ADVANCED TREATMENT OF BIOLOGICALLY TREATED CHEMICAL INDUSTRY WASTEWATER PRODUCING ORGANIC PEROXIDES USING FENTON AND ADSORPTION PROCESSES

Ali Rıza Dinçer[1], Deniz İzlen Çifçi[1], Demet Darcan[2], İbrahim Feda Aral[3*]

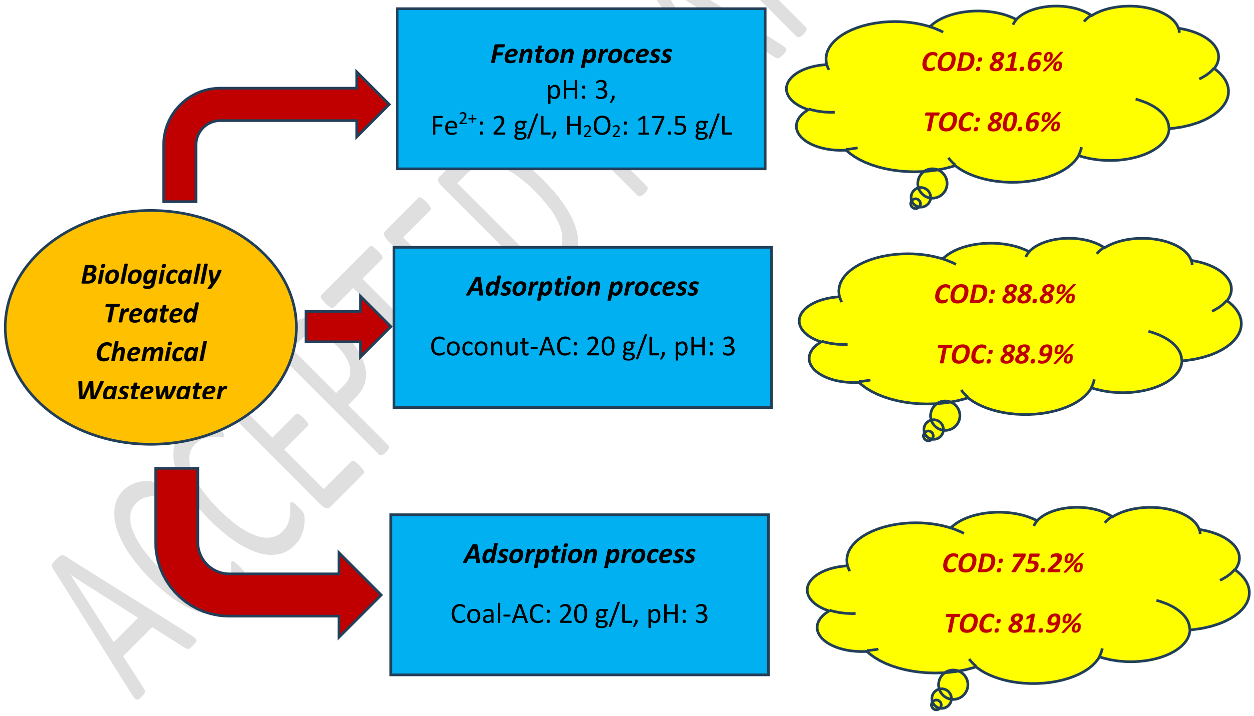
[1] Tekirdağ Namık Kemal University, Corlu Engineering Faculty, Department of Environmental Engineering, Çorlu, Tekirdağ, Turkey, A.R. Dinçer: adincer@nku.edu.tr, D.I. Çifçi: dicifci@nku.edu.tr,

[2]Akpa Chemical, Muratlı-Tekirdağ, demet@akpakimya.com

[3] Tekirdağ Namık Kemal University, Corlu Engineering Faculty, Department of Civil Engineering, Çorlu, Tekirdağ, Turkey, iaral@nku.edu.tr

[*]Corresponding author: İbrahim Feda Aral: iaral@nku.edu.tr

Graphical Abstract



Abstract

In this study, the advanced treatment of biologically treated chemical industrial wastewater from organic peroxide production was investigated using Fenton and adsorption processes. In the Fenton oxidation process, wastewater treatment was performed at different Fe^{2+} and H_2O_2 concentrations, pH values, and oxidation times to determine the optimal treatment conditions and treatment kinetics. In the adsorption process, wastewater treatment was conducted using coconut-based activated carbon (Coconut-AC) and coal-based activated carbon (Coal-AC) at different pH values, activated carbon doses, and adsorption times to determine the best treatment conditions, adsorption kinetics, and isotherms. In Fenton oxidation, COD (4680 mg/L), TOC (1022 mg/L), and organic peroxide removal were 81.6%, 80.6%, and 77.3%, with 1 h oxidation at pH 3, 2 g/L Fe^{2+}, and 17.5 g/L H_2O_2, respectively. In the adsorption process, better wastewater removal was achieved with Coconut-AC than with Coal-AC. At pH 3, with a 20 g/L activated carbon dose, 88.8% COD, 88.9% TOC, and 86.4% organic peroxide removal were obtained with Coconut-AC after 24 h of adsorption, while 75.2% COD, 81.9% TOC, and 54.5% organic peroxide removal were observed with Coal-AC. Although the SO_4^{2-} concentration in the wastewater increased with Fenton oxidation, 30.8% SO_4^{2-} removal was observed with Coconut-AC and 10.6% with Coal-AC. The cost was 15.77 \$/m^3 in Fenton oxidation under optimal conditions, compared to 15.87 \$/m^3 in the adsorption processes with Coconut-AC and Coal-AC. As a result, the adsorption process with Coconut-AC achieved higher wastewater treatment efficiency than Fenton oxidation, while the cost per m^3 of wastewater remained nearly the same. Moreover, SO_4 removal was effectively achieved in the adsorption process

Keywords: Adsorption, COD removal, cost analysis, Fenton oxidation, organic matter removal, TOC removal, organic peroxide, wastewater treatment

1.Introduction

Organic peroxides are widely used as crosslinkers, catalysts, or initiators in the chemical industry, drug synthesis, and polymerization reactions (Yan et al., 2024a; Zhu et al., 2024). Organic peroxides have a large market due to their use in the production of many materials, such as rubber, plastic, resin, and polymers. The demand for organic peroxides is increasing, because the number and capacity of facilities producing organic peroxides are also growing (Yan et al., 2024a; Liu et al., 2021). However, due to the large amount of water used in their production, the volume of wastewater generated is also quite high (Yan et al., 2024b). As water recycling has become one of the main focuses of sustainable development, the reuse of wastewater generated in industries is becoming widespread (Maruthai et al., 2025). Wastewater from the production of organic peroxides has low biodegradability and is toxic due to the presence of pollutants that are resistant to degradation (Yan et al., 2024b). Additionally, these wastewaters have high sulfate and organic peroxide concentrations, making them very difficult to treat with conventional wastewater treatment systems (Yan et al., 2024b; Dinçer et al., 2021). Therefore, additional treatment with advanced processes is required.

Advanced oxidation processes enable the removal of persistent and difficult to treat organic pollutants by producing the non-selective and highly reactive oxidizing agent •OH (hydroxyl) radical (Gómez et al., 2023). Fenton oxidation, one of the advanced oxidation processes, has been shown to be effective in treating many complex industrial wastewaters (Gómez et al., 2023; Gholami et al., 2022). In the Fenton oxidation of leather dyeing industrial wastewater with 0.981 mM Fe^{2+} and 5.38 mM H_2O_2 at pH 3.15, 82% COD, 92% TOC, and 97% color removal were achieved (Gómez et al., 2023). In the Fenton oxidation of pulp and paper wastewater with 15 mM Fe^{2+} and 15 mM H_2O_2 at pH 3, 78% COD removal was achieved (Gholami et al., 2022). Additionally, 85% COD removal was achieved in the treatment of coking wastewater with Fenton oxidation, and 77% TOC removal was achieved in the treatment of swine wastewater with Fenton oxidation (Verma et al., 2020; Toor et al., 2021).

