

Article

Magnetite, Hematite and Zero-Valent Iron as Co-Catalysts in Advanced Oxidation Processes Application for Cosmetic Wastewater Treatment

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Abstract: Background: There is a need for more effective methods of industrial wastewater treatment. Methods: Cosmetic wastewater was collected and subjected to $\text{H}_2\text{O}_2/\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3/\text{Fe}^0$ and UV/ $\text{H}_2\text{O}_2/\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3/\text{Fe}^0$ process treatment. Results: Total organic carbon (TOC) was decreased from an initial 306.3 to 134.1 mg/L, 56.2% TOC removal, after 120 min of treatment for 1:1 $\text{H}_2\text{O}_2/\text{COD}$ mass ratio and 500/500/1000 mg/L $\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3/\text{Fe}^0$ catalyst doses. The application chromatographic analysis allowed for the detection and identification of pollutants present in the wastewater. Identified pollutants were removed during the treatment processes. Processes carried out at a pH greater than 3.0 were ineffective. The UV process was more effective than the lightless process. Conclusions: The applied processes are effective methods for wastewater treatment. Chromatographic results confirmed the effectiveness of the treatment method. The kinetics of the process were described by the modified second-order model. On the basis of ANOVA results, the hypothesis regarding the accuracy and reproducibility of the research was confirmed.



Citation: Bogacki, J.; Marcinowski, P.; Bury, D.; Krupa, M.; Ścieżyńska, D.; Prabhu, P. Magnetite, Hematite and Zero-Valent Iron as Co-Catalysts in Advanced Oxidation Processes Application for Cosmetic Wastewater Treatment. *Catalysts* **2021**, *11*, 9. <https://dx.doi.org/10.3390/catal11010009>

Received: 20 November 2020

Accepted: 22 December 2020

Published: 24 December 2020

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Keywords: industrial wastewater; advanced oxidation processes; zero valent iron; magnetite; hematite

1. Introduction

The cosmetics market is booming and it is one of the fastest growing consumer markets. It globally generated EUR 474.2 billion in 2019. The coronavirus pandemic resulted in a decrease in industry revenues in 2020 by only 1.2%, to EUR 468.3 billion [1].

The constantly increasing production of cosmetics is accompanied by the side effect of producing increasing amounts of waste and wastewater. Cosmetic wastewater (CW) is created by washing production lines with water with surfactants and disinfectants, so CW contains the same compounds as those that are present in cosmetics. A typical industrial-scale CW treatment method is coagulation coupled with dissolved air flotation (C/DAF) followed by biological treatment [2,3]. This method is highly effective, but not enough [4] to remove micropollutants considered to be particularly harmful, such as polycyclic musk, UV filters, heavy metals, and microplastics [5–11]. Fragrances and UV filters are contaminants of emerging concern (CEC) [5]. The most commonly used and thus detected in the polycyclic musk environment are galaxolide (1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-cyclopenta[g]benzopyran, HHCB) and tonalide (6-acetyl-1,1,2,4,4,7-hexamethyltetraline, AHTN), while the most important UV filters are benzophenone-3 (2-hydroxy-4-methoxyphenyl)-phenylmethanone, BP-3) and 4-MBC (4-methylbenzylidene camphor). These compounds often have the potential for bioaccumulation and also show estrogenic activity [6]. Heavy metals such as Zn, Cu, and Fe are typically used in cosmetics as physical UV filters, dyes, or enzyme components. However, even metals such as silver or bismuth are used as bactericides or mask ingredients [7]. Plastics are usually chemically

inert, but under environmental conditions, they are broken down into microscopic grains that penetrate the body even at the cellular level. Their content in organisms increases as they move up the food chain [8]. Due to their persistence to decomposition, they form layers or even islands floating on the water or they accumulate in the soil or bottom sediments, depending on their density [9]. There is a need to develop a policy for dealing with substances that are components of cosmetics [10]. Cosmetic micropollutants during treatment in a biological treatment plant do not decompose but pass into the sludge phase [6]. Their presence is detected in globally collected environmental samples, in concentrations usually below 100 µg/L or 100 µg/kg, depending on sample type [11].

In order to increase the effectiveness of CW treatment, the possibilities of improving classically used coagulation and DAF processes were investigated [12–15]. Advanced oxidation processes (AOPs) [15–19] and the improvement of biological treatment [20–23] were also tested. Attempts were also made to improve the entire treatment, including both chemical and biological methods [24–26].

Many alternatives to classical coagulation and DAF for CW treatment technologies are being developed. Promising ones are AOPs, consisting of the effective generation of strong oxidants, namely radicals. In the case of AOPs in which the production of radicals is catalyzed by the presence of Fe²⁺ ions (Fenton's process and its modifications), a major problem [27] is to ensure the appropriate quantity and availability of Fe²⁺ ions. The amount of Fe²⁺ ions in a solution is influenced by many factors, including pH, the efficiency of Fe²⁺ ion recovery from Fe³⁺, and the rate of Fe²⁺ ion release from the carrier. This problem is solved in two ways: by controlling the Fe²⁺/Fe³⁺ ions ratio or by the controlled continuous introduction of Fe²⁺ ions into the solution. Both strategies pose numerous technical difficulties when applied in practice; therefore, iron-based heterogeneous cocatalysts are gaining interest. Among them are Fe⁰ (metallic iron, zero-valent iron, ZVI), Fe₂O₃ (hematite), and Fe₃O₄ (magnetite) [28–31]. Oxides act through coordinating surface sites of Fe²⁺ that form complexes with contaminants and reduce them [28].

The aim of this study is to determine the effectiveness of the joint use of Fe⁰, Fe₂O₃, and Fe₃O₄ as mutually supportive catalysts using synergy effects in the AOP treatment of industrial wastewater. This is the first article where Fe₂O₃, Fe₃O₄, and Fe⁰ were mutually used in one process as co-catalysts supporting modified Fenton processes to treat cosmetic wastewater.

