

## APPLICATION OF POTASSIUM FERRATE(VI) FOR OXIDATION OF SELECTED POLLUTANTS IN AQUATIC ENVIRONMENT – SHORT REVIEW

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### Abstract

The paper provides comprehensive information on the recent progress of the use of potassium ferrate(VI) ( $K_2FeO_4$ ) for the removal of selected pollutants from water and wastewater.  $K_2FeO_4$  provides great potential for diverse environmental applications without harm to the natural environment. Therefore  $K_2FeO_4$  was used in removal of cyanides from gold ore purification processes, degradation of dyes and organic compounds in wastewater and algae removal in the water treatment process. The quoted research results indicate that  $K_2FeO_4$  due to its strong oxidizing and coagulating properties, could be an alternative to the use of Advanced Oxidation Processes (AOPs) or be an additional option to conventional methods of water and wastewater treatment. As a result of using  $K_2FeO_4$ , the emerge intermediates of the impurities decomposition are nontoxic or show less toxicity than the initial substrates. The use of  $K_2FeO_4$  is also associated with certain limitations of technical and technological nature, which requires further research in order to use its high efficiency in the degradation of various types of contamination on a technical scale.

Keywords: Potassium ferrate(VI);  $K_2FeO_4$ ; Cyanides; Organic compounds; Dyes; Algae.

## 1. INTRODUCTION

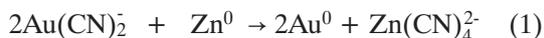
Treatment of industrial wastewater due to its varied quantitative and qualitative composition is a complex issue, which is still the subject of numerous studies. An example of wastewater whose cleaning up causes many problems are wastewater from dyes, textile, polygraph and mining industry. Industry wastewater is characterized by considerable nuisance and environmental toxicity. First of all, their composition contains dyes and other substances such as: mineral and silicone oils, polycyclic aromatic hydrocarbons, pesticides, detergents, inorganic acids, strong oxidants used as bleaching agents, as well as adhesives and alkali [1]. What is more industrial wastewater has an intense

color, a various inhibitors and toxic agents contained in them are poorly biodegradable, sometimes they are characterized by variations in the composition, reaction and pollution load [2]. Due to the diverse nature of mentioned wastewater, various methods (like sorption, coagulation, biodegradation or chemical oxidation) of their treatment, or combining several of them, must be used. Potassium ferrate(VI) has a high value redox potential (2.2 V in acidic solutions), only the fluorine (2.9 V) and the OH hydroxyl radical (2.8 V) have a higher values [3]. Because of this it could be a very effective reagent in various fields including applications in water oxidation catalysis, waste remediation and high capacity battery cathodes production [4]. Moreover it can kill microorganisms, eliminate organ-

ic and inorganic contaminants and eliminate suspended/colloidal materials due to its high oxidizing potential and ability to simultaneously generate ferric cations, which can act as a coagulant. Generally the products of decomposed contaminants are water and carbon dioxide and also intermediate products are less toxic than the previous ones. In addition, during the reduction of  $\text{FeO}_4^{2-}$  ions to Fe(III) compounds the coagulation and adsorption process of contaminants takes place on the iron  $\text{Fe}^{3+}$  hydroxide flocs. Very often Fe(VI) salts are called environmentally friendly and therefore potassium ferrate(VI) is often called “environmentally friendly oxidant” [5]. For many years, various research investigations have been carried out on the application of  $\text{K}_2\text{FeO}_4$  for the degradation of various pollutants in water and wastewater. In this paper authors focused on pollutants deriving from the industry and mining like: cyanides, organic compounds, dyes and also removal of algae from potable water.

