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EVALUATION OF OPERATIONAL PARAMETERS AND ITS RELATION ON THE STOICHIOMETRY OF FENTON'S OXIDATION TO TEXTILE WASTEWATER

Article Highlights

- Operation conditions for implementation of the Fenton process were re-evaluated
- COD/H₂O₂, COD/Fe²⁺ and H₂O₂/Fe²⁺ ratios were optimized by physico-chemical studies
- The effects of important parameters on TOC and color removal were investigated
- A new operational table was produced on the basis of stoichiometric ratios
- Time-dependant dosing of H₂O₂ helps to obtain higher efficiency levels

Abstract

The operation conditions for the implementation of the Fenton process are of utmost importance because there are problems related to the proportion of H₂O₂ dosage to COD and Fe²⁺ dosage to the specified H₂O₂ amount. The relevant literature shows that COD/H₂O₂ ratios range between 0.0084 and 113.9. Similarly, the COD/Fe²⁺ ratio varies between 0.079 and 292.6, while the H₂O₂/Fe²⁺ ratio varies between 0.09 and 287. Moreover, the ratio of the maximum value to the minimum value used in the operations on the basis of COD is 13560 for COD/H₂O₂ (0.0084-113.9), 2210 for COD/Fe²⁺ (0.079-174.7), and finally 3190 for H₂O₂/Fe²⁺ (0.09-287). The aim of this study was to re-evaluate these values that significantly differ from each other with specific emphasis on textile wastewater and considering stoichiometric ratios. Results showed that values ranging between 0.43 and 4.0 for COD/H₂O₂ and those ranging between 0.75 and 3.0 for H₂O₂/Fe²⁺ are more suitable. The results showed that in a Fenton process conducted by dosing H₂O₂ at different times, the TOC reduction efficiencies increased from 80.8 up to 88.9%. Similarly, the color reduction efficiency also rose from 96.5 to 98.7%.

Keywords: Fenton's oxidation; operational parameters; oxidation; stoichiometric ratio, TOC removal.

Wastewaters are treated physically, chemically, and biologically. The physical methods use separation processes rather than a treatment processes. At the end of these processes, contaminants are generated in a concentrated manner [1]. At the end of the biological processes, on the other hand, one of the contaminants that one emerges is sludge [2]. Even

though the contaminants generated by chemical methods, such as clarification-type processes, are different, they are still present inside the chemical sludge [3], whereas the contaminants can be fully avoided by using advanced treatment processes. The oxidation processes in particular aid in the complete elimination of these contaminants. The Fenton process has a special characteristic among the other oxidation processes. The difference of the Fenton process is that it generates •OH, which helps introduce the synergistic effect of peroxide, an oxidant, the iron catalysis [4]. This process is especially efficient for COD parameters that are difficult to reduce, when the BOD/COD ratio is low. When a Fenton process is applied to a COD parameter, which cannot be reduced by means

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of other processes, high efficiencies can be obtained. The reason for this is that the oxidation capacity of hydroxyl radicals is higher than the other oxidants [4]. Based on this, one can conclude that the Fenton process can be used on a variety of wastewaters such as those produced by activities related to textiles [5], leachates [6], paints [7], olive mills [8], pharmaceuticals [9], tanneries [10] and surfactants [11]. In addition, whenever the desired level of efficiency cannot be obtained by biological refinement, the Fenton process can also be used as a final treatment method to shift *COD* values to the desired levels [12].

In spite of these advantageous characteristics, the Fenton process brings about a number of important economic problems [13]. The major reason behind this is that normally the peroxide dose and the amount of iron to be used cannot be finely adjusted. The addition of peroxide and iron in measurements that are less than needed causes low efficiency levels. On the other hand, excessive use of peroxide creates problems, not only because it requires reduction (reduction of excessive peroxide), but also it results in additional costs. Similarly, the addition of excessive iron also brings about extra costs and also results in extremely significant operational problems such as the sludge caused by too much iron. For these reasons, the selection of operational conditions for a Fenton process is of utmost importance in terms of a correct and efficient operation [4].

The aim of this study was to avoid eventual redundant and excessive H_2O_2 and Fe^{2+} additions, and hence to prevent the formation of redundant sludge and excessive peroxide, based on the stoichiometric ratios that should be ensured by selecting the appropriate operational conditions. In addition, a physico-chemical study was carried out on a textile wastewater sample, by using less chemicals on the basis of stoichiometric ratios, and it was aimed to demonstrate that high reduction efficiencies can actually be obtained by using low amounts of chemicals.

MATERIALS AND METHODS

Selection of operational parameters

In this study, the effects of the operational conditions such as initial pH value, and $\text{COD}/\text{H}_2\text{O}_2$ and $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratios on the Fenton process were investigated. Since the priority of this study was to define $\text{COD}/\text{H}_2\text{O}_2$ and $\text{H}_2\text{O}_2/\text{Fe}^{2+}$, these parameters were investigated in more detail. After defining the optimum values, an optimization study was carried out on the basis of pH values. Finally, the effect of adding the initial peroxide by dosing on the results was analysed.