2. Results

2.1. Raw Wastewater

CW parameters used in the experiments are shown in Table 1. Low values of parameters indicating the content of organic compounds (total organic carbon, TOC and chemical oxygen demand, COD), and the almost complete absence of suspended solids (TSS) and nitrogen compounds (total Kjeldahl nitrogen, TNK), indicated the effective operation of the preliminary treatment (C/DAF) at the production plant. The very high value of the electrolytic conductivity indicated significant wastewater salinity that cannot be derived from only aluminum coagulants used in wastewater treatment in the factory or reagents for pH correction. Despite the high five day biochemical oxygen demand (BOD₅) value and theoretically high potential susceptibility to biological treatment (described as BOD₅/COD ratio, 0.382), even a small amount of raw cosmetic wastewater has a negative effect on biological wastewater treatment plants, hence the need for further treatment.

Table 1. Cosmetic wastewater parameters.

Parameter	Unit	Value
TOC	mg/L	306.3
COD	mg/L	904
BOD ₅	mg/L	345
TSS	mg/L	7
pH	-	8.7
Conductivity	mS/cm	13.8
Surfactants	mg/L	7
TKN	mg/L	<0.1

2.2. Kinetics Matching

In the case of the classical Fenton process, it involves catalytic radical oxidation and final coagulation combined with coprecipitation. The applied modification of the process causes the concentration of iron (II) ions to change due to the dissolution of metallic iron—Fe (II)—amount constantly increasing. In addition, as a result of UV irradiation, there is an increased reduction in iron (III) during the Fenton reaction to iron (II), which results in at least a theoretical decrease in homogeneous catalyst demand. The use of magnetite and hematite as cocatalysts, and metallic iron, leads to the appearance of the surface of solid catalyst heterogeneous processes, including sorption or ion exchange. All these processes are at least partially independent and sometimes even antagonistic. Therefore, describing the kinetics of the treatment process is not easy. Four equations were used to describe the kinetics:

- First-order reaction with respect to the TOC value:

$$\text{TOC} = \text{TOC}_0 \times e^{-kt} \quad (1)$$

- Second-order reaction with respect to the TOC value:

$$\text{TOC} = (kt + 1/\text{TOC}_0)^{-1} \quad (2)$$

- Modified first-order reaction with respect to the TOC value:

$$\text{TOC} = (\text{TOC}_0 - b) \times e^{-kt} + b \quad (3)$$

- Modified second-order reaction with respect to the TOC value:

$$\text{TOC} = (kt + (\text{TOC}_0 - b)^{-1})^{-1} + b \quad (4)$$

Equations (1) and (2) are the descriptions of the usual first- and second-order kinetics. Typically, however, the kinetics of a specific chemical reaction is described with clearly defined substrates and products. In the case of the description of wastewater, it is a complex mixture of many chemical compounds present in various concentrations. From a practical point of view, it is not possible to determine the concentrations of all chemical compounds and, most importantly, to predict all chemical reactions taking place. Therefore, collective parameters such as BOD₅, COD, and TOC are described. In the case of treatment processes where hydrogen peroxide is used, it may remain after the process. While we ran the process to ensure that it was decomposed (and iodometrically checked), the decomposition of hydrogen peroxide takes time. Hydrogen peroxide is a well-known disruptor in COD measurement. During radical oxidation, wastewater is at least partially sterilized, which also affects BOD determination. Although both disturbing factors (in the determination of BOD and COD) can be eliminated, from a practical point of view, it is easier to use TOC notation, which is considered more reliable and unambiguous in its interpretation. Therefore, it was decided to describe all kinetics in relation to one collective TOC parameter. The idea behind first- and second-order kinetics is that the reaction can be

completed, i.e., until the substrate is completely used. Under the conditions of our experiment, this means zeroing the TOC value and complete decomposition of the pollutants. However, it is not possible to obtain complete TOC elimination. There is always a certain amount left, hence the idea to modify the description of kinetics. As such, there was a certain number of compounds that could be removed in our process, but some would be persistent to decomposition. The amounts of these substances can be described as possible and impossible to remove TOC. Value “b” Equations (3) and (4), represents the content of this persistent, so-called “hard” TOC. The remaining amount of nonpersistent TOC can still be decomposed, and the description is related to first- or second-order kinetics. An example of the application of four kinetic models is presented in Figure 1. The best match was obtained for the modified second-order kinetics model.

