

APPLICATION OF POTASSIUM FERRATE(VI) IN THE TREATMENT OF SELECTED WATER AND WASTEWATER POLLUTANTS – SHORT REVIEW

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Abstract

The paper presents the application of potassium ferrate(VI) (K_2FeO_4) for the removal of selected pollutants from water and wastewater. The research results on the degradation of endocrine disrupting compounds (EDCs), decomposition of surfactants (SPCs), personal care products (PCPs), pharmaceuticals and their metabolites have been reviewed. Due to K_2FeO_4 strong oxidizing and coagulating properties, high stability, non-toxic by-products and non-selectivity it is sometimes called “environmentally friendly oxidant”. Due to this reasons K_2FeO_4 can be a multi-purpose water and wastewater treatment chemical and an alternative to advanced oxidation processes (AOPs).

Keywords: Potassium ferrate(VI), K_2FeO_4 , EDCs, SPCs, PCPs, Pharmaceuticals.

1. INTRODUCTION

Water is used as an indispensable component in almost every area of economic life. The energy, mining, food, dye and other industries consume a significant amount of water for technological processes, at the same time contaminating it. These impurities can appear in dissolved form as well as in the form of suspensions. It is often thought that dissolved impurities are more dangerous than in the form of suspensions. However, it has been proven that suspensions of both natural origin and discharged into wastewater, together with the pollutants adsorbed on them, also adversely affect the entire aquatic ecosystem. It is also important, that in suspensions a higher content of toxic impurities is generally observed compared to bottom sediments [1]. Contaminants getting in the aquatic environment, can have a negative impact on them and

accumulate in other components of the natural environment, e.g. in groundwater or soil. A huge progress in many fields of technology, entailing the production of a large number of products, causes formation of new impurities. Despite the availability of a large number of water and wastewater treatment methods, degradation of the aquatic environment still occurs in many parts of the world. Therefore, it is necessary to develop new, effective methods degradation of pollutants and the use of Fe(VI) compounds for wastewater treatment is part of this trend. Fe(VI) salts, such as K_2FeO_4 (potassium ferrate(VI)) [2] (Fig. 1) are strong oxidants, and their redox potential is even higher than permanganates and dichromates. Table 1 shows redox potentials of selected oxidants. Analysis of these values indicates that K_2FeO_4 is characterized by one of the highest values of the redox potential, which in consequence is associated with its very strong oxidizing

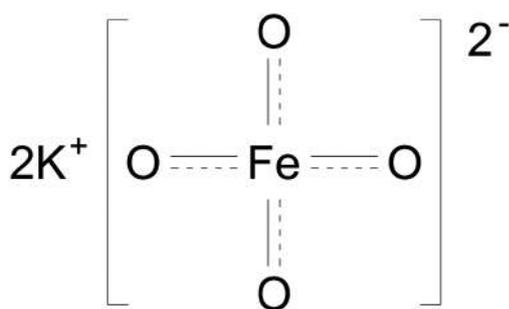


Figure 1.
Structural formula of K_2FeO_4 [2]

properties. Only the fluorine and the $\bullet OH$ (hydroxyl radical) have a higher value of the redox potential.

Under appropriate conditions, Fe(VI) ions are even able to oxidize water and the reaction products are hydrogen protons and oxygen [4]. They are also characterized by the ability to oxidize compounds containing, e.g. sulfur, nitrogen, in particular phenols, amines, aniline and alcohols [5, 6]. Generally, all pollutants are degraded to water and carbon dioxide or intermediates, which are less toxic than initial substrates, which makes Fe(VI) salts environmentally friendly and therefore potassium ferrate(VI) is often called “environmentally friendly oxidant” [7]. High oxidation capacity and non-toxic decomposition products allow to use K_2FeO_4 for the degradation of various organic and inorganic compounds. During the reduction of Fe(VI) to Fe(III) emerge a coagulation and adsorption of contaminants on the formation of

flocs of iron(III) hydroxide. Potassium ferrate(VI) does not react with bromide ions, which avoids the formation of carcinogenic bromates. Among many methods of obtaining K_2FeO_4 it can distinguish three most common and proven methods of synthesis (wet, dry and electrochemical synthesis) [6].

