_2O_2 treatment that denotes significant role of non-selective attack of $HO^{\bullet}$ in both oxidation processes [94].

Applications of the Fenton reaction demonstrated high potential for effective degradation of wide range of environmental pollutants including the recalcitrant ones [45]. The process ability to degrade and mineralise the target pharmaceutical is closely related to the pH, the water matrix, and the pollutant/H_2O_2/catalyst ratio [6, 49]. Proper adjusting of the treatment conditions is required for successful implementation of the H_2O_2/Fe^{2+} system. The main advantage of this system is substantially lower cost of the treatment if compared to the ozonation, UV-photolysis and photocatalytic processes [95].

Several studies proved advanced performance of photo-Fenton compared the Fenton process for removal of various pharmaceuticals [6, 49, 96]. Nevertheless, no significant difference in decomposition rate of three pharmaceuticals by the Fenton and photo-Fenton treatment was found by Giri and Golder [96]. Still, mineralisation rate was higher in the photo-Fenton treatment.

Catalá et al. [97] observed that the photo-Fenton treatment led to high removal of drugs using very low concentrations of the oxidant. The concentration of all compounds present in the river water was reduced by more than 70% using UV–VIS light only. Nevertheless, degradation of drugs did not ensure toxicity elimination.

Alalm et al. [98] found that very high concentrations of the oxidant (0.5-2.0 g/L) and the catalyst as well as long treatment time (60-120 minutes) were required for elimination of four pharmaceuticals by solar-photo-Fenton at pH 3, accordingly, resulting in high operation cost even under optimal treatment conditions. At higher pH values (5-10) not more than 68% removal of the compounds was observed.

The recent studies on the pharmaceuticals' degradation by the Fenton and photo-Fenton oxidation allow concluding that the performance of these processes for degradation of the pharmaceuticals is compound dependent and the case specific.

The persulphate based AOTs have been recently used for the oxidation of organic compounds in aqueous matrices. High aqueous stability, cost-effectiveness and innocuous end products make persulphate oxidation a preferable option for *in situ* groundwater remediation among the other AOTs. However, only few studies concerning pharmaceuticals abatement using activated persulphate systems are found in the literature [99-102].

1.4 Aims of the study

The main aim of the present research was to clarify the potential of different AOTs in degradation of pharmaceuticals in aqueous matrices, and as a result to enlarge the current knowledge of $HO^{\bullet}$- and $SO_4^{\bullet-}$-AOTs application for water, wastewater, and groundwater treatment.

The objectives of the present research were as follows:

- to assess and compare the efficacy of ozone, UV photolysis, O_3/UV, O_3/UV/H_2O_2, H_2O_2/UV, H_2O_2/Fe^{2+}, and H_2O_2/Fe^{2+}/UV system application for SMX and IBP degradation in pure water matrix, urea matrix and wastewater matrix;
- to study and compare the efficacies of UV photolysis, H_2O_2 photolysis, homogeneous and heterogeneous Fenton/photo-Fenton processes for degradation of DCF as well as to identify the main DCF photo-transformation products;
- to investigate and compare the performance of LFX degradation and mineralisation in Fenton (H_2O_2/Fe^{2+}), $S_2O_8^{2-}/Fe^{2+}$ and combined Fenton/persulphate ($H_2O_2/S_2O_8^{2-}/Fe^{2+}$) systems along with identification of transformation products;
- to study and compare the performance of LFX degradation and mineralisation in different activated persulphate systems ($S_2O_8^{2-}/Fe^{2+}$, $S_2O_8^{2-}/H_2O_2$ and $S_2O_8^{2-}/OH^-$);
- to analyse the influence of activator and oxidant dosage, pH, and oxidation duration on pharmaceuticals' degradation efficacy in the studied advanced chemical oxidation techniques as the basis for optimisation of treatment conditions to achieve the maximum practicable treatment efficacy.

2. MATERIALS AND METHODS

2.1 Chemicals and materials

All chemicals were of analytical grade and were used without further purification. Working solutions were freshly prepared in double-distilled water (*Papers I, II*) or ultrapure water (Millipore Simplicity® UV System; *Papers III, IV*). Sodium hydroxide and sulphuric acid aqueous solutions were used to adjust the pH.

Synthetic solutions of SMX and IBP were prepared by dissolving respective pharmaceutical (100 mg/L) in double-distilled water (pure water matrix), in 20 g/L urea aqueous solution (urea matrix), or in secondary treatment effluent (wastewater matrix). The structures and main properties of studied pharmaceuticals as well the main characteristics of the secondary effluent are presented in *Paper I, Table 1* and *Paper I, Table 2*, respectively.

Working solutions with initial DCF concentration of 100 mg/L were prepared in double-distilled water. The structure and basic data concerning DCF are presented in *Paper II, Table 1*. Goethite (α-FeOOH) with the specific surface area 112.5 m^2/g was used as a heterogeneous activator (*Paper II*).

Model solutions with initial LFX concentration of 75 μM were prepared in ultrapure water. The structure and main properties of the studied antibiotic are presented in *Paper III, Figure 1* and in the *Chemicals and materials* section of *Paper IV*, respectively.

2.2 Experimental procedure

The ozonation, O_3/H_2O_2, O_3/UV and O_3/H_2O_2/UV experiments (*Paper I*) were carried out in semi-continuous bubble reactor (for details see *Experimental procedure* section in *Paper I*). Ozone produced by laboratory ozone generator from pure oxygen was bubbled through 1 L of selected aqueous matrix containing SMX or IBP. In all trials, the ozone concentration in the feed-gas was kept at 5±0.25 mg/L and the gas flow rate at 1 L/min. The duration of ozone treatment was 1-5 h until at least 90% elimination of the target compound was attained. The ozonation experiments were carried out at different pH values.

A mercury low-pressure OSRAM lamp with an energy input of 10 W located in a quartz tube inside a reactor was used as an UVC source in direct UV photolysis (*Papers I, II*), UV/H_2O_2 (*Papers I, II*), O_3/UV (*Paper I*), O_3/H_2O_2/UV (*Paper I*) and photo-Fenton processes (*Papers I, II*). The incident UV radiation photon flux at 254 nm measured by potassium ferrioxalate actinometry [103] was 3.48±0.16 μEinstein/s (*Paper I*) and 3.59±0.12 μEinstein/s (*Paper II*). The temperature (22±1 °C) in the reactor was maintained using a cooling jacket.

All trials of the Fenton (*Papers I-III*), persulphate (*Papers III, IV*) and combined Fenton/persulphate (*Paper III*) processes were performed in batch mode and in non-buffered solutions at ambient room temperature (*Papers I-IV*).

SMX, IBP, DCF solutions (1 L), or LFX solutions (0.4 L) were treated in a cylindrical glass reactor with a permanent agitation speed for a period of 2 (*Paper II*), 3 (*Papers III, IV*) or up to 5 h (*Paper I*). The pH of the samples was adjusted to 3 (*Papers I, III, IV*) or 5 (*Papers I, II*), if not specified otherwise. The activator $FeSO_4 \cdot 7H_2O$ (*Papers I-IV*) or α-FeOOH (*Paper II*) was added, and after complete dissolution of the catalyst or after establishment of the adsorption/desorption equilibrium between the pharmaceutical and the catalyst particles, oxidation was initiated by adding H_2O_2 (*Papers I-IV*), $Na_2S_2O_8$ (*Papers III, IV*) or $H_2O_2/Na_2S_2O_8$ (*Paper III*). The molar ratio of H_2O_2/Fe^{2+} was kept constant at 10:1 (*Papers I, II*). Samples were withdrawn at pre-determined time intervals (*Papers I-IV*) and filtered through a Millipore filter (0.45 μm) (*Paper II*). The oxidation quenching was done by the addition of NaOH (1 M) to adjust pH to ~9 (*Papers I, II*) or Na_2SO_3 at a $[oxidant]_0/SO_3^{2-}$ molar ratio (m/m) of 1/10 (*Papers III, IV*). The experiments on adsorption effect of goethite (*Paper II*) and on pharmaceuticals oxidation with non-activated hydrogen peroxide (*Papers I-IV*) or persulphate (*Papers III, IV*) were conducted in identical reactors and treatment conditions for the respective Fe^{2+}-activated oxidation trials. In the case of Fenton/persulphate and peroxide-activated persulphate, both oxidants were added simultaneously.

The direct UV photolysis, UV/H_2O_2 process and photo-Fenton experiments were carried out in identical reactors and treatment conditions for the respective Fenton oxidation trials. For details see the *Experimental procedure* section of *Papers I* and *II*.

All experiments were duplicated; the results of the analysis are presented as the mean with a standard deviation less than 5%.

2.3 Analytical methods

SMX, IBP, and DCF concentrations during the experiments were quantified using a high performance liquid chromatograph (HPLC) CLAS MPm (Labio Ltd.) equipped with a microcolumn MAG 0 (1.5 × 50 mm) Biospher PSI 100 C18 (particle size, 5 μm) and UV/Vis detector SAPHIRE. Samples were filtered through a Millipore filter (0.45 μm) prior to measurement of SMX, IBP, and DCF concentrations by HPLC. The concentration of LFX was quantified by means of high performance liquid chromatography combined with a diode array detector (HPLC-PDA, Prominence SPD-M20A, Shimadzu) equipped with a Phenomenex Gemini (150×2.0 mm, 1.7 μm) NX-C18 (110 Å, 5 μm) column.

The concentration of pharmaceuticals was determined by using the standard chemical to fit the retention time. Identification of major DCF (*Paper II*) and LFX (*Paper III*) transformation products was performed with a gas chromatograph GC-2010 (Shimadzu, Kyoto, Japan) equipped with a GCMS-QP2010 Plus mass selective detector and with a high-performance liquid chromatography combined with a mass spectrometer (HPLC-MS, Shimadzu LC-MS 2020), respectively. All the details of pharmaceuticals residual concentrations analysis and by-products identification are presented in the *Analytical methods* section of *Papers I-IV*.

The pH measurements were performed using a digital pH meter (Model CG-840, Schott) (*Papers I, II*) or a digital pH/ion meter (Mettler Toledo S220) (*Papers III, IV*). The total iron concentration in the solution was quantified with phenanthroline method [104] (*Papers I, II*). The initial H_2O_2 concentration in the stock solutions was measured spectrophotometrically at λ=254 nm; the residual H_2O_2 concentration in the treated samples was measured at λ=410 nm with Ti^{4+} [105] by a Heλios-β UV/vis spectrophotometer (Thermo Electron Corporation) (*Papers I-IV*). The residual persulphate concentration in the treated samples was measured spectrophotometrically at λ=446 nm with o-dianisidine [106] (*Papers III, IV*). Non-purgeable organic carbon (NPOC) was measured by a TOC analyser multi N/C® 3100 (Analytik Jena) (*Papers III, IV*). The chemical oxygen demand (COD) was determined by the closed reflux titrimetric method according to [104] (*Papers I, II*). The correction of hydrogen peroxide interference on COD test was done by the correlation equation according to [107] (*Paper II*).

3. RESULTS AND DISCUSSION

Different AOTs were applied for degradation of pharmaceuticals in aqueous matrices (Table 4).

Table 4. AOTs applied for the synthetic aqueous solutions treatment.

Pharmaceutical	Treatment technologies	Paper
SMX, IBP	ozonation, UV photolysis, O_3/H_2O_2, O_3/UV, O_3/H_2O_2/UV, UV/H_2O_2, H_2O_2/Fe^{2+}, H_2O_2/Fe^{2+}/UV	*I*
DCF	UV photolysis, UV/H_2O_2, H_2O_2/Fe^{2+}, H_2O_2/α-FeOOH, H_2O_2/Fe^{2+}/UV, H_2O_2/α-FeOOH/UV	*II*
LFX	H_2O_2/Fe^{2+}, $S_2O_8^{2-}/Fe^{2+}$, $H_2O_2/S_2O_8^{2-}/Fe^{2+}$	*III*
LFX	$S_2O_8^{2-}/Fe^{2+}$, $S_2O_8^{2-}/H_2O_2$, $S_2O_8^{2-}/OH^-$	*IV*

The efficacy of applied processes was assessed mainly on the basis of target compound degradation (*Papers I-IV*), oxidant consumption (*Papers I-IV*) as well as COD (*Paper II*) and NPOC reduction (*Papers III, IV*).

3.1 Ozonation and ozone-based processes

Ozonation, O_3/H_2O_2, O_3/UV, and O_3/H_2O_2/UV processes were studied for degradation of SMX and IBP in three different aqueous matrices (*Paper I*). The obtained data processing revealed that target compounds degradation by ozonation and ozone-based processes followed a pseudo-first-order kinetic law during an entire reaction and may be described with regard to the pharmaceutical concentration through eq. 42:

$$\frac{dC}{dt} = -k_1 \times C \qquad (42)$$

where k_1 is the pseudo-first order rate constant and C is the pharmaceutical concentration. The $-k_1$ constants were calculated from the slopes of the straight lines by plotting $\ln(C/C_0)$ as a function of time t through linear regression. The values of the kinetic constants and 90% conversion times ($T_{90\%}$) were calculated for conventional ozonation and other ozone-based processes as presented in *Paper I, Table 3*.

In general, both pharmaceuticals were degraded by ozonation and related processes whereas the removal efficiency increased with increasing pH of aqueous matrix. Accordingly, ozonation at pH 11 led to more than 1.5 and 4.5 times faster SMX and IBP degradation, respectively, compared to experiments carried out at acidic pH values (*Paper I, Table 3*), indicating the ability of radicals' reactions to improve the efficacy of target compounds oxidation. The application of O_3/UV system proved to be ineffective in acceleration of SMX

degradation, but resulted in faster IBP decomposition (*Paper I, Table 3*). Similarly, the addition of H_2O_2 into O_3 and O_3/UV system did not accelerate the removal of SMX compared to ordinary ozonation and only slightly improved IBP degradation (*Paper I, Table 3*). The ineffectiveness of O_3/H_2O_2 and O_3/H_2O_2/UV systems to enhance substantially degradation of both pharmaceuticals can be explained by formation of H_2O_2 observed during ozonation and O_3/UV oxidation in aqueous matrix, leading to insignificant impact of supplementary added H_2O_2 on the degradation of SMX and IBP. Irrespective of the pH value used in ozonation and related processes, the degradation of IBP was considerably less effective than SMX decomposition.

The influence of wastewater and urea matrix on ozonation and related processes efficacy was studied as well. The results indicated a negligible impact of the urea addition on the performance of SMX and IBP degradation in ozonation, O_3/UV and O_3/H_2O_2 systems (*Paper I, Table 3*). Conversely, the pharmaceuticals oxidation with ozone and related processes in the wastewater matrix was retarded as compared to the results obtained for the pure water matrix, most likely due to the presence of organic and inorganic constituents in the secondary treatment effluent (*Paper I, Table 2*) acting as scavenges and consequently inhibiting the degradation of target compounds.

3.2 UV and H_2O_2 photolysis

UV photolysis and UV/H_2O_2 process were applied for degradation of SMX and IBP (*Paper I*), and DCF (*Paper II*) in aqueous matrix.

Similarly to ozone-based processes, the degradation of SMX, IBP and DCF by UV and H_2O_2 photolysis followed the pseudo-first order kinetic law and may be described by eq. 42. The values of the calculated kinetic constants and $T_{90\%}$ of SMX and IBP degradation by UV and UV/H_2O_2 processes presented in *Paper I, Table 4*. According to the results IBP proved to be more resistant to UV photolysis than SMX, and thus the $T_{90\%}$ for SMX and IBP degradation by oxidation at pH 3 and 5 was 28 and 275 min, respectively, in the pure water matrix. The addition of H_2O_2 to UV photolysis accelerated IBP degradation but resulted in negligible increase in SMX's decomposition efficacy (*Paper I, Table 4*). Accordingly, the IBP degradation by UV/H_2O_2 process at an IBP/H_2O_2 m/m of 1/1.2 and 1/3 was 3.2 and 7.5 times faster, respectively, as compared to the direct photolysis. Irrespective of the studied aqueous matrix, UV photolysis of SMX resulted in extended formation of H_2O_2. With regard to IBP degradation by direct photolysis, the H_2O_2 formation was detected in urea and wastewater matrices, not in the pure water matrix. In general, the urea and wastewater matrix proved to have a negative impact on the direct photolysis of SMX as well as UV and H_2O_2 photolysis of IBP (*Paper I, Table 4*). The wastewater's suspended matter may contribute to the light attenuation in a water layer, both by light absorption and light scattering, as well as impede the degradation of the target compound via its adsorption and shielding effects. Dissolved components of the wastewater may induce radical scavenging, consequently retarding the degradation of pharmaceuticals.

The DCF degradation by UV photolysis at pH 5 resulted in only 85% pharmaceutical decomposition during 2 h of oxidation. In the case of direct photolysis started at pH 7 and 9, a fast decrease in pH to acidic values was observed (*Paper II, Figure 1*), but the $T_{90\%}$ for DCF was 115 and 80 min, respectively (*Paper II, Figure 2*). The application UV/H_2O_2 process at elevated H_2O_2 concentrations and alkaline conditions resulted in faster DCF degradation as compared to direct photolysis (*Paper II, Figure 2*). Accordingly, the $T_{90\%}$ decreased from 48 to 28.5 min for UV and H_2O_2 photolysis (DCF/H_2O_2 m/m of 1/6, pH 11), respectively. Overall UV and H_2O_2 photolysis DCF degradation efficacy was assessed by measuring COD. The highest achieved COD removal was 15% after 2 h of oxidation, indicating the formation of more resistant to the photo-degradation DCF transformation products.

The blank experiments for the H_2O_2 oxidation of SMX, IBP, and DCF were conducted as well; none of the studied pharmaceuticals underwent degradation within 120 min.

3.3 Fenton-based processes

The classical Fenton (*Papers I-III*), heterogeneous Fenton-based (*Paper II*) and photo-Fenton (*Papers I, II*) processes were studied for pharmaceuticals degradation in aqueous matrix.

Paper I

Irrespective of the oxidant dose, the degradation of SMX by Fenton process proceeded fast at the initial stage of the oxidation, and afterwards it was retarded or even totally terminated (*Paper I, Figure 1*) mainly due to the complete utilisation of H_2O_2 in the system. In general, the SMX degradation efficacy proved to be directly proportional to the amount of H_2O_2 added. Thus, the Fenton oxidation at a SMX/H_2O_2/Fe^{2+} m/m/m of 1/4/0.4 and 1/8/0.8 resulted in the respective $T_{90\%}$ of 36.5 and 10 min. Similarly to the results of SMX decomposition, the degradation of IBP was fast during the first few minutes of oxidation, and afterwards it was retarded or totally terminated (*Paper I, Figure 2*). Generally, IBP was found to be more resistant to the Fenton oxidation compared to SMX, and thus under studied treatment conditions the complete IBP removal was not attained. The fastest IBP degradation was observed at an IBP/H_2O_2/Fe^{2+} m/m/m of 1/20/2 with the $T_{90\%}$ of 270 min. Notably, the residual H_2O_2 concentration was observed in all the studied Fenton systems even after 5 h of oxidation.

The application of photo-Fenton process enhanced the degradation of SMX and IBP, enabling considerably faster the complete removal of pharmaceuticals and utilising substantially lower oxidant doses compared to the Fenton process (*Paper I, Figures 3 and 4*). The complete degradation of SMX and IBP was observed even at a pharmaceutical/H_2O_2/Fe^{2+} m/m/m of 1/2/0.2 with the respective $T_{90\%}$ of 17 and 76 min.

The impact of the wastewater and urea matrix on the degradation of pharmaceuticals by Fenton and photo-Fenton processes was evaluated. Accordingly, the influence of urea addition on the IBP degradation by Fenton oxidation was negligible (*Paper I, Figure 2*). Conversely, the photo-Fenton oxidation of the target compound resulted in the $T_{90\%}$ of 33.5 to 128 min for the pure water and urea matrix, respectively (*Paper I, Figure 4*). The oxidation in the wastewater matrix led to the reduced efficacy of IBP degradation by Fenton (*Paper I, Figure 2*) and photo-Fenton system (*Paper I, Figure 4*). The degradation of SMX by Fenton process was retarded in both the urea and wastewater matrix (*Paper I, Figure 3*). Thus, the SMX oxidation at a $SMX/H_2O_2/Fe^{2+}$ m/m/m of 1/3/0.3 in pure water, urea, and wastewater matrix resulted in the respective $T_{90\%}$ of 40, 135 and 140 min. Conversely, the impact of the matrix on SMX decomposition by photo-Fenton process was insignificant (*Paper I, Figure 3*).

Paper II

The efficacy of Fenton process to degrade DCF was very moderate at pH 5. Accordingly, only a 25% DCF decomposition was attained after 2-h oxidation at a $DCF/H_2O_2/Fe^{2+}$ m/m/m of 1/3/0.3. The increase in initial pH to 7 resulted in improved DCF degradation with 40 and 70% of degraded DCF by oxidation at a $DCF/H_2O_2/Fe^{2+}$ m/m/m of 1/3/0.3 and 1/8/0.8, respectively. The results of H_2O_2/α-FeOOH process application demonstrated no removal of DCF during 2 hours of the heterogeneous Fenton reaction irrespective of the DCF/H_2O_2 m/m in the range of 1/2 – 1/12. Prolonged 24-h oxidation experiments resulted in less than 5% degradation of DCF. The data obtained within sorption experiments indicated negligible DCF adsorption on the α-FeOOH surface.

The results of DCF degradation by homogeneous photo-Fenton process revealed similarity with the UV/H_2O_2 system (at the same pH 7), but in general slower DCF degradation compared to direct photolysis. The efficacy of goethite-activated photo-Fenton system was to some extent higher compared to the UV/H_2O_2 process, mainly with increase in H_2O_2 concentration and pH value (*Paper II, Figures 3 and 4*). Thus, the $T_{90\%}$ was decreased from 115 to 69 min and from 80 to 42 min by the application of heterogeneous photo-Fenton process (DCF/H_2O_2 m/m of 1/6) at pH 7 and 9, respectively, as compared to direct photolysis. The H_2O_2 decomposition in the studied heterogeneous photo-Fenton systems was up to 30% at pH 7 and 9 and less than 5% at pH 11, probably, due to the oxidant auto-decomposition at elevated pH values. The highest efficacy in DCF degradation by H_2O_2/α-FeOOH/UV system was attained at a DCF/H_2O_2 m/m of 1/20 and pH 11 with the $T_{90\%}$ of 23.5 min (*Paper II, Figure 4*).

COD removal was ≤ 15% after 2-h oxidation in all the studied Fenton-based systems at pH 5, 7 and 9. As to the Fenton-based oxidation at pH 11 and elevated oxidant concentrations, the COD reduction was up to 60%, indicating a high overall efficacy of the process under strongly alkaline conditions.

The LFX degradation by the classical Fenton oxidation proved to follow a pseudo-first-order kinetic law and may be described by with regard to the pharmaceutical concentration through eq. 42. The values of the kinetic constants were calculated for the Fenton oxidation at different LFX/H_2O_2/Fe^{2+} m/m/m as presented in *Paper III, Table 1*.

In general, the application of Fenton process demonstrated a high oxidation efficacy, resulting in complete LFX removal in less than 2 h even at a low oxidant ratio of 1/5/0.5 (LFX/H_2O_2/Fe^{2+}, m/m/m) (*Paper III, Figure 2*). A further increase in H_2O_2 concentration at the same H_2O_2/Fe^{2+} ratio led to faster LFX degradation, contributing to a decrease in the oxidation time needed to remove LFX completely. The highest performance was observed at a LFX/H_2O_2/Fe^{2+} m/m/m of 1/20/2 with the complete target compound decomposition within 6 min (*Paper III, Figure 2*). In the majority of trials the H_2O_2/Fe^{2+} m/m was maintained at 10/1, but in order to reduce the amount of activator added as well as the final cost of the treatment, the effect of the twofold-lower H_2O_2/Fe^{2+} m/m ratio of 20/1 was studied as well. The results indicated decrease in the LFX degradation rate and less effective oxidant utilisation for the Fenton oxidation at a LFX/H_2O_2/Fe^{2+} m/m/m of 1/10/0.5 compared to 1/10/1 (*Paper III, Table 1*). Conversely, the application of H_2O_2/Fe^{2+} m/m of 5/1 and 2.5/1 in the Fenton system resulted in rapid and ineffective hydrogen peroxide decomposition, leading to termination of LFX degradation and mineralisation (*Paper III, Table 1*).

Irrespective of the applied LFX/H_2O_2/Fe^{2+} ratio, the mineralisation was considerably less effective than pharmaceutical degradation. The tendency of NPOC reduction was similar for all studied conditions and in general was enhanced with increases in Fenton reagent dose as presented in *Paper III, Figure 3*. Conversely, the extent of improvement was strongly dependent on the dose of Fenton reagent applied. Therefore, NPOC removal was 26, 36.5, and 37.5% after 3-h oxidation at a LFX/H_2O_2/Fe^{2+} m/m/m of 1/10/1, 1/15/1.5, and 1/20/2, respectively.

The results of non-activated H_2O_2 oxidation at a LFX/H_2O_2 m/m of 1/10 indicated no pharmaceutical removal and more than 99% of unused oxidant in solution.

3.4 Activated persulphate processes

The performance of LFX degradation in aqueous solutions in Fe^{2+}-activated $S_2O_8^{2-}$(*Papers III, IV*) and combined H_2O_2/$S_2O_8^{2-}$ (*Paper III*), peroxide-activated $S_2O_8^{2-}$ (*Paper IV*), and base-activated $S_2O_8^{2-}$ (*Paper IV*) systems was evaluated and compared.

In all the studied $S_2O_8^{2-}$ systems, a fast decomposition of LFX was observed during the first minute (the first measured time point after the beginning of the reaction), and then the target compound was gradually degraded within the remaining reaction time. Accordingly, the entire reaction can be divided into

two main phases: the first period of fast LFX degradation and the second period of gradual LFX oxidation. Additionally, the obtained data processing showed that LFX degradation by non-activated $S_2O_8^{2-}$ as well as ferrous ion- and peroxide-activated $S_2O_8^{2-}$ processes followed a pseudo-first-order kinetic law during the second reaction period and may be described with regard to the LFX concentration through eq. 42.

Non-activated persulphate oxidation

The results of LFX degradation by non-activated $S_2O_8^{2-}$ at a LFX/$S_2O_8^{2-}$ m/m of 1/10 and pH 3 indicated the negligible efficacy in pharmaceutical degradation, and thus only 7% of LFX was removed in the first fast period with a $k_1 \times 10^{-2}$ of 0.04 1/min for the second stage, and more than 95% of the unreacted oxidant was observed after 3-h oxidation.