Also, a comparative analysis between the first 9 studies and the study-set between 29 and 38 will provide further insight regarding the effect of dosing the peroxide to add to the results.

Wastewater characteristics

Textile wastewater was selected as the study case. The textile wastewater samples were taken from the Akinal textile factory (Cevizlibag, Istanbul, Turkey) and kept at 4 °C. The wastewater parameters were regularly measured during this study. The main characteristics of the textile wastewater samples used in the experiments are shown in Table 1.

Table 1. Characterization of textile wastewater from Akinal textile factory; *SD* - standard deviation

Parameter	Unit	Mean + <i>SD</i>
Chemical oxygen demand (<i>COD</i>)	mg/L	1625±40
Five-day biochemical oxygen demand (<i>BOD</i> ₅)	mg/L	570±15
<i>BOD</i> ₅ / <i>COD</i>	-	0.35
<i>TOC/COD</i>	-	0.32
pH	-	4.3±0.1
Total organic carbon (<i>TOC</i>)	mg/L	524±10
Color	Pt-Co	545±10
Conductivity	µS/cm	2370±50

Fenton's oxidation

A stock solution of 10 g/L of Fe^{2+} was prepared by dissolving $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Merck Chemical Corp.) in distilled water. In addition to iron sulfate reagent, 30% H_2O_2 solution (Merck Chemical Corp.) with a density of 1.11 kg/L was used in the oxidation process. In each oxidation test, 500 mL of textile wastewater sample was collected from the textile industry effluent. In the first step of Fenton's oxidation process, the pH of the textile wastewater was adjusted to the desired value by the addition of 1 M H_2SO_4 and 1 M NaOH. During the whole oxidation process, the pH of samples were also set at the desired value by adding these reagents (1 M H_2SO_4 and 1 M NaOH) gradually in addition to the pre-adjustment of the pH. The $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and H_2O_2 solutions were then added to the effluent sample and conducted for 5 min of rapid mixing at 120 rpm using a Jar Test Equipment (VELP Scientifica, FC6S). The effluent sample was then gently stirred at 10 rpm for 25 min. After the flocculation process, the sample transferred to a graduated settling column for 30 min of settling. 100 mL of supernatant sample was then collected for the further analyses (*TOC* and color) after the settling process. In order to prevent interferences in analytical measurements, the pH of collected supernatant sample

was increased to about 6.0 by adding 6 M NaOH gradually to precipitate Fe^{2+} in the form of $\text{Fe}(\text{OH})_3$. Finally, the MnO_2 reagent was then added to remove the residual H_2O_2 from the collected supernatant [26].

Analytical procedure

The pH of wastewater samples was measured by a pH meter (WTW series pH 720) and a pH probe (WTW, pH-Electrode Sentix 41). The color of wastewater samples was measured with a Hach Lange spectrophotometer (model: DR 5000) and determined as platinum-cobalt (Pt-Co) color unit according to method 120. Electrical conductivity was measured by using a multimeter instrument (Hach Lange HQ 40D). The total organic carbon (TOC) was measured by using a Hach Lange IL 550 TOC/TN analyzer. All other experimental analyses were performed by the procedures described in the Standard Methods of APHA [34]. These parameters were determined by the procedures described in method numbers of 5220 C (closed reflux, titrimetric method for COD) and 5210 B (5-day BOD test). The deionized water used in the experiments was supplied from a purification system (Meck Millipore Direct-Q 3, 5, 8 Ultrapure Water Systems). The analyses were carried out at least three times for each sample to assess method precision. Stability of the oxidation process and components of wastewater samples were monitored in the Environ-

mental Engineering Laboratory at Yildiz Technical University in Istanbul, Turkey.

RESULTS AND DISCUSSION

Literature review on the Fenton's oxidation process

When the data reported in the relevant literature are investigated, it is seen that the doses selected both for peroxide and Fe^{2+} parameters differ greatly from each other, even when they are proportional to the COD values. A variety of the most recent studies, selected among those available in the literature, are shown in Table 2.

The cells in normal characters in Table 2 are those directly reported by the mentioned studies. The cells given in bold characters, on the other hand, were calculated based on the values reported in those studies, because each study reported a different ratio ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$, $\text{COD}/\text{H}_2\text{O}_2$, $\text{COD}/\text{Fe}^{2+}$, $\text{Fe}^{2+}/\text{H}_2\text{O}_2$, $\text{H}_2\text{O}_2/\text{COD}$ and $\text{Fe}^{2+}/\text{H}_2\text{O}_2$). The obtained results are quite interesting for a number of reasons. As seen in Table 2, the H_2O_2 values determined on the basis of COD are given in terms of concentrations. Similarly, Fe^{2+} , which are determined based on the added H_2O_2 amount in terms of a mole ratio, are also reported in terms of concentrations. However, although it is more practical to report these values in terms of concentrations, this brings about an impor-