- Wet synthesis consists of the preparation of sodium ferrate(VI) (Na_2FeO_4), in the reaction of $FeCl_3$ with $NaClO_3$ (at a concentration greater than 12%), in the presence of $NaOH$. Then KOH is added to the solution until precipitation of K_2FeO_4 [7]. However, this method requires many subsequent purification operations, such as: crystallization with 3 mol/L KOH , washing with anhydrous CH_3OH to obtain a solid K_2FeO_4 , with purity > 90%. The above method, without using mentioned purification processes of the synthesis products, makes it possible to obtain a technical K_2FeO_4 , containing only 10–15% pure compound.
- Dry synthesis is the process of oxidation of iron compounds at high temperatures and involves the heating of iron oxides, for examples Fe_2O_3 , with potassium and sodium hydroxides or oxides and potassium nitrate and sodium nitrate at a temperature of 420–600°C. Depending on the molar ratios of the mixture components and temperature, the process proceeds in different efficiency and enables to obtain the final product with a purity of up to 99.9%.
- Electrochemical synthesis consists in dissolving an anode made of metallic iron in an aqueous solu-

Table 1.
Redox potentials of selected oxidants [3, modified]

Element/Compound	Chemical reaction	E^0 , V
Chlorine	$Cl_{2(g)} + 2e^- \rightleftharpoons 2Cl^-$	1.358
	$ClO^- + H_2O + 2e^- \rightleftharpoons Cl^- + 2OH^-$	0.841
Chlorate(I)	$HClO + H^+ + 2e^- \rightleftharpoons Cl^- + H_2O$	1.482
Chlorine(IV) oxide	$ClO_{2(aq)} + 2e^- \rightleftharpoons ClO_2^-$	0.954
Chlorate(VII)	$ClO_4^- + 8H^+ + 8e^- \rightleftharpoons Cl^- + 4H_2O$	1.389
Fluorine	$F_{2(g)} + 2e^- \rightleftharpoons 2F^-$	2.87
Hydroxyl radical	$OH^\bullet + H_2O_2 \rightleftharpoons H_2O + HO_2^\bullet$	2.76
Ozone	$O_3 + 2H^+ + 2e^- \rightleftharpoons O_2 + 2H_2O$	2.076
Hydrogen peroxide	$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	1.776
Oxygen	$O_{2(g)} + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	1.229
Permanganate	$MnO_4^- + 4H^+ + 3e^- \rightleftharpoons MnO_2 + 2H_2O$	1.679
	$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	1.507
Dichromate	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	1.33
Ferrate(VI)	$FeO_4^{2-} + 8H^+ + 3e^- \rightleftharpoons Fe^{3+} + 4H_2O$	2.2
	$FeO_4^{2-} + 8H_2O + 3e^- \rightleftharpoons Fe(OH)_3 + 8H_2O$	0.7

tion, which is associated with very low efficiency of the process and obtaining a low purity of the product. Only the use of a solution of concentrated hydroxides (KOH, NaOH) instead of water results in K_2FeO_4 of high purity [8, 9].

Various research investigations have been carried out on the application of K_2FeO_4 as an oxidizer in industrial wastewater treatment, because this method is characterized by high efficiency of pollutant degradation. Selected applications of K_2FeO_4 for the degradation of various pollutants in water and wastewater, such as EDCs, PCPs, SPCs, pharmaceuticals are presented below.

