Simona Kliś[1], Maciej Thomas[2,*], Krzysztof Barbusiński[3], Klaudiusz Gołombek[4], Łukasz Krzemiński[4], Marek Chyc[5]

Removal of Azo Dye Acid Red 27 from Aqueous Solutions Using Classical and Modified Fenton Reagent with Zero-Valent Iron

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[1] Central Mining Institute,
Plac Gwarków 1, 40-166 Katowice, Poland

[2] Chemiqua Company,
ul. Skawińska 25/1, 31-066 Kraków, Poland,
* e-mail: biuro@chemiqua.pl

[3] Silesian University of Technology, Institute of Water and Wastewater Engineering,
ul. Konarskiego 18, 44-100 Gliwice, Poland

[4] Silesian University of Technology, Institute of Engineering Materials and Biomaterials,
ul. Konarskiego 18a, 44-100 Gliwice, Poland

[5] State Higher Vocational School in Tarnów, Institute of Mathematical and Natural Sciences,
ul. Mickiewicza 8, 33-100 Tarnów, Poland

Abstract
The article compares the classic Fenton reagent (Fe^{2+}/H_2O_2) with its modification with zero-valent iron (ZVI/H_2O_2) to remove azo dye Acid Red 27 from aqueous solutions at a concentration of 100 mg/l. For both methods, the most favorable parameter values were determined at which visual discoloration of the solutions tested was obtained (for Fe^{2+}/H_2O_2: pH = 3.5, H_2O_2 = 60 mg/l, Fe^{2+}/H_2O_2 = 0.3, t = 15 min, and for ZVI/H_2O_2: pH = 3, H_2O_2 = 40 mg/l, ZVI = 80 mg/l, t = 15 min). Under these conditions, the COD value was reduced by 71.5% and 69.2% for the classic Fenton and its modification, respectively. A reduction in toxicity was also obtained for Aliivibrio fischeri bacteria to below 25% by using the Microtox test. ZVI digestion at acidic pH for 10 minutes allowed to shorten the reaction time by about four times – from 15 to 4 minutes. BET analysis showed that the specific surface area increases with the digestion time, which significantly accelerates the reaction. The visual discoloration of aqueous solutions was obtained, and the final COD values were very small, ranging from 49-53 mg O_2/l. According to the Aliivibrio fischeri toxicity classification test for water samples, all solutions of dyes tested can be considered as non-toxic (toxicity value <25%). In the study presented, results of decreasing the COD value and concentration of the dye in the ZVI/H_2O_2 method obtained are slightly worse compared to the Fe^{2+}/H_2O_2 method. However, taking the decolouration time as a criterion, a four times faster decolouration time was obtained in the ZVI/H_2O_2 method, compared to the Fe^{2+}/H_2O_2 method.

Key words: *Acid Red 27, Fenton reagent, modified Fenton reagent, Zero-Valent Iron, wastewater treatment.*

Introduction

Synthetic dyes, due to the possibility of their large quantity production by chemical synthesis, their chemical stability and wide range of colours, are characterised by versatile application. Most of their global production is used in the textile industry for dyeing textiles, which is associated with the production of a significant amount of industrial wastewater. For example, azo dye Acid Red 27 is used for dyeing wool, silk, and leather, it is also used in the food and photographic industry. As estimated, approx. 280 000 tonnes of coloured wastewater are produced annually in the textile industry [1]. These wastewaters, insufficiently purified when entering water ecosystems, may contribute to the reduction of light transmission, which, in consequence, affects the course of photosynthesis and results in an increased oxygen deficit in water [2]. In addition, textile wastewater is characterised by a high content of organic compounds of different chemical structure, and in consequence of the different toxicological properties, they cause mutagenic or carcinogenic properties in these wastewaters [3]. For these reasons, despite the fact that the use of toxic compounds is limited to the production and processing of textiles, more and more attention is being paid to the use of effective methods of wastewater treatment. Unfortunately, conventional methods are not always effective in removing this type of wastewater. For example, biological methods allow for a high degree of dye removal from wastewater. On the other hand, organisms used in biological methods are susceptible to the temperature of sewage, the impact of heavy metals or residual dyes present in wastewater, and to the toxicity of wastewater, which causes a decrease in the efficiency of the methods used. In addition, a very long reaction time is needed for dye decolouration. The Advanced Oxidation Processes (AOPs), which enable the effective degradation of organic pollutants, as a result of generating hydroxyl radicals (•OH) with very strong oxidising activity, are one of the increasingly high-quality industrial wastewater treatment methods. In addition, these radicals may contribute to the inactivation of pathogenic microorganisms and parasites as well as reduce the toxicity of wastewater in the biological aspect [4]. Due to the simple technological solutions, the wide availability of reagents and high efficiency, the most frequently used processes involve the Fenton reagent (Fe^{2+}/H_2O_2) in an acidic