Table 2. Comparison of different process typologies on Fenton's oxidation

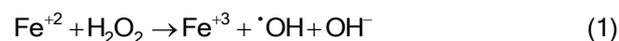
<i>COD</i> / mg L ⁻¹	pH	Time min	H_2O_2 dosage mg/L	Fe^{2+} dosage mg/L	<i>t</i> / °C	<i>COD</i> / H_2O_2	<i>COD</i> / Fe^{2+}	$\text{H}_2\text{O}_2/\text{Fe}^{2+}$	Reference
5320	2-9	60	340-15300	280-5600	-	0.35-15.65	0.95-19	0.2-10	[14]
-	2.5-7	5-240	60-450	0-15	-	-	-	4-45	[15]
3242	2-6	30-120	16950-42375	200-1000	-	0.076-0.19	3.24-16.21	33.9-169.5	[16]
1140	2-8	0-60	1000-6500	150-1000	-	0.175-1.14	1.14-7.6	3.2-21.67	[17]
11987	2-4	90	13185- 52742.8	217-8686	-	0.23-0.91	1.38-55.2	10-100	[18]
314-404	2-5	0-100	-	-	-	0.126-0.315	0.609-3.125	1.99-9.90	[19]
564	2.5-7.0	0-300	102-510	22.4-100.8	30-60	1.11-5.53	5.6-25.2	0.61-2.43	[5]
176 ± 13.2	3-5	0-180	187-2240	560-2240	-	0.079-0.94	0.079-0.314	1-3	[20]
725	4	0-30	0-100	0-50	-	7.25-72.5	14.5-145	5-10	[21]
25624	0.75-3.75	35-255	225-900	500-4500	-	28.47-113.9	5.69-51.25	0.09-1.35	[22]
1200	5	-	50-300	20-160	-	4-24	7.5-60	0.5-5	[23]
2150-2770	2-5.5	-	19300-57750	222-2196	25-70	0.043- 0.127	1.12-11.08	96-287	[24]
7500-8400	5.4-9.1	0-150	5780-18,020	300-3000	-	0.44-1.37	2.65-26.5	1.93-34	[25]
1750	2-7	60	200-1200	100-1000	-	1.46-8.75	1.75-17.5	0.5-12	[26]
2533	1.5-3.5	30	44000-266000	552-2210	20-40	0.0095-0.058	1.15-4.59	19.91-201.1	[27]
69600-174000	3-5	0-240	1700-5100	204-3050	-	13.65-102	22.82-57	1.67-8.33	[28]
1670	3-7	0-180	15000-200000	13.8-1380	5-20	0.0084-0.111	1.21-121	0-5	[29]
4528	1-7	30-240	100-800	100-800	-	5.66-45.28	5.66-45.28	0.4-5	[30]
11620-85300	3	-	19800-55200	1250-5000	-	0.23-3.40	6.4-25.6	8-22	[31]
575-2271	2.25-2.47	40	39.0-252.9	13.0-84.3	-	2.27-58	6.82-174.69	3.0	[32]

tant problem. When these values are proportioned to *COD* or as $\text{H}_2\text{O}_2/\text{Fe}^{2+}$, they result in values that greatly differ from each other.

As can be seen from Table 2, the $\text{COD}/\text{H}_2\text{O}_2$ ratio ranged between 0.0084 and 113.9. Similarly, $\text{COD}/\text{Fe}^{2+}$ ratios varied between 0.079 and 174.7, and $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratios varied between 0.09 and 287. These intervals are quite high. Since adding less H_2O_2 than necessary brings about problems in terms of efficiency, and excessive H_2O_2 causes problems not only in efficiency but also in the reduction of excessive peroxide, these large intervals pose a great challenge in this oxidation process. For this reason, the ratio of *COD* to the amount of H_2O_2 used should be determined stoichiometrically [33]. Reactions occur smoothly by using 10% more than the stoichiometric ratios. More than this amount should not be used as this will cause excessive $\cdot\text{OH}$ in water. The stoichiometric $\text{COD}/\text{H}_2\text{O}_2$ ratios to be used in the Fenton processes can be found in the literature [8]. Based on the stoichiometric ratio [8], it can be stated that for 2.125 g of H_2O_2 (or 0.0625 mol H_2O_2), 1 g of *COD* (or 1 g $\text{O}_2 = 0.03125$ mol O_2) is needed with a ratio of about 0.471. Considering a 10% margin of safety, it was determined that the $\text{COD}/\text{H}_2\text{O}_2$ ratio should be equal to 0.428 or higher. This is due to the fact that it is important for economic reasons to evaluate this ratio in proportions such as 1:1, even 1:0.5 and 1:0.25, rather than 1:2.125, considering the synergistic effect. Therefore, it is quite plausible to use values ranging between 0.428 and 4.0 for the $\text{COD}/\text{H}_2\text{O}_2$ ratio. The $\text{COD}/\text{H}_2\text{O}_2$ ratios lower than 0.428 indicate use of excessive peroxide, which might result in significant problems from an engineering perspective.

