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The Optimization of Advanced Oxidation Processes for the Degradation of Industrial Pollutants

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Abstract: The suitability of advanced oxidation processes to industrial pollutants was evaluated. Three dyes were selected for research: Indigo carmine, Tartrazine, and Allura red AC. Single processes (oxidation by H_2O_2, Fenton process, ozonation), and hybrid processes (O_3 + H_2O_2, O_3 + Fenton) were applied. The results of the research obtained indicated that the use of hydrogen peroxide alone is not effective in the degradation of the analyzed dyes (max. efficiency was 9.38%). The use of the Fenton process (1 mg of Fe^{2+}, 15 µL of H_2O_2, pH = 3) allows for the complete decolorization of all dyes tested, while the time for each dye is different (2 min for Indigo carmine, 15 min for Tartrazine, and 30 min for Allura red AC). Ozonation is effective in removing only Indigo carmine. Thirty minutes of ozonation (pH = 5.5) results in a 97% elimination of this dye, while for Tartrazine and Allura red AC, the results were 8.46% and 4.32%, respectively. The addition of H_2O_2 and Fe(II) ions during ozonation accelerates the degradation of Indigo carmine (from 30 min to 1 min) and increases the elimination degree to approx. 80% of Tartrazine and Allura red AC. It has been proven that AOPs, for example, the Fenton process and ozonation, are sustainable in removing industrial pollutants, e.g., dyes.

Keywords: dyes degradation; AOPs; Fenton process; ozonation process; hybrid process; oxidation; optimization; industrial pollutants

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1. Introduction

The intensive development of many industries, including the production of synthetic dyes, generates increasing levels of pollution, which, together with the high absorption of water, results in a degradation of the quality of the water and soil environment [1,2]. There are estimated to be over 100,000 known commercial dyes with a production exceeding 7×10^5 tons per year, used, among others, in paper mills, textile plants, the food industry, and the plastic industry [3,4]. The textile industry is one of the most important industries in the world, but it is also one of the largest wastewater generators responsible for surface water pollution and ecotoxicity due to the inefficient fixation of textile dyes in fabrics.

Textile industries are included in the restricted group of the largest wastewater generators owing to the large amounts of water used in the coloring processes. An average textile mill producing approximately 1.6 million liters of effluent per day. Fifty-four percent of the dyed effluents are released into the environment by this industry, and approx. 280,000 tons of textile dyes are discharged into water every year. An average concentration of 300 mg/L of synthetic dyes, including highly genotoxic and carcinogenic azo dyes, is present in the textile effluents [5].

About 10–15% of all dyes used in the industry enter the aquatic environment in the form of industrial wastewater (so-called colored wastewater), which significantly affects the deterioration of the environment and poses a serious threat to living organisms [5,6]. Synthetic dyes have a toxic effect because many of them are xenobiotics, highly stable, and resistant to chemical, biological, and photolytic decomposition [7,8]. The intense coloration, low biodegradability, and often toxic nature of colored wastewater make conventional wastewater treatment methods insufficiently effective [9]. Untreated colored wastewater enters surface water, and with it, colored xenobiotics, creating the risk of their accumulation in the environment [10,11]. The treatment of organic wastewater is becoming an increasingly critical issue in sustainable development, as it contains a large number of refractory and toxic organic pollutants. Conventional separation and transformation technologies are inefficient in the treatment of refractory and toxic organic pollutants.

Different textile wastewater treatment methods have been used, including physical, chemical, and biological treatment methods. Other techniques utilized for the removal of dyes include aerobic and anaerobic reactors in biochemical techniques, dissolved air flotation, and an electrocoagulation system in physicochemical techniques [12]. Physical treatment methods include adsorption, flocculation, coagulation, and photocatalytic purification. The performance of these treatment technologies depends upon their application and is also influenced by the type of textile effluents, and the stability of the dye toward light and oxidizing agents complicates the treatment of textile effluents. These methods have advantages over other treatment methods due to their low operating cost and ease of operation [13]. Adsorption is a process commonly used in wastewater treatment from various industries. Some adsorbents are very effective in the removal of dyes from textile wastewater. Mostly natural and synthetic materials were used as adsorbents for the treatment of dyes from textile wastewater. Quansah et al. (2020) [14] conducted a study in which a nascent rice husk was used to remove methylene blue and crystal violet from textile wastewater. The maximum percentage removal was up to 95% for both dyes (at 25 °C, pH 4–10, the concentration of methylene blue and crystal violet was 0.05–0.5 g/L and 0.1–1 g/L). The adsorption process has been reported to exhibit high color removal efficiency and adsorbent regeneration ability. However, its application is limited by sludge generation and high costs of adsorbent disposal [15]. Coagulation/flocculation is one of the most popular unit operations in water and wastewater treatment trains. Dye removal by coagulation is not based on the partial decomposition of dye compounds; thus, no potentially harmful and toxic intermediates are produced. Furthermore, this process can be used in large-scale operations with relatively high operability and cost effectiveness. A limitation of this technique is that some high-soluble, low-molecular, and cationic dyes might not be effectively removed. The removal of coagulated sludge could be another restriction associated with this technique [15,16]. Biological processes for the removal of dyes are environmentally friendly and cost-competitive methods that have been used for decades. However, biological procedures are typically very time-consuming, are less flexible in design, and are not applicable for the removal of several classes of dyes [17–19]. The removal of dyes from wastewater is often associated with the need to combine several methods, including sorption, oxidation, coagulation, filtration, and biodegradation.

In recent years, there has been a growing interest in so-called "sustainable chemistry", i.e., ecological and environmentally friendly chemistry. In practice, this means that a new approach has been developed to the issue of synthesis, processing, and the use of chemical substances, related to reducing the risk to human health and the environment. It means designing, manufacturing, and using products in chemical technologies that allow for achieving large economic benefits and are at the same time environmentally friendly. During the design and conduct of chemical processes, the amount of energy, nonrenewable raw materials, and water used should be reduced. The concept of "sustainable chemistry" also requires reducing the number of pollutants and waste produced at every stage of production and producing chemical products that can be reused or recycled. An important area of activity within sustainable chemistry is the search for new ways to accelerate and catalyze chemical processes. Catalysis plays an extremely important role in preventing and eliminating the effects of environmental pollution. This role is manifested both in the scope of basic research and in industrial applications. Catalytic reactions usually result in reduced energy requirements and increased selectivity. In recent years, advanced oxidation processes (AOPs) have become an increasingly popular alternative in industrial wastewater treatment. These methods involve the decomposition of organic compounds using strong oxidants characterized by high oxidation potential [20–24].