environment. The oxidation process with the Fenton reagent allows to achieve the full mineralisation of organic compounds (decomposition to CO_2 and H_2O), while the process of incomplete oxidation usually leads to the decomposition of pollutants into simpler compounds with a lower molecular weight and toxicity than the initial substances [5, 6]. Currently, research is conducted not only with the use of alternative methods of pollutant oxidation in wastewater, but also well-known methods are modified (e.g Fenton's process). One of the research trends is the use of alternative sources of iron ions in the Fenton reaction. In this case, it indicates the possibility of using, among others, iron-containing zeolites (Fe-doped ZnO on a zeolite matrix) [7], metal nano oxides (Fe_3O_4-MnO_2) [8], steel swarfs [9] and nano iron [10,11]. A very promising and, at the same time, alternative source of iron(II) ions is zero-valent iron (ZVI), which in an acidic environment is digested with the formation of Fe(II) ions, which is a substrate in reaction with H_2O_2, resulting in the formation of hydroxyl radicals [11]. The main advantage of ZVI is that it is an alternative source of Fe(II) ions. A previous study on the decolouration of aqueous solutions of Acid Red 73 (AR73) with an initial concentration of 200 mg/l showed that the efficiency of dye removal increased (in the ranges studied) with an increase in the ZVI dose (0-0.4 mg/l), the amount of H_2O_2 (0-3 mM), the stirring speed (0-140 rpm) and temperature (20-40 °C), but decreased with an increase in pH. For the most favorable process conditions (H_2O_2 = 2 mM, pH = 3, 100 rpm, 20 °C, 30 min.), the final concentration of AR73 was 6.4 mg/l, which was associated with high removal efficiency (96.8%) [12]. Studies carried out for solutions of dyes belonging to different classes: azo dye (Reactive Brilliant Red K-2G-RBR), antraquinone dye (Reactive Brilliant Blue, KN-R-RBB) and triphenylmethane dye (Malachite Green-MG) showed that the pH value of the reaction had little effect on the efficiency of decolouration, with an increase in the ZVI dose resulting in a significant increase in decolorization efficiency while reducing the reaction time. In the most favorable process conditions and for different reaction times (pH = 2, ZVI = 2 g/l, dye concentration = 698 mg/l, reaction time 2 min.), the decolouration efficiency for RBR was 97.9%, for RBB 95.7% (pH = 4.2, ZVI = 2 g/l, dye concentration = 692 mg/l, 10 min), and for MG 99.2% (pH = 7, ZVI = 2 g/l, dye concentration = 686 mg/l, 30 min.) [13]. In the article presented, zero-valent iron (ZVI) was used for the decolouration of aqueous solutions of azo dye Acid Red 27 (AR27). The aim of the research was to determine the most favorable parameters for the classic and modified Fenton reagent (ZVI/H_2O_2) to obtain the decolouration of aqueous solutions of AR27 dye. In addition, for post-reaction solutions purified in the most favorable conditions of the process parameters determined, the efficiency of reducing COD and toxicity was analysed, as well as the surface area size, pore size distribution and size of unreacted ZVI.

Materials

ZVI was used for the tests, with an Fe content (based on a quality certificate) greater than 99.5% (Selkat, Poland), which contained particles with dimensions of 150-250 μm (12.2%), 45-150 μm (67.0%) and up to 45 μm (20.8%) as well as trace amounts of particles larger than 250 μm. In the research, aqueous solutions of Acid Red 27 (C.I. 16185, $C_{20}H_{14}N_2O_{10}S_3$, Acid Amaranth I, technical grade – the manufacturer does not give the content of pure dye in the commercial product due to trade secret, Boruta Zachem SA, Poland), $FeSO_4 \cdot 7H_2O$ and 30% H_2O_2 (Avantor Performance Materials, Poland) were used. For pH correction, 10% H_2SO_4 and NaOH solutions were used (Avantor Performance Materials, Poland), as well as MnO_2 (Sigma-Aldrich, Germany) of analytical grade to remove residual H_2O_2.