The adsorption process has become a preferred tertiary treatment for industrial wastewater due to its high removal capacity for persistent organic compounds (Feng et al., 2020; Jorge et al., 2022; Kushwaha et al., 2010). The effectiveness of this process, which involves the retention of pollutants in wastewater on the surface of the adsorbent material by physical or chemical mechanisms, varies depending on factors such as the properties of the adsorbent, the properties of the pollutants and the current operating conditions (Selvanarayanan et al., 2024). COD removal was 98% in cork wastewater treatment combined flocculation and adsorption process (Ge et al., 2018). In the treatment of winery wastewater combined coagulation-flocculation, Fenton oxidation, and adsorption process (with bentonite), 81% COD and 72% TOC removal were obtained (Jorge et al., 2022). In the coagulation and adsorption of mixed (textile and chemical industry) industrial wastewater with coconut-based activated carbon, 97.5% COD and 95.5% TOC removal was achieved (Enfiyeci and Çifçi, 2025). In the treatment of dairy wastewater pretreated by coagulation or electro-coagulation using the adsorption process, around 80% TOC removal was achieved at the adsorption stage (Al-Qodah et al., 2024; 2025).

When the literature is examined, it is evident that there are very few studies on the treatment of wastewater generated by industries producing organic peroxides (Yan et al., 2024a; 2024b; Dinçer et al., 2021). The treatment of organic peroxide wastewater using the ozone oxidation process with a CeO_2-C catalyst has been investigated, yielding 28.1% COD removal, while oxidation with iron-carbon microelectrolysis resulted in 35.7% COD removal (Yan et al., 2024a; 2024b). In our previous study on organic peroxide wastewater, 83.3% COD and 71.1% TOC removal were achieved using nanofiltration after Fenton oxidation (Dinçer et al., 2021). The chemical industry generates quite complex wastewater due to the diversity of chemicals produced. Studies on the treatment of chemical wastewater from which organic peroxides are produced are also quite limited. This study, unlike the aforementioned study, examined the Fenton oxidation and adsorption treatment processes applied to wastewater subjected to biological treatment at an organic peroxide production facility. Thus, the treatment performance of chemical wastewater from which organic peroxides are produced using both processes was evaluated and compared.

The aim of this study is to research the advanced treatability of biologically treated chemical industry wastewater producing organic peroxides using Fenton and adsorption processes. The study examines the effects of Fe^{2+} and H_2O_2 concentrations, pH, and oxidation time in Fenton oxidation, and determines the kinetics of the process. In the adsorption process, adsorption was performed using coconut-based and coal-based activated carbons, and the effects of pH, adsorbent dose, and adsorption time were investigated. Adsorption isotherms and kinetics were also determined. Finally, a cost analysis was conducted for both processes and compared. The novelty of this study lies in the fact that the wastewater used was sourced from the chemical industry where organic peroxides are produced, and there is a lack of sufficient research on the treatment of such wastewater.

2.Material and Method

2.1Biologically treated chemical industrial wastewater characterization

The chemical industry wastewater, which contains various chemicals with organically bound peroxides, is located in the Muratlı/Tekirdağ region. Wastewater produced in the chemical industry is first treated with aerobic biological treatment after coagulation, and then it is sent to the Muratlı Organized Industrial Zone wastewater treatment plant after final sedimentation. This study investigates the advanced treatment of biologically treated chemical industry wastewater. The properties of the biologically treated wastewater are presented in Table 1. The COD and TOC concentrations of the wastewater are 4680 and 1022 mg/L, and it contains 0.22% H_2O_2 and 10,640 mg/L SO_4^{2-}, respectively.

Table 1. Characterization of biological treated chemical industry wastewater producing organic peroxide

Parameter	Unit	Value
pH	-	7.41
Conductivity	mS/cm	11.91±0.17
Turbidity	NTU	30.3±0.5
COD	mg/L	4680±17
TOC	mg/L	1022±12
H_2O_2	%	0.22±0.01
SO_4^{2-}	mg/L	10640±249

2.2 Fenton oxidation experiments

Fenton oxidation studies were carried out by placing 200 mL of wastewater in a 600 mL beaker and mixing at 45 rpm for 1 h using Jar Test. After adding Fe^{2+} (as $FeSO_4.7H_2O$, CAS: 7782-63-0) to 200 mL of biologically treated chemical wastewater, the pH was adjusted to 3 with a pH meter using H_2SO_4 (CAS: 7664-93-6). H_2O_2 (30%, CAS: 7722-84-1) was added to the wastewater and oxidation was carried out for 1 h. At the end of oxidation, the pH value of the wastewater was adjusted to the range of 7.5-8.0 with 6 N NaOH (CAS: 1310-73-2) using a pH meter, and precipitation was allowed to occur for 30 min. Samples were taken from the clear upper wastewater and the necessary analyses were carried out.

In Fenton studies, by performing wastewater treatment at 8 different H_2O_2 concentrations up to 22.5 g/L at 2.0 g/L Fe^{2+} concentration to determine the required H_2O_2 concentration for wastewater treatment. Then, by performing wastewater treatment at 8 different Fe^{2+} concentrations up to 2.25 g/L at 17.5 g/L H_2O_2 concentration to determine the required Fe^{2+} concentration for wastewater treatment. In addition, by performing wastewater treatment at 5 different pH values between pH 2 and 4 at 2 g/L Fe^{2+} and 17.5 g/L H_2O_2, the optimum pH value for wastewater treatment was determined. Finally, oxidation kinetics were calculated by wastewater treatment at different oxidation times up to 2.0 h at 2 g/L Fe^{2+} and 17.5 g/L H_2O_2 concentration at pH 3.

2.3 Adsorption experiments

Coconut based activated carbon (Coconut-AC) and coal based activated carbon (Coal-AC) were used in the adsorption studies. The properties of these activated carbons were detailed in a previous study (Enfiyeci and Çifçi, 2025). Adsorption studies were conducted by placing 100 mL of wastewater in a 250 mL conical flask and shaking at 150 rpm. After adding activated carbon to the wastewater, the pH was adjusted using a pH meter with H_2SO_4 and NaOH. After adsorption was performed on the wastewater shaker at 150 rpm, the activated carbon was separated by centrifugation (4000 rpm for 5 min). In the adsorption studies, adsorption was carried out at pH values of 3, 5, 7, 9, and 11, using a dose of 25 g/L of Coconut-AC or Coal-AC, and the pH value that provided the best wastewater treatment was determined. Then, the activated carbon dose that provided the best wastewater treatment was determined by adsorbing at different activated carbon doses (5, 10, 15, 20, 25, 30, and 35 g/L) at pH 3. Finally, adsorption kinetics and the adsorption isotherm were determined.

2.4 Analysis methods

COD analyses were carried out according to the closed reflux-titrimetric method given in the standard method on APHA5220C. TOC, organic peroxide and SO_4^{2-} analyses were carried out in AKPA Chemical R&D laboratory.

3. Results and Discussions

3.1 Fenton oxidation process

3.1.1 Effect of H_2O_2 concentrations

In the wastewater treatment study carried out with only a 2 g/L Fe^{2+} concentration (without adding H_2O_2), 9.7% COD and 25.3% TOC removal were achieved (Fig. 1). While COD and TOC removal increased to 60.0% and 66.3% with a 5 g/L H_2O_2, an increase in COD and TOC removal was observed up to a 17.5 g/L H_2O_2 concentration. The highest COD and TOC removals were obtained at 81.6% and 80.6% at 17.5 g/L H_2O_2, and COD and TOC removal decreased to 79.5% and 71.1% at 20 g/L H_2O_2, respectively. COD removal decreased from 4680 to 1039 mg/L, while TOC removal decreased from 1022 to 260 mg/L at 2 g/L Fe^{2+} and 17.5 g/L H_2O_2. H_2O_2 reacts with HO• and acts as a scavenger of HO• radicals, producing hydroperoxyl radicals (HO_2•) at excessive H_2O_2 concentrations (Machado et al., 2023). Although HO• radicals are also reactive against organic pollutants, they have less oxidizing power and slower kinetics than HO• radicals, thus slowing down wastewater treatment (Babuponnusami et al., 2014; Machado et al., 2023). Organic peroxide in the wastewater decreased by 50.0% in the wastewater treatment study with only a 2 g/L Fe^{2+} concentration (without adding H_2O_2), while it increased to 77.3% in Fenton oxidation with a 17.5 g/L H_2O_2. Despite the increase in H_2O_2 concentration in Fenton oxidation, similar organic peroxide removal can be achieved. This is due to the use of H_2O_2 added by Fenton oxidation in the production of hydroxyl radicals (Dinçer and Çifçi, 2021). While the SO_4^{2-} concentration in the wastewater was 10,640 mg/L, it increased to 12,564 mg/L in the wastewater treatment study with only a 2 g/L Fe^{2+} concentration (without adding H_2O_2). This is due to the H_2SO_4 used to adjust the pH value to 3 after Fe^{2+} was added to the wastewater.