The advanced oxidation process is one of the sustainable emerging technologies for treating refractory organic contaminants present in different industrial wastewaters such as textile, paper, and pulp, pharmaceuticals, petrochemicals, and refineries. Some examples of these processes are ozonation, the Fenton process, oxidation by hydrogen peroxide, photo-Fenton, photo-ozone, photo-hydrogen peroxide, and photo-catalysts [25–29].

The Fenton reaction is a so-called radical reaction in which the substrates, intermediates, or end products are free radicals. The chemistry of the Fenton reaction is based on the catalyzed decomposition of hydrogen peroxide (H_2O_2) into hydroxyl radicals ($HO^\bullet$) in an acidic reaction environment according to Equations (1)–(10) [27]:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^- + \bullet OH \tag{1}$$

$$^\bullet OH + H_2O_2 \rightarrow HO_2^\bullet + H_2O \tag{2}$$

$$2HO^\bullet \rightarrow H_2O_2 \tag{3}$$

$$H_2O \rightarrow {}^\bullet OH + H^\bullet \tag{4}$$

$$^\bullet OH + RH \rightarrow H_2O + R^\bullet \tag{5}$$

$$R^\bullet + O_2 \rightarrow ROO^\bullet \tag{6}$$

$$R^\bullet + Fe^{3+} \rightarrow R^+ + Fe^{2+} \tag{7}$$

$$ROO^\bullet + RH \rightarrow ROOH + R^\bullet \tag{8}$$

$$ROOH + Fe^{2+} \rightarrow RO^\bullet + Fe^{3+} + HO^- \tag{9}$$

$$ROOH + Fe^{3+} \rightarrow ROO^\bullet + Fe^{2+} + H^+ \tag{10}$$

The catalyst for breaking the bond in the peroxide group is most often divalent iron ions. It is also possible to use other transition metal ions, e.g., copper or manganese [12,13]. $HO^\bullet$ radicals formed during catalyzed decomposition of H_2O_2 are characterized in the literature as strong, nonselective oxidants. The high oxidation potential of $HO^\bullet$ (2.76 V) enables the oxidation of poorly biodegradable substances. The homogeneous Fenton process for wastewater treatment has shown relevant advantages over other advanced oxidation processes, as it is a suitable and affordable way to degrade organic molecules in aqueous media. For instance, Fenton reagents are inexpensive and easy to handle and store, and the reaction is conducted at ambient temperature and pressure. Despite its simplicity and ease of use, Fenton's reagent does not find a wider practical application in the degradation of wastewater pollutants. This is due to the lack of comprehensive scientific studies proving that the use of Fenton's reagent can be an effective and therefore commonly used method of treating industrial wastewater that is difficult to neutralize using traditional technologies. The nonselective oxidizing effect of OH radicals provide a basis for assuming that Fenton's reagent will effectively purify wastewater containing various types of difficult-to-degradable pollutants at the same time. The current challenge in environmental engineering is to find alternative solutions to the conventional Fenton process (Fe^{2+}/H_2O_2), which will not only increase its efficiency and cost-effectiveness but also develop a method that meets the assumption of sustainable development and green chemistry. Currently, alternative solutions are being sought for the conventional Fenton process (Fe^{2+}/H_2O_2), which will allow it to increase in efficiency and cost-effectiveness. The most common modifications include the use of alternative sources of catalyst and oxidant as well as supporting the classic process, e.g., ozonation (O_3–Fenton), UV radiation (UV–Fenton), or electrochemical methods (electro–Fenton) [14,17].

Ozonation is capable of oxidizing pollutants through a direct reaction with ozone or indirectly after the formation of hydroxyl radicals [30]. Ozonation is a very effective method in treating wastewater containing recalcitrant compounds and is considered one of the most attractive alternatives to solve the color problem in industrial wastewater. The disadvantages of ozonation include a high production cost, low solubility and stability in water, and the incomplete mineralization of some pollutants [31,32]. A simple mechanism for the decomposition of ozone in an aqueous solution is illustrated in the following equations, Equations (11)–(16).

$$O_3 + HO^- \rightarrow HO_2^\bullet + O_2^{-\bullet} \tag{11}$$

$$O_3 + HO_2^\bullet \rightarrow {}^\bullet OH + 2O_2 \tag{12}$$

$$O_3 + {}^\bullet OH \rightarrow O_3^\bullet + {}^\bullet OH \tag{13}$$

$$O_3^\bullet \rightarrow {}^\bullet O + O_2 \tag{14}$$

$${}^\bullet O + H+ \rightarrow {}^\bullet OH \tag{15}$$

$${}^\bullet OH + HO_2^\bullet \rightarrow H_2O + O_2 \tag{16}$$

The novelty of this work is applying the Fenton process and ozonation processes (single O_3, O_3 + H_2O_2, O_3 + Fenton process) to eliminate industrial pollutants using dyes (Indigo carmine, Tartrazine, and Allura red AC) as examples. The innovative nature of the conducted research is the application of processes in real solutions without pH correction.

2. Materials and Methods

2.1. Chemicals and Materials

The dyes (Indigo carmine, Tartrazine, Allura red AC) were purchased from Sigma-Aldrich, Saint Louis, MO, USA). The characteristics of the dyes are presented in Table S1. Stock dye solutions of 1 dm^3 volume and 50 mg/dm^3 concentration were prepared by dissolving them in distilled water. The dye solutions prepared were stored under conditions protected from light and at 4 °C. The colors of the prepared solutions are shown in Figure S1. The resulting dye samples were analyzed spectrophotometrically, and calibration curves (0–50 mg/dm^3) were prepared for each dye, adjusting the wavelength to λ = 610 nm for Indigo carmine, λ = 427 nm for Tartrazine, and λ = 500 nm for Allura red AC. The dye concentration was analyzed using a HACH LANGE DR 3900 spectrophotometer (Ames, IA, USA).

Hydrochloric acid (HCl), sodium hydroxide (NaOH), hydrogen peroxide (H_2O_2), and $FeSO_4 \cdot 7H_2O$ were obtained from Chempur (Poland). All reagents used in this study were analytical grade.

