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Treatment of Real Textile Wastewater by Using Potassium Ferrate(VI) and Fe(III)/H$_2$O$_2$. Application of *Aliivibrio Fischeri* and *Brachionus plicatilis* Tests for Toxicity Assessment

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Abstract

The paper presents the possibility of applying combined chemical oxidation processes using potassium ferrate(VI) (K$_2$FeO$_4$) and Fe(III)/H$_2$O$_2$ for the treatment of real wastewater from the textile industry characterised by an increased content of organic substances (COD = 1920 mg O$_2$/l). The use of both processes under optimal conditions included the use of the RSM method (Response Surface Methodology) in order to make it possible to decrease the COD of the wastewater by 75.4% (final COD = 472 mg O$_2$/l). The toxicity of wastewater treated under the most favourable conditions, determined using two test organisms (Aliivibrio fischeri and Brachionus plicatilis), decreased by 33 and 45%, respectively. In some cases the method described can be used on a larger scale.

Key words: *potassium ferrate(VI), textile wastewater, Fenton-like reaction, toxicity assessment.*

Introduction

The textile industry is one of the largest and oldest in the world [1]. It produces three main types of fibres, i.e.: cellulose, protein and synthetic. Many inorganic and organic compounds (including dyes) are used in textile factories in order to give fabrics specific properties. Dyes used in the textile industry, are classified as reactive, direct, naphthol and indigo. For dyeing cellulose fibres, reactive, direct, vat and sulphur dyes are used, in the case of wool: acid, metal-complex and special reactive dyes, for polyester fibres (PE): disperse dyes, for polyamide fibres (PA): acid, metal-complex (type 1:2), reactive and special disperse dyes, and for polyacrylic fibres (PAN): cationic and basic dyes. Other types of fibre such as protein fibres usually require the use of acid and lanaset dyes. In general, disperse, direct and basic dyes are used for the dyeing of synthetic fibres [2-6]. The increasing demand for fabrics to be attractive not only in terms of their functional properties but also visual ones, encourages the use of colouring agents, which is also associated with the growing demand for dyes and the increase in their production. It was estimated that the global consumption of reactive dyes in 1988-2004 increased almost three times and amounted to 178,000 tonnes in 2004 [7]. Similarly, the global export and import of direct dyes increased from 53,848 tonnes (1992) to

181,998 tonnes (2011), and dispersion dyes – from 150,000 tonnes (1998) to 570,000 metric tonnes (2011). In the case of acid dyes, which also comprise an important group, it reached 680,000 tonnes (2011) [8]. The dye manufacturing industry represents a relatively small part of the entire chemical industry, but global dye production is estimated at almost 800,000 tonnes per year [9]. In addition, technological processes used in the textile industry are characterised by a significant demand for water, which is variable and depends, among others, on the type of fabric produced. It is assumed that on average it is 80-150 m^3 of water per 1 ton of product [10]. Other authors state that with a daily production of 12-20 tons of textiles, water consumption may vary in the range of 1,000-3,000 m^3 [11-12]. About 30-40% of water is used for main chemical processes and dyeing, while 60-70% is consumed in washing processes [13]. The considerable demand of textile industry processes for water on the one hand and the necessity of using many chemical compounds of organic (mainly dyes) and inorganic origin on the other results in the creation of a large amount of wastewater with diverse chemical composition. Due to the fact that some of the dyes used are toxic, the resulting wastewater is a serious environmental problem and is characterised by low susceptibility to biodegradation [14]. In some cases, dyes may degrade under anaerobic conditions. As a result of this process, potentially carcinogenic

compounds may be formed and then be found in the food chain [15]. In addition, wastewater containing high concentrations of dyes is characterised by a negative impact on surface waters, because they prevent the penetration of light and oxygen into deeper layers of water and, in this way, may prevent the normal functioning and development of aquatic organisms [16]. The physicochemical parameters of industrial wastewater vary widely and depend on many factors, including the technical and technological level of industrial plants. In general, the physicochemical parameters of wastewater depend on the dyeing technology of different fibres. The data quoted in the reference literature indicate that individual values of physicochemical parameters may vary within the range of 25-65 °C, 3.9-14 (pH), 90.7-5,980 mg/l (total dissolved solids, TDS), 0-7 mg/l (dissolved oxygen, DO), 41-2,430 mg O$_2$/l (chemical oxygen demand, COD), 10-786 mg/l (biochemical oxygen demand, BOD), 24.9-3.950 mg/l (total suspended solids, TSS) and 250-63,750 μS/cm (electrical conductivity, EC) [13]. The problem of dyeing wastewater treatment is very important, among others, due to high TDS values, the non-biodegradable character of dyes present in wastewater as well as to the presence of free chlorine and dissolved silica [17]. Conventional processes involving the chemical precipitation and subsequent coagulation and flocculation of precipitates are usually ineffective and should only be used as pre-treatment

Parameter	Unit	Value ± expanded uncertainty
pH	–	8.1±0.1
Conductivity	*μS/cm*	6250±313
Total Dissolved Solids	mg/l	5590±559
Total Suspended Solids	mg/l	865±87
Chloride	mg/l	480±48
Sulphate	mg/l	356±36
BOD$_5$	mg O$_2$/l	430±65
COD	mg O$_2$/l	1920±288
TOC	mg/l	590±89
Toxicity (*Aliivibrio fischeri*)	% of toxicity effect	99
Toxicity (*Brachionus plicatilis*)	% of mortality	100

Table 1.b. Toxicological parameters of treated textile wastewater.

