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Investigation of treatability of automotive industry wastewaters by coagulation-flocculation, fenton and UV/H_2O_2

Otomotiv endüstrisi atıksularının koagülasyon- flokülasyon, fenton ve UV/H_2O_2 prosesleri ile arıtılabilirliğinin incelenmesi

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Abstract

In the automotive industry, painting operations have emerged as a major source of environmental concerns. In this study, the treatability of wastewater obtained from the automotive industry painting process was investigated by using coagulation-flocculation, ultraviolet/hydrogen peroxide (UV/H_2O_2), and Fenton processes. The effects of pH, coagulant, and anionic polymer doses were examined for three different coagulants in the coagulation-flocculation process. Optimal conditions were determined based on chemical oxygen demand (COD) and turbidity removal efficiency. As a result of the study, the optimum conditions for the coagulant identified as ferric chloride, which achieved the highest COD removal of 49.6% and turbidity removal of 74.4%, were determined as pH 8, coagulant dose of 400 mg L^{-1}, and anionic polymer dose of 1 mg L^{-1}. In the second stage of the study, Fenton and UV/H_2O_2 processes were applied to the effluent of the coagulation-flocculation process to increase the removal efficiency. When the results were evaluated, it was observed that the maximum COD removal efficiency of 63.4% was attained under the conditions of pH 3 and 400 mg L^{-1} H_2O_2 concentration applied in the UV/H_2O_2 process. However, in the Fenton process, a maximum COD removal efficiency of only 51% was achieved. From this study, it can be concluded that the UV/ H_2O_2 process applied after coagulation-flocculation increases the removal efficiency and can be an alternative and effective treatment process for wastewater from the automotive painting process.

Keywords: Automotive industry, Coagulation-flocculation, Fenton, UV/H_2O_2

Özet

Otomotiv endüstrisinde boyama prosesleri, çevresel endişelerin ana kaynaklarından biri olarak ortaya çıkmaktadır. Bu çalışmada otomotiv endüstrisi boyama prosesinden elde edilen atıksuyun koagülasyon-flokülasyon, ultraviyole/hidrojen peroksit (UV/H_2O_2) ve Fenton prosesleri ile arıtılabilirliği incelenmiştir. Koagülasyon-flokülasyon prosesinde farklı pH, koagülant ve anyonik polimer dozlarının etkisi karşılaştırılmış ve optimum şartlar kimyasal oksijen ihtiyacı (KOİ) ve bulanıklık giderim verimine göre belirlenmiştir. Çalışma sonucunda en yüksek %49.6 KOİ ve %74.4 bulanıklık giderim veriminin elde edildiği koagülant olarak tespit edilen demir (III) klorür için optimum koşullar pH 8, koagülant konsantrasyonu 400 mg L^{-1} ve anyonik polimer dozu 1 mg L^{-1} olarak belirlenmiştir. Giderim verimini arttırmak amacıyla koagülasyon-flokülasyon prosesi çıkış suyuna Fenton ve UV/H_2O_2 prosesleri uygulanmıştır. Sonuçlar değerlendirildiğinde maksimum KOİ giderim verimi pH=3 ve 400 mg L^{-1} H_2O_2 konsantrasyonunda uygulanan UV/ H_2O_2 prosesi ile % 63.4 olarak elde edilmiştir. Ancak Fenton prosesinde ise maksimum %51 KOİ giderimi sağlanabilmiştir. Bu çalışmadan, koagülasyon flokülasyon ardından uygulanacak UV/H_2O_2 prosesinin giderim verimini arttırdığı ve otomotiv endüstrisi boyama prosesi atıksuları için alternatif ve etkili bir proses olabileceği sonucuna varılmıştır.

Anahtar kelimeler: Otomotiv endüstrisi, Koagülasyon-flokülasyon, Fenton, UV/H_2O_2

1 Introduction

The automotive industry is a continuously evolving sector shaped by technological innovations and consumer demands. It also holds significant economic value, with high export capacity and importance in terms of employment. However, due to the complex processes involved, it exhibits considerably high rates of water and energy consumption. Numerous natural resources are consumed throughout the automobile manufacturing process, and a variety of hazardous and non-hazardous gaseous, liquid, and solid wastes are produced [1]. Therefore, waste management, compliance with environmental regulations, recycling initiatives, and sustainability practices are of great significance for this sector.

Wastewaters originating from the automotive industry, obtained from various processes, exhibit diverse characteristics and, due to their contents, can pose significant environmental issues within industrial effluents. The painting, assembling, surface finishing, metal casting, and production of metal and plastic components are some of these processes [2, 3]. The wastewater from these processes contains pollutants such as paints, heavy metals, phosphate, solids in the suspension, chemical oxygen demand (COD),

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biological oxygen demand (BOD), detergents, oils, and are extremely dangerous because of their toxic content, although they are not voluminous [4]. Among these processes, one of the most hazardous is the painting process, due to the use of hazardous chemicals and resulting waste [5]. Despite the automotive industry having advanced technologies and production facilities, the wastewater from the painting process, in particular, leads to high levels of environmental pollution due to its high COD, heavy metal, and phosphorus content [6]. In many studies, the painting and coating process takes the lead in the environmental issues caused by vehicle manufacturing, constituting 60-80% of environmental risks [7-10]. It is known that the typical COD of the paint shop wastewater varies between 1400-11400 mg L^{-1}, and this value can differ depending on the equipment used, operational/cleaning processes, and the type of chemicals used [11-13]. It is seen that various treatment processes are applied under different conditions to make such wastewater comply with discharge standards [2]. In Turkey, discharge limits that must be adhered to on a sectoral basis have been established and published in the “Water Pollution Control Regulation.” In this regulation, discharge limits for vehicle factories are specified [14].

