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Organic material removal from bilge water by chemical treatment processes

Kimyasal arıtım yöntemleriyle sintine suyundan organik madde giderimi

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Abstract

Uncontrolled discharged of bilge water from sea vessels is one of the major pollutants for marine ecosystem due to its high amount petroleum and oil content. In this research, organic material removal from bilge water by using coagulation - flocculation and Fenton oxidation was investigated. In coagulation-flocculation experiments, the effects of different coagulants and their dosages on COD removal were examined. Ferrous sulphate presented the best performance to remove organic material. The maximum COD removal efficiency was achieved as 40.7±0.7%, and the optimum coagulant dosage was determined as 250 mg L^{-1}. Regarding Fenton oxidation, different Fe^{2+} and H_2O_2 concentrations as well as different Fe^{2+}/H_2O_2 ratios were tested to identify optimum operational conditions. COD removal efficiency of 59.0±0.2% was achieved at 6 mM Fe^{2+} ions. The highest COD removal efficiencies were obtained at 30 mM H_2O_2 and Fe^{2+}/H_2O_2: 1/5. Despite the fact that Fenton oxidation presented a better performance for organic material removal than coagulation-flocculation, COD concentration in the effluent could not meet the discharge limits. Therefore, Fenton oxidation under optimum operational conditions was considered as an effective pre-treatment method to remove organic materials from bilge water.

Keywords: Bilge water, Coagulation-Flocculation, Fenton oxidation, COD removal.

Öz

Yüksek petrol ve yağ içeriği nedeniyle gemilerden kontrolsüz şekilde deşarj edilen sintine suyu deniz ekosistemi için başlıca kirleticilerden biri olarak kabul edilir. Bu çalışmada, koagülasyon - flokülasyon ve Fenton oksidasyonu kullanılarak sintine suyundan organik madde giderimi incelenmiştir. Farklı koagülantlar ve dozajlarının KOİ giderimi üzerine etkisi araştırılmıştır. Koagülasyon-flokülasyonda, demir sülfat organik madde gideriminde en iyi performansı göstermiştir. Maksimum KOİ giderim verimi %40.7±0.7 olarak sağlanmıştır ve optimum koagülant dozajı 250 mg L^{-1} olarak belirlenmiştir. Fenton oksidasyonundaki optimum işletim koşullarını belirlemek için farklı Fe^{2+} ve H_2O_2 konsantrasyonlarıyla birlikte farklı Fe^{2+}/H_2O_2 oranları test edilmiştir. 6 mM Fe^{2+} iyonu konsantrasyonu KOİ giderim verimi %59.0±0.2 olarak elde edilmiştir. En yüksek KOİ giderim verimleri 30 mM H_2O_2 konsantrasyonunda ve Fe^{2+}/H_2O_2: 1/5'te bulunmuştur. Fenton oksidasyonu organic madde gideriminde koagülason-flokülasyon prosesinden daha iyi bir performans göstermesine ragmen çıkış numunesindeki KOİ konsantrasyonu deşarj limiti sağlamamaktadır. Bu sebeple optimum işletim koşullarındaki Fenton oksidasyonu sintine suyundan organik madde gideriminde etkili bir ön arıtım metodu olarak düşünülmüştür.

Anahtar kelimeler: Sintine suyu, Koagülasyon-Flokülasyon, Fenton oksidasyonu, KOİ giderimi.

1 Introduction

With the increase in the globalization in the last decades, the importance of transportation between countries and continents has increased. Marine transportation is more preferable than any other transportation methods because it is cost effective and it has a greater loading capacity than the others [1]. Around 20% of marine pollution is resulted from sea vessels and it depends on ship types and their routes as well as environmental conditions [2]. Bilge water is the major pollutant caused by ships, which contains high amount of petroleum and oil [3].

Bilge water is collected in the lowest part of ship's hull and it is a corrosive mixture of wastewater and sea water [4]. Although the pollution characteristic of bilge water is highly dependent on the type of sea vessels and operational conditions; bilge water typically includes fuel, oil-grease, detergents and surfactants, solvents and salts [5],[6]. Uncontrolled discharge of high amount of bilge water decrease the concentration of dissolved oxygen and the sun light penetration by forming a layer on the surface because oil has lower gravity than water, as well as it could cause a massive death of fishes and birds by sticking their gills and feathers, respectively [7]. In order to control and prevent the negative impact of bilge water on marine environment, the discharge standards set by International Maritime Organization (IMO) should be met before discharging bilge water (<15 ppm oil-grease) [8].