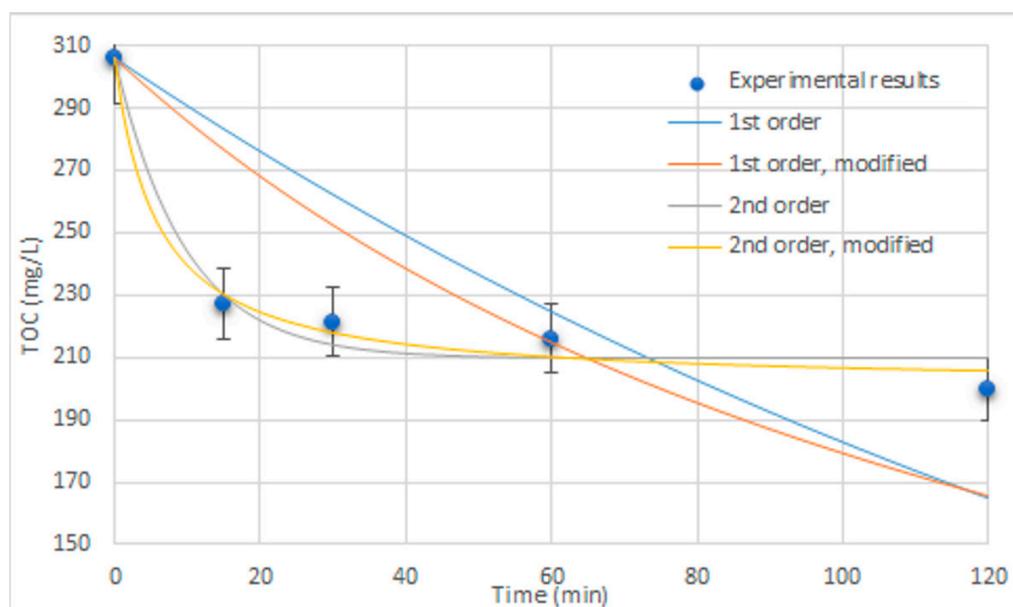


Figure 1. Example kinetic model results: 1500/1500/1000 $\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3/\text{Fe}^0$ doses (mg/L) $\text{H}_2\text{O}_2/\text{COD}$ mass ratio 1:1, UV irradiation, pH = 3.0.

2.3. Treatment Processes

Detailed doses and proportions of the reagents used during the research on CW catalytic treatment are presented in Table S1, while treatment results are shown in Figures 2–5.

Treatment is more effective as the process takes longer to run. The use of UV light increases the effectiveness of the treatment compared to a non-light-assisted process with the same doses of reagents.

In each of the non-light-assisted experiments, the most intensive TOC removal, around 50 mg/L, was obtained in the first 15 min. Such a situation could be observed, for, e.g., 2:1 $\text{H}_2\text{O}_2/\text{COD}$ ratio and 250/250/1500 mg/L $\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3/\text{Fe}^0$ catalyst doses (Figure 3). In the mentioned sample, after 30 min of the process, TOC was 221.7 mg/L; for 15 min from the first measurement, it was decreased by 27 mg/L. During subsequent measurements made at 15-, 30-, and 60-min time differences, TOC decreased more slowly. A better treatment effect was obtained by using a lower ratio of 1:1 $\text{H}_2\text{O}_2/\text{COD}$. The lowest TOC, 182.0 mg/L, was obtained for 1:1 $\text{H}_2\text{O}_2/\text{COD}$ ratio and 500/500/3000 mg/L $\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3/\text{Fe}^0$ catalyst doses after a 120 min process time (Figure 2). The second-lowest TOC, 198.4 mg/L, was for 1:1 $\text{H}_2\text{O}_2/\text{COD}$ ratio and 500/500/1000 mg/L $\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3/\text{Fe}^0$ catalyst doses. The highest TOC 218.0 mg/L, only 28.8% TOC removal after a 120-min process time, was obtained for 375/375/250 mg/L $\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3/\text{Fe}^0$ catalyst doses and 2:1 $\text{H}_2\text{O}_2/\text{COD}$ ratio. On the basis of the presented data, for non-light-assisted processes, with regard to catalyst doses at constant values of hydrogen peroxide, lower TOC values were achieved for higher doses of the catalysts: 4000 mg/L, slightly lower for 2000 mg/L,

and the lowest for 1000 mg/L. In most cases, lower values of TOC were recorded for the lower 1:1 H₂O₂/COD ratio. The TOC values determined after the treatment process with the 2:1 H₂O₂/COD ratio were higher than the value for 1:1 H₂O₂/COD ratio. The exception was the process involving 1000 mg/L of hematite, 1000 mg/L of magnetite, and 2000 mg/L of metallic iron, in which the difference was 40 mg/L.

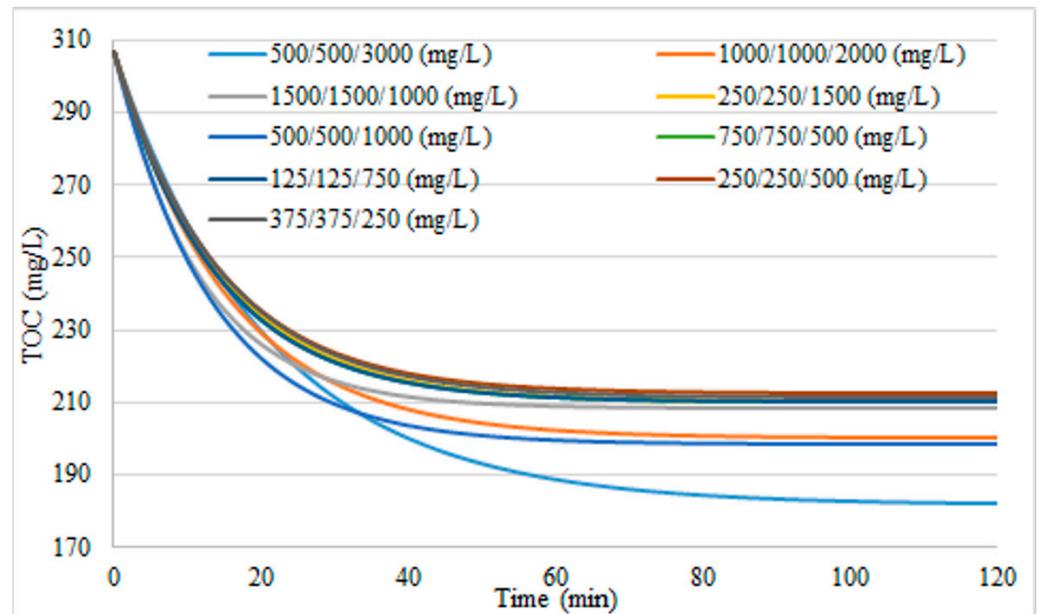


Figure 2. Cosmetic wastewater (CW) treatment results with different Fe₃O₄/Fe₂O₃/Fe⁰ doses (mg/L) H₂O₂/COD mass ratio 1:1, without UV irradiation, pH = 3.0.