Conditions of experiments

To the reactors containing 500 ml of 100 mg/l AR27 solution, an appropriate amount of ZVI was added and mixed using a coagulator (JLT 6, VELP Scientifica, USA) at 400 rpm. The pH-value was then adjusted with 10% H_2SO_4 to the presumed value, an appropriate amount of 30% H_2O_2 added, and the reaction was carried out for the established time. In the next stage, 10% NaOH was added to adjust the pH to 9.5±0.1 to stop the reaction, precipitate the iron compounds and decompose the remaining H_2O_2. Samples were centrifuged (10 min., 3000 rpm) in a centrifuge (MPW 360, Precision Mechanics, Poland) and the concentration of H_2O_2 was determined in the supernatant. Residual H_2O_2 was removed with MnO_2 and the concentration of AR 27 determined. For the most favorable process conditions, the COD value and toxicity in the purified solutions were determined. Before the toxicity test, the samples were further neutralised to a pH of 7.0 ± 0.1 with 10% H_2SO_4. The effect of 4 parameters (H_2O_2 and ZVI concentration, pH value and reaction time) on the final concentration of AR27 was analysed in the most favourable process conditions. COD values and the toxicity of the purified solutions were determined. The following parameter ranges were adopted in the test: pH: 2-5, reaction time: 0-30 min., H_2O_2:20-100 mg/l and ZVI: 60-100 mg/l [14.15]. Similarly, tests were carried out for the classical Fenton reagent, using $FeSO_4 \cdot 7H_2O$ instead of ZVI. For reactors containing 500 ml of 100 mg/l AR27 solution, an appropriate amount of $FeSO_4 \cdot 7H_2O$ was added and mixed using a magnetic stirrer (MS06, ChemLand, Poland) at 400 rpm. The pH was then adjusted with 10% H_2SO_4 to the presumed value, an appropriate amount of 30% H_2O_2 added, and the reaction was carried out for the established time. Then scientists proceeded according to the ZVI/H_2O_2 method. The following ranges of parameters were accepted: pH: 2-5, reaction time: 0-30 min., H_2O_2:50-90 mg/l, and $FeSO_4 \cdot 7H_2O$: 5-25 mg/l.

Analytical methods

The pH-value was measured using a pH meter equipped with a combined pH electrode (CPC-502, Elmetron®, Poland) [16]. The concentration of AR27 was determined using a UV-VIS spectrophotometer (Nanocolor® Linus, Macherey Nagel, Germany) at a wavelength of λ = 520 nm. COD was determined by the dichromate method using sealed tubes by using a spectrophotometer, type PF-11 (Macherey Nagel, Germany) [17], the presence of residual H_2O_2 was determined by the manganometric method [18]. The residue H_2O_2, which in the post-reaction solutions would cause an overestimation of COD [19], was removed with a small excess of MnO_2. The toxicity of the aqueous solutions before and after the reaction was tested according to the MicrotoxOmni Screening Test procedure (Microtox Model 500, Modern Water, Poland) [20]. Indicator organisms were subjected to 15 min. exposure on samples, and the test result was expressed as a percentage of bioluminescence inhibition. The results were compared to a control sample (2% NaCl). ZVI morphology studies were performed using a scanning