2.2. Degradation Experiments

2.2.1. Use of H_2O_2 to Dye Degradation

Oxidation reactions were carried out on a 4-station magnetic stirrer at a constant stir-ring speed of 100 rpm under ambient conditions (ambient temperature, atmospheric pressure). The beakers with a capacity of 100 cm^3 were filled with 50 cm^3 of solutions of Indigo carmine/Tartrazine/Allura red AC dyes at a concentration of 50 mg/dm^3. Each process was carried out at the initial pH value of the dye solutions (5.5) and using a pH correction to a value of 3 ± 0.2 using a hydrochloric acid solution. The first stage of the study consisted of evaluating the effectiveness of the oxidation process of the dyes tested by adding 30% hydrogen peroxide in the form of hydrogen peroxide to the individual solutions at a dose of 15, 30, and 60 µL. The oxidation processes of the mixture containing Indigo carmine, Tartrazine, and Allura red AC were carried out for 30 min. After this time, the samples were collected and neutralized with sodium hydroxide solution and then analyzed.

The degree of removal of dye in the oxidation processes was calculated according to Equation (17).

$$\%E = (C_0 - C)/C_0 \cdot 100\% \tag{17}$$

where

%E—percentage degree of elimination;
C_0—initial dye concentration, [mg/dm^3];
C—dye concentration after the process, [mg/dm^3].

2.2.2. Use of the Fenton Process to Dye Degradation

The Fenton process was carried out on a 4-station magnetic stirrer at a constant stirring speed of 100 rpm under ambient conditions (ambient temperature, atmospheric pressure). The beakers with a capacity of 100 cm^3 were filled with 50 cm^3 of basic solutions of Indigo carmine/Tartrazine/Allura red AC dyes at a concentration of 50 mg/dm^3. Each process was carried out at the initial pH value of the basic dye solutions (5.5) and using a pH correction to 3 ± 0.2 using a hydrochloric acid solution. The catalyst was then introduced in the form of $FeSO_4 \cdot 7H_2O$ salt solution to the dyes in the amount corresponding to 1, 2, 5, and 10 mg Fe^{2+} and the oxidant (hydrogen peroxide) at a dose of 15, 30, and 60 µL. The oxidation process was carried out for a maximum of 30 min.

2.2.3. Use of the Ozonation Process to Degradation of Dyes

In the tests, an ozone generator (Korona L 20 AQUASWIM, Korona lab, Piotrków Trybunalski, Poland) with a capacity of 20 g/h was used. Beakers with a capacity of 100 cm^3 were filled with 50 cm^3 of basic solutions of Indigo carmine/Tartrazine/Allura red AC dyes at a concentration of 50 mg/dm^3. Each process was carried out at the initial pH value of the basic dye solutions (5.5). The ozonation process was carried out for a maximum of 35 min. Furthermore, the ozonation process was combined with oxidation using hydrogen peroxide (15 µL) and the support of the Fenton process (15 µL of H_2O_2, 1 mg Fe^{2+}).

2.3. Cost Analysis of Processes Conducted

The cost for Fenton process included the costs of energy consumption and cost of chemicals. Operating costs are directly dependent on the efficiency of treatment processes. To facilitate comparison of reaction performance, an indicator called EE/O (electrical energy required to reduce pollutant concentration by one order of magnitude in one cubic meter of water or wastewater) was applied. The EE/O values were calculated based on Equation (18):

$$\frac{\mathrm{EE}}{\mathrm{O}} = \frac{\mathrm{P}\cdot \mathrm{t}\cdot 1000}{\mathrm{V}\cdot 60\log\left(\frac{\mathrm{C_0}}{\mathrm{C_t}}\right)}\left[\frac{\mathrm{kWh}}{\mathrm{m^3}}\right] \tag{18}$$

where

P—the power input of the ozone generator, the magnetic stirrer [kW];
t—reaction time [min];
V—the volume of the effluent [L];
C_t—the final concentration of dye;
C_0—initial concentration of dye.

3. Results and Discussion

3.1. Use of H_2O_2 to Degrade Dyes

The test results on the effect of hydrogen peroxide alone on the degradation of Indigo carmine, Tartrazine, and Allura red AC are presented in Figure 1 and Table 1.

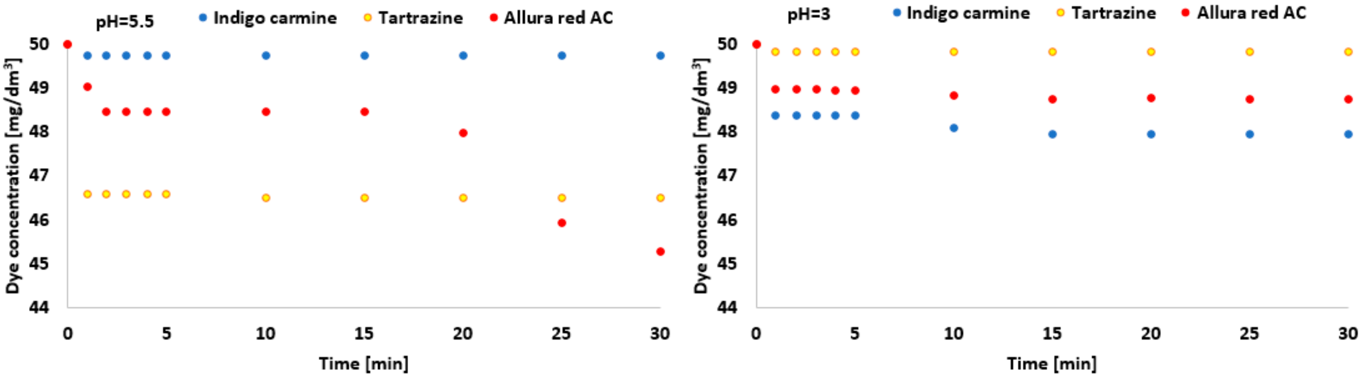

Figure 1. Effect of time and pH (5.5 and 3) on dye degradation (H_2O_2 dose: 15 µL, volume samples: 50 cm^3, dye concentration: 50 mg/dm^3).