1.1. Degradation of Endocrine Disrupting Chemicals (EDCs)

EDCs (Endocrine Disrupting Chemicals) are chemical compounds that disrupt the hormonal balance of the body. They are common in everyday life, because they are used for the production of plastic packaging, they are found in cleaning agents and detergents and also a part of medicines or plant protection products. EDCs also include natural origin compounds that, despite their origin, also destabilize the functioning of the endocrine system. In this group, hormonal compounds can also be distinguished, which after entering the body may negatively affect its homeostasis [10]. Table 2 presents examples of compounds obtained by chemical synthesis and natural compounds, classified as EDCs.

Table 2.
EDCs division depending on the origin [11]

EDCs obtained by synthesis	Natural EDCs
Bisfenol A	Progesterone
Bisfenol F	Testosterone
17- α -ethynylestradiol (EE2)	Androsterone
Genistein	15- β -estradiol (E2)
Biochanin A	Estrone (E1)

EDCs are a serious threat to human and animal health, especially if they enter the aquatic environment in a direct way (plant protection products, animal faeces) and uncontrolled. The biggest problem is the lack of adaptation of technologies used in water and wastewater treatment plants for the removal of these compounds. For the first time this problem was noticed and described in 1993 by Colbrom *et al.* [12]. During several years of research in the Great Lakes (USA), where mainly the chemical and heavy indus-

try is located, several generations of animals inhabiting this area were examined. As a result of research, it was found that the next generations are physically weaker and thus the incidence of various types of diseases, increases with subsequent generations. Colbrom *et al.* [12] determined that substances escaping from industrial plants into the environment are permanently accumulated in animal organisms and destabilize their hormonal system. She also proved that these substances cause changes in the embryonic phase of animals and on this basis, the conclusion is that these substances also threaten people [12]. Therefore, the search for methods allowing effective removal of EDCs from the natural environment was started. However, the applied physical processes, such as membrane methods, were characterized by different effectiveness of removal of individual compounds, as shown in Table 3. The very strong oxidizing properties of potassium ferrate(VI) cause, that this compound is a place of interest to many scientists around the world, including endocrine disrupting compounds (EDCs). Conventional methods of purification are not effective, due to the huge amount and variety of pollutants. Most of the chemical compounds used in wastewater treatment processes have a low or selective effect, and the use of K_2FeO_4 under appropriate process conditions (pH, temperature, time, dose) allows for complete degradation or significant EDCs reduction in wastewater [13, 14].

Table 3.
Percentage removal of EDCs in membrane processes [11]

EDCs	Effectiveness, %
Bisfenol A (BPA)	18–99
Testosterone	30–60
17- α -ethynylestradiol (EE2)	34–60
15- β -estradiol (E2)	8–90
Estrone (E1)	10–95

At the Hong Kong University, research was carried out on various methods of removing EDCs by using K_2FeO_4 . Two Bisphenol A compounds (BPA) were tested – used in the production process of plastic packaging, paper, cosmetics and cleaning products, and 17- α -ethynylestradiol (EE2) – a component of contraceptives [15]. First of all, the strong oxidizing properties of K_2FeO_4 were used to degrade the tested compounds. During tests, the effect of pH and reaction time on the oxidation efficiency of the tested compounds were determined and in the case of BPA a schematic sequence of changes taking place

Table 4.
Percentage removal of EDCs in K_2FeO_4 oxidation [17]

EDCs	Removed compound, % removal of EDCs			
	1	5	30	180
Reaction time, min.				
Bisfenol A (BPA)	99.8	99.8	99.8	99.8
Testosterone	53.0	78.9	81.4	85.7
17- α -ethynylestradiol (EE2)	99.0	99.0	99.0	99.0
15- β -estradiol (E2)	98.0	98.0	98.0	98.0
Estrone (E1)	99.3	99.3	99.3	99.3