Ferrous ion-activated persulphate oxidation

The efficacy of the $S_2O_8^{2-}/Fe^{2+}$ system in LFX oxidation was studied at different LFX/$S_2O_8^{2-}$ and $S_2O_8^{2-}/Fe^{2+}$ ratios, and the results are presented in *Paper III, Figures 4, 5* and *Paper IV, Figure 2*. In the case of the $S_2O_8^{2-}/Fe^{2+}$ system, the two-stage kinetic model was observed not only for LFX degradation but also for $S_2O_8^{2-}$ decomposition (*Paper IV, Figures 2 and 4*). Accordingly, more than 31 and 56% of LFX along with 7 and 11% of $S_2O_8^{2-}$ was decomposed during the first minute and the rest of the 3-h oxidation, respectively, in $S_2O_8^{2-}/Fe^{2+}$ systems at a LFX/$S_2O_8^{2-}/Fe^{2+}$ m/m/m of 1/10/1. The values of the kinetic constants calculated for the $S_2O_8^{2-}/Fe^{2+}$ system at the studied LFX/$S_2O_8^{2-}/Fe^{2+}$ molar ratios are presented in *Paper III, Table 2*. The obtained results indicated a steady improvement in the LFX degradation rate with the increase in applied persulphate dose at a fixed LFX/Fe^{2+} and $S_2O_8^{2-}/Fe^{2+}$ ratio (*Paper III, Figure 4 and Table 2*). Accordingly, a higher-than-threefold increase in the LFX degradation rate at a LFX/$S_2O_8^{2-}/Fe^{2+}$ m/m/m of 1/40/1 compared to 1/5/1 was achieved. In trials with the fixed $S_2O_8^{2-}/Fe^{2+}$ m/m of 10/1, the $k_1 \times 10^{-2}$ of the second reaction period was 0.93, 2.42, and 5.74 1/min for the $S_2O_8^{2-}/Fe^{2+}$ oxidation at a LFX/$S_2O_8^{2-}/Fe^{2+}$ of 1/10/1, 1/20/2, and 1/30/3, respectively. The results of LFX oxidation at a LFX/$S_2O_8^{2-}/Fe^{2+}$ m/m/m of 1/20/2 and different initial pH are presented in *Paper III, Figure 6 and Table 2*. The efficacy of LFX degradation proved to decrease gradually with the increase in the initial pH.

The data on the LFX mineralisation extent in the $S_2O_8^{2-}/Fe^{2+}$ system are presented in *Paper III, Figure 7* and *Paper IV, Figure 3*. Accordingly, the NPOC concentration remained nearly unchanged after 3-h oxidation at a LFX/$S_2O_8^{2-}/Fe^{2+}$ m/m/m lower than 1/20/2 (more than 97% of residual concentration). The highest obtained mineralisation under the studied treatment conditions was 11% at a LFX/$S_2O_8^{2-}/Fe^{2+}$ m/m/m of 1/30/3, mainly indicating the accumulation of by-products in the oxidised LFX aqueous solution.

Peroxide-activated persulphate oxidation

To evaluate the efficacy of LFX degradation by peroxide-activated $S_2O_8^{2-}$ oxidation, the effect of $S_2O_8^{2-}$ and H_2O_2 dose was studied (*Paper IV, Figure 5 and Table 2*). The results demonstrated to some extent improvement in the pharmaceutical decomposition at a LFX/$S_2O_8^{2-}$/H_2O_2 of 1/10/10 compared to non-activated $S_2O_8^{2-}$ oxidation at a LFX/$S_2O_8^{2-}$ m/m 1/10, and thus 8% of LFX removed in the first stage with $k_1 \times 10^{-2}$ of 0.07 1/min for the second gradual period and more than 99% of residual H_2O_2 (residual $S_2O_8^{2-}$ was not measured) after 3 h of oxidation was observed. Conversely, the efficacy of LFX degradation in the $S_2O_8^{2-}$/H_2O_2 system was considerably lower compared with the $S_2O_8^{2-}$/Fe^{2+} oxidation at the same LFX/$S_2O_8^{2-}$ ratios (*Paper IV, Figures 2 and 5*). In general, the obtained data indicated a strong necessity for careful optimisation of the $S_2O_8^{2-}$/H_2O_2 system in order to attain a practical LFX degradation (*Paper IV, Figures 5, 6 and Table 2*). The highest LFX degradation efficacy was observed at a LFX/$S_2O_8^{2-}$/H_2O_2 m/m/m of 1/15/5 with 16 and 25% of LFX removed during the first minute and overall oxidation time, respectively. Similarly to LFX degradation, the most effective utilisation of H_2O_2 was observed at a LFX/$S_2O_8^{2-}$/H_2O_2 m/m/m of 1/15/5 with only 15% of utilised H_2O_2, indicating the high potential of prolonged oxidation for subsequent increase in treatment efficacy. Notably, the efficacy of LFX removal by the $S_2O_8^{2-}$/H_2O_2 oxidation decreased with the increase in pH (*Paper IV, Table 2)*. Additionally, the efficacy of LFX mineralisation in the peroxide-activated $S_2O_8^{2-}$ process was assessed, and the results obtained indicated negligible NPOC removal with the highest achieved mineralisation of 1-2%.

Combined ferrous ion-activated hydrogen peroxide/persulphate oxidation

The results of LFX degradation by the H_2O_2/$S_2O_8^{2-}$/Fe^{2+} system are presented in *Paper III, Figure 8* and *Table 3*. In the main, a more rapid decrease in residual LFX concentration was observed during the first minute in the H_2O_2/$S_2O_8^{2-}$/Fe^{2+} system compared with the $S_2O_8^{2-}$/Fe^{2+} and Fenton processes, indicating the synergic action of both processes. Conversely, considering the two-fold higher activator dose added into the combined system, the overall performance of the combined process in LFX decomposition was generally higher than in the $S_2O_8^{2-}$/Fe^{2+} system but somewhat lower than in the Fenton process, mainly indicating the presence of concurrent reactions of the oxidant with the activator in the combined system (*Paper III, Table 3*). Accordingly, 31(39), 55(86) and 51(81)% of the initial LFX concentration was removed during the first minute of oxidation by the $S_2O_8^{2-}$/Fe^{2+} system at a LFX/$S_2O_8^{2-}$/Fe^{2+} m/m/m of 1/10/1(2), the Fenton process at a LFX/H_2O_2/Fe^{2+} m/m/m of 1/10/1(2), and the combined H_2O_2/$S_2O_8^{2-}$/Fe^{2+} system at a LFX/H_2O_2/$S_2O_8^{2-}$/Fe^{2+} m/m/m/m of 1/10/10/1(2), respectively. In the case of the combined H_2O_2/$S_2O_8^{2-}$/Fe^{2+} system, residual concentrations of hydrogen peroxide in samples was measured (*Paper III, Table 3*). Accordingly, it was ascertained that only 58% of hydrogen peroxide was

used during 3 h of oxidation at a LFX/H_2O_2/$S_2O_8^{2-}$/Fe^{2+} m/m/m/m of 1/10/10/1. A twofold increase in activator dose (LFX/H_2O_2/$S_2O_8^{2-}$/Fe^{2+} m/m/m/m of 1/10/10/2) improved the consumption of H_2O_2 in the combined system, and only 14% of residual oxidant was detected after 3 h of reaction indicating a necessity to double the activator dose in the combined system in order to achieve competitive results.

Additionally, the efficacy of the combined process in LFX mineralisation was assessed, and the results obtained are presented in *Paper III, Figure 9*. Similarly to LFX degradation, the NPOC removal in the H_2O_2/$S_2O_8^{2-}$/Fe^{2+} system was essentially improved compared with particular Fe^{2+}-activated $S_2O_8^{2-}$ oxidation, but it was mainly lower than in the respective Fenton process. Thus, 26(24), 1(1) and 14(21)% NPOC removal was observed after 3 h of oxidation by the Fenton system at a LFX/H_2O_2/Fe^{2+} m/m/m of 1/10/1(2), the $S_2O_8^{2-}$/Fe^{2+} process at a LFX/$S_2O_8^{2-}$/Fe^{2+} m/m/m of 1/10/1(2), and the combined H_2O_2/$S_2O_8^{2-}$/Fe^{2+} system at a LFX/H_2O_2/$S_2O_8^{2-}$/Fe^{2+} m/m/m/m of 1/10/10/2(2), respectively.

Base-activated persulphate oxidation

The results of LFX degradation by the $S_2O_8^{2-}$/OH^- oxidation are presented in *Paper IV, Figure 7 and Table 3*. The efficacy of LFX degradation in the base-activated $S_2O_8^{2-}$ was strongly dependent on the LFX/$S_2O_8^{2-}$ ratio applied. Accordingly, LFX removal was 6/14 and 13/18% after the first minute/3-h oxidation at a LFX/$S_2O_8^{2-}$ m/m of 1/5 and 1/10, respectively. An increase in the $S_2O_8^{2-}$ dose from 1/10 to 1/20 (LFX/$S_2O_8^{2-}$, m/m) resulted in 4 and 7% of supplementary pharmaceutical removal during the first minute and 3-h oxidation, respectively, indicating the efficacy of elevated oxidant dose application to enhance LFX removal. Conversely, the utilisation of $S_2O_8^{2-}$ proved more effective at moderate LFX/$S_2O_8^{2-}$ molar ratio of 1/10, but still resulted in 94% of unused $S_2O_8^{2-}$ in solution after 3-h oxidation. Thus, in the case of $S_2O_8^{2-}$/OH^- system the prolonged treatment could be a reasonable solution to improve the performance of pharmaceutical degradation. Similarly to the $S_2O_8^{2-}$/H_2O_2 system, the mineralisation in the $S_2O_8^{2-}$/OH^- process was noticeably less effective than LFX degradation and in general resulted in <1% of NPOC removal. Taking into account the treatment performance, oxidant utilisation and mineralisation extent, the base-activated $S_2O_8^{2-}$ system proved the less effective for LFX degradation in aqueous solution among other studied activated persulphate systems (*Paper IV, Figure 8*).

3.5 Identification of major transformation products

Transformation products (TPs) were studied for DCF (*Paper II*) and LFX (*Paper III*) degradation by application of different AOTs.

Paper II

The obtained results indicated similar GC-MS chromatogram patterns for UV photolysis, hydrogen peroxide photolysis, and heterogeneous photo-Fenton process. Two photo-TPs were detected; other transformation products were in trace concentrations (below the method detection limits). The main detected photo-TP with formula $C_{14}H_9C_{l2}NO$ (MW 277 g/mol) was identified as 1-(2,6-dichlorophenyl)indolin-2-one. The other observed photo-TP with formula $C_{14}H_{10}ClNO$ (MW 243 g/mol) could be identified as C-2 (8-chloro-9H-carbazole-1-acetic aldehyde). The analysis of mass spectrum of the latter TP indicated mass differences of Δ=28 and Δ=35 pointing to the existence of one chlorine atom and an aldehyde function.

Paper III

Six TPs characterised by different m/z ratios were identified (*Paper III, Table 4*) by LC-MS analysis in the positive ESI. LC-MS analysis allowed for the identification of the same TPs during LFX oxidation by H_2O_2/Fe^{2+}, $S_2O_8^{2-}/Fe^{2+}$, and $H_2O_2/S_2O_8^{2-}/Fe^{2+}$ systems. The identity of TPs for all studied systems verifies $HO^{\bullet}$ as the main oxidative specie in the studied processes. The chemical structures of TPs presented in *Paper III, Table 4* were mainly suggested on the basis of the well-known reactivity of $HO^{\bullet}$ with unsaturated and tertiary amine compounds. The major reaction pathways observed during pharmaceutical degradation in the studied systems included defluorination (TP4), piperazinyl substituent transformation (TP1, TP3, TP5), and quinolone moiety modifications (TP2, TP6). Moreover, the results of LC-MS analyses revealed that the TPs identified progressively disappeared after complete elimination of LFX in the studied AOTs.

4. CONCLUSIONS

The main conclusions of this thesis are summarised in the following points:

- In general, the application of UV/H_2O_2 and photo-Fenton process demonstrated the highest potential for degrading SMX, IBP, and DCF in aqueous solutions. On the whole, the UV treatment and related processes may be recommended for practical applications for pharmaceuticals degradation in water and wastewater.
- The impact of the matrix on the degradation of pharmaceutical was obvious for all the studied AOTs, and thus the elimination rates determined in the pure water cannot be directly used to predict the oxidation of SMX and IBP in the wastewater.
- The Fenton, $S_2O_8^{2-}/Fe^{2+}$ and combined $H_2O_2/S_2O_8^{2-}/Fe^{2+}$ systems proved promising techniques for the oxidation of LFX in aqueous solution. The performance of the Fenton and activated persulphate processes in LFX degradation was as follows: the Fenton system > the combined Fenton/$S_2O_8^{2-}$ system > the $S_2O_8^{2-}/Fe^{2+}$ system > the $S_2O_8^{2-}/H_2O_2$ system > the $S_2O_8^{2-}/OH^-$ system. A similar tendency was observed for NPOC removal, and, accordingly, the highest mineralisation was obtained in the Fenton system followed by the combined process. The findings in this study strongly suggested that all considered activated persulphate systems with prolonged oxidation period could be a reliable technology for wastewater and groundwater remediation contaminated by the LFX.
- Overall, the results obtained within this study provide fundamental information essential for the practicable application of AOTs to treat pharmaceuticals contamination in water, wastewater and groundwater.

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ABSTRACT

Degradation of Pharmaceuticals by Advanced Oxidation Technologies in Aqueous Matrices

The presence of pharmaceuticals in surface water bodies, groundwater and wastewater streams has become a subject of worldwide environmental concern. These compounds originate mainly from industrial, agricultural, and domestic wastes and represent one of the greatest challenges to environmental technology due to the intrinsic high toxicity, low biodegradability and resistance to conventional biological treatment methods to the overwhelming majority of pharmaceuticals. The application of advanced oxidation technologies (AOTs), particularly radical-based processes, seems to be the most viable solution to the problem of pharmaceuticals contamination because of their principal advantage of rapid and predominantly non-selective degradation of multiple organic contaminants along with reduction in toxicity of treated aqueous matrices.

Accordingly, the main aim of the present study was to evaluate the potential of different AOTs, including direct UV photolysis and ozonation, in degradation of pharmaceuticals representing two important groups of drugs such as non-steroidal anti-inflammatory analgesics (ibuprofen (IBP), diclofenac (DCF)) and antimicrobial drugs (sulfamethoxazole (SMX), levofloxacin (LFX)) in aqueous matrices.

The other objectives of the present research were as follows:

- to assess and compare the efficacy of ozone, UV photolysis, O_3/UV, O_3/UV/H_2O_2, H_2O_2 photolysis, Fenton (H_2O_2/Fe^{2+}), and photo-Fenton (H_2O_2/Fe^{2+}/UV) system application for SMX and IBP degradation in pure water matrix, urea matrix and wastewater matrix;
- to study and compare the efficacies of UV photolysis, H_2O_2 photolysis, homogeneous and heterogeneous Fenton/photo-Fenton processes for degradation of DCF as well as to identify the main DCF photo-transformation products;
- to investigate and compare the performance of LFX degradation and mineralisation in Fenton, $S_2O_8^{2-}/Fe^{2+}$ and combined Fenton/persulphate ($H_2O_2/S_2O_8^{2-}/Fe^{2+}$) systems along with identification of transformation products.
- to study and compare the performance of LFX degradation and mineralisation in ferrous ion-, peroxide-, and base-activated persulphate systems;
- to analyse the influence of activator and oxidant dosage, pH, and oxidation duration on pharmaceuticals' degradation efficacy in the studied AOTs as the basis for optimisation of treatment conditions to achieve the maximum practicable treatment efficacy.

The result of the present study indicated that the implementation of AOTs is a promising solution for different pharmaceuticals degradation in different aqueous matrices in a single treatment step. Accordingly, the application of

UV/H_2O_2 and photo-Fenton process demonstrated the highest potential for degrading SMX, IBP, and DCF in aqueous solutions. Notably, it was found that the impact of the matrix on the degradation of pharmaceutical was obvious for the treatment efficacy of all the studied AOTs, and thus the elimination rates determined in the pure water cannot be directly used to predict the oxidation of pharmaceuticals in more complex aqueous systems. Considering the UV treatment as a trustworthy and widely used technique for drinking water and wastewater disinfection, the UV-induced degradation of pharmaceuticals could be achieved as a valuable side effect. Therefore, based on the findings of this study, the UV treatment and related processes may be recommended for practical applications for pharmaceuticals degradation in drinking water and wastewater.

The application of Fenton, $S_2O_8^{2-}/Fe^{2+}$, and novel combined $H_2O_2/S_2O_8^{2-}/Fe^{2+}$ systems proved to be promising treatment methods for the degradation of LFX in aqueous solution. The performance of the Fenton and activated persulphate processes in LFX oxidation as well as mineralisation was as follows: the Fenton system > the combined Fenton/$S_2O_8^{2-}$ system > the $S_2O_8^{2-}/Fe^{2+}$ system > the $S_2O_8^{2-}/H_2O_2$ system > the $S_2O_8^{2-}/OH^-$ system. In general, all studied activated persulphate systems with prolonged oxidation period proved to be a reliable technology for remediation of groundwater contaminated with LFX. Nevertheless, the findings in this study strongly suggested that prudently adjusted novel combined Fenton/persulphate oxidation could be the most promising technology for LFX degradation in wastewater and especially in groundwater.

On the whole, the outcomes of this work could provide fundamental information essential for the practicable application of AOTs to treat water, wastewater and groundwater contaminated with pharmaceuticals.

KOKKUVÕTE

Ravimite lagundamine vesikeskkonnas süvaoksüdatsioonitehnoloogiatega

Ravimite olemasolu pinna- ja põhjavees ning heitvee suublates on saanud ülemaailmseks keskkonnaprobleemiks. Peamiselt tööstustest, põllumajandusest ja olmejäätmetest pärinevad ühendid on kõrge toksilisuse, madala biolagundatavuse ja tavapärastele bioloogilistele töötlusmeetoditele allumatuse tõttu üheks suurimaks keskkonnatehnoloogia alaseks väljakutseks. Kõige tõenäolisemaks lahenduseks ravimitega seotud reostusele on eelkõige radikaalide aktiivsusel põhinevate süvaoksüdatsioonitehnoloogiate (SOT) rakendamine. SOT peamine eelis on kiire ja valdavalt mitte-selektiivne erinevate orgaaniliste lagundamine ning töödeldud vee toksilisuse vähendamine.

Võttes arvesse eelpool toodut, oli käesoleva töö peamiseks eesmärgiks hinnata erinevate SOT, sealhulgas otsese UV-fotolüüsi ja osoonimise, efektiivsust kahe olulise ravimigrupi hulka kuuluvate ühendite lagundamisel vees/reovees. Uuritavateks ühenditeks olid mittesteroidsete põletikuvastaste valuvaigistite alla kuuluvad ibuprofeen (IBP) ja diklofenak (DCF) ning mikroobivastaste ravimite alla kuuluvad sulfametoksasool (SMX) ja levofloksatsiin (LFX).

Töö kõrvaleesmärgid olid järgmised:

- hinnata ja võrrelda osoonimise, UV-fotolüüsi, O_3/UV, O_3/UV/H_2O_2, H_2O_2 fotolüüsi, Fentoni (H_2O_2/Fe^{2+}) ja foto-Fentoni (H_2O_2/Fe^{2+}/UV) süsteemi rakendamise efektiivsust SMX ja IBP lagundamisel puhtas vees, uureat sisaldavas vees ning reovees;
- uurida ja võrrelda UV-fotolüüsi, H_2O_2 fotolüüsi, homogeense ja heterogeense Fenton-/foto-Fenton-protsessi tõhusust DCF lagundamiseks ning määrata peamised DCF fotomuundumise produktid;
- uurida ja võrrelda LFX lagunemist ja mineraliseerumist Fenton-protsessis, $S_2O_8^{2-}/Fe^{2+}$ ja kombineeritud Fenton/persulfaat ($H_2O_2/S_2O_8^{2-}/Fe^{2+}$) süsteemides ning identifitseerida vaheproduktid;
- uurida ja võrrelda LFX lagunemist ja mineraliseerumist kahevalentse raua, peroksiidi ja leelisega aktiveeritud persulfaadi süsteemides;
- analüüsida rakendatud SOT aktivaatori ja oksüdandi doosi, pH ja oksüdatsiooniaja mõju ravimite lagundamise efektiivsusele, mille põhjal leida optimaalsed töötlemistingimused.

Tööst saadud tulemused näitasid, et SOT eraldiseisev rakendamine on perspektiivikas mitmesuguste ravimite lagundamiseks erinevates vee maatriksites. Töö käigus tõestati, et UV/H_2O_2 ja foto-Fenton-protsess olid SMX, IBP ja DCF lagundamiseks tõhusaimad meetodid. Leiti, et vee/reovee omadused mõjutasid ravimite lagundamist kõikide uuritud SOT puhul ning sellest tulenevalt ei saa puhta vee puhul saadud tulemusi kasutada vahetuks võimalike efektiivsuste prognoosimiseks keerukamates vee maatriksites (looduslikud veed/reoveed). Arvestades UV-töötluse laialdast kasutamist

joogivee ja heitvee desinfitseerimisel, võib UV-aktiveeritud ravimite lagundamist pidada perspektiivikaks. Seega võib antud tulemuste põhjal soovitada UV-töötluse ja sellel põhinevate protsesside rakendamist ravimite lagundamiseks vees ja heitvees.

Rakendatud Fenton, $S_2O_8^{2-}/Fe^{2+}$ ja uudne kombineeritud $H_2O_2/S_2O_8^{2-}/Fe^{2+}$ süsteem osutusid tõhusateks LFX lagundamiseks vees. Fenton- ja aktiveeritud persulfaadi protsesside efektiivsused LFX lagundamisel ning mineraliseerimisel olid järgnevad: Fentoni süsteem > kombineeritud Fenton/$S_2O_8^{2-}$ süsteem > $S_2O_8^{2-}/Fe^{2+}$ süsteem > $S_2O_8^{2-}/H_2O_2$ süsteem > $S_2O_8^{2-}/OH^-$ süsteem. Üldiselt osutusid kõik uuritud pikendatud oksüdatsiooniajaga aktiveeritud persulfaadi süsteemid tõhusateks LFX kõrvaldamiseks põhjaveest. Siiski saab antud töös leitud uudset kombineeritud Fenton/persulfaadi oksüdatsiooni (eelneva optimeerimisega) pidada perspektiivikaimaks tehnoloogiaks LFX lagundamiseks eelkõige põhjavees ja heitvees.

Kokkuvõttes on antud töö tulemused oluliseks aluseks SOT rakendamiseks ravimitega saastunud vee, heitvee ja põhjavee töötlemisel.

APPENDIX A

PAPER I

Epold, I., Dulova, N., Veressinina, Y., Trapido, M. Application of ozonation, UV photolysis, Fenton treatment and other related processes for degradation of ibuprofen and sulfamethoxazole in different aqueous matrices. – *Journal of Advanced Oxidation Technologies*, 2012, 15(2), 354-364.

Application of Ozonation, UV Photolysis, Fenton Treatment and other Related Processes for Degradation of Ibuprofen and Sulfamethoxazole in Different Aqueous Matrices

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Abstract:
Two pharmaceuticals ibuprofen (IBP) and sulfamethoxazole (SMX) were treated with ozone and advanced oxidation processes (AOPs): UV photolysis, O_3/H_2O_2, O_3/UV, O_3/H_2O_2/UV, H_2O_2/UV, the Fenton and photo-Fenton process. The efficacy of AOPs for degradation of pharmaceuticals as well as the impact of the matrix (pure water, urea and wastewater) on drugs' decay was evaluated. The experimental study has been carried out using concentration of the pharmaceuticals in the level of 100 mg/L. IBP was more resistant to all types of treatment than SMX. Ozonation was effective for removal of SMX and IBP when carried out under alkaline conditions. The ultimate elimination of SMX could be achieved with UV photolysis, whereas more rapid removal of IBP was attained with H_2O_2/UV. The complete SMX removal and more than 90% IBP degradation by the ordinary Fenton treatment were reached with oxidant overdosing only. Additional UV-radiation improved substantially the performance of the Fenton oxidation for elimination of both pharmaceuticals. The elimination rates determined in the pure water cannot be directly used to predict the oxidation of SMX and IBP in the wastewater.

Keywords: AOPs; pharmaceuticals; UVC radiation; urea; wastewater

Introduction

Traces of organic contaminants or micropollutants: pesticides, biocides, pharmaceuticals, and personal care products are frequently detected in drinking water sources. These compounds are constituents of wastes from industrial, agricultural, military, commercial and domestic operation and represent one of the greatest challenges to environmental technology. Many of listed compounds have high resistance to conventional biological treatment but can be oxidized to different extent by common disinfectants such as ozone and chlorine (1). Micropollutants reach humans and animals via drinking water or through the food chain and present a long-term risk to wildlife and human health (2).

Among the various micropollutants, pharmaceuticals have been a particular concern during last decade as these micropollutants have been identified in aquatic environments such as drinking and surface water, groundwater, wastewater treatment plant (WWTP) effluent and sludge, seawater and sediments (3). The sources of pharmaceuticals in natural water systems may be manufacturing operations in pharmaceutical industry and therapeutical use of them for human and animals. High amount of pharmaceuticals have also been used as growth promoters in intensive farming (4). Human and animal pharmaceuticals are partially metabolized in the organism and excreted with urine as the parent substance or/and as metabolites (5, 6). Usually, pharmaceuticals are detected in the higher μg/L range in hospital effluents, lower μg/L range in municipal wastewater and ng/L in surface, ground- and seawater (7, 8).

The main way to combat with residues of pharmaceuticals is to avoid their spread to water bodies and streams through improvement of wastewater treatment. Conventional treatment methods used in water purification (coagulation, flocculation, sedimentation, sand filtration, and disinfection with chlorine) and wastewater treatment (primary settling, activated sludge or trickling filter, and secondary settling) are known to be ineffective for removal of pharmaceuticals present in raw water and wastewater (9, 10). Therefore, in order to meet standards for wastewater discharge, the development of appropriate end-of-pipe wastewater treatment technologies that may improve the situation within relatively short time is a crucial issue.