Table 1. The effect of the H_2O_2 dose on the degradation of dyes (reaction time: 1 min, volume samples: 50 cm^3, dye concentration: 50 mg/dm^3).

pH	Dose of H_2O_2 (30%)	Degradation Efficiency [%]		
		Indigo Carmine	Tartrazine	Allura Red AC
5.5	15 µL	0.5	6.82	3.06
	30 µL	0	0	0
	60 µL	0	0	0
3	15 µL	3.2	0.3	2
	30 µL	2.1	0	2.4
	60 µL	6.4	0	0

The results of the research obtained indicate that the use of hydrogen peroxide alone is not effective in the degradation of dyes (Indigo carmine, Tartrazine, and Allura red AC). Neither increasing the dose of hydrogen peroxide nor extending the contact time of the oxidant with the removed dyes resulted in significant discoloration of the solutions. The same can be said about the change in the pH value from 5.5 to 3. The highest degree of degradation for the tested substances is 6.4%, 6.98%, and 9.38%, respectively, for Indigo carmine, Tartrazine, and Allura red AC. Similar results were obtained in studies conducted by Barbusiński (2003) [29], which consisted of decolorizing an aqueous solution containing the azo dye Acid red 18. Hydrogen peroxide alone was used in the concentration range of 50 to 500 mg/dm^3 at pH 3.5. As a result, the absorbance value decreased only from 10% to 23% for the minimum and maximum doses, respectively. Other studies [33,34] also confirmed the low oxidizing power of H_2O_2 for the degradation of Reactive black 5 and Reactive blue 2 dyes.

Such a low efficiency or even no oxidation of the dyes tested resulted from the insufficient amount of hydroxyl radicals produced. Therefore, further studies focused on the Fenton reaction. In this process, the use of an additional reagent, a catalyst in the form of iron ions, causes a greater amount of •OH to be generated, making the degradation of organic compounds more effective (according to Equation (1)) [35].

3.2. Use of the Fenton Process to Dye Degradation

Figure 2 shows that the pH value of the reaction solution is a parameter that significantly affects the oxidation efficiency of organic compounds during the Fenton process. With the change in the pH value from 5.5 ± 0.2 to 3 ± 0.2, a significant increase in the decolorization efficiency of solutions with Tartrazine and Allura red AC was observed. The highest concentration reduction dynamics were observed for the Tartrazine dye, where from the efficiency of 43.7%, 49.1%, and 52.7% for pH 5.5, an increase was obtained to the values of 90.5%, 83%, and 91.3% (for pH 3), respectively. The efficiency of the Fenton reaction also increased for the Allura red AC dye. At a higher pH value, the decolorization efficiency was lower, which could be caused by the precipitation of iron (III) hydroxide by iron ions, leading to the deactivation of the catalyst and thus reducing the amount of generated hydroxyl radicals. Better dye degradation at pH 3 resulted from the higher reduction potential of •OH [36]. Nidheesh et al. (2013) [37] stated that lowering the pH of the reaction medium is an important step in the Fenton process. The degradation of organic matter is more effective at pH 3, and hydrogen peroxide and iron ions are more stable.

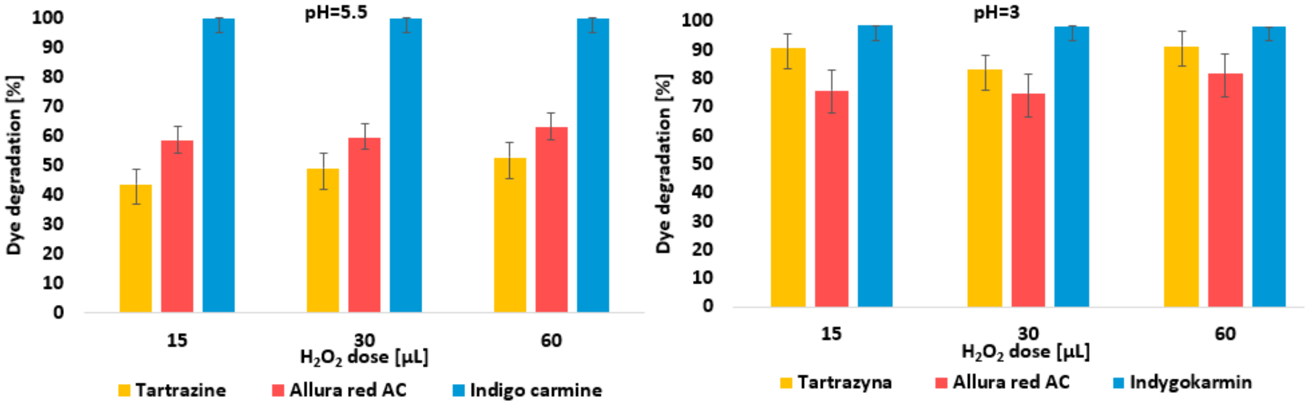

Figure 2. The influence of pH (5.5 and 3) and the H_2O_2 dose on the removal efficiency of Indigo carmine, Tartrazine, and Allura red AC dyes (Fe^{2+} dose: 1 mg, reaction time: 5 min, volume samples: 50 cm^3, dye concentration: 50 mg/dm^3).

Studies conducted by Chen et al. (2009) [38], Bouasla et al. (2010) [39], and Mansoorian et al. (2014) [40] also showed that pH 3 is the optimal parameter in the oxidation process of dyes (such as Acridine, Methyl Violet 6B, Reactive red 198, Reactive blue 19).

The degradation process of the Indigo carmine dye was the only one to be more effective at a higher pH value. Changing the pH value from 5.5 to 3 reduced the degree of discoloration only by several percent.

The next parameter of the Fenton process analyzed was the dose of hydrogen peroxide. In the case of the oxidation processes of the Tartrazine and Allura red AC dyes at pH 5.5 ± 0.2, it can be seen that increasing the dose of hydrogen peroxide causes an increase of several percent in the effects of the degradation of the compounds tested. In turn, after the process is carried out at a lower pH value, this relationship can be formulated by comparing the use of the smallest dose with a 4-fold dose (60 µL). The greatest increase in efficiency was observed after the catalytic process for Allura red AC dye in which the dose of oxidant was increased from 15 µL to 60 µL (an increase in efficiency from 75.7% to 81.5%). The intensification of the degradation efficiency of the Tartrazine and Allura red AC dyes in the Fenton process was due to the increase in the generated $^{\bullet}OH$ radicals by using higher concentrations of the oxidant [36]. In the case of the oxidation process of the Tartrazine dye, a 4-fold increase in the amount of hydrogen peroxide compared to the initial dose at pH 3 did not significantly affect the technological effects obtained (efficiency increased by 0.8%). Giwa et al. (2020) [41] obtained similar results in studies on the removal of methylene blue dye in the Fenton process. The dose of hydrogen peroxide was increased twice to 80 mmol, recording a better degradation of the dye by only 1.2% (with the reaction parameters: Fe^{2+} dose: 4 mmol, pH: 3).