In the literature, various treatment techniques have been experimented with and their effectiveness investigated to treat wastewater originating from automotive paint processes and other manufacturing stages. According to result of study carried out by Kuybu [15], the wastewater has subjected to treatment processes such as sand filtration, activated carbon adsorption, ultrafiltration, and reverse osmosis (RO). In the first treatment stage, sand filtration achieved a 90% removal efficiency for suspended solids (SS), in the activated carbon adsorption process, a 68% removal of COD, a 58% removal of nitrate (NO_3) was observed, and finally, after the application of the reverse osmosis process, a 99% removal efficiency in conductivity output values was achieved.

In another study applying the electrocoagulation process for automotive industry wastewater, it was possible to achieve, at optimum parameter values, 95% oil removal, 87.4% COD removal, and 70.6% mineralization values. Additionally, a final biodegradability of 0.54 (BOD_5/COD) was reached [16]. In a study examining treatment with an anaerobic sequential batch biofilm reactor, it was reported that an 88% removal efficiency was achieved at a volumetric loading rate (VLR) of 3.09 g COD/L day [12].

Among various treatment techniques in the literature, it has been suggested that physical-chemical technologies including coagulation-flocculation and advanced oxidation processes may be suitable for the treatment of such wastewater [17]. Coagulation-flocculation is one of the important processes used in the treatment of water and industrial wastewater [18]. This process is widely preferred due to its high removal efficiency, ease of application, as well as its lower energy requirements compared to alternative technologies, and economic efficiency [19]. The coagulants added to wastewater disrupt the electrostatic charges of colloidal and dissolved substances in the water, neutralizing particle charges. In this way, particles come together to form larger and more rapidly settling masses [20, 21]. The most commonly preferred coagulants in the coagulation-flocculation process are aluminum sulfate (alum), iron(II) sulfate, iron(III) chloride, and iron chloro-sulfate ($FeClSO_4$) [10]. Every coagulant exhibits optimal pollutant removal at an ideal pH and functions best in a particular pH range. The width of this pH range is influenced by the type of coagulant used, the characteristics of the wastewater, and the coagulant dosage [22].

Advanced oxidation processes are based on the production of hydroxyl radicals (E^0=2.8 eV) [23]. One of these processes, Fenton oxidation, is based on the formation of highly potent oxidizing hydroxyl radicals through the reaction of H_2O_2 with Fe^{2+} ions in an acidic environment [24, 25]. Hydroxyl radicals (OH·) rapidly mineralize most practically organic pollutants and transform them into less or non-toxic products. The commonly acknowledged mechanism of the Fenton process is illustrated in Equation (1)–(3) [26].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\cdot + OH^- \tag{1}$$
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2\cdot + H^+ \tag{2}$$
$$Fe^{3+} + HO_2\cdot \rightarrow Fe^{2+} + H^+ + O_2 \tag{3}$$

The efficiency of the Fenton reaction varies depending on various parameters such as pH, temperature, concentrations of reactants, and the quantities of organic and inorganic pollutants [24]. The main advantages of the process include reasonable initial investment costs, high pollutant removal efficiencies, ecological safety, low toxicity for potential subsequent biological treatment, partial inactivation of toxic and recalcitrant compounds, stability in treating various chemical substances, and operability without the need for additional equipment [25].

In the UV/H_2O_2 oxidation process, the primary oxidizing agent is the hydroxyl radical, which is generated through UV radiation in the presence of hydrogen peroxide. These radicals react with organic pollutants, chemically oxidizing organic matter. In this way, a H_2O_2 decomposition-formation cycle occurs. The mechanism of the UV/H_2O_2 process is illustrated in Equation (4)–(6) [27, 28].

$$H_2O_2 + h\nu \rightarrow 2OH\cdot \tag{4}$$
$$H_2O_2 + OH\cdot \rightarrow H_2O + HO_2\cdot \tag{5}$$
$$HO_2\cdot + HO_2\cdot \rightarrow H_2O_2 + O_2 \tag{6}$$

In other words, UV light triggers the decomposition of hydrogen peroxide into two hydroxyl radicals. Subsequently, these radicals engage with organic pollutants, initiating the chemical oxidation of organic matter. The reaction time depends on the pollution load and the complexity of the wastewater. The reaction is completed at the end of a certain period, and even if the process continues beyond that time, no increase in efficiency is observed [29]. The UV/H_2O_2 process also offers advantages such as no sludge formation during treatment and suitability for operation under ambient conditions [30].