Ozonation and advanced oxidation processes (AOPs) are a particularly attractive option among the advanced technologies that may be used to remove pharmaceuticals. Successful elimination of some

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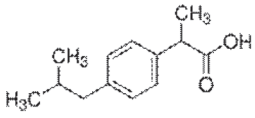
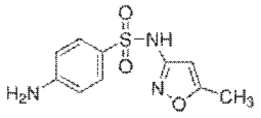
Table 1. The structures and main properties of studied pharmaceutical.

Pharmaceutical	Ibuprofen	Sulfamethoxazole
Abbreviation in text	IBP	SMX
Formula	$C_{13}H_{18}O_2$	$C_{10}H_{11}N_3O_3S$
Molecular formula		
CAS Nr.	15687-27-1	723-46-6
Molecular weight, g/mol	206.28	253.28
pK_a	4.9 (35)	pK_{a1} = 1.60; pK_{a2} = 5.7 (33)

pharmaceuticals by ozonation (11-17), improved (catalytic) ozonation (18-20), photolytic degradation (3, 17, 21-24), photocatalytic oxidation (3, 4, 25, 26), the Fenton-based treatment including photo-Fenton and electro-Fenton processes (3, 7, 27-33), sonolysis (34, 35) and gamma irradiation (36) has been reported. However, no individual oxidative method is universally applicable or highly effective for every kind of pharmaceuticals.

Pharmaceuticals are designed to cause effect on humans and animals in trace concentration. Consequently, even low concentrations of pharmaceuticals in the environment have to be avoided as they can cause various toxic effects on any level of biological hierarchy (3). Between the various pharmaceutical compounds present in the environment, special emphasis has been given to antibiotics, because of their potential role in the development of multi-resistant strains of bacteria (37).

The efficiency of AOPs for the removal of pharmaceuticals has typically been studied in pure/ultrapure water (demineralised water) whereas the applicability of such results for natural water and wastewater remains uncertain. Only few studies considering ozonation and AOPs application for the treatment of wastewater treatment plant (WWTP) effluents spiked with pharmaceuticals were recently published (12, 30, 38, 39).

In the current study two pharmaceuticals, ibuprofen (IBP) and sulfamethoxazole (SMX), representing two important groups of drugs such as analgesics and antibiotics, both widely consumed all over the world, were investigated. IBP is a non-steroidal anti-inflammatory, analgesic and antipyretic drug. IBP belongs to the group of propionic acid derivatives and is available under various trademarks over-the-counter in most countries. SMX, one of the most widely synthesized sulfonamides, is frequently used in medicine to treat bronchitis and urinary tract infections and also in veterinary, for prevention and treatment of infections, as well as a growth promoter (4).

The degradation of IBP and SMX in water was done by application of ozone and AOPs: UV-photolysis, ozonation combined with UV-radiation and/or hydrogen peroxide, the Fenton and photo-Fenton process, and hydrogen peroxide photolysis. Besides obtaining data on the efficacy of different AOPs for removal of IBP and SMX in aqueous solution, the study aimed to compare the efficacy of these processes for elimination of the above-mentioned pharmaceuticals in three different water matrices: pure water matrix, urea matrix and wastewater (secondary treatment effluent from WWTP) matrix. Some recent works on the photocatalysis (40, 41) and photo-Fenton-process (42) for removal of pharmaceuticals in WWTP effluent have proved the efficacy of alternative processes such as AOPs for the treatment of such kind of wastewater.

Materials and Methods

Chemicals and Materials

Sulfamethoxazole and ibuprofen were purchased from Sigma-Aldrich; acetonitrile (99.8%, isocratic grade for HPLC) was obtained from Baker. The structures and the basic data concerning investigated pharmaceuticals are presented in Table 1. All other chemicals were of analytical grade and used without further purification.

The model stock solutions of SMX and IBP were prepared by dissolving respective pharmaceutical in double-distilled water (pure water matrix). Urea (20 g/L) as the main component of urine was added in some experiments to simulate treatment of wastewater coming from no-mix toilets (urea matrix). The secondary effluent after activated sludge treatment with simultaneous phosphorus precipitation and pre-anoxic zone from the local WWTP was used in some trials as a wastewater matrix. The main characteristics of the secondary effluent are summarised in Table 2. In the experiments with wastewater matrix SMX and IBP were added directly to the secondary effluent. The stock solutions were alkalified and stirred for several

Table 2. The main parameters of the secondary effluent.

Parameter	Value
pH	7.6
COD, mg [O_2]/L	33
BOD_7, mg [O_2]/L	10
BOD_7/COD	0.30
Electrical conductivity, μS/cm	1050
Total solids (TS), mg/L	600
Total suspended solids (TSS), mg/L	12
Phosphate, mgP/L	0.75
Total iron, mg/L	0.4
NH_4 mgN/L	0.22
Nitrate, mgN/L	4.2

hours to ensure complete dissolution. The initial concentration of pharmaceutical was maintained 100 mg/L in all cases. Although this concentration is far from the expected levels in the environment, it can be assumed that the degradation pathway is the same. As the solubility of IBP is low under acidic conditions, the experiments with IBP were conducted at initial pH≥5. Sodium hydroxide and sulphuric acid aqueous solutions (0.1 N) were used for pH adjustment.

Experimental Procedure

The ozonation, O_3/H_2O_2, O_3/UV and O_3/H_2O_2/UV experiments were carried out in 1.5 L Ace European-style three-neck flask with an ozone diffuser (Ø 3.5 cm; porous size 0.1 mm) located 1.5 cm above the reactor's bottom. Ozone produced by laboratory ozone generator (Trailigaz Labo) from pure oxygen was bubbled through 1 L of selected aqueous matrix containing SMX or IBP. In all trials, the ozone concentration in the feed-gas was kept at 5 ± 0.25 mg/L and the gas flow rate at 1.0 L/min. The initial and residual concentrations of ozone in the gas phase, measured at λ=258 nm with a PCI-Wedeco ozone monitor (WEDECO Environmental Technologies Inc., USA), were used for the calculation of ozone inlet and consumed doses. Samples were withdrawn at selected time intervals; the duration of ozone treatment was from 60 to 300 minutes until at least 90% elimination of the pharmaceutical was attained. The ozonation experiments were carried out at different pH values. In O_3/UV and O_3/H_2O_2/UV experiments, the UV lamp was located in the centre inside the reactor. The initial concentration of hydrogen peroxide in the O_3/H_2O_2 process and O_3/H_2O_2/UV system was 1 mM.

A mercury low-pressure OSRAM lamp with an energy input of 10 W located inside the reactor in a quartz tube was used as an UV source in direct UV photolysis, H_2O_2/UV, O_3/UV, O_3/H_2O_2/UV and photo-Fenton processes. The UV radiation intensity at 254 nm measured by potassium ferrioxalate actinometry (43) was 3.48 ± 0.16 μEinstein/s. The lamp was turned on at least 10 min before the trial to insure constant output. The constant temperature in the reactor was maintained using a cooling jacket.

All Fenton process trials were carried out in the batch mode and in un-buffered solutions. A standard procedure consisted of treating 1 L of selected aqueous matrix containing SMX or IBP in glass reactor with a permanent agitation speed (200-300 rpm). The reactant was let to react until all the hydrogen peroxide was consumed or for a period up to 300 minutes. Samples were withdrawn at selected time intervals and the reaction was stopped by adding 2 drops of 1 N aqueous solution of NaOH to each test tube.

The Fenton reaction (H_2O_2/Fe^{2+}) was initiated by adding hydrogen peroxide (0.8-10 mM) to the acidified stock solution (pH 3 and pH 5 for SMX and IBP, respectively) containing a known amount of Fe^{2+} ion. The initial molar ratio of H_2O_2/Fe^{2+} was kept constant at 10:1, which is optimal according to (44). The photo-Fenton experiments were carried out in the same reactor and treatment conditions as those used for the Fenton experiments with the UV lamp located inside the reactor. In the photo-Fenton trials the concentration of hydrogen peroxide was in the range of 0.8-1.5 mM.

The direct UV photolysis and H_2O_2/UV experiments were carried out in the same reactor (1 L of selected aqueous matrix containing SMX or IBP in a glass reactor with a constant agitation speed for a period of 200-300 min). SMX and IBP solutions were treated at pH 3 and pH 5, respectively. The concentration of H_2O_2 was in the range of 0.6-2.4 mM.

Additionally, blank experiments on IBP and SMX oxidation with hydrogen peroxide were conducted in the same reactor and treatment conditions as the respective Fenton-based treatment trials.

All experiments were duplicated and the data on SMX and IBP concentrations was verified with at least three replicates. The results of the analysis of initial and treated samples are presented as the mean with the standard deviation below 3% in all cases. The experiments were performed at 22±1 °C.

Analytical Methods

SMX and IBP concentrations during the experiments were quantified using a high performance liquid chromatograph (HPLC) CLAS MPm (Labio Ltd.) equipped with a microcolumn MAG 0 (1.5 × 50 mm) Biospher PSI 100 C18 (particle size, 5 μm) and UV/VIS detector SAPHIRE. The isocratic method with a mobile phase containing 35% acetonitrile and 0.1% of acetic acid in Milli-Q water (Millipore Gradient System)

was used. The flow rate of 50 μL/min and absorbance wavelength of 254 nm were maintained for determination of SMX. The flow rate and absorbance wavelength for determination of IBP were 100 μL/min and 226 nm, respectively. Samples were filtered through a Millipore filter (0.45 μm) prior to measurement of SMX and IBP concentrations by HPLC. The concentration of SMX and IBP was determined by using the external standard.

The pH measurements were performed using a digital pH meter (Model CG-840, Schott). The electrical conductivity (EC) was measured using a digital EC meter (Model HI9032, HANNA Instruments). The total iron concentration in the solution was quantified with phenanthroline method (45). The initial hydrogen peroxide concentration in stock solutions was determined spectrophotometrically by measurement of the absorption of hydrogen peroxide at λ=254 nm (molar extinction coefficient of 19.6 L/mol·cm (46)), using Heλios-β UV/VIS (Thermo Electron Corporation). The residual hydrogen peroxide concentration was measured by the spectrophotometric method with Ti^{4+} (Heλios-β UV/VIS, Thermo Electron Corporation) (46). COD and BOD_7 of the wastewater were determined according to (45). The concentration of NO_3^- and PO_4^{3-} ions in the wastewater was measured by means of ion chromatography with chemical suppression of eluent conductivity (761 Compact IC, Metrohm) coupled with a METROSEP A Supp 5 analytical column (4×150 mm).

Results and Discussion

Ozonation and Related Treatment

The chemical oxidation with ozone proved an effective process for degradation of various micropollutants (14). As ozonation is widely used for drinking water (and rarely for wastewater) disinfection and other purposes, the knowledge of the degradation rate of pharmaceuticals is important for predicting the treatment efficacy at real conditions.

The steady state concentrations of dissolved ozone were attained within initial five minute of the ozonation. The degradation of investigated pharmaceuticals in aqueous matrices followed a pseudo-first order kinetic law and can be described with regard to the pharmaceutical concentration:

$$\frac{dC}{dt} = -k_{1\times} C \qquad (1)$$

where k_1 is the pseudo-first order rate constant.

The $-k_1$ constants were calculated from the slopes of the straight lines by plotting $\ln(C/C_0)$ as a function of time t, through linear regression (r^2>0.985). Table 3 summarise 90% conversion times ($T_{90\%}$) and the pseudo-first order rate constants for the degradation of SMX and IBP by conventional ozonation and other ozone-based processes.

Both pharmaceuticals were degraded by ozonation whereas the removal efficiency increased with increasing pH of aqueous solution (Table 3). Ozonation conducted at pH 11 led to the complete removal of pharmaceuticals in more than 1.5 and 4.5 times faster for SMX and IBP, respectively, compared to experiments carried out in acidic conditions. Thus, 90% removal of SMX and IBP with ozonation at pH 11 required 15 and 45 min, respectively. This fact can evidence the ability of indirect (radicals) reactions to accelerate the degradation of the target compounds.

The fast reaction of SMX with ozone observed in the present study is in agreement with several recently published data (14, 16). The high reactivity of ozone with SMX is due to the presence of nucleophilic points in the molecular structure of SMX that are selectively attacked by ozone (Table 1). The results of SMX ozonation at pH between 3 and 11 showed an increase in ozonation rate with increasing pH (Table 3), similarly to results obtained by Dantas et al. (14) and Garoma et al. (16). The SMX is a compound that presents three possible species in water according to the pH and pK_a values (1.6 and 5.7): the protonated (SMX^+), the non-protonated (SMX) and the anionic (SMX^-) molecule. Thus, the increase of k_1 with pH was expected, because the deprotonated SMX, which is known to have higher reactivity towards ozone compared to protonated one (48), becomes predominant as the pH increases.

No trials were conducted at pH lower than 5 due to relatively low value of the acid dissociation of IBP (pK_a = 4.9), since in acidic medium the solubility of IBP decreases sharply, leading to translucent suspensions due to precipitation. Above the pK_a value ionic IBP is the predominant form, and has higher reactivity towards ozone that the protonated molecule (11). The results indicated (see Table 3) that independent of pH IBP appeared to be more ozone resistant compared to SMX.

The degradation of IBP was accelerated substantially when O_3/UV treatment was carried out at acidic conditions (Table 3). Thus, the $T_{90\%}$ of IBP at pH 5 was 64 minutes, which is approximately 3.7 times less than in ozonation. In the case of pH 11 only slight increase in $T_{90\%}$ from 41.5 to 45 min for ozonation and O_3/UV process, respectively, was observed.

The addition of hydrogen peroxide to ozonation process is known to increase the ozone decay and accelerates its decomposition into hydroxyl radicals. At elevated pH values hydrogen peroxide reacts with ozone when present as an anion, HO_2^-. Whenever the

Table 3. 90% conversion times ($T_{90\%}$) and the pseudo-first order rate constants (k_1) of SMX and IBP degradation by ozonation and ozone-based processes.

Treatment method	Matrix	pH	$T_{90\%}$ (min)	k_1 (1/min) × 10^{-2}	mg pharmaceutical removed/mg ozone consumed
SMX					
Ozonation	pure water	3	31.5	8.52±0.32	1.96±0.16
Ozonation	pure water	7	16	12.72±0.60	2.40±0.12
Ozonation	pure water	11	15	13.20±0.34	1.36±0.07
Ozonation	urea	7	17.5	12.24±0.43	2.15±0.20
Ozonation	wastewater	7	26	9.36±0.24	1.28±0.25
O_3/UV	pure water	3	34	7.86±0.38	1.10±0.05
O_3/H_2O_2	pure water	3	35	7.68±0.27	1.38±0.03
O_3/H_2O_2/UV	pure water	3	29	8.76±0.40	1.10±0.17
IBP					
Ozonation	pure water	5	236	1.06±0.05	1.20±0.12
Ozonation	pure water	8	183	1.25±0.05	1.40±0.01
Ozonation	pure water	11	45	5.06±0.20	1.20±0.09
Ozonation	urea	11	45	4.99±0.21	1.11±0.13
Ozonation	wastewater	5	275	0.79±0.03	0.90±0.12
Ozonation	wastewater	11	118	2.00±0.12	0.67±0.06
O_3/UV	pure water	5	64	3.85±0.19	0.60±0.09
O_3/UV	pure water	11	41.5	5.98±0.24	0.86±0.22
O_3/UV	urea	11	43.5	5.59±0.25	0.82±0.02
O_3/UV	wastewater	5	85	2.57±0.13	0.61±0.08
O_3/H_2O_2	pure water	5	235	1.09±0.06	0.91±0.04
O_3/H_2O_2/UV	pure water	5	61	4.22±0.22	0.70±0.16

concentration of hydrogen peroxide is above 10^{-7} M and the pH-value less that 12, HO_2^- has a greater effect than OH^- on the decomposition rate of ozone in water. However, it does not affect greatly the extent of micropollutant degradation for compounds slowly reacting with ozone (e.g., IBP) (49). The results of the present study indicated the increased rate of O_3 decay and only negligible increase in the rate of IBP degradation by O_3/H_2O_2 (Table 3). Similarly, the addition of H_2O_2 to O_3/UV system only slightly increased the overall process efficacy.

As to SMX, O_3/UV, O_3/H_2O_2 treatment and even such a powerful oxidation system as O_3/H_2O_2/UV did not accelerate the removal of SMX compared to ordinary ozonation (Table 3). The ineffectiveness of hydrogen peroxide to improve degradation of both pharmaceuticals can be explained by observed formation of hydrogen peroxide during both ozonation and O_3/UV treatment of SMX and IBP aqueous solutions. Thus, hydrogen peroxide impact has been already presented in both studied systems and additional amount of oxidant did not significantly accelerate the degradation of SMX and IBP that is in concordance with results obtained by Masten and Hoigne (50).

The wastewater matrix usually has an impact on the removal of the target compound with ozonation and other AOPs as the organic and inorganic admixtures present in water can compete for oxidants including the non-selective hydroxyl radicals and, consequently, impede the elimination of pharmaceuticals. Examples for those so-called scavengers are bicarbonate and carbonate ions as well as the dissolved organic carbon.

Furthermore, the influence of urea, the main urine component, on the efficacy of the different AOPs was evaluated. It is supposed that source separation of urine that contains many of the pharmaceuticals and their metabolites may offer the more effective solution to the problem of pharmaceuticals in the environment. Due to the higher concentrations of micropollutants, the treatment is expected to be more efficient in urine than in diluted wastewater (51). The information of urea impact on the degradation efficiency of pharmaceuticals can be important for the treatment of wastewater coming from no-mix toilets.

The addition of urea did not influence notably the performance of drugs' ozonation independent of investigated pharmaceutical (Table 3). But the wastewater matrix retarded the degradation of pharmaceuticals with ozone compared to their elimination from the pure water matrix. The wastewater contained dissolved and suspended organics and some inorganic constituents (Table 2) that act as scavenges and consequently inhibit the degradation of pharmaceuticals. The retardation of pharmaceuticals' decay in the wastewater was less obvious in the acidic ($T_{90\%}$ increased from 236 to 275 min for IBP) and the neutral medium

Table 4. 90% conversion times ($T_{90\%}$) and the pseudo-first order rate constants (k_1) of SMX and IBP degradation by UV photolysis and H_2O_2/UV process.

Treatment method	Matrix	H_2O_2 (mM)	$T_{90\%}$ (min)	k_1 (1/min) × 10^{-2}
SMX				
UV photolysis	pure water	-	28	8.94±0.05
UV photolysis	urea	-	38	6.66±0.33
UV photolysis	wastewater	-	44	6.12±0.16
H_2O_2/UV	pure water	0.8	29	8.76±0.32
H_2O_2/UV	pure water	1.2	27	9.12±0.21
H_2O_2/UV	pure water	2.4	26	9.30±0.35
IBP				
UV photolysis	pure water	-	275	0.77±0.04
UV photolysis	urea	-	>300	0.59±0.02
UV photolysis	wastewater	-	>300	0.38±0.02
H_2O_2/UV	pure water	0.6	85.5	2.48±0.10
H_2O_2/UV	pure water	1.5	42	5.79±0.15
H_2O_2/UV	urea	1.5	67	3.46±0.15
H_2O_2/UV	wastewater	1.5	119	1.94±0.06

($T_{90\%}$ increased from 16 to 26 min for SMX). At pH 11, the $T_{90\%}$ in wastewater matrix was more than 2.6 times longer compared to pure water matrix.

Similarly to ozonation the degradation of pharmaceuticals in the urea matrix was slightly retarded when O_3/UV and O_3/H_2O_2 systems were used. In the case of wastewater the inhibiting impact of matrix was more obvious. In addition, during both ozonation and O_3/UV treatment of SMX and IBP in urea and wastewater matrices the formation of hydrogen peroxide was detected, but in a lower extent than in the pure water matrix.

Photolysis and Hydrogen Peroxide Photolysis

Photodegradation can occur by direct absorption of radiation of the target molecule (direct photolysis) or by reaction with reactive intermediates (hydroxyl radicals (•OH) or other reactive species). Such intermediates are intensively generated when irradiation is combined with a strong oxidant, e.g. hydrogen peroxide (hydrogen peroxide photolysis). The efficacy of photodegradation depends on the absorbance spectrum of the pharmaceutical, the concentration of hydrogen peroxide employed, the type of the radiation source, and the matrix. It is known that many of pharmaceuticals undergo photodegradation easily. Therefore, the photolytic degradation and hydrogen peroxide photolysis of IBP and SMX was studied. Several studies on SMX (4, 25, 52) and IBP (53) degradation by black light (UVA) and solar light photolysis were published recently, indicating low efficiency of the process for both pharmaceuticals. In the present study a low-pressure mercury lamp emitting at 254 nm was used as it is commonly utilised in water/wastewater treatment for disinfection purposes.

SMX absorbs light within the range between 240 and 310 nm, and thus it is prone to undergo germicidal ultraviolet light photolysis. The photolysis of SMX is also known to be strongly affected by the pH (52). At the neutral and basic pH values SMX is in its anionic form (pK_a values 1.6 and 5.7), which is the most stable form (36). Thus, pH=3 was maintained during all photolysis trials.

IBP absorbs mainly at lower wavelengths (in the range of 200-240 nm) and presents absorbance minimum at approximately 250 nm. Therefore, degradation of IBP by UV photolysis with application of low pressure lamp was expected to be slow.

Similarly to ozone-based processes, each individual decomposition curve of UV photolysis and H_2O_2/UV treatment showed the pseudo-first order rate behaviour. Table 4 summarises the calculated formal pseudo-first order rate constants and $T_{90\%}$ of SMX and IBP degradation by UV and H_2O_2/UV processes.

The application of direct photolysis (i.e. UV treatment alone) resulted in complete removal of both pharmaceuticals (Table 4). Analogous to ozonation, IBP was found to be much more resistant to UV photolysis than SMX. Thus, the $T_{90\%}$ for SMX and IBP was 28 and 275 min, respectively, in the pure water matrix.

The addition of hydrogen peroxide to photolysis accelerated IBP degradation (Table 4). The k_1 of IBP degradation by H_2O_2/UV process increased by factor of 3.2 and 7.5 for hydrogen peroxide concentration of 0.6 and 1.5 mM, respectively. The observed increase in IBP degradation efficacy is most likely due to the photochemical cleavage of hydrogen peroxide to yield hydroxyl radicals by light absorption. In the case of SMX, the hydrogen peroxide photolysis showed

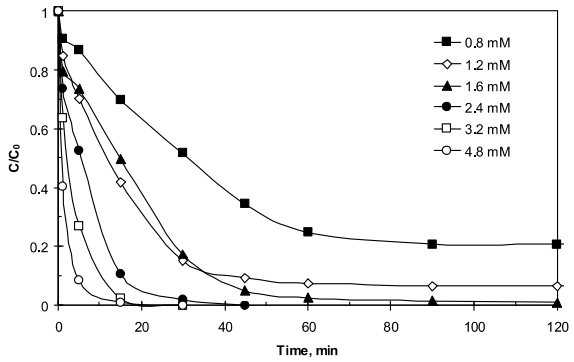


Figure 1. SMX degradation by the Fenton treatment at different H_2O_2 concentrations.

negligible increase in drug's removal efficacy when compared with direct photolysis.

It should be mentioned that during UV photolysis of SMX independently on aqueous matrix used the extended formation of hydrogen peroxide was observed. As to IBP photolysis, H_2O_2 formation was not detected in the pure water matrix. However, the application of UV photolysis in urea and wastewater matrices resulted in formation of hydrogen peroxide.

The matrix proved to have the impact on the direct photolysis of SMX as well as direct photolysis and H_2O_2/UV treatment of IBP (Table 4). The results indicated a slight deceleration in pharmaceuticals' degradation rates due to urea addition to the system. The latter is in accordance with the data formerly reported by Felis and Miksch (22). The degradation of IBP by direct photolysis and hydrogen peroxide photolysis was definitely retarded in the wastewater matrix. Thus, the k_1 value decreased by 2 and 3 times for UV photolysis and H_2O_2/UV treatment, respectively. The impact of wastewater matrix on the degradation of SMX was not as evident as in the case of IBP; however, retardation was observed as well (Table 4). The wastewater's suspended matter may contribute to the light attenuation in a water layer, both by light absorption and light scattering, as well as impede the degradation of the target compound via its adsorption and shielding effects. Some components of the wastewater may also induce radical scavenging, consequently retarding the degradation of pharmaceuticals.

The Fenton and Photo-Fenton Treatment

The Fenton's reagent and its modifications were found to be very effective for the degradation of various pharmaceuticals (27). However, for successful application, the Fenton process has to be carefully optimized. In practical applications, an optimal H_2O_2 concentration (molar ratio of hydrogen peroxide to contaminant) is a key to effective degradation of the target compound and to the reduction of oxidant consumption. The reaction medium pH is another important factor. The acidic conditions (pH ca 3.0) promote the most efficient generation of •OH-radicals and avoid the iron precipitation. However, there is evidence that the fast pH drop during the very beginning of the reaction may be responsible for the effective elimination of target compounds even at initial solution pH values close to neutral.

In order to verify the Fenton process efficacy, blank experiments of pharmaceuticals degradation by hydrogen peroxide oxidation alone were conducted. No changes in SMX and IBP concentrations were observed for H_2O_2 dosages in the range form 0.8 to 10 mM and treatment duration of 2 h.

Independent of the oxidant dose, the degradation of SMX by the Fenton treatment proceeded fast at the initial stage of the oxidation, and afterwards it was retarded or even totally terminated (Figure 1). In the latter case, the reaction ceased due to complete utilization of hydrogen peroxide in the system. In general, hydrogen peroxide was fully consumed during 2 h of SMX degradation in all Fenton treatment trials. The decay of SMX was directly proportional to the amount of H_2O_2 employed. Thus, application of 0.8 mM H_2O_2 (corresponding to H_2O_2/SMX molar ratio of 2) was not enough to achieve the complete degradation of SMX in the Fenton system. Twofold increase in H_2O_2 concentration up to 1.6 improved effectively drug's removal and resulted in $T_{90\%}$ of 36.5 min. To accelerate the elimination of SMX by the Fenton treatment, the concentration of hydrogen peroxide must be further raised. Accordingly, the ultimate SMX degradation was achieved within 15-30 minutes of treatment at H_2O_2 dosage of 3.2 and 4.8 mM, whereas the $T_{90\%}$ was 10 and 4.5 minutes, respectively.