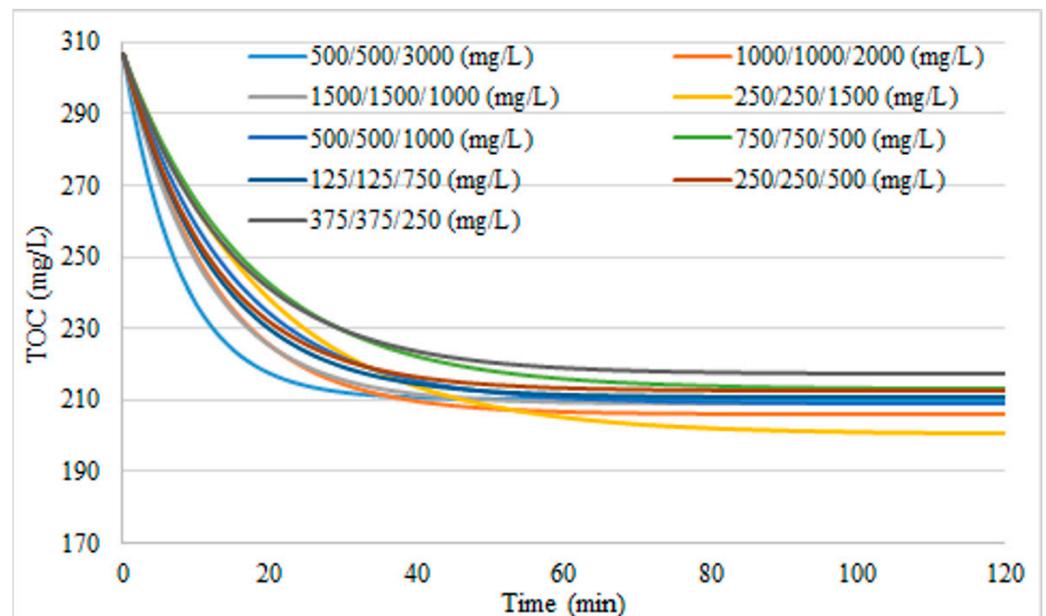


Figure 3. CW treatment results with different Fe₃O₄/Fe₂O₃/Fe⁰ doses (mg/L) H₂O₂/COD mass ratio 2:1, without UV irradiation, pH = 3.0.

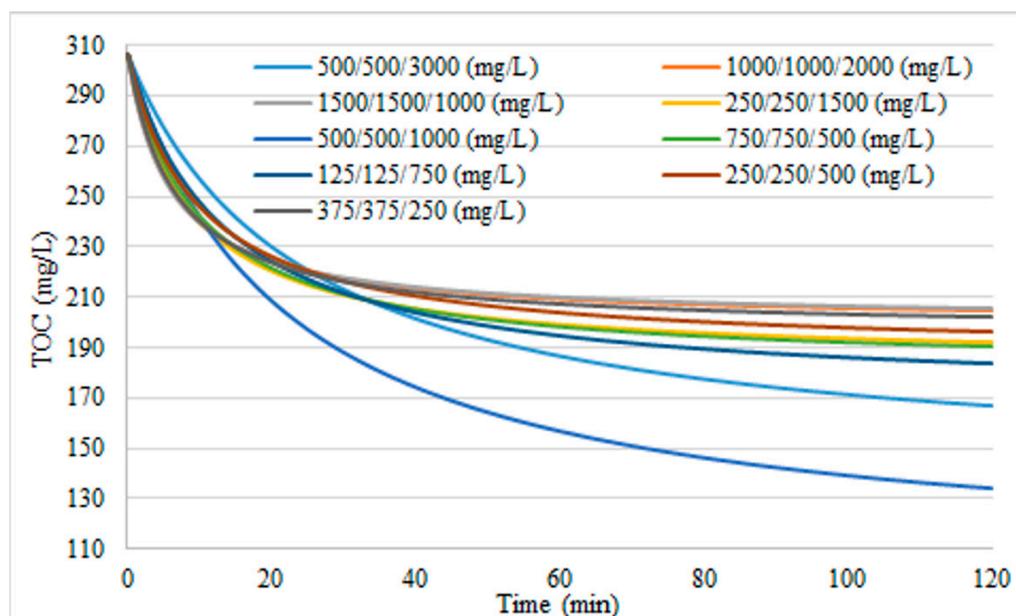


Figure 4. CW treatment results with different $\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3/\text{Fe}^0$ doses (mg/L) $\text{H}_2\text{O}_2/\text{COD}$ mass ratio 1:1, UV irradiation, pH = 3.0.

