



## RESEARCH ARTICLE

### Treatment of dye-producing chemical industry wastewater by persulfate advanced oxidation

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#### ABSTRACT

A dye-producing chemical industry wastewater in Çorlu (Tekirdağ) is treated by the coagulation-flocculation process of the wastewater. However, the wastewater discharged after coagulation-flocculation still has a very high COD (4402 mg L<sup>-1</sup>) with very high proportion of dissolved COD (4316 mg L<sup>-1</sup>). Therefore, the aim of this study is to achieve higher COD and color removal in wastewater using Fe<sup>2+</sup>/S<sub>2</sub>O<sub>8</sub> or UV/S<sub>2</sub>O<sub>8</sub> oxidation process after coagulation-flocculation. The processes in the oxidation of this industrial wastewater using Fe<sup>2+</sup>/S<sub>2</sub>O<sub>8</sub> and UV/S<sub>2</sub>O<sub>8</sub> were examined and the effect of COD/Fe<sup>2+</sup>/S<sub>2</sub>O<sub>8</sub> ratio (in Fe<sup>2+</sup>/S<sub>2</sub>O<sub>8</sub>) or COD/S<sub>2</sub>O<sub>8</sub> ratio (in UV/S<sub>2</sub>O<sub>8</sub>), pH and oxidation time were evaluated in the study. While high organic matter and color removal was observed in acidic conditions for both processes, optimum pH were 3 and 6 in Fe<sup>2+</sup>/S<sub>2</sub>O<sub>8</sub> and UV/S<sub>2</sub>O<sub>8</sub> oxidation processes, respectively. In Fe<sup>2+</sup>/S<sub>2</sub>O<sub>8</sub> oxidation, 61.1% of COD removal and above 97% of color (UV<sub>436</sub>, UV<sub>525</sub> and UV<sub>620</sub>) removal was obtained at 1/8/8 of COD/Fe<sup>2+</sup>/S<sub>2</sub>O<sub>8</sub> ratio and pH 3 after 1 h oxidation. In UV/S<sub>2</sub>O<sub>8</sub> oxidation (COD/S<sub>2</sub>O<sub>8</sub> ratio 1/8, pH 6), 54.4% of COD and 98% of color (UV<sub>436</sub>, UV<sub>525</sub> and UV<sub>620</sub>) removals were achieved after 4 h oxidation. As a result, both Fe<sup>2+</sup>/S<sub>2</sub>O<sub>8</sub> and UV/S<sub>2</sub>O<sub>8</sub> oxidation processes were applied to ensure discharge standards for color removal from this chemical industry wastewater are effective methods as they provide over 97% color removal. Moreover, COD removal efficiency was approximately 55-60% in both methods.

**Keywords:** Activation, kinetics, oxidation, persulfate, industrial wastewater treatment

#### 1. INTRODUCTION

The chemical industry is considered a highly polluting sector. Generally, the chemical industry does not alter chemical products and processes and prefers to deal with the end of the pipe for the management of wastewater [1]. The chemical industry produces special chemicals such as adhesives, sealants, catalysts, coatings, plastic adhesives, and personal care products such as pharmaceuticals, soaps, detergents, shampoos, creams from various raw materials [1]. One of the chemical industries, the dye-producing chemical industry uses many different raw materials (aniline, soluble, etc.), auxiliary chemicals, dyes and intermediates, many of which can be toxic to the environment and have carcinogenic effects in humans [2]-[3]. Auxiliary chemicals, dyes and intermediates include many agents, phosphates, polyamide resins, acrylic coatings and the wastewaters formed have high organic matter, non-biodegradable and toxic substances [4].

Advanced oxidation technologies are suitable and effective method for the treatment of high non-biodegradable and persistent organic pollutants in industrial wastewaters [5]. Although hydroxyl (OH<sup>•</sup>) production processes such as Fenton and UV photocatalysis oxidation processes have been used as advanced oxidation processes for many years, interest in the persulfate oxidation processes for producing the sulfate radical has increased for persistent organic pollutant removal in recent years [6]. SO<sub>4</sub><sup>•-</sup> has become an alternative to OH<sup>•</sup> radical for the organic compound degradation and wastewater treatment due to the high redox potential (2.5-3.1 V) and longer lifetime (3-4.10<sup>-5</sup> s) [7].

Methods such as heat, UV, alkaline, metal ions and activated carbon is used to activate the persulfate to generate sulphate free radicals [8]-[9]. Many studies showed that the sulfate radical based treatment is very effective and promising results for various organic pollutants and dye treatment [9]-[10]. However, the

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studies generally focused on leachate treatment, and it was stated that UV/S<sub>2</sub>O<sub>8</sub>, Fe/S<sub>2</sub>O<sub>8</sub> oxidation processes were effective for the treatment of landfill leachate [11]-[16]. In addition, studies show that the UV/S<sub>2</sub>O<sub>8</sub> or Fe/S<sub>2</sub>O<sub>8</sub> oxidation processes can be used in the treatment of petrochemical wastewater that 66-69% of COD removal could be achieved up to 120 min oxidation [17]-[19]. Treatment of dye-producing chemical industry wastewater by UV/S<sub>2</sub>O<sub>8</sub> or Fe/S<sub>2</sub>O<sub>8</sub> persulfate oxidation has not been studied yet. Studies on the comparison of iron and UV activation methods for persulfate oxidation are insufficient and it could not be determined which method was more effective for organic matter removal. In this study, the chemically treated wastewater of a chemical industry, which produces dyes for textile, paper, plastic (masterbatch) and metal industries was trying to be treated by UV/S<sub>2</sub>O<sub>8</sub> and Fe/S<sub>2</sub>O<sub>8</sub> persulfate oxidation method. The wastewater of this industry is quite complex and much polluted in terms of organic matter and color so to treat it very hard. The aim of this study is to compare iron and UV activation methods for persulfate oxidation process in terms of COD and color removal efficiencies. For this purpose, the optimum pH, oxidation time and persulfate doses in both methods were determined and the kinetic evaluations of the processes were also made.