Another important parameter is the $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratios. When the effect of H_2O_2 ions is determined (in those studies where different doses of H_2O_2 are added), a single dose is specified and used for the Fe^{2+} . However, while the specified Fe^{2+} amounts are excessive for low doses of H_2O_2 , it is generally insufficient for high doses of peroxide additions. Although the higher doses normally induce better results, this is not completely due to the oxidation effect of $\cdot\text{OH}$. The added Fe^{2+} transform a part of the H_2O_2 into $\cdot\text{OH}$, while the oxidation effect of the remaining H_2O_2 plays an important role in the increase of efficiency. More Fe^{2+} additions might help transform all H_2O_2 into $\cdot\text{OH}$ and therefore increase the oxidation capacity; however, it is not economically feasible to use the oxidation capacity of peroxide rather than forming more $\cdot\text{OH}$. For this reason, in order to obtain more correct results, the ratio of H_2O_2 to Fe^{2+} should be kept constant, rather than fixing the H_2O_2 amount in Fe^{2+} opti-

mization or the Fe^{2+} amount in H_2O_2 optimization. To this end, for the first peroxide optimization, a $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio, which is well-balanced in terms of its stoichiometric value and reported to be successful by the relevant literature, should be specified and iron dosing should be carried out based on this ratio. Then, the most suitable $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratios should be defined by keeping the specified optimum H_2O_2 dose constant and modifying the Fe^{2+} amount. When the literature regarding the $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratios are investigated, it is seen that the values reported change range within a very wide interval. In certain studies [22] the $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio is equal to 0.09, while in some others [24] this value may rise to 287. The ratio of these two values is as high as 3190, which clearly shows that a suitable value for the $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio should be defined by means of optimization studies. By taking the added Fe^{2+} ions and the amount of $\cdot\text{OH}$ formed by H_2O_2 into account, the stoichiometric ratios to be used should be defined. The stoichiometric equation and ratio to be used for $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ is given below:



When this equation is stoichiometrically investigated, it is seen that for 56 g of Fe^{2+} , 34 g of H_2O_2 is needed with a ratio of about 0.607. By also considering a 10% margin of safety for the addition of Fe^{2+} , the new ratio can be defined as 0.552. An addition of Fe^{2+} greater than the amount resulting in this ratio will bring about extra costs and also undesired chemical sludge at the end of the reaction. Therefore, lower ratios should not be used. It should be kept in mind that the proportional lower limit for Fe^{2+} concentration corresponding to the upper limit of the ratio to use is 0.55. In this study, as can be seen also in Table 3, the performance of the reaction was evaluated by using the lower amounts of Fe^{2+} , such as the ratios equal to 1 and 2.

Another proportional expression that is representative for a Fenton process is $\text{COD}/\text{Fe}^{2+}$. As a matter of fact, these two parameters are not directly inter-related. This value is specified based on the H_2O_2 concentration. When the stoichiometric ratios are considered, the proportional values suggested to obtain a synergistic effect and less chemical use are as follows:

Stoichiometric ratio: $\text{COD}/\text{H}_2\text{O}_2/\text{Fe}^{2+}$: 1/2.125/3.5

Economical ratio: $\text{COD}/\text{H}_2\text{O}_2/\text{Fe}^{2+}$: 1/2.125-0.25/3.5-0.35

The calculated ratios were obtained by considering 10% more than the maximum stoichiometric ratio. The minimum values, on the other hand, were

Table 3. Experimental runs and operational parameters

Runs	COD/H ₂ O ₂	H ₂ O ₂ /Fe ²⁺	Initial pH	Dosing
1	0.428	0.55	3.00	-
2	0.5	0.55	3.00	-
3	0.6	0.55	3.00	-
4	0.8	0.55	3.00	-
5	1.0	0.55	3.00	-
6	1.2	0.55	3.00	-
7	1.4	0.55	3.00	-
8	1.6	0.55	3.00	-
9	1.8	0.55	3.00	-
10	2.0	0.55	3.00	-
11	0.5	0.55	3.00	-
12	0.5	0.75	3.00	-
13	0.5	1.0	3.00	-
14	0.5	1.2	3.00	-
15	0.5	1.4	3.00	-
16	0.5	1.6	3.00	-
17	0.5	1.7	3.00	-
18	0.5	1.8	3.00	-
19	0.5	1.9	3.00	-
20	0.5	2.0	3.00	-
21	0.5	1.0	2.00	-
22	0.5	1.0	2.25	-
23	0.5	1.0	2.50	-
24	0.5	1.0	2.75	-
25	0.5	1.0	3.25	-
26	0.5	1.0	3.50	-
27	0.5	1.0	3.75	-
28	0.5	1.0	4.00	-
29	0.5	1.0	3.00	1
30	0.5	1.0	3.00	2
31	0.5	1.0	3.00	3
32	0.5	1.0	3.00	4
33	0.5	1.0	3.00	5
34	0.5	1.0	3.00	10
35	0.5	1.0	3.00	15
36	0.5	1.0	3.00	30
37	0.5	1.0	3.00	45
38	0.5	1.0	3.00	60
39	0.5	1.0	3.00	60
40	0.5	1.0	3.00	60
41	0.5	1.0	3.00	60
42	0.5	1.0	3.00	60
43	0.5	1.0	3.00	60