Many different methods have been applied for the treatability of bilge water in the literature; including membrane processes [6],[9],[10], electrochemical processes [3],[11],[12], and biodegradation [13]-[15]. These are effective methods to treat bilge water and to separate oil and water; however, these processes require high energy.

In the economical perspective, coagulation-flocculation, and advanced oxidation process (Fenton oxidation) have presented alternative treatment methods for bilge water. Coagulation-flocculation and Fenton oxidation are highly efficient processes for wastewater treatment, and they have been used to remove organic materials in many different industrial wastewaters such as cheese whey [16], pesticide [17], pulp and paper mills

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[18], pharmaceutical [19], dye [20] and leachate [21]. In coagulation, the negative surface charges on the colloidal suspended solids are neutralized with opposite charged ions by adding chemicals and the neutralized particles are formed flocs in flocculation [17]. In Fenton oxidation, organic matters are broken down via hydroxyl radicals having high oxidation potential which are formed after serial reactions by catalysing hydrogen peroxide with ferrous salts under high acidic conditions [21].

Turkey has an international strategical importance due to its geopolitical location where is the connection point of Asia and Europe. With the increase in marine transportation, Istanbul Bosporus (41°K, 29°D) has been severely polluted by bilge water [22]. In Haydarpasa Waste Collection Plant, Haydarpaşa Port, İstanbul, bilge water has been treated by coagulation-flocculation. The process flow scheme for Haydarpasa Waste Collection Plant is presented in Figure 1. Polyaluminium chloride (PAC), and polyelectrolyte are used as coagulant, and coagulant aid, respectively. Organic material concentration in the effluent differed from 450 to 550 mg COD L^{-1}, corresponding to the removal efficiency of COD was in the range of 60-85% [22]. However, COD concentration in the effluent could not meet the discharge standard set in Table 19 at Su Kirliliği Kontrol Yönetmeliği (SKKY) (Water Pollution Control Regulations) [23].

This research aims to develop the current coagulation-flocculation by using different coagulants (i.e., ferrous sulphate, ferric chloride, aluminium sulphate, polyaluminium chloride) and additionally propose an alternative process as Fenton oxidation to increase the removal efficiency of organic materials from bilge water. In this scope, optimum coagulant dosages for each coagulant were determined. The optimum operational conditions (the dosage of ferrous salt [Fe^{2+}] and hydrogen peroxide [H_2O_2] and the optimum ratio of [Fe^{2+}] /[H_2O_2]) were identified.

2 Materials and methods

2.1 Bilge Water

Bilge water that was used in this study was collected from Haydarpasa Waste Collection Plant. Sampling point was the influent of chemical treatment unit (Figure 1).

Although oil and water were firstly separated, samples still contained oil. The characterization of bilge water was summarized in Table 1.

Table 1. The characterization of bilge water.

Parameter	Concentration (mg L^{-1})
Chemical Oxygen Demand (COD)	1100
Soluble Chemical Oxygen Demand (sCOD)	900
Oil-Grease	900
Chloride (Cl^-)	5700
Suspended Solids (SS)	100
Volatile Suspended Solids (VSS)	90

2.2 Experimental setup and operational conditions

2.2.1 Coagulation-Flocculation

500 mL bilge water samples were transferred in 1 L beakers. In order to determine the optimum coagulant dosage, different concentrations of ferrous sulphate, ferric chloride, aluminium sulphate, polyaluminium chloride (PAC) were added (Table 2).