## 2. MATERIALS AND METHODS

### 2.1. Wastewater characterization

Wastewater was taken from dye-producing chemical industry. In this industry, dispersed dyes, reactive dyes, acrylic dyes, acid dyes, digital inks, digital auxiliaries, pigments and chemical groups of liquid, powder and dispersion products used in the textile industry are produced. Hybrid electrostatic powder paint for metal industry, and paper auxiliaries, brown paint, optical brightener and performance chemicals for the paper industry are also produced. The wastewater in this chemical industry is chemically treated using FeCl<sub>3</sub> as a coagulant and then transferred to the central wastewater treatment plant of the industrial zone in Çerkezköy, Tekirdağ. The wastewater used in the study was taken after the coagulation-flocculation process. The characterization of the wastewater is given in Table 1. As seen from Table 1, although the wastewater is the chemically treated, the COD concentration is quite high, but the majority of the COD is in soluble form. In addition, the low TSS concentration in the wastewater shows that the particulate matter in the wastewater is low due to chemical treatment as expected. The color (UV<sub>436</sub>-UV<sub>525</sub>-UV<sub>620</sub>) values in the wastewater are quite high and the wastewater has a brown-red color.

**Table 1.** The characterization of the wastewater

Parameter	Unit	Concentration
pH	-	7.84
EC	mS cm <sup>-1</sup>	6.84
TSS	mg L <sup>-1</sup>	87±2.0
VSS	mg L <sup>-1</sup>	42±2.6
NH <sub>3</sub> -N	mg L <sup>-1</sup>	12.1±1.6
TKN	mg L <sup>-1</sup>	37.3±1.6
Total COD	mg L <sup>-1</sup>	4402±135
Soluble COD	mg L <sup>-1</sup>	4316±41
UV <sub>254</sub>	abs.	13.2±0.53
UV <sub>280</sub>	abs.	10.4±0.34
UV <sub>436</sub>	abs.	4.79±0.33
UV <sub>525</sub>	abs.	0.91±0.03
UV <sub>620</sub>	abs.	0.65±0.02

### 2.2. Fe<sup>2+</sup>/S<sub>2</sub>O<sub>8</sub> oxidation process

Jar test method was used for the treatment of wastewater with Fe<sup>2+</sup>/S<sub>2</sub>O<sub>8</sub> oxidation process. 200 mL wastewater, required amount of FeSO<sub>4</sub>.7H<sub>2</sub>O (Sigma-Aldrich, 215422) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (Merck, 1.05091) were added to the 600 mL beaker. pH was adjusted to the desired value and wastewater were stirred for 60 min at 60 rpm. Then pH was adjusted to about 7.5 with 6 N NaOH to precipitate excess iron and settled for 1 h. After 1 h of precipitation, sample was taken from the supernatant and centrifuged for 5 min at 4000 rpm for the analysis. COD/Fe<sup>2+</sup>/S<sub>2</sub>O<sub>8</sub> (as g/g/g) ratio was used

to evaluate the effect of the Fe<sup>2+</sup> and S<sub>2</sub>O<sub>8</sub> concentration. Also, effect of pH (2-7) and oxidation time (0.5-4 h) were investigated in the experiments.

### 2.3. UV/S<sub>2</sub>O<sub>8</sub> Oxidation Process

UV/S<sub>2</sub>O<sub>8</sub> oxidation experiments were conducted by using 500 mL graduated cylinder (active volume 300 mL). Required amount of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> were added to the wastewater and the pH was adjusted to the desired value. 12 watts of mercury vapor lamp (model Hg F15-05, Eurotech) at 254 nm was positioned in the center of the cylinder for the UV-C irradiation [20].

Wastewater was stirred with magnetic stirrer at about 60 rpm during the UV irradiation. The samples were taken at certain times and centrifuged for 5 min at 4000 rpm before the analysis. The effect of the COD/S<sub>2</sub>O<sub>8</sub> (as g/g) ratio, pH and oxidation time were evaluated the oxidation studies.

## 2.4. Analysis

The pH was measured using a pH meter (WTW pH 315j). Color (UV<sub>436</sub>-UV<sub>525</sub>-UV<sub>620</sub>) and humic substance (UV<sub>254</sub>-UV<sub>280</sub>) of the wastewater were determined using a UV spectrophotometer (Shimadzu UV-2401 PC instrument). UV<sub>254</sub> is used for aromatic and unsaturated organic compounds and UV<sub>280</sub> is represented aromaticity [21]. Total COD, soluble COD, total suspended solids (TSS), volatile suspended solids (VSS), total Kjeldahl nitrogen (TKN) and ammonia nitrogen (NH<sub>3</sub>-N) was analyzed based on the Standard Methods for the Examination of Water and Wastewater [22]. The chemical oxygen demand (COD) was determined using a closed reflux colorimetric method. S<sub>2</sub>O<sub>8</sub> concentration was measured according to Liang et al. [23]. The removal efficiencies of COD, UV<sub>254</sub>, UV<sub>280</sub> or color were obtained using the following Eq. 1.

$$\text{Removal Efficiency(\%)} = \frac{C_0 - C_t}{C_0} \quad (1)$$

where C<sub>0</sub> is the initial COD (mg L<sup>-1</sup>), UV<sub>254</sub>, UV<sub>280</sub> or color (m<sup>-1</sup>) concentration and C<sub>t</sub> refer to the COD (mg L<sup>-1</sup>), UV<sub>254</sub>, UV<sub>280</sub> or color (m<sup>-1</sup>) concentration at time t or at the end of the treatment, respectively.