defined as one tenth of the maximum value, specified considering the synergistic effect. Optimization work to be carried out between these values is thought to help define more appropriate operational condition, addressing higher efficiencies and lower chemical

consumptions. The operational conditions specified in this study were optimized at each stage before passing to the next one, with the aim to increase the efficiency by using optimum values in the subsequent study-sets. The obtained results were discussed under different sub-titles in this section.

Effect of COD/H₂O₂ ratio

The most important parameter in a Fenton process is the hydrogen peroxide ratio. As the H₂O₂ amount increases, the oxidation capacity and efficiency also increase. However, the dose to apply should be suitable to the amount of organic contaminants in the water. Otherwise, less H₂O₂ than needed will reduce the efficiency level, while excessive H₂O₂ amounts will increase operational costs. Therefore, the optimization of H₂O₂ amount is of utmost importance in the Fenton oxidation process. The color and TOC reduction efficiencies obtained for different doses specified on the basis of stoichiometric ratios are given in Figure 1. The studies were carried out with a pH value equal to 3.0, as an average of the interval 2-4. The H₂O₂/Fe²⁺ ratio was taken as 0.55, which is the most suitable value from a stoichiometric perspective.

When Figure 1 is closely examined, it is seen that increasing COD/H₂O₂ ratios (or decreasing peroxide amounts) adversely affect efficiency, since lower peroxide amounts decrease the formation rate of the •OH radicals, and consequently lower the oxidation capacity of the process. Therefore, the highest efficiency level was obtained when COD/H₂O₂ ratio was equal to 0.5. When the COD/H₂O₂ ratio was taken as 0.5, the resulting TOC and color reduction values were 80.2 and 96.1%, respectively. Based on these results, 0.5 was accepted to be the optimum value for the COD/H₂O₂ ratio and used for the optimization of H₂O₂/Fe²⁺ ratio in the next step.

Effect of H₂O₂/Fe²⁺ ratio

In redox reactions, the Fe²⁺ ratio that helps form •OH is also as important as the H₂O₂ in the Fenton oxidation process. Similarly to the hydrogen peroxide dosing, the use of higher than necessary Fe²⁺ doses will result in additional costs. Using an insufficient amount of Fe²⁺, on the other hand, will result in inefficiently completed redox reactions, which are needed for the formation of •OH. Therefore, the Fe²⁺ doses to add must be optimized for better results. To this end, a series of studies were carried out using H₂O₂/Fe²⁺ doses, determined in compliance with stoichiometric ratios. The obtained results are given in Figure 2. In these studies, the pH was 3.0, which is the average value for the 2-4 interval. The COD/H₂O₂ ratio, on the

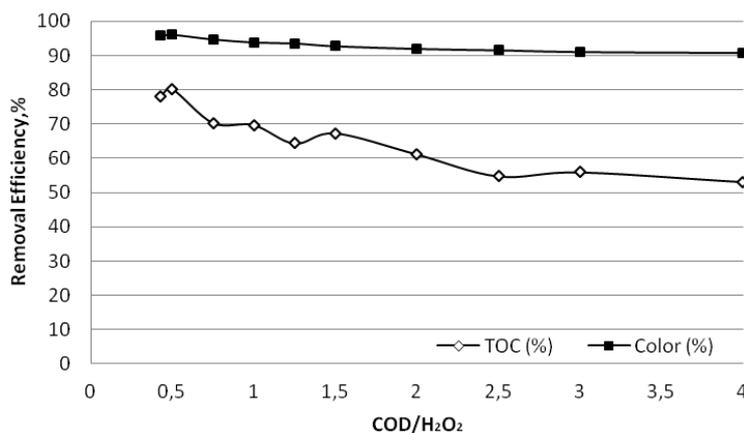


Figure 1. Effects of COD/H₂O₂ ratio on color and TOC removal efficiencies ($H_2O_2/Fe^{2+} = 0.55$, pH 3.0, reaction time = 30 min).