## 2. DEGRADATION OF CYANIDES ORIGINATING FROM THE MINING AND PROCESSING OF GOLD ORE

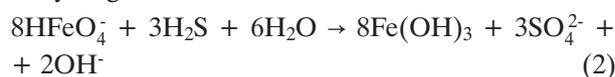
One of the most profitable industries in the world are gold mines. The current development of technology, especially computer technology, causes a continuous increase in the demand for this raw material. Gold is an irreplaceable raw material for the production of high-quality conductors, connectors or other technical accessories. The process of gold mining and processing is a complicated operation and one ton of ore gives an average of 6.5 g Au. The extracted rocks are milled to a suitable thickness and an aqueous solution of metal cyanides is added. Under the influence of air oxygen, Au from minerals reacts with  $\text{CN}^-$  ions forming the  $\text{Au}(\text{CN})_2^-$  complex, after which the compound is reduced with Zn metal in accordance with the reaction (1):



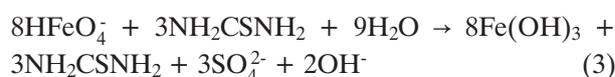
After the separation of metallic gold, significant amounts of wastewater are generated, which must be treated [5, 6]. They are characterized by high pH value, high content of heavy metals (among others: Zn, Cd, Cu, Ni, Bi, U), very high content of cyanides, sulfur compounds (sulfides, sulfites), they also contain traces of gold compounds as well as organic compounds. Due to the high toxicity, post-mining wastewater should be cleaned, however, one effective method of treatment has not been developed. To

treat these wastewater, methods such as ozonation, chlorination, oxidation with  $\text{H}_2\text{O}_2$ , sedimentation and biological methods are used [7]. The most important module for the purification of this type of wastewater should be their oxidation, mostly based on the ozonation or chlorination process. Unfortunately, both these processes have major disadvantages: ozonation is a cost-intensive process, whereas chlorination causes secondary pollution of wastewater with chlorine compounds [6]. In order to reduce the costs of wastewater treatment and to obtain at least a partial distribution of pollutants,  $\text{K}_2\text{FeO}_4$  was used for this purpose. Under laboratory conditions,  $\text{K}_2\text{FeO}_4$  oxidized many compounds present in wastewater from a gold mine. The following are the compounds found in post-mining wastewater, oxidized by  $\text{K}_2\text{FeO}_4$  [7]:

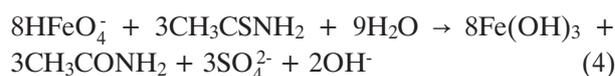
- Hydrogen sulfide



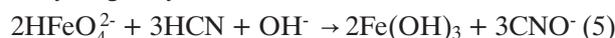
- Thiourea



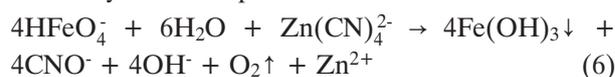
- Thioacetamide



- Hydrogen cyanide



- Zinc-cyanide complex



In the course of the research, the main focus was put on the degradation of zinc-cyanide complex and free cyanides, because they constitute the largest load of pollutants in post-mining wastewater. By selecting the appropriate pH and reaction time, zinc-cyanide complex was completely removed. In addition, the further activity of  $\text{K}_2\text{FeO}_4$  on intermediates of cyanide oxidation, at low pH, allowed their complete decomposition to carbon dioxide and nitrites [6]. The rate of oxidation of  $\text{CN}^-$  ions depended largely on the pH of the reaction. The tests showed that the oxidation reaction was the fastest in the range of pH 7.5–8, while with the increase of pH, the reaction rate was reduced. In addition, if the  $\text{FeO}_4^{2-}$  ions concentration was five times higher than the concentration of  $\text{CN}^-$  ions (100  $\mu\text{M}$ ), the cyanide half-life was 9.3 s at 15°C. Addition of 0.01 g  $\text{K}_2\text{FeO}_4$  to a mine wastewater sample containing 680  $\mu\text{M}$  total cyanides and 200  $\mu\text{M}$