The pseudo first order kinetics of COD, UV<sub>254</sub>, UV<sub>280</sub>, UV<sub>436</sub>, UV<sub>525</sub> or UV<sub>620</sub> is calculated according to Eq. 2 [23];

$$\ln \frac{C_t}{C_0} = -k_1 \cdot t \quad (2)$$

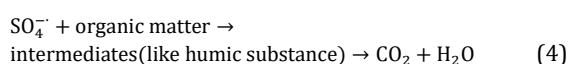
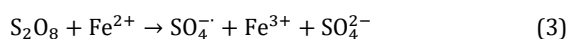
where C<sub>0</sub> is the initial pollutant as COD (mg L<sup>-1</sup>), UV<sub>254</sub>, UV<sub>280</sub>, UV<sub>436</sub>, UV<sub>525</sub> or UV<sub>620</sub> (m<sup>-1</sup>) concentration and C<sub>t</sub> refer to the pollutant as COD (mg L<sup>-1</sup>), UV<sub>254</sub>, UV<sub>280</sub>, UV<sub>436</sub>, UV<sub>525</sub> or UV<sub>620</sub> (m<sup>-1</sup>) concentration at time t, respectively. k<sub>1</sub> is the pseudo first order kinetic constant rate as (h<sup>-1</sup>).

## 3. RESULTS AND DISCUSSION

### 3.1. Fe<sup>2+</sup>/S<sub>2</sub>O<sub>8</sub> oxidation process

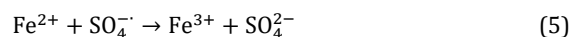
#### Effect of Fe<sup>2+</sup> concentration for Fe<sup>2+</sup>/S<sub>2</sub>O<sub>8</sub> oxidation process

Fe<sup>2+</sup>/S<sub>2</sub>O<sub>8</sub> ratio is an important parameter for the persulfate oxidation. When the S<sub>2</sub>O<sub>8</sub> activated with Fe<sup>2+</sup> ion, sulfate radical (SO<sub>4</sub><sup>•-</sup>) was generated in the system and then oxidation occurs by reacting organic matter with sulfate radicals. The reactions were given in Eq. 3 and Eq. 4 [14].



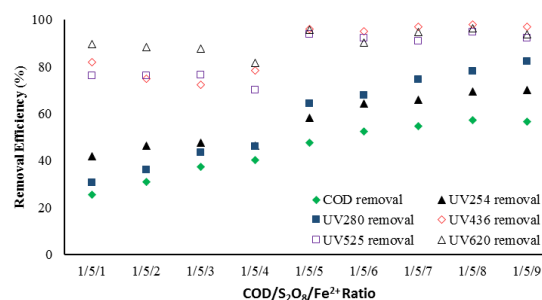
However, in the case of excessive amounts of Fe<sup>2+</sup>, a scavenging effect of sulfate radicals occurs due to the

reaction between Fe<sup>2+</sup> and SO<sub>4</sub><sup>•-</sup> and oxidation efficiency decreases (Eq. 5) [24]-[25].



The effect of Fe<sup>2+</sup> ions on COD and color removal efficiencies were investigated by keeping COD/S<sub>2</sub>O<sub>8</sub> ratio (1/5) constant of the COD/S<sub>2</sub>O<sub>8</sub>/Fe<sup>2+</sup> ratio. It was observed that 25.4% COD removal was achieved at the lowest Fe<sup>2+</sup> concentration (at COD/S<sub>2</sub>O<sub>8</sub>/Fe<sup>2+</sup>:1/5/1) and COD removal efficiency increased up to 57.2% (at COD/S<sub>2</sub>O<sub>8</sub>/Fe<sup>2+</sup>:1/5/8) as the Fe<sup>2+</sup> concentration increased (Fig. 1). A slight decrease of COD removal (56.5%) showed in 1/5/9 ratio due to the scavenger effect of excessive Fe<sup>2+</sup> on the sulfate radical. When the COD/S<sub>2</sub>O<sub>8</sub>/Fe<sup>2+</sup> ratio is between 1/5/1 and 1/5/4, UV<sub>254</sub> removal is close to each other, while UV<sub>280</sub> removal is lower than UV<sub>254</sub> removal. This suggests that COD/S<sub>2</sub>O<sub>8</sub>/Fe<sup>2+</sup> ≤ 1/5/4 is insufficient and further oxidation is needed to break down organic matter. After the COD/S<sub>2</sub>O<sub>8</sub>/Fe<sup>2+</sup> > 1/5/4, UV<sub>280</sub> removal started to increase and in parallel UV<sub>254</sub> removal also enhanced.