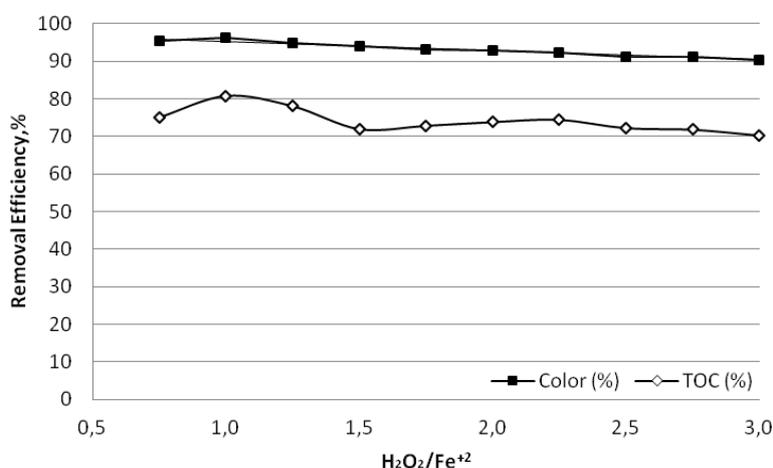


Figure 2. Effects of H₂O₂/Fe²⁺ ratio on color and TOC removal efficiencies (COD/H₂O₂ = 0.5, pH 3.0, reaction time = 30 min).

other hand, was 0.5, which was found to be the optimum value.

When the obtained results are investigated, it is clearly seen that increasing H₂O₂/Fe²⁺ ratios (or decreasing Fe²⁺ amounts) slightly decrease the color and TOC reduction levels. Increasing the H₂O₂/Fe²⁺ ratios indicates insufficient Fe²⁺ additions. Consequently, a lower efficiency level can be observed due to the inhibition of the formation of •OH. The optimum value for the H₂O₂/Fe²⁺ ratio was found to be 1.0. The color and TOC reduction values determined by using these values were 80.8 and 96.2%, respectively.

Effect of pH on TOC and color removal

Like in all chemical reactions, for a Fenton oxidation process to be able to be carried out efficiently, there is a suitable pH interval. For a Fenton reaction, it is known that this interval corresponds to the acidic range (generally between 2.0 and 4.0) [33,35]. An optimization study on pH level was carried out to further elaborate on this value between 2.0 and 4.0. The results obtained from this study are shown in

Figure 3. This optimization was carried out by taking H₂O₂/Fe²⁺ and COD/H₂O₂ ratios as 1.0 and 0.5, respectively, which were found to be the optimum values in previous studies.

When the obtained results are investigated, it is seen that the highest efficiency levels are obtained with a pH value equal to 3.0, because maintaining the pH value constant at 3.0 (also at the previous optimization studies) increased the reliability of the results obtained from these optimization studies. Under these circumstances, the color and TOC reduction efficiencies were found to be 80.8 and 96.2%, respectively. The results indicated that both TOC and color removal levels were lower, compared to results obtained when the pH value was kept equal to 3.0. This could be due to the decrease in the synergistic effect of H₂O₂ and Fe²⁺ [26].

Effect of H₂O₂ dosing on TOC and color removal

•OH plays an active role in the reaction mechanism of the Fenton oxidation process as oxidant. For the formation of these radicals, the addition of H₂O₂ -

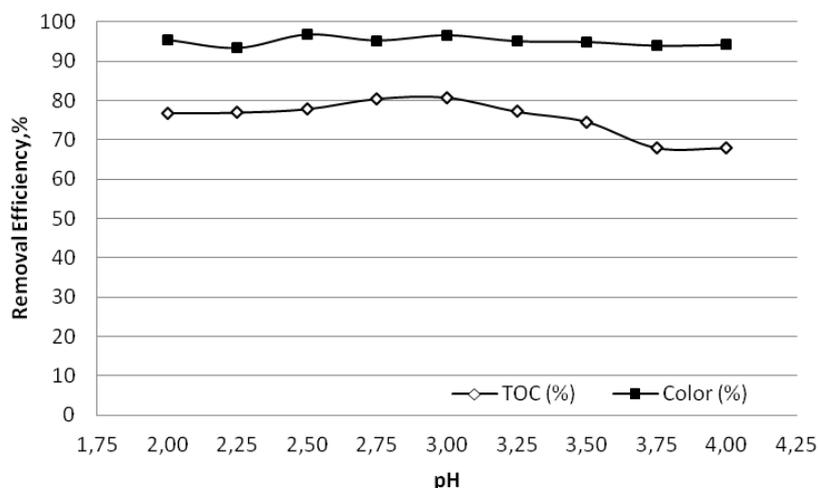


Figure 3. Effects of pH on color and TOC removal efficiencies ($COD/H_2O_2 = 0.5$, $H_2O_2/Fe^{2+} = 1.0$, reaction time = 30 min).

in one go, or in different time periods during the reaction - is of great importance. For this aim, a series of studies have been conducted regarding different dosing types in photo-Fenton and solar photo-Fenton procedures [36-37]. In classical Fenton studies, on the other hand, the addition of single-step H_2O_2 is generally preferred [38-40]. At this stage of the study, the effects of different H_2O_2 dosing on color and TOC reduction were attempted to be investigated. To this end, the single-step method was not preferred and the dosing of H_2O_2 addition was carried out in multiple steps (2 times (per 15 min), 3 times (per 10 min), 4 times (per 7.5 min), 5 times (per 6 min), 6 times (per 5 min), 10 times (per 3 min), 15 times (per 2 min), 30 times (per 1 min), and 45 times (per 40 s)) in 30 s and in continuous mode.