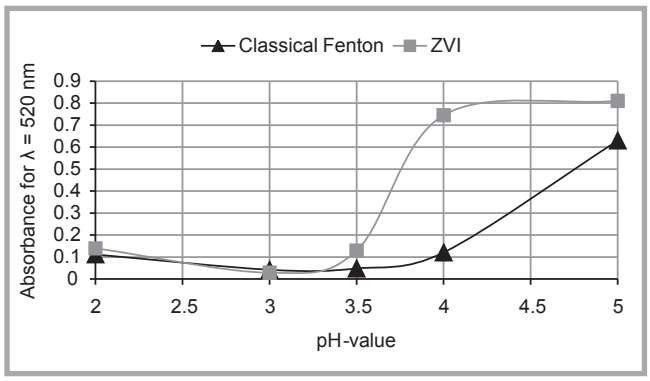

Figure 1. *AR27 dye solution absorbance as a function of pH.*

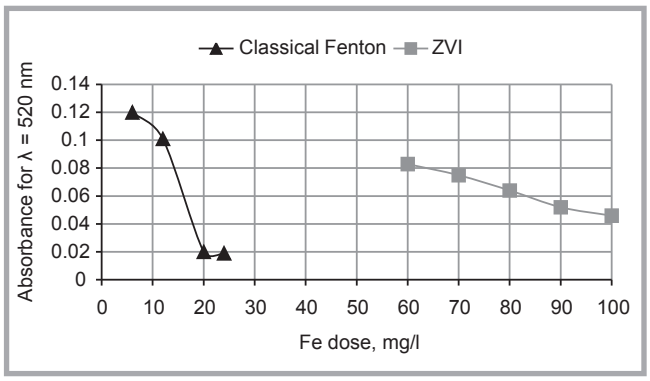

Figure 2. *AR27 dye solution absorbance as a function of Fe dose (mg/l).*

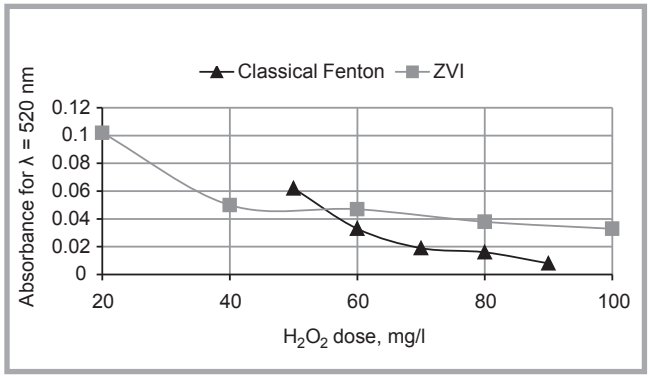

Figure 3. *AR27 dye solution absorbance as a function of H_2O_2 dose (mg/l).*

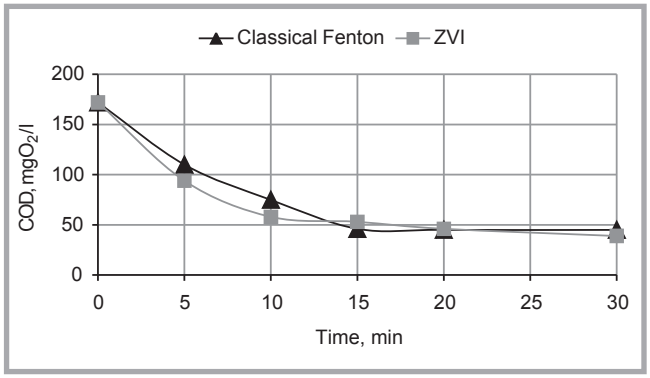

Figure 4. *COD values for AR27 dye solutions in the most favourable conditions (Fe^{2+}/H_2O_2 method: pH = 3,5, H_2O_2 = 60 mg/l, Fe^{2+}/H_2O_2 = 0,3, reaction time = 30 min. ZVI/H_2O_2 method: pH = 3, H_2O_2 = 40 mg/l, ZVI = 80 mg/l, reaction time = 30 min).*

electron microscope (SEM Supra 35, Zeiss, Germany), equipped with a scattered X-ray EDS detector and Schottsky emitter. For imaging of the surface topography of ZVI particles, a detector of backscattered electrons and secondary SE electrons at a 15-20 kV accelerating voltage was used. The surface properties of ZVI before and after digestion were also investigated using a surface analyser (Gemini VII 2390, Micromeritics, USA). Surface investigations were performed based on the analysis of BET isotherms and measuring the size and distribution of BJH pores using the low-temperature N_2 adsorption/desorption analysis method at 77K [21].

Results and discussion

The aqueous solution of 100 mg/l AR27 dye used in the study was characterised by pH = 7.2, COD = 172 mg O_2/l and the toxicity was 86%. In the test using *Aliivibrio fischeri* bacteria, according to the classification criterion of environmental samples adopted [22], it was marked as highly toxic. In the first stage of the tests (for the Fe^{2+}/H_2O_2 process), the most favourable pH value of the reaction was determined for an initial concentration of H_2O_2 = 60 mg/l, Fe^{2+}/H_2O_2 = 0.3 and reaction time of 15 min. (***Figure 1***). The most favourable pH values (within the pH range 2-5) for which the absorbance values were the lowest (0.042 and 0.048, respectively) were obtained for pH in the range of 3-3.5; however, without obtaining visual decolouration. Thus, for both pH values differences in the absorbance values determined were small, pH 3.5 was taken as the most favourable value for further studies, which was additionally associated with a lower consumption of H_2SO_4 for acidifying the solution. As the pH value increased, the absorbance values determined also increased in the range of 0.121-0.630. In the next stage, different Fe^{2+}/H_2O_2 ratios were tested. A ratio of 0.3 (corresponding to a concentration of 20 mg Fe^{2+}/l) was found to be the most advantageous value, at which the absorbance after 15 minutes of the oxidation process was 0.041 (concentration of the dye – 2 mg/l), which was associated with obtaining a visual decolouration of the solution (***Figure 2***). In addition, for lower values of the Fe^{2+}/H_2O_2 ratio (0.1 and 0.2, respectively), after 15 minutes no visual decolouration of the AR27 solution was obtained. In the next stage of the research, the most favourable dose of H_2O_2 was determined at constant values of the remaining parameters, i.e. pH = 3.5, Fe^{2+}/H_2O_2 = 0.3 and reaction time = 15 min. The effect of the H_2O_2 dose in the range of 50-90 mg/l on the effectiveness of decolouration was analysed. Studies showed that visual decolouration was obtained for a dose of H_2O_2 = 60 mg/l and higher; however, a dose of 60 mg/l was considered as the most favourable (***Figure 3***). On the basis of the tests conducted, the most favourable process conditions were finally adopted: pH = 3.5, H_2O_2 = 60 mg/l, Fe^{2+}/H_2O_2 = 0.3 and reaction time = 15 min. Under these conditions, the effectiveness of removing AR27 from the solution was 99.6%, while the decrease in the COD value was 71.5% (COD = 49 mg O_2/l). In the reaction time range of 15-30 minutes, no further decrease in COD values was noted (***Figure 4***). In addition, under the same conditions of the oxidation process, the toxicity of the samples was reduced to