When the examine of the consumed S<sub>2</sub>O<sub>8</sub>, observation of the residue S<sub>2</sub>O<sub>8</sub> in treated wastewater up to 1/5/4 ratios indicated that Fe<sup>2+</sup> concentration was insufficient to generate the sulfate radicals. 100% of S<sub>2</sub>O<sub>8</sub> has been converted to the sulfate radicals between 1/5/5 and 1/5/9 ratios. UV<sub>254</sub> and UV<sub>280</sub> represent the aromatic organic compounds in water and are used as a humic substance concentration index in the literature [26]-[27]. UV<sub>280</sub> removal enhanced with increasing the Fe<sup>2+</sup> while the removal of UV<sub>254</sub> showed no significant change between 1/5/8 and 1/5/9. Meanwhile, more than 90% color (UV<sub>436</sub>-UV<sub>525</sub>-UV<sub>620</sub>) removal was observed above 1/5/5 ratio.

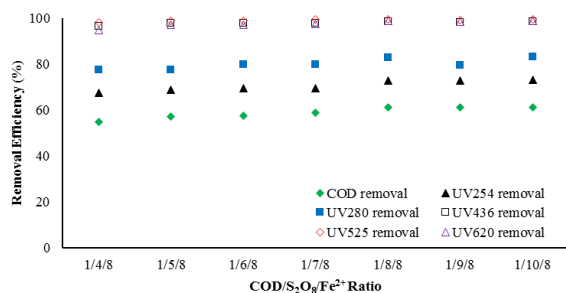


**Fig 1.** Effect of Fe<sup>2+</sup> concentration on the COD, UV<sub>254</sub>, UV<sub>280</sub> and color (UV<sub>436</sub>-UV<sub>525</sub>-UV<sub>620</sub>) removal (pH: 2, oxidation time: 60 min)

#### Effect of S<sub>2</sub>O<sub>8</sub> concentration on Fe<sup>2+</sup>/S<sub>2</sub>O<sub>8</sub> oxidation process

S<sub>2</sub>O<sub>8</sub> concentration is important in the sulfate oxidation process for wastewater treatment since sulfate radicals are generated by the S<sub>2</sub>O<sub>8</sub>. However, when the excessive amount of S<sub>2</sub>O<sub>8</sub> is added into the system, the sulfate radicals formed can react with each other by the effect of collision and reformed to S<sub>2</sub>O<sub>8</sub> [25].

When the amount of COD/S<sub>2</sub>O<sub>8</sub>/Fe<sup>2+</sup> ratio increased from 1/4/8 to 1/8/8, COD removal efficiency increased from 54.9% to 61.1%, UV<sub>254</sub> removal efficiency increased from 67.6% to 72.8% and UV<sub>280</sub> removal efficiency enhanced from 77.7% to 82.8% (Fig 2).

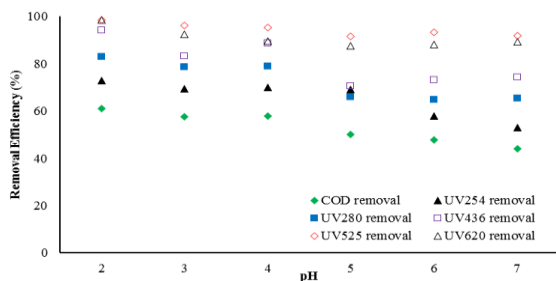


**Fig 2.** Effect of S<sub>2</sub>O<sub>8</sub> concentration on the COD, UV<sub>254</sub>, UV<sub>280</sub> and color (UV<sub>436</sub>-UV<sub>525</sub>-UV<sub>620</sub>) removal (pH: 2, oxidation time: 60 min)

The most appropriate COD/S<sub>2</sub>O<sub>8</sub>/Fe<sup>2+</sup> ratio was 1/8/8 due to the fact that no significant change in COD, UV<sub>254</sub> and UV<sub>280</sub> removal was observed in the applications after 1/8/8, and the residual S<sub>2</sub>O<sub>8</sub> in the treated wastewater increased after the 1/8/8 ratio. In addition, color (UV<sub>436</sub>-UV<sub>525</sub>-UV<sub>620</sub>) removal were higher than 95% between 1/4/8 and 1/10/8 of COD/S<sub>2</sub>O<sub>8</sub>/Fe<sup>2+</sup> ratios while UV<sub>436</sub>, UV<sub>525</sub> and UV<sub>620</sub> removals in 1/8/8 ratio were 98.5%, 99.4% and 98.8%, respectively. This result was consistent with the literature that when the stabilized leachate was treated using Fe<sup>2+</sup>/S<sub>2</sub>O<sub>8</sub> oxidation process, the highest COD removal was observed at Fe<sup>2+</sup>/S<sub>2</sub>O<sub>8</sub> molar ratio 1:1 [12]. In the treatment of leachate using COD/S<sub>2</sub>O<sub>8</sub>/Fe<sup>2+</sup> oxidation process, the best COD removal was obtained as 76.2% at 90 mM Fe<sup>2+</sup> with COD/S<sub>2</sub>O<sub>8</sub> 1/6.7 after 120 min oxidation [11].

**Effect of pH for Fe<sup>2+</sup>/S<sub>2</sub>O<sub>8</sub> oxidation process**

One of the critical factors in the treatment of wastewater by Fe<sup>2+</sup>/S<sub>2</sub>O<sub>8</sub> oxidation process is the solution pH due to the control of free sulfate radical and Fe<sup>2+</sup> ions [28]. As can be seen from Fig. 3, the removal efficiencies of COD, UV<sub>254</sub> and UV<sub>280</sub> decreased as the pH of the wastewater increased. The decrease of the removal efficiencies between pH 2 and 4 was very negligible, but when the pH was increased from 4 to 7, the COD, UV<sub>254</sub> and UV<sub>280</sub> removal efficiency decreased from 57.7% to 44.0%, from 70.0% to 53.0% and from 78.9% to 68.5%, respectively. This finding is compatible with the literature.