Parameter	Unit	Value
Toxicity (*Aliivibrio fischeri*)	% of toxicity effect	66 (after 15 min. exposure time)
Toxicity (*Brachionus plicatilis*)	% of mortality	15 (after 15 min. exposure time)
		25 (after 30 min. exposure time)
		55 (after 45 min. exposure time)

processes. As a result of their use, the impurities present in the liquid phase (wastewater) are transferred to the precipitate, without the possibility of oxidation (degradation) of dyes and organic compounds contained in the wastewater. Moreover, an additional problem is the storage or processing of deposits that contain substances potentially dangerous to the natural environment. In the subject literature there is a prevailing view that the methods and chemicals used for wastewater treatment should be characterised not only by high efficiency in removing pollutants, but they should also be environmentally friendly and implement the principles of 'green chemistry'. This concept is very well suited to the use of potassium ferrate(VI) (K$_2$FeO$_4$), which is an 'environmentally friendly oxidant', and its use in wastewater technology is related to its ability to efficiently oxidise many organic pollutants while producing non-toxic Fe(OH)$_3$ [18]. The oxidising agent is, which contains Fe(VI) ion, characterised by a stronger oxidising action in an acidic (2.20 V) rather than alkaline (0.72 V) [19] environment as well as by the simultaneous reduction of Fe(VI) to Fe(III) and precipitation of Fe(OH)$_3$ with coagulant activity. K$_2$FeO$_4$ is characterised by unique properties unlike those of any other chemicals used in wastewater treatment. Conducting the process in an acidic environment causes that, depending on the pH, some Fe(III) ions (at higher pH values) may precipitate in the form of Fe(OH)$_3$ and some (at lower pH values) remain in the aqueous environment in the form of hydrated Fe[(H$_2$O)$_6$]$^{3+}$ cat-

ion, which can be used as a substrate for a Fenton-like reaction. In the case of the classic Fenton reaction, Fe(II) ions are used, which in an acidic environment enable the catalytic decomposition of H$_2$O$_2$ and the formation of •OH radicals. In order to produce •OH radicals, it is also possible to use Fe(III) ions, according to *Equations (1)* and *(2)*:

$$Fe^{3+} + H_2O_2 \rightarrow HO_2^{\bullet} + Fe^{2+} + H^+ \quad (1)$$

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

The reaction rate (•OH formation) with Fe(III) ions (Fenton-like reaction) is lower than when using Fe(II) ions, because it is limited by the rate of Fe(II) ion production according to reaction (1) [20-21]. The application of the Fenton reaction after the oxidation process with K$_2$FeO$_4$ allows the use of Fe(III) ions present in the reaction solution (due to K$_2$FeO$_4$ decomposition in the oxidation-reduction process) to produce •OH in the reaction with H$_2$O$_2$ as a result of the Fenton-like reaction. It enables more effective oxidation of organic impurities (owing to two stages of oxidation). The aim of the research presented was to select the most favourable purification conditions (maximum reduction of COD) of actual dyeing wastewater using K$_2$FeO$_4$ (pH, reaction time, K$_2$FeO$_4$ concentration) and H$_2$O$_2$ (pH, reaction time, H$_2$O$_2$ concentration). For the treated wastewater, after application of the combined process K$_2$FeO$_4$ and Fe(III)/H$_2$O$_2$, for which the greatest decrease in COD was obtained, toxicity was tested in relation to *Aliivibrio fischeri* and *Brachionus plicatilis*.

Materials

The tests used technical K$_2$FeO$_4$ (Envifer®, Nano Iron, s.r.o., Czech Republic), which contained 40% of pure K$_2$FeO$_4$ and 30% H$_2$O$_2$ (Sigma-Aldrich, Germany). For pH correction, solutions of NaOH and H$_2$SO$_4$ at concentrations of 25% were used. As a flocculant, 0.05% Furoflock CW277 solution (Chemische Fabrik Wocklum GmbH & Co. KG, Germany) was used. Solid MnO$_2$ (Sigma – Aldrich, Germany) was utilised to remove the remaining H$_2$O$_2$. Chemical reagents of analytical purity and distilled water were used in the tests. Wastewater utilised in the research came from a production plant located in Eastern Europe. Values of selected physicochemical and toxicological parameters of the industrial wastewater are presented in *Table 1.a*.