0%. The results obtained in terms of the efficiency of removing the AR27 dye correspond with those by other authors for azo dye Reactive Black 5 and Disperse Red 343 (97.5% and 100%, respectively) [23, 24]. The results obtained for the classic Fenton reagent are shown in ***Table 1***. In the next stage of the research (for the ZVI/H_2O_2 process), a ZVI composition analysis (by the EDS method) was carried out, which showed that the commercial product contained 100% pure iron. Analysis of the morphology with the SEM method (***Figure 5***) revealed a fairly regular (homogeneous) surface structure of the ZVI under study, with a visibly large number of agglomerates (integrated particles) and a small number of pores. In the first stage, the most favourable pH value of the process was determined with the ZVI concentration = 100 mg/l, H_2O_2 = 60 mg/l and a reaction time of 15 min. (***Figure 1***). The lowest absorbance values were obtained at pH = 3, but without visual discolouration. When the pH value ranged from 3.5 to 5, the absorbance values also increased – from 0.130 to 0.811, and therefore pH = 3 was considered as the most favourable for further testing. Next, the effect of ZVI concentration on the decolouration effect was analysed with constant values of the remaining parameters, i.e.: pH = 3, H_2O_2 = 60 mg/l and thereaction time = 15 min. It was shown (***Figure 2***) that as the concentration of ZVI increased, in the range of 60-100 mg/l, the absorbance values decreased in the range of 0.083-0.046, respectively. For a ZVI dose = 80 mg/l after 15 minutes of reaction, a visual decolouration of the test solution AR27 was obtained. The ZVI concentration above was adopted for further studies. In the subsequent part of the experiments, the most favourable concentration of H_2O_2 was determined, enabling visual decolouration of the AR27 solution. A H_2O_2 concentration in the range of 20-100 mg/l was used, with constant values of the remaining reaction parameters, i.e. pH = 3, ZVI = 80 mg/l and the reaction time = 15 min. The results obtained (***Figure 3***) showed that with an increase in the H_2O_2 dose, the absorbance values decreased in the range of 0.102-0.033. After exceeding the threshold dose of 40 mg/l, visual discolouration was obtained, and only slight changes in absorbance were noted. Therefore, the dose above was considered the most beneficial. Then, based on the the most favorable conditions of the modified Fenton process finally determined

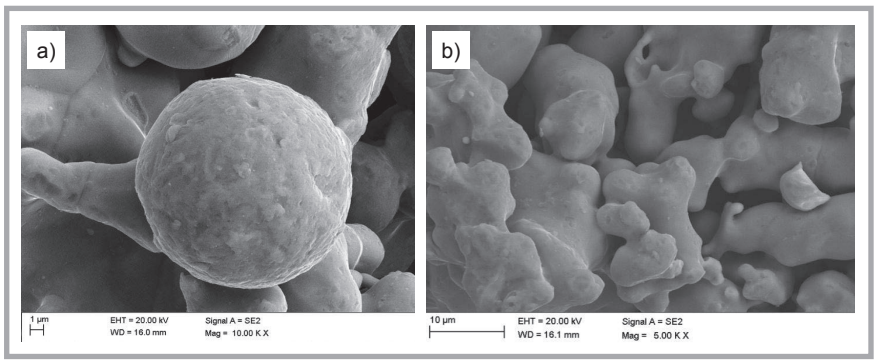

Figure 5. *SEM analysis of ZVI: a) 5000x, b) 10000x.*

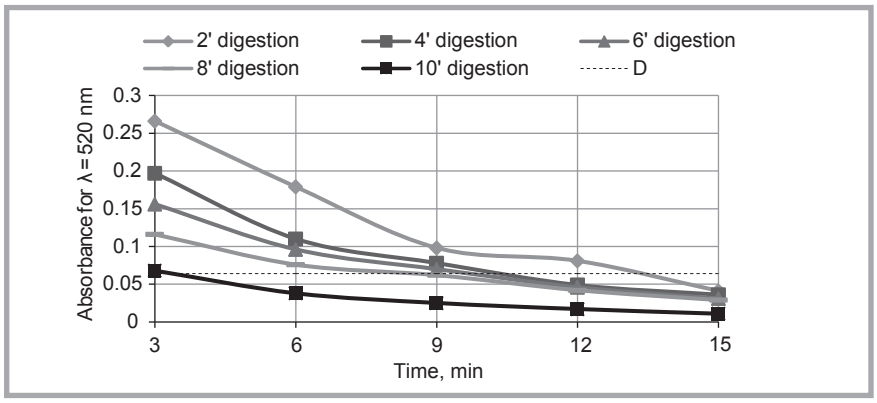

Figure 6. *AR27 dyes solution absorbance as a function of the time of ZVI digestion (pH = 3, H_2O_2 = 40 mg/l, ZVI = 80 mg/l, D – discolouration by absorbance = 0,064).*