free cyanides resulted in 77% removal of free cyanides and 59.4% removal of total cyanides. More  $K_2FeO_4$  addition (0.128 g) to the same sample resulted in complete removal of free cyanides and 98% removal of total cyanides [7]. The use of  $K_2FeO_4$  in the technology of wastewater treatment coming from gold mines can bring many benefits, both economical, and ecological. This method is much cheaper than, e.g. ozonation and its final products are potentially harmless to the environment. The results of other studies [8] aimed at testing the possibility of removing cyanides (free cyanides and several complex cyanide compounds) in water in alkaline conditions ( $pH > 11$ ) with  $K_2FeO_4$  indicate that the rate of free cyanide removal by oxidation of  $K_2FeO_4$  was greater at pH 11 than at pH of 12. A total oxidation was obtained at Fe(VI):CN ratio 2.67 and at pH 11.  $K_2FeO_4$  did not degrade all cyanide complexes, but removed complexes with copper, zinc and cadmium. In addition, the ions of these metals were removed by coagulation on the basis of sorption on the flocs of the resulting  $Fe(OH)_3$ . At the same time, rapid oxidation of copper-complexes was observed and the oxidation of nickel and silver cyanides complexes were incomplete. It can be assumed that complexes of cyanides with  $Ni^{2+}$  ions have been removed to some extent, but it was not possible to remove complexes with silver ions [8]. Similar research on copper-cyanide and nickel-cyanide complexes was conducted by Lee and Tiwari [9]. Degradation of the cyanide complex (1 mM) with copper removal

(0.095 mM) was carried out at different doses of  $K_2FeO_4$  in the range of 0.3–2 mM at pH 10. Potassium ferrate(VI) (1 mM) was found to easily oxidize cyanides (final concentration 0.03 mM). Reduced to  $Fe(OH)_3$  also contributed to the removal of free copper ions (final concentration 0.002 mM), which formed after the breakdown of the complex. The influence of pH on the degradation of copper-cyanide complexes was also investigated. Raising the pH from 10 to 13 did not affect the oxidation of cyanides, but allowed for the removal of 99% of the initial amount of copper ions. In a strongly alkaline environment, copper ions may precipitate as a result of co-precipitation together with the simultaneously occurring  $Fe(OH)_3$ . Similar studies [9] were conducted for nickel-cyanide complexes where the concentration of the cyanide was 1 mmol/L, including initial nickel concentration of 0.17 mmol/L, dose of Fe(VI) was 2 mmol/L, pH range 10–12. At pH 10, partial cyanide oxidation (64.2%) and partial nickel removal (15.2%) were achieved. Increasing the pH to 12 resulted in a deterioration of the obtained results. Under these conditions, a cyanide removal efficiency (51%) was obtained and nickel removal was only 1% in relation to the initial values. Therefore, the use of potassium ferrate(VI) has allowed decomposition of copper-cyanide complexes, while the oxidation of nickel-cyanide complexes may require a long reaction time. Literature data [8, 10–27] indicate that it is also possible to decompose other inorganic compounds, which are summarized in Table 1.

**Table 1.**  
Inorganic compounds susceptible to decomposition by using  $K_2FeO_4$

Compound/Ion	Molar mas, g/mol	Literature
HCN	27.03	Costarramone et al., 2010 [8], Sharma et al., 1998 [10]
$SCN^-$	58.08	Sharma et al., 2002 [11], Gonzalez – Merchan et al., 2016 [12]
$Cd(CN)_4^{2-}$	216.48	Yngard et al., 2008 [13], Tiwari & Lee, 2011 [14]
$Fe(CN)_4^{2-}$	159.91	Sharma V.K., 2011 [15]
$Zn(CN)_4^{2-}$	169.45	Yngard et al., 2007 [16]
$Ni(CN)_4^{2-}$	162.76	Yngard et al., 2008 [13], Osathaphan et al., 2014 [17]
$Cu(CN)_4^{3-}$	167.62	Tiwari & Lee, 2011 [14], Sharma et al., 2005 [18]
$NH_2OH$	33.03	Sharma V.K., 2011 [15]
$N_2H_4$	32.05	Sharma V.K., 2011 [15]
$H_2S$	34.08	Sharma et al., 1997 [19], Talaickhoazni et al., 2016 [20]
$SO_3^{2-}$	80.06	Johnson & Bernard, 1992 [21], Read et al., 2001 [22]
$S_2O_3^{2-}$	112.13	Johnson & Read, 1996 [23]
$S_3O_6^{2-}$	192.19	Read et al., 2005 a,b [24, 25]
$S_5O_6^{2-}$	256.32	Read et al., 2005 a,b [24, 25]
$As^{3+}$	74.92	Fan et al., 2007 [26], Lee et al., 2003 [27]