Analytical methods

The pH value was determined using an Inolab® pH/Ion/Cond 750 and SenTix® 81 electrode (WTW, Germany) [22]. The content of K$_2$FeO$_4$ in Envifer by 505 nm was determined using a UV-VIS spectrophotometer (Cary® 50 UV-VIS, Varian Inc., Australia) [23]. The COD value after removing the excess of H$_2$O$_2$ by means of solid MnO$_2$ was determined by the standard dichromate method using a Nanocolor® 500D spectrophotometer (Macherey-Nagel, Germany) [24]. The content of H$_2$O$_2$ in samples of purified wastewater was determined by the manganometric method after filtering the sample through a syringe membrane filter (0.45μm) [25]. Wastewater toxicity before and after the reaction was tested according to the Microtox® Omni screening test procedure (Microtox® M500, Modern Water PLC, United Kingdom) [26]. The test result was expressed as a percentage of bioluminescence inhibition resulting from the inhibition of metabolic processes of indicator organisms subjected to 15 min. exposure to the wastewater sample, relative to the control test. A 2% NaCl solution was used as a control test. Toxicity against *Brachionus plicatilis* was tested in accordance with [27-28] using neonates of *Rotifer B. plicatilis* due to the relatively high conductivity of real wastewater (6,250±313 μS/cm). Although the *Aliivibrio fischeri* test is the standard procedure, *Brachionus plicatilis* is also used for model tests in ecology and toxicology. 20 ml of the wastewater was diluted with 200 ml of synthetic seawater containing 20 neonates of *Rotifer*

Table 2. *Plan of experiment.* **Note:** * the Envifer dose for pure K_2FeO_4 was calculated, ** centre of plan, *** after 30 min. oxidation by using K_2FeO_4, **** after 30 min. oxidation using K_2FeO_4 and 30 min. oxidation using $Fe(III)/H_2O_2$.

Run	Experiment conditions			Experiment results (value ± expanded uncertainty)				
	pH	K_2FeO_4, g/l	H_2O_2, g/l	CODI***, g O_2/l	% removal of CODI	CODII****, g O_2/L	% removal of CODII	% increase in COD removal
1	3.00	0.075	1.000	1.280±0.192	37.1	1.150±0.173	40.1	3
2	3.00	0.075	3.000	1.220±0.183	36.5	0.980±0.147	49.0	12.5
3	3.00	0.275	1.000	0.990±0.149	48.4	0.960±0.144	50.0	1.6
4	3.00	0.275	3.000	0.930±0.140	51.6	0.840±0.126	56.3	4.7
5	6.00	0.075	1.000	1.375±0.206	28.4	1.340±0.201	30.2	1.8
6	6.00	0.075	3.000	1.390±0.209	27.6	1.310±0.197	31.8	4.2
7	6.00	0.275	1.000	0.990±0.149	48.4	0.980±0.147	49.0	0.6
8	6.00	0.275	3.000	1.020±0.153	46.9	0.950±0.143	50.5	3.6
9	2.00	0.175	2.000	1.710±0.257	10.9	1.700±0.255	11.5	0.6
10	7.00	0.175	2.000	1.770±0.266	7.8	1.760±0.264	8.3	1.3
11	4.50	0.007	2.000	1.865±0.269	2.9	1.710±0.257	10.9	8.0
12	4.50	0.343	2.000	0.440±0.066	77.1	0.320±0.048	83.3	6.2
13	4.50	0.175	0.318	0.810±0.122	57.8	0.800±0.120	58.3	0.5
14	4.50	0.175	3.682	0.795±0.119	58.6	0.610±0.092	68.2	9.6
15(C)**	4.50	0.175	2.000	0.790±0.119	58.9	0.510±0.077	73.4	14.5
16 (C)**	4.50	0.175	2.000	0.785±0.118	59.1	0.520±0.078	72.9	13.8

B. plicatilis in each millilitre. The control sample contained, instead of the test sample, 20 ml of synthetic seawater. After an incubation time of 15, 30 and 45 min, the number of viable and dead organisms in 1 ml of culture was calculated using an Eclipse E200-LED trinocular microscope (Nikon Instruments Europe B.V., Netherlands). The result was calculated as a percentage of mortality.