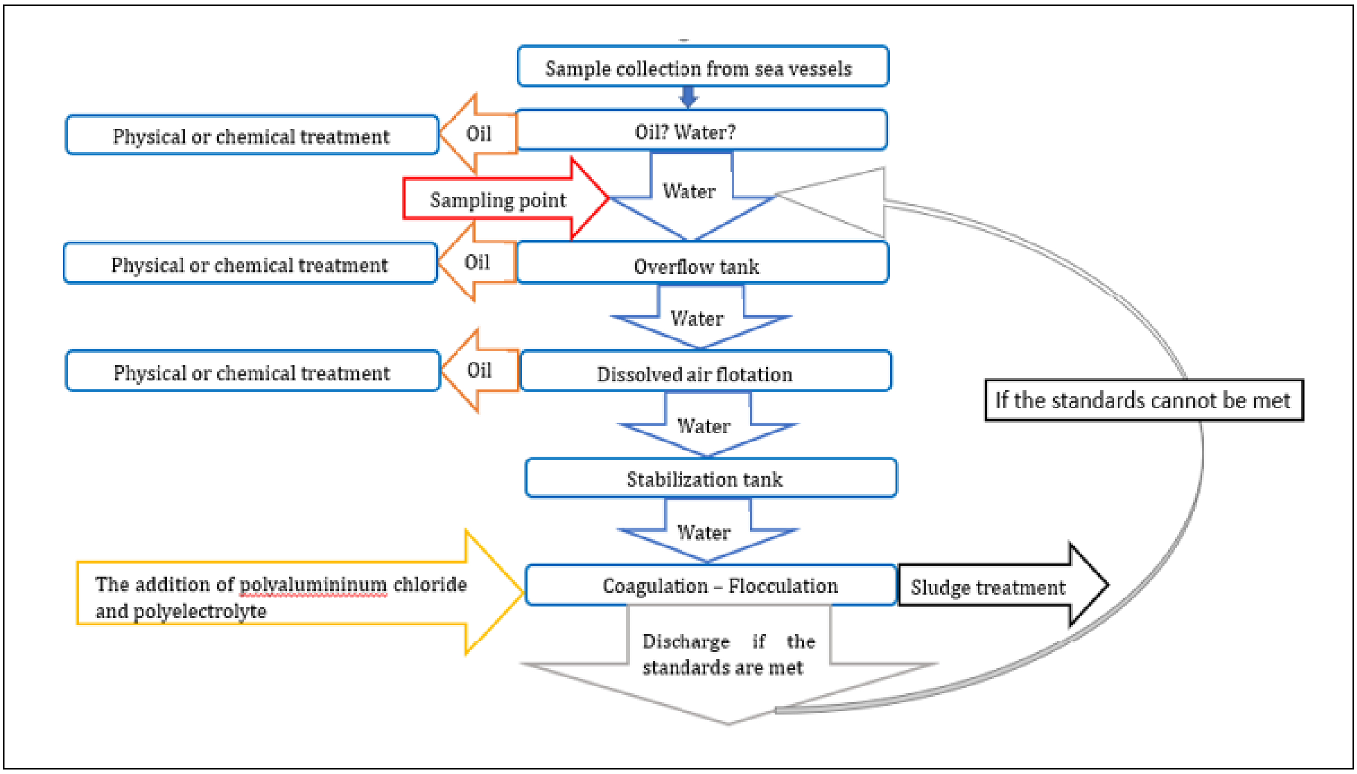

Figure 1. The process diagram for Haydarpaşa waste collection plant.

Table 2. Experimental plan for coagulation-flocculation.

Experiment Number	Coagulant	pH	Coagulant dosage (mg L^{-1})
1	Ferrous Sulphate ($FeSO_4$)	9.5	50
			100
			150
			200
			250
2	Ferric Chloride ($FeCl_3$)	10.0	50
			100
			150
			200
			250
3	Aluminium Sulphate ($Al_2(SO_4)_3$)	5.0	25
			75
			100
			150
			200
			250
4	Polyaluminium Chloride (PAC)	5.0	50
			100
			150
			200
			250
			300

pH was adjusted the optimum values for each coagulant recommended by Oz [24], using 1 N H_2SO_4 and 0.5 N NaOH by a pH meter (WTW Inolab pH*7110). Samples were placed in the jar test setup with 6 stirrers (WiseStir). Coagulation and flocculation lasted for 2 minutes and 30 minutes at the stirring rate of 100 rpm and 30 rpm, respectively. Samples were left for the precipitation for an hour. After precipitation, sCOD was analysed by filtering the samples with a 0.45 µm syringe filter.