### 3. DEGRADATION OF ORGANIC COMPOUNDS

Natural organic matter (NOM) is a large group of organic carbon compounds occurring in the natural environment, both land and water. It is a matter composed of organic compounds from residues of living organisms, such as plants or animals. Organic molecules can also be produced by chemical reactions, with the basic NOM structures formed from cellulose, tannins, cutin and lignin, as well as from proteins, lipids and carbohydrates. Organic matter is very important for the flow of nutrients in the environment and plays an important role in water retention in soil. The same ability of natural organic matter that helps in the retention of water in the soil, however, poses problems for current methods of water treatment. In an aqueous environment, organic matter binds to metal ions and minerals and due to its high reactivity, it can produce by-products that are harmful to the environment and people [28]. Therefore, researchers are trying to find new ways of drinking water treatment, e.g. using  $K_2FeO_4$  for several reasons [29]:

- the reaction rate of  $K_2FeO_4$  and NOM can affect the rate of Fe(III) formation, which can be used as an in-situ coagulant,
- NOM causes the water color, which affects its aesthetic and health effect,
- NOM is a precursor to some disinfection by-products that affect health,
- NOM increases the solubility of metals in water by complexing them.

So far, little research has been done on the degradation of NOM, and those available in the scientific circuit focus on one or two types of substances such as humic acid (HA) or fulvic acid (FA) [30–34]. Research conducted by Qu et al. [30] showed that the use of  $K_2FeO_4$  to oxidize FA extracted from the bottom sediment of the Chinese water reservoir, allowed for 90% removed of this acid. The applied dose of FA was 2 mg/L, and  $K_2FeO_4$  6.8 mg/L, at pH 7.1–7.8. Lim and Kim [32], indicate that  $K_2FeO_4$  easier removes NOM at pH 3 than at pH 7.8 or 11. On the other hand, Gan et al. [34], provide further data on not only NOM removal but also the reduction of by-products. The authors oxidized the natural organic matter (FA and HA) from the Suwannee River in the USA (Dissolved Oxygen Content, DOC 3 mg/L, pH 7) and achieved a 12% and 28% reduction in DOC using 1 mg/L and 20 mg/L  $K_2FeO_4$  respectively. Most of the

previous work concerned only the oxidation of some NOM fractions using  $K_2FeO_4$  or was not carried out in experimental conditions similar to water treatment conditions. Sun et al. [35], proposed a novel DEET (N,N-diethyl-3-toluamide) oxidation process by the combined use of  $K_2FeO_4$  and sulfite ions. The obtained test results indicated that sulfites in combination with  $K_2FeO_4$  can significantly improve the DEET degradation rate. At the beginning, the researchers checked how degradation works with  $Na_2SO_3$  and  $K_2FeO_4$  used separately, and then in a combination of both compounds. After 30 min of reaction using only  $Na_2SO_3$  (dose 400  $\mu M$ ) at pH 8, practically no degradation of DEET was observed (initial and final concentration was 10  $\mu M$ ). A similar situation took place using only  $K_2FeO_4$  (converted to Fe(VI) ions at 100  $\mu M$ ), under the same reaction conditions. The combination of  $K_2FeO_4$  and  $Na_2SO_3$  allowed to remove 78% DEET from the solution within 10 seconds. It was also checked how the initial concentration of DEET affects its degradation efficiency. At a constant concentration of Fe(VI) ions (100  $\mu M$ ) and  $Na_2SO_3$  (400  $\mu M$ ) for DEET < 7  $\mu M$ , almost complete removal of DEET (95%) in 10 s, at pH 8 was achieved. For doses of 7  $\mu M$  < DEET < 30  $\mu M$ , only a 45% removal, in 10 s, at pH 8 was noted. The effectiveness of DEET degradation in the Fe(VI)/ $Na_2SO_3$  system was closely related to the doses of both reagents, the initial concentration of DEET and the pH value. It was also shown that the presence of humic acids, chloride, bicarbonate and carbonate ions, clearly inhibited the decomposition of DEET [35].