Table 5.
EDCs compounds susceptible to K_2FeO_4 degradation

Compound	Molecular formula	Molar mass, g/mol	Literature
4-Methylphenol	$C_{10}H_{12}O$	108.14	Lee <i>et al.</i> , 2005 [18], Wang and Feng, 2013 [19]
Estradiol	$C_{18}H_{24}O_2$	272.39	Lee <i>et al.</i> , 2005 [18], Li and Dong, 2016 [20]
Bisphenol A	$C_{15}H_{16}O_2$	228.29	Lee <i>et al.</i> , 2005 [18], Li <i>et al.</i> , 2008 [21]
Phenol	C_6H_6O	94.11	Lee <i>et al.</i> , 2005 [18], Peings <i>et al.</i> , 2015 [22]
Nonylphenol	$C_{15}H_{24}O$	220.36	Anquandah and Sharma, 2009 [23]
Octylphenol	$C_{14}H_{22}O$	206.33	Anquandah and Sharma, 2009 [23]
α -Ethinylestradiol	$C_{20}H_{24}O_2$	296.40	Li <i>et al.</i> , 2008 [21], Lee <i>et al.</i> , 2009 [24]
Dimethylamino-benzaldehyde (DMAB)	$C_8H_{11}N$	121.18	Lee and von Gunten, 2010 [25]
Tetrabromo-bisphenol A	$C_{15}H_{12}Br_4O_2$	543.88	Yang <i>et al.</i> , 2014 [26]

during the process was created. The pH effect in the range of 8–10.5 was tested and it was shown that at pH 9.2 the oxidation processes of BPA and EE2 proceed with the highest efficiency. The studies' results have shown that with the reduction of Fe(VI) ions, oxidation of BPA and EE2 occurs. The initial concentrations of both compounds were 0.1 mM. A concentration of Fe(VI) ions of 0.5 mM was used for BPA and the reaction was carried out at pH 9.2 for 10 min. A concentration of Fe(VI) ions of 0.4 mM was used for EE2 and the reaction was carried out as before at pH 9.2 for 10 min. With properly selected parameters it was possible to remove completely (99.99%) both pollutants from wastewater. Another tested compound that belongs to the EDCs group is tetrabromobisphenol A (TBBPA). In this case, the initial concentration of TBBPA 1.84 μ M and the concentration of Fe(VI) 25.25 μ M were used. The tests were carried out on a laboratory scale, in the pH range 5–11, during 30 min. Under the most favorable conditions (pH 7, 30 min., 25°C) 99.06% degradation of TBBPA was achieved. During the research, 11 intermediates were identified and possible degradation pathways were proposed. Total degradation by potassium ferrate(VI) included processes of debromination, substitution, deprotonation and oxidation [16]. Chinese researchers have examined over a dozen compounds belonging to EDCs. The characteristic feature of these compounds was the presence

of phenolic moieties in their molecules. The initial concentration of each EDCs was 100 μ g/L, the dose of K_2FeO_4 was 10 mg/L, and the tests were carried out at pH 7 at 23°C. Samples were collected at 1, 5, 30 and 180 min. from the start of the experiment. Table 4 presents the results obtained during the tests for selected compounds.

Analyzing the results, it is clear that by using K_2FeO_4 , 99% of EDCs contained in wastewater can be removed except for testosterone (85.7%), which in the case of the tested compounds indicates very high efficiency of this oxidant. In addition, the study showed that the oxidation of EDCs containing phenolic moieties proceeds according to the mechanism of electrophilic oxidation, which involves the formation of a phenoxy radical, followed by the formation of quinone and bisphenol as by-products. In addition, the oxidation process could change the molecular structure of the target compounds, leading to a reduction in estrogen activity [17]. Currently, many researchers deal with the subject of degradation of various compounds belonging to EDCs. In Table 5 there are several examples along with literature data.