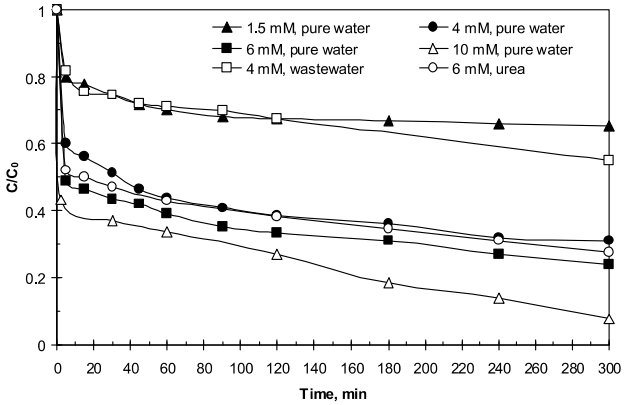


Figure 2. IBP degradation by the Fenton treatment at selected H_2O_2 concentrations in different matrices.

IBP was found to be more resistant to the Fenton treatment than SMX. Similar to SMX, the degradation of IBP was fast during the first few minutes of oxidation, and afterwards it was retarded or totally terminated. In the Fenton-based treatment the initial pH value of all IBP solutions was maintained at 5. However, the results indicated rapid pH drop below the pK_a value of IBP (4.9) during the first minutes after hydrogen peroxide addition. Below the pK_a value of IBP the formation of visible precipitate in the reactive Fenton system was observed. Thus, the Fenton process was retarded after several minutes of reaction and the solubility of IBP was the main limiting factor. On the other hand, sharply increased IBP/H_2O_2 molar ratio might also have an adverse effect on the overall treatment efficacy as hydrogen peroxide present in excess can compete with the pharmaceutical for the hydroxyl radicals generated in the Fenton system.

The results of IBP degradation by the Fenton treatment are presented in Figure 2. Under current treatment conditions the complete IBP removal was not achieved. The highest IBP degradation was observed at hydrogen peroxide concentration of 10 mM with $T_{90\%}$ of 270 min. The degradation of IBP was directly proportional to the amount of H_2O_2 employed. However, hydrogen peroxide was not fully consumed in all cases. For example, almost 77 and 50% of initial 4 and 6 mM of hydrogen peroxide, respectively, remained unconsumed after 2 h of the Fenton treatment. H_2O_2 residual concentration was observed in reaction system even after prolonged experiment (overall treatment duration 5 h).

Because the pharmaceuticals readily underwent photolytic degradation, the photo-Fenton treatment was expected to enhance the efficacy of the pharmaceuticals' degradation compared to the Fenton process. The synergetic action of UV light leading to the increase of reactive species via photo-Fenton reaction may accelerate the elimination of organic compounds. Indeed, the photo-Fenton treatment enhanced the decay of both pharmaceuticals, enabling complete removal at significantly higher rate and utilising substantially lower oxidant doses compared to the Fenton process (Figures 3 and 4). The entire degradation was observed even at low H_2O_2 dosages of 0.8 and 1 mM with $T_{90\%}$ of 17 and 76 min for SMX and IBP, respectively (corresponding to H_2O_2/pharmaceutical molar ratio of 2). According to the above-mentioned, there is no sense in using more than 0.8 mM H_2O_2 for successful removal of SMX in the pure water matrix. However, for faster elimination of IBP, 1.5 mM hydrogen peroxide concentration ($T_{90\%}$ of 33.5 min) or even higher could be recommended if the photo-Fenton treatment is utilised (Figure 4).

The impact of the wastewater/urea matrix on the decay of SMX and IBP was contradictory. No significant impact of urea addition on the decay of IBP during the Fenton treatment was observed (Figure 2). The photo-Fenton treatment of IBP was not affected by urea during the initial stage of the oxidation but subsequently was followed by definite deceleration of IBP decay resulting in $T_{90\%}$ increase from 33.5 to 128 min for the pure water and urea matrix, respectively (Figure 4). The treatment of IBP in the wastewater matrix indicated the reduced efficacy of IBP degradation by the Fenton process (Figure 2) and somewhat deceleration of IBP decay in the photo-Fenton system (Figure 4).

The degradation of SMX in urea and wastewater matrices was definitely retarded at the initial stage of the Fenton treatment (Figure 3). Thus, the $T_{90\%}$ was increased from 40 min in the pure water matrix to 135

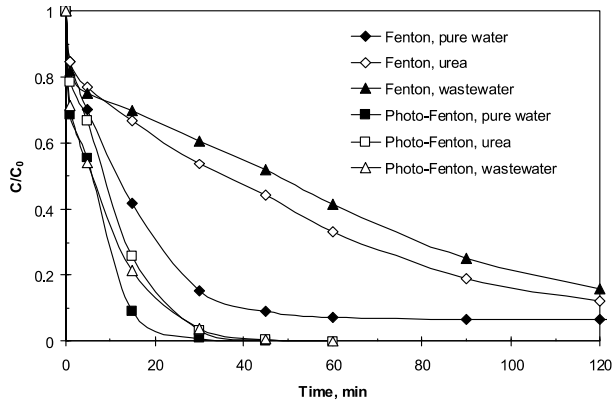


Figure 3. The impact of the matrix on the degradation of SMX by the Fenton and photo-Fenton treatment (1.2 mM H_2O_2).

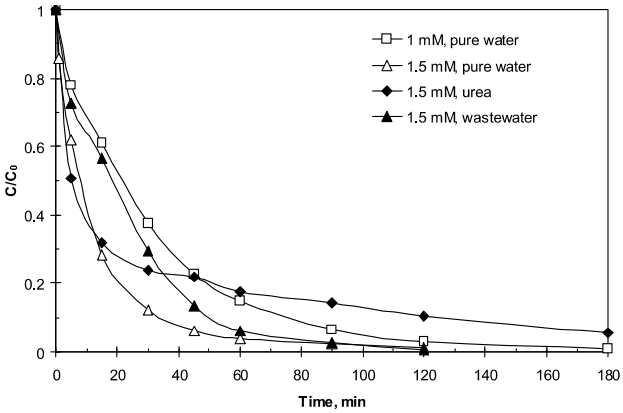


Figure 4. IBP degradation by the photo-Fenton treatment at selected H_2O_2 concentrations in different matrices.

and 140 min in urea and wastewater matrices, respectively (1.2 mM H_2O_2). The impact of the matrix on SMX decay by the photo-Fenton process was minor and mainly observed during the first 30 minutes of the treatment (Figure 3). For effective elimination of both pharmaceuticals by the photo-Fenton treatment in the wastewater/urea matrix, the prolonged treatment seems to be more reasonable than the increase in oxidant dose.

Conclusions

The impact of the matrix on the degradation of both pharmaceuticals was obvious for all AOPs. Consequently, elimination rates determined in the pure water cannot be directly used to predict the oxidation of SMX and IBP in the wastewater.

The ability of studied AOPs to destroy the two pharmaceuticals was different. IBP was more resistant to all types of treatment, especially to the Fenton's reagent, compared to SMX. The recommendations for practical application should take into account the cost of the treatment. Our primary estimations utilizing the approach published earlier (54) have shown that the operation cost for the photo-Fenton treatment should remain in the range of 0.6-1.0 €/m^3. The operation cost of the ozonation is 0.4-0.6 €/m^3; however, the total cost will be significantly higher due to high investments (54). Thus the photo-Fenton treatment could be considered for elimination of studied pharmaceuticals in practice.

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PAPER II

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Degradation of diclofenac in aqueous solution by homogeneous and heterogeneous photolysis

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Abstract

Background: Pharmaceuticals have arisen as emerging environmental pollutants due to their potential impact on humans, animals and microorganisms even at low concentrations. Conventional wastewater treatment plants are known to be ineffective for removal of many pharmaceuticals present in wastewater. Advanced oxidation processes are one of the most promising treatment technologies for degradation of such persistent compounds. The current study was focused on the efficacies of various oxidation processes for degradation of diclofenac (DCF) as one of the most widespread pharmaceuticals.

Methods: The efficacy of UV photolysis, hydrogen peroxide photolysis, homogeneous and heterogeneous Fenton/photo-Fenton treatment for removal of DCF from aqueous solution was examined. The impact of pH, hydrogen peroxide concentration, and catalyst type on DCF removal was assessed. The identification of DCF photo-degradation products with GC-MS (EI) technique was carried out.

Results: According to results of the present study direct photolysis proved main contributing reaction pathway in all studied systems with UV irradiation. Fast decrease in pH value observed during all studied processes started at pH 5, 7, and 9 led to the system controlled by DCF precipitation-degradation-re-dissolution conditions. The enhanced efficacy of promoted photolysis proved dependent on the rate of pH decrease to value below pK_a at the beginning of the process. After reaching acidic pH values of the surrounding solution the DCF degradation was controlled by the solubility independently of treatment method applied. The highest DCF degradation efficacy was attained by the heterogeneous photo-Fenton treatment at initial pH 11. Thus, DCF 90% conversion time decreased from 48 to 23.5 min for UV photolysis and heterogeneous photo-Fenton process (3.8 mM H_2O_2), respectively.

Conclusions: DCF was quite resistant to all tested processes. The application of the Fenton-based treatment and UV/H_2O_2 did not show vital advantages compared to UV photolysis when the initial pH was 7 or 9. Direct photolysis proved main process contributing to DCF degradation in all studied systems combined with UV irradiation. The present study was the first to evaluate the efficacy of photo-Fenton catalysed by goethite for DCF degradation in aqueous solution. The latter proved the most efficient one among the Fenton-based processes.

Keywords: Advanced oxidation processes, photolysis, photo-Fenton process, pharmaceutical, UVC radiation, goethite

Background

The presence of pharmaceutical residues in municipal, surface, ground- and even drinking water is an emerging environmental problem due to the potential impact on human health and the environment even at low concentrations. Pharmaceuticals used by human or animal are only partially consumed in the organism and excreted through urine or faeces in unchanged or/and metabolized form. Drugs are released into the wastewater not only after medical application, but also during manufacturing and improper disposal of unused or expired medicines. Unit operations used in wastewater treatment plants (WWTP) are known to be ineffective for removal of many pharmaceuticals present in wastewater. Consequently, effluents finally released into the receiving water bodies contain from ng L^{-1} to μg L^{-1} of these pollutants [1-2].

Among the various pharmaceuticals, non-steroidal anti-inflammatory drugs (NSAIDs) are of the greatest environmental interest due to their widespread availability. Diclofenac (2-(2,6-dichlorophenylamino)phenylacetic acid, DCF) is one of the most consumed NSAIDs (annual DCF consumption estimated as 940 tons [3]) commonly used in medical care as an analgesic, antiarthritic and antirheumatic agent. Being resistant to biodegradation, it is ubiquitously present in the aquatic environment and detected in effluents of WWTP [3]. This pharmaceutical is relatively stable in the environment, but similar to others NSAIDs is sensitive to photolysis. DCF is known to undergo solar radiation induced photochemical decomposition in surface waters. However, it is still one of the most frequently

detected compounds in water at concentrations up to 2 μg L^{-1} [4]. Although the ecotoxicity of DCF is relatively low, in combination with other drugs present in water, the toxic effects increase considerably [5]. Conventional WWTP, typically based on biological processes, are capable of removing some substances, but non-biodegradable compounds (*e.g.* DCF) may escape the treatment.

Advanced oxidation processes (AOPs) are one of the most promising treatment technologies for successful degradation of pharmaceuticals in aqueous matrices [6]. Several AOPs have been tested for DCF removal from water/wastewater including photolysis and UV/H_2O_2 process [6-7], homogeneous Fenton/photo-Fenton oxidation [2,5], heterogeneous catalytic oxidation with H_2O_2 [9], *etc.* However, among the various advanced oxidation technologies proposed for the degradation of DCF the heterogeneous Fenton-based process with goethite catalyst has not yet been investigated.

The main drawbacks associated with homogeneous catalysts in the Fenton process are the narrow pH range of operation to avoid the formation and subsequent precipitation of iron oxyhydroxide and the need to recover dissolved iron ions from the treated solution by supplementary treatment process. The application of heterogeneous catalyst (*e.g.* naturally occurring minerals) in the Fenton treatment overcomes the above-mentioned problems and results in extended periods of catalyst life without requiring regeneration or replacement, in easy removal of the catalyst from the treated water by sedimentation or filtration, and in Fenton-like reactions over a wide range of pH value [10]. The heterogeneous Fenton-based processes involving naturally occurring minerals (hematite a-Fe_2O_3, goethite a-FeOOH, magnetite Fe_3O_4, *etc.*) proved feasible alternative for water/wastewater treatment [11]. Goethite has been recognized as the preferred mineral oxide catalyst since it appears to have the fastest reaction with H_2O_2 [12].

In the present study the degradation of DCF using UV photolysis, H_2O_2 photolysis, homogeneous and heterogeneous Fenton/photo-Fenton processes was investigated. The efficacies of various oxidation processes on DCF removal from aqueous solution were compared. The identification of main by-products of DCF degradation by AOPs applied was carried out.

Methods

Chemicals and materials

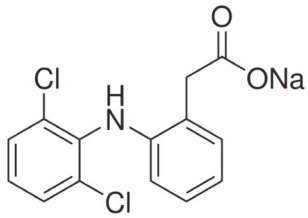
Diclofenac sodium salt and goethite (α-FeOOH, 30-50 mesh) were purchased from Sigma-Aldrich; acetonitrile (99.8%, isocratic grade for HPLC) was obtained from Baker. The structure and the basic data concerning DCF are presented in **Table 1.** The specific surface area of goethite was measured by multipoint N_2-BET analysis using a sorptometer KELVIN 1042 (COSTECH Instruments) as 112.5 m^2 g^{-1}. All other chemicals were of analytical grade and used without further purification.

Stock solutions with initial DCF concentration of 100 mg L^{-1} were prepared in twice-distilled water. The solution was mixed for several hours to achieve complete DCF dissolution. As the solubility of DCF is low below the pK_a value (4.15), all experiments were conducted at initial pH ≥5. Sodium hydroxide and sulphuric acid aqueous solutions were used for pH adjustment.

Experimental procedure

A mercury low-pressure OSRAM lamp with an energy input of 10 W located in a quartz tube inside the reactor was used as an UV source. The incident UV radiation photon flux at 254 nm measured by potassium ferrioxalate actinometry [13] was 3.59 ± 0.12 μ Einstein s^{-1}. The constant temperature (22±1°C) in the reactor was maintained using a cooling jacket. All Fenton-based process trials were carried out in batch mode and in non-buffered solutions. DCF solutions were treated in 1 L cylindrical glass reactor with permanent

Table 1. The structure and main properties of studied pharmaceutical

Pharmaceutical	**Diclofenac sodium salt**
Empirical formula	$C_{14}H_{10}Cl_2NNaO_2$
Molecular formula	
CAS Nr.	15307-79-6
Molecular weight, g mol^{-1}	318.13
pK_a	4.15 [3]

agitation at a speed to provide complete mixing for uniform distribution and full suspension of iron catalyst particles for a period of 120 min; samples were withdrawn at selected time intervals and filtered through a Millipore filter (0.45 μm). The reaction was stopped by adding 2 drops of 1 M aqueous solution of NaOH.

The homogeneous Fenton reaction (H_2O_2/Fe^{2+}) was initiated by adding H_2O_2 (0.94-2.5 mM) to DCF solution (pH 5 or pH 7) containing a known amount of Fe^{2+} ion. The molar ratio of H_2O_2/Fe^{2+} was kept invariable at 10:1. Heterogeneous Fenton-based treatment trials (H_2O_2/α-FeOOH) were carried out with 1 g L^{-1} of goethite at pH values of 7. The suspensions were continuously stirred for 30 min prior to H_2O_2 addition to establish the adsorption/desorption equilibrium between the DCF and the catalyst particles.

The photo-Fenton experiments were carried out in the same reactor and treatment conditions as the Fenton experiments with the UV lamp located inside the reactor. In the homogeneous photo-Fenton trials the concentration of hydrogen peroxide was in the range of 0.63-1.9 mM; the pH value of the stock solution was adjusted to 7. The heterogeneous photo-Fenton experiments were carried at pH values of 7, 9 and 11 with H_2O_2 concentration from 0.63 to 3.8 mM.

The direct UV photolysis and H_2O_2/UV experiments were carried out in the same reactor (1 L of stock DCF solution in a glass reactor with a permanent agitation speed for a period of 120 min). The pH value of the stock solution was in the range of 5 to 11. The H_2O_2 concentration varied from 0.63 to 1.9 mM.

Additionally, the experiments on adsorption effect of goethite and DCF oxidation with non-catalyzed hydrogen peroxide were conducted in the same reactor and treatment conditions as the respective Fenton-based treatment trials. All experiments were duplicated and the data on DCF concentration was verified with at least three replicates. The results of the analysis of initial and treated samples are presented as the mean, with the standard deviation below 4% in all cases.

Analytical methods

DCF concentrations were quantified by means of a CLAS MPm (Labio Ltd.) high performance liquid chromatograph equipped with a MAG 0 (1.5 × 50 mm) Biospher PSI 100 C18 (particle size, 5 μm) microcolumn and UV/VIS detector SAPHIRE. The isocratic method with a solvent mixture of 50% acetonitrile and 0.1% of acetic acid in water was applied. Samples were analyzed at a flow rate of 70 μL min^{-1} and absorbance wavelength of 254 nm. The concentration of DCF was determined by using the standard chemical to fit the retention time.

The total iron concentration was quantified with phenanthroline method [14]. The initial hydrogen peroxide concentration in stock solutions was determined spectrophotometrically by measurement of the absorption of hydrogen peroxide at λ=254 nm. The residual hydrogen peroxide concentration was measured by the spectrophotometric method with Ti^{4+} [15]. The chemical oxygen demand (COD) was determined by the closed reflux titrimetric method according to [14]. The correction of hydrogen peroxide interference on COD test was done by the correlation equation according to [16].

Identification of DCF degradation by-products

The samples from selected trials were concentrated to dryness by water evaporation at room temperature and re-dissolved in methanol to a final volume of 2 mL.

GC-MS measurements were performed with a gas chromatograph GC-2010 (Shimadzu, Kyoto, Japan) equipped with a GCMS-QP2010 Plus mass selective detector. The column flow was maintained at 1.66 mL min^{-1}. The analytes were separated in a ZB-5MS column (30 m × 0.32 mm × 0.25 μm). The oven temperature program was 1.0 min at 105°C, 25°C min^{-1} to 180°C, 5°C min^{-1} to 250°C, 20°C min^{-1} to 270 (holding time 3 min). The interface temperature was set at 280°C. The injector and the ion source temperature were 270 and 250°C, respectively. The MS detector was operated in the EI mode, scanning in the range of 50-400 m/z.

Results and Discussion

UV photolysis and UV/H_2O_2 process

DCF effectively absorbs UV light in the range between 200 and 300 nm with the absorption maximum at 273 nm, which tails well over 300 nm when the spectrum is measured up to 400 nm. In general, DCF is known to undergo both long wave and short wave UV photolysis. The former may occur even in natural surface water systems.

The experiments of UV photolysis and UV/H_2O_2 treatment of DCF were performed as preliminary trials for subsequent assessment of homogeneous and heterogeneous photo-Fenton treatment efficacy. In direct photolysis trials a spontaneous pH drop to 3.5 due to formation of hydrochloric and carboxylic acids was observed leading to precipitation of DCF (**Figure 1**). DCF is very water soluble in neutral-alkaline medium (50 g L^{-1}), but has low solubility (23.7 mg L^{-1}) at pH below pK_a value [17]. Thus, under such acidic conditions, DCF precipitates from the solution.

In UV photolysis at pH 5, DCF was completely precipitated at the beginning and the process kinetics was entirely governed by the continuous re-dissolution of DCF. 90% conversion was not achieved during 2 h of oxidation and the highest DCF removal was 85%. Therefore, DCF degradation was still occurring at pH around 3.5, even though it had undergone slight precipitation during the treatment, due to simultaneous precipitation-degradation-re-dissolution process. Similar observation was reported by [5]. In the case of direct photolysis experiment started at pH 7 and 9, fast decrease in pH also led to the system controlled by DCF re-dissolution process (**Figure 1**). However, in both cases 90% conversion was achieved in 115 and 80 min for

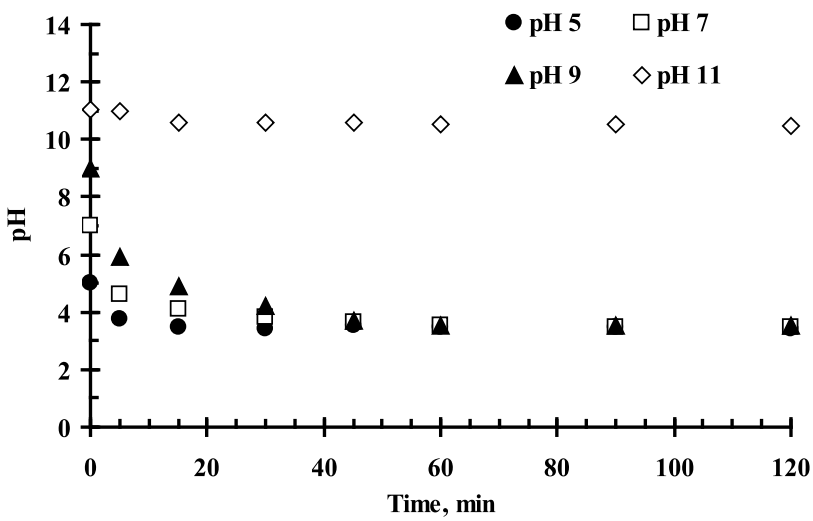


Figure 1. Change in pH during DCF degradation by UV photolysis at different initial pH values.

pH 7 and 9, respectively (**Figure 2**). Faster DCF removal compared to the trial at pH 5 was mainly due to effective drug degradation at the beginning of the treatment, i.e. pending pH decrease from initial to below pK_a value.

Rivas *et al.,* [**18**] suggested that addition of free radical promoters does not enhance the efficiency of UV photolysis when irradiated substances have relatively high values of quantum yield (φ) and molar absorption coefficient (ε); moreover, a negative effect can be experienced. Reported ε and φ for DCF UV photolysis at 254 nm are 4260±130 M^{-1} cm^{-1} and 0.272±0.046 mol $Einstein^{-1}$, respectively [**19**]. On the other hand, Vogna *et al.,* [**20**] found that addition of hydrogen peroxide to UV system effectively induced DCF degradation. In the present study, different concentrations of hydrogen peroxide were tested to increase UV photolysis efficacy.

Similar to UV photolysis the efficacy of UV/H_2O_2 process proved dependent on the solubility equilibrium of DCF controlled by the pH of the surrounding solution. The results indicated that DCF transformation in the UV/H_2O_2 process was influenced by direct photolysis; *i.e.* UV photolysis was responsible for 85-100% of DCF degradation by UV/H_2O_2 system (**Figure 2**). The addition of 0.63 and 0.94 mM H_2O_2 resulted in negligible efficacy enhancement or even in worse DCF reduction compared to UV photolysis independently of the initial pH value. Further increase in H_2O_2 concentration to 1.9 mM led to improvement in DCF degradation with pH increase from 7 to 11 (**Figure 2**). Thus, 90% conversion time ($T_{90\%}$) decreased from 48 to 28.5 min for UV photolysis and UV/H_2O_2 process at pH 11, respectively.

Blank trials with non-catalyzed hydrogen peroxide were performed at the same initial concentrations as the photo-catalytic experiments. No degradation of DCF was detected during 2 h of H_2O_2 oxidation.

Overall UV and hydrogen peroxide photolysis treatment efficacy was assessed by measuring COD. Low mineralization (not exceeding 15% after 2 h of oxidation) was observed in any case according to measured COD values. This fact indicated the formation of intermediates, which are more resistant to the photo-degradation than DCF itself.

The Fenton and photo-Fenton treatment

The Fenton process trials (H_2O_2/Fe^{2+}) were conducted at pH 5 and 7. The experiments with initial pH 5 indicated rapid pH decrease below pK_a value, resulting in the system completely controlled by precipitation-degradation-re-dissolution process. DCF removal during 2 h was very moderate, *e.g.* 25% in trial with 0.94 mM H_2O_2. The increase in initial pH to 7 resulted in improved DCF removal (40 and 70% of DCF were degraded during the Fenton treatment at 0.94 and 2.5 mM H_2O_2 concentration, respectively). However, fast pH decrease was still observed in systems with pH 7 indicating effective degradation of DCF at the beginning of the Fenton reaction and subsequent slow removal

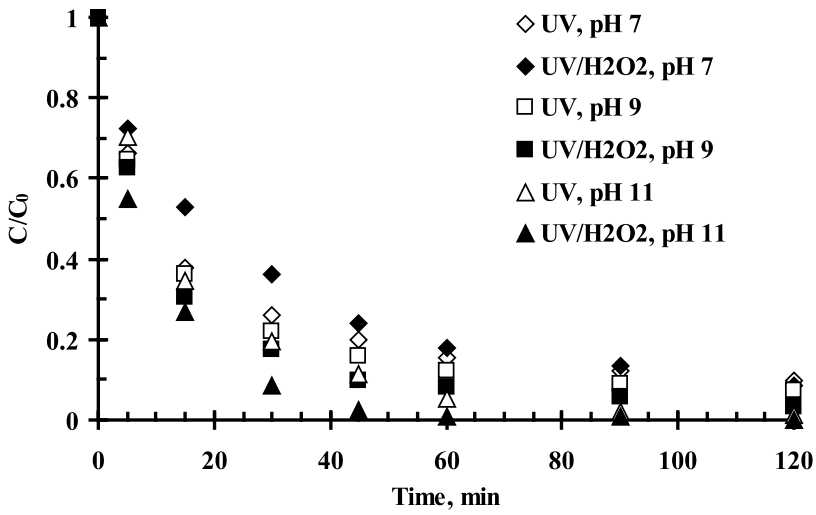


Figure 2. DCF degradation by UV photolysis and UV/H_2O_2 process (1.9 mM H_2O_2) at different pH values.

influenced by drug's re-dissolution.

As to the heterogeneous Fenton process, the goethite catalysed Fenton-based reaction is a surface controlled process that depends on H_2O_2 concentration, on the iron mineral surface area and on other system parameters (pH, *etc.*). The overall heterogeneous reaction will include various steps such as diffusion of chemicals to the surface, surface complex formation, actual electron transfer, desorption of products, and regeneration of the reactive sites [10].