### 4. REMOVAL OF DYES

In the nineteenth century, a lot of methods were developed for obtaining synthetic dyes on a larger scale. Since then, about 10.000 synthetic dyes have been created, often with a complicated chemical structure, which in most cases displaced natural dyes from production [36, 37]. Currently, artificial colors are used in various industries, especially in the textile, pulp and paper, pharmaceutical, cosmetics and food industries. The highest consumption of dyes is recorded in the textile industry. Pigment dyes, which are organic and inorganic substances difficult to biodegradable, may occur in many types of wastewater [38]. These dyes can effectively inhibit photosynthesis and biochemical pathways in the organisms of various plants and animals living in the aquatic

environment [39]. In addition, some of the dyes may have toxic, mutagenic, teratogenic or carcinogenic effects on various aquatic organisms [40]. Additionally, the surface waters are a source of water for people. There has been a long-standing interest in ways of degradation of dyes present in industrial wastewater. Various methods of this type of wastewater treatment were developed, including physico-chemical methods (adsorption, coagulation, filtration, ion exchange), chemical (ozonation, chlorination), Advanced Oxidation Processes (AOPs) such as photochemical methods (UV-photolysis, photo-Fenton reaction, processes using ultrasounds, UV/H<sub>2</sub>O<sub>2</sub> processes, UV/O<sub>3</sub> and others) and chemical methods (Fenton reaction, oxidation by O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>, electrochemical oxidation). Although the above methods have been successfully used to eliminate dyes from contaminated water, they have many limitations due to the need to use specific adsorbents, chemical substances (including catalysts), enzymes, as well as specific technological conditions (e.g. high temperature, pressure, UV radiation). Among the AOPs methods used for the degradation of dyes in wastewater, the Fenton reagent (Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>) and its modifications has been quite often used for some time [41, 42]. The advantage of using the Fenton reagent is the high oxidation potential of the resulting hydroxyl radicals and the fact that the Fenton reaction occurs at ambient temperature and normal pressure. An interesting alternative for using AOPs processes for the degradation of dyes in wastewater, landfill leachate and other types of wastewater is using K<sub>2</sub>FeO<sub>4</sub>, due to the very high oxidation potential of Fe(VI) ions and the formation of usually less toxic or non-toxic by-products in relation to the initial impurities [43]. Potassium ferrate(VI) has been used as an oxidizing and coagulating agent for the degradation of methylene blue (MB) present in dye wastewater. The authors [44] used Fourier-transform infrared spectroscopy (FTIR) to study degraded MB molecules after using K<sub>2</sub>FeO<sub>4</sub>. The dye concentration was 1 mg/L, the dose of K<sub>2</sub>FeO<sub>4</sub> 20–250 mg/L, pH 7–8, and the reaction time 20 min. The obtained results showed that the peaks characteristic for this dye disappeared, which proved that it was completely degraded. In addition, the MB removal efficiency was estimated by measuring the UV–VIS adsorption spectrum with the K<sub>2</sub>FeO<sub>4</sub> solution. The pure MB solution showed maximum absorbance at 664 nm, however, the absorbance measured after the reaction showed no peak in the electron spectrum, suggesting that the dye was completely oxidized. The most