2.2.2 Fenton oxidation

500 mL samples were added in 1 L beakers. Samples were placed on a hotplate (Gerhardt) to adjust their temperature as 20°C by a thermometer (IsoLab). pH was set as 3 using 1 N H_2SO_4 and 0.5 N NaOH by a pH meter. Ferrous salt and hydrogen peroxide were added from the stock solutions of 1 M [Fe^{2+}] and 2 M [H_2O_2] (35% by volume), respectively. Table 3 presents the concentration of Fe^{2+} and H_2O_2 that were used for the experiments. Samples were placed in jar test setup with 6 stirrers, and they were stirred at 200 rpm for 30 minutes. The oxidation process maintained for 2 hours. Supernatant phase of samples was transferred in 500 mL beakers after completing the oxidation, and pH was adjusted as 7.5. Samples were settled for 2 hours. After the settlement, sCOD was measured by filtering the samples with a 0.45 µm syringe filter.

Hydrogen peroxide concentration was measured because of its interference on COD analysis. Therefore, COD concentrations were corrected using Eq. (1) recommended by Kang [25].

$$COD(H_2O_2)\left(\frac{mg}{L}\right) = 0.4706\,[H_2O_2] - 4.06 * 10^{-5}\,[H_2O_2]^2 \quad (1)$$

Table 2. Experimental plan for Fenton oxidation.

Experiment Number	[Fe^{2+}] molarity (mM)	[H_2O_2] molarity (mM)	[Fe^{2+}]/[H_2O_2] Ratio
5	1	30	
	2	30	
	3	30	
	4	30	
	5	30	
	6	30	
6	6	30	
	6	60	
	6	120	
	6	180	
	6	240	
7	1	5	1/5
	2	10	1/5
	3	15	1/5
	4	20	1/5
	5	25	1/5
	6	30	1/5
8	1	10	1/10
	2	20	1/10
	3	30	1/10
	4	40	1/10
	5	50	1/10
	6	60	1/10
9	1	20	1/20
	2	40	1/20
	3	60	1/20
	4	80	1/20
	5	100	1/20
	6	120	1/20
10	1	30	1/30
	2	60	1/30
	3	90	1/30
	4	120	1/30
	5	150	1/30
	6	180	1/30

2.3 Analytical procedure and chemicals

COD, SS, VSS, and oil-grease were analysed following SM 5220 D, SM 2540 D, SM 2540 E, and SM 5520 D, respectively [26]. Chloride was analysed by using Mohr Method. The chemicals used in this study were purchased from MERCK or similar manufacturer at an equivalent purity.

2.4 Statistical analysis

Analyses were conducted in duplicates and the data were reported as average ± standard deviation. One-way analysis of variance (ANOVA) was performed by using IBM SPSS Statistics 23. *post hoc* Tukey test was conducted in order to compare between the different means once *p* value is lower than 0.05.

3 Results and discussion

3.1 Coagulation-flocculation

50, 100, 150, 200, and 250 mg $FeSO_4$ L^{-1} were tested at pH: 9.5 to identify the effect of ferrous sulphate on COD removal from bilge water Figure 2(a). COD concentration decreased sharply with the increase in ferrous sulphate concentration from 50 mg L^{-1} to 250 mg L^{-1} (from 930.0 ± 40.0 mg L^{-1} to 652.5±7.5 mg L^{-}), corresponding to the removal efficiency of COD increased from 15.5±3.6% to 40.7±0.7% (*p*=0.01). Thus, the optimum ferrous sulphate dosage was obtained as 250 mg L^{-1}. There is a good agreement with the literature. Katip [17] studied organic material removal from pesticide industry wastewater by coagulation-flocculation and obtained 42% of COD removal efficiency at 250 mg L^{-1} $FeSO_4$ concentration. However, lower organic material removal efficiencies were reported at higher ferrous sulphate concentrations [16],[27]. Higher coagulant dosages cause sludge problem.