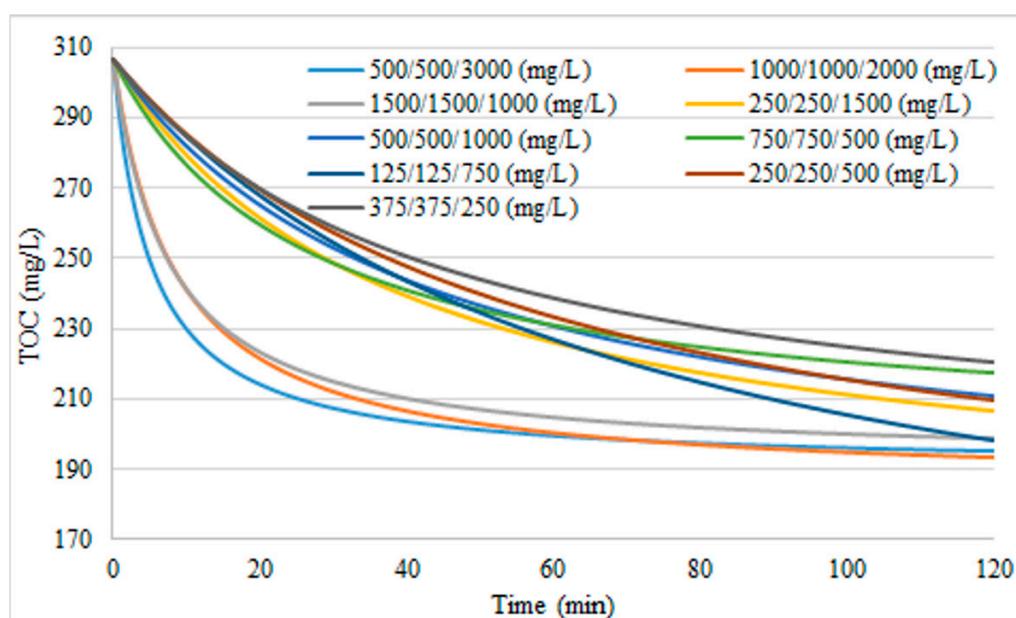


Figure 5. CW treatment results with different $\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3/\text{Fe}^0$ doses (mg/L) $\text{H}_2\text{O}_2/\text{COD}$ mass ratio 2:1, UV irradiation, pH = 3.0.

In the light-assisted process, the lowest TOC, 134.1 mg/L (56.2% TOC removal), was obtained after 120 min for 1:1 $\text{H}_2\text{O}_2/\text{COD}$ ratio and 500/500/1000 mg/L $\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3/\text{Fe}^0$ catalyst doses (Figure 5). In the initial phase of the process, a slower decrease in TOC value was visible for the 2:1 $\text{H}_2\text{O}_2/\text{COD}$ ratio, to 260–270 mg/L. However, a faster decrease was observed in the mixture of iron compounds mass equal to 4000 mg/L. This may indicate that the weight of the catalysts was optimal for the higher dose of hydrogen peroxide and accelerated the process. For smaller total catalyst concentrations, 2:1 $\text{H}_2\text{O}_2/\text{COD}$ ratio led to the inhibition of the reaction. The decrease in TOC value for 4000 mg/L of catalyst 2:1 $\text{H}_2\text{O}_2/\text{COD}$ ratio was comparable with that in samples with a lower oxidant concentration for up to 30 min. After this time, for the 1:1 $\text{H}_2\text{O}_2/\text{COD}$ ratio, reactions slowed down significantly. An exception may be the sample of 500/500/1000 mg/L $\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3/\text{Fe}^0$

catalyst doses, where TOC decreased throughout the experiment. In this case, the hetero-catalytic reaction could have contributed to the steady decline. The optimal selection of reagent doses ensured the decomposition of the organic pollutants on the surface of the catalysts. For a higher concentration of the oxidant, the given doses of the catalysts did not give an outstanding result, and at a lower concentration of H_2O_2 , it had a greater effect on TOC decomposition. In the experiments where the concentration of iron compounds was 4000 mg/L, there was no visible difference in the rate of the processes, resulting from the concentration of hydrogen peroxide. For the experiments carried out at the concentration of iron compounds of 2000 and 1000 mg/L, however, there was a difference according to the dose of hydrogen peroxide. Lower concentrations of the oxidant resulted in faster TOC removal in the first few minutes of the experiment. At higher concentrations, removal was slower, and more time was required for the reaction to come to a halt. Even though the reaction took longer, in most cases, efficiency for TOC removal at a higher concentration of H_2O_2 did not exceed the effectiveness for the 1:1 H_2O_2 /COD ratio. The exceptions were the concentrations of 1000/1000/3000 mg/L $Fe_3O_4/Fe_2O_3/Fe^0$, in which efficiency was higher at a higher oxidant concentration.

Additionally, an experiment was performed that demonstrated the influence of pH on the efficiency of the pollutant oxidation process (Figure 6). The process was the most effective at pH 2 and 3. The processes carried out at a pH greater than 3 were ineffective, and the decrease in TOC value from 15 min until the end of the experiment was not significant. At pH 2 and 3, TOC decrease was visible throughout the process. At pH 2, sediment in the sample was swollen and occupied the largest volume compared to in the other samples. Sediment after the process carried out at pH 4 was a reddish color and had a volume comparable to that in the processes at pH 3. Obtained sediment during the experiment at pH 5 was brown, and its amount was the smallest in comparison to that formed during the process at other pH values. In the experiment carried out at pH 6, the sediment after the process was reddish, and its structure was comparable to that of the sediment at pH 3 and 4. The red may have indicated the presence of iron (III) hydroxide, which is formed at a high solution pH.