However, no significant change was observed in SO_4^{2-} concentration at different H_2O_2 concentrations in Fenton oxidation.

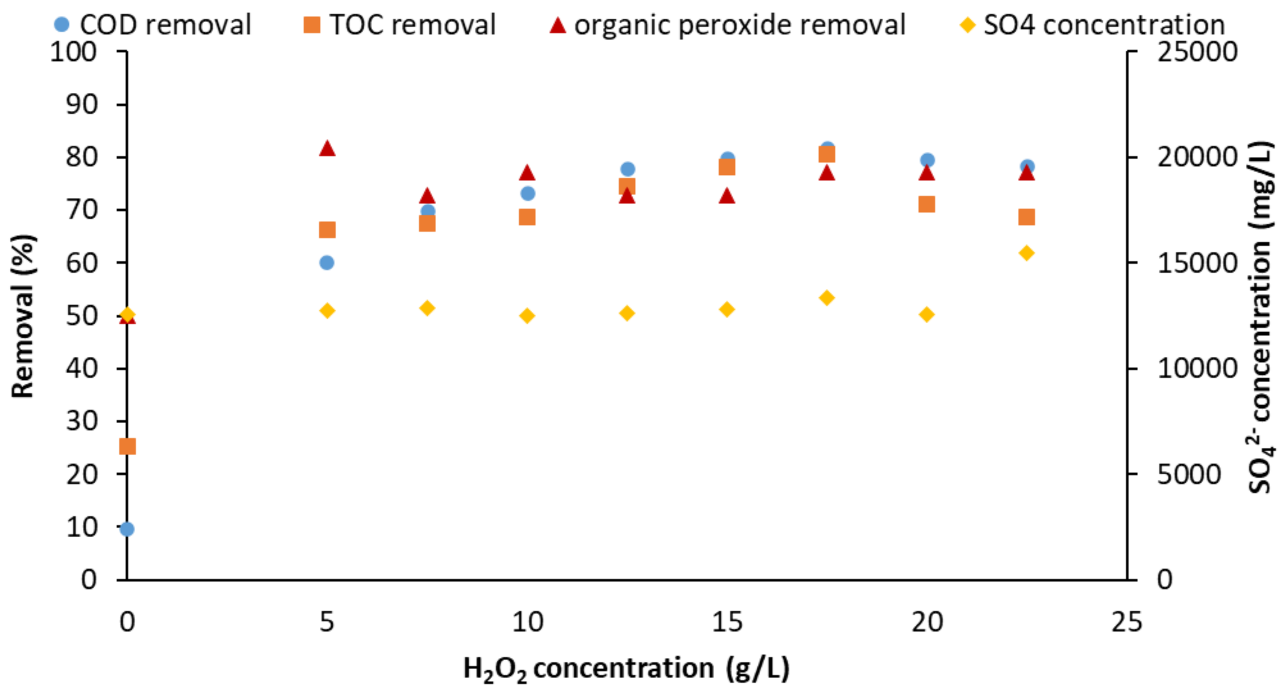


Figure 1. COD, TOC and organic peroxide removal efficiency at different H_2O_2 concentration (Fe^{2+}: 2.0 g/L, t: 60 min, pH: 3)

3.1.2 Effect of Fe^{2+} concentrations

COD removal increased from 54.0% to 79.4% as the Fe^{2+} concentration increased from 0.5 to 1.5 g/L, and reached 81.6% at a 2 g/L Fe^{2+} (Fig. 2). COD concentrations at 0.5, 1.5, and 2.0 g/L Fe^{2+} concentrations were 2152, 963, and 863 mg/L, respectively. As a similiar trend to COD, TOC removal observed as 50.0%, 72.2%, and 80.6% at 0.5, 1.5, and 2 g/L Fe^{2+}concentrations, respectively. A decrease in COD and TOC removal was observed at a 2.25 g/L Fe^{2+} concentration. Since there is not enough H_2O_2 in the presence of excess iron ions, it does not increase the production of hydroxyl radicals. On the contrary, it causes an increase in the amount of iron sludge, the total dissolved solids in the treated wastewater, and the scavenger effect (Babuponnusami et al., 2014; Ribeiro et al., 2021). While organic peroxide removal increased to 86.4% at a Fe^{2+} concentration of 0.5 g/L, increasing Fe^{2+} concentrations above 0.5 g/L did not provide a significant change in organic peroxide removal. The SO_4^{2-} concentration increased compared to the inlet wastewater, reaching values of up to 14,140 mg/L. This is due to the increase in the H_2SO_4 concentration used to adjust the pH to 3 with the increase in Fe^{2+} addition.

In the treatment of biologically treated chemical industry wastewater producing organic peroxides by Fenton oxidation, the optimum conditions were found to be pH 3, 2.0 g/L Fe^{2+}, and 17.5 g/L H_2O_2 and the H_2O_2/Fe^{2+} molar ratio was 14.4. Under these conditions, 81.6% COD and 80.6% TOC removal were achieved after 1 h of oxidation. In our previous study with industrial wastewater containing organic peroxide, the H_2O_2/Fe^{2+} molar ratio was found to be 32.8 (Dinçer et al., 2021). It is observed that in the case of Fenton oxidation applied after the biological treatment of chemical wastewater containing organic peroxides, the H_2O_2/Fe^{2+} ratio decreases. In the Fenton oxidation of industrial container and drum cleaning wastewater, the H_2O_2/Fe^{2+} molar ratio was found to be 32.9, 19.2, and 13.2 in three wastewater samples, and 91%, 97%, and 95% COD removal achieved (Güneş et al., 2018). In the Fenton oxidation of textile wastewater, the optimum H_2O_2/Fe^{2+} ratio was found to be 19.6, and 74% COD removal achieved (GilPavas et al., 2017). In the Fenton oxidation of water-based paint wastewater, the H_2O_2/Fe^{2+} ratio was found to be 10.0, and 81% COD removal achieved (Mamadiev et al., 2011).

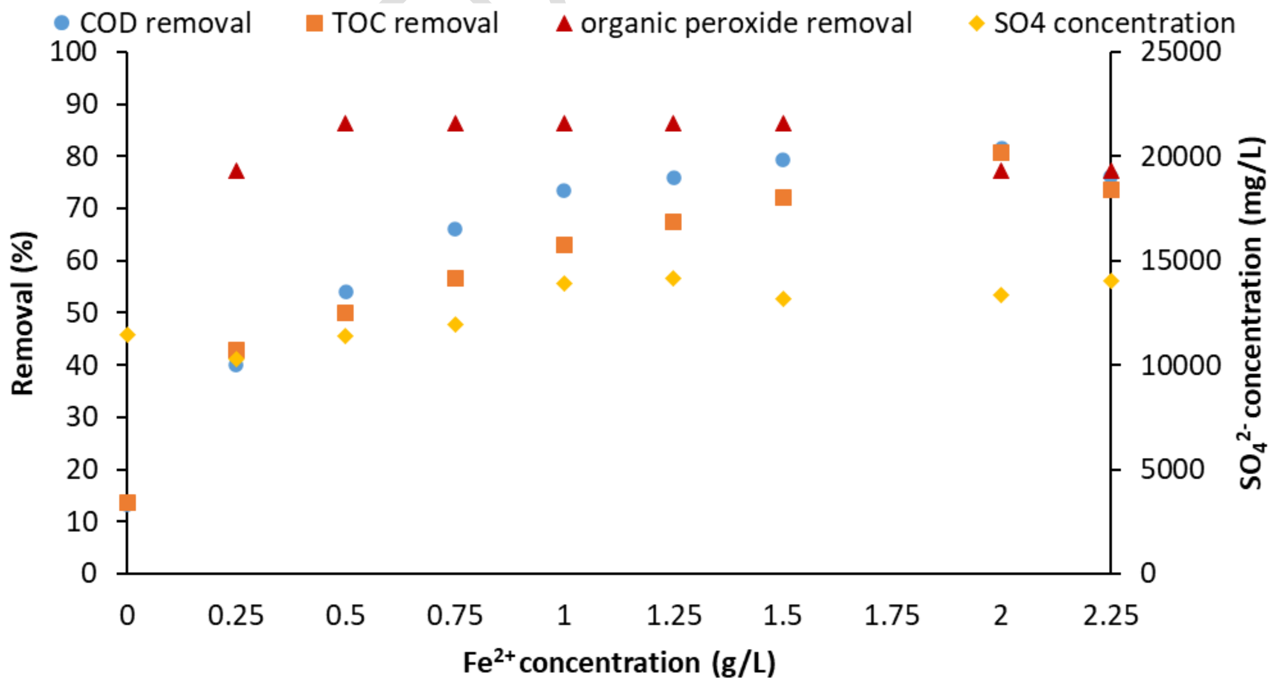


Figure 2. COD, TOC and organic peroxide removal efficiency at different Fe^{2+} concentration (H_2O_2: 17.5 g/L, t: 60 min, pH: 3)

3.1.3 Effect of pH

COD and TOC removals were 69.8% and 67.9% at pH 2 and both of them increased to 81.6% and 80.6%, as the pH value increased to 3, respectively (Fig. 3). COD and TOC removals decreased above pH 3.5. COD and TOC removals were 69.9% and 69.2% at pH 4. Similar removal was observed at all pH values for organic peroxide removal. However, the SO_4^{2-} concentration increased to 18,238 mg/L at pH 2 and 14,107 mg/L at pH 2.5 due to the use of H_2SO_4 for pH adjustment.