Figure 2(b) demonstrated the effect of Ferric chloride dosages (50, 100, 150, 200, and 250 mg $FeCl_3$ L^{-1}) on COD removal from bilge water (pH was set as 10). The behaviour of COD removal is similar to the one that was observed in Figure 1(a) for ferrous sulphate. There was a significant reduction in COD concentration from 994.0 ± 0.0 mg L^{-1} to 833.6 ± 15.0 mg L^{-1} (p=0.03) with increasing ferric chloride dosage from 50 mg L^{-1} to 150 mg L^{-1}. COD removal efficiency increased from 9.8±0.0% to 24.2±1.4%. Further increases in ferric chloride concentration did not present any statistical differences (p>0.05). Therefore, the optimum ferric chloride dosage was reported as 150 mg L^{-1}. Although similar COD removal efficiency was reported as 26% at higher ferric chloride concentration (400 mg L^{-1}) [16], greater organic material removal efficiencies were achieved (from 43% to 75.6%) in previously published studies [17],[27],[28]. This situation could be attributed to ferric chloride dosages, and wastewater characterizations which were used.

The effect of aluminium sulphate dosages on organic material removal from bilge water was presented in Figure 2(c). 25, 75, 100, 150, 200, and 250 mg L^{-1} aluminium sulphate were examined at pH: 5. COD concentration decreased significantly from 872.6±32.6 mg L^{-1} to 734.1±4.1 mg L^{-1} between 25-150 mg $Al_2(SO_4)_3$ L^{-1}, corresponding to the removal efficiency of COD increased sharply from 20.7±3.0% to 33.3±0.4% (p=0.028). With a further increase in aluminium sulphate dosage, any statistical differences were not observed (p>0.05), so that 150 mg L^{-1} aluminium sulphate was chosen as the optimum dosage. Verma et al. [27] identified the optimum Alum dosage of 3500 mg L^{-1} with 33.1% of organic material removal efficiency from petrochemical wastewater. Lower COD removal efficiency was obtained as 29% [16] whereas Katip [17] achieved almost one and half times higher organic material removal (47%) than the one which was reported in this study by using 300 mg L^{-1} Alum. This fluctuation could be resulted from different operational conditions for coagulation-flocculation experiments.

50, 10, 150, 200, 250, and 300 mg PAC L^{-1} were tested at pH: 5 to determine the effect of PAC dosages on organic material removal from bilge water. Although COD removal efficiency decreased slightly with incrementing PAC dosage from 50 to 100 mg L^{-1} (p = 0.758), a significant increase was achieved in the removal efficiency of COD (from 21.4±3.6 to 37.3±3.6%) between 100 and 200 mg L^{-1} PAC, corresponding to a sharp decrease in COD concentration from 865.0±40.0 to 690.0±40.0 mg L^{-1}(p=0.037) (Figure 2(d). COD concentration and the removal efficiency of COD fluctuated with a further increase in PAC concentration, which were not statistically different (p > 0.05). Therefore, 200 mg PAC L^{-1} was preferred as the optimum dosage for COD removal from bilge water. Greater organic material removal was observed at higher PAC concentrations in the literature [27],[28].

It can be clearly seen in Figure 2 that over the optimum dosage did not present any significant differences in organic material removal from bilge water. This situation could be attributed the fact that colloidal particles are restabilized at the excessive coagulant dosage.