Considering these factors, the main objective of this study is to explore the feasibility of treating wastewater produced during the painting process in the automotive industry. The study includes a two-step approach, starting with coagulation-flocculation and then assessing the effectiveness of two distinct advanced oxidation processes: Fenton and UV/H_2O_2.

Optimum conditions were determined by evaluating the results obtained under different process conditions. The removal efficiencies after treatment were evaluated based on COD and turbidity parameters. The results obtained will contribute to reducing the environmental impact of wastewater from the automotive industry painting process and help in the development of alternative treatment methods for similar wastewater.

2 Materials and methods

2.1 Wastewater collection and characterization

Wastewater used in this study was obtained from the wastewater treatment plant equalization tank entrance of a facility located in Aksaray and operating in the painting of plastic exterior parts. The wastewater samples were stored in the laboratory at 4^0C. During the wastewater characterization, analyses were conducted for COD (SM 5220 C), Conductivity (SM 2510 B), Turbidity (SM 2130B), pH (SM 4500B), Total Nitrogen (EN ISO 12260), Ammonium NH_4-N (SM 4500), and Phosphate PO_4-P (SM 4500 P) [31]. The main physico-chemical characteristics of this wastewater are summarized in Table 1.

Table 1. Characterization of the automotive industry painting process wastewater used in the study.

Parameters	Unit	Concentration/Value
COD	(mg L^{-1})	14744±734.54
TDS	(mg L^{-1})	4.13±0.02
pH	-	7.29±0.12
EC	(mS cm^{-1})	4.76±0.08
Turbidity	(NTU)	682.20±12.97
NH_4	(mg L^{-1})	5.29±0.65
NH_4-N	(mg L^{-1})	4.12±0.51
PO_4	(mg L^{-1})	17.98±1.05
PO_4-P	(mg L^{-1})	5.78±0.11
NO_3	(mg L^{-1})	153.27±5.23
NO_3-N	(mg L^{-1})	35.29±5.23

2.2 Experimental setups

Within the scope of this study, treatability studies of wastewater taken from the automotive industry painting process output were conducted in two phases: first, chemical treatment, and then advanced oxidation processes applied to the effluent of the chemical treatment. The processes used for the wastewater treatment are summarized in the flow diagram in Figure 1.

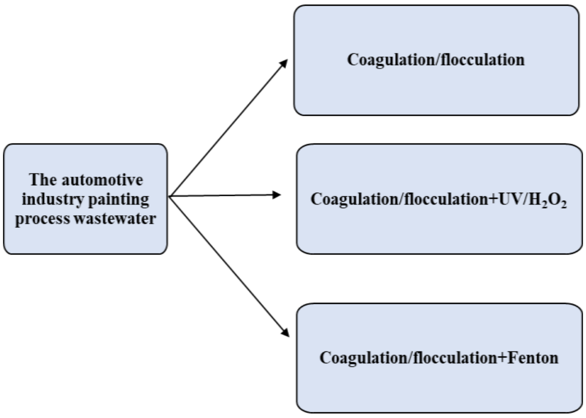

Figure 1. Treatment processes applied for wastewater treatment of automotive industry painting process.

2.2.1 Coagulation-flocculation process

In coagulation-flocculation studies, three different coagulants were used: aluminum sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$, M= 666.42 g mol^{-1}), iron (II) sulfate ($FeSO_4 \cdot 7H_2O$, M= 278.2 g mol^{-1}), and iron (III) chloride ($FeCI_3 \cdot 6H_2O$, M=270.32 g mol^{-1}). Anionic polymer (SNF Floerger Flopam AN 905 PWG) was used as a coagulant aid.

Coagulation-flocculation experiments were carried out in the classical jar test (Velp-Scientifica JLT6) setup and at room temperature (24 ± 2^0C). At the beginning of the study, 2 g L^{-1} stock coagulant solutions were prepared using ultrapure water. To determine the optimum pH, 200 mL wastewater samples were placed in 500 mL beakers, and pH values were adjusted to selected values between 4, 5, 6, 7, 8, and 9. pH adjustment was carried out with 6 N sodium hydroxide (NaOH) and 6 N sulfuric acid (H_2SO_4) solutions. The prepared wastewater samples were mixed rapidly at 100 rpm for 3 minutes and then slowly mixed at 30 rpm for 20 minutes. After mixing, the wastewater was left to precipitate for 30 minutes. The COD and turbidity levels were measured in the supernatant samples. At this stage, the coagulant doses in each beaker were kept constant.

In the second stage of the coagulation-flocculation studies, coagulant doses ranging from 30, 60, 120, 200, 300, and 400 mg L^{-1} were studied at the determined optimum pH value. Finally, an anionic polymer study was carried out at doses between 0.25-0.50-1-2-3, and 4 mg L^{-1} at the determined optimum coagulant dose and pH value. Thus, the optimum pH, coagulant, and anionic polymer dosage were determined. All studies were repeated for three coagulants.