The results showed no removal of DCF during 2 hours of the heterogeneous Fenton reaction independent of H_2O_2 concentration in the range of 0.63-3.8 mM. The amount of the total dissolved iron in the bulk solution for H_2O_2/α-FeOOH system was less than 0.03 mg L^{-1} after 120 min of oxidation, indicating solely heterogeneous pathway of reaction. Some decrease in H_2O_2 concentration observed during the goethite catalyzed Fenton-based oxidation is most likely due to partial H_2O_2 decomposes to oxygen and water at the surface of the heterogeneous catalysts without producing dissolved radicals [10]. Prolonged experiments with overall duration of 24 h resulted in negligible degradation of DCF with less than 5% removal. The sorption experiments demonstrated no DCF removal due to adsorption on the catalyst surface.

Since solely H_2O_2 did not led to complete mineralization of DCF by UV/H_2O_2 process the photo-Fenton treatment proved promising alternative to enhance DCF degradation in aqueous solution. Similar to direct and hydrogen peroxide photolysis the photo-Fenton process (both homogeneous and heterogeneous) kinetics were governed by the continuous re-dissolution of DCF. Thus, trials with initial pH 7 and 9, demonstrated pH decrease to 3.5 during the experiment.

The homogeneous photo-Fenton treatment was conducted at initial pH 7. Iron precipitated at this pH value producing highly light-absorbing iron hydroxide colloids. In general, photo-reductive decomposition of ferric-complexes can release ferrous iron to the solution, which will produce additional hydroxyl radicals in the presence of hydrogen peroxide. The results of DCF removal revealed similarity among the homogeneous photo-Fenton process and UV/H_2O_2 system (pH 7). Thus, DCF degradation was slower during UV/H_2O_2/Fe^{2+} process compared to direct photolysis at neutral pH value. This fact can be explained by faster decrease in pH below pK_a value leading to the treatment process controlled by continuous DCF re-dissolution.

The heterogeneous photo-Fenton trials were conducted at pH in the range from 7 to 11. Generally, minerals containing ferric oxides (*e.g.* goethite) need ultraviolet radiation to accelerate the reduction of Fe^{3+} to Fe^{2+}. The results of goethite catalysed photo-Fenton system indicated similarity to UV/H_2O_2 process as the increase in H_2O_2 concentration and pH led to additional DCF removal if compared to direct photolysis (**Figures 3** & **4**). Thus, $T_{90\%}$ was decreased from 115

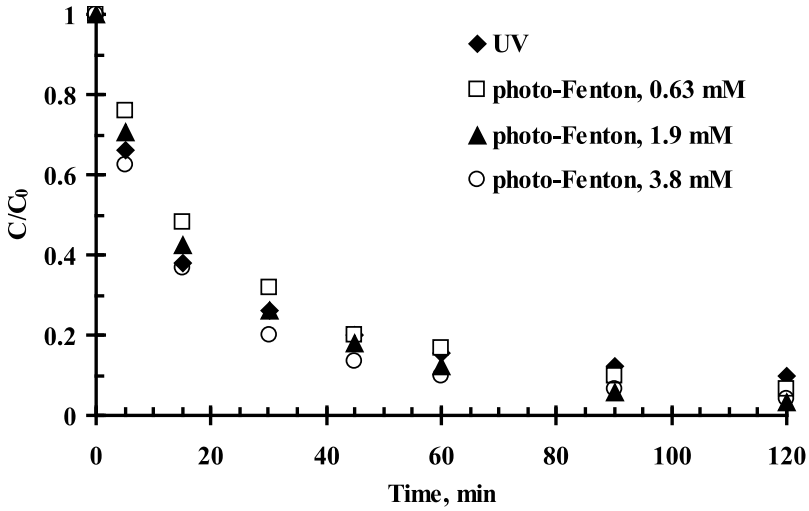


Figure 3. DCF degradation by heterogeneous photo-Fenton treatment (pH 7) at different H_2O_2 concentrations.

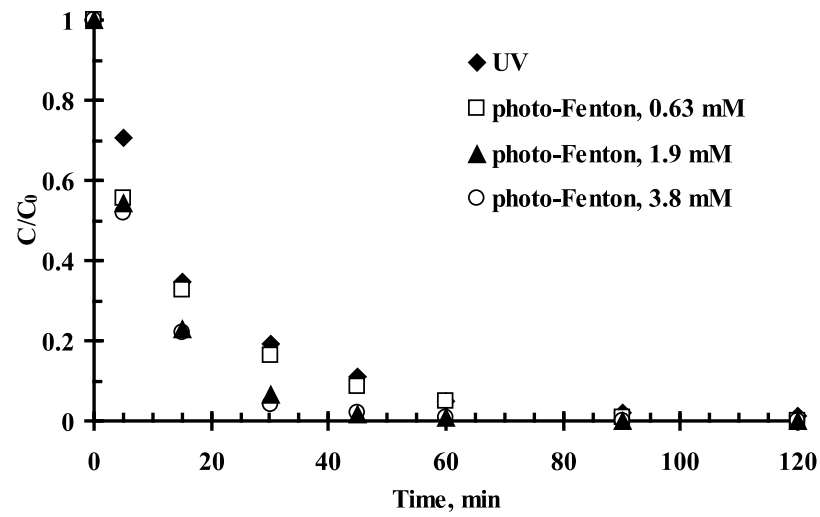


Figure 4. DCF degradation by heterogeneous photo-Fenton treatment (pH 11) at different H_2O_2 concentrations.

to 69 min and from 80 to 42 min for photo-Fenton treatment (1.9 mM H_2O_2) at pH 7 and 9, respectively, if compared to direct photolysis. The H_2O_2 utilization in the heterogeneous photo-Fenton and UV/H_2O_2 processes was comparable as well and resulted in 25-30% at pH 7 and 9. At pH 11 residual H_2O_2 concentrations was less than 5% in all cases, probably due to H_2O_2 auto-decomposition at elevated pH values.

The efficacy of promoted photolysis proved dependent on the rate of pH decrease (from initial to value below pK_a) at the beginning of the process. After reaching acidic pH of the surrounding solution the DCF degradation was stable and controlled by the solubility independently of treatment method applied. The highest efficacy improvement was attained in UV/H_2O_2/α-FeOOH system at pH 11, where pH decreased only to 10, and the process was not determined by the solubility equilibrium of DCF. The $T_{90\%}$ for UV photolysis and heterogeneous photo-Fenton process (3.8 mM H_2O_2) was 48 and 23.5 min, respectively (**Figure 4**).

Similar to UV and UV/H_2O_2 systems, no substantial mineralization of DCF was observed in any studied Fenton-based process with initial pH 7 and 9. COD removal was ca 15% after 2 h of oxidation. In the case of pH 11 and elevated H_2O_2 concentration (1.9 mM), COD was essentially reduced (up to 60%) indicating overall efficacy of the process under strongly alkaline conditions.

Identification of intermediates

In the present study, no derivatization procedures were undertaken prior to injection of the samples into GC-MS (EI) system, and highly polar or non-volatile by-products could escape the scope of the technique. Identification of by-products was done by comparison of full-scan mass spectra of the peaks with mass spectral library (NIST/EPA/NIH (NIST 08)) or by identification of the fragmentation patterns.

The results of the present study indicated similar GC-MS chromatogram patterns for UV photolysis, UV/H_2O_2 and UV/H_2O_2/α-FeOOH systems. Two photo-transformation products were detected; other by-products were in trace concentrations (below the method detection limits) even during the first few minutes of DCF degradation. The main detected photo-transformation product with formula $C_{14}H_9Cl_2NO$ (MW 277) was identified as 1-(2,6-dichlorophenyl) indolin-2-one. This compound was also reported [4] as one of the major photo-decomposition products of DCF in pure water. However, the application of GC-MS for sample analysis could be the reason for such observation, since 1-(2,6-dichlorophenyl)indolin-2-one can be formed due to a high temperature used in this method. The other observed photo-transformation product with formula $C_{14}H_{10}ClNO$ (MW 243) was apparently described as C-2 (8-chloro-9H-carbazole-1-acetic aldehyde) [21]. The analysis of mass spectrum of the latter by-product indicated mass differences of Δ=28 and Δ=35 pointing to the existence of one chlorine atom and an aldehyde function. In order to prove this assumption further detailed analysis is required.

Conclusions

DCF was quite resistant to all tested AOPs. The application of the Fenton-based treatment and UV/H_2O_2 did not show vital advantages compared to UV photolysis when the initial pH was 7 or 9. Direct photolysis proved main process contributing to DCF degradation in all studied systems combined with UV irradiation. The fast pH decrease of the surrounding solution to 3.5 observed during all studied processes started at pH 5, 7 and 9 led to system controlled by DCF precipitation-degradation-re-dissolution. The efficacy of UV/H_2O_2, homogeneous and heterogeneous photo-Fenton systems proved dependent on time of pH decrease at the beginning of the process. After reaching pH values below DCF pK_a the degradation was controlled by the solubility independently of treatment method applied. The present study was the first to evaluate the efficacy of photo-Fenton catalysed by goethite for DCF degradation in aqueous solution. The latter proved the most efficient one among the Fenton-based processes. The identification of DCF degradation by-products by GC-MS (EI) technique was done indicating 1-(2,6-dichlorophenyl)indolin-2-one and 8-chloro-9H-carbazole-1-acetic aldehyde as two detectable photo-transformation products.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

IE contributed to research design, fulfilled the experiments and analyses, contributed to data interpretation and drafted the manuscript. ND contributed in conception, research design, data interpretation and manuscript draft. MT contributed in conception, research design and manuscript draft. All authors approved the manuscript.

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PAPER III

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Degradation of levofloxacin in aqueous solutions by Fenton, ferrous ion-activated persulfate and combined Fenton/persulfate systems

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HIGHLIGHTS

- The treatment efficacy was as follows: $H_2O_2/Fe^{2+} > H_2O_2/S_2O_8^{2-}/Fe^{2+} > S_2O_8^{2-}/Fe^{2+}$.
- The combined Fenton/persulfate process proved effective in LFX removal.
- Six LFX transformation products were identified in all studied systems.
- $HO^{\cdot}$ was proposed as the predominant radical in all studied systems.

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ABSTRACT

The efficacies of Fenton (H_2O_2/Fe^{2+}), Fe^{2+}-activated persulfate ($S_2O_8^{2-}/Fe^{2+}$) and combined Fenton/persulfate ($H_2O_2/S_2O_8^{2-}/Fe^{2+}$) systems for degrading levofloxacin (LFX) in aqueous solutions were investigated and compared. The LFX degradation by classical Fenton oxidation followed a pseudo-first-order kinetic law during the entire reaction. In the case of the $S_2O_8^{2-}/Fe^{2+}$ and $H_2O_2/S_2O_8^{2-}/Fe^{2+}$ systems, a fast degradation of LFX was observed within the first minute, and then the target compound was gradually degraded within the remaining reaction time. Notably, without consideration of the first minute, the rest of the LFX degradation in the $S_2O_8^{2-}/Fe^{2+}$ system also followed the pseudo-first-order kinetic model. The application of combined Fenton/persulfate oxidation was promising, and after careful adjustment of oxidants and activator doses, it demonstrated a considerable improvement in LFX degradation compared with the Fe^{2+}-activated persulfate system and a somewhat similar efficacy to the Fenton process. Among the studied processes, the H_2O_2/Fe^{2+} system showed the highest performance both in LFX degradation and mineralization, followed by the combined $H_2O_2/S_2O_8^{2-}/Fe^{2+}$ process. Six LFX transformation products were identified by LC–MS analysis in all studied systems, indicating that hydroxyl radicals are the predominant oxidative species in H_2O_2/Fe^{2+}, $S_2O_8^{2-}/Fe^{2+}$, and $H_2O_2/S_2O_8^{2-}/Fe^{2+}$ processes. In summary, all studied radical-based advanced oxidation technologies proved to be promising techniques for the treatment of wastewater and in situ groundwater containing LFX, with a particularly high potential for the combined Fenton/persulfate system.

1. Introduction

Antibiotics have become a greater focus point of investigation due to the high frequency of their detection in the environment and the rapid increase in the formation and spread of bacterial resistance. Among antimicrobial agents, fluoroquinolones (FQs) are the most frequently identified antibiotics in wastewater and surface water [1]. FQs are known to be excreted mainly in unmetabolized form, only partially degraded by processes used in wastewater treatment plants (WWTPs), and, when released into the environment, found in surface waters mostly in their active form [1,2]. Levofloxacin (LFX) is a synthetic broad-spectrum antibiotic of the fluoroquinolone drug class used to treat severe or life-threatening bacterial infections. Similarly to other FQs, it is known to be extremely resistant to conventional biological oxidation and usually escapes intact from WWTPs [1,3]. As a result, permanent LFX occurrence in WWTP effluent may cause long-term concerns such as bioaccumulation and toxicity in the environment. To prevent the escape of LXF into receiving water bodies as well as to solve the problems of existing contamination, radical-based advanced oxidation technologies could be applied as the main or supplementary (polishing step) technique in water/wastewater/groundwater treatment.

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The application of hydroxyl radical-based advanced oxidation technologies (HO•-AOTs) has shown a great potential to degrade persistent and bio-refractory organic compounds presented in wastewater, surface water, groundwater and soil [4–7]. The advantages of HO•-AOTs as treatment techniques include high reaction rates and non-selective oxidation due to hydroxyl radicals (HO•, E° = 2.73 V [8]), which allow the simultaneous degradation of multiple contaminants and potentially reduce the toxicity of contaminated aqueous media [7]. The Fenton treatment is widely studied and used HO•-AOT for water/wastewater purification [9–11] and in situ groundwater/soil remediation [12,13] based on the generation of HO• from hydrogen peroxide (H_2O_2) with ferrous iron ions (Fe^{2+}) acting as a homogeneous activator at preferably acidic pH. The commonly accepted mechanism of the Fenton reaction consists of a sequence of reactions, where HO• are produced through Eq. (1) and the activator is regenerated in accordance with Eq. (2) or from the reaction of ferric iron ions (Fe^{3+}) with organic radicals [8]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + HO^- \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \quad (2)$$

Recently, an innovative treatment technology based on persulfate oxidation has been studied as an alternative to conventional HO•-AOTs both for water/wastewater treatment [14–18] and in situ chemical oxidation applications [13,19]. The persulfate anion ($S_2O_8^{2-}$) is a strong oxidant (E° = 2.1 V, Eq. (3)), which through activation forms an even stronger sulfate radical ($SO_4^{\bullet-}$, E° = 2.6 V, Eq. (4)) [20]. The main methods used for $SO_4^{\bullet-}$ generation are heat, UV light or ultrasound activation, transition metal activation, alkaline activation, or peroxide activation [20,21]:

$$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-} \quad (3)$$

$$S_2O_8^{2-} + \text{activator} \rightarrow SO_4^{\bullet-} + (SO_4^{\bullet-} + SO_4^{2-}) \quad (4)$$

Sulfate radical-based advanced oxidation technologies ($SO_4^{\bullet-}$-AOTs) have several advantages over HO•-AOTs. Accordingly, unlike HO•, $SO_4^{\bullet-}$ is more stable and selective for oxidizing unsaturated bonds and aromatic constituents [22]. In general, the high oxidation efficiencies of $SO_4^{\bullet-}$ in combination with the slow rate of consumption of the precursor oxidant make $SO_4^{\bullet-}$-AOTs a very effective option for the degradation of persistent organic pollutants.

Among different transition metals used in persulfate activation, iron in its ferrous form is the most frequently studied metal (Eq. (5)) [20]. In general, the Fe^{2+}-activated persulfate system contains many similarities to the Fenton process, mainly owing to the fact that the structure of the persulfate molecule is basically a symmetrically substituted derivative of hydrogen peroxide. However, due to the several drawbacks intrinsic to $S_2O_8^{2-}/Fe^{2+}$ systems, its widespread application for water/wastewater treatment is rather limited. Accordingly, the excess Fe^{2+} presented in the activated system results in the scavenging of $SO_4^{\bullet-}$ through Eq. (6), leading to inhibition of the oxidation of target contaminants:

$$S_2O_8^{2-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{\bullet-} \quad (5)$$

$$SO_4^{\bullet-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} \quad (6)$$

Additionally, similar to the Fenton system, Fe^{2+} activation works effectively only at acidic pH values because of fast iron precipitation such as ferric hydroxycomplexes at pH > 4. Finally, unlike the H_2O_2/Fe^{2+} system in which Fe^{3+} is reduced to Fe^{2+} after formation (Eq. (2)), the Fe^{3+} that forms in Eq. (5) is more stable in the $S_2O_8^{2-}/Fe^{2+}$ system, which leads to the ceasing of the activation reaction [23,24].

To overcome, or at least alleviate, the limitations of Fe^{2+}-activated persulfate as well as combine the main benefits of both AOTs, the joint Fenton/persulfate system is proposed in this work. Therefore, the purpose of this study was to investigate and compare the performance of LFX degradation in Fenton (H_2O_2/Fe^{2+}), $S_2O_8^{2-}/Fe^{2+}$ and combined Fenton/persulfate ($H_2O_2/S_2O_8^{2-}/Fe^{2+}$) systems. In general, the application of Fe^{2+}-activated hydrogen peroxide and persulfate has been studied for the degradation of different classes of organic contaminants; however, the data on the use of the latter process for degrading FQs, including LFX, have not been fully evaluated. Accordingly, the degradation of LFX by various AOTs has been investigated under different treatment conditions for ozonation [3,25,26], hydrogen peroxide photolysis [3], photocatalysis in the presence of TiO_2 [26], and sonolysis in H_2O_2/Fe_3O_4 system [27]. Moreover, the potential of combined Fenton/persulfate system for antibiotics and other micropollutants degradation is discussed for the first time. It is anticipated that the results of this study could provide fundamental support for FQ-contaminated wastewater and especially groundwater remediation using these techniques in practical application. To the best of our knowledge, this is the first study on the degradation and identification of reaction intermediates for any FQ with sulfate radical and joint hydroxyl/sulfate radical action.

2. Materials and methods

2.1. Chemicals and materials

Levofloxacin (Fig. 1; $C_{18}H_{20}FN_3O_4$, ⩾98%, molecular weight 361.37 g mol^{-1}, pK_a 5.33 and 8.07 [28]), hydrogen peroxide (PERDROGEN™, ⩾30%), sodium persulfate ($Na_2S_2O_8$, ⩾99%), ferrous sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$, ⩾99%), and sodium sulfite (Na_2SO_3, ⩾98%) were purchased from Sigma–Aldrich. All other chemicals of analytical grade were used without further purification. Stock solutions were prepared in ultrapure water (Millipore Simplicity® UV System). NaOH and H_2SO_4 aqueous solutions were used to adjust the pH.

2.2. Experimental procedure

All trials of the Fenton, persulfate and combined Fenton/persulfate processes were performed in batch mode and in non-buffered solutions at ambient room temperature (21 ± 1 °C). LFX solutions (75 μM, 0.4 L) were treated in a 0.6-L cylindrical glass reactor with a permanent agitation speed (400 rpm) for a period of 3 h. The pH of the samples was adjusted to 3 with H_2SO_4 (0.5 M), if not specified otherwise. The activator ($FeSO_4{\cdot}7H_2O$) was added, and after complete dissolution of the catalyst, oxidation was initiated by adding H_2O_2, $Na_2S_2O_8$ or $H_2O_2/Na_2S_2O_8$. Samples were withdrawn at pre-determined time intervals. The oxidation quenching was done by the addition of Na_2SO_3 at a $[\text{oxidant}]_0/SO_3^{2-}$ molar ratio (m/m) of 1/10. The experiments on LFX oxidation with non-activated hydrogen peroxide or persulfate were conducted in identical reactors and treatment conditions for the respective Fe^{2+}-activated oxidation trials. In the case of

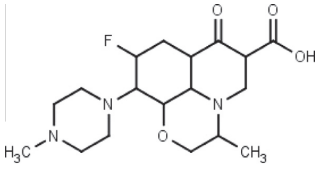


Fig. 1. Molecular structure of levofloxacin.

peroxide-activated persulfate, both oxidants were added simultaneously. All experiments were duplicated; the results of the analysis are presented as the mean with a standard deviation less than 5%.

2.3. Analytical methods

The concentration of LFX was quantified by means of high performance liquid chromatography combined with a diode array detector (HPLC-PDA, Prominence SPD-M20A, Shimadzu) equipped with a Phenomenex Gemini (150 × 2.0 mm, 1.7 μm) NX-C18 (110 Å, 5 μm) column. The isocratic method with a solvent mixture of 10% acetonitrile and 90% acetic acid aqueous solution (0.1%) was applied. The flow rate was maintained at 200 μL min^{-1}. Samples were scanned at 190–800 nm and analyzed at λ = 295 nm. The concentration of LFX was determined by using the standard chemical to fit the retention time.

The pH was measured using a digital pH/ion meter (Mettler Toledo S220). The initial hydrogen peroxide concentration in the stock solutions was measured spectrophotometrically at λ = 254 nm (the molar extinction coefficient of H_2O_2 at 254 nm is 19.6 L mol^{-1} cm^{-1}); the residual hydrogen peroxide concentration in the treated samples was measured by a spectrophotometric method with Ti^{4+} at λ = 410 nm [29] by a Heλios-β UV/VIS spectrophotometer (Thermo Electron Corporation). The residual persulfate concentration in the treated samples was measured spectrophotometrically at λ = 446 nm with o-dianisidine [30]. Non-purgeable organic carbon (NPOC) was measured by a TOC analyzer (multi N/C® 3100, Analytik Jena).

2.4. Identification of LFX degradation by-products

The samples from selected trials were analyzed by high-performance liquid chromatography combined with a mass spectrometer (HPLC–MS, Shimadzu LC–MS 2020). Phenomenex Gemini-NX 5u C18 110A 150 × 2.0 mm column, inner diameter 1.7 μm, was used with an isocratic eluent mixture, 0.1% acetic acid aqueous solution (90%, v/v) and acetonitrile (10%, v/v) with a total flow rate of 0.2 mL min^{-1}. Mass spectra were acquired in full-scan mode (scanning in the range 50–500 *m/z*). The instrument was operated in positive ESI mode, and the results obtained with MS detector were handled using Shimadzu LabSolutions software.

3. Results and discussion

3.1. Fenton process

First, the performance of Fenton oxidation in LFX degradation was evaluated. The main goal of this study was the adjustment of H_2O_2/Fe^{2+} system parameters to achieve target compound removal in a reasonable amount of time. The results of LFX oxidation by the classical Fenton process is presented in Fig. 2.

The obtained data processing revealed that LFX degradation by Fenton oxidation followed a pseudo-first-order kinetic law during an entire reaction and may be described with regard to the LFX concentration through Eq. (7):

$$\frac{dC_{LFX}}{dt} = -k_1 \times C_{LFX} \quad (7)$$

where k_1 is the pseudo-first-order rate constant and C_{LFX} is the LFX concentration. The $-k_1$ constants were calculated from the slopes of the straight lines by plotting $\ln(C/C_0)$ as a function of time t through linear regression. The values of the kinetic constants were calculated for the Fenton oxidation at different LFX/H_2O_2/Fe^{2+} molar ratios as presented in Table 1.

As was expected, the Fenton process demonstrated a high oxidation efficacy, resulting in complete LFX removal in less than 2 h and a respective $k_1 \times 10^{-2}$ value of 4.85 ± 0.18 min^{-1} even at a low oxidant ratio of 1/5/0.5 (LFX/H_2O_2/Fe^{2+}, m/m/m). A further increase in oxidant dosage at the same H_2O_2/Fe^{2+} ratio led to faster LFX degradation, contributing to a decrease in the oxidation time needed to remove LFX completely. The highest performance was achieved at a LFX/H_2O_2/Fe^{2+} m/m/m of 1/20/2 with a $k_1 \times 10^{-2}$ value of 116.11 ± 2.2 min^{-1} and complete target compound elimination within 6 min. In the majority of trials the molar ratio of H_2O_2/Fe^{2+} was maintained at 10/1, which was found to be an optimal ratio in our previous studies [5,31]. However, in order to reduce the amount of activator added as well as the final cost of the treatment, the effect of the twofold-lower H_2O_2/Fe^{2+} m/m ratio of 20/1 was also studied. As a result, a greater-than-threefold decrease in the LFX degradation rate with $k_1 \times 10^{-2}$ values of 6.98 ± 0.22 and 20.81 ± 0.7 min^{-1} for the Fenton oxidation at a LFX/H_2O_2/Fe^{2+} m/m/m of 1/10/0.5 and 1/10/1, respectively, was observed, indicating irrationality of the decrease in activator dose. Similarly, the utilization of hydrogen

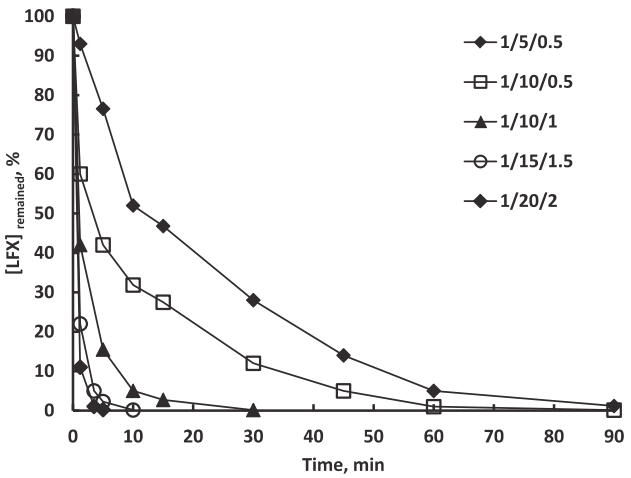


Fig. 2. Degradation of LFX by the H_2O_2/Fe^{2+} process (LFX/H_2O_2/Fe^{2+} is a molar ratio, $[LFX]_0$ = 75 μM.)

Table 1
Kinetic parameters of LFX degradation by the H_2O_2/Fe^{2+} process under different treatment conditions.