favorable dye degradation conditions were also determined: K<sub>2</sub>FeO<sub>4</sub> concentration 70 mg/L, pH 7 and reaction time 20 min. Potassium ferrate(VI) was also used as an oxidizer to remove Orange II dye from an aqueous solution. The effectiveness of the discoloration of the Orange II dye using K<sub>2</sub>FeO<sub>4</sub>, KMnO<sub>4</sub> and ferrate(VI)-hypochlorite liquid mixture was investigated [45]. Oxidant concentrations were 10 mg/L, dye concentration 50 mg/L, pH 3 and reaction time 10 min. Under these conditions a decolorization efficiency for KMnO<sub>4</sub> solution was 17.7%, 62% for K<sub>2</sub>FeO<sub>4</sub> solution and 95.2% for ferrate(VI)-hypochlorite liquid mixture. The obtained results indicate the possibility of rapid destruction of chromophores and aromatic rings in the dye tested, especially in the case of K<sub>2</sub>FeO<sub>4</sub> and ferrate(VI)-hypochlorite liquid mixture. Potassium ferrate(VI) also effectively degraded azo dye (Brilliant Red X–3B). It was shown that the pH value, the initial concentration of the dye and the dose of K<sub>2</sub>FeO<sub>4</sub>, had a significant influence on the efficiency of the oxidation process. Under the most favorable conditions, in which the starting dose of the dye in the aqueous solution was 49.2 mg/L, K<sub>2</sub>FeO<sub>4</sub> concentration 25 mg/L, pH 8.4, after 20 min reaction, 99% discoloration was obtained. The disappearance of the color was much faster than the decrease in the COD and TOC values, since after 60 minutes of reaction only 42% reduction of the COD value and 9% decrease of the TOC value were obtained. This was most likely caused by the destruction of chromophores and the formation of various by-products, such as: naphthalene, phthalic acid, 1-isocyanato-phenol, azobenzene, muconic acid and hydroquinone [46]. What is more, Han et al. [47] investigated the effect of anions on the decolorization of X–3B dye by K<sub>2</sub>FeO<sub>4</sub> and KMnO<sub>4</sub>. It has been shown that the presence of Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> had a positive effect on decolorization while the addition of CO<sub>3</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup> ions influenced inhibition. The effect of concentration of oxidants, dye concentration, pH and solution temperature on color removal was also investigated, as well as the effectiveness of COD and TOC removal. The ability of X–3B to decolorize with K<sub>2</sub>FeO<sub>4</sub> was better than with KMnO<sub>4</sub>. When the concentration of the dye was 100 mg/L, and the concentration of oxidants was 150 mg/L, 100% removal of the dye for K<sub>2</sub>FeO<sub>4</sub> was found at room temperature, and only 62% removal of color by KMnO<sub>4</sub>. However, at a higher temperature of 60°C, 80% discoloration was obtained for K<sub>2</sub>FeO<sub>4</sub>,

and only 60% for  $\text{KMnO}_4$ . It was also shown that in a wide pH range (4–9)  $\text{K}_2\text{FeO}_4$  had high dye bleaching efficiency of over 85%. The percent removal of COD and TOC for  $\text{K}_2\text{FeO}_4$  was 58% and 24% respectively, while for  $\text{KMnO}_4$ , 42% and 10% respectively [47]. Thomas et al. [48] applied the Taguchi method to optimize the purification process of synthetic wastewater with the use of  $\text{K}_2\text{FeO}_4$ . The research was carried out with the use of synthetic wastewater (sodium lauryl sulfate,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ,  $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ ,  $\text{NaOH}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaCl}$ ,  $\text{CH}_3\text{COOH}$ , Acid Green 16–AG16), differing in the concentration of dye AG16 (20, 120 and 220 mg/L).  $\text{K}_2\text{FeO}_4$  at 25, 125 and 225 mg/L was used. The tests were carried out in three pH ranges: 2, 7 and 12 and in 10, 30 and 50 min. For planning and optimization, the Taguchi method was used for 4 input parameters (pH, reaction time, AG16 concentration and  $\text{K}_2\text{FeO}_4$  concentration) for which 9 experiments were performed, in accordance with the adopted experimental design. Test result analysis allowed to indicate the optimal values for individual input parameters (pH 2, time 50 min, AG 16–20 mg/L,  $\text{K}_2\text{FeO}_4$  – 125 mg/L). Under these conditions, visual discoloration of wastewater was obtained (AG 16–0.4 mg/L, decrease by 98%), color removal (66 mg Pt/L, decrease by 88%) and DOC (249 mg/L, decrease by 37%) [49].