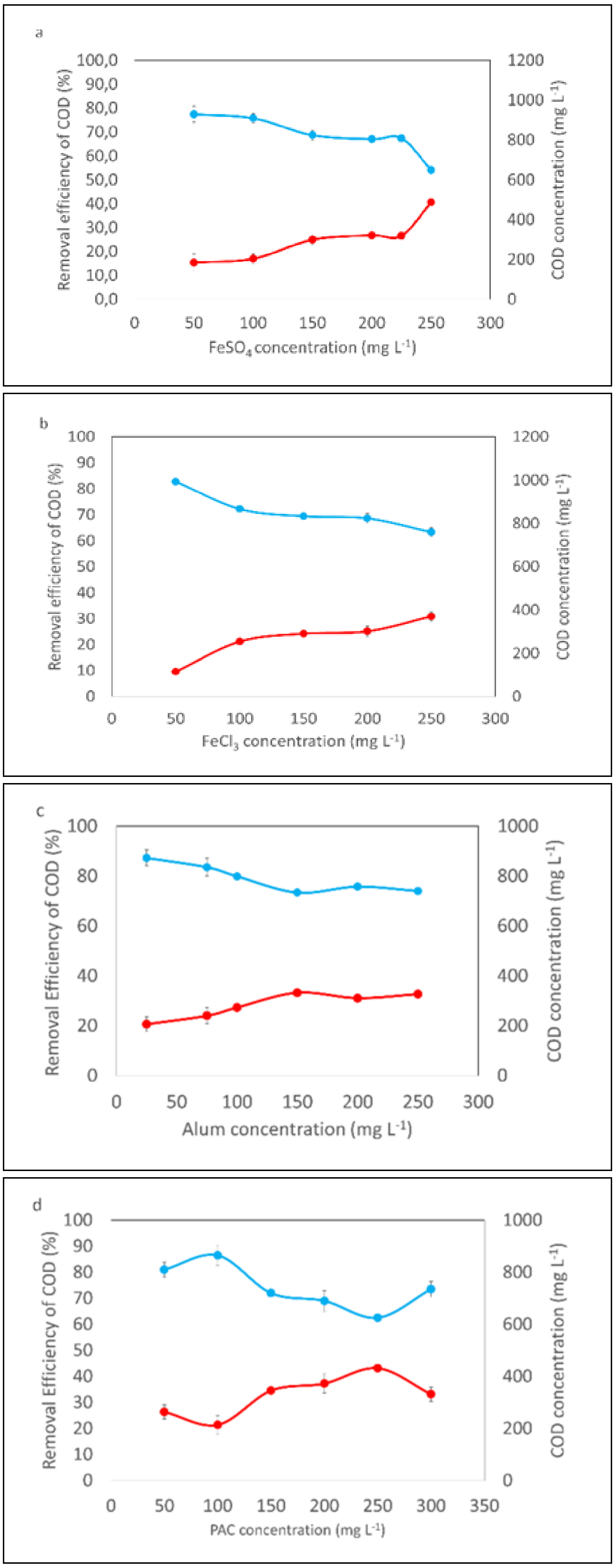

Figure 2. The effect of different coagulant dosages on removal efficiency of COD and COD concentration. (a): $FeSO_4$; (b): $FeCl_3$; (c): $Al_2(SO_4)_3$; and (d): PAC.

Their surface charges become positive due to the adsorption of coagulant [27],[28]. Furthermore, less amount of coagulant can contribute to reducing sludge production [29]. Although the highest COD removal efficiency was achieved as 40.7±0.7% using ferrous sulphate as coagulant, COD concentration in the effluent could not meet the discharge standard set in Table 19 at SKKY (400 and 300 mg L^{-1} COD for the composite sample for 2 h and 24 h, respectively) [23]. Therefore, Fenton oxidation was proposed as an alternative process for the treatment of bilge water in Haydarpasa Waste Collection Plant.

3.2 Fenton oxidation

3.2.1 Optimum Fe^{2+} and H_2O_2 concentration

[Fe^{2+}] molarity was adjusted as 1, 2, 3, 4, 5, and 6 mM at 30 mM H_2O_2 for the experiments of the optimum ferrous concentration to treat bilge water by Fenton oxidation Figure 3(a). COD concentration significantly decreased from 777.5±0.0 mg L^{-1} to 550.3 ± 20.0 mg L^{-1} with the increase in ferrous molarity from 1 mM to 2 mM, corresponded to a sharply increase in the removal efficiency of COD from 29.3±0.0% to 50.0±1.8% (p=0.001). Further increases in ferrous concentration did not present any statistical differences on COD removal ($p > 0.05$). However, the highest COD removal efficiency was obtained as 59.0±0.2%, corresponding to the lowest COD concentration of 450.8±2.5 mg L^{-1} at 6 mM Fe^{2+}. Thus, the optimum [Fe^{2+}] molarity was identified as 6 mM. This situation could be attributed to the fact that more hydroxyl radicals are generated by the reaction between ferrous ion and hydrogen peroxide (Eq. (2)); and hydroxyl radicals that was formed can degrade more organic matters [20]. There are two possible reasons to reduce organic materials oxidation at greater ferrous concentration;

(i) Excessive Fe^{2+} can also interact with hydroxyl radicals and generate ferric (Fe^{3+}) (Eq. (3)) and,

(ii) The reaction between ferric and hydrogen peroxide forms hydroperoxyl radicals, having lower oxidation potential than hydroxyl radicals (Eq. (4)) [30].