LFX/H_2O_2/Fe^{2+}, m/m/m ([LFX]$_0$ = 75 μM)	Initial/final pH (t = 3 h)	$[H_2O_2]_{remained}$, % (t = 3 h)	Pseudo-first-order constant, $k_1 \times 10^{-2}$ min^{-1} (r^2 > 0.98)
1/2.5/1	3/3	0	11.12 ± 0.11[a]
1/5/1	3/2.98	0	14.64 ± 0.28
1/5/0.5	3/2.99	0	4.85 ± 0.18
1/10/0.5	3/2.98	33	6.98 ± 0.22
1/10/1	3/2.98	11	20.81 ± 0.7
1/10/2	3/2.97	0	158.53 ± 3.48
1/15/1.5	3/2.95	10	62.26 ± 1.5
1/20/2	3/2.94	0.5	116.11 ± 2.2

[a] r^2 = 0.95.

peroxide was more effective in the case of the LFX/H_2O_2 m/m of 1/10 with H_2O_2/Fe^{2+} m/m maintained at 10/1 compared with 20/1, resulting in a residual oxidant concentration three times lower after the 3-h treatment (Table 1). Notably, the effect of the twofold-higher H_2O_2/Fe^{2+} m/m ratio of 5/1 was studied as well, mainly as a blank experiment for the combined Fenton/persulfate system. The results indicated a greater-than-sevenfold increase in the LFX degradation rate at a LFX/H_2O_2/Fe^{2+} m/m/m of 1/10/2 compared to the oxidation at a LFX/H_2O_2/Fe^{2+} m/m/m of 1/10/1, but complete hydrogen peroxide utilization within 60 min (Table 1). In general, the application of H_2O_2/Fe^{2+} m/m of 5/1 and 2.5/1 in the Fenton system resulted in rapid and ineffective hydrogen peroxide decomposition, leading to termination of LFX degradation and NPOC removal.

Irrespective of the applied Fenton reagent dose, the mineralization was considerably less effective than target compound removal. The tendency of NPOC removal was similar for all studied conditions and in general was enhanced with increases in Fenton reagent dose as presented in Fig. 3. Conversely, the extent of improvement was strongly dependent on the LFX/H_2O_2/Fe^{2+} m/m/m applied. Accordingly, NPOC removal was 26% and 36.5% after 3-h oxidation at a LFX/H_2O_2/Fe^{2+} m/m/m of 1/10/1 and 1/15/1.5, respectively. A further increase in the LFX/H_2O_2/Fe^{2+} m/m/m from 1/15/0.5 to 1/20/2 resulted in only 1% of supplementary mineralization, indicating the inefficacy of an application of an elevated oxidant dose to enhance NPOC removal, mainly due to the stability of LFX transformation products (TPs) formed during Fenton oxidation.

To confirm the predominant radical mechanism of target compound decomposition in the H_2O_2/Fe^{2+} system, the oxidative potential of non-activated hydrogen peroxide was studied as well. The results of antibiotic oxidation at a LFX/H_2O_2 m/m of 1/10 indicated no LFX removal and more than 99% of unused H_2O_2 in solution after 3 h of treatment.

In general, the Fenton process proved to be an efficient technique for LFX degradation with a substantially lower efficacy in reducing mineralization. These results are consistent with data obtained by other authors concerning FQs and their transformation product removal by HO·-AOTs [3,32,33].

3.2. Ferrous-ion activated persulfate process

The performance of the $S_2O_8^{2-}/Fe^{2+}$ system in LFX oxidation was studied at different LFX/$S_2O_8^{2-}$ and $S_2O_8^{2-}/Fe^{2+}$ ratios. The effect of oxidant and activator dose on the efficacy of Fe^{2+}-activated persulfate LFX oxidation was evaluated, and the results are presented in Figs. 4 and 5.

In the case of the $S_2O_8^{2-}/Fe^{2+}$ system, a fast decomposition of LFX and persulfate was observed during the first minute (the first measured time point after the beginning of the reaction), and then the target compound along with persulfate was gradually degraded within the remaining reaction time. Thus, more than 31% and 56% of LFX was removed during the first minute and the rest of the 3-h oxidation, respectively, in $S_2O_8^{2-}/Fe^{2+}$ systems at a LFX/$S_2O_8^{2-}/Fe^{2+}$ m/m/m of 1/10/1 (Fig. 4 and Table 2). Accordingly, the entire reaction can be divided into two main

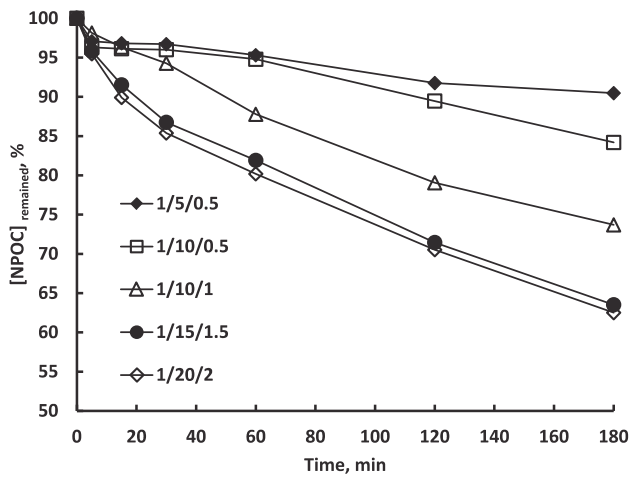


Fig. 3. Reduction of NPOC by the H_2O_2/Fe^{2+} process (LFX/H_2O_2/Fe^{2+} is a molar ratio, [LFX]$_0$ = 75 μM).

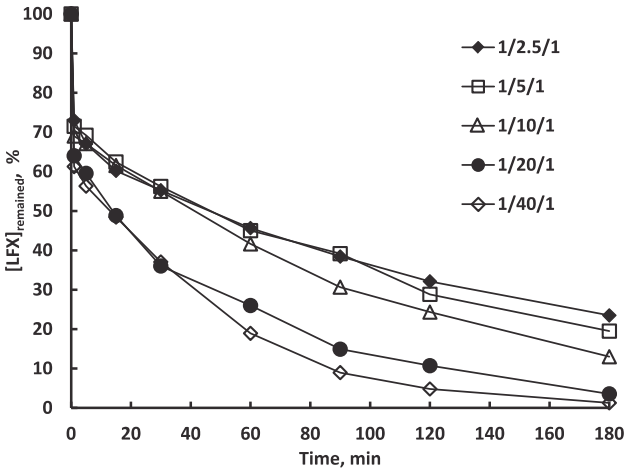


Fig. 4. Degradation of LFX by the $S_2O_8^{2-}/Fe^{2+}$ process: effect of initial $S_2O_8^{2-}$ concentration (LFX/$S_2O_8^{2-}$/Fe^{2+} is a molar ratio, $[Fe^{2+}]_0$ = 75 μM).

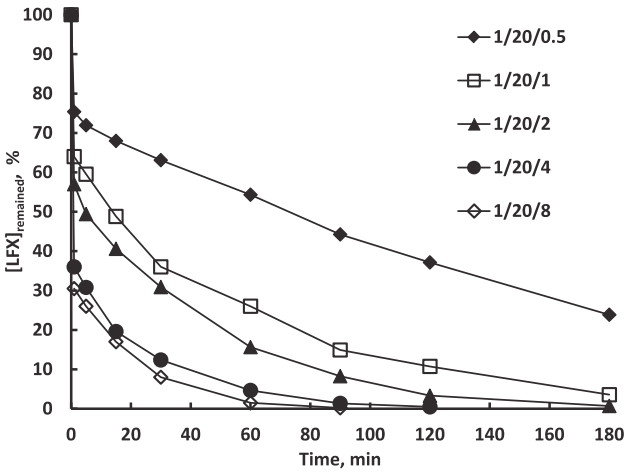


Fig. 5. Degradation of LFX by the $S_2O_8^{2-}/Fe^{2+}$ process: effect of initial Fe^{2+} concentration (LFX/$S_2O_8^{2-}$/Fe^{2+} is a molar ratio, $[S_2O_8^{2-}]_0$ = 1.5 mM).

Table 2
Kinetic parameters of LFX degradation by the $S_2O_8^{2-}/Fe^{2+}$ process under different treatment conditions.

LFX/$S_2O_8^{2-}$/Fe^{2+}, m/m/m ($[LFX]_0$ = 75 μM)	Initial/final pH (t = 3 h)	$[S_2O_8^{2-}]_{remained}$, % (t = 3 h)	$[LFX]_{remained}$, % (t = 1 min)	Pseudo-first-order constant, $k_1 \times 10^{-2}$ min^{-1} (r^2 > 0.99)
1/2.5/1	3/2.97	51	73	0.61 ± 0.01
1/5/1	3/2.89	60.5	71.5	0.72 ± 0.02
1/10/0.5	3/2.87	91	75	0.65 ± 0.02
1/10/1	3/2.82	67	69	0.93 ± 0.02
1/10/2	3/2.88	45	61	2.23 ± 0.05
1/20/0.5	3/2.88	95	75	0.62 ± 0.02
1/20/1	3/2.76	88	64	1.57 ± 0.05
1/20/2	3/2.77	65	57	2.42 ± 0.04
1/20/2	5/3.01	63	61	2.41 ± 0.06
1/20/2	7/3.04	68	64	2.33 ± 0.04
1/20/2	9/3.18	78.5	69	1.44 ± 0.03
1/20/4	3/2.74	62	36	3.61 ± 0.08
1/20/8	3/2.63	56	30.5	5.58 ± 0.13
1/30/3	3/2.66	65	44	5.74 ± 0.15
1/40/1	3/2.77	91.5	61	2.18 ± 0.06

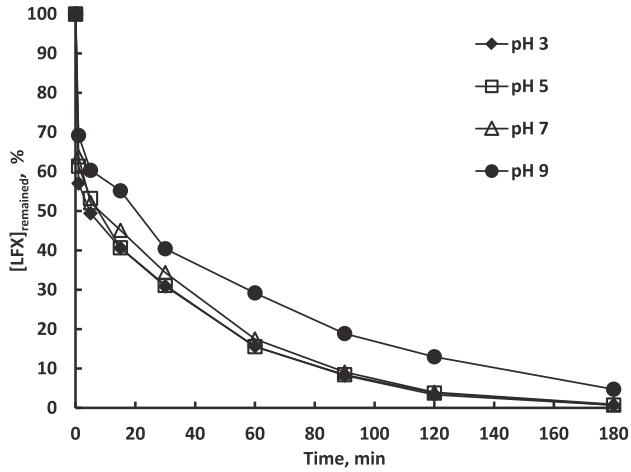


Fig. 6. Degradation of LFX by the $S_2O_8^{2-}/Fe^{2+}$ process: effect of initial pH (LFX/$S_2O_8^{2-}/Fe^{2+}$ molar ratio of 1/20/2, $[LFX]_0$ = 75 μM).

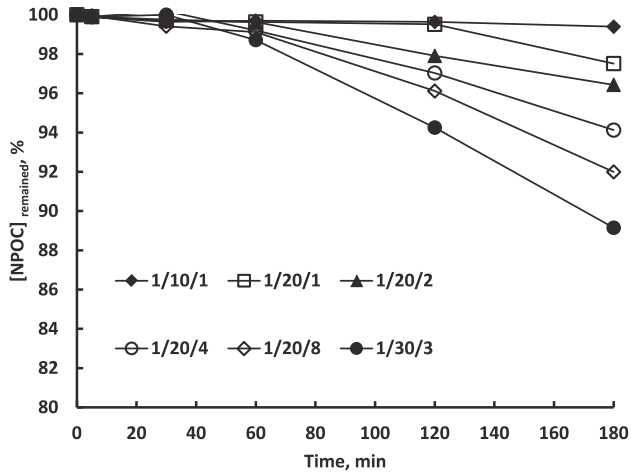


Fig. 7. Reduction of NPOC by the $S_2O_8^{2-}/Fe^{2+}$ process (LFX/$S_2O_8^{2-}/Fe^{2+}$ is a molar ratio, $[LFX]_0$ = 75 μM).

phases: the first period of fast LFX degradation and persulfate decomposition and the second period of gradual LFX oxidation simultaneously with steady persulfate consumption. This observation can be explained by fast generation of $SO_4^{\cdot-}$ through the decomposition of persulfate immediately after activation and rapid accumulation of Fe^{3+} through the complete oxidation of Fe^{2+}. Fe^{3+} alone proved to be an ineffective activator of persulfate decomposition even at acidic pH values [24]. Conversely, the existence of the second period of gradual LFX and persulfate decomposition suggests the presence of other routes for reducing the activator and supporting $SO_4^{\cdot-}$ generation. According to the available literature, the $SO_4^{\cdot-}$ generated in $S_2O_8^{2-}/Fe^{2+}$ systems may further undergo conversion to HO· depending on pH levels in accordance with Eq. (8) [20]:

$$SO_4^{\cdot-} + H_2O \rightarrow HO^{\cdot} + H^+ + SO_4^{2-} \quad (8)$$

As a result, the radicals $SO_4^{\cdot-}$/HO· can be presented either individually or simultaneously in the activated persulfate system. Moreover, the recent study of Wu et al. [34] proved the generation and even the dominant role of HO· in the $S_2O_8^{2-}$/Fe/citric acid system. The presence of HO· in the reactive system can eventually lead to the generation of hydrogen peroxide through Eq. (9):

$$2HO^{\cdot} \rightarrow H_2O_2 \quad (9)$$

Therefore, the second phase of gradual LFX degradation in $S_2O_8^{2-}/Fe^{2+}$ systems can be explained by the continuous reduction of Fe^{3+} in the reaction with organic radicals as presented in Eq. (10), by the formation of hydrogen peroxide and the subsequent direct reduction of Fe^{3+} through Eq. (2), or by the combined action of both listed processes.

$$R^{\cdot} + Fe^{3+} \rightarrow Fe^{2+} + \text{products} \quad (10)$$

Therefore, similar to the Fenton oxidation trials, without consideration of the first minute (the rapid reaction period), the rest of the performance of LFX degradation in the $S_2O_8^{2-}/Fe^{2+}$ system followed the pseudo-first-order kinetic model. The values of the kinetic constants calculated for the $S_2O_8^{2-}/Fe^{2+}$ system at the studied LFX/$S_2O_8^{2-}/Fe^{2+}$ ratios are presented in Table 2.

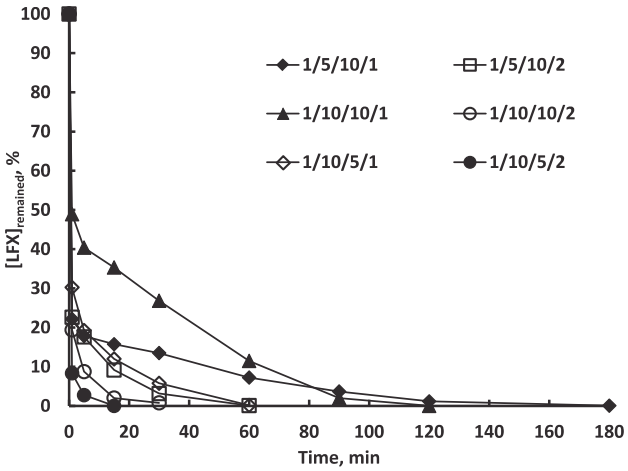


Fig. 8. Degradation of LFX by the $H_2O_2/S_2O_8^{2-}/Fe^{2+}$ process (LFX/H_2O_2/$S_2O_8^{2-}$/Fe^{2+} is a molar ratio, $[LFX]_0$ = 75 μM).

Table 3
Kinetic parameters of LFX degradation by the $H_2O_2/S_2O_8^{2-}/Fe^{2+}$ process under different treatment conditions.

LFX/H_2O_2/$S_2O_8^{2-}$/Fe^{2+}, m/m/m/m ($[LFX]_0$ = 75 μM)	Initial/final pH (t = 180 min)	$[H_2O_2]_{remained}$, % (t = 180 min)	$[LFX]_{remained}$, % (t = 1 min)
1/2.5/10/1	3/2.74	8.5	86
1/5/10/1	3/2.71	23	22
1/5/10/2	3/2.73	0.8	23
1/10/10/1	3/2.86	42	49
1/10/10/2	3/2.7	14	19
1/10/5/1	3/2.81	29	30
1/10/5/2	3/2.75	0	8
1/10/2.5/1	3/2.98	17	35

The obtained results indicated a stable improvement in the LFX degradation rate with the increase in applied persulfate dose at a fixed LFX/Fe^{2+} and $S_2O_8^{2-}/Fe^{2+}$ m/m ratio (Fig. 4 and Table 2). Accordingly, a greater-than-threefold increase in the LFX degradation rate with $k_1 \times 10^{-2}$ values of 0.72 ± 0.02 and 2.18 ± 0.06 min^{-1} for the $S_2O_8^{2-}/Fe^{2+}$ oxidation at a LFX/$S_2O_8^{2-}/Fe^{2+}$ m/m/m of 1/5/1 and 1/40/1, respectively, was observed. In the case of trials with the fixed $S_2O_8^{2-}/Fe^{2+}$ molar ratio of 10/1, the $k_1 \times 10^{-2}$ of the second reaction period was 0.93 ± 0.02, 2.42 ± 0.04, and 5.74 ± 0.15 for the Fe^{2+}-activated persulfate oxidation at a LFX/$S_2O_8^{2-}/Fe^{2+}$ of 1/10/1, 1/20/2, and 1/30/3, respectively. Similarly, the decomposition of LFX during the fast reaction period improved with the increase in oxidant dose, indicating a more comprehensive LFX oxidation until the added activator is completely oxidized through Eqs. (5) and (6). In general, the efficacy of target compound degradation in the $S_2O_8^{2-}/Fe^{2+}$ system was considerably lower compared with the Fenton process at the same LFX/oxidant/Fe^{2+} ratios. Thus, the application of elevated LFX/$S_2O_8^{2-}/Fe^{2+}$ m/m/m of 1/20/2 and 1/30/3 resulted in >99% LFX removal only after 3 and 1.5 h of oxidation, respectively. Meanwhile, in the case of the H_2O_2/Fe^{2+} system, LFX degradation was completed in less than 45 min at a LFX/H_2O_2/Fe^{2+} m/m/m of 1/10/1. The lower observed performance, compared with the Fenton process, can be explained by the fast depletion of the activator in the $S_2O_8^{2-}/Fe^{2+}$ system. To control the activator-consuming reaction presented in Eq. (6), Fe^{2+}-activated persulfate oxidation can be adjusted by correction of the activator dose. Accordingly, five $S_2O_8^{2-}/Fe^{2+}$ m/m ratios of 40/1, 20/1, 10/1, 5/1, and 2.5/1 were evaluated at the same LFX/$S_2O_8^{2-}$ m/m of 1/20. A further increase in activator dose was not studied due to the ultimately increasing amount of residual iron waste along with cost of the treatment process. The results indicated equally faster LFX degradation in both reaction periods and persulfate decomposition at a LFX/$S_2O_8^{2-}/Fe^{2+}$ m/m/m ratio of 1/20/8 (Fig. 5 and Table 2). However, considering the high stability of persulfate along with its high acidity ensuring acidic pH values in reaction media, prolonged oxidation at a $S_2O_8^{2-}/Fe^{2+}$ m/m of 10/1 could be a more reasonable alternative to the elevated activator dose (5/1 and higher) both for water/wastewater treatment as well as in situ applications.

The pH value of the solution is known to be an important parameter affecting degradation of organic contaminants. Therefore, the effect of initial pH on the degradation of LFX in the $S_2O_8^{2-}/Fe^{2+}$ system was also evaluated. The results of LFX oxidation at a LFX/$S_2O_8^{2-}/Fe^{2+}$ m/m/m of 1/20/2 and different initial pH values (3, 5, 7 and 9) are presented in Fig. 6 and Table 2. The efficacy of LFX degradation was found to decrease gradually with the increase in the initial pH value. Accordingly, a 1.7-fold decrease in k_1 value of the second reaction period and 12% lower removal of LFX during 1 min was observed at initial pH 9 compared to pH 3. Conversely, the obtained results revealed the comparable performance of LFX degradation in the $S_2O_8^{2-}/Fe^{2+}$ system at initial pH values of 3, 5 and 7, indicating a high potential of this process for in situ applications at natural pH values. This observation is in agreement with previous studies in literature concerning organic contaminants degradation by activated persulfate processes [14,24,35]. Notably, the solution pH in all trials decreased to around 3 after 3 h of oxidation, mainly due to acidity of oxidant and its decomposition products, metal-related acidity and acidic LFX decomposition by-products (Table 2).

The efficacy of the Fe^{2+}-activated persulfate system in the degradation of transformation products was evaluated as well, and the data are presented in Fig. 7. Similar to LFX degradation, the extent of mineralization in the $S_2O_8^{2-}/Fe^{2+}$ system was considerably lower than in the H_2O_2/Fe^{2+} system. Thus, the NPOC concentration remained nearly unchanged after 3 h of oxidation at a LFX/$S_2O_8^{2-}/Fe^{2+}$ m/m/m lower than 1/20/2 (more than 97% of residual concentration). The highest obtained NPOC removal under the studied treatment conditions was 11% at a LFX/$S_2O_8^{2-}/Fe^{2+}$ m/m/m of 1/30/3, mainly indicating the accumulation of TPs in the oxidized LFX aqueous solution.

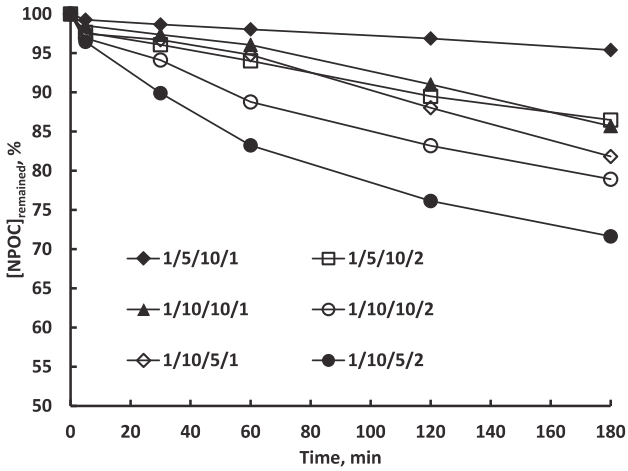


Fig. 9. Reduction of NPOC by the $H_2O_2/S_2O_8^{2-}/Fe^{2+}$ process (LFX/H_2O_2/$S_2O_8^{2-}$/Fe^{2+} is a molar ratio, $[LFX]_0$ = 75 μM).

Generally, it is known that $S_2O_8^{2-}$ itself is a strong but relatively stable oxidant. Furthermore, under acidic conditions the breakdown of $S_2O_8^{2-}$ into $SO_4^{\cdot-}$ can be promoted by H^+ in accordance with Eqs. (11) and (12) [14]:

$$S_2O_8^{2-} + H^+ \rightarrow HS_2O_8^- \quad (11)$$

$$HS_2O_8^- \rightarrow H^+ + SO_4^{\cdot-} + SO_4^{2-} \quad (12)$$

Therefore, the efficacy of LFX degradation by non-activated persulfate at a LFX/$S_2O_8^{2-}$ m/m of 1/10 at pH 3 was studied. According to the results, only 7% of LFX was removed in the first stage with a $k_1 \times 10^{-2}$ of 0.04 min^{-1} for the second gradual period, and more than 95% of the residual $S_2O_8^{2-}$ was observed after 3 h of oxidation, indicating the negligible efficacy of $S_2O_8^{2-}$ oxidation in LFX degradation. The termination of persulfate oxidation with the subsequent gradual degradation of LFX suggests, however, the radical-based target compound degradation mechanism. The reaction inhibition in this case was most likely caused by the preference of $SO_4^{\cdot-}$-to-$SO_4^{\cdot-}$ reactions over $SO_4^{\cdot-}$-to-LFX reactions. Accordingly, the predominant oxidation effect in the$S_2O_8^{2-}/Fe^{2+}$ system proved to be due to the addition of the activator rather than acidic $S_2O_8^{2-}$ decomposition.

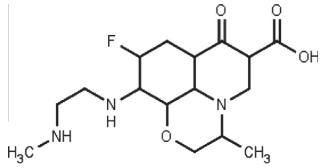
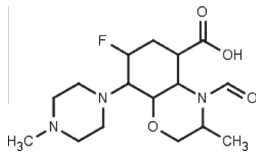
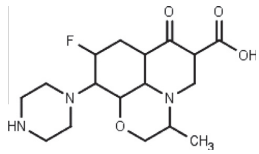
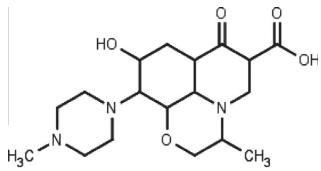
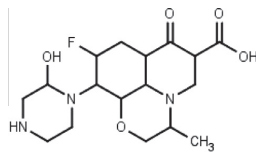
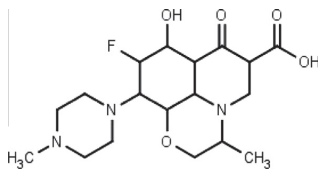
3.3. Combined Fenton/persulfate process

The combined $H_2O_2/S_2O_8^{2-}/Fe^{2+}$ system was studied in order to facilitate the activator regeneration in $S_2O_8^{2-}/Fe^{2+}$ systems as well as to evaluate the possible advantages of the simultaneous action of Fe^{2+}-activated hydrogen peroxide and persulfate.

To evaluate the efficacy of LFX degradation by combined non-activated persulfate and hydrogen peroxide oxidation, the blank experiment at a LFX/H_2O_2/$S_2O_8^{2-}$ m/m/m of 1/10/10 was conducted. The results indicated similarities in the performance of the $H_2O_2/S_2O_8^{2-}$ system and non-activated persulfate oxidation with only 8% of LFX removed in the first stage with $k_1 = 0.07 \times 10^{-2}$ - min^{-1} for the second gradual period and more than 99% of residual H_2O_2 after 3 h of oxidation. Notably, in both non-activated and Fe^{2+}-activated combined systems LFX decomposition was divided to two oxidation periods. However, the rate of LFX degradation followed the pseudo-first order in the second period of oxidation only in the $H_2O_2/S_2O_8^{2-}$ system. Therefore, in the case of combined Fenton/persulfate oxidation systems, the values of kinetic constants were not calculated because the data did not fit any kinetic model. The results of LFX degradation activated by the combined system are presented in Fig. 8 and Table 3.