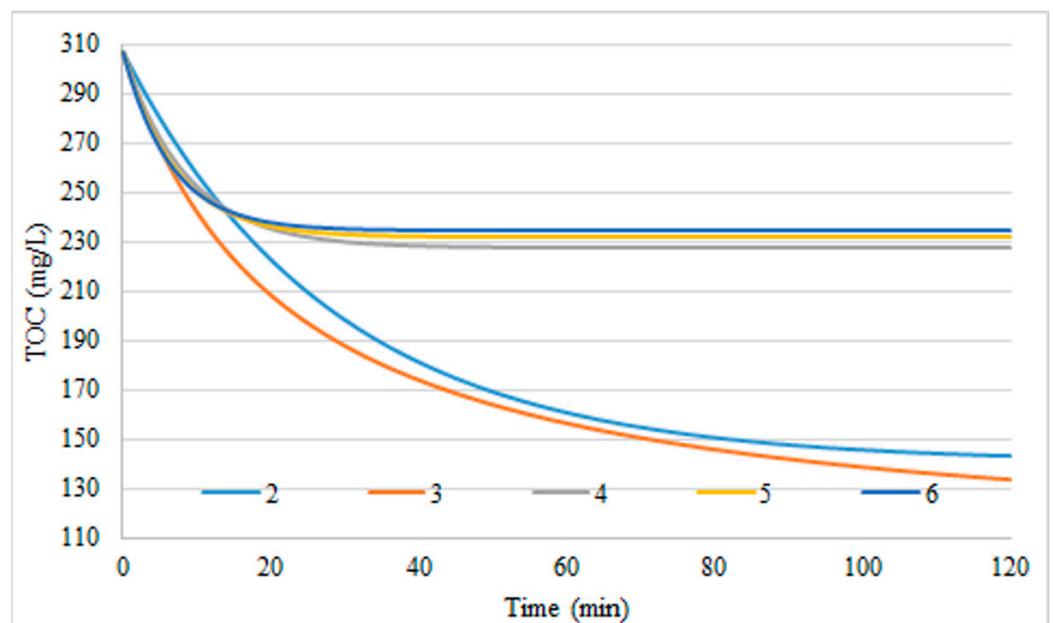


Figure 6. CW treatment results at different pH, 500/500/1000 $Fe_3O_4/Fe_2O_3/Fe^0$ doses (mg/L) H_2O_2 /COD mass ratio 1:1, UV irradiation.

H_2O_2 is a weak acid. Its stability increases with a decrease in pH value, which may impede its catalytic decomposition into a hydroxyl ion and radical. However, these effects

were not strongly observed during the experiment. Hydrogen peroxide under alkaline conditions decomposes rapidly with the evolution of oxygen. For this reason, no attempt was made to operate the process under alkaline conditions. However, the presence of the formation of oxygen bubbles hindering the sedimentation of the formed sludge was observed in all experiments at the termination stage of the Fenton reaction. In the case of iron (II) and (III), its source in the process was twofold: the surface of stable iron oxides magnetite and hematite, and the dissolution of metallic iron. The solubility (corrosion) of metallic iron occurs quickly under strongly acidic conditions; under neutral conditions, the process is very slow. Therefore, in neutral conditions, contact between the reactants is difficult to achieve during the entire duration of the process. In an acidic environment, due to the constant increase in the content of dissolved iron, its availability, and thus the intensity of the Fenton reaction, increases steadily with time. Additionally, the form of iron is strongly pH-dependent. At pH 5, iron hydroxides with small solubility begin to form, and the coagulation process begins. For iron hydroxide, due to minimal solubility, the optimal value for carrying out the coagulation process was around 6.0 and above 8.5. This was another reason for abandoning the experiment in alkaline conditions, as radicals were terminated on the sludge flocs, which resulted in rapidly decreasing process efficiency.

The statistical analysis was described on the basis of Miller [32]. ANOVA was used to determine the magnitude of variability in the average concentrations of TOC and to check whether differences in the average test results for TOC for individual process conditions (for different doses of catalysts) may have been caused by random errors (Tables S2 and S3, Figures S4 and S5).

Variance is estimated using two methods: the method determining the variability within a given sample, and variability between samples. The difference in the performed tests was the different durations and reagent doses of the process. The above statement is a null hypothesis.

If the hypothesis were true, then there would be no large difference between calculated values. If the hypothesis were not true, then the between-group estimate would be greater than the intergroup estimate. This is due to the high variability between samples. To check if the difference was significant, Snedecor's one-sided F test with $\alpha = 0.05$ was performed.

The following null hypothesis was made for ANOVA: the tests were performed accurately, and reproducibility was achieved in TOC results. The value of the F parameter was lower than that of the critical F, which means that the hypothesis is true. The mean values in the samples were similar, and similar conclusions were found during TOC analysis. Even the optimal value did not significantly differ from the other values. From the perspective of the performed tests, this is a favorable phenomenon, as it proved the accuracy and repeatability of the performed tests. However, the process itself was not effective, and from the perspective of the conducted process, its effectiveness was not favorable.

2.4. HS-SPME-GC-MS Analysis

Head space-solid phase micro extraction-gas chromatography-mass spectrometry (HS-SPME-GC-MS) analysis results are shown in Table 2. GC-MS chromatograms, for raw and treated samples (the sample with the lowest TOC after the process was selected), are shown in Figures S1 and S2.

The identified compounds were mainly cosmetic bases (e.g., decamethyltetrasiloxane or decamethylcyclopentasiloxane) and fragrances (e.g., 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-cyclopenta(g)-2-benzopyran (galaxolide) or 4-isopropenyl-1-methyl-1-cyclohexene (limonene)).

All compounds detected with HS-SPME-GC-MS were removed during the treatment process. No new compound was detected during the process. HS-SPME-GC-MS is a useful tool that can be used to confirm the high efficiency of the treatment process.

Table 2. Raw wastewater head space-solid phase micro extraction–gas chromatography–mass spectrometry (HS-SPME–GC–MS) analysis results.