(ZVI/H_2O_2), i.e. pH = 3, H_2O_2 = 40 mg/l, ZVI = 80 mg/l, changes in COD values were determined with the reaction time in the range of 0-30 min. (***Figure 4***). After 15 minutes of reaction, the COD value was reduced to 53 mg O_2/l, with an initial value of 172 mg O_2/l, which corresponded to a decrease in the COD value of 69.2%. In addition, under these conditions, the removal efficiency of AR27 was 99%. For the most favorable parameter values determined, the toxicity of post-reaction solutions was also established. It was shown that the use of both methods made it possible to reduce the toxicity of solutions to below 25%. In ***Table 1*** the test results obtained for both methods are summarised. Other authors (in the context of colour removal efficiency using ZVI and ultrasounds) obtained a high decolourisation efficiency (91.2%) for Direct Blue 71 azo dye. In the study, a concentration of DB71 = 50 mg/l, a ZVI dose = 0.3 g/l, pH = 2.5, reaction time = 20 minutes, and ultrasonic power = 95 W were used [25].

Table 1. *Comparison of most favorable oxidation conditions and effects obtained for AR27 using Fe^{2+}/H_2O_2 and ZVI/H_2O_2 processes.*

Parameter \ Method	Fe^{2+}/H_2O_2	ZVI/H_2O_2
pH	3.5	3
Reaction time, min.	15	15
ZVI concentration Fe^{2+}/H_2O_2; (Fe^{2+}), mg/l	– 0.3; (20)	80 –
H_2O_2 concentration, mg/l	60	40
Initial concentration of dye, mg/l	100	100
Final concentration of dye, mg/l	0.4	1.0
% of dye removal	99.6	99.0
Initial COD value, mg O_2/l	172	172
Final COD value, mg O_2/l	49	53
% of COD value reduction	71.5	69.2
Initial toxicity, %	86	86
Final toxicity, %	<25	<25

Table 2. *Comparison of different ZVI digestion times and changes in its surface area and pore size.*

Digestion time, min	Visual decolouration time, min	Surface area (BET), m^2/g	Pore diameter (BET), nm	Total pore volume (BJH), cm^3/g	Pore diameter (BJH), nm
0	15	<0.01	<0.01	<0.01	<0.01
2	15	11.22	6.14	0.0158	5.36
4	12	9.85	5.9	0.0127	5.25
6	12	5.15	11.4	0.0104	7.27
8	9	9.98	8.59	0.0174	6.20
10	4	11.95	6.55	0.0178	5.29

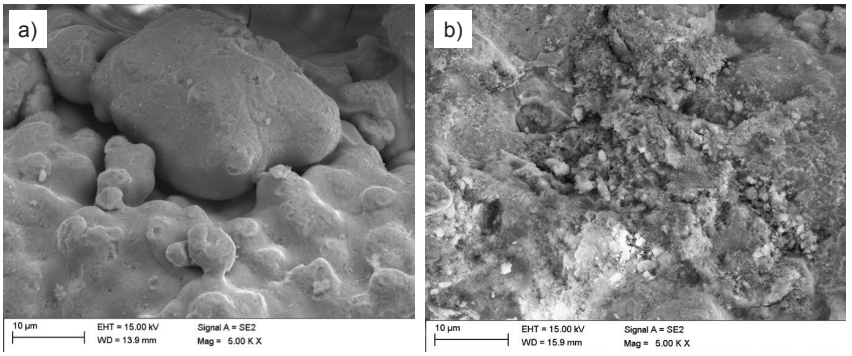

Figure 7. *SEM analysis of ZVI after digestion (pH = 3, H_2O_2 = 40 mg/l, ZVI = 80 mg/l), magnification 5000x: a) 2 min, b) 4 min.*

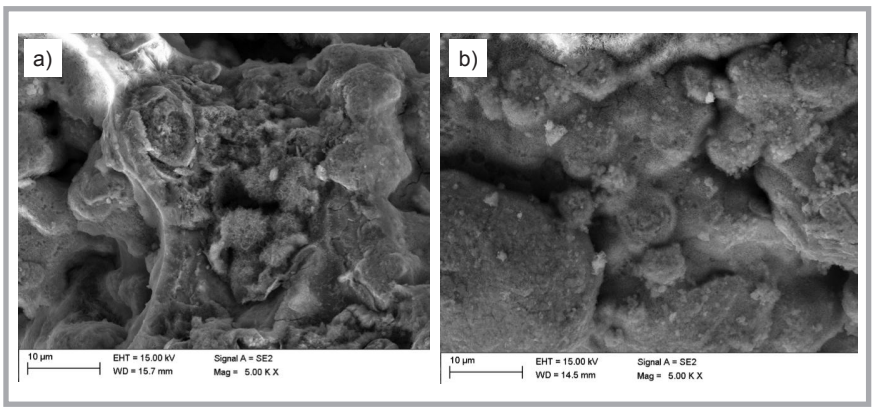

Figure 8. *SEM analysis of ZVI after digestion (pH = 3, H_2O_2 = 40 mg/l, ZVI = 80 mg/l), magnification 5000x: a) 6 min, b) 8 min.*