The obtained results clearly showed that time-dependent dosing of H_2O_2 might help to obtain higher efficiency levels. It was seen that by carrying out dosing at an extended period of time, TOC reduction efficiency rose from 80.8 up to 88.9% for the same amount of dosing. Similarly, the color reduction efficiency also increased from 96.5 to 98.7% by time-dependent dosing of H_2O_2 . The higher occurrence rate of the reactions by dosing is also reflected in the efficiency levels. An instantaneous dosing will play the role of the oxidation capacity of peroxide instead of turning all the peroxide into $\cdot OH$ at one time. Therefore, it is apparent that the dosing of hydrogen peroxide for an extended period of time will considerably improve the reduction efficiency levels.

CONCLUSIONS

This study aimed to provide the synchronization between studies carried out on the operation con-

ditions intrinsic to the Fenton process that is effectively used for strong organic compounds. When the stoichiometric ratios are not considered, the excessive use of chemicals results in not only additional costs, but also in the formation of undesired amounts of sludge. Similarly, the use of insufficient amounts of reactant results in low reduction efficiencies. Therefore, an evaluation of the most recent studies on the Fenton process in the relevant literature was made, and the need for such a study was demonstrated. From a dosing point of view, it was shown that an apparent increase in efficiency levels can be obtained in the Fenton processes. At the same time, synchronization in operational conditions can be provided and the efficiency of different studies carried out in this field can be compared to each other more easily. An equivalent reduction in efficiency levels can be obtained with lower chemical consumptions when the stoichiometric ratios are taken into consideration.

REFERENCES

- [1] D. Squire, J. Murrer, P. Holden, C. Fitzpatrick, *Desalination* **108** (1997) 143-147
- [2] P. Kampas, S.A. Parsons, P. Pearce, S. Ledoux, P. Vale, J. Churchley, E. Cartmell, *Water Res.* **41** (2007) 1734-1742
- [3] F. Ilhan, U. Kurt, O. Apaydin, M.T. Gonullu, *J. Hazard. Mater.* **154** (2008) 381-389
- [4] E. Neyens, J. Baeyens, *J. Hazard. Mater.* **98** (2003) 33-50
- [5] S. Karthikeyan, A. Titus, A. Gnanamani, A.B. Mandal, G. Sekaran, *Desalination* **281** (2011) 438-445
- [6] D. Hermosilla, M. Cortijo, C.P. Huang, *Sci. Total Environ.* **407** (2009) 3473-3481
- [7] U. Kurt, Y. Avsar, M.T. Gonullu, *Chemosphere* **64** (2006) 1536-1540