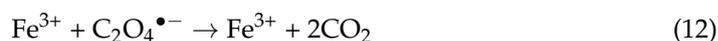
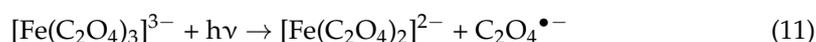
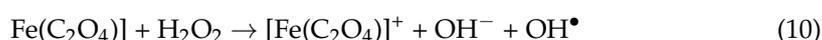
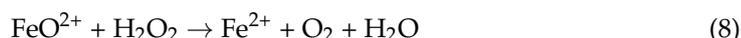
No.	Retention Time (s)	Peak Area	Compound Name
1	842.56	263936015	2,2,4,6,6-pentamethylheptane
2	914.76	76933033	2-ethyl-1-hexanol
3	922.12	55446786	4-isopropenyl-1-methyl-1-cyclohexene
4	969.37	40480391	decamethyltetrasiloxane
5	995.26	135240755	6-ethyl-2-methyl-6-hepten-2-ol
6	1042.25	407718598	3,7-dimethyl-3-octanol
7	1049.08	376591195	3,7-dimethyl-1,6-octadien-3-ol
8	1126.13	376591195	decamethylcyclopentasiloxane
9	1191.81	87920970	5-methyl-2-(1-methylethyl)-cyclohexanol
10	1220.03	87920970	3,7-dimethyl-1,6-octadien-3-ol
11	128073	342408048	dodecamethylpentasiloxane
12	1344.91	201821493	2,6-dimethyloctane
13	13.92.76	84107649	tridecane
14	1424.61	293329202	dodecamethylcyclohexasiloxane
15	1441.31	523263467	2,2,4,4,6,8,8-heptamethylnonane
16	1473.59	439161977	undecylcyclohexane
17	1667.25	592268444	2-dodecanol
18	1791.80	913690562	hexadecamethylheptasiloxane
19	1842.23	471919073	hexadecane
20	1933.23	175348881	di-n-octyl ether (1,1'-oxybisoctane)
21	1938.56	193030178	cyclopentaneacetic acid, 3-oxo-2-pentyl-,methyl ester
22	1968.92	152991091	7a-isopropenyl-4,5-dimethyloctahydro-1H-inden-4-yl)methanol
23	1978.11	93958573	unidentified compound
24	2035.27	1390556189	2-butyloctanol
25	2067.00	474433634	2,4-dimethyl-1-heptanol
26	2074.26	161503287	isobutyl nonyl carbonate
27	2091.65	569595240	2-methyl-1-decanol
28	2115.29	467909425	oxalic acid, cyclohexylmethyl tridecyl ester
29	2150.05	226358082	unidentified compound
30	2206.07	980264063	1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-cyclopenta(g)-2-benzopyran
31	2210.77	678685873	1-hexadecanol
32	2307.06	327313756	ether, di-n-octyl-(1,1'-oxybis-octane),
33	2374.06	79843231	1-methylethyl hexadecanoate

3. Discussion

An innovative solution was applied that has not yet been used as a cosmetic wastewater treatment technique, nor has it appeared in other industries. After separate analysis of the effectiveness of each catalyst, metallic iron with hematite and metallic iron with magnetite [33], the compounds were combined to create a unique mixture in order to check its properties and effectiveness during the treatment of cosmetic wastewater. The highest efficiency of the process was achieved when using the catalyst proportion in which there was a significant advantage of metallic iron and a comparable lower dose of magnetite and hematite (quantitative ratio of the compounds was 250/250/1500 mg/L). The lowest efficiency of the process was obtained when the catalyst was used, in which a significantly lower dose of metallic iron of 250 mg/L, and slightly higher concentrations of hematite and magnetite were used, 375 mg/L in all cases. When using a total concentration of 2000 mg/L of the mixed catalyst, the process was the most effective. The lowest concentrations were obtained with the use of a lower dose of 1000 mg/L reagent. The lower dose was insufficient to efficiently perform oxidation. When a higher dose of hydrogen peroxide was used, the process was also not as effective as when a higher dose of the mixed catalysts was used.

Analyzing the obtained results, they complied with those of earlier research [33], indicating that the excess of hydrogen peroxide adversely affects the performed process, decreasing its effectiveness.

The use of a higher dose of the oxidant caused a lower efficiency in TOC removal from CW. Excess hydrogen peroxide is an inhibitor of the reaction. Then, a process may take place (reaction Equation (5)) where a hydroperoxide radical is formed (oxidation-reduction potential 1.7 V) which is much less reactive than the hydroxyl radical (2.8 V). Hydroperoxide radicals react with hydroxyl radicals (reaction Equation (6)) to form a water molecule and an oxygen molecule. Reactive molecules merge with each other to form substrates that are not strong oxidants.



Intermediate compounds are formed in the catalytic cycle. One is oxoiron $\text{Fe}^{\text{IV}}\text{O}$ [34], which is formed as a result of the reaction initiating the Fenton process, described by reaction Equation (7).

With an excess of hydrogen peroxide, oxoiron reacts with it and forms Fe^{2+} , oxygen, and water (reaction (8)). This is a reaction that stops the process. Oxoiron is also involved in the oxidation of organics (reaction (9)), which is much slower than the one with the hydroxyl radical.

Factors accelerating the formation of radicals may be ligands present in CW, which form complexes and chelates with iron. The oxalate ligand reacts with hydrogen peroxide to form a hydroxyl radical according to reaction Equation (10). Oxalates (diethyl, dimethyl, diisopropyl, diisobutyl, sodium) are present in cosmetics and thereby also in CW. In acidic conditions, at a low pH of 3.0, acid hydrolysis of oxalates esters could take place.

The process was supported by UV radiation (full emission spectrum is shown in Figure S3), so its influence on reaction kinetics in the presence of oxalates should be considered. Absorbed radiation causes the decarboxylation of the ligand with the release of CO_2 and reduction in Fe^{3+} to Fe^{2+} (reactions (11) and (12)). The oxidation of organic compounds occurs at high speed in the presence of oxalates. Complex compounds with carboxylic acids under UV radiation reduce the iron, and alkyl radical and carbon dioxide are produced (reaction (13)). These reactions lead to the fast mineralization of organic compounds in wastewater.

Improperly selected doses of catalysts (too small an amount of iron) have a negative effect on the high-efficiency treatment process. Regardless of the amount of catalyst and hydrogen peroxide, the effectiveness of the treatment processes increases with time.