Experimental procedure

The tests were carried out at a constant temperature of 20±1 °C, in beakers containing 500±2.5 ml of the wastewater examined, which was mixed with a magnetic stirrer at a constant speed (250 rpm, MS11, Wigo, Poland). A sample of Envifer® (K_2FeO_4) was added to a measured wastewater sample, the pH adjusted with 25% H_2SO_4 to a certain value, and the reaction was continued for a specified time (oxidation by using K_2FeO_4). After this time, a given amount of 30% H_2O_2 was added, and mixing was continued for the prescribed time. After completion of the oxidation (oxidation by using K_2FeO_4 and $Fe(III)/H_2O_2$), the pH was adjusted to 7-7.5 to precipitate Fe(III). 1 ml of 0.05% Furoflock CW277 solution was added and only stirred to precipitate the sediment. Determination of COD values was carried out after oxidation with only K_2FeO_4 (designated as COD I) and after oxidation with K_2FeO_4 and $Fe(III)/H_2O_2$ (designated as COD II). The removal of excess H_2O_2 by means of solid MnO_2 was applied only after the $Fe(III)/H_2O_2$ process. Optimisation of the COD removal

process was carried out using Response Surface Methodology (RSM) and Statistica 13 software (Tibco Software Inc., USA). The statistical analysis was influenced by the reaction time, the pH of the environment, and by the concentrations of K_2FeO_4 and H_2O_2 in the COD value of the dyeing wastes tested. Selection of the range of independent variables was made on the basis of the results of studies of other authors regarding the oxidation of pollutants in textile wastewater using K_2FeO_4 and Fenton's reagent [29-30]. The stirring speed (250 rpm), reaction time (30 min for each oxidation step), and temperature (20±1 °C) were adopted as constant values. As independent variables, pH (3-6), K_2FeO_4 (0.075-0.275 g/l) and H_2O_2 (1-3 g/l) concentrations were assumed. As a result of experimental planning, a research plan was obtained consisting of 16 experiments (two in the centre of the plan) for 3 independent factors (**Table 2**). The results of experimental investigations are presented in graphs of the response surface, which enabled a precise analysis of the influence of the independent variables studied (pH, K_2FeO_4 and H_2O_2 concentrations) on the value of the dependent variable (COD). For the most favourable values of the process parameters determined, a verification experiment was carried out, after which the toxicity of the treated wastewater (after neutralisation to pH 7-7.5 and removal of H_2O_2) was tested using *Aliivibrio fischeri* and *Brachionus plicatilis*. All experiments were performed three times, and the results presented are an arithmetic mean.

Results and discussion

Determination of the K_2FeO_4 content in the commercial product (Envifer®) was performed by the spectrophotometric method and the test results obtained showed that it contained 40% pure K_2FeO_4, which was used to convert Envifer® doses into the pure K_2FeO_4 utilised in the study. The actual dye wastewaters used in the tests (**Table 1**) were characterised by a slightly alkaline reaction (8.1±0.1), large values of electrical conductivity (6,250±313 μS/cm) and by a significant content of dissolved substances (5,590±559 mg/l). In addition, the TOC and COD values in raw wastewater (590±89 mg O_2/l and 1920±288 mg/l) determined indicated a significant content of organic compounds in the wastewater analysed. Other authors obtained similar results for pH (3.9-14), COD (41-2,430 mgO$_2$/l) and EC (250-63,750 μS/cm) [13]. Other test results (for average values of 10 wastewater samples) indicate a similar pH value (8.5) and sulphate concentration (412 mg/l) but increased chloride concentration (846 mg/l) [31]. The toxicity values were 99 and 100% (for *Aliivibrio fischeri* and *Brachionus plicatilis*, respectively). Wastewater treatment was carried out in the first stage using K_2FeO_4 and in the second stage with the K_2FeO_4 and $Fe(III)/H_2O_2$ process. The oxidation time in both cases was 30 minutes, and tests were carried out in accordance with the experiment schedule presented in **Table 2**. A plan of 16 experiments was devised for three input factors (pH, K_2FeO_4, H_2O_2) whose implementation enabled

Table 3. *Analysis of the experiment with the central composite design using Statistica 13 – sheet of estimator effects ANOVA.* **Note:** *L-linear effect, Q-quadratic effect, *parameter is statistically significant for p<0,05, p-probability value.*

| Parameter	Evaluation of effects: COD II, g O_2/L, R^2 = 0.8799, R^2_{adj} = 0.7999 3 parameter, 1 block, 16 experiments & MS=0.0393								
	Effect	Standard error	p-value*	-95% confidence intervals	+95% confidence intervals	Factor	Standard error of factor	95% confidence intervals	+95% confidence intervals
Constant value	0.5272	0.1398	0.0044	0.2109	0.8435	0.5272	0.1398	0.2109	0.8435
pH (L)	0.1100	0.1073	0.3323	-0.1328	0.3528	0.0550	0.0537	-0.0664	0.1764
pH (Q)	0.8008	0.1303	0.0002	0.5061	1.0955	0.4004	0.0651	0.2530	0.5478
K_2FeO_4 (L)	-0.4962	0.1074	0.0013	-0.7391	-0.2533	-0.2481	0.0537	-0.3695	-0.1266
K_2FeO_4 (Q)	0.2957	0.1305	0.0497	0.0005	0.5910	0.1479	0.0653	0.0002	0.2955
H_2O_2 (L)	-0.0981	0.1073	0.3848	-0.3408	0.1447	-0.0490	0.0537	-0.1704	0.0724
H_2O_2 (Q)	0.0760	0.1303	0.5740	-0.2187	0.3707	0.0380	0.0651	-0.1094	0.1854