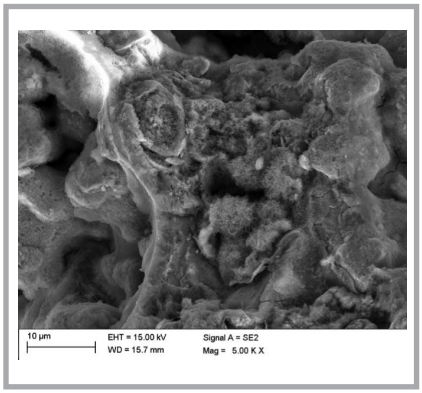

Figure 9. *SEM analysis of ZVI after 10 min digestion (pH = 3, H_2O_2 = 40 mg/l, ZVI = 80 mg/l), magnification 5000x.*

In another study [26] whose aim was to evaluate the efficiency of alumina-coated multi-walled carbon nanotubes, removing two azo dyes – Reactive Red 198 (RR 198) and Reactive Blue 19 (RB19) from aqueous solutions was carried out. In the most favourable conditions for RR 198 (pH = 3, 25 °C, adsorbent dose = 0.5 g/l, 150 minutes) and for RB 19 (pH = 3, 25 °C, adsorbent dose = 0.4 g/l, 180 minutes), the maximum removal efficiency was 91.54% and 93.51%, respectively. This method was very efficient, like the ZVI method, but it required a longer time reaction. Similar studies were carried out with the use of multiwalled carbon nanotubes (MWCNTs) for the decolourisation of Direct Blue 71 (DB 71) [27]. The maximum efficiency of DB 71 removal – 96.44% was observed at pH = 3, 90 minutes, adsorbent dose = 0.6 g/l, and dye concentration = 25 mg/l, better removal efficiency of the same dyes was obtained by [28]. Researchers compared the Fenton method with the ZVI method. In the most favourable conditions for Fenton (pH = 3, 25 °C, H_2O_2/Fe^{2+} concentration = 11.3 mM, 10 minutes) and ZVI (pH = 3, 25 °C, H_2O_2/Fe^{3+} concentration = 5.1 mM, 10 minutes) in the Fenton reaction, maximum efficiency was obtained at 94.70% and 99.31% for RR 198 and RB 19, respectively, while in the ZVI method maximum efficiency removal for RR 198 and RB 19 was 94.8% and 99.43%, respectively. The final stage of the research was to determine the rate of decolouration of the AR27 solution in dependance on the ZVI digestion time in an acidic medium (H_2SO_4) with respect to changes in the ZVI specific surface area. It was foreseen that longer ZVI digestion should lead to the release of more Fe^{2+} ions to the solution, which will result in the formation of more hydroxyl radicals and, consequently, contribute to faster and more efficient dye degradation. Results of the tests showed that extending the digestion time caused a reduction in the reaction time necessary to obtain a visual discolouration (***Figure 6***). For undigested ZVI and after 2 min of its dissolution, visual decolouration of the solution was obtained after 15 min. of the process duration (***Table 2***). However, 10 min of ZVI digestion resulted in visual decolouration after just 4 min. of the reaction, which was associated with an almost fourfold reduction in the time process. Similar results of the effect of the ZVI digestion time on the rate of obtaining the visual decolouration of azo dye Acid Red 18 solution at a concentration of 100 mg/l were obtained by other authors [29], who showed that as the ZVI digestion time was extended (in powder form, particle size <100 µm), the process of visual decolouration takes place faster (10 min digestion of ZVI in the test solution at pH = 3, decolouration time reduced from 11 to 5 minutes). After the ending of the reaction (ZVI/H_2O_2), images were also taken using SEM (***Figures 7, 8*** and ***9***) to observe changes in the ZVI morphology. SEM analysis showed that as the digestion time increased, the ZVI surface became rougher and was characterised by the presence of more pores. The surface area of ZVI and pore size were also inve-