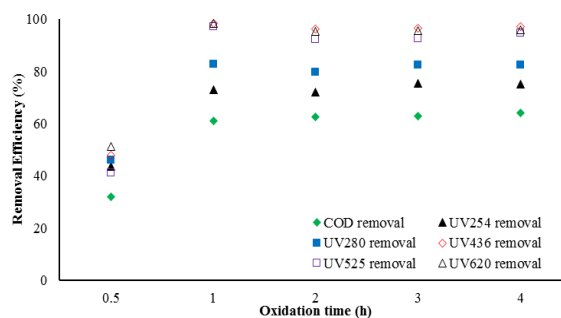
**Fig 3.** Effect of pH on the COD, UV<sub>254</sub>, UV<sub>280</sub> and color (UV<sub>436</sub>-UV<sub>525</sub>-UV<sub>620</sub>) removal (COD/ Fe<sup>2+</sup>/S<sub>2</sub>O<sub>8</sub> ratio 1/8/8, oxidation time: 60 min)

Asha et al. [12] achieved the highest COD removal for stabilized leachate treatment with Fe/S<sub>2</sub>O<sub>8</sub> was in the range of pH 3-4 and stated that COD removal decreased when the pH was above 4 [12]. Likewise, the highest treatment efficiency of leachate with the Fe<sup>2+</sup>/S<sub>2</sub>O<sub>8</sub>

process was obtained at pH 3, and the COD removal decreased as the pH increased [11]. In other study, maximum COD removal efficiency was found as 69% at pH 3 under Fe<sup>2+</sup>/S<sub>2</sub>O<sub>8</sub> ratio of 6 for the treatment saline recalcitrant petrochemical wastewater [18]. Because when the pH is above 4, iron deactivation occurs which leads to the formation of iron hydroxide complexes having the high stability and low catalytic activity [14], [28]-[29]. Another reason for increasing removal efficiencies at pH ≤ 4 is that H<sub>2</sub>O<sub>2</sub> is produced by the hydrolysis of S<sub>2</sub>O<sub>8</sub> and together with H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> may form extra OH radicals by Fenton reaction [30]. While the pH change did not have a significant effect on color (UV<sub>436</sub>-UV<sub>525</sub>-UV<sub>620</sub>) removal, it can be seen that a slight color removal decreased with increasing pH.

**Effect of oxidation time on Fe<sup>2+</sup>/S<sub>2</sub>O<sub>8</sub> oxidation process**

The effect of oxidation time on Fe<sup>2+</sup>/S<sub>2</sub>O<sub>8</sub> oxidation process is shown in Fig 4. COD, UV<sub>254</sub> and UV<sub>280</sub> as well as color removal tended to increase rapidly up to 1 h reaction. After 1 h of oxidation, no significant change in color removal was observed. Similar to color removal, COD, UV<sub>254</sub> and UV<sub>280</sub> removal increased rapidly during the first hour oxidation period and no significant change was observed after 1 h of oxidation time.



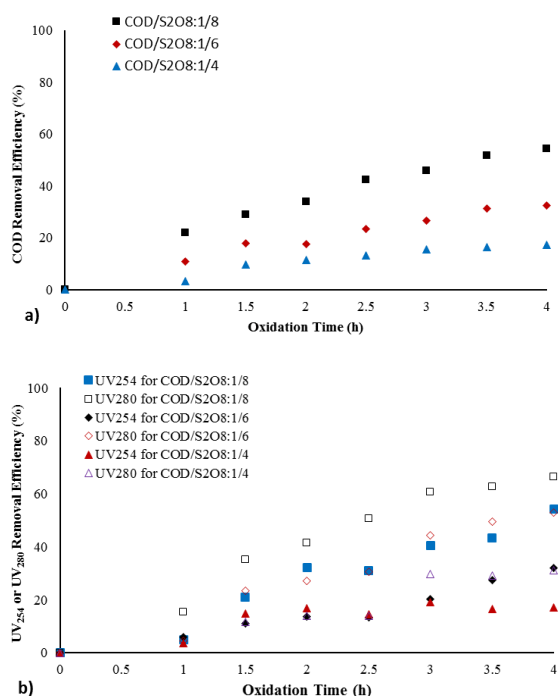
**Fig 4.** Effect of oxidation time on the COD, UV<sub>254</sub>, UV<sub>280</sub> and color (UV<sub>436</sub>-UV<sub>525</sub>-UV<sub>620</sub>) removal (COD/ Fe<sup>2+</sup>/S<sub>2</sub>O<sub>8</sub> ratio 1/8/8, pH:2, oxidation time: 60 min)

At the end of 1 h of oxidation, COD, UV<sub>254</sub> and UV<sub>280</sub> removal efficiencies were obtained as 61.1%, 72.8% and 82.8%, which increased to 64.1%, 75.0% and 82.5% after 4 h oxidation, respectively. UV<sub>436</sub>, UV<sub>525</sub> and UV<sub>620</sub> removal efficiencies of 1/8/8 ratio were obtained as 47.7%, 40.9% and 51.1% after 0.5 h oxidation time and 98.4%, 97.1% and 98.4% removal efficiencies were obtained after 1 h oxidation, respectively. In a study for treating petroleum refinery wastewater using Fe<sup>2+</sup>/S<sub>2</sub>O<sub>8</sub> oxidation process, 66.6% of COD removal was observed at 302.9 mg L<sup>-1</sup> of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 20.3 mg L<sup>-1</sup> FeSO<sub>4</sub>.7H<sub>2</sub>O and 4.8 of pH after 1 h oxidation [17]. Rahmat and Ahmadi [18] reported that maximum COD removal was achieved after 30 min oxidation time and COD concentration remained same up to 120 min oxidation time for the treatment of saline recalcitrant petrochemical wastewater using Fe<sup>2+</sup>/S<sub>2</sub>O<sub>8</sub> oxidation process [18].