In previous studies, the optimum pH value was determined to be 3 for the treatment of various wastewaters, such as textile, mixed industrial wastewater, pulp and paper wastewater, leather dyeing, and coking wastewater by Fenton oxidation (Enfiyeci and Çifçi, 2025; Çalık and Çifçi, 2022; Gholami et al., 2022; GilPavas et al., 2017; Gómez et al., 2023; Metin and Çifçi, 2023; Verma et al., 2020). When the pH value was below 3, stable or unreactive species such as oxonium ions (H_3O^+) and iron complexes such as $[Fe(H_2O)_6]^{2+}$ are formed, which cause slower reactions (Gómez et al., 2023; Patil et al., 2023; Verma et al., 2020). Iron begins to precipitate and •OH consumption occurs during this reaction at high pH values (Gómez et al., 2023; Patil et al., 2023; Verma et al., 2020).

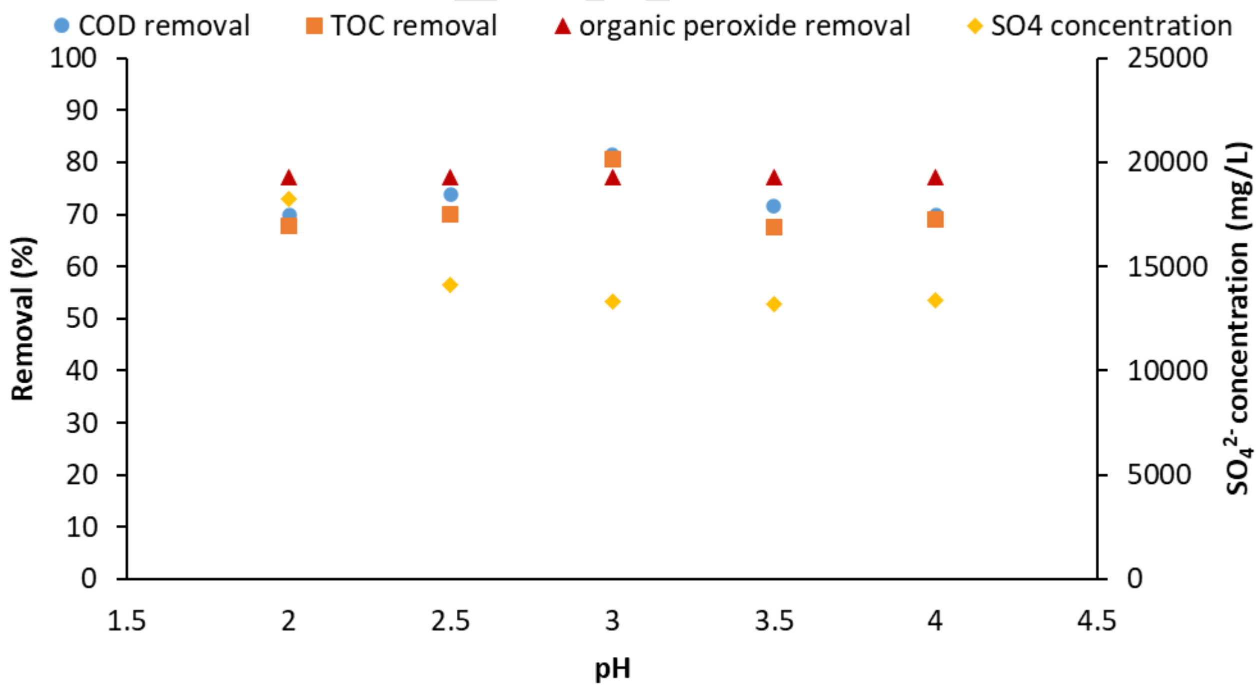


Figure 3. COD, TOC and organic peroxide removal efficiency at different pH value (Fe^{2+} concentration: 2 g/L, H_2O_2: 17.5 g/L, t: 60 min)

3.1.4 Effect of oxidation time

COD, TOC, organic peroxide removal efficiencies obtained at pH 3, 2 g/L Fe^{2+} and 17.5 g/L H_2O_2 concentrations at different oxidation times are given in Fig. 4. While COD and TOC removal in wastewater continued during 1 h of oxidation, no significant change was observed in wastewater treatment between 1 and 2 h. COD removal was 52.3%, 69.3% and 81.6% and TOC removal was 52.3%, 63.9% and 80.6% at 0.25, 0.5 and 1 h oxidation times, respectively.

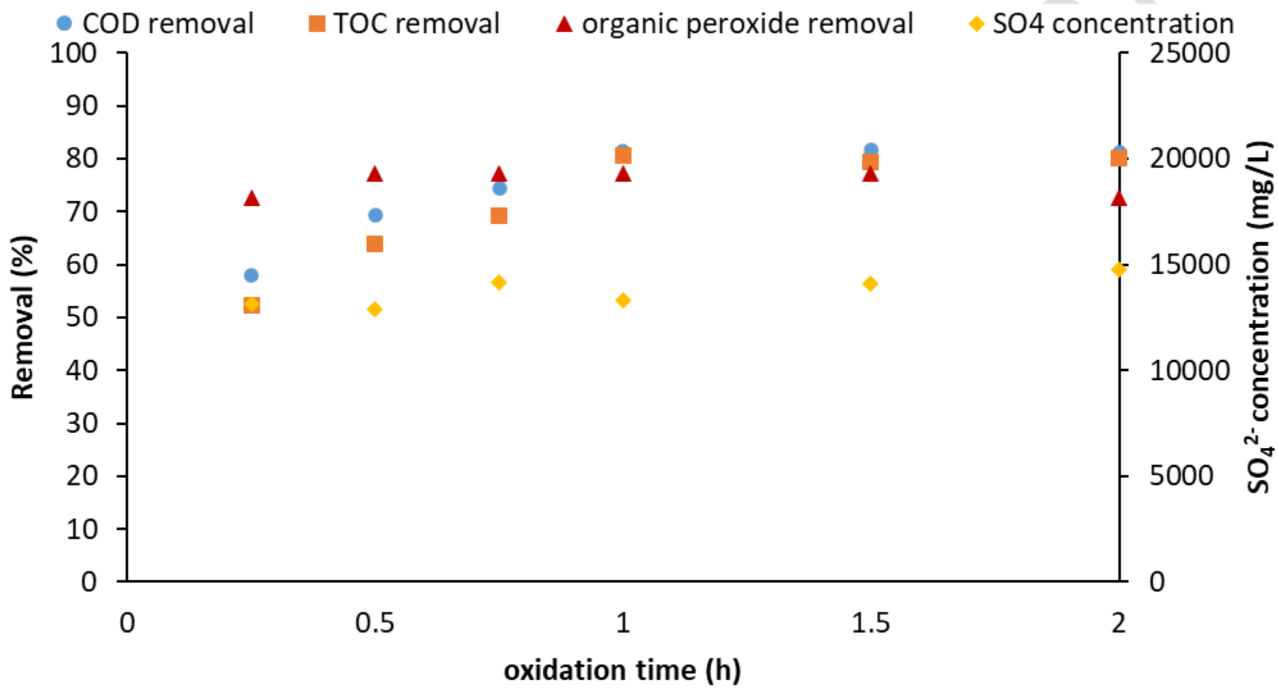


Figure 4. COD, TOC and organic peroxide removal efficiency at different pH value (Fe^{2+} concentration: 2 g/L, H_2O_2: 17.5 g/L, pH: 3)

COD and TOC concentrations and kinetic parameters obtained in the treatment of biologically treated chemical wastewater at pH 3, 2 g/L Fe^{2+} and 17.5 g/L H_2O_2 for different oxidation time were determined and the parameters are given in Table 2. 1st order and 2nd order kinetic models were calculated with the formulas given below (Gholami et al., 2022).

$$ln\frac{C}{C_0} = -k_1 t \qquad (1)$$

$$\frac{1}{C_0} - \frac{1}{C} = -k_2 t \qquad (2)$$

Here C_0 represents the initial COD or TOC concentration (mg/L), C represents the COD or TOC concentration at time t. t represents the oxidation time in hours. k_1 (h^{-1}) and k_2 ($(mg/L)^{-1} \cdot h^{-1}$) are the first and second order kinetic constants. As seen in Table 2, in the treatment of chemical industry wastewater producing organic peroxides by Fenton oxidation after biological treatment, COD and TOC removal in the Fenton oxidation process is more suitable for the 2nd order kinetic model.