An analysis of the data obtained after the process of removing the Indigo carmine dye at pH 5.5 shows that complete degradation of the compound was obtained regardless of the applied oxidant dose. In the case of the reaction at pH 3, the highest efficiency of 98.6% was obtained using the lowest dose of H_2O_2 (15 µL). A further increase in the concentration of hydrogen peroxide did not affect the better efficiency of the decolorization of the mixtures. According to data from the current literature, at high concentrations of H_2O_2, $^{\bullet}OH$ is captured, and this leads to the formation of hydroperoxide radicals $HO_2^{\bullet}$ with a lower oxidizing potential than $^{\bullet}OH$. This results in a decrease in the efficiency of the degradation of organic pollutants [38].

The next parameter optimized was the reaction time of the catalytic process (Figure 3). When the mechanism of the Fenton process for the degradation of the Indigo carmine dye from water is analyzed, it can be seen that this dye is the most susceptible to the applied processes. Significant color fading was observed after just the first 10 s, with 100% removal achieved after approximately 2 min. The most resistant to degradation is the Allura red AC dye. Removal above 90% was achieved after as long as 25 min of reaction. In turn, the complete mineralization of Tartrazine was obtained after 15 min of the Fenton reaction. Based on the literature review [40–43], it can be concluded that in most experiments, the Fenton process is the fastest in the first minutes of the reaction. Over time, the increase is small, or there is no further degradation of pollutants. For example, the authors of Ramirez et al. (2005) [44] in studies on the removal of Orange II dye showed that extending the reaction time from 10 min to 2 h increased efficiency from 97% to 99% (with reaction parameters: pH: 3, H_2O_2 dose: 15 mmol, Fe^{2+}/H_2O_2 weight ratio: 0.05).

Indigo carmine is particularly used in the textile industry to dye jean clothes. Although Indigo carmine is considered safe at low levels and its use is approved in the European Union and the United States, elevated amounts of this compound in wastewater are harmful to the environment and human health [45]. Since the textile industry generates effluents with high concentrations of this dye, the removal of this chemical from wastewaters has been of continuing research interest [46–52].

Due to the 100% degradation of the Indigo carmine dye obtained in the classical Fenton process (with reaction parameters: pH 5.5, Fe^{2+} dose: 1 mg, H_2O_2 dose: 15 µL, reaction time: 5 min), more studies were performed based on maximization of oxidation effects for the remaining two dyes. The effect of increasing catalyst doses and reaction time on the oxidation power obtained from the Fenton mixture was determined. Initially, the amount of iron (II) ions in the reaction medium was increased from 1 mg to 2 mg using the previous three constant doses of hydrogen peroxide (15, 30, 60 µL) and the optimal pH of 3. A two-fold increase in the amount of catalyst in the Fenton process resulted in a better degradation of the Tartrazine dye by 12.1% and 4.2% for H_2O_2 doses of 30 and 60 µL, respectively (Figure 4). The use of a solution of hydrogen peroxide in the amount of 15 µL and 2 mg Fe^{2+} resulted in a lower degree of discoloration than in the case of a dose of 1 mg Fe^{2+}. As evidenced by data from the scientific literature [53,54], increasing the dose of iron ions (II) increases the efficiency of the catalytic decomposition of hydrogen peroxide, but their excess (above the optimal concentration, which should be determined experimentally) acts as a so-called radical scavenger, causing the •OH generated to bond.

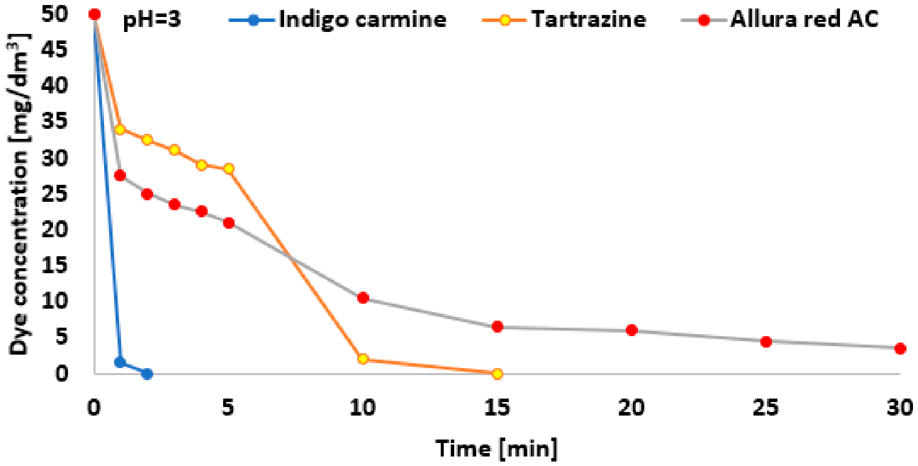

Figure 3. The effect of time on the degradation of dyes (H_2O_2 dose: 15 µL, Fe^{2+} dose: 1 mg, pH = 3, volume samples: 50 cm^3, dye concentration: 50 mg/dm^3).

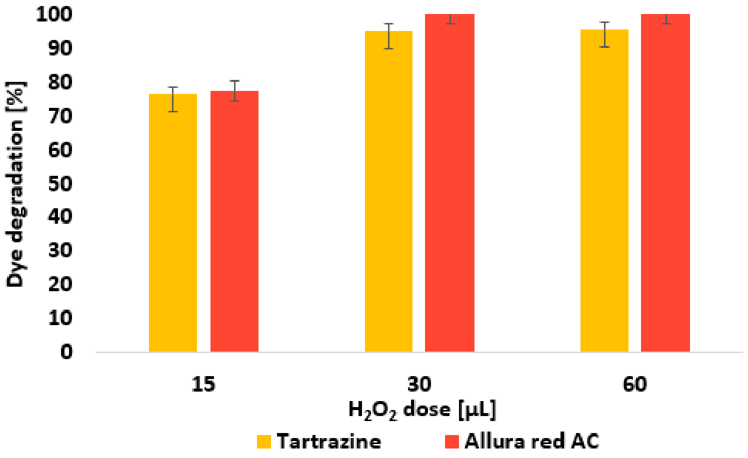

Figure 4. The effect of Fe^{2+} dose (2 mg) and H_2O_2 doses on dye removal efficiency after a reaction time of 5 min at pH 3 (volume samples: 50 cm^3, dye concentration: 50 mg/dm^3).