Overall, a more rapid decrease in residual LFX concentration was observed during the first minute in the $H_2O_2/S_2O_8^{2-}/Fe^{2+}$ system compared with the $S_2O_8^{2-}/Fe^{2+}$ and H_2O_2/Fe^{2+} processes, indicating the synergic action of both processes. Conversely, considering the two-fold higher activator dose added into the combined system, the overall performance of the $H_2O_2/S_2O_8^{2-}/Fe^{2+}$ process in LFX decomposition was generally higher than in the $S_2O_8^{2-}/Fe^{2+}$ system but somewhat lower than in the Fenton process, mainly indicating the presence of concurrent reactions of the oxidant with the activator in the combined system (Table 3). Accordingly, 31(39)%, 55(86)% and 51(81)% of the initial LFX concentration was removed during the first minute of oxidation by the Fe^{2+}-activated persulfate system at a LFX/$S_2O_8^{2-}/Fe^{2+}$ m/m/m of 1/10/1(2), the Fenton process at a LFX/H_2O_2/Fe^{2+} m/m/m of 1/10/1(2), and the combined Fenton/persulfate system at a LFX/H_2O_2/$S_2O_8^{2-}/Fe^{2+}$ m/m/m/m of 1/10/10/1(2), respectively. To adjust the $H_2O_2/S_2O_8^{2-}$ ratio, the effect of hydrogen peroxide and persulfate doses was studied at a fixed amount of activator (LFX/Fe^{2+} m/m of 1/1). The observed variation in LFX removal efficacies at different $H_2O_2/S_2O_8^{2-}$ ratios indicated a strong necessity for careful optimization of the combined Fenton/persulfate system (Fig. 8 and Table 3). Thus, the decrease in $H_2O_2/S_2O_8^{2-}$ molar ratio from 10/10 to 5/10 at a fixed LFX/$S_2O_8^{2-}/Fe^{2+}$ m/m/m of 1/10/1 resulted in 51% and 78% LFX removal within the first minute of oxidation, respectively. A further decrease in the $H_2O_2/S_2O_8^{2-}$ molar ratio to 2.5/10 demonstrated only 14% LFX removal during the first minute of reaction. Conversely, the highest overall performance of the combined process among the abovementioned systems was achieved at a LFX/H_2O_2/$S_2O_8^{2-}/Fe^{2+}$ m/m/m/m of 1/10/10/1 with >99.9% LFX decomposition within 120 min, indicating the positive effect of hydrogen peroxide addition on Fe^{2+}-activated persulfate efficacy. In the case of trials with a fixed LFX/H_2O_2/Fe^{2+} ratio (1/10/1, m/m/m), a decrease in persulfate dose resulted in faster LFX degradation that was more similar to the efficacy of the treatment by the Fenton process, indicating the inhibitive effect of persulfate on the performance of the H_2O_2/Fe^{2+} system.

Table 4
Protonated molecular ions obtained from MS analysis of oxidation transformation products (TPs).

Compound	MS (m/z)/MW (g mol^{-1})	Reaction pathway proposed	Chemical structure proposed
TP1	336/335	+2[H] −[C_2H_4]	
TP2	338/337	+[HO] +[O] −[C_2O_2H]	
TP3	348/347	+[H] −[CH_3]	
TP4	360/359	+[HO] −[F]	
TP5	364/363	+[HO] +[H] −[CH_3] −[H]	
TP6	378/377	+[HO] −[H]	

In the case of the combined $H_2O_2/S_2O_8^{2-}/Fe^{2+}$ system, residual concentrations of persulfate were not measured due to interference caused by the presence of hydrogen peroxide in samples. Conversely, the presence of residual persulfate still allowed the measurement of unused hydrogen peroxide (Table 3). Accordingly, it was ascertained that only 58% of hydrogen peroxide was used during 3 h of oxidation at a LFX/$H_2O_2/S_2O_8^{2-}/Fe^{2+}$ m/m/m/m of 1/10/10/1. A twofold increase in activator dose (LFX/$H_2O_2/S_2O_8^{2-}/Fe^{2+}$ m/m/m/m of 1/10/10/2) improved the consumption of hydrogen peroxide in the combined system, and only 14% of residual oxidant was detected after 3 h of reaction. Similarly, a more effective utilization of hydrogen peroxide was observed at a LFX/$H_2O_2/S_2O_8^{2-}/Fe^{2+}$ m/m/m/m of 1/5/10/2 compared with 1/5/10/1, indicating a necessity to double the activator dose in the combined system in order to achieve competitive results.

Additionally, the efficacy of the combined $H_2O_2/S_2O_8^{2-}/Fe^{2+}$ process in NPOC removal was assessed, and the results obtained are presented in Fig. 9. Similar to LFX degradation, the extent of mineralization in the combined Fenton/persulfate system was essentially improved compared with particular Fe^{2+}-activated persulfate oxidation, but it was mainly lower than in the respective Fenton process. Thus, 26(24)%, 1(1)% and 14(21)% NPOC removal was observed after 3 h of oxidation by the H_2O_2/Fe^{2+} system at a LFX/H_2O_2/Fe^{2+} m/m/m of 1/10/1(2), the $S_2O_8^{2-}/Fe^{2+}$ process at a LFX/$S_2O_8^{2-}/Fe^{2+}$ m/m/m of 1/10/1(2), and the combined $H_2O_2/S_2O_8^{2-}/Fe^{2+}$ system at a LFX/$H_2O_2/S_2O_8^{2-}/Fe^{2+}$ m/m/m/m of 1/10/10/2(2), respectively.

According to the results obtained within this study, the application of the combined Fenton/persulfate system with carefully adjusted hydrogen peroxide and activator doses could be a feasible

solution for the degradation of LFX and other FQs both in water/wastewater treatment as well as in situ applications.

3.4. Identification of major transformation products

Along with the degradation of LFX, six TPs characterized by different m/z ratios were identified (Table 4). Only the positive ESI mode was used in MS analyses due to the higher response in the positive mode for both LFX and TPs. LC–MS analysis allowed for the identification of the same TPs during LFX oxidation by Fe^{2+}-activated hydrogen peroxide, persulfate and combined hydrogen peroxide and persulfate systems. The identity of TPs for all studied systems verifies $HO^{\cdot}$ as the main oxidative specie in the H_2O_2/Fe^{2+}, $S_2O_8^{2-}/Fe^{2+}$, and $H_2O_2/S_2O_8^{2-}/Fe^{2+}$ systems. In the case of the Fe^{2+}-activated persulfate system, the obtained results are consistent with previously published studies, indicating $HO^{\cdot}$ as predominant oxidative species [34,36].

The chemical structures of TPs presented in Table 4 were mainly suggested on the basis of the well-known reactivity of $HO^{\cdot}$ with unsaturated and tertiary amine compounds. Moreover, the proposed TPs are generally in agreement with the structures of TPs observed by other research groups during FQ degradation by $HO^{\cdot}$-AOTs [3,32,33,37,38].

The major reaction pathways observed during LFX oxidation in all studied systems included defluorination (TP4), piperazinyl substituent transformation (TP1, TP3, TP5), and quinolone moiety modifications (TP2, TP6). Additionally, the results of LC–MS analyses revealed that the TPs identified progressively disappeared after complete elimination of LFX in all studied systems.

4. Conclusions

The H_2O_2/Fe^{2+}, $S_2O_8^{2-}/Fe^{2+}$ and combined $H_2O_2/S_2O_8^{2-}/Fe^{2+}$ systems proved to be promising techniques for the degradation of LFX in aqueous solution. The performance of the studied processes in target compound oxidation was as follows: the Fenton process > the combined Fenton/persulfate system > the Fe^{2+}-activated persulfate process. A similar tendency was observed for NPOC removal, and, accordingly, the highest mineralization was obtained in the H_2O_2/Fe^{2+} system followed by the combined $H_2O_2/S_2O_8^{2-}/Fe^{2+}$ process. The identification of transformation products revealed the presence of six compounds similar to all studied systems, which gradually disappeared after complete LFX degradation.

The findings in this study strongly suggested that prudently adjusted combined Fenton/persulfate oxidation could be a feasible technology for wastewater and especially groundwater remediation contaminated by the LFX. Generally, the results obtained within this study provide fundamental information essential for the practicable application of $HO^{\cdot}/SO_4^{\cdot-}$-AOTs to treat FQ contamination in water/wastewater and groundwater.

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PAPER IV

Epold, I., Dulova, N. Oxidative degradation of levofloxacin in aqueous solution by $S_2O_8^{2-}/Fe^{2+}$, $S_2O_8^{2-}/H_2O_2$ and $S_2O_8^{2-}/OH^-$ processes: A comparative study. – *Journal of Environmental Chemical Engineering*, 2015, 3(2), 1207-1214.

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ABSTRACT

The performance of levofloxacin (LFX) degradation in aqueous solutions in ferrous ion-activated persulfate ($S_2O_8^{2-}$/Fe^{2+}), peroxide-activated persulfate ($S_2O_8^{2-}$/H_2O_2), and base-activated persulfate ($S_2O_8^{2-}$/OH^-) systems was evaluated and compared. The LFX degradation by all studied activated persulfate systems was divided into two oxidation periods: a fast degradation of target compound within the first minute and subsequent gradual oxidation within the remaining reaction time. Notably, without consideration of the first minute, the rest of the LFX degradation in the $S_2O_8^{2-}$/Fe^{2+} and $S_2O_8^{2-}$/H_2O_2 system followed the pseudo-first-order kinetic model. Among the studied activation techniques, the Fe^{2+}-activated persulfate system demonstrated the highest efficacy in LFX degradation, mineralization and persulfate utilization, followed by the peroxide-activated persulfate oxidation. Generally, all studied sulfate radical-based advanced oxidation technologies proved to be promising tool for the treatment of LFX contaminated water/wastewater and, especially, groundwater.

Introduction

Antibiotics are one of the most important pharmaceuticals used worldwide in human and veterinary medical practices [1]. The primary pathways for antibiotics release in to the environment are wastewater treatment plants (WWTPs) effluents, animal waste and municipal landfill leachate [2]. Once administered, antibiotics are metabolized to varying degrees, and then excreted as metabolites or unchanged parent compounds, which subsequently can undergo further modifications due to biological and chemical processes in both WWTPs and receiving water bodies [3]. Nevertheless, antibiotics are known to be resistant to conventional biological oxidation and usually escape intact from WWTPs, causing long-term concerns in the environment such as bio-accumulation and contributing to the spread of antibiotic resistance in microorganisms. Particularly, the continuous introduction of antibiotics into the environment can affect natural waters quality and potentially impact drinking water supplies, ecosystem and human health [1,3]. Thus, developing effective treatment technology for degradation of antibiotics in aqueous matrices is of a great scientific, environmental and public concern.

The application of advanced oxidation technologies (AOTs) could be a viable solution for the prevention of antibiotics escape into the environment as well as for the in situ treatment of already existing groundwater contamination. The radicals involved in AOTs are mainly the hydroxyl radical ($HO^{\bullet}$, $E^{\circ} = 2.73$ V [4]) and sulfate radical ($SO_4^{\bullet-}$, $E^{\circ} = 2.5–3.1$ V [5,6]). The former can be generated by combination of strong oxidants (hydrogen peroxide, ozone) with activators (transition metals, semiconductors), UV/vis and ultrasound irradiation [7]. The $HO^{\bullet}$ reacts with organic compounds mainly by abstracting hydrogen-atom from C—H, N—H, or O—H bonds, adding to double and triple bonds, or adding to aromatic rings [4,8]. The advantages of $HO^{\bullet}$-AOTs as aqueous matrices treatment techniques include high reaction rates and non-selective oxidation due to $HO^{\bullet}$, which allow the simultaneous degradation of multiple organic contaminants including pharmaceuticals [2,9–16]. The most common technique used for $SO_4^{\bullet-}$ generation is persulfate activation by heat, transition metal, UV or ultrasound irradiation, base, or peroxide [17,18] in accordance with Eq. (1):

$$S_2O_8^{2-} + \text{activator} \rightarrow SO_4^{\bullet-} + (SO_4^{\bullet-} + SO_4^{2-}) \quad (1)$$

The activated persulfate oxidation has several advantages over $HO^{\bullet}$-AOTs. Accordingly, different from hydroxyl radicals, sulfate radicals are more stable, more selective for oxidizing unsaturated bond and aromatic constituents, and preferably undergo electron

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transfer reactions with organics [17,18]. The $SO_4^{\bullet-}$-AOTs have been recently used for the degradation of organic pollutants in aqueous matrices [19–24]. However, only few studies concerning antibiotics abatement using activated persulfate systems can be found in the literature [25,26]. Generally, high aqueous stability, relatively low cost and benign end products make persulfate oxidation a promising choice for in situ groundwater treatment among the other AOTs.

Owning to the advantages of cost effectiveness, high activity and the environmentally friendly nature, ferrous iron (Fe^{2+}) has been commonly selected as the activator of persulfate in practical applications [17]:

$$S_2O_8^{2-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{\bullet-} + SO_4^{2-} \quad (2)$$

Moreover, several studies have shown that Fe^{2+}-activated persulfate system proved effective to degrade various persistent organic pollutants in aqueous matrices [27–30]. Conversely, the data on the use of other persulfate activation techniques promising for in situ applications such as peroxide and base have not been fully evaluated.

In the present study, a broad-spectrum antibiotic of the fluoroquinolone (FQ) drug class levofloxacin (LFX) was selected as the target compound due to its and other FQs frequent detection in aquatic environment [31]. LFX is principally used to treat severe or life-threatening bacterial infections, since it has substantial activity against a broad array of Gram-positive and -negative bacteria [32]. Similarly to other FQs, it is known to be extremely resistant to conventional biological oxidation and usually escapes intact from wastewater treatment plants [31,33]. The main goal of this work was to investigate and compare the performance of LFX degradation and mineralization in $S_2O_8^{2-}/Fe^{2+}$, $S_2O_8^{2-}/H_2O_2$ and $S_2O_8^{2-}/OH^-$ systems. To the best of our knowledge, the comparison of different persulfate activation techniques efficacies for FQs as well as other antibiotics degradation in aqueous matrices has not been investigated yet. Generally, the data obtained within this study provides valuable knowledge for further implementation in water/wastewater treatment and in situ groundwater purification by means of activated persulfate oxidation.

Materials and methods

Chemicals and materials

Hydrogen peroxide (Perdrogen™, ≥30%), ferrous sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$, ≥99%), levofloxacin (Fig. 1; $C_{18}H_2OFN_3O_4$, ≥98%, molecular weight 361.37 g mol^{-1}, pK_a 5.33 and 8.07 [34], log K_{ow} − 0.39 [35]), sodium persulfate ($Na_2S_2O_8$, ≥99%), and sodium sulfite (Na_2SO_3, ≥98%) were purchased from Sigma–Aldrich. All other chemicals of analytical grade were used without further purification. Stock solutions were prepared in ultrapure water (Millipore Simplicity® UV System).

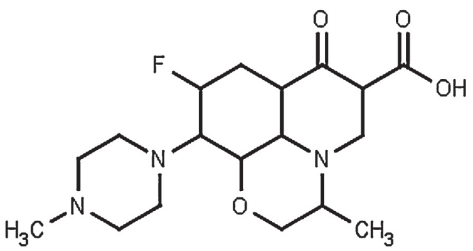

Fig. 1. Molecular structure of levofloxacin.

Sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4) aqueous solutions were used to adjust the pH.

Experimental procedure

All the persulfate oxidation trials were performed in batch mode and in non-buffered solutions at ambient room temperature (21 ± 1 °C). LFX solutions (75 μM, 0.4 L) were treated in a 0.6 L cylindrical glass reactor with a permanent agitation speed (400 rpm) for a period of 3 h. The pH of the samples was adjusted to 3 with H_2SO_4 (0.5 M), if not specified otherwise. The activator ($FeSO_4{\cdot}7H_2O$) was added, and after its complete dissolution, oxidation was initiated by adding $Na_2S_2O_8$. Samples were withdrawn at pre-determined time intervals. The oxidation quenching was done by the addition of Na_2SO_3 at a $[oxidant]_0/SO_3^{2-}$ molar ratio (m/m) of 1/10. The experiments on LFX oxidation with non-activated persulfate or hydrogen peroxide, base-activated (pH 11) and peroxide-activated persulfate were conducted in identical reactors and treatment conditions for the respective Fe^{2+}-activated oxidation trials. In the case of peroxide-activated persulfate, both oxidants were added simultaneously. All experiments were duplicated; the results of the analysis are presented as the mean with a standard deviation less than 5%.

Analytical methods

The pH was measured using a digital pH/Ion meter (Mettler Toledo S220). The initial hydrogen peroxide concentration in the stock solutions was measured spectrophotometrically at λ = 254 nm; the residual hydrogen peroxide concentration in the treated samples was measured as described in Dulov et al. [15] at λ = 410 nm by a Heλios-β UV/vis spectrophotometer (Thermo Electron Corporation). The residual persulfate concentration in the treated samples was measured spectrophotometrically at λ = 446 nm with *o*-dianisidine [36]. Non-purgeable organic carbon (NPOC) was measured by a TOC analyzer multi N/C® 3100 (Analytik Jena).

The concentration of LFX was quantified by means of high performance liquid chromatography combined with a diode array detector (HPLC-PDA, Prominence SPD-M20A, Shimadzu) equipped with a Phenomenex Gemini (150 × 2.0 mm, 1.7 μm) NX-C18 (110 Å, 5 μm) column. The isocratic method with a solvent mixture of 10% acetonitrile and 90% acetic acid aqueous solution (0.1%) was applied. The flow rate was maintained at 200 μL/min. Samples were scanned at 190–800 nm and analyzed at λ = 295 nm. The concentration of LFX was determined by using the standard chemical to fit the retention time.

Results and discussion

In all studied persulfate systems, a fast decomposition of the target compound during 1 min (the first measured time point after the beginning of the reaction) with subsequent gradual degradation within the remaining reaction time was observed. Accordingly it was suggested to divide the entire persulfate oxidation reaction into two main phases: the first period of rapid LFX degradation and the second period of steady target compound oxidation. Additionally, the obtained data processing revealed that LFX degradation by non-activated persulfate as well as Fe^{2+}-and peroxide-activated persulfate process followed a pseudo-first-order kinetic law during the second reaction period and may be described with regard to the LFX concentration through Eq. (3):

$$\frac{dC_{LFX}}{dt} = -k_1 \times C_{LFX} \quad (3)$$

where k_1 is the pseudo-first-order rate constant and C_{LFX} is the LFX concentration. The $-k_1$ constants were calculated from the slopes of the straight lines by plotting $\ln(C/C_0)$ as a function of time t through linear regression.

Non-activated persulfate oxidation

First, the performance of non-activated persulfate in LFX degradation was studied. The persulfate ion ($S_2O_8^{2-}$) is known to be a strong but relatively stable oxidant, which under acidic conditions can hypothetically breakdown into $SO_4^{\bullet-}$ in accordance with Eqs. (4) and (5) [37]:

$$S_2O_8^{2-} + H^+ \rightarrow HS_2O_8^- \quad (4)$$

$$HS_2O_8^- \rightarrow H^+ + SO_4^{\bullet-} + SO_4^{2-} \quad (5)$$

Therefore, the efficacy of LFX degradation by non-activated persulfate at an LFX/$S_2O_8^{2-}$ m/m of 1/10 and pH 3 was evaluated. The results indicated the negligible efficacy of non-activated $S_2O_8^{2-}$ oxidation in target compound degradation, and thus only 7% of LFX was removed in the first fast period with a $k_1 \times 10^{-2}$ of 0.04 min^{-1} for the second stage, and more than 95% of the unreacted $S_2O_8^{2-}$ was observed after 3 h of oxidation. The observed two-stage kinetic model of LFX degradation by non-activated persulfate process suggests, however, the radical-based target compound oxidation mechanism. The inhibition of oxidation in this case was presumably caused by the preference of $SO_4^{\bullet-}$-to-$SO_4^{\bullet-}$ reactions over $SO_4^{\bullet-}$-to-LFX reactions.

Ferrous ion-activated persulfate oxidation

The performance of the $S_2O_8^{2-}/Fe^{2+}$ system in target compound and oxidation by-products removal was studied at different LFX/$S_2O_8^{2-}$ and $S_2O_8^{2-}/Fe^{2+}$ ratios. The effect of oxidant and activator dose on the efficacy of LFX degradation and mineralization in the $S_2O_8^{2-}/Fe^{2+}$ oxidation was evaluated, and the results are presented in Figs. 2 and 3.

In the case of the $S_2O_8^{2-}/Fe^{2+}$ system, the two-stage kinetic model was observed not only for LFX degradation but also for persulfate decomposition (Figs. 2 and 4). Accordingly, more than 31 and 56% of LFX was removed as well as 7 and 11% of persulfate was decomposed during the first minute and the rest of the 3 h oxidation, respectively, in $S_2O_8^{2-}/Fe^{2+}$ systems at an LFX/$S_2O_8^{2-}$/Fe^{2+} m/m/m of 1/10/1.

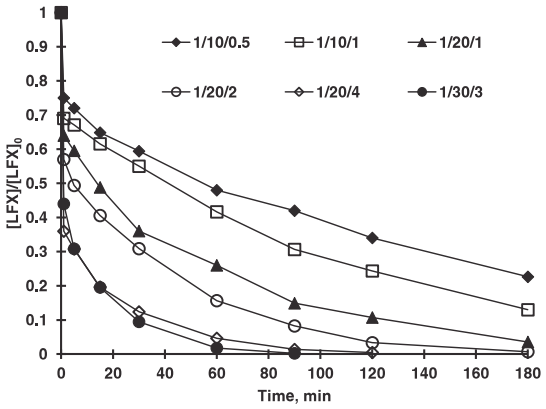

Fig. 2. Degradation of LFX in the $S_2O_8^{2-}/Fe^{2+}$ system (LFX/$S_2O_8^{2-}/Fe^{2+}$ is a molar ratio, $[LFX]_0 = 75$ μM).

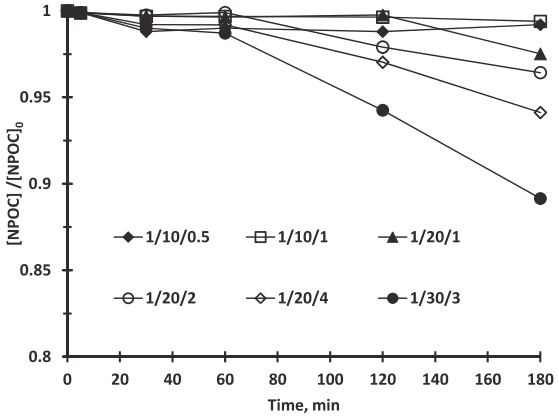

Fig. 3. Reduction of NPOC in the $S_2O_8^{2-}/Fe^{2+}$ system (LFX/$S_2O_8^{2-}/Fe^{2+}$ is a molar ratio, $[LFX]_0 = 75$ μM).

This observation can be explained by fast generation of $SO_4^{\bullet-}$ through the decomposition of persulfate immediately after activation and rapid accumulation of ferric ion (Fe^{3+}) through the complete oxidation of activator in accordance with Eqs. (2) and (6). Subsequently, ineffectiveness of Fe^{3+} to activate persulfate decomposition even at acidic pH values [38] led to fast inhibition of the oxidation of target compound.

$$SO_4^{\bullet-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} \quad (6)$$

Conversely, the existence of the second period of gradual LFX degradation and steady persulfate decomposition suggests the presence of other routes for reducing the activator and supporting $SO_4^{\bullet-}$ generation. Recently, the simultaneous existence of both $SO_4^{\bullet-}$ and $HO^{\bullet}$ in the $S_2O_8^{2-}/Fe^{2+}$ system was demonstrated by Wu et al. [39]. Therefore, the second phase of gradual LFX degradation in $S_2O_8^{2-}/Fe^{2+}$ systems can be explained by the continuous reduction of Fe^{3+} in the reaction with organic radicals as presented in Eq. (7), by the formation of hydrogen peroxide in accordance with Eq. (8), and the subsequent direct reduction of Fe^{3+} through Eq. (9), or by the combined action of both listed processes.

$$R^{\bullet} + Fe^{3+} \rightarrow Fe^{2+} + \text{products} \quad (7)$$

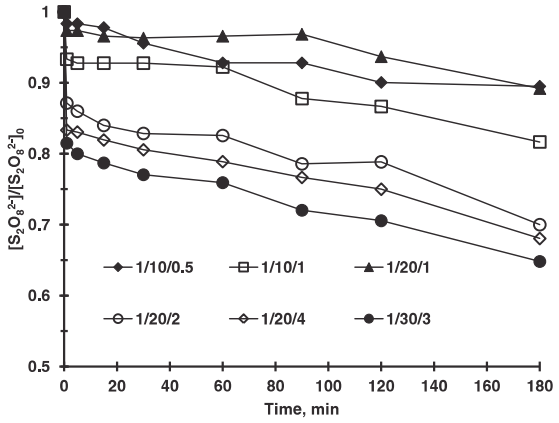

Fig. 4. Decomposition of $S_2O_8^{2-}$ in the $S_2O_8^{2-}/Fe^{2+}$ system (LFX/$S_2O_8^{2-}/Fe^{2+}$ is a molar ratio, $[LFX]_0 = 75$ μM).

Table 1
Kinetic parameters of LFX degradation in the $S_2O_8^{2-}/Fe^{2+}$ system under different treatment conditions ($[LFX]_0 = 75\ \mu M$).

LFX/$S_2O_8^{2-}$/Fe^{2+}, m/m/m	$pH_{initial}$	$[LFX]_{removed}$, % ($t = 1$ min)	Pseudo-first-order constant, $k_1 \times 10^{-2}\ min^{-1}$ ($r^2 > 0.99$)
1/10/0.5	3	25	0.65 ± 0.02
1/10/1	3	31	0.93 ± 0.02
1/20/1	3	36	1.57 ± 0.05
1/20/2	3	43	2.42 ± 0.04
1/20/2	5	39	2.41 ± 0.05
1/20/2	7	36	2.33 ± 0.03
1/20/2	9	31	1.44 ± 0.04
1/20/4	3	64	3.61 ± 0.08
1/30/3	3	56	5.74 ± 0.15

$$2HO^{\bullet} \rightarrow H_2O_2 \quad (8)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \quad (9)$$

The termination of oxidation in the $S_2O_8^{2-}/Fe^{2+}$ systems is believed to occur through Eq. (6) and Eqs. (10)–(13) [4,40]:

$$HO_2^{\bullet} + HO^{\bullet} \rightarrow H_2O + O_2 \quad (10)$$

$$SO_4^{\bullet-} + HO^{\bullet} \rightarrow HSO_5^- \quad (11)$$

$$HO_2^{\bullet} + SO_4^{\bullet-} \rightarrow HSO_4^- + O_2 \quad (12)$$

$$SO_4^{\bullet-} + SO_4^{\bullet-} \rightarrow S_2O_8^{2-} \quad (13)$$

As it was above-mentioned, without consideration of the first minute, the rest of the performance of LFX degradation in the $S_2O_8^{2-}/Fe^{2+}$ system followed the pseudo-first-order kinetic model. The values of the kinetic constants calculated for the $S_2O_8^{2-}/Fe^{2+}$ system under different treatment conditions are presented in Table 1.