Table 2. Kinetic parameters obtained from the Fenton oxidation

Parameter	**k_1 (h^{-1})**	**R^2**	**k_2 ($(mg/L)^{-1}h^{-1}$)**	**R^2**
COD	1.8765	0.9628	0.0009	0.9935
TOC	1.7165	0.9753	0.0037	0.9811

3.2 Adsorption process

3.2.1 Effect of pH

The highest removals of COD (72.4%), TOC (84.2%), and organic peroxide (86.4%) were achieved at pH 3, while a decrease in removal efficiencies was observed with increasing pH in adsorption studies using Coconut-AC (Fig. 5). COD removal was 53.5% and 50.1%, while TOC removal was 71.2% and 48.6% using Coconut-AC at pH 7 and pH 11, respectively. The highest removals of COD (56.9%), TOC (79.8%), and organic peroxide (60.9%) were obtained at pH 3 in adsorption studies using Coal-AC. COD removal was 34.4% and 32.8%, and TOC removal decreased to 35.4% and 20.7% using Coal-AC at pH 7 and pH 11, respectively.

Since hydroxyl ions are abundant in basic conditions, competition occurs between OH^- and negatively charged organic matter (Enfiyeci and Çifçi, 2025; Meng et al., 2018). In adsorption studies with activated carbon, the highest removal of cork wastewater was observed at pH 3.5, mineral processing wastewater at pH 2, and mixed (textile and chemical industry) industrial wastewater at pH 3 (Ge et al., 2018; Meng et al., 2018).

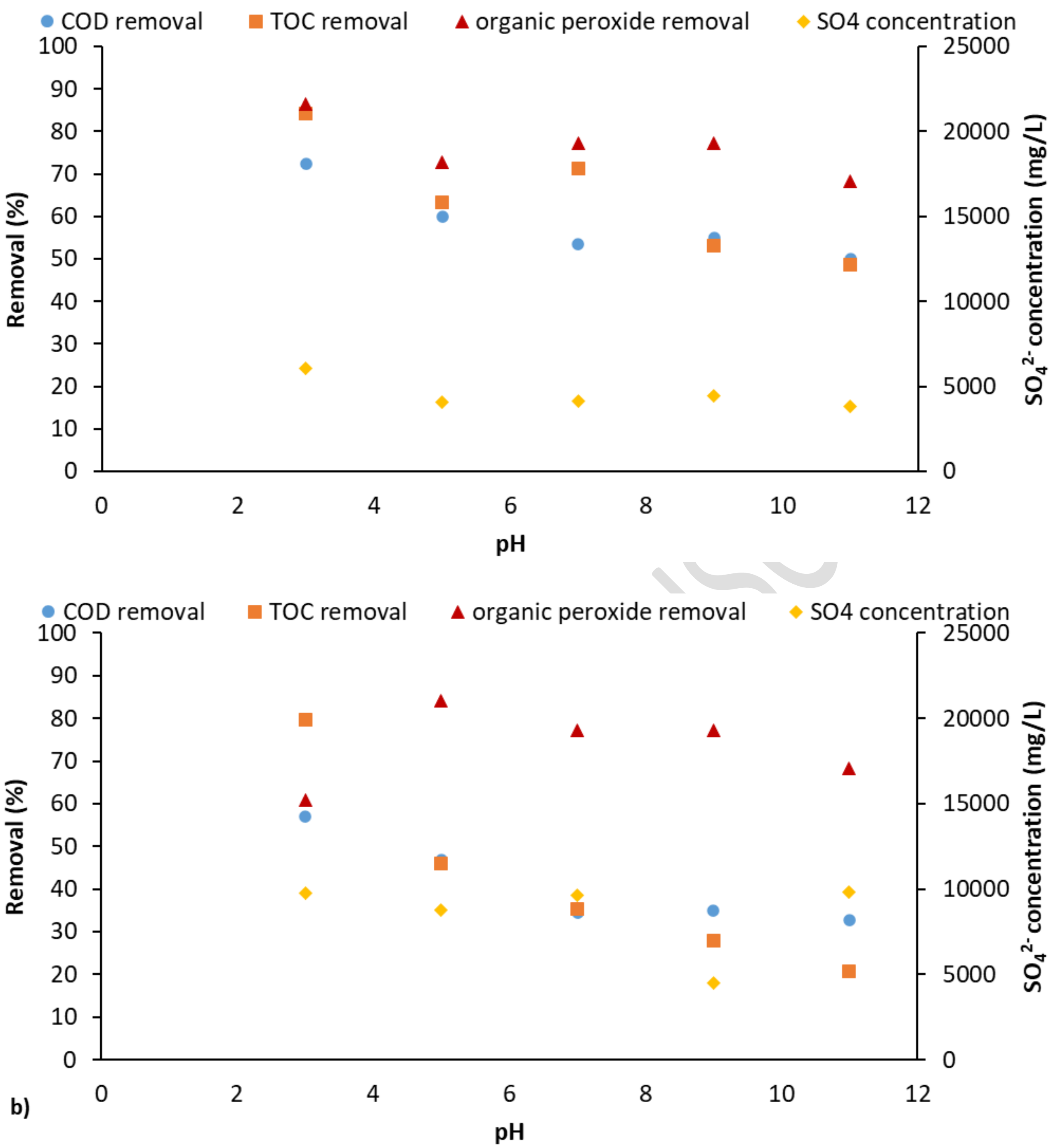


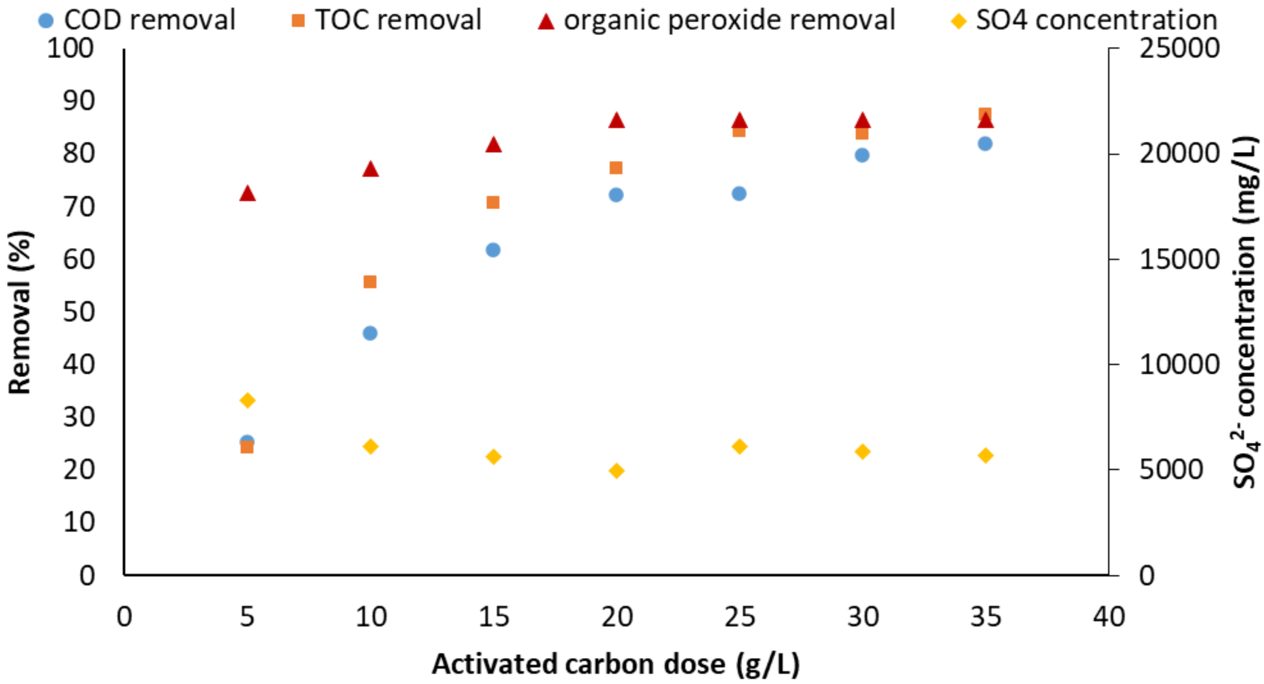
Figure 5. COD, TOC and organic peroxide removal at different pH value a) for Coconut-AC, b) for Coal-AC (Coconut-AC or Coal-AC: 25 g/L, t: 1 h)