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + {}^{\cdot}OH + H_2O \qquad (2)$$

$$Fe^{2+} + {}^{\cdot}OH \rightarrow OH^{\cdot} + Fe^{3+} \qquad (3)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO^{\cdot}_2 + H \qquad (4)$$

Similar COD removal trend against ferrous concentration was observed in the previous studies [19],[20],[30],[31]. The optimum concentration of ferrous salt and COD removal efficiencies in the literature differed from 1 mg Fe^{2+} L^{-1} to 4 g Fe^{2+} L^{-1} and from 22.4 to 95%, respectively. Optimum Fe^{2+} concentration and COD removal efficiency which was reported in this study are in the range of those in the literature.

Figure 3(b) presented the effect of H_2O_2 on organic material removal via Fenton process. 30, 60, 120, 180, and 240 mM H_2O_2 were tested at 6 mM Fe^{2+}. COD removal efficiency and COD concentration varied from 50.9 ± 5.2% to 59.2 ± 0.5% and from 448.3 ± 5.0 to 540.0 ± 57.5 mg L^{-1}, respectively. However, these changes were not different statistically ($p > 0.05$), so that the optimum H_2O_2 concentration was determined as 30 mM from the economical perspective. Argun [19] reported that COD removal efficiencies varied between 72 - 79% in the range of 500-6000 mg L^{-1} H_2O_2. Regardless of H_2O_2 concentration, 87.6-92.1% of COD removal efficiency was obtained [32]. Despite the similar behaviour, there is also a discrepancy with many previous studies which reported that the removal efficiency of COD incremented until the optimum H_2O_2 concentration and decreases with a further increase [20],[30],[31],[33]. This situation could be attributed to the fact that H_2O_2 reacts with Fe^{2+} to generate more hydroxyl radicals according to Eq. 2 and, the reaction between the excessive H_2O_2 and hydroxyl radicals can form hydroperoxyl radicals (Eq. (5)), which resulted in the decrease in organic removal [34].

$$H_2O_2 + {}^{\cdot}OH \rightarrow HO^{\cdot}_2 + H_2O \qquad (5)$$

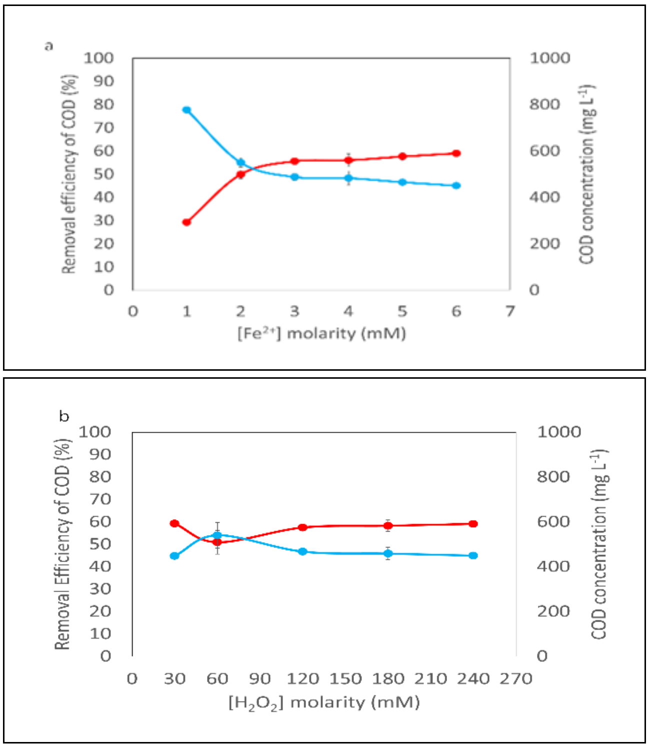

Figure 3. The effect of different molarities of Fenton oxidation's reactives on COD removal efficiency and COD concentration, (a): Fe^{2+}; and (b): H_2O_2.

3.2.2 Optimum Fe^{2+}/H_2O_2 ratio

Figure 4 demonstrated the effect of Fe^{2+}/H_2O_2 ratios on COD removal from bilge water.