2.2.2 UV/H_2O_2 process

At this stage of the study, UV/H_2O_2, an advanced oxidation process, was applied to the wastewater taken from the exit of the coagulation-flocculation process carried out under optimum conditions. The UV/H_2O_2 process was carried out on 350 ml wastewater samples placed in a photoreactor PURFECT 01 model, emitting light at 50 Hz, 220 V, 254 nm. In the study, firstly, the pH values of the wastewater samples were adjusted to 3, 5, 7, and 9 to determine the optimum pH value. Before the samples were given to the reactor, the H_2O_2 stock solution prepared at 250 g L^{-1} concentration was added to the beakers on the magnetic stirrer in a volume that would provide a constant 400 mg L^{-1} H_2O_2 concentration. For the H_2O_2 stock solution, 30% H_2O_2 with a density of 1.11 g cm^{-3}, obtained from Merck, was used. During the optimal pH studies, samples were collected from the UV reactor outlet at 5, 10, 15, 30, 45, 60, 75, and 90 minutes. In the second stage of the study, different H_2O_2 concentrations ranging from 300 to 800 mg L^{-1} were investigated at the optimum pH value determined in the first stage. The experimental setup used in the UV/ H_2O_2 process is provided in Figure 2.

.

Figure 2. The experimental setup used in the feasibility study of treating with the UV/H_2O_2 process

2.2.3 *Fenton process*

In order to improve the COD removal efficiency, the Fenton process was applied by taking the wastewater coagulated under optimum conditions. Thus, it was aimed to evaluate a second alternative and determine the optimum conditions for the advanced treatment process that can be applied after coagulation. All studies on the Fenton process were carried out at pH<3.5 and 250 mL volume. 6 N H_2SO_4 solution was added to the beakers in the required amounts to ensure pH<3.5. Since it is known in the literature that the Fenton process is effective at low pH levels (<3.5) according to the operational procedure, an optimum pH study was not conducted within the scope of this study [32-34]. During the process, the beakers in the jar test setup were stirred for a total of 30 minutes, with 5 minutes at a high speed of 200 rpm and 25 minutes at a slow speed of 15 rpm. When the process time was completed, the pH was increased again to 8-8.5 with 6N NaOH solution to stop the formation of $OH^{\cdot}$ radicals and terminate the process.

At the end of the process, the samples in the beakers were left to settle for 60 minutes. In the last stage, COD analyses were performed on the samples taken from the upper phase of each beaker.

3 Results and discussions

3.1 *Determining optimum pH for coagulation flocculation*

One of the preferred and important processes in the treatment of water and industrial wastewater is the coagulation-flocculation process [18]. This process is easy to apply and, at the same time, is a highly effective method for the removal of heavy metals and inorganic compounds [10]. In this study, experiments were conducted with aluminum sulfate (alum), iron (II) sulfate, and iron (III) chloride coagulants at pH values of 4, 5, 6, 7, 8, and 9 using a jar test apparatus. The results obtained for all three coagulants were comparatively evaluated, as seen in Figure 3. The optimum pH values for aluminum sulfate, iron (III) chloride, and iron (II) sulfate were determined to be 7, 9, and 8, respectively. At these pH values, COD removal efficiencies were found to be 28.06%, 44.16%, and 39.44%, while turbidity removal efficiencies were 45.24%, 72.88%, and 76.37%, respectively.

COD and turbidity removal efficiencies showed a decreasing trend at pH values higher and lower than the specified optimum pH values for each coagulant. The pH parameter is an effective factor on the physicochemical properties of wastewater as well as the removal rate of pollutants in the water [35]. In the chemical coagulation process, the pH value determines the dominant hydrolysis species in destabilization with hydrolyzed metal coagulants. The pH value at which the most efficient hydrolysis species of the coagulant are formed in the process is of great importance for the achievement of optimal coagulation [22, 36, 37].

In a study from the literature, COD removal was aimed at the wastewater obtained from a spare parts manufacturing facility for automobiles using the coagulation-flocculation process, and in parallel with this study, investigations were carried out on the optimum pH, coagulant dosage, and anionic polymer dosage. In experiments conducted for three different coagulants, the optimum pH was found to be 7 for aluminum sulfate, and at this pH, a COD removal of 36% was achieved. For iron (III) chloride, the optimum pH was determined to be 6, with a COD removal of 51% [38]. In another study, iron (III) chloride was used as a coagulant in the treatment of wastewater from the automotive industry, and a COD removal of 80% was achieved under the conditions of pH 8 and a coagulant dosage of 0.8 mL^{-1} [10].

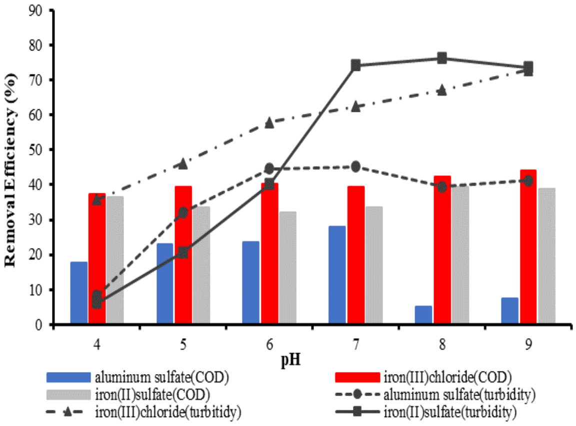

Figure 3. Effect of pH on the COD and, turbidity removal by coagulation-flocculation process

3.2 *Determining optimum coagulant dose for coagulation flocculation*

During the second phase of coagulation-flocculation studies, the impact of varying coagulant concentrations on the efficiency of COD and turbidity removal was investigated. For each coagulant, coagulant doses ranging from 30 to 400 mg L^{-1} were studied at the optimum pH values obtained in the first stage. The results obtained are presented in Figure 4.