3.2.2 Effect of Coconut-AC or Coal-AC dose

As the Coconut-AC dose increased from 5 to 30 g/L, a decrease in COD and TOC removal was observed, while no significant change was seen at the 35 g/L dose (Fig. 6). COD removal was 25.3%, 79.8%, and 81.9%, and TOC removal was 24.2%, 83.9%, and 87.3% at 5, 30, and 35 g/L Coconut-AC, respectively. The SO_4^{2-} concentration was 8335 mg/L at 5 g/L Coconut-AC, and it decreased by

21.7%. The SO_4^{2-} concentration was 5901 mg/L, representing a 44.5% decrease at 30 g/L Coconut-AC. Organic peroxide removal increased to 86.4% with increasing Cocounut-AC dose up to 20 g/L, while no significant change was observed in organic peroxide removal after 20 g/L dose.

Similarly, in adsorption studies with Coal-AC, COD and TOC removal increased as the activated carbon dose increased from 5 to 30 g/L, with no significant change in removals observed at 35 g/L. COD and TOC removal were 20.1% and 15.6% at the 5 g/L Coal-AC dose, and 72.5% and 84.4% at the 30 g/L Coal-AC dose, respectively. COD and TOC removal reached 73.5% and 83.3% at the 35 g/L Coal-AC dose, respectively. The SO_4^{2-} concentration was 9335 mg/L, and a decrease of 12.3% was observed. The highest organic peroxide removal, 68.2%, was achieved at the 20 g/L Coal-AC dose, and increasing the Coal-AC dose beyond 20 g/L did not result in any further improvement in organic peroxide removal.



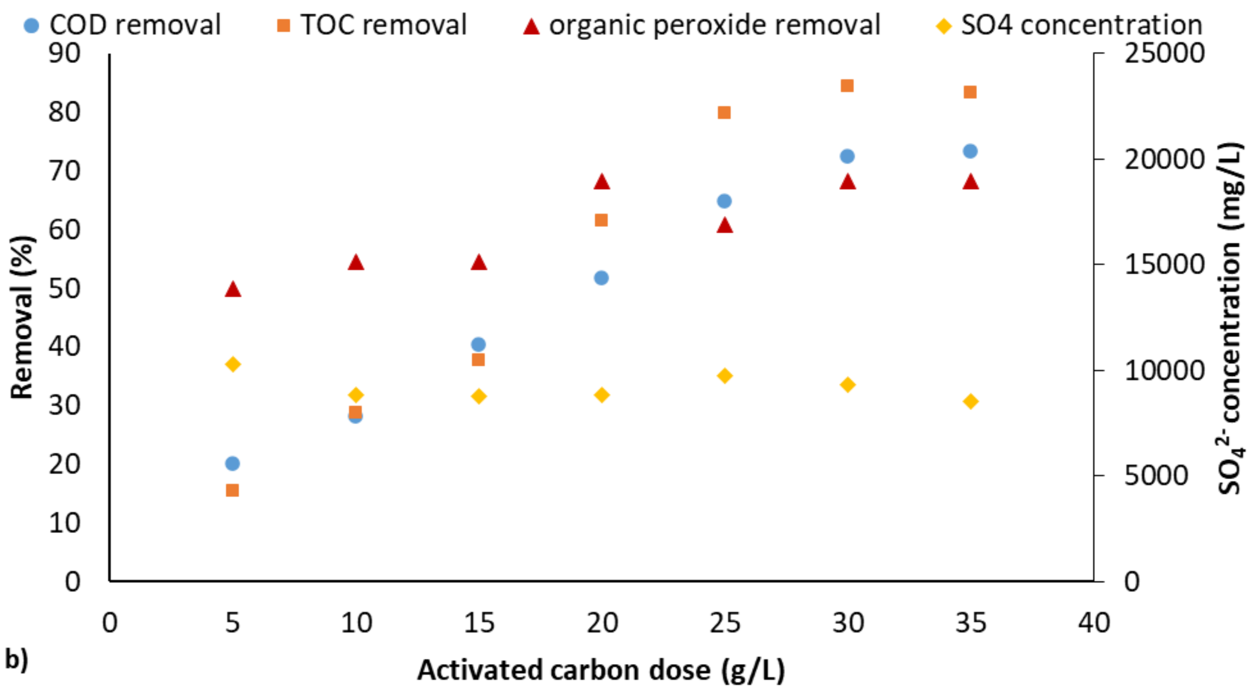


Figure 6. COD, TOC and organic peroxide removal at different activated carbon dose a) Coconut-AC, b) Coal-AC (pH: 3, t: 1 h)

3.2.3 Effect of adsorption time and adsorption kinetic models

COD removal with Coconut-AC was 72.3%, 76.6%, and 88.8% at the end of 1, 5, and 24 h of adsorption, while TOC removal was 84.2%, 84.4%, and 89.4%, respectively (Fig. 7). COD removal with Coal-AC was 51.8%, 61.7%, and 75.2% at 1, 5, and 24 h of adsorption, while TOC removal was 79.8%, 81.0%, and 83.1%. It was observed that COD and TOC removal in wastewater occurred rapidly within the first hour of adsorption with both activated carbons, after which the treatment rate slowed down.