The same reaction parameters (Fe^{2+} dose: 2 mg, H_2O_2 doses: 15, 30, 60 µL, pH: 3) were used in the elimination process of the Allura red AC dye. A higher catalyst dose along with the use of 15 µL H_2O_2 slightly improved the efficiency of the process (an increase of 1.5%). The lower oxidizing power of Fenton's reagent in the processes in which the lowest dose of H_2O_2 was used was probably due to an insufficient amount of oxidant compared to the catalyst dose used [55]. Low concentrations of hydrogen peroxide can result in a smaller amount of free radicals generated and, consequently, a slower rate of oxidation of pollutants [56]. A significantly higher reduction level was observed in the concentration of Allura red AC dye in the reaction using 30 and 60 µL of hydrogen peroxide (an increase of 25.5% and 18.5%, respectively).

One of the most commonly used synthetic dyes in the food industry is Allura red AC, an azo dye added mainly to soft drinks, candies, ice cream, and bakery products. In many countries, the use of Allura red AC has been banned due to its toxicity (USA, India, Denmark, Belgium, France, Germany, Switzerland, Sweden, Austria, and Norway) [57]. In the European Union, it is a permitted ingredient in human food but has not been approved for the production of animal feed due to its potential genotoxicity [58,59]. This dye is not recommended for consumption by children, and products containing it should have additional information on the label: "may have an adverse effect on the activity and attention of children" [60]. Allura red AC is capable of reduction by azoreductase enzymes in intestinal bacteria and liver cells, releasing aromatic amines into the body, which cause headaches in adults and hyperactivity and concentration problems in children [57].

Tartrazine (Acid yellow 23) is a synthetic lemon yellow anionic azo dye found under the number E102 in many food, cosmetic, and pharmaceutical products [61,62]. According to Harasym and Bogacz-Radomska, 2016 [63], Tartrazine is characterized by good resistance to light and temperature. Furthermore, it dissolves very well in water (20 g/100 mL at 25 °C), but this makes its identification in industrial wastewater difficult [57,64]. The allowable daily dose (ADI) of this dye is 0–7.5 mg/kg bw. [57]. Many authors [62,64,65] emphasize that the consumption of Tartrazine is not indifferent to our body and, in high concentrations, can cause allergic reactions, migraines, depression, weakness, eczema, and anxiety. Furthermore, excessive consumption by children can cause attention deficit hyperactivity disorder (ADHD) [65].

Further processes for Tartrazine and Allura red AC dyes were performed using a higher catalyst dose (5 and 10 mg of Fe^{2+} ions). The remaining process parameters remained unchanged. It was noted that increasing the Fe^{2+} dose resulted in a slight deterioration of the decolorization effects or inhibition of the reaction (Figure 5). For example, for the degradation process of Tartrazine and Allura red AC dyes using 10 mg of Fe^{2+} (instead of 2 mg) and 60 µL of H_2O_2, the decrease in efficiency was 2.4% and 2.0%, respectively. The results obtained are consistent with the reports in the literature [28,35,39,66], which show that an increase in the concentration of iron (II) ions increases the degree of removal of organic compounds, but only to a certain level. Above the optimal concentration of the catalyst present in the reaction medium, Fe^{2+} ions can act as radical scavengers by reacting with the formed $^{\bullet}OH$. This leads to the inhibition of the further oxidation of pollutants or even a decrease in efficiency. For example, Mandal et al. (2010) [67] in the Fenton process, by increasing the catalyst dose four times, obtained a 2.8-fold increase in COD reduction efficiency (at pH 3.5 and reaction time: 24 h). An additional increase in the amount of Fe^{2+} (above 6 mg/dm^3) resulted in a slight decrease in efficiency.

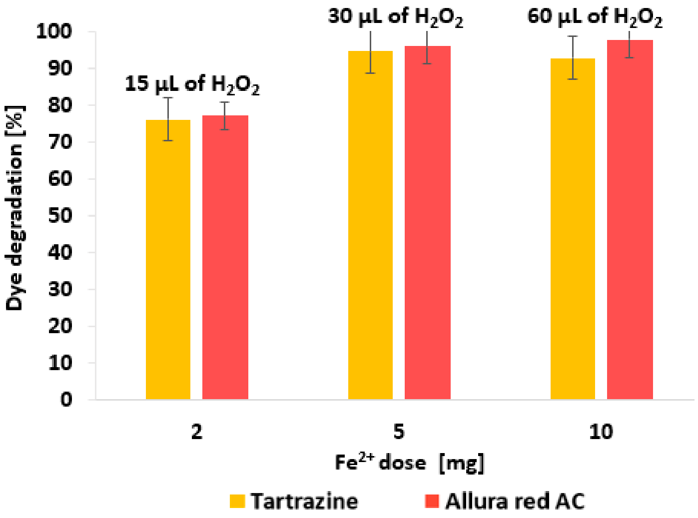

Figure 5. The effect of Fe^{2+} and H_2O_2 dose (15, 30, 60 µL) on the efficiency of dye removal after a reaction time of 5 min at pH = 3 (volume samples: 50 cm^3, dye concentration: 50 mg/dm^3).

3.3. Use of the Ozonation Process to Degradation of Dyes

Figure 6 shows the results obtained during the ozonation process. For the Indigo carmine dye only, satisfactory results of solution decolorization were obtained. Thirty minutes of ozonation resulted in a dye reduction of 97.1%. Similar results were obtained in studies conducted by Ortiz et al. (2016) [68]. The Tartrazine and Allura red AC dyes did not decompose in contact with ozone. The removal efficiency using ozone depends on the chemical structure of the dye, the presence of oxidizable functional groups, and the reaction conditions. Ozone is a strong oxidizing agent that primarily reacts with double bonds, aromatic groups, and electron-donating functional groups in dye molecules. Indigo carmine contains an aromatic system and double bonds within its indigo structure, which are highly susceptible to oxidation. This dye contains one sulfone group (-SO_3H), which affects its water solubility and stability. In contrast, Tartrazine contains sulfonic groups (-SO_3H) and double bonds within its azo structure (-N=N-). Sulfonic groups can slow down the reaction, as they are stable and increase the dye's hydrophilicity, which directly affects the removal efficiency. Allura red AC is characterized by azo groups (-N=N-), aromatic rings, and sulfonic groups in its structure. Similar to Tartrazine, ozone will initially break the azo bonds and aromatic rings. Indigo carmine lacks as many stabilizing groups (e.g., sulfonic groups) as Tartrazine and Allura red AC, making it less resistant to degradation [68].