1.2. Degradation of surfactants (SPC)

Surfactants are surface active agents, widely used in many areas of life, such as economy, industry, agriculture, pharmacy and molecular medicine. They are

also used as basic components of washing, cleaning, foaming agents, emulsifiers and are included in medicines and ready-made formulations of plant protection products also containing herbicides [27, 28]. Surfactants are made of a hydrophilic and hydrophobic group and are usually divided into four types: anionic, cationic, amphoteric and non-ionic. If SPC are present in a given system at low concentration, they have the ability to adsorb on the surface or interface of the system, changing to some extent its free energy [29]. Due to its physicochemical properties (formation of micelles in contact with water), they adsorb on the water surface, which causes the following problems [30]:

- difficult penetration of oxygen into the depth of natural waters, which hinders the development of living organisms, as well as limits self-purification of water reservoirs in biodegradation processes,
- oxygen consumption during biochemical degradation of surfactants, which may lead to the formation of oxygen deficit in water ecosystems,
- adsorption of surfactants on fish gills, formation of complexes with proteins and as a consequence interfering with gill's work and impaired respiratory fish system,
- foaming of water, causing disturbances in the operation of water devices, such as turbines or aerating devices in wastewater treatment plants.

Due to the high durability and very slow surfactants degradation in the natural environment, research is conducted on their degradation. The degradation of

cetylpyridinium chloride (CPC) was carried out with K_2FeO_4 , 98% purity [31]. The study of the efficiency of CPC mineralization was performed indirectly by measuring the total organic carbon (TOC) in the reaction mixture. With a molar ratio of K_2FeO_4 : CPC = 1:1, the TOC removal was 78% in 30 min. (pH 9.2, initial concentration of CPC and Fe(VI) 80.7 μ M and 80.8 μ M respectively).

1.3. Degradation of Personal Care Products (PCPs)

Personal Care Products (PCPs) used to improve the quality of life are a unique group of new environmental pollutants, due to their natural ability to cause physiological effects in humans at low doses. More and more studies have confirmed the presence of PCPs in various environmental components, which raises concerns about potentially harmful effects on humans and animals. The environmental risk posed by these pollutants is assessed in the light of the sustainability, bioaccumulation and toxicity criteria of these compounds. PCPs include disinfectants, fragrances (musk, galaxolide, tonalide, celestolide), UV filters (benzophenols-3, homosalate, octyl-methoxycinnamate, octyl-dimethyl-PABA) and some cosmetics ingredients (glycine, glycerylglycine) [32, 33]. The research results presented below concerned the analysis of degradation products of glycine and glycerylglycine and the determination of the kinetics of the decomposition reactions of these compounds. For this purpose, solutions of the above substances at a concentration of 200 μ M and a

Table 6.
PCPs compounds susceptible to K_2FeO_4 degradation

Compound	Molecular formula	Molar mass, g/mol	Literature
Ibuprofen	$C_{13}H_{18}O_2$	206.29	Lee and von Gunten, 2010 [25]
Atenolol	$C_{14}H_{22}N_2O_3$	266.34	Lee and von Gunten, 2010 [25]
Menadione Sodium Bisulfite	$C_{11}H_9NaO_5S$	276.24	Yang <i>et al.</i> , 2012 [17]
Carbamazepine	$C_{15}H_{12}N_2O$	236.27	Yang <i>et al.</i> , 2012 [17]
Benzophenone-3	$C_{14}H_{12}O_3$	228.25	Diaz-Cruz and Barcelo, 2015 [35]
Triclosan (TCS)	$C_{12}H_7Cl_3O_2$	289.54	Diaz-Cruz and Barcelo, 2015 [35]
Glycerylglycine	$C_4H_8N_2O_3$	132.12	Noorhasan <i>et al.</i> , 2010 [34]
Sulfamethizole	$C_9H_{10}N_4O_2S_2$	270.33	Wu <i>et al.</i> , 2018 [36]
Ciprofloxacin	$C_{17}H_{18}FN_3O_3$	331.35	Zhou and Jiang, 2015a [37]
Penicillin G	$C_{16}H_{18}N_2O_4S$	334.39	Zhou and Jiang, 2015a [37]
Cephalexin	$C_{16}H_{17}N_3O_4S$	347.39	Karlesa <i>et al.</i> , 2014 [38]
Sulfamethoxazole	$C_{24}H_{29}N_7O_6S$	543.60	Noorhasan <i>et al.</i> , 2010 [34]
Diatrizoic acid	$C_{11}H_9I_3N_2O_4$	613.90	Anquandah <i>et al.</i> , 2011 [39]
Propranolol	$C_{16}H_{21}NO_2$	259.35	Anquandah <i>et al.</i> , 2013 [40]
Tetracycline	$C_{22}H_{24}N_2O_8$	444.40	Sharma <i>et al.</i> , 2015 [41]