the determination of baseline values (CODI and CODII) for each experiment. These were carried out after the first and second oxidation stage, respectively. The use of K_2FeO_4 to remove COD from the treated wastewater resulted in obtaining purified wastewater characterised by a reduced content of organic compounds. The smallest value of CODI (in treated wastewater) was obtained in experiment 12 (440 mg O_2/l), while the highest in experiment 11 (1.865 mg O_2/l), which corresponded to a decrease in the COD value in relation to the initial value (1.920 mg O_2/l) of 77.1% and 2.9%, respectively. The percentage reduction in the COD value after the first oxidation step using K_2FeO_4 thus varied from 2.9-77.1%. Analysis of the results presented in **Table 2** indicates that higher percentages of COD removal were obtained for wastewater using a higher dose of K_2FeO_4 at the same pH value (experiments 1-4). When the same dose of K_2FeO_4 (0.275 g/l) and process run at different pH values (3 and 6) were used, similar or slightly better results were obtained for the treated wastewater at lower pH (experiments 3, 4, 7 and 8). If extreme pH values were used, i.e. 2 and 7 (experiments 9, 10) and an identical K_2FeO_4 dose (0.175 g/l), the decrease in COD was low, amounting to 10.9 and 7.8%, respectively. Other researchers observed similar tendencies. At the optimal dose of K_2FeO_4, the largest decrease in the COD value of the wastewater tested was observed at pH ca. 4.5. At the same time, a decrease in process efficiency was observed for extreme values (pH 3 and 6) [29]. In the second stage of the research, the process of oxidation of organic compounds in wastewater was continued with the use of •OH radicals resulting from the reaction of Fe(III) ions present in the wastewater with the addition of H_2O_2. In this case, the smallest percentage decrease in COD (relative to the ini-

tial value) was obtained in experiments 10, 11 and 9 (8.3, 10.9 and 11.5%, respectively), whereas the highest was in experiments 12, 15 and 16 (83.3, 73.4 & 72.9%, respectively). In the case of experiment 11, the use of a very small dose of K_2FeO_4 (0.007 g/l) in the first stage resulted in the presence of a small amount of Fe(III) ions in the treated wastewater. In light of the above, it should be assumed that the amount of •OH radicals formed was also negligible after the addition of H_2O_2. In spite of this, a decrease in the COD value of 10.9% was observed in this case after the second stage. Therefore it is probable that in the case of the wastewater under investigation, the decrease in COD was caused by the use of a strong oxidiser (K_2FeO_4), the action of Fe(III) with H_2O_2 •OH radicals and probably, to some extent, by that of H_2O_2 itself. It cannot be ruled out that oxidising compounds were present in the wastewater under the influence of the weak oxidant, which is H_2O_2 (at a concentration of 2 g/l). It is clear that the Fe(III) ions present in the wastewater after the K_2FeO_4 oxidation process may have some minor function in removing the colour and contaminants from it. In addition, Fe(II) ions were immediately oxidised to Fe(III) ions due to the formation of free radicals (•OH). It seems that in this case the importance of Fe(II) ions in removing colours and contaminants is negligible. The efficiency of COD removal from wastewater is the result of oxidation and, to a small extent, the coagulation (Fe(III)) processes. **Table 3** presents the values of ANOVA estimators for normalised values of the input quantities (pH, K_2FeO_4, H_2O_2). The statistical analysis carried out indicated that the value of CODII (treated wastewater from the second stage) is mainly influenced by 3 statistically significant parameters (p<0.05), i.e. pH, K_2FeO_4 (L) and K_2FeO_4 (Q). From the statistical point of view, H_2O_2