### 3.2. UV/S<sub>2</sub>O<sub>8</sub> oxidation process

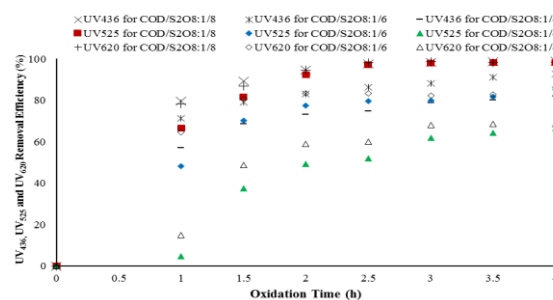
#### Effect of COD/S<sub>2</sub>O<sub>8</sub> ratio for UV/S<sub>2</sub>O<sub>8</sub> oxidation process

To determine the effect of COD/S<sub>2</sub>O<sub>8</sub> ratio on the COD, UV<sub>254</sub> and UV<sub>280</sub> removal efficiencies at initial pH 6, three different COD/S<sub>2</sub>O<sub>8</sub> ratios (1/4, 1/6 and 1/8) were used (Fig 5). When the COD/S<sub>2</sub>O<sub>8</sub> ratio was increased from 1/4 to 1/8 after 4 hours of oxidation, COD, UV<sub>254</sub> and UV<sub>280</sub> removal efficiencies increased from 17.4%, 17.1% and 31.3% to 54.4%, 54.3% and 66.5%, respectively. The increase in pollutant removal by UV/S<sub>2</sub>O<sub>8</sub> is related to the formation of free sulphate radicals after activation of persulfate by UV irradiation. (Eq. 7) [15], [31].



**Fig 5.** Effect of COD/S<sub>2</sub>O<sub>8</sub> ratio (a) on the COD removal (pH:6); (b) on the UV<sub>254</sub> and UV<sub>280</sub> removal (pH:6)

UV<sub>436</sub>, UV<sub>525</sub> and UV<sub>620</sub> removal efficiencies were increased after 4 hours oxidation (Fig 6). The UV<sub>436</sub>, UV<sub>525</sub> and UV<sub>620</sub> removals were obtained over 95% after 2.5 h oxidation. The UV<sub>436</sub>, UV<sub>525</sub> and UV<sub>620</sub> removal efficiencies were 97.5%, 97.2% and 98.2% at 1/8 of COD/S<sub>2</sub>O<sub>8</sub> ratio after 2.5 h oxidation, respectively. At the end of 4 h oxidation, the UV<sub>436</sub>, UV<sub>525</sub> and UV<sub>620</sub> removals were reached 92.9%, 85.2% and 86.3% at 1/6 of COD/S<sub>2</sub>O<sub>8</sub> ratio, while they were remained 82.1%, 66.5% and 68.5% at 1/4 of COD/S<sub>2</sub>O<sub>8</sub> ratio.



**Fig 6.** Effect of COD/S<sub>2</sub>O<sub>8</sub> ratio on the color (UV<sub>436</sub>-UV<sub>525</sub>-UV<sub>620</sub>) removal (pH:6)

#### Effect of pH for UV/S<sub>2</sub>O<sub>8</sub> oxidation process

The effect of the initial pH on the removal of organic matter and color was investigated using the initial pH of 3, 6 and 10. The removal efficiencies of COD, UV<sub>254</sub> and UV<sub>280</sub> were increased by increasing the initial pH from 3 to 6 (Fig 7). However, when the initial pH increased to 10, the COD, UV<sub>254</sub> and UV<sub>280</sub> removal efficiencies decreased after 4 h of oxidation, they were 31.8%, 30.7% and 55.5% respectively.

Maximum COD, UV<sub>254</sub> and UV<sub>280</sub> removal efficiencies were obtained at pH 6. This finding is consistent with the literature that the highest pollutant removal with persulfate oxidation has been achieved at near neutral pH levels [32]-[34]. The highest COD removal was obtained at pH 6 and 8.2 values in the treatment of pulp and paper wastewater by UV/S<sub>2</sub>O<sub>8</sub> oxidation [34]. In some studies related to oxidation of organic substances (1H-benzotriazole, N,N-diethyl-m-toluamide, chlorophene, 3-methylindole, and nortriptyline hydrochloride, trichloroethylene) with sulfate radicals, the activation energy of the reactions was found to be the lowest at pH 7 and therefore the removal efficiencies were reported to be higher at this pH [32], [35]. In this study, it is thought that a similar result was obtained because chemical industry wastewaters which contain many different organic materials were used. In the range of pH 7-10.5, SO<sub>4</sub><sup>•-</sup> and OH<sup>•-</sup> radicals are present in solution and the OH<sup>•-</sup> radical is predominant, which may reduce the removal efficiency at basic conditions [33], [36]. Although the removal of UV<sub>254</sub> and UV<sub>280</sub> at pH 3 and 10 were close to each other, COD removal was higher at pH 10 than pH 3.