stigated. In ***Table 2***, results of the BET/BJH analysis of ZVI surface properties after the digestion process are presented. The test results obtained (***Figure 10***) showed that ZVI digestion in the H_2SO_4 solution significantly influences the development of the surface and increases its porosity. BET analysis of non-digested ZVI showed a specific surface area less than 0.01 m^2/g (under the conditions of measurement), indicating a porous surface structure in the pore size range examined or a small adsorption of N_2 on the adsorbent surface, resulting from its physicochemical properties; thus making it impossible to precisely determine the distribution and pore size of the undigested material. Results of the ZVI digested surface analysis showed the effect of the acidic environment on ZVI surface properties, where ZVI digestion was found to increase the specific surface area to 11.22 m^2/g in 2 min., gaining an average pore size of 6.14 nm. Extending the ZVI digestion time in an acidic environment up to 6 min resulted in an increase in pore size to 11.4 nm (BET) respectively, while reducing the total pore volume, which consequently reduced the specific surface area to 5.15 m^2/g. However, further extending the digestion time to 8 and 10 min caused an increase in the specific surface area up to 11.95 m^2/g and in the pore size to slightly higher values (6.55 nm) than those obtained during 2 min. of ZVI digestion (6.14 nm). Therefore, based on the changes observed in surface properties as well as the absorbance changes in the AR27 dye solutions for different ZVI digestion times, it can be concluded that extending the digestion time successively increases the amount of Fe^{2+} ions released regardless of the surface state of the ZVI particles. Research conducted by other authors confirms that a longer digestion time results in an increase in the amount of Fe^{2+} ions released into the environment [30].

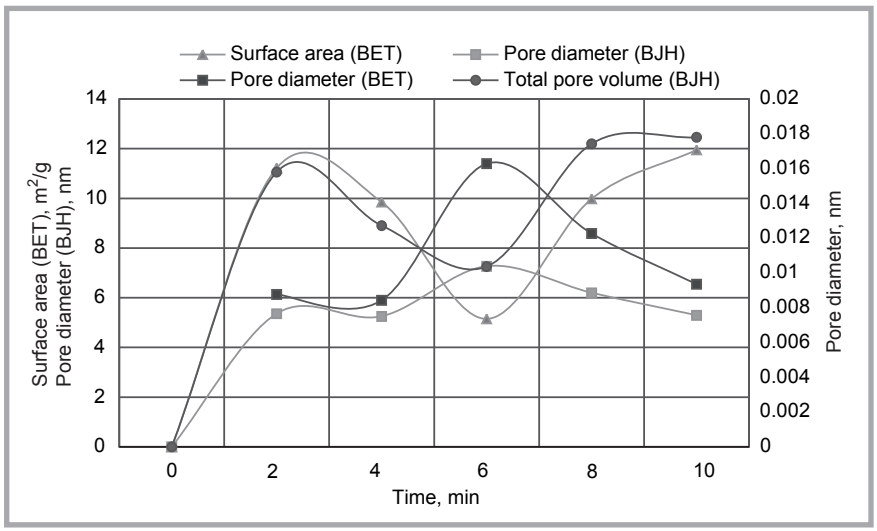

Figure 10. *Effect of digestion time on the surface properties of ZVI particles obtained by the BET/BJH method.*

Conclusions

The use of both methods (Fe^{2+}/H_2O_2 and ZVI/H_2O_2) for the oxidation of AR27 in an aqueous solution resulted in a colour reduction of 99.6% and 99%, respectively, and obtaining a visual decolouration of the solutions tested. The final concentrations of AR27 in post-reaction solutions for both methods used were 0.4 mg/l and 1 mg/l, for Fe^{2+}/H_2O_2 and ZVI/H_2O_2, respectively. Using the Fe^{2+}/H_2O_2 method, a slightly higher degree of COD reduction was obtained (71.5%) than in the case of the ZVI/H_2O_2 method (69.2%). In both cases, small final COD values were obtained in the range of 49-53 mg O_2/l. According to the toxicity classification for water samples, the test solution of AR27 dye with an initial toxicity of 86% in relation to *Aliivibrio fischeri*, after both methods of purification, can be considered as non-toxic (toxicity <25%). In addition, 10 min. of ZVI digestion allowed to shorten the reaction time (to obtain visual decolouration) from 15 to 4 minutes. BET analysis confirmed that the surface area of ZVI increased as a result of digestion, which caused the transition of more Fe^{2+} ions to the solution, accelerating the removal of AR27 from the test solution. It is likely that the increase in pore size is associated with the dissolution of the walls of the smaller pores and their combination in bigger ones. In turn, the disappearance of micropores and small mesopores reduces the specific surface area. A longer time digestion (8 and 10 min) may result in the formation of new pores or the opening of pores already present in the material. All things considered, the use of both methods allows to obtain similar results in the context of AR27 removal efficiency, COD and toxicity. The modified Fenton method, in comparison to the classic Fenton reagent, has the additional advantage that the reaction can be accelerated by dissolving the ZVI earlier, which in the research results presented allowed to reduce the decolourisation time almost four times. Results of decreasing the COD value and concentration of the dye obtained in the ZVI/H_2O_2 method are slightly worse compared to the Fe^{2+}/H_2O_2 method. Taking the decolouration time as a criterion, a four times faster decolouration time was obtained in the ZVI/H_2O_2 method, compared to the Fe^{2+}/H_2O_2 method.

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