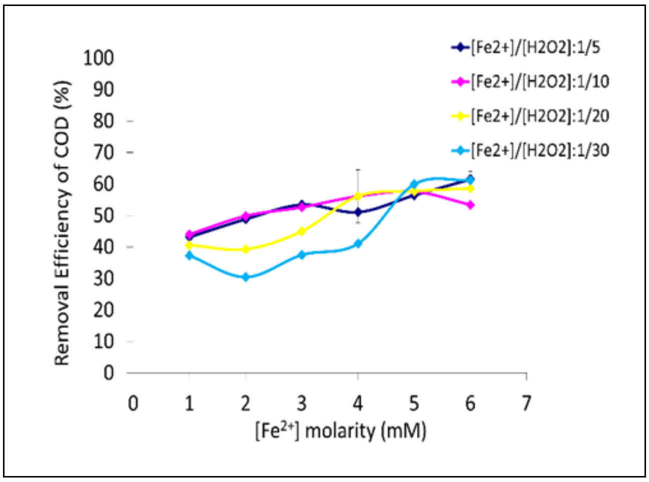

Figure 4. The effect of Fe^{2+}/H_2O_2 ratios on the removal efficiency of COD.

Fe^{2+}/H_2O_2 ratio was adjusted as 1/5, 1/ 10, 1/20, and 1/30 by using a set of $[Fe^{2+}]$ molarity of 1, 2, 3, 4, 5, and 6 mM and H_2O_2 was adjusted by depending on Fe^{2+}/H_2O_2 ratio. It can be clearly seen in Figure 4, greater COD removal efficiencies achieved at lower Fe^{2+}/H_2O_2 ratios (1/5 and 1/10) between 1 and 3 mM Fe^{2+}, and COD removal efficiencies fluctuated with the Fe^{2+}/H_2O_2 ratios at higher Fe^{2+} concentrations, which were not significantly different (p>0.05). Moreover, the Fe^{2+}/H_2O_2 ratio of 1/5 and 1/10 did not presented statistically differences on organic material removal (p>0.05). Therefore, the optimum Fe^{2+}/H_2O_2 ratio was identified as 1/5 to reduce the requirement chemical from the economical perspective. There is a good agreement with the previous study. Organic material removal from pharmaceutical industry by Fenton oxidation was studied and the optimum Fe^{2+}/H_2O_2 was reported as1/5 [19].

In this section, Fenton oxidation was investigated as an alternative process to coagulation-flocculation that has been used for the treatment of bilge water at Haydarpaşa Waste Collection Plant. The maximum removal efficiency of COD was achieved as 59.0 ± 0.2%, corresponding to the residual organic material concentration of 450.8 ± 2.5 mg L^{-1}. Thus, the optimum operational conditions were determined as 6 mM Fe^{2+}, 30 mM H_2O_2 and the Fe^{2+}/H_2O_2: 1/5.

In summary, greater organic material removal was obtained by using Fenton oxidation compared to the ones which were reported by coagulation-flocculation. The difference of COD removal efficiencies between these two processes can be resulted from the hydroxyl radicals that are produced by Fenton oxidation, which have a high oxidation potential to organic materials from bilge water. Ferrous sulphate was found as the optimum coagulant with the maximum COD removal efficiency of 40.7 ± 0.7% at optimum dosage of 250 mg L^{-1} for coagulation-flocculation. Regarding Fenton oxidation, the optimum $[Fe^{2+}]$ identified was 6 mM with the removal efficiency of COD of 59.0±0.2. Although the different H_2O_2 concentrations and Fe^{2+}/H_2O_2 ratios did not present any significant differences on COD removal, the optimum H_2O_2 concentration and Fe^{2+}/H_2O_2 ratio were preferred as 30 mM and 1/5, respectively. Higher COD removal efficiency was achieved by Fenton oxidation than using coagulation - flocculation. However, COD concentration in the effluent could not meet the discharge limits. Fenton oxidation under optimum operational conditions is recommended as a pre-treatment process for organic materials removal from bilge water. After Fenton oxidation, advanced physicochemical treatment methods are suggested to improve the efficiency of organic material removal from bilge water.

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5 Authors contributions statements

Çiğdem ÖZ (corresponding author) carried out the laboratory analyses, analysed the data made the literature research, wrote, and submitted the manuscript. Ender ÇETİN contributed to identifying the research problem and research gap.

6 Ethics commitee approval and conflict of interest statement

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, and this paper is not required the research ethics committee approval.

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