No significant change in color removal was observed at pH 6 and 10. The UV<sub>436</sub>, UV<sub>525</sub> and UV<sub>620</sub> absorbances removal efficiencies were high at both pH 10 and pH 6, and over 90% removal of UV<sub>436</sub>, UV<sub>525</sub> and UV<sub>620</sub> was achieved at pH 6 after 2 h of oxidation (Fig 8). UV<sub>436</sub> decolorization at pH 3 was close to that of pH 6 and 10; however UV<sub>525</sub> and UV<sub>620</sub> absorbances removal at pH 3 remained considerably lower than pH 6 and 10. Compared COD, UV<sub>254</sub>, UV<sub>280</sub> removal with color removal efficiency, both organic matter removal and color removal at pH 3 remain low according to pH 6 and 10.

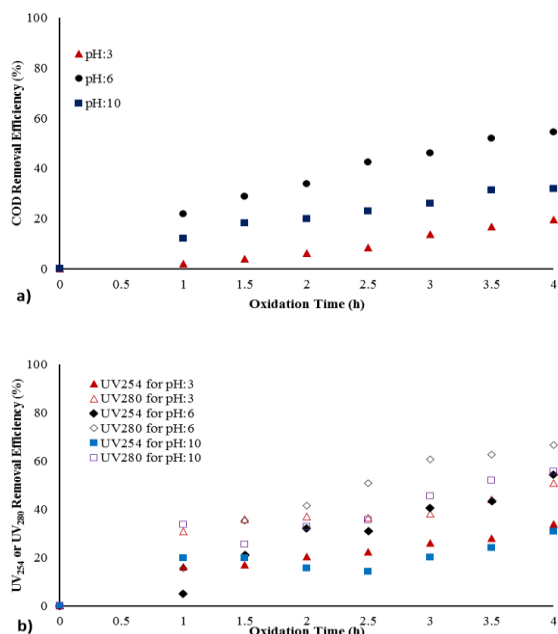


Fig 7. Effect of pH (a) on the COD removal (COD/S<sub>2</sub>O<sub>8</sub> ratio 1/8); (b) on the UV<sub>254</sub> and UV<sub>280</sub> removal (pH:6) (COD/S<sub>2</sub>O<sub>8</sub> ratio 1/8)

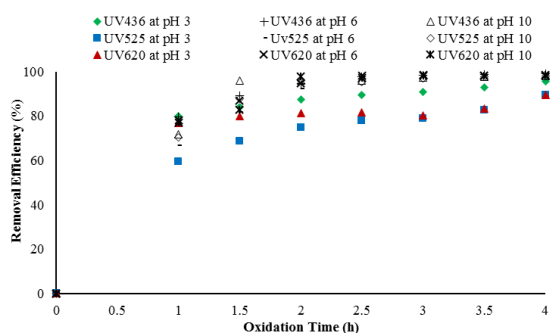


Fig 8. Effect of pH on the color (UV<sub>436</sub>-UV<sub>525</sub>-UV<sub>620</sub>) removal (COD/S<sub>2</sub>O<sub>8</sub> ratio 1/8)

### 3.3. Kinetic evaluation of Fe<sup>2+</sup>/S<sub>2</sub>O<sub>8</sub> and UV/S<sub>2</sub>O<sub>8</sub> oxidation process

Fe<sup>2+</sup>/S<sub>2</sub>O<sub>8</sub> and UV/S<sub>2</sub>O<sub>8</sub> oxidation of dye-producing chemical industrial wastewater is fitted better pseudo first order kinetic model for COD, UV<sub>254</sub>, UV<sub>280</sub>, UV<sub>436</sub>, UV<sub>525</sub> and UV<sub>620</sub> removals. The pseudo first order rate constants (k<sub>1</sub>) for Fe<sup>2+</sup>/S<sub>2</sub>O<sub>8</sub> oxidation process were 0.9074 h<sup>-1</sup>, 1.2689 h<sup>-1</sup>, 1.6557 h<sup>-1</sup>, 3.5816 h<sup>-1</sup>, 3.0519 h<sup>-1</sup> and 3.5731 h<sup>-1</sup> for COD, UV<sub>254</sub>, UV<sub>280</sub>, UV<sub>436</sub>, UV<sub>525</sub> and UV<sub>620</sub> removal at 1/8/8 COD/S<sub>2</sub>O<sub>8</sub>/Fe<sup>2+</sup> ratio and pH 2, respectively (Table 2). The pseudo first order rate constants (k<sub>1</sub>) for COD, UV<sub>254</sub>, UV<sub>280</sub>, UV<sub>436</sub>, UV<sub>525</sub> and UV<sub>620</sub> removal were 0.2071 h<sup>-1</sup>, 0.1731 h<sup>-1</sup>, 0.2816 h<sup>-1</sup>, 1.4335 h<sup>-1</sup>, 1.3059 h<sup>-1</sup> and 1.4727 h<sup>-1</sup> at 1/8 ratio of UV/S<sub>2</sub>O<sub>8</sub> and pH 6, respectively.