## 5. REMOVAL OF ALGAE

Eutrophication, the increase in the fertility of waters, is caused by the growing pollution of the natural environment with biogenic substances, mainly nitrogen and phosphorus compounds, which are used, among others, in agriculture. Eutrophication causes the excessive development of phytoplankton organisms, which in consequence is associated with the reduction of light transmittance to deeper parts of water reservoirs, overgrowth of hydrotechnical devices and release of various toxins to the aquatic environment by algae. Unfortunately, for many reasons, the causes of water eutrophication can not be completely eliminated, which necessitates the elimination of phytoplankton in water treatment stations. Phytoplankton (algae, cyanobacteria) removal processes in water treatment plants mainly boil down to coagulation, sedimentation and or filtration processes. These processes allow the removal of nearly all phytoplankton, however, remains the problem of the water smell and the presence of toxic compounds (anatoxin-a, anatoxin-a(s), aplysiatoxin,

cylindrospermopsin, microcystin LR, nodularin R, saxitoxin), secreted by algae. In order to eliminate these problems, oxidation processes using strong oxidants, e.g. chlorine compounds or ozone are used. The addition of an oxidant also increases the efficiency of the coagulation process itself, and reduces the need for coagulant [49]. The results of research conducted using  $\text{K}_2\text{FeO}_4$ , as a compound supporting the coagulation process and aimed at the elimination of odor and toxic compounds, indicated the possibility of effective use of this oxidant. During the tests, the water from the water reservoir in which the eutrophication processes took place was treated. The presence of organisms such as *Chlorella*, *Spirogyra*, *Chlorococoum* and *Scenedesmus* were found mainly in this water. The concentration of algae ranged from  $8 \cdot 10^6$  to  $2 \cdot 10^7$  organisms per liter.  $\text{K}_2\text{FeO}_4$  and  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  in different doses was used as a coagulant. Studies [49] have shown that with the increasing dose of coagulant and  $\text{K}_2\text{FeO}_4$ , the efficiency of removing algae from the tested water was increased. The use of the coagulant itself did not cause a large removal of algae, only the addition of  $\text{K}_2\text{FeO}_4$ , resulted in increasing removal efficiency by up to 60%. The research also showed that the process was most effective during the first 5 minutes, for the highest dose of  $\text{K}_2\text{FeO}_4$  (5 mg/L) used, with the time extension not improving the effects. The use of  $\text{K}_2\text{FeO}_4$  also made it possible to reduce the coagulant dose. It was found that the addition of  $\text{K}_2\text{FeO}_4$  significantly supports the process of removing phytoplankton in two ways. Firstly it eliminates toxic (anatoxina, anatoxin-a(s), aplysiatoxin, cylindrospermopsin, microcystin LR, nodularin R, saxitoxin) and odorous compounds, and secondly, the product of reduction of  $\text{K}_2\text{FeO}_4$  is  $\text{Fe}(\text{OH})_3$ , which by forming a flocculated suspension supports the process of coagulation [49]. Although  $\text{K}_2\text{FeO}_4$  is considered as an universal oxidizing agent, earlier studies [49] have focused only on the oxidation of individual impurities (algae cells or their toxins). According to [50] the presence of iron has a negative effect on the efficiency of water treatment because of acceleration of toxins synthesis. The results of subsequent studies [51] have shown that the use of  $\text{K}_2\text{FeO}_4$  enables inactivation of algae cells and degradation of toxins. Next, the  $\text{Fe}^{3+}$  ions formed, resulting from the reduction of potassium ferrate(VI), initiate cell coagulation in situ. The initial concentration of algae cells ( $4.26 \cdot 10^4$  cells/mL at pH 5.5 and  $5.16 \cdot 10^4$  cells/mL at pH 7.5) decreased to zero at doses of  $\text{K}_2\text{FeO}_4$  7–10 mg/L. At a pH higher