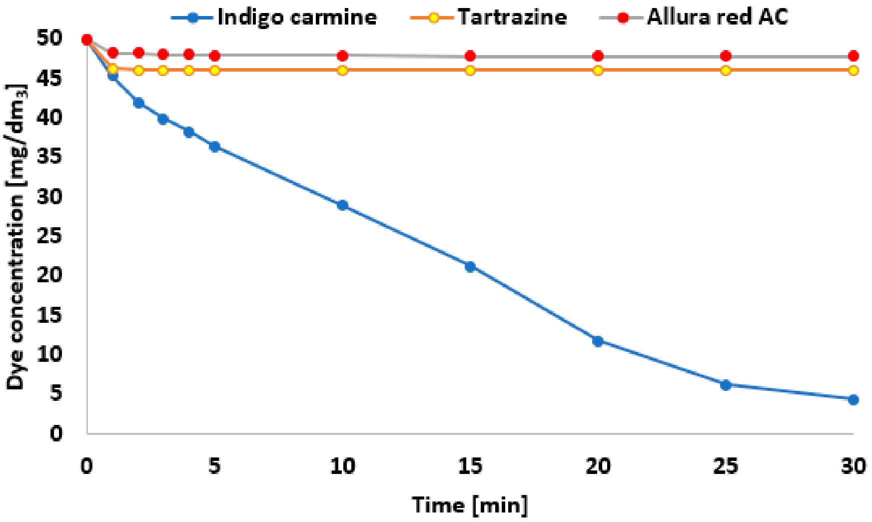

Figure 6. Effect of ozonation time on dye degradation (pH = 5.5, volume samples: 50 cm^3, dye concentration: 50 mg/dm^3).

Ozonation is capable of oxidizing pollutants through a direct reaction with ozone or indirectly after the formation of hydroxyl radicals [69]. Ozonation is a very effective method in treating wastewater containing recalcitrant compounds and is considered one of the most attractive alternatives to solve the problem of color in industrial wastewater [70,71]. The disadvantages of ozonation include high production cost, low solubility and stability in water, and the incomplete mineralization of some pollutants [32]. As a consequence of this limitation and the relatively low availability of hydroxyl radicals, some of these dyes are not effectively removed when this technology is applied. For this reason, in the next stage, the ozonation process is combined with oxidation using hydrogen peroxide itself (Figure 7).

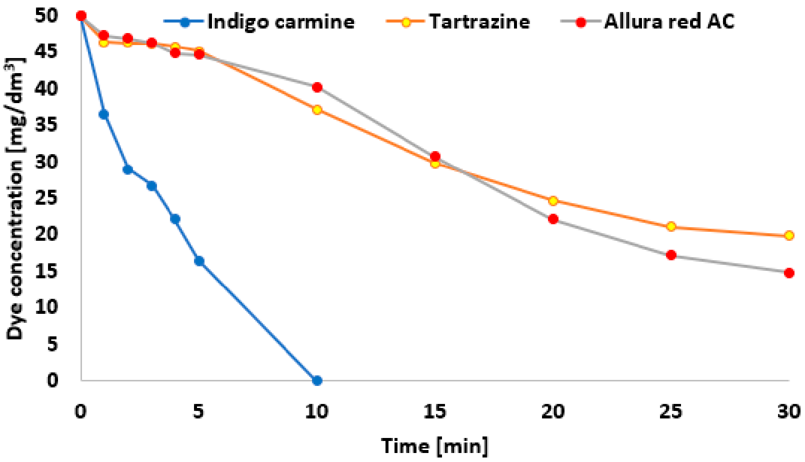

Figure 7. Effect of ozonation time on dye degradation with presence of H_2O_2 (H_2O_2 dose: 15 µL, pH = 5.5, volume samples: 50 cm^3, dye concentration: 50 mg/dm^3).

The addition of H_2O_2 to the solution subjected to ozonation caused an acceleration of the discoloration effect in the case of Indigo carmine and a significant increase in the elimination efficiency of Tartrazine and Allura red AC despite the fact that hydrogen peroxide alone did not cause such a large removal of dyes (Table 1). In the case of combining ozonation and oxidation with hydrogen peroxide, a synergistic effect was observed. Just 10 min of the hybrid process was enough to achieve the complete elimination of Indigo carmine. For Tartrazine, the maximum elimination rate was 60.2%, and for Allura red AC, it was up to 70.4%. Combining O_3 with H_2O_2 improves single ozonation performance while keeping the required dose of ozone as low as possible. Through the application of this process, hydroxyl radical production increases with respect to ozonation alone, thus allowing for larger removals of ozone-refractory compounds for equivalent doses of ozone [72].

The last process used to remove the dyes was the ozonation process combined with the Fenton process. The results are shown in Figure 8. Already within the first minute of the process, 100, 64.8, and 64.6% were obtained for Indigo carmine, Tartrazine, and Allura red AC, respectively. The results indicate a significant acceleration of dye degradation compared to single processes. Extending the process time resulted in only a slight increase in degradation efficiency. When comparing the time of 1 min and 30 min, an increase of 14.6% and 15.4% is observed for Tartrazine and Allura red AC, respectively.

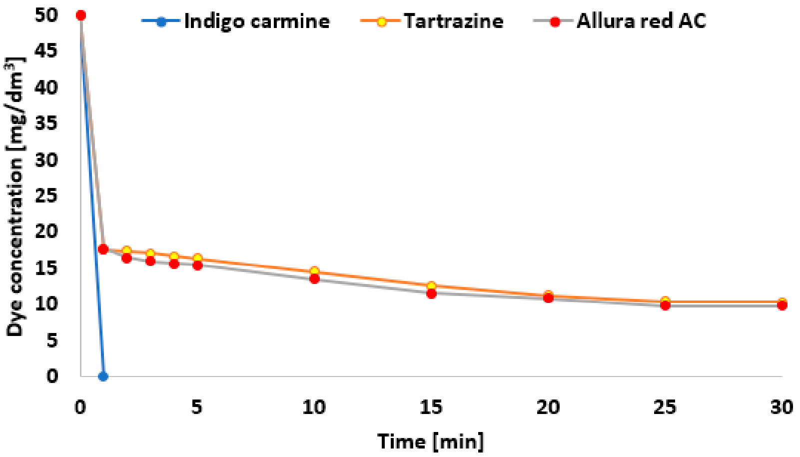

Figure 8. Effect of ozonation + Fenton process on dye degradation (H_2O_2 dose: 15 µL, Fe^{2+} dose: 1 mg, pH = 5.5, volume samples: 50 cm^3, dye concentration: 50 mg/dm^3).