K_2FeO_4 solution at a concentration of 200 to 400 μM were used, and the reaction was carried out at pH 4–10, at 25°C, for up to 30 min. A 99% degradation of glycine and glycyglycine was obtained at a K_2FeO_4 concentration of 100 μM , at pH 9, in 10 min. Under the oxidation conditions depicted, the amount of K_2FeO_4 used was equal to the amount of mole glycine. At the twice molar amount of glycine, the byproducts were ammonia, carbon dioxide and iminodiacetate (IDA) and nitriloacetate (NTA). Researchers also calculated the half-lives of both amines (at pH 7) during the oxidation of K_2FeO_4 (10 mg/L). The half-life for primary and secondary amines (IDA) was 42 s, and for tertiary amines (NTA) – 33 min. [34]. The presented test results indicate that K_2FeO_4 can remove the pollutants to a significant extent under appropriate conditions. Other examples of degradation of various compounds belonging to PCPs are shown in Table 6 along with literature data.

1.4. Degradation of pharmaceuticals and their metabolites

One of the modern tasks of wastewater treatment technology is the implementation of effective methods for the removal of pharmaceuticals and their metabolites in wastewater treatment plants, due to the reason that technologies currently used in wastewater treatment plants are not adapted to the removal of this type of micro-pollutants. Also currently used processes of surface water treatment are not able to remove these micro-pollutants. The lack of such activities causes getting pharmaceuticals and their metabolites into the water cycle in nature, and along with drinking water into human and animal organisms, which may cause a number of health problems [42]. Chemically, pharmaceuticals and their metabolites are compounds from various chemical groups for which no uniform removing method has been developed. Currently, the Advanced Oxidation Processes (AOPs) are being used for this purpose, but it is most often carried out on a laboratory scale, because there are no legal regulations forcing operators of the wastewater treatment plant to implement effective methods of pharmaceutical disposal. In addition, these methods do not remove individual pharmaceuticals to an equal degree [43]. An alternative may be using K_2FeO_4 as a strong oxidant. In this field, research on the degradation of sulfamethoxazole (SMX), which is a popular bacteriostatic antibiotic (chemotherapeutic agent) with medium duration