than 7.5, the removal of solid particles was almost impossible, probably because coagulation occurs when the surface charge of the particles decreases. During that time, it has been proven that at the same time toxins (anatoxin-a, anatoxin-a(s), aplysiatoxin, cylindrospermopsin, microcystin LR, nodularin R, saxitoxin) produced by algae can be broken down at each pH value tested. The highest degree of their degradation was achieved at pH 5.5, which resulted from higher effectiveness of  $K_2FeO_4$  at this pH value. These studies were the first step towards the use of  $K_2FeO_4$  as a promising agent for the oxidation of many surface eutrophication products simultaneously [51]. Studies on the kinetics of  $K_2FeO_4$  reactions with selected compounds causing the taste and smell of algae in water were also carried out by Shin et al. [52]. The olefinic compounds were tested: 1-penten-3-one,  $\beta$ -ionone, trans,cis-2,6-nonadienal,  $\beta$ -cyclocitral, cis-3-hexen-1-ol and non-olefinic compounds, such as: 2-isopropyl-3-methoxypyrazine (IPMP), geosmin, 2-methylisoborneol (MIB), originating from Lake Dongbok and the Nakdong River. First, the QSAR (Quantitative Structure Activity Relationships) model was used to predict and evaluate the elimination efficiency of organic compounds, which was then confirmed experimentally. The results of the tests showed that the olefinic compounds were characterized by a significant reactivity to  $K_2FeO_4$  ( $\kappa_{app}=34\text{--}639M^{-1}s^{-1}$ ) at pH 7. Non-olefinic compounds (geosmin and MIB) showed only insignificant reactivity to  $K_2FeO_4$  ( $\kappa_{app}<0.6 M^{-1}s^{-1}$ ) at pH 7. The reaction rate of the olefinic compounds was greater when increasing the ferrite concentration in the range of 0.2–1 mM. The elimination of these compounds was much faster than the prediction of the model, which indicates the emergence of new pathways for their degradation, e.g. by cleaving the double bond, which is associated with the formation of aldehydes. Based on the obtained results, it can be concluded that  $K_2FeO_4$  can be effective in the process of removing phytoplankton and inactivating compounds that cause a specific taste and smell of water. It is also a much more effective substitute for chlorine and ozone and also does not create environmentally harmful end products. In addition, the resulting  $Fe(OH)_3$  behaves like a coagulant, which is associated with a lower need for a basic coagulant.

## 6. CONCLUSIONS

Potassium ferrate(VI) is a very promising oxidizing compound, which is still mainly in the field of laboratory research.  $K_2FeO_4$  has many unique properties – it is non-toxic and environmentally friendly. As a result of using  $K_2FeO_4$ , products with significantly lower toxicity than toxicity of starting substrates or non-toxic products are usually formed. What is more  $K_2FeO_4$  can act bi-directionally, i.e. as the oxidant in the first stage and as a coagulant in the second stage of the purification processes. As a result of contact with contaminants, it acts as an oxidizer, on the other hand, when  $Fe(VI)$  ions are simultaneously reduced to  $Fe(III)$ ,  $Fe(OH)_3$  can be precipitated, and acts as a coagulant. Moreover, potassium ferrate(VI) does not act selectively and can degrade all kinds of pollutants. Literature studies indicate the possibility of using  $K_2FeO_4$  for the decomposition of many contaminants like: metal cyanides, organic compounds, dyes and algae present in water and wastewater. 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. The wider implementation of  $K_2FeO_4$  method on a technical scale, as in any case, requires further research on a wider scale and also reduction of production costs. The application of  $K_2FeO_4$  for removal of another types of pollutants (endocrine disrupting chemicals, surface active agents, personal care products and pharmaceuticals) will be the subject of next review paper.

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