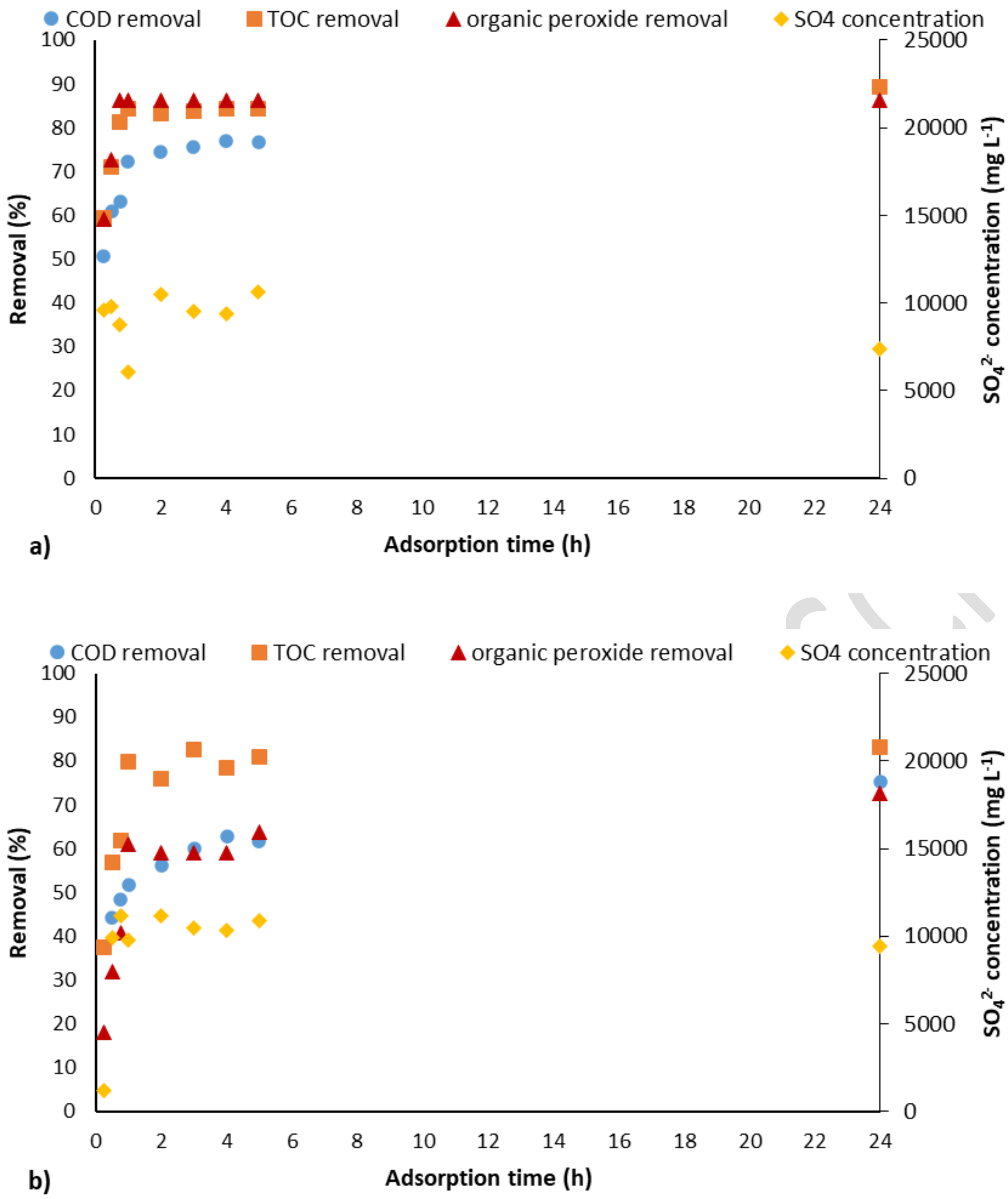


Figure 7. COD, TOC and organic peroxide removal at different adsorption time a) Coconut-AC, b) Coal-AC (pH: 3, Coconut-AC or Coal-AC: 20 g/L)

Using the COD and TOC concentrations obtained at different adsorption times, pseudo 1st order and pseudo 2nd order kinetic models were applied according to the formulas found in the literature (Wang and Guo, 2020). It was found that the pseudo 2nd order kinetic model better describes the adsorption process for both activated carbons (Table 3). This suggests that the rate-limiting step in the adsorption of biologically treated chemical industry wastewater from organic peroxide production with Coconut-AC and Coal-AC is surface adsorption, including chemical adsorption (El-Naas et al., 2010).

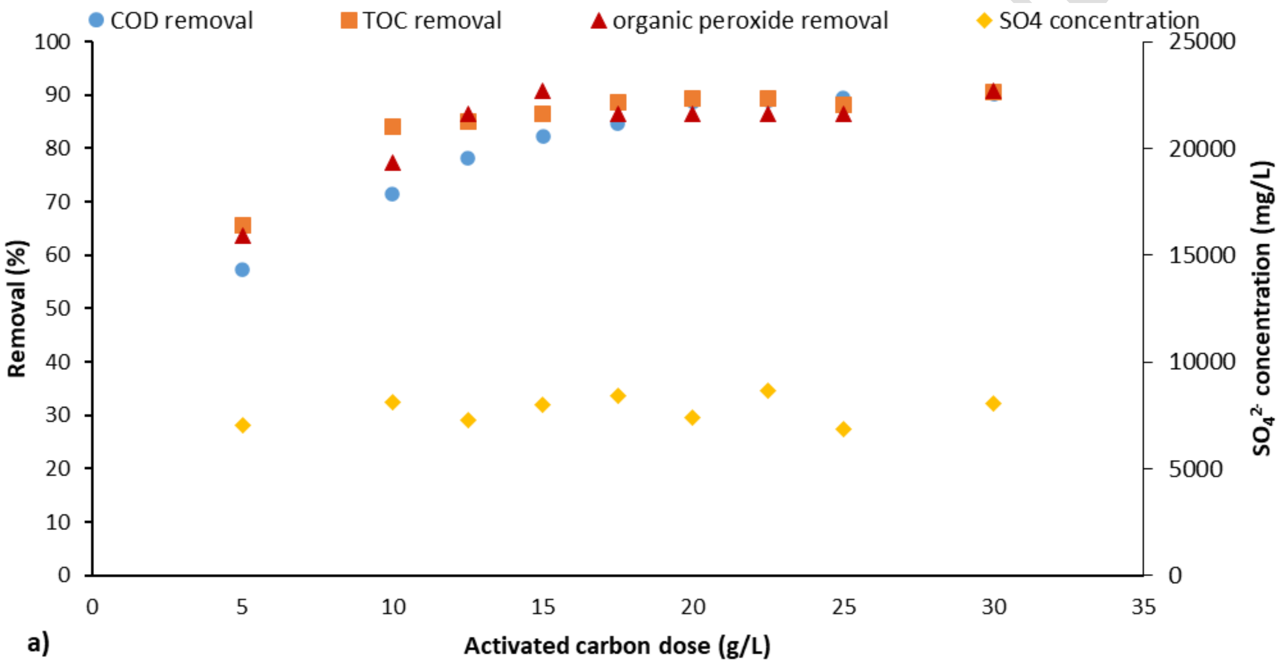
Additionally, adsorption studies on dairy wastewater, biologically treated papermaking wastewater, and refinery wastewater with activated carbon have also shown a better fit for the pseudo 2nd order kinetic model (El-Naas et al., 2010; Feng et al., 2020; Kushwaha et al., 2010). The q_e values calculated according to the pseudo 2nd order kinetic model were 208.3 mg/g for COD and 45.9 mg/g for TOC with Coconut-AC, and 151.5 mg/g for COD and 43.3 mg/g for TOC with Coal-AC.

Table 3. Adsorption kinetic model constants using Coconut-AC and Coal-AC

Pollutants		**Pseudo 1st order kinetic**			**Pseudo 2nd order kinetic**		
			Coconut-AC				
	q_e (measured) (mg/g)	**k_1 (h^{-1})**	**q_e (calculated) (mg/g)**	**R^2**	**k_2 ((g/mg) h^{-1})**	**q_e (calculated) (mg/g)**	**R^2**
COD	207.71	0.2949	85.37	0.6198	11.52	208.33	0.9991
TOC	45.71	0.3965	11.36	0.4874	132.01	45.87	0.9999
			Coal-AC				
	q_e (measured)	**k_1**	**q_e**	**R^2**	**k_2**	**q_e**	**R^2**
COD	176.00	0.2753	93.05	0.7441	26.41	151.52	0.9992
TOC	42.46	0.6868	15.51	0.5742	102.62	43.29	0.9968

3.2.4 Adsorption isotherm models

Adsorption isotherms are important to determine the equilibrium distribution and interaction between the pollutants and the adsorbent in wastewater (Al-Qodah et al., 2023). To establish the Langmuir and Freundlich adsorption isotherm models, adsorption was carried out with different doses of Coconut-AC or Coal-AC for 24 h, and the obtained COD, TOC, and organic peroxide removal efficiencies are shown in Figure 8. COD and TOC removal increased up to a 20 g/L activated carbon dose, and no significant change observed at 20 and 30 g/L doses using Coconut-AC. COD removal was 57.2%, 71.6%, 88.8%, and 90.2% and TOC removal was 65.6%, 84.0%, 89.4%, and 90.5% at 5, 10, 20, and 30 g/L Coconut-AC doses, respectively. COD and TOC removal increased up to a 22.5 g/L activated carbon dose using Coal-AC. COD removal was 42.2%, 50.6%, 78.4%, and 79.0 and TOC removal was 45.0%, 67.9%, 85.8%, and 86.7% % at 5, 10, 22.5, and 30 g/L Coal-AC doses. Adsorption isotherms were constructed using the results from 24 h adsorption at various activated carbon doses.