concentration (L and Q) was defined as a non-significant parameter (p > 0.05). Values of the determination coefficient (R^2) and improved determination coefficient (R^2_{adj}), which are a measure of the quality of model fit to experimental values, were 0.8799 and 0.7999, respectively, which indicated a good fit of the model to experimental values. In addition, the value of the mean square error was also small (MS = 0.0393). Results of verification of the adequacy of model coefficients were obtained out using ANOVA. The verification performed confirmed the significance of the three main input parameters, as shown in the Pareto chart (**Figure 1**). Estimators of standardised effects were grouped according to their absolute value, and the vertical line marked minimal values of the statistically significant effects, at a significance level of p = 0.05. From the statistical point of view, the CODII value of the treated wastewater, and thus the combined efficiency of the combined oxidation processes, was influenced mostly by pH (Q), K_2FeO_4 (L) and K_2FeO_4 (Q), while to the smallest extent by H_2O_2 (L) and H_2O_2 (Q). In addition, the relationship between the values observed and estimated, shown in **Figure 2**, indicates the correlation of both types of parameters. **Figure 3.a** shows the dependence of the initial value (CODII) on the pH and concentration of K_2FeO_4. Model studies have shown that the lowest CODII values (<0.5 g O_2/l), assuming a constant value for H_2O_2 (2 g/l), can be obtained in the pH range 3.75-5 at a concentration of K_2FeO_4 in the range of 0.18-0.33 g/l. If a constant value for K_2FeO_4 (0.175 g/l) was assumed, the smallest CODII values (<0.6 g O_2/l, **Figure 3.b**) were obtained for a pH value in the range 3.75-5.2 at an H_2O_2 concentration in the range 1.1-4.2 g/l. In this case, the condition for obtaining purified wastewater with a low CODII value is the course of the process
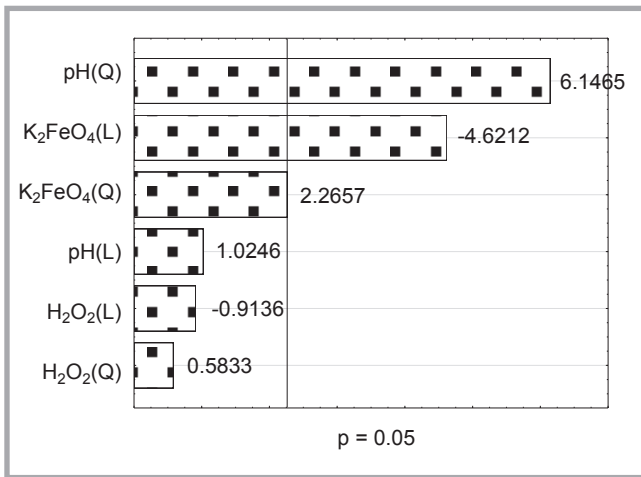
Figure 1. *Pareto chart – absolute value of standardised assessment of effects (COD II, g O₂/l, 3 value, 1 block, 16 experiments, MS = 0.0393, L-linear effect, Q-quadratic effect).*
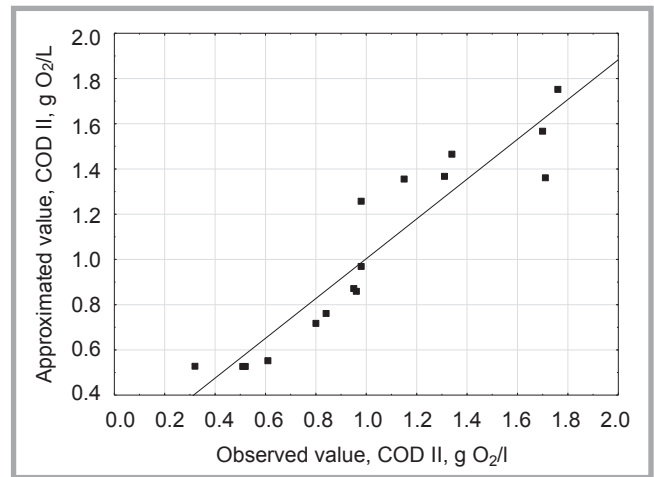
Figure 2. *Estimated vs. observed value plots (COD II, g O₂/l, 3 value, 1 block, 16 experiments, MS = 0.0393).*
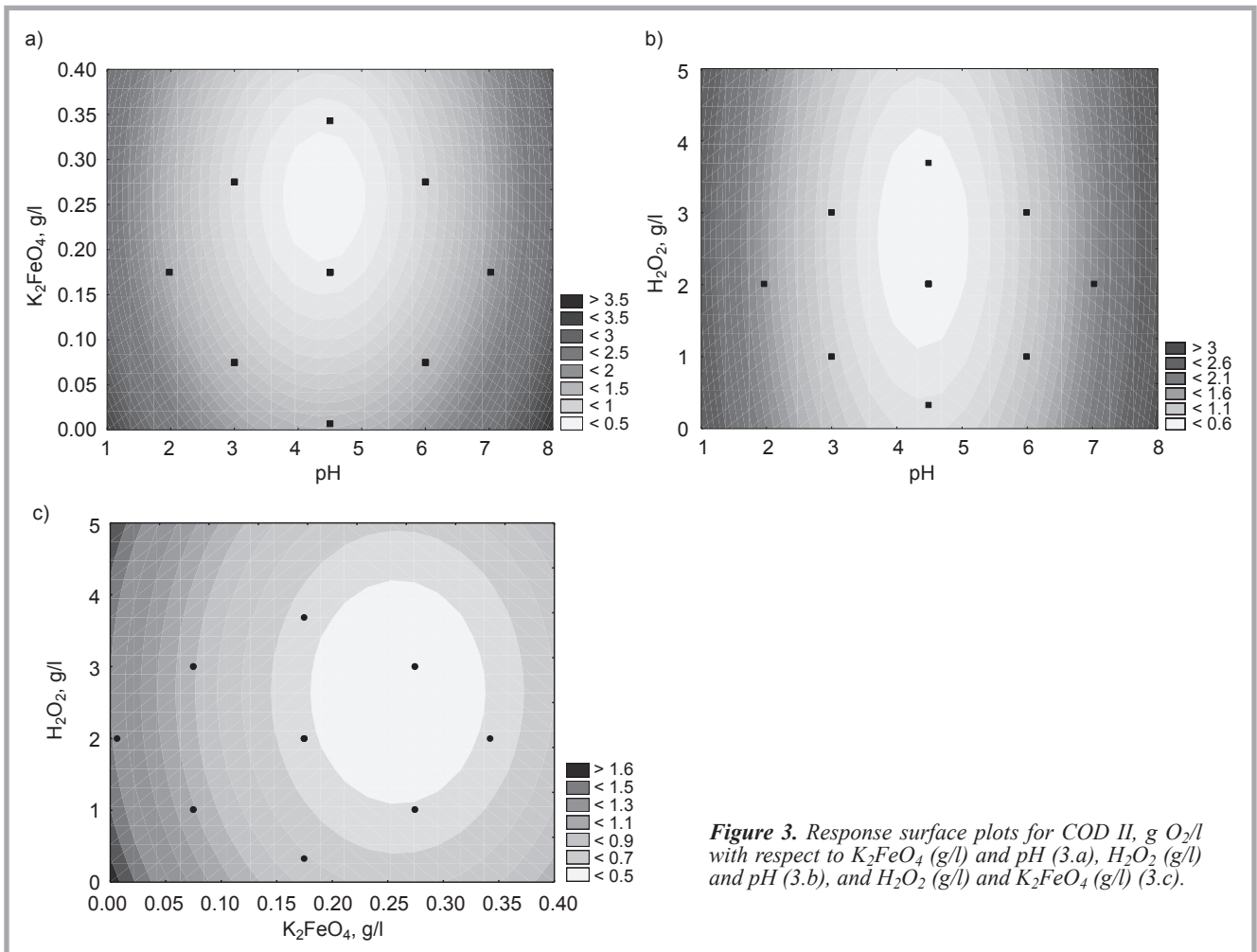