of action, was conducted. It has the ability to penetrate into the cerebrospinal fluid, it also achieves high concentration in the urine and is generally used as a combined preparation with trimethoprim. SMX is a compound that causes a number of side effects, including allergies, irritation of the skin and gastrointestinal tract and disorders of the blood clotting process, which may lead to hemorrhages [44]. K_2FeO_4 (purity 98%) was added to an aqueous solutions containing SMX and the tests were carried out at various pH ranges. The concentration of SMX in the tested samples was over 1 mM, and the concentration of K_2FeO_4 was in the range of 0.75–0.001 M. It was observed that over time, the concentration of K_2FeO_4 decreased, which was a sign of the SMX oxidation reaction. The oxidation reaction proceeded fastest (within the first 2 min.) at pH 7 (the range from 6.5 to 9.5 was tested). It has been shown that K_2FeO_4 is also effective in sulfonamides degradation, and the occurred by-products are less toxic [45]. Considering above results, it can be assumed that also other chemicals used in pharmacotherapy will be degraded by oxidation under the influence of K_2FeO_4 [43, 44]. Diclofenac (DCF) is another compound often used in pharmacotherapy. It is used in family medicine and rheumatology, which affects the musculoskeletal system, causing a reduction in pain and inflammation. DCF can cause renal cell mutation, damage to fish tissue or even death. Due to its widespread use by patients, it has been recognized as an impurity that has recently gained interest in the scientific world. Because DCF is characterized by bio-resistant properties, it cannot be removed by conventional biological methods, hence it is necessary to look for other effective, economical and environmentally friendly technologies. Zhao *et al.* [45] conducted research on the DCF decomposition. The initial concentration of DCF in synthetic wastewater was 80 μM , K_2FeO_4 concentration was 0.2 M, and the tests were carried out at 25°C for 3 min. A 89% DCF removal was obtained. Researchers proposed 6 different DCF degradation pathways, including hydroxylation, decarboxylation, C-N cleavage, dehydrogenation, formylation and dechlorination-hydroxylation. Fluoroquinolones (FQs) belong to broad-spectrum antibiotics against Gram-negative and Gram-positive bacteria and are often used to treat humans and animals. After penetrating into aquatic ecosystems, they can induce transcriptional changes in microorganisms, thus contributing to the creation of new genes by duplicating existing ones and developing resistant bacteria. In addition, it was found that mixtures of

fluoroquinolones with other pharmaceutical agents may act to inhibit growth and cause genotoxicity in aquatic organisms [46, 47]. K_2FeO_4 oxidation susceptibility tests were conducted with reference to five different fluoroquinolone antibiotics (FQ's), such as: flumequine (FLU), enrofloxacin (ENR), norfloxacin (NOR), ofloxacin (OFL) and marbofloxacin (MAR) [48]. The research was carried out using five different types of water: pure (or deionized) water, tap water, synthetic water, filtered natural river water and synthetic wastewater, which were enriched with one of the antibiotics, whose initial concentrations were $30 \mu\text{M}$. The antibiotic FLU was first tested and the reactions were carried out at 25°C for 10 min. at pH 7. The effect of Fe(VI):FLU molar ratio on the degree of its degradation was investigated. At the beginning, the most favorable Fe(VI):FLU ratio and reaction time were determined. The studies included the following molar ratios: 5:1, 10:1, 20:1, 50:1 and 100:1. Table 7 shows the percentage removal of FLU in the oxidation process using K_2FeO_4 .

For the Fe(VI):FLU ratio of 5:1 and 100:1, FLU

Table 7.
Percentage removal of FLU in the oxidation process using K_2FeO_4

Fe(VI):FLU ratio	Percentage removal after 10 min. reaction
Without Fe(VI)	0%
5:1	12%
10:1	29%
20:1	50%
50:1	95%
100:1	100%

degradation took place in the first 2 min. reaction, and lengthening the time to 10 minutes did not result in greater removal of the antibiotic. It can also be seen that for a ratio of 50:1 and 100:1, the percent removal of FLU was similar (95% and 100%). It is possible that an extended reaction time would result in the complete removal of FLU at a 50:1 ratio. In the next stage, the effect of the Fe(VI):FQ's ratio on the degradation of the remaining four antibiotics was examined, as shown in Fig. 2.

The analysis of the obtained test results indicates the complete removal of FQ's from the purified model wastewater, for the various Fe(VI):FQ's ratios. For ENR and OFL it was a 15:1 ratio, for NOR 10:1, and for MAR 20:1. The results of the tests showed that smaller molar ratios were have sufficient than in the case of FLU. The effect of humic acid (HA) and ions (Cl^- , SO_4^{2-} , NO_3^- , HCO_3^- , Na^+ , K^+ , Ca^{2+} , Cu^{2+} , Fe^{3+})