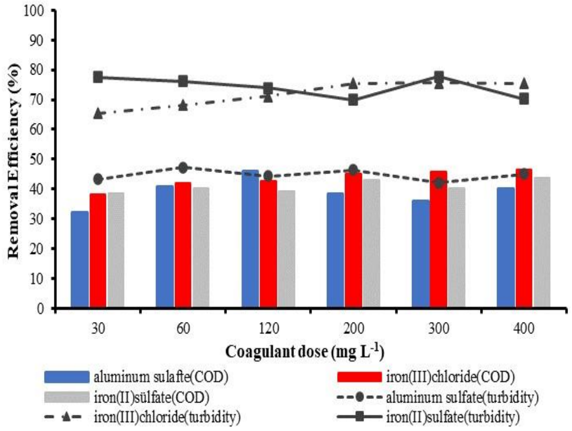

Figure 4. Effect of coagulant dose on COD and turbidity removal by coagulation-flocculation process (pH=7 for $Al_2(SO_4)_3$, pH=9 for $FeCI_3$, pH=8 for $FeSO_4$)

The optimum coagulant doses were determined as 120 mg L^{-1} for aluminum sulfate and 400 mg L^{-1} for iron (III) chloride and iron (II) sulfate, with COD removal efficiencies of 45.87%, 46.64%, and 43.87%, respectively, at these concentrations. Turbidity removal efficiencies were found to be 44.42% for aluminum sulfate, 75.54% for iron (III) chloride, and 70.25% for iron (II) sulfate. In coagulation-flocculation processes, commonly used inorganic metal salts include aluminum sulfate, iron sulfate, ferric chloride, and ferric chlorosulfate. Among these, iron salts are generally more effective than aluminum salts. [10].

When the obtained COD removal efficiencies are evaluated, it can be observed that the removal efficiency is lower at concentrations below or above the optimum dose. In particular, in the studies conducted for ferric chloride and ferrous sulfate, higher coagulant doses were tested after obtaining the highest removal efficiencies at 400 mg L^{-1}. However, it was determined that the removal efficiency decreased at higher concentrations. In a similar study using aluminum sulfate and ferric chloride as coagulants, the maximum COD removal efficiency for aluminum sulfate was determined to be 46% at the optimum coagulant dose of 100 mg L^{-1}, while for ferric chloride, the maximum COD removal efficiency reached 60% at a coagulant concentration of 200 mg L^{-1}. In the same study, it was noted that parallel to these study results, the use of higher coagulant concentrations led to a decrease in removal efficiency [38]. In another study conducted on wastewater from the automotive industry, PAC and $FeCl_3$ were utilized as coagulants. A COD removal efficiency of 85% was achieved with a PAC dosage of 1.0 mL L^{-1} at pH 6.5, while for $FeCl_3$, the highest removal efficiency, 80%, was determined at a dosage of 0.8 mL L^{-1} and pH 9.5 [10]. According result of study carried out by Karchiyappan [3], three types of processes, namely ozonation (ON), Electro-Fenton process (EFP), and chitosan-based coagulation (CBC), have been employed for the removal of turbidity from automotive industry wastewater. By the model, optimal conditions for each process resulted in a turbidity removal rate exceeding 55%.

3.3 *Determining optimum anionic polymer dose for coagulation flocculation*

In the final stage of the coagulation-flocculation process studies, the effect of the anionic polymer as a coagulant aid was investigated by testing varying doses ranging from 0.25 to 4 mg L^{-1} The results obtained from the experiments carried out by keeping the optimum coagulant dose and pH values determined separately for each coagulant are given in Figure 5.

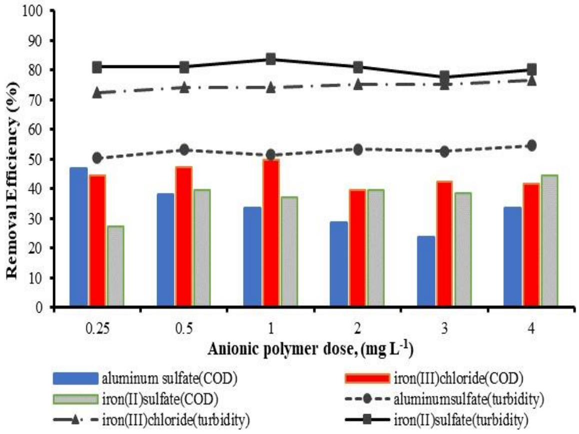

Figure 5. Effect of anionic polymer dose on COD and turbidity removal by coagulation-flocculation process (pH=7 and coagulant dose=120 mg L^{-1} for $Al_2(SO_4)_3$, pH=9 and coagulant dose=400 mg L^{-1} for $FeCI_3$, pH=8 and coagulant dose=400 mg L^{-1} for $FeSO_4$)