Figure 3. *Response surface plots for COD II, g O₂/l with respect to K₂FeO₄ (g/l) and pH (3.a), H₂O₂ (g/l) and pH (3.b), and H₂O₂ (g/l) and K₂FeO₄ (g/l) (3.c).*

with small changes in pH (3.75-5.2), while H_2O_2 concentrations for which CODII values are smaller than 0.6 g O₂/l may vary within quite wide limits. Model tests showed that H_2O_2 is not a significant parameter in the case of the treated wastewater (**Figure 1**), and therefore an optimal effect is possible over a wide range of concentrations (**Figure 3.b**). **Figure 3.c** shows the dependence of CO-DII values on K_2FeO_4 and H_2O_2 concentrations at a constant pH of 4.5. In the case analysed, model tests showed that obtaining wastewater with a CODII value of <0.5 g O₂/l is possible at concentrations of K_2FeO_4 and H_2O_2 in the range of 0.17-0.34 and 1.1 to 4.2 g/l, respectively. For critical values of particular parameters calculated from the model (pH 4.40, K_2FeO_4 0.259 g/l and H_2O_2 2.65 g/l), the minimum value for CODII approximated on the basis of the model was 0.405 g O₂/l. In order to conduct experimental verification of the model, three experi-
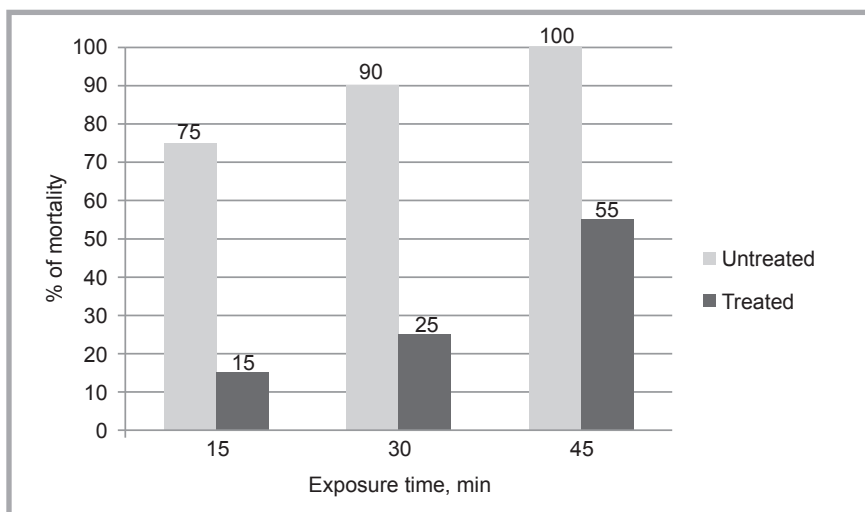
Figure 4. *Toxicity of untreated and treated (K_2FeO_4 and $Fe(III)/H_2O_2$) wastewater (% of mortality of Brachionus plicatilis after 15, 30 and 45 min. exposure time).*