These results confirmed that ozonation and its combination techniques (O_3/H_2O_2 and $O_3/Fe^{2+}/H_2O_2$) have effectiveness in destroying contaminants through a direct reaction (E_0 = 2.08 V) and hydroxyl-radical-induced oxidation (E_0 = 2.80 V) [61].

3.4. Cost Analysis

The cost of the Fenton process, ozonation, and hybrid process has been estimated. The parameters and characteristics of the processes are presented in Table 2. The cost analysis is preliminary because it only includes the costs of operating parameters at the bench scale, including energy consumption, H_2O_2, and Fe^{2+} costs. When the process is applied in full-scale, capital cost, equipment maintenance, and depreciation costs should be included. The ozonation process was not included in the cost analysis due to the lack of degradation of two of the three dyes. The total costs of the processes used range from 92.28 to 1632 PLN/m^3. Process costs depend on the process used and dye removal. The lowest cost is for Indigo carmine removal regardless of the degradation method. The cheapest and fastest method for removing this dye is the hybrid method, i.e., a combination of ozonation and the Fenton process. An additional advantage of this process is that it is carried out in an environment without changing the pH value. The most unfavorable economic is the process of combining ozonation with hydrogen peroxide.

Table 2. Cost analysis.

Fenton Process (pH = 3; 1 mg of Fe^{2+}; 15 µL of H_2O_2)			
Cost analysis	Indigo Carmine (2 min)	Tartrazine (15 min)	Allura Red AC (30 min)
EE/O [kWh/m^3]	58.82	441.18	882.35
Elektricity cost [PLN/m^3]	36.47	273.53	547.06
H_2O_2 cost [PLN/m^3]	68.98	68.98	68.98
Fe^{2+} cost [PLN/m^3]	11.1	11.1	11.1
Total cost [PLN/m^3]	116.55	353.61	627.14
Ozonation + H_2O_2 (pH = 5.5; 15 µL of H_2O_2)			
Cost analysis	Indigo carmine (10 min)	Tartrazine (30 min)	Allura red AC (30 min)
EE/O [kWh/m^3]	196.46	2521	1886.8
Elektricity cost [PLN/m^3]	121.8	1563.02	1169.82
H_2O_2 cost [PLN/m^3]	68.98	68.98	68.98
Total cost [PLN/m^3]	190.79	1632	1238.8
Ozonation + Fenton process (pH = 5.5; 15 µL of H_2O_2; 1 mg of Fe^{2+})			
Cost analysis	Indigo carmine (1 min)	Tartrazine (30 min)	Allura red AC (30 min)
EE/O [kWh/m^3]	19.65	1456.3	1415.1
Elektricity cost [PLN/m^3]	12.2	902.9	877.4
H_2O_2 cost [PLN/m^3]	68.98	68.98	68.98
Fe^{2+} cost [PLN/m^3]	11.1	11.1	11.1
Total cost [PLN/m^3]	92.28	982.98	957.48

The current electricity rate in Poland is 0.62 PLN/kWh. Price of 30% H_2O_2 is 29.90 PLN/L. Price of $FeSO_4 \cdot 7H_2O$ is 111 PLN/kg.

The studies conducted were small-scale (small volume of reaction solution), so in the next stage of the research, an optimized process applied on an industrial scale to treat real wastewater containing dyes should be evaluated. In advanced oxidation technologies, in parallel to the oxidation processes using $^{\bullet}OH$ radicals, reactions of their "capture" also occur. Apart from excess H^+ and Fe^{2+} ions, other substances acting as radical scavengers are bicarbonate and carbonate ions. The action of hydroxyl radicals is also inhibited by humic compounds, complexing compounds, formaldehyde, tert-butyl alcohol, phosphate and bromide ions, and organic acids, e.g., citric, oxalic, formic, and acetic acids present in water and sewage [54]. It can be expected that in real industrial wastewater, the costs will increase significantly due to the much higher required doses of reagents or the longer process time.

4. Conclusions

The application of the classical Fenton process enables the effective degradation of the dyes Indigo carmine, Tartrazine, and Allura red AC from aqueous solutions. Fenton's reagent was characterized by high oxidizing power compared to that of hydrogen peroxide, which turned out to be insufficient in the degradation of the selected dyes. The research carried out showed that the reaction with Fenton's reagent depends on many factors, i.e., the pH value of the reaction, a medium dose of oxidant and catalyst, the reaction time, and the type of substance being removed. Of all the compounds removed, the Indigo carmine dye turned out to be the most susceptible to the applied processes because high degradation occurred in the shortest reaction time (reaction time: 60 s, pH = 3, H_2O_2 dose: 15 µL, Fe^{2+} dose: 1 mg). In contact with ozone, only Indigo carmine was subject to degradation of more than 90% (pH = 5.5, volume samples: 50 cm^3, dye concentration: 50 mg/dm^3). However, the duration of ozonation had to be much longer compared to the Fenton process (reaction time: 30 min). The combination of the ozonation process with the addition of hydrogen peroxide increased the degree of the decolorization of Tartrazine and Allura red AC solutions. The obtained degradation degree was 60.2% (for Tartrazine) and 70.4% (for Allura red AC) after 30 min of the process (H_2O_2 dose: 15 µL, pH = 5.5). The complete decolorization of the Indigo carmine dye was accelerated from 30 to 10 min. Even better results were recorded in the O_3–Fenton hybrid process (H_2O_2 dose: 15 µL, Fe^{2+} dose: 1 mg, pH = 5.5). For Indigo carmine, 100% removal was achieved after 60 s, while the final degradation of Tartrazine and Allura red AC after 30 min was 79.4% and 80.4%, respectively. It has been proven that the Fenton process, ozonation, and ozonation-based processes are effective in removing dye pollutants from water samples despite not correcting the pH value to 3.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/su17051908/s1, Figure S1: Colors of dye solutions at a concentration of 50 mg/dm3 (1–Indigo carmine, 2–Tartrazine, 3–Allura red AC); Table S1: The selected parameters of the dyes.

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