- [8] M.S. Lucas, J.A. Peres, J. Hazard. Mater. **168** (2009) 1253-1259
- [9] N.S.S. Martinez, J.F. Fernandes, X.F. Segura, A.S. Ferrer, J. Hazard. Mater., B **101** (2003) 315-322
- [10] U. Kurt, O. Apaydin, M.T. Gonullu, J. Hazard. Mater. **143** (2007) 33-40
- [11] S.H. Lin, C.M. Lin, H.G. Leu, Water Res. **33** (1999) 1735-1741
- [12] K. Yetilmezsoy, Environ. Sci. Pollut. Res. **19** (2012) 2227-2237
- [13] P. Canizares, R. Paz, C. Saez, M.A. Rodrigo, J. Environ. Manag. **90** (2009) 410-422
- [14] J.H. Park, I.H. Cho, S.W. Chang, J. Environ. Sci. Heal., B **41** (2006) 109-120
- [15] M.J. Abdul, M. Kumar, S. Vigneswaran, J. Kandasamy, J. Ind. Eng. Chem. **18** (2012) 137-144
- [16] R. Li, C. Yang, H. Chen, G. Zeng, G. Yu, J. Guo, J. Hazard. Mater. **167** (2009) 1028-1032
- [17] D. Guclu, N. Sirin, S. Sahinkaya, M.F. Sevimli, Environ. Prog. Sustain. **32** (2013) 176-180
- [18] M.I. Badawy, R.A. Wahaab, A.S. El-Kalliny, J. Hazard. Mater. **167** (2009) 567-574
- [19] C.C. Su, M.P. Asa, C. Ratanatamskul, M.C. Lu, Sep. Purif. Technol. **83** (2011) 100-105
- [20] X. Zhu, J. Tian, R. Liu, L. Chen, Sep. Purif. Technol. **81** (2011) 444-450
- [21] S.F. Kang, C.H. Liao, M.C. Chen, Chemosphere **46** (2002) 923-928
- [22] K.V. Padoley, S.N. Mudliar, S.K. Banerjee, S.C. Deshmukh, R.A. Pandey, Chem. Eng. J. **166** (2011) 1-9
- [23] X. Wang, G. Zeng, J. Zu, J. Hazard. Mater. **153** (2008) 810-816
- [24] I. Gulkaya, G.A. Surucu, F.B. Dilek, J. Hazard. Mater. **136** (2006) 763-769
- [25] L. Chu, J. Wang, J. Dong, H. Liu, X. Sun, Chemosphere **86** (2012) 409-414
- [26] K. Yetilmezsoy, S. Sakar, J. Hazard. Mater. **151** (2008) 547-558
- [27] T. Mandal, D. Dasgupta, S. Mandal, S. Datta, J. Hazard. Mater. **180** (2010) 204-211
- [28] M. Ahmadi, F. Vahabzadeh, B. Bonakdarpour, E. Mofarrah, M. Mehranian, J. Hazard. Mater. **123** (2005) 187-195
- [29] L.M. Nieto, G. Hodaifa, S. Rodriguez, J.A. Gimenez, J. Ochando, Chem. Eng. J. **173** (2011) 503-510
- [30] J. Li, Z. Luan, L. Yu, Z. Ji, Desalination **284** (2012) 62-65
- [31] B. Bianco, I.D. Michelis, F. Veglio, J. Hazard. Mater. **186** (2011) 1733-1738
- [32] R.F. Yu, H.W. Chen, K.Y. Liu, W.P. Cheng, P.H. Hsieh, J. Chem. Technol. Biotech. **85** (2010) 267-278
- [33] J. Blanco, F. Torrades, M.D. Varga, J.G. Montano, Desalination **286** (2012) 394-399
- [34] APHA (American Public Health Association), Standard Methods for the Examination of Water & Wastewater, 21th ed., Washington DC, 2005
- [35] E.L. Kochany, J. Kochany, Chemosphere **73** (2008) 745-750
- [36] D.P. Garcia, G. Buitron, J. Hazard. Mater. **217-218** (2012) 293-300
- [37] E.O. Gomez, J.C.M. Ubeda, J.D.A. Hervas, J.L.C. Lopez, L.S.J. Jorda, J.A.S. Perez, J. Hazard. Mater. **237-238** (2012) 223-230
- [38] H. Zhang, H.J. Choi, C.P. Huang, J. Hazard. Mater., B **125** (2005) 166-174
- [39] D.L. Wu, W. Wang, Q.W. Guo, Y.H. Shen, Chem. Eng. J. **214** (2013) 278-284
- [40] S. Dogruel, T.O. Hanci, Z. Kartal, I.A. Alaton, D. Orhon, Water Res. **43** (2009) 3974-3983.

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NAUČNI RAD

PROCENA RADNIH PARAMETARA I NJIHOV ODNOS SA STEHIOMETRIJOM FENTON OKSIDACIJE OTPADNE VODE TEKSTILNE INDUSTRIJE

Radni uslovi Fentonovog procesa su od najveće važnosti jer postoje problemi vezani za odnos doziranja H_2O_2 sa HPK i doziranja Fe^{2+} sa specifičnom količinom H_2O_2 . Relevantna literatura pokazuje da su vrednosti odnosa HPK/ H_2O_2 u opsegu između 0,0084 i 113,9. Slično, odnos HPK/ Fe^{2+} je u opsegu između 0,079 i 292,6 dok odnos H_2O_2/Fe^{2+} varira između 0,09 i 287. Pored toga, odnos maksimalne i minimalne vrednosti korišćenih na bazi HPK ima vrednost 13560 za odnos HPK/ H_2O_2 (u opsegu od 0,0084 do 113,9), 2210 za odnos HPK/ Fe^{2+} (u opsegu od 0,079 do 174,7) i konačno 3190 za odnos H_2O_2/Fe^{2+} (u opsegu od 0,09 do 287). Cilj ovog rada je da ponovo proceni ove vrednosti koje se značajno razlikuju jedna od druge sa posebnim naglaskom na otpadne vode tekstilne industrije uz razmatranje stehiometrijskih odnosa. Ovi rezultati pokazuju da su vrednosti u opsegu od 0,43 do 4,0 za HPK/ H_2O_2 dok su vrednosti u opsegu od 0,75 do 3,0 mnogo pogodnije za H_2O_2/Fe^{2+} . Takođe, ovi rezultati pokazuju da doziranje H_2O_2 u različitim vremenima Fentonovog procesa može da poveća efikasnost smanjenja ukupnog organskog ugljenika od 80,8 do 88,9%. Slično, efikasnost smanjenja obojenosti se povećava sa 96,5 na 98,7%.

Ključne reči: Fentonova oksidacija, radni parametri, oksidacija, stehiometrijski odnos, uklanjanje ukupnog organskog ugljenika.