The optimum anionic polymer doses were determined as 0.25 mg L^{-1} for aluminum sulfate, 1 mg L^{-1} for ferric chloride, and 4 mg L^{-1} for ferrous sulfate. The COD removal efficiencies for aluminum sulfate, ferric chloride, and ferrous sulfate were found to be 46.64%, 49.60%, and 44.57%, respectively. When evaluating turbidity removal, the results obtained for each coagulant showed that an increase in the anionic polymer dose did not lead to a significant change in turbidity removal efficiency. However, turbidity removal efficiencies increased significantly compared to the previous stage where only coagulants were used. At the optimum anionic polymer doses, we determined by evaluating the turbidity and COD removal efficiencies together, 50%, 74% and 80% turbidity removal efficiencies were determined for alum, iron (III) chloride and iron (II) sulfate, respectively.

Furthermore, in this stage of the study, to assess the influence of the sedimentation time applied at the end of the coagulation-flocculation process, turbidity measurements were taken not only at 30 minutes but also at 60 minutes after the process. The obtained turbidity values are presented in Figure 6. The increase in sedimentation time was observed to have no significant effect on turbidity removal. When comparing all three coagulants, it was observed that iron (II) sulfate was more effective in turbidity removal compared to the other two coagulants. However, it did not provide the same level of performance in COD removal.

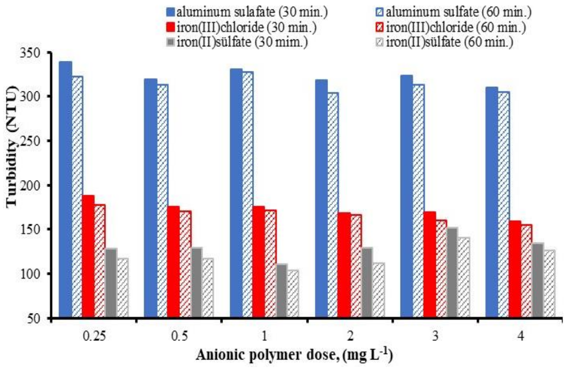

Figure 6. Effect of anionic polymer dosage and settling time in turbidity removal by coagulation-flocculation process.

As a part of the wastewater treatment study on automotive industry painting process effluents, the initial stage involved the coagulation-flocculation process. The obtained optimal conditions and removal efficiencies for three different coagulants are summarized in Table 2.

3.4 *Effect of UV/H_2O_2 process on COD removal*

Advanced oxidation processes are primarily employed for the removal of challenging and hazardous pollutants present in industrial wastewater, surface waters, and groundwater. These processes generate highly potent and non-selective oxidizing species, known as hydroxyl radicals (OH·), to facilitate the degradation of pollutants [39]. In this study, UV/H_2O_2, one of the advanced oxidation processes, was studied in the automotive industry painting process wastewater taken from the output of the coagulation-flocculation process carried out under optimum conditions. Similarly, there are studies in the literature where advanced oxidation processes are applied to wastewater taken from the output of the coagulation-flocculation process for different wastewater types [40, 41]. Firstly, the results obtained from the UV/H_2O_2 process studies carried out at different pH values are given in Figure 7.

It was observed that higher COD removal efficiencies were obtained at lower pH values. The highest COD removals of 63.39%, 57.90%, 51.43% and 50.49% were obtained at pH values of 3-5-7 and 9, respectively. Maximum COD removal was achieved at pH=3 and 30 minutes with a removal percentage of 63%. This can be stated as the rapid decomposition of hydroxyl radicals and hydrogen peroxide at low pH values, as in similar studies. [42]. When many studies on this subject are examined, it has been stated that the oxidizing ability of H_2O_2 decreases and becomes unstable at high pH values and has a negative effect on the oxidation reaction and significantly reduces the formation of OH radicals. However, at low pH value (pH<2), $H_3O_2^+$ is formed and in this case, the formation of OH radical becomes difficult. [25, 39, 43].

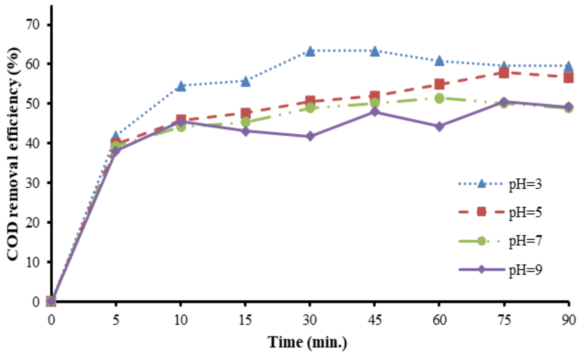

Figure 7. Effect of pH on the COD removal during UV/H_2O_2 process (H_2O_2 = 400 mg L^{-1}).

At this stage, where the effect of pH on the UV/H_2O_2 process was examined, samples were taken at different times until the end of the 90-minute oxidation period. Thus, the effect of oxidation time on the removal efficiency was observed. It was observed that the increase after 30 minutes did not have significant effect on COD removal efficiencies at all pH values.