Table 4. *Analysis of the experiment with the central composite design using Statistica 13 – verification of the adequacy of the model using ANOVA.* **Note:** *L – linear effect, Q – quadratic effect, SS – predicted residual error of sum of squares, MS – mean square error, F – statistics, p – probability value.*

Entrance	Evaluation of effects: COD II, g O_2/L, R^2 = 0.8799, R^2_{adj} = 0.7999 3 parameter, 1 block, 16 experiments & MS=0.0393			
	SS	MS	F	p
pH (L)	0.0413	0.0413	1.0498	0.3323
pH (Q)	1.4858	1.4858	37.7796	0.0002
K_2FeO_4 (L)	0.8398	0.8398	21.3551	0.0013
K_2FeO_4 (Q)	0.2019	0.2019	5.1334	0.0497
H_2O_2 (L)	0.0328	0.0328	0.8346	0.3848
H_2O_2 (Q)	0.0134	0.0134	0.3403	0.5740
Error	0.3539	0.0393	–	–

ments were carried out using the critical values of input parameters indicated, obtaining an average value for CODII = 0.472±0.071 g O_2/l. Taking into account the uncertainty of COD determination (±15%), the experimental value obtained (CODII) corresponds to the value calculated from the model (0.405±0.061 and 0.472±0.071 g O_2/l, respectively). In the research presented, the decrease in COD was 75.4%. Other researchers using conventional activated sludge (CAS), followed by effluent polishing with a sand filter and activated carbon observed less efficiency (81.6%) [31].

Wastewater toxicity

The toxicity of the treated wastewater obtained in verification experiments was tested using *Aliivibrio fischeri* and *Brachionus plicatilis*. The tests carried out showed that the combination of chemical oxidation methods (K_2FeO_4 i $Fe(III)/H_2O_2$) used in the treatment of dyeing wastewater, under optimal conditions determined using RSM, caused a reduction in the toxic effect in relation to *Aliivibrio fischeri* to 66%, as compared to the initial value for raw wastewater of 99% (**Table 1.b**). Tests with *Brachionus plicatilis* (**Figure 4**) showed that the raw wastewater was characterised by high toxicity relative to the test organism used, which increased as a result of lengthening the exposure time (15, 30 and 45 min), being 75, 90 and 100%, respectively. In the case of treated wastewater, the use of two methods of chemical oxidation (K_2FeO_4 and $Fe(III)/H_2O_2$) resulted in an expected reduction in toxicity to 15, 25 and 55%, respectively (**Figure 4**). The degree of toxicity reduction determined using both methods (by 33% for *Aliivibrio fischeri* and 45% for *Brachionus plicatilis*) may be related to the formation of intermediate oxidation products of pollutants present in the wastewater, which are also characterised by some toxicity, albeit less than in the starting substances. Research into Direct Blue 86 oxidation and the toxicity of oxidation products allowed to obtain better results in the context of the reduction of wastewater toxicity (reduc-

tion of toxicity from 80 to 20%, as compared to *Brachionus plicatilis*). However, in this case, studies were carried out with a 100 mg/l dye solution in distilled water [27]. Based on the toxicity tests conducted using *Aliivibrio fischeri* according to the standardised method [26], raw wastewater should be classified as highly toxic (range 75.1-100% of the toxic effect), whereas the treated wastewater obtained – as toxic (range 50.1-75% of the toxic effect) [32].

Conclusions

The paper presents the results of using two methods of advanced chemical oxidation (K_2FeO_4 and $Fe(III)/H_2O_2$) for the treatment of real dyeing wastewater. The use of the RSM method to plan and optimise the purification process made it possible to determine optimal conditions (pH 4.40, K_2FeO_4 0.259 g/l and H_2O_2 2.65 g/l) of the process for which a decrease in COD from 1.920±0.288 to 0.472±0.071 g O_2/l was obtained (the value forecasted from the model was 0.405±0.061 g O_2/l). For wastewater treated under optimal process conditions, for which the COD reduction was 75.4%, a reduction in wastewater toxicity of 33% for *Aliivibrio fischeri* and 45% for *Brachionus plicatilis* were noted. The possibility of the formation of intermediate products with reduced toxicity in treated wastewater as compared to those present in untreated wastewater was found due to the chemical oxidation processes. Moreover the use of these oxidation methods has made it possible to reduce the class of wastewater toxicity and to reduce the amount of organic compounds in wastewater.

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