The longest process time, 120 min, was the most effective. The 15 min process time was the least effective, as this was not enough time to carry out the treatment process. However, the duration and higher costs of the process should be considered, and the optimal time should be selected so as to maintain high efficiency with an appropriate cost of treatment. For lightless processes and 120-min process time, the process is no longer profitable, and an equally high efficiency was achieved after 60 min of treatment. Such an observation was not made in the case of light-assisted processes. For them, extending the process time to 120 min is still profitable. The process showed the greatest efficiency in relation to its duration during the first 15 min, and TOC was mostly decreased in a short period of time. Then, sequential TOC measurements showed lower speed of the treatment process.

Most of the studies that used hematite or magnetite were carried out on pollutants present in components. For example, hematite was used as a catalyst by Araujo et al. [35]. In total, 20 g of hematite and a dose of 800 mg/L of hydrogen peroxide allowed for achieving 99% treatment efficiency of the process after 120 min. Our research was carried out for much lower catalyst doses and a different type of contaminant with a much more complex matrix (wastewater from the cosmetic industry).

In samples taken after 15- and 30-min process time, a large amount of evolving gas bubbles was visible because of the decomposition of unreacted hydrogen peroxide. The color of the precipitate depended on the ratio of iron to magnetite and hematite. Dependence was visible; the greater the amount of metallic iron in the sample was, the more orange the sediment was. No greenish sediment was observed, which would indicate the presence of Fe^{2+} ions. On this basis, it was concluded that the oxidant doses were correctly selected.

There was a separation in the sediment phases into an upper rusty one (oxidized iron) and lower black one (magnetite, metallic iron). The exact mechanism of the separation process is unknown, but this could be due to the difference between densities, as iron hydroxide has a lower density than that of magnetite and metallic iron.

4. Materials and Methods

4.1. Wastewater

Samples of real cosmetic wastewater, pre-treated by coagulation coupled with dissolved air flotation, were taken for the tests. The samples were taken from an industrial plant located in Poland.

4.2. Treatment Process

Zero-valent iron (Ferox Target, 325 mesh) was supplied by Hepure (Hillsborough, NJ, USA). Hematite (10 μm) was supplied by Kremer (Aichstetten, Germany); magnetite (10 μm) was supplied by Kremer (Aichstetten, Germany); 30% H_2O_2 solution was supplied by Stanlab (Lublin, Poland).

Doses of H_2O_2 , Fe^0 , magnetite, and hematite were selected in preliminary tests. Treatment processes were carried out in a 1.5 L reactor filled with 1 L of the sample, stirred at 300 rpm (Heidolph MR3000, Schwabach, Germany). pH in the treatment processes was set to 3.0, unless otherwise stated. The experiment on the influence of pH on the efficiency of the process was carried out at pH 2.0, 3.0, 4.0, 5.0 and 6.0. Samples were taken after 15, 30, 60 and 120 min of the process. The process was stopped as a result of alkalization to pH 9.0 with 3M NaOH (POCh, Gliwice, Poland).

The source of radiation was medium-pressure Fe/Co 400W lamp type HPA 400/30 SDC with 94W UVA power (Philips, Amsterdam, The Netherlands). The lamp spectrum is shown in Figure S3. Details of the experiment setup are shown in Table S1.

4.3. Analytical Methods

Total organic carbon (TOC), five-day biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), total Kjeldahl nitrogen (TKN), total suspended solids (TSS), ammonia, surfactants, pH, and conductivity were determined according to the standard methods.

TOC was determined using a TOC-L analyzer (Shimadzu, Kyoto, Japan) with an OCT-L8-port sampler (Shimadzu, Kyoto, Japan). Chromatographic analysis was conducted with an Agilent 7890A (Santa Clara, CA, USA) gas chromatograph coupled with a Leco TruTOF (St. Joseph, MI, USA) mass spectrometer. The detailed methodology is described elsewhere [33].

5. Conclusions

Due to the increasing consumption of cosmetics, an effective and inexpensive method of CW treatment is needed. The effective treatment of CW in accordance with applicable

legal standards is difficult. The results of this research confirmed the effectiveness of the pretreatment of wastewater currently used by most industrial plants with the use of C/DAF.

CW can be effectively treated with both the UV/H₂O₂/Fe₃O₄/Fe₂O₃/Fe⁰ and the H₂O₂/Fe₃O₄/Fe₂O₃/Fe⁰ process. The condition for the application of an effective CW treatment by catalytic oxidation is the use of an appropriate dose of hydrogen peroxide as a catalyst.

The best match of the results to kinetic models was obtained by second-order equations with a modification, taking into account the amount of undegraded compounds during the treatment process.

On the basis of the ANOVA results, the hypothesis regarding the accuracy and reproducibility of the research was confirmed.

Supplementary Materials: The following are available online at <https://www.mdpi.com/2073-4344/11/1/9/s1>, Table S1: Experimental setup, Table S2: One-way analysis of variance for mean values of TOC for 1:1 H₂O₂/COD ratio, Table S3: One-way analysis of variance for mean values of TOC for 2:1 H₂O₂/COD ratio. Figure S1: GC-MS chromatogram: Raw wastewater, Figure S2: GC-MS chromatogram: Treated wastewater, 500/500/1000 mg/L Fe₃O₄/Fe₂O₃/Fe⁰ catalyst doses, 1:1 H₂O₂/COD ratio, pH = 3.0, 120 min, Figure S3: The emission spectrum of the lamp, Figure S4: Anova plots of the UV/H₂O₂/Fe₃O₄/Fe₂O₃/Fe⁰ process, Figure S5: Anova plots of the H₂O₂/Fe₃O₄/Fe₂O₃/Fe⁰ process.

Author Contributions: Conceptualization, methodology, writing—original draft preparation, review and editing, supervision: J.B. and P.M.; laboratory work and data processing: J.B., P.M., D.B., M.K., D.Ś. and P.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Acknowledgments: The authors thank Hepure for providing ZVI Ferox Target samples as research material.

Conflicts of Interest: The authors declare no conflict of interest.

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