In the second step of the UV/H_2O_2 studies, varying H_2O_2 concentrations between 300 and 800 mg L^{-1} were investigated to determine the effect of H_2O_2 concentration, while keeping the pH value constant at 3. The results are presented in Figure 8. The maximum COD removal efficiency of 63.4% was obtained at a concentration of 400 mg L-^{1} H_2O_2. The highest COD removal efficiencies obtained at 500, 600 and 800 mg L^{-1} H_2O_2 concentrations were determined as 50%, 51% and 51%, respectively. It was observed that an increase in H_2O_2 concentration beyond 400 mg L^{-1} did not significantly affect the COD removal efficiency. The reason for this is that, as explained in similar studies, when hydrogen peroxide concentration is added above the optimum values, it can consume hydroxyl radicals in the solution and act as a scavenger for hydroxyl radicals [39]. On the other hand, at hydrogen peroxide concentrations below the optimum level, an insufficient amount of hydroxyl radicals is generated, which can lead to a decrease in removal efficiency [30].

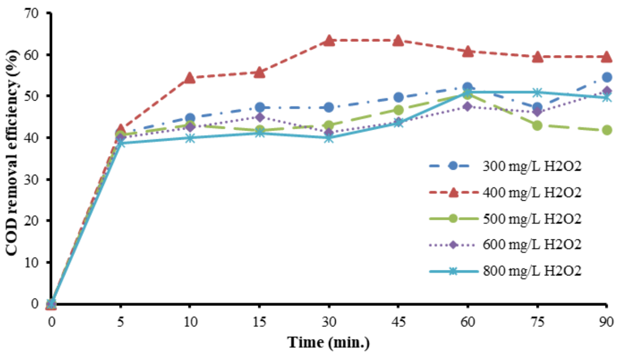

Figure 8. Effect of H_2O_2 dose on the COD removal during UV/H_2O_2 process (pH=3)

Table 2. The optimum process conditions for COD and turbidity removal through coagulation-flocculation and the obtained removal efficiencies (Rapid mixing: 3 min at 100 rpm; slow mixing: 20 min at 30 rpm).

Coagulants	**Optimum conditions**			**Removal efficiencies (%)**		
	pH	**Coagulant dose (mg L^{-1})**	**Anionic polymer dose (mg L^{-1})**	**COD**	**Turbidity (Settling time:30 min.)**	**Turbidity (Settling time:60 min.)**
$Al_2(SO_4)_3.18H_2O$	7	120	0.25	46.6	50.3	52.7
$FeCl_3.6H_2O$	9	400	1	49.6	74.2	74.9
$FeSO_4.7H_2O$	8	400	4	44.6	80.2	81.4

3.5 *Effect of Fenton process on COD removal*

In the final stage of the study, the wastewater obtained after treatment under the determined optimum conditions in the coagulation-flocculation process was subjected to the Fenton process. In recent years, the Fenton process has been efficiently used for the removal of many hazardous organic compounds from wastewater [44]. In the literature, the most suitable pH value for the Fenton process is generally accepted to be in the range of 3-3.5; therefore, an optimum pH study was not conducted in this research [25, 44-46]. Firstly, H_2O_2 concentrations ranging from 250-1500 mg L^{-1} were studied at a fixed Fe^{2+} concentration of 100 mg L^{-1}. When the results given in Figure 9 are examined, the highest COD removal was obtained as 47.57% at 250 mg L^{-1} H_2O_2 concentration. The COD removal efficiencies ranging from 40% to 42% were achieved at H_2O_2 concentrations of 500, 750, 1000, 1250, and 1500 mg L^{-1}. As shown in Figure 9, the increase in H_2O_2 concentration did not significantly impact the removal efficiency. In the Fenton process, the concentration of H_2O_2 plays a crucial role in determining the overall efficiency of the degradation process. The source of OH radicals formed in Fenton oxidation is hydrogen peroxide. Typically, it has been observed that an increase in hydrogen peroxide dosage leads to a higher percentage of pollutant degradation [44, 47]. However, the generated OH· is not selective toward either the pollutants or the excess H_2O_2 in the solution [48]. Therefore, the concentration of H_2O_2 should be adjusted to achieve the optimum dosage. In this study 250 mg L^{-1} H_2O_2 was chosen optimum dose. The presence of an excess of H_2O_2 beyond the optimum level in the environment, ferric ions react with hydrogen peroxide to form HO_2•, which has a lower oxidizing ability, leading to the formation of iron hydroxyl sludge. In this case, the Fenton process can lead to an increase in COD and pollution in the treated water [44, 49, 50].

In the second stage of the study for the Fenton process, Fe^{2+} concentrations ranging from 25-150 mg L^{-1} were studied. The results are presented in Figure 10. The highest COD removal was determined as 51.14% at 75 mg L^{-1} Fe^{2+} concentration. COD removal efficiencies obtained at Fe^{2+} concentrations below and above this concentration were lower. Thus, the optimum Fe^{2+} concentration in the Fenton process applied for automotive industry painting process wastewater was determined as 75 mg L^{-1}.