In a study by Pourehie and Saien [17], k<sub>1</sub> value of COD was calculated 0.0218 min<sup>-1</sup> under the optimum conditions as 302.9 mg/L K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 20.3 mg/L FeSO<sub>4</sub>.7H<sub>2</sub>O and 4.8 pH for treating petroleum refinery wastewater using UV/Fe<sup>2+</sup>/S<sub>2</sub>O<sub>8</sub> oxidation process [17]. In addition, according to a study on the treatment of petrochemical wastewater by UV/S<sub>2</sub>O<sub>8</sub> and UV/S<sub>2</sub>O<sub>8</sub>/Fe<sup>2+</sup> oxidation processes, k<sub>1</sub> value for COD removal was calculated as 0.018 min<sup>-1</sup> and 0.0188 min<sup>-1</sup>, respectively [19].

The oxidation rate in UV/S<sub>2</sub>O<sub>8</sub> oxidation process was lower than Fe<sup>2+</sup>/S<sub>2</sub>O<sub>8</sub> oxidation process. For COD, UV<sub>254</sub> and UV<sub>280</sub> using Fe<sup>2+</sup>/S<sub>2</sub>O<sub>8</sub> treatment, k<sub>1</sub> values were 4.38, 7.33 and 5.88 times higher than UV/S<sub>2</sub>O<sub>8</sub> treatment. In addition, the color (UV<sub>436</sub>, UV<sub>525</sub> and UV<sub>620</sub>) removal rates were found to be about 2.3-2.5 times higher in Fe<sup>2+</sup>/S<sub>2</sub>O<sub>8</sub> process. Above 90% of color (UV<sub>436</sub>, UV<sub>525</sub> and UV<sub>620</sub>) removal efficiency could be achieved by Fe<sup>2+</sup>/S<sub>2</sub>O<sub>8</sub> oxidation process in 1 h, while UV/S<sub>2</sub>O<sub>8</sub> oxidation process was obtained in 2 h.

Table 2. Pseudo first order kinetic constants of Fe<sup>2+</sup>/S<sub>2</sub>O<sub>8</sub> and UV/S<sub>2</sub>O<sub>8</sub> oxidation

Parameter	Fe <sup>2+</sup> /S <sub>2</sub> O <sub>8</sub> oxidation process (COD/S <sub>2</sub> O <sub>8</sub> /Fe <sup>2+</sup> ratio 1/8/8)		UV/S <sub>2</sub> O <sub>8</sub> oxidation process (COD/S <sub>2</sub> O <sub>8</sub> ratio 1/8)	
	k <sub>1</sub> (h <sup>-1</sup> )	R <sup>2</sup>	k <sub>1</sub> (h <sup>-1</sup> )	R <sup>2</sup>
	COD	0.9074	0.9857	0.2071
UV <sub>254</sub>	1.2689	0.9937	0.1731	0.9372
UV <sub>280</sub>	1.6557	0.9645	0.2816	0.9793
UV <sub>436</sub>	3.5816	0.8366	1.4335	0.9924
UV <sub>525</sub>	3.0519	0.8301	1.3059	0.9818
UV <sub>620</sub>	3.5731	0.8510	1.4727	0.9841

#### 4. CONCLUSIONS

The treatment of dye-producing chemical industrial wastewater using  $\text{Fe}^{2+}/\text{S}_2\text{O}_8$  or  $\text{UV}/\text{S}_2\text{O}_8$  oxidation process was investigated in this study. In  $\text{Fe}^{2+}/\text{S}_2\text{O}_8$  oxidation process, optimum COD/ $\text{Fe}^{2+}/\text{S}_2\text{O}_8$  ratio, pH and oxidation time were found to be 1/8/8, 3 and 1 h. In these conditions, COD,  $\text{UV}_{254}$ ,  $\text{UV}_{280}$ ,  $\text{UV}_{436}$ ,  $\text{UV}_{525}$  and  $\text{UV}_{620}$  removal efficiencies in this chemical industrial wastewater were obtained as 61.1%, 72.8%, 82.8%, 98.4%, 97.1% and 98.4%, respectively. In  $\text{UV}/\text{S}_2\text{O}_8$  oxidation process, COD,  $\text{UV}_{254}$ ,  $\text{UV}_{280}$ ,  $\text{UV}_{436}$ ,  $\text{UV}_{525}$  and  $\text{UV}_{620}$  removal efficiencies were 54.4%, 54.3%, 66.5%, 98.9%, 98.2% and 98.3% at 1/8 of COD/ $\text{S}_2\text{O}_8$  ratio and pH 6 after 4 h oxidation time, respectively. While more than 97% color removal can be achieved in both  $\text{Fe}^{2+}/\text{S}_2\text{O}_8$  and  $\text{UV}/\text{S}_2\text{O}_8$  oxidation processes, it was seen that organic matter removal was lower in  $\text{UV}/\text{S}_2\text{O}_8$  oxidation process when COD,  $\text{UV}_{254}$  and  $\text{UV}_{280}$  parameters are examined. In the  $\text{Fe}^{2+}/\text{S}_2\text{O}_8$  oxidation process, high COD and color removal efficiencies were achieved compared to  $\text{UV}/\text{S}_2\text{O}_8$  oxidation process and also the oxidation time was shorter (the oxidation rate was higher). The results showed that both  $\text{Fe}^{2+}/\text{S}_2\text{O}_8$  and  $\text{UV}/\text{S}_2\text{O}_8$  oxidation processes were effective and suitable methods for removal of especially color parameter in this chemically treated dye-producing chemical industry wastewater. Although the organic matter removal (as COD,  $\text{UV}_{254}$ ) was higher in the  $\text{Fe}^{2+}/\text{S}_2\text{O}_8$  oxidation process, the amount of  $\text{Fe}^{2+}$  used in this process and the amount of sludge formed should also be taken into account for economic evaluation.

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