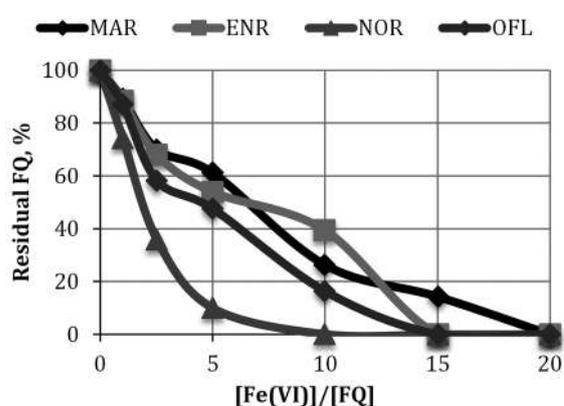


Figure 2.
The effect of different Fe(VI)/FQ's ratios on the antibiotics degradation (pH 7, T = 25°C , concentration of FQ's = $30 \mu\text{M}$) [48]

on the effectiveness of FLU removal was also investigated. The presence of ions and HA reduces the effectiveness of removing antibiotics, e.g. 15 mg of HA in solutions reduced the effectiveness of the reaction by 40% and the presence of individual ions (5 mM) by about 50%. Based on the conducted tests, it can be concluded that K_2FeO_4 is desirably used for the purification of various types of surface water or wastewater containing antibiotics, the degree of their removal depends, among others, on the Fe(VI) dose, pH and reaction time.

2. CONCLUSIONS

The development of the industry is related to the use of significant amounts of water for technological processes, which causes its pollution and often causes a negative impact on the natural environment. This is connected with the need to clean it, in order to prevent degradation of the natural environment. In addition to the currently used purification methods: physical, chemical and biological, which often do not give satisfactory results, further, more innovative methods of wastewater treatment are being developed. One of such very promising and alternative methods, which are still mainly in the field of laboratory research, may be the use of K_2FeO_4 , which is a compound with highly oxidizing and coagulating properties [49, 50, 51]. On the one hand, as a result of contact with contaminants, it acts as an oxidizer, while Fe(VI) ions are simultaneously reduced to Fe(III), $\text{Fe}(\text{OH})_3$ can be precipitated, which acts as a coagulant. Either AOPs methods or use of K_2FeO_4 have many advantages, but also disadvantages, which generate costs. First of all in AOPs methods costs are

generated by reagents used in a reaction (H_2O_2 , $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, H_2SO_4 , NaOH). Secondly AOPs methods generate precipitates that need to be disposed. On the other hand, the method using K_2FeO_4 currently is too expensive to use on a technical scale, especially when it is used pure K_2FeO_4 . Using technical K_2FeO_4 enable to reduce technological costs, due to the fact that this product is much cheaper. Another advantages are the lack of using additional oxidizers like H_2O_2 and it is no need to acidify the reaction environment, because K_2FeO_4 , in most cases, has also an oxidizing effect at neutral pH. Although as in AOPs methods some precipitates are generated, which need to be disposed. Some research and an economic analysis should be done, before using both methods. Nowadays K_2FeO_4 is used for water purification in lakes or soil remediation. K_2FeO_4 was successfully used to remove EDCs, such as bisphenol A, testosterone, progesterone and other contaminations, with the efficiency varying from 78 to 95%. Similarly, K_2FeO_4 was used to remove PCPs, which was associated with the removal of 99% of their initial amount. Potassium ferrate(VI) also showed high reactivity to pharmaceuticals such as sulfamethoxazole, diclofenac and fluoroquinolones. Despite its high efficiency K_2FeO_4 was not widely used on a large scale, probably due to high synthesis and treatment costs. However, it should be noted that at the current stage of research and experience, the use of K_2FeO_4 on a larger scale is also related to technical and technological constraints, mainly the complicated and costly process of its production. There is still a need for further intensive research into the use of K_2FeO_4 for a wide range of environmental applications.

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