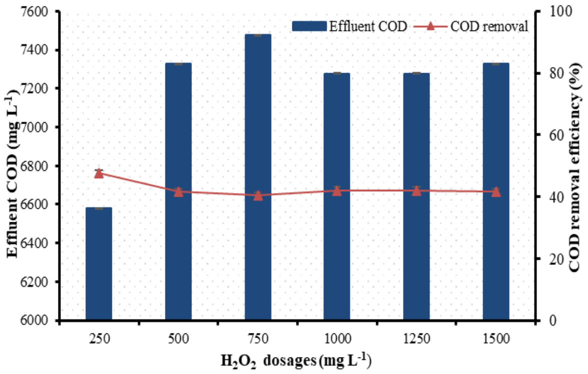

Figure 9. Effect of H_2O_2 dose on the COD removal during Fenton process (pH =3-3.5 and Fe^{2+} =100 mg L^{-1}).

In Fenton oxidation, Fe^{2+} ion reacts with H_2O_2 and forms OH radicals. In the absence of Fe^{2+} ion and since OH radicals cannot be formed; effective oxidation does not occur. The reaction rate and the production of the OH radical increase simultaneously with the rise in the concentration of this ion. Nevertheless, an excessive increase in Fe^{2+} ion concentration may lead to an undesirable increase in the total dissolved solid content or the quantity of suspended iron at the process outlet [25, 44, 50, 51].

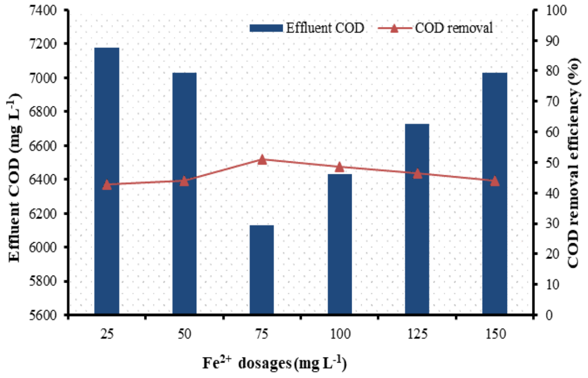

Figure 10. Effect of Fe^{2+} dose on the COD removal during Fenton process (pH =3-3.5 ve H_2O_2=250 mg L^{-1}).

In a similar study conducted for the painting process in the automotive industry, the initial COD value, which was 4435 mg L^{-1}, could only be reduced to 4365 mg L^{-1} at the process outlet using the Fenton process. It has been stated that this situation is probably due to the presence of high stability and permanence antioxidant substances used as additives in paints and the non-degradability of these substances [17].

4 Conclusions

In this study, the wastewater wastewater generated from an automotive industry painting process was investigated for turbidity and COD removal efficiencies. The raw wastewater was obtained from the balancing tank entrance of the treatment plant. The wastewater was initially treated with coagulation-flocculation, followed by the application of advanced oxidation processes, specifically Fenton and UV/H_2O_2, to the effluent from this process. The coagulation-flocculation studies were conducted using three different coagulants: aluminum sulfate (alum), iron (II) sulfate and iron (III) chloride achieved %47, %50, and, %45 for COD removal, and %50, %74, and, %80 for turbidity removal, respectively. According to these results, it was determined that the most suitable coagulant is iron (III) chloride, and the optimum conditions for this coagulant are pH=9, 400 mg L^{-1} H_2O_2, and 1 mg L^{-1} anionic polymer dose.

In the second stage of the study, the aim was to enhance the COD removal efficiency by applying UV/H_2O_2 and Fenton advanced oxidation processes separately to the wastewater obtained from the coagulation-flocculation process carried out under optimum conditions and using iron (III) chloride as the coagulant. As a result of the studies conducted on the UV/H_2O_2 process, the optimum conditions were determined as pH=3, H_2O_2 concentration of 400 mg L^{-1}, and a process time of 30 minutes. Under these optimum conditions, it was found that the COD removal efficiency increased from 50% to 63.4%. Additionally, it was determined that there is a decreasing trend in COD removal efficiency at H_2O_2 concentrations above 400 mg L^{-1} in the UV/H_2O_2 process. However, when the Fenton process was applied to the wastewater obtained from the coagulation-flocculation process, it did not result in a significant increase in COD removal. This can be attributed to the nature and concentration of contaminants that could potentially hinder the effectiveness of the Fenton process.

In light of all these results, the discharge limit of 300 mg L^{-1} for the COD parameter cannot be achieved in the effluent of both treatment processes. However, compared to similar industrial wastewaters in the literature, the COD value of the studied wastewater is quite high. Therefore, the achieved 63.4% COD removal with coagulation-flocculation + UV/H_2O_2 processes is significant. This can contribute to reducing the potential adverse effects of automotive industry painting process wastewaters or similar industrial wastewaters on the environment. In future research, alternative advanced oxidation processes, as well as relatively new and updated applications of Fenton, could be employed for the treatment of wastewater from the automotive industry dyeing process, with a particular focus on COD removal.

Conflict of interest

The author declares that there is no conflict of interest.

Similarity rate (iThenticate): 19 %

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