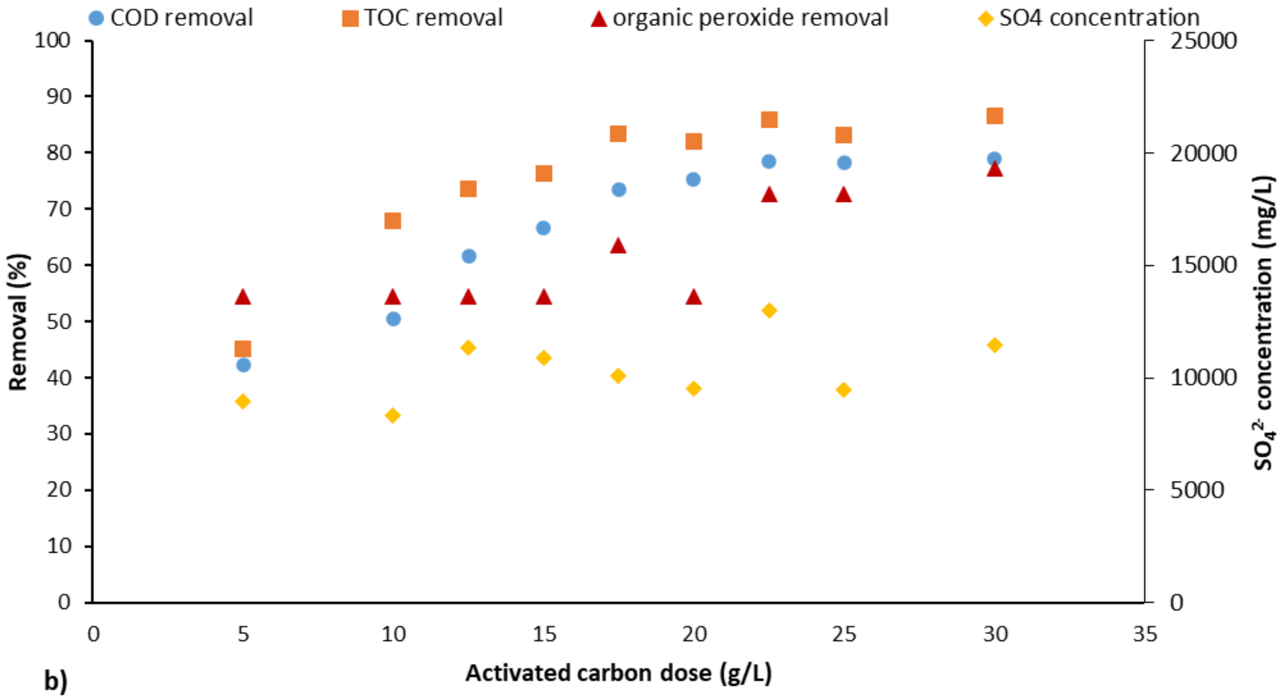


Figure 8. COD, TOC and organic peroxide removal at different activated carbon dose a) Coconut-AC, b) Coal-AC (pH: 3, t: 24 h)

Langmuir and Freundlich adsorption isotherms were calculated according to the literature (Adedeji et al., 2023). When comparing the Langmuir and Freundlich isotherm models, it was found that the adsorption of biologically treated chemical industry wastewater produced with organic peroxide was more suitable for the Freundlich isotherm model with both Coconut-AC and Coal-AC (Table 4). This indicates that COD and TOC adsorption occurs on heterogeneous surfaces in both Coconut-AC and Coal-AC adsorption (Adedeji et al., 2023).

In the Freundlich isotherm, when 1/n is less than 1, it indicates that the adsorption is favorable (Boubaker and Ridha, 2021). It has been observed that the adsorption of paper industry wastewater with activated carbon and the adsorption of biologically treated papermaking wastewater with magnetic activated carbon are also more suitable for the Freundlich isotherm model (Boubaker and Ridha, 2021; Feng et al., 2020).

Table 4. Adsorption isotherm model constants using Coconut-AC and Coal-AC

Pollutants	Langmuir isotherm	Freundlich isotherm
	Coconut-AC	

	q_{max} (mg/g)	K_L (L/mg)	R^2	1/n	K_F ((mg/g)(L/g)^n)	R^2
COD	1428.6	0.0003	0.6119	0.775	1.393	0.9561
TOC	1250	0.0003	0.0155	1.102	0.241	0.8523
Coal-AC						
	q_{max}	K_L	R^2	1/n	K_F	R^2
COD	1250	0.0001	0.2018	0.824	0.495	0.8596
TOC	232.6	0.0012	0.5983	0.750	0.850	0.8950

3.3 Cost analysis

The treatment performances and cost analyses of chemical industry wastewater using Fenton oxidation and adsorption processes are provided in Table 5. For the cost analysis, the values given in the literature for the costs of $FeSO_4$ (\$0.47 kg^{-1}) and H_2O_2 (\$0.64 kg^{-1}) used in Fenton oxidation, as well as activated carbon (\$0.45 kg^{-1}) used in the adsorption process (Metin and Çifçi, 2023; Mukherjee et al., 2022; Sayın et al., 2022). The current electricity cost in Turkey is \$0.127 per kWh (Enfiyeci and Çifçi, 2025).

In Fenton oxidation, COD decreased from 4680 to 863 mg/L at pH 3, with 2 g/L Fe^{2+} and 17.5 g/L H_2O_2 concentrations, resulting in an 81.6% COD removal. The treatment cost was \$15.77 m^{-3}, with the cost per kg of COD removed calculated at \$4.13.

In the adsorption using Coconut-AC, 81.9% COD removal was achieved after 1 h of adsorption at pH 3 and a 35 g/L Coconut-AC dose. The treatment cost was \$15.87 m^{-3}, with the cost per kg of COD removed being \$4.14. When 20 g/L Coconut-AC was used at pH 3 for 24 h of adsorption, COD removal increased to 88.8%, and the cost decreased to \$11.90 m^{-3}, with the cost per kg of COD removed dropping to \$2.86.

The lowest COD removal and highest cost were observed in the adsorption using Coal-AC. In the adsorption with Coal-AC, 73.5% of COD removal was achieved after 1 h of adsorption at pH 3 with a 35 g/L Coal-AC dose, resulting in a treatment cost of \$15.87 m^{-3}, with the cost per kg of COD removed being \$4.61. COD removal reached 75.2% at pH 3, 20 g/L Coal-AC dose and 24 h of adsorption, and the cost decreased to \$11.90 m^{-3}, with the cost per kg of COD removed at \$3.38.

Table 5. Cost analysis of biologically treated chemical industry wastewater producing organic peroxides using Fenton and adsorption process

COD			**Cost**	**Cost per kg COD**
Inlet (mg/L)	**Outlet (mg/L)**	**Removal (%)**	**($/m³)**	**removed ($)**
Fenton (pH: 3, Fe^{2+}: 2 g/L, H_2O_2: 17.5 g/L, t: 1 h)				
4680	863	81.6	15.77	4.13
Adsorption (Coconut-AC) (pH: 3, Coconut-AC: 35 g/L, t: 1 h)				
4680	846	81.9	15.87	4.14
Adsorption (Coconut-AC) (pH: 3, Coconut-AC: 20 g/L, t: 24 h)				
4680	526	88.8	11.90	2.86
Adsorption (Coal-AC) (pH: 3, Coal-AC: 35 g/L, t: 1 h)				
4680	1241	73.5	15.87	4.61
Adsorption (Coal-AC) (pH: 3, Coal-AC: 20 g/L, t: 24 h)				
4680	1160	75.2	11.90	3.38

4. Conclusions

In this study, the treatment of biologically treated chemical industry wastewater producing organic peroxides was investigated using Fenton oxidation and adsorption processes. The optimal conditions for Fenton oxidation was obtained at pH 3, with 2 g/L Fe^{2+} and 17.5 g/L H_2O_2 for 1 h of treatment and COD, TOC, and organic peroxide removals were obtained as 81.6%, 80.6%, and 77.3%, respectively. The COD and TOC removal by Fenton oxidation was found to be more suitable for pseudo 2nd order kinetics.

In the adsorption process, 88.8% COD, 88.9% TOC, and 86.4% organic peroxide removal were achieved at pH 3 and 20 g/L activated carbon dose after 24 h using Coconut-AC. In these conditions, 75.2% COD, 81.9% TOC, and 54.5% organic peroxide removal were observed using Coal-AC. The adsorption kinetics for both Coconut-AC and Coal-AC more suitable for the pseudo 2nd order kinetic model, while the adsorption isotherms were more fitting for the Freundlich model.

The cost was \$15.77 m^{-3} in Fenton oxidation under optimal conditions, compared to \$15.87 m^{-3} for the adsorption process with either Coconut-AC or Coal-AC. The cost per kg of COD removed was calculated as \$4.13 in Fenton oxidation, while it was \$2.86 using Coconut-AC and \$3.38 using Coal-AC.

In conclusion, although the cost per m^3 of wastewater treated was similar for all methods, the adsorption process using Coconut-AC provided superior treatment performance compared to Fenton oxidation and Coal-AC. Moreover, the lowest cost per kg of COD removed was achieved with Coconut-AC, and SO_4^{2-} removal was also observed during its adsorption process. The SO_4^{2} concentration (10640 mg/L) in wastewater generated in the chemical industry, where organic peroxides are produced, is high. Therefore, it is important to ensure SO_4^{2-} removal in addition to organic matter removal. While SO_4^{2-} removal cannot be achieved in the Fenton oxidation process, the use of coconut-AC in the adsorption process would be advantageous in this process. Future studies should focus on optimizing the regeneration and reuse of activated carbons to increase economic and environmental sustainability. Additionally, combining Fenton oxidation with adsorption in a hybrid treatment system could be investigated to further improve organic and sulfate removal efficiencies.

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Data Availability Statement

Data are available upon request.

Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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