The obtained results indicated a stable improvement in the LFX degradation rate with the increase in applied oxidant dose at the same $S_2O_8^{2-}/Fe^{2+}$ ratio. Accordingly, the $k_1 \times 10^{-2}$ of the second reaction period was 0.93 ± 0.02, 2.42 ± 0.04, and 5.74 ± 0.15 min^{-1} for the $S_2O_8^{2-}/Fe^{2+}$ oxidation at an LFX/$S_2O_8^{2-}/Fe^{2+}$ m/m/m of 1/10/1, 1/20/2, and 1/30/3, respectively. Similarly, the decomposition of LFX during the first stage of reaction improved with the increase in oxidant dose, indicating a more comprehensive target compound oxidation until the added activator is completely oxidized through Eqs. (2) and (6). In the case of $S_2O_8^{2-}$ decomposition, a more obvious dependence on oxidant dose was observed during the first minute, with almost similar tendency of decomposition within the rest of 3 h oxidation. Unlike LFX degradation, the extent of mineralization in the $S_2O_8^{2-}/Fe^{2+}$ system was considerably lower, mainly indicating the accumulation of transformation products in the reaction mixture. Consequently, the NPOC concentration remained nearly unchanged after 3 h of oxidation at an LFX/$S_2O_8^{2-}/Fe^{2+}$ m/m/m lower than 1/20/2 (less than 3% mineralization). The highest obtained NPOC removal under the studied treatment conditions was 11% at an LFX/$S_2O_8^{2-}/Fe^{2+}$ m/m/m of 1/30/3.

The pH value of the solution is known to be an important parameter affecting degradation of organic contaminants. Therefore, the effect of initial pH on the degradation of LFX by Fe^{2+}-activated persulfate was evaluated. The results of LFX oxidation at an LFX/$S_2O_8^{2-}/Fe^{2+}$ m/m/m of 1/20/2 and four different pH values (3, 5, 7 and 9) are presented in Table 1. The efficacy of LFX degradation was found to decrease gradually with the increase in the initial pH value. Accordingly, a 1.7-fold decrease in k_1 value of the second reaction period and 12% lower removal of LFX during 1 min was observed at initial pH 9 compared to pH 3. Conversely, the obtained results revealed the comparable performance of LFX degradation in the $S_2O_8^{2-}/Fe^{2+}$ system at initial pH values of 3, 5 and 7, indicating a high potential of this process for in situ applications at natural waters pH values. Notably, the solution pH in all trials decreased to around 3 after 3 h of oxidation, mainly due to acidity of oxidant and its decomposition products, metal-related acidity and acidic LFX decomposition by-products.

In order to suppress the activator-consuming and $SO_4^{\bullet-}$-scavenging reaction presented in Eq. (6), the adjustment of $S_2O_8^{2-}/Fe^{2+}$ system by correction of the activator dose was studied. Accordingly, three $S_2O_8^{2-}/Fe^{2+}$ m/m ratios of 20/1, 10/1, and 5/1 were evaluated at a fixed LFX/$S_2O_8^{2-}$ m/m of 1/20. The results indicated equally faster target compound degradation and persulfate decomposition in both reaction periods as well as better mineralization at a $S_2O_8^{2-}/Fe^{2+}$ m/m ratio of 5/1 (Figs. 2–4, Table 1). However, considering the high stability of persulfate along with its high acidity ensuring acidic pH values in reaction media, prolonged oxidation at a $S_2O_8^{2-}/Fe^{2+}$ m/m of 10/1 could be a more reasonable alternative to the elevated activator dose (5/1 and higher) both for water and wastewater treatment as well as for in situ groundwater decontamination.

Peroxide-activated persulfate oxidation

To evaluate the efficacy of LFX degradation by peroxide-activated persulfate oxidation, the effect of persulfate and hydrogen peroxide dosages was studied (Fig. 5). Similarly to the

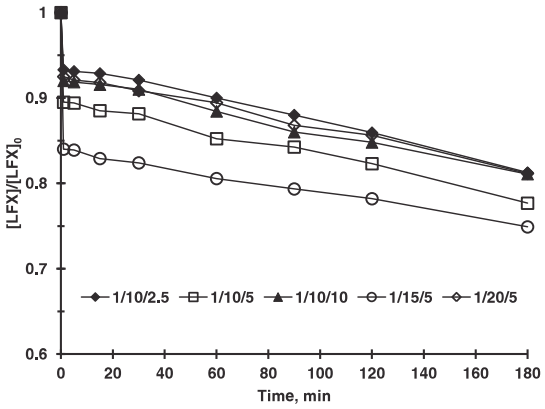

Fig. 5. Degradation of LFX in the $S_2O_8^{2-}/H_2O_2$ system (LFX/$S_2O_8^{2-}/H_2O_2$ is a molar ratio, $[LFX]_0 = 75\ \mu M$).

Table 2
Kinetic parameters of LFX degradation in the $S_2O_8^{2-}/H_2O_2$ system under different treatment conditions ($[LFX]_0 = 75$ μM).

LFX/$S_2O_8^{2-}$/H_2O_2, m/m/m	$pH_{initial}$	$[LFX]_{removed}$, % ($t = 1$ min)	Pseudo-first-order constant, $k_1 \times 10^{-2}$ min^{-1} ($r^2 > 0.99$)
1/10/2.5	3	10	0.08 ± 0.003
1/10/5	3	10.5	0.08 ± 0.002
1/10/5	5	10	0.06 ± 0.001
1/10/5	7	10.5	0.05 ± 0.002
1/10/5	9	10	0.02 ± 0.002
1/10/10	3	8	0.07 ± 0.003
1/15/5	3	16	0.06 ± 0.001
1/20/5	3	7.5	0.07 ± 0.002

non-activated and Fe^{2+}-activated persulfate system LFX degradation in $S_2O_8^{2-}/H_2O_2$ process was divided to two oxidation periods and the rate of LFX degradation followed the pseudo-first order in the second steady oxidation stage (Table 2). Notably, in the case of the $S_2O_8^{2-}/H_2O_2$ system, residual concentrations of persulfate were not measured due to interference caused by the presence of hydrogen peroxide in samples. Conversely, the presence of residual persulfate still allowed the measurement of unused hydrogen peroxide, and the results are presented in Fig. 6.

The obtained results demonstrated to some extent improvement in the target compound decomposition at an LFX/$S_2O_8^{2-}/H_2O_2$ of 1/10/10 compared to non-activated persulfate oxidation at an LFX/$S_2O_8^{2-}$ m/m 1/10, and thus 8% of LFX removed in the first stage with $k_1 \times 10^{-2}$ of 0.07 min^{-1} for the second gradual period and more than 99% of residual H_2O_2 after 3 h of oxidation was observed. Conversely, the efficacy of LFX degradation in the $S_2O_8^{2-}/H_2O_2$ system was considerably lower compared with the $S_2O_8^{2-}/Fe^{2+}$ oxidation at the same LFX/$S_2O_8^{2-}$ ratios (Figs. 2 and 5). To adjust the $S_2O_8^{2-}/H_2O_2$ ratio and as a result to improve the overall efficacy of the peroxide-activated persulfate system, the effect of hydrogen peroxide and persulfate dosages was studied at a fixed LFX/$S_2O_8^{2-}$ and LFX/H_2O_2 ratio, respectively. The obtained results indicated a strong necessity for careful optimization of the $S_2O_8^{2-}/H_2O_2$ system (Fig. 5, Table 2). Accordingly, the increase in $S_2O_8^{2-}/H_2O_2$ molar ratio from 1/1 to 2/1 at a fixed LFX/$S_2O_8^{2-}$ m/m of 1/10 resulted in 8 and 10.5% LFX removal within the first minute of oxidation, respectively. A further increase in the $S_2O_8^{2-}/H_2O_2$ molar ratio to 4/1 resulted in similar 10% LFX removal within the first minute of oxidation, indicating the irrationality of further decrease in hydrogen peroxide dose. In the case of trials with a fixed LFX/H_2O_2 ratio (1/5, m/m), an increase in $S_2O_8^{2-}/H_2O_2$ molar ratio from 2/1 to 3/1 resulted in faster LFX degradation during the first period. A further increase in the $S_2O_8^{2-}/H_2O_2$ ratio to 4/1 demonstrated decrease in target compound oxidation efficacy. Thus, the highest LFX degradation efficacy was observed at an LFX/$S_2O_8^{2-}/H_2O_2$ m/m/m of 1/15/5 with 16 and 25% of LFX removed during the first minute and overall oxidation time, respectively. Irrespective of the applied $S_2O_8^{2-}/H_2O_2$ molar ratio, the performance of peroxide-activated persulfate in LFX degradation during the second oxidation period was comparable, and thus the kinetic constants ($k_1 \times 10^{-2}$) ranged from 0.06 to 0.08 min^{-1}. Similarly to LFX degradation, the most effective utilization of hydrogen peroxide was observed at an LFX/$S_2O_8^{2-}/H_2O_2$ m/m/m of 1/15/5 with only 15% of utilized H_2O_2, indicating the high potential of prolonged oxidation for subsequent increase in treatment efficacy. Additionally, the efficacy of LFX oxidation by-products degradation in the $S_2O_8^{2-}/H_2O_2$ system was assessed, and the results obtained indicated negligible NPOC removal with the highest achieved mineralization of 1–2%.

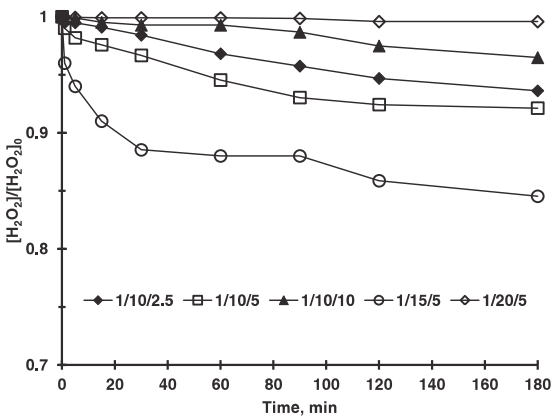

Fig. 6. Decomposition of H_2O_2 in the $S_2O_8^{2-}/H_2O_2$ system (LFX/$S_2O_8^{2-}/H_2O_2$ is a molar ratio, $[LFX]_0 = 75$ μM).

To evaluate the effect of initial pH on the performance of LFX degradation in the $S_2O_8^{2-}/H_2O_2$ system, the target compound degradation at an LFX/$S_2O_8^{2-}/H_2O_2$ m/m/m of 1/10/5 was additionally studied at pH 5, 7 and 9 (Table 2.). Similarly to the $S_2O_8^{2-}/Fe^{2+}$ system, the efficacy of LFX removal in the $S_2O_8^{2-}/H_2O_2$ process decreased with the increase in the initial pH value. Accordingly, a 4-fold decrease in k_1 value of the second reaction period was observed at initial pH 9 compared to pH 3. This observation is in agreement with previous studies in literature concerning organic contaminants degradation by activated persulfate processes [19,37,38].

To clarify the predominant mechanism of LFX decomposition in the $S_2O_8^{2-}/H_2O_2$ system, the oxidative potential of non-activated hydrogen peroxide was studied as well. The results of target compound oxidation at an LFX/H_2O_2 m/m of 1/10 indicated no LFX removal and more than 99% of unused H_2O_2 in solution after 3 h of treatment. Generally, it is known that a dual oxidant system utilizing $S_2O_8^{2-}$ and H_2O_2 combines the reactivity of peroxide in the reduction of target organic contaminants with the enhanced stability of persulfate and involves the simultaneous generation of $HO^\bullet$ and $SO_4^{\bullet-}$ [17]. However, the mechanism of peroxide activation of persulfate is still uncertain; the suggested activation mechanisms include the $HO^\bullet$ generated from peroxide or the heat from the exothermic hydrogen peroxide reactions [17]. The later can be described with the sequence of reaction proposed by Tsao and Wilmarth [41] for the $S_2O_8^{2-}/H_2O_2$ system at $T = 30$ °C, where the chain initiation was suggested to be caused by the thermal decomposition of $S_2O_8^{2-}$ through Eq. (14). Additionally, it was assumed that direct peroxide activation through Eq. (15) plays an insignificant part in the initiation of persulfate decomposition to $SO_4^{\bullet-}$.

$$S_2O_8^{2-} \rightarrow 2SO_4^{\bullet-} \quad (14)$$

$$S_2O_8^{2-} + H_2O_2 \rightarrow SO_4^{\bullet-} + HO_2^\bullet + HSO_4^- \quad (15)$$

Then, the chain-carrying step can be described through Eqs. (16)–(19) and the termination of the oxidation in accordance with Eqs. (10)–(13).

$$SO_4^{\bullet-} + H_2O \rightarrow HO^{\bullet} + SO_4^{2-} + H^+ \quad (16)$$

$$HO^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \quad (17)$$

$$HO_2^{\bullet} + S_2O_8^{2-} \rightarrow HSO_4^{-} + SO_4^{2-} + O_2 \quad (18)$$

$$HO_2^{\bullet} + H_2O_2 \rightarrow HO^{\bullet} + H_2O + O_2 \quad (19)$$

According to the results obtained within this study, the application of the peroxide-activated system with carefully adjusted activator dose and preferably prolonged treatment period could be a viable solution for the degradation of LFX and other micropollutants in water/wastewater and especially groundwater were naturally occurring iron could play a significant role in subsequent improvement of the overall treatment efficacy.

Base-activated persulfate oxidation

The results of LFX degradation by the $S_2O_8^{2-}$/OH^- system are presented in Fig. 7 and Table 3. In the case of base-activated persulfate system, the values of kinetic constants were not calculated for the second oxidation period because the data did not fit any kinetic model.

The efficacy of LFX degradation in the base-activated persulfate was strongly dependent on the LFX/$S_2O_8^{2-}$ ratio applied. Accordingly, LFX removal was 6/14 and 13/18% after 1 min/3 h oxidation at an LFX/$S_2O_8^{2-}$ m/m of 1/5 and 1/10, respectively. A further increase in the oxidant dose from 1/10 to 1/20 (LFX/$S_2O_8^{2-}$, m/m) resulted in 4 and 7% of supplementary LFX removal during 1 min and 3 h oxidation, respectively, indicating the efficacy of elevated oxidant dose application to enhance target compound removal. Conversely, the utilization of persulfate proved more effective at moderate LFX/$S_2O_8^{2-}$ molar ratio of 1/10, but still resulted in 94% of unused $S_2O_8^{2-}$ in solution after 3 h of treatment. Therefore, in the case of $S_2O_8^{2-}$/OH^- system the prolonged oxidation could be a reasonable solution to improve the performance of target compound degradation. Similarly to the $S_2O_8^{2-}$/H_2O_2 system, the mineralization in the $S_2O_8^{2-}$/OH^- system was noticeably less effective than LFX degradation and in general resulted in less than 1% of NPOC removal. Taking into account the treatment performance, oxidant utilization and mineralization extent, the base-activated persulfate system proved the less effective for LFX degradation in aqueous solution among other studied activated persulfate systems (Fig. 8).

Table 3
Kinetic parameters of LFX degradation in the $S_2O_8^{2-}$/OH^- system under different treatment conditions ([LFX]$_0$ = 75 μM).

LFX/$S_2O_8^{2-}$, m/m	[LFX]$_{removed}$, % (t = 1 min)	[$S_2O_8^{2-}$]$_{remained}$, % (t = 180 min)
1/5	6	94.5
1/10	13	94
1/15	14.5	96
1/20	17	98

A possible mechanism of base activation of persulfate was suggested by Furman et al. [42]. The initial step of the proposed mechanism is the base-catalyzed hydrolysis of $S_2O_8^{2-}$ to peroxomonosulfate ion (SO_5^{2-}) and sulfate ion (SO_4^{2-}) through Eq. (20) with subsequent formation of hydroperoxide (HO_2^-) in accordance with Eq. (21). Then, the HO_2^- reduces another persulfate molecule, generating $SO_4^{\bullet-}$ and superoxide ($O_2^{\bullet-}$) through Eq. (22). Furthermore, in highly alkaline conditions, the $SO_4^{\bullet-}$ reacts with OH^- to form $HO^{\bullet}$ in accordance with Eq. (23).

$$S_2O_8^{2-} + H_2O \rightarrow SO_5^{2-} + SO_4^{2-} + 2H^+ \quad (20)$$

$$SO_5^{2-} + H_2O \rightarrow HO_2^{-} + SO_4^{2-} + H^+ \quad (21)$$

$$HO_2^{-} + S_2O_8^{2-} \rightarrow SO_4^{\bullet-} + SO_4^{2-} + H^+ + O_2^{\bullet} \quad (22)$$

$$SO_4^{\bullet-} + OH^- \rightarrow SO_4^{2-} + HO^{\bullet} \quad (23)$$

The $SO_4^{\bullet-}$ and $HO^{\bullet}$ generated in Eqs. (22) and (23) proceed through propagation and scavenging reactions, Eqs. (10)–(13), in base-activated persulfate system, resulting mainly in the generation of molecular oxygen. The $O_2^{\bullet-}$ is likely scavenged by $HO^{\bullet}$ and $SO_4^{\bullet-}$ through Eqs. (24) and (25), respectively, and thus expected

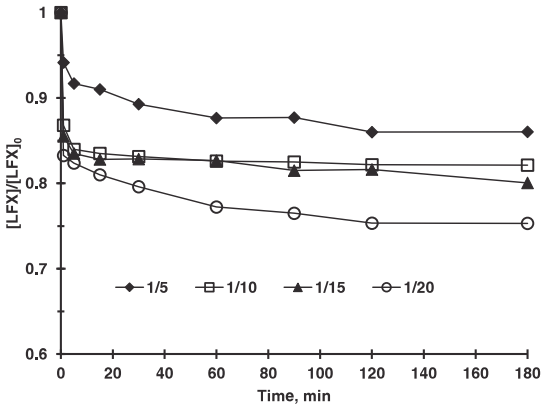

Fig. 7. Degradation of LFX in the $S_2O_8^{2-}$/OH^- system (LFX/$S_2O_8^{2-}$ is a molar ratio, [LFX]$_0$ = 75 μM).

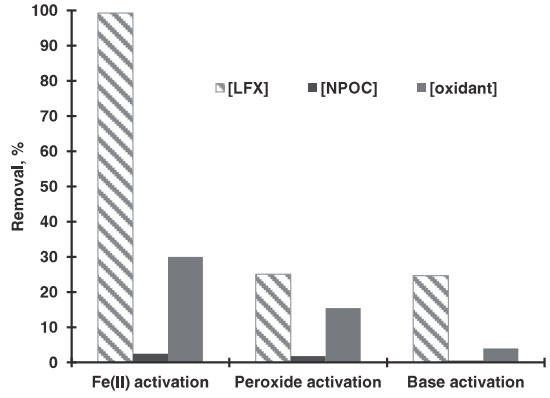

Fig. 8. Removal of LFX, NPOC and oxidant after 3 h of oxidation in the $S_2O_8^{2-}$/Fe^{2+} system (LFX/$S_2O_8^{2-}$/Fe^{2+} m/m/m of 1/20/2, [LFX]$_0$ = 75 μM), $S_2O_8^{2-}$/H_2O_2 system (LFX/$S_2O_8^{2-}$/H_2O_2 m/m/m of 1/15/5), and $S_2O_8^{2-}$/OH^- system (LFX/$S_2O_8^{2-}$ m/m of 1/20).

to have a negligible impact on the overall oxidative potential of the $S_2O_8^{2-}/OH^-$ system.

$$HO^{\bullet} + O_2^{\bullet-} \rightarrow O_2 + OH^- \quad (24)$$

$$SO_4^{\bullet-} + O_2^{\bullet-} \rightarrow SO_4^{2-} + O_2^{\bullet} \quad (25)$$

Generally, it is suggested that alkaline activation is one of the least efficient approaches due to the very fast decomposition of persulfate under alkaline conditions [17]. However, the results of the present study indicated the fast decomposition of persulfate only during the first fast period of target compound degradation with the subsequent gradual decomposition during the rest of reaction in the $S_2O_8^{2-}/OH^-$ system, indicating a high potential of prolonged oxidation to enhance the overall treatment efficacy mainly for in situ applications.

Conclusions

The ferrous ion-activated, peroxide-activated and base-activated persulfate systems proved to be promising techniques for the degradation of LFX in aqueous solution. The main conclusions of this work are summarized in the following points:

- The performance of the studied processes in target compound oxidation was as follows: the $S_2O_8^{2-}/Fe^{2+}$ system > the $S_2O_8^{2-}/H_2O_2$ system > the $S_2O_8^{2-}/OH^-$ system.
- The highest mineralization and more complete persulfate utilization were observed in the Fe^{2+}-activated persulfate system followed by the peroxide-activated persulfate oxidation.
- The results obtained within this study suggested that all studied activated persulfate systems with prolonged oxidation period could be a reliable technology for wastewater and groundwater remediation contaminated by the LFX.

Generally, the findings in this study may provide important insight for further implementation in the treatment of FQ contamination in water/wastewater and, especially, groundwater.

Acknowledgments

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APPENDIX B

ELULOOKIRJELDUS

1. Isikuandmed

Ees- ja perekonnanimi: Irina Epold
Sünniaeg ja -koht: 05.09.1984, Tallinn
Kodakondsus: Eesti
E-posti aadress: irina.epold@gmail.com

2. Hariduskäik

Õppeasutus (nimetus lõpetamise ajal)	Lõpetamise aeg	Haridus (eriala/kraad)
Tallinna Tehnikaülikool	2008	Tehnikateaduste magistrikraad
Tallinna Tehnikaülikool	2006	Tehnikateaduste bakalaureusekraad
Tallinna 53.Keskkool	2003	Keskharidus

3. Keelteoskus (alg-, kesk- või kõrgtase)

Keel	Tase
Eesti keel	kõrgtase
Vene keel	kõrgtase (emakeel)
Inglise keel	algtase
Saksa keel	kesktase

4. Teenistuskäik

Töötamise aeg	Tööandja nimetus	Ametikoht
2014-2014	Tallinna Tehnikaülikool	insener
2006-2011	AS Tallinna Vesi	projekti koordinaator

5. Kaitstud lõputööd

Tehnikateaduste magistrikraad: Исследование свойств гидравлических жидкостей на основе соевого и рапсового масел (Hüdrovedelike omaduste uurimine soja- ja rapsiõli baasil). Tallinna Tehnikaülikool, 2008, Juhendaja: Rein Muoni.

6. Teadustöö põhisuunad

4. Loodusteadused ja tehnika, 4.11. Keemia ja keemiatehnika, P305 Keskkonnakeemia (Süvaoksüdatsiooniprotsessid vee ja reovee puhastamiseks)
1. Bio- ja keskkonnateadused, 1.9. Keskkonnaohtlikke aineid käsitlevad uuringud, P305 Keskkonnakeemia (Mikrosaasteainete lagundamine süvaoksüdatsiooniprotsessidega)

7. Uurimisprojektid

IUT1-7 Keemiatehnikapõhine lähenemisviis prioriteetsete saasteainete ja uute esilekerkivate mikrosaasteainete kõrvaldamisele veest/reoveest ja pinnasest: täiustatud oksüdatsioonitehnoloogiate kasutamine ja optimeerimine

SF0142719s06 Tehnoloogiliste protsesside intensiivistamine aktuaalsete keskkonnaprobleemide lahendamiseks

ETF8186 Esiletulevate orgaaniliste mikrosaasteainete eemaldamine veest/reoveest täiustatud Fenton-protsessidega

CURRICULUM VITAE

1. Personal data

Name: Irina Epold
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2. Education

Educational institution	Graduation year	Education (field of study/degree)
Tallinn University of Technology	2008	M.Sc. in Engineering
Tallinn University of Technology	2006	B.Sc. in Engineering
Tallinn Secondary 53th School	2003	High school education

3. Language competence/skills (fluent, average, basic skills)

Language	Level
Estonian	fluent
Russian	fluent (mother tongue)
English	basic skills
German	average skills

4. Professional employment

Period	Organisation	Position
2014-2014	Tallinn University of Technology	engineer
2006-2011	AS Tallinna Vesi	project manager

5. Defended theses

M.Sc. thesis: Исследование свойств гидравлических жидкостей на основе соевого и рапсового масел (Investigation of properties of hydraulic fluids on the base of soybean and canola oil). Tallinn University of Technology, 2008. Supervisor: Rein Muoni.

6. Main areas of scientific work

4. Natural Sciences and Engineering, 4.11. Chemistry and Chemical Technology, P305 Environmental chemistry (Advanced oxidation processes for water/wastewater treatment)
1. Biosciences and Environment, 1.9. Research into Substances Hazardous to the Environment, P305 Environmental chemistry (Degradation of micropollutants by advanced oxidation processes)

7. Research projects

IUT1-7 Chemical engineering approach to removal of priority pollutants and emerging micropollutants from water/wastewater and soil: implementation and optimisation of advanced oxidation technologies

SF0142719s06 Intensification of technological processes for the solution of actual environmental problems

ETF8186 Removal of emerging organic micropollutants from water and wastewater by application of advanced Fenton-based processes

DISSERTATIONS DEFENDED AT TALLINN UNIVERSITY OF TECHNOLOGY ON *CHEMISTRY AND CHEMICAL ENGINEERING*

1. **Endel Piiroja**. Oxidation and Destruction of Polyethylene. 1993.

2. **Meili Rei**. Lihatehnoloogia teaduslikud alused. Fundamentals of Food Technology. 1995.

3. **Meeme Põldme**. Phase Transformations in Hydrothermal Sintering Processing of Phosphate Rock. 1995.

4. **Kaia Tõnsuaadu**. Thermophosphates from Kovdor and Siilinjärvi Apatites. 1995.

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39. **Jelena Hruljova**. Role of Specifically Interacting Solvents in Solvent Swelling of Kukersite Oil Shale Kerogen. 2014.

40. **Irina Klimova**. Modification of Ammonium Nitrate Fertilizer. 2014.

41. **Julia Krasulina**. Upgrading of Liquid Products from Estonian Kukersite Oil Shale by Catalytic Hydrogenation. 2015.