

Article

Treatment of Bilge Water by Fenton Oxidation Followed by Granular Activated Carbon Adsorption

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Abstract: Due to its high oil content, the discharge of bilge water from ships is one of the most important pollutants in marine ecosystem. In this research, we investigated the treatment of bilge water for Haydarpasa Waste Collection Plant by Fenton oxidation followed by granular activated carbon (GAC) adsorption. We applied the following optimum operational conditions for Fenton oxidation: $[\text{Fe}^{2+}]$: 6 mM; $[\text{H}_2\text{O}_2]$: 30 mM; and the ratio of $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$: 1/5. Adsorption was performed in the effluent sample of Fenton oxidation. The effects of different adsorption periods, adsorbent concentrations, temperature, and pH were examined. Additionally, Freundlich and Langmuir isotherm models were applied. We obtained the following optimum operational conditions: 24 h, 2 g of GAC L^{-1} , 20 °C, and pH = 6. We observed an $89.5 \pm 1.9\%$ of Chemical Oxygen Demand (COD) removal efficiency under these conditions. Data generated from the experiments fit both isotherm models well, though we preferred the Langmuir isotherm model to the Freundlich isotherm model because the former's regression coefficient (0.90) was larger than that reported for the Freundlich isotherm model (0.78). The potential to treat bilge water by Fenton oxidation followed by granular activated carbon is promising for the Haydarpasa Waste Collection Plant.

Keywords: marine pollution; bilge water; COD removal; advanced oxidation; adsorption



Citation: Öz, Ç.; Çetin, E. Treatment of Bilge Water by Fenton Oxidation Followed by Granular Activated Carbon Adsorption. *Water* **2021**, *13*, 2792. <https://doi.org/10.3390/w13192792>

Academic Editors: Laura Bulgariu and Antonio Panico

Received: 1 September 2021

Accepted: 3 October 2021

Published: 8 October 2021

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1. Introduction

The importance of transportation between countries and continents has increased as a result of globalization. Specifically, the rate of marine transportation has increased due to its larger loading capacity compared to other transportation methods, which has induced marine pollution [1,2]. In the context of marine pollution, sea vessels (i.e., ships) are considered to be among the main marine pollutants. Around 20% of marine pollution is caused by sea vessels, with levels depending on ship types and conditions, as well as their routes [3]. Bilge water is considered to be sea vessels' major pollutant because it contains high amounts of petroleum and oil [4].

Bilge water is stored in the lowest internal part of a ship's hull below the engine room and boiler, and it is a corrosive mixture of wastewater and sea water [5]. Although the pollution characteristic of bilge water depends on the type of vehicle and its operation mode, pollutants typically found in bilge water include fuels, oils, grease, detergents, surfactants, solvents, and salts [6,7]. The adverse effects of discharging bilge water on marine habitat are: (i) reductions of dissolved oxygen and sunlight penetration caused by a layer formed on the surface due to its lower oil density than water and (ii) the massive death of fish and birds caused by the bilge water sticking on their gills and feathers, respectively [8]. Therefore, the discharge standard set by International Maritime Organization (IMO) (<15 ppm oil/grease) should be met before discharging bilge water [9].

Turkey's geographical location has international strategic importance regarding marine transportation between two continents, Europe and Asia. Therefore, Istanbul

Bosporus (41° N, 29° E) has been severely contaminated by bilge water [10]. Bilge water is first collected by waste collection ships; then stored in different tanks depending on the types of waste in Haydarpaşa Waste Collection Plant, Istanbul, Turkey; and finally pumped out at the wastewater treatment plant. The coagulation–flocculation process is performed to treat bilge water. Haydarpaşa Waste Reception Plant’s flow diagram is demonstrated in Figure S1. Although COD removal efficiency varies from 60 and 85%, with organic material concentration from 450 to 550 mg COD L⁻¹ [10], the discharge standard set in Su Kirliliği Kontrol Yönetmeliği (SKKY) (Water Pollution Control Regulations) [11] regarding COD concentration in the effluent cannot be met. Many different methods for the treatment of bilge water, including membrane processes [7,12,13], electrochemical processes [2,4,14], and biodegradation [15–17], have been studied. However, their applicability can be scrutinized from an economical perspective due to their high energy requirements. Physicochemical processes (i.e., Fenton oxidation and granular activated carbon adsorption) could be also used for the removal of organic materials [18,19]. Fenton oxidation an advanced oxidation process that is simple to apply, has low capital costs, and is based the formation of hydroxyl radicals by using ferrous salts with H₂O₂ at acidic pH [20]. Adsorption removes organic and inorganic pollutants by binding adsorbates on the outer surfaces of adsorbent. Granular activated carbon is a commonly used adsorbent [19].

The treatment of bilge water with a moving bed biofilm reactor has been studied, and the greatest obtained COD removal efficiency was as 86% [21]. Mazioti A.A. et al. [22] investigated the treatment of bilge water by anaerobic digestion via granular sludge, and they reported that methane production and COD removal efficiency significantly increased after adding zero valent iron and activated charcoal, respectively. In addition, the removal efficiency of organic materials differed in the range of 36.2–71% when electrochemical processes such as electrocoagulation and electro-Fenton were applied for bilge water treatment [4]. In our previous study, Fenton oxidation was proposed as a pre-treatment process for bilge water collected at Haydarpaşa Waste Reception Plant due to the fact that the effluent could not meet the discharge standards. We identified the optimum operational conditions as [Fe²⁺]: 6 mM; [H₂O₂]: 30 mM; and the ratio of [Fe²⁺]/[H₂O₂]: 1/5 [23]. Furthermore, Ramirez-Sosa D.R. et al. [24] reported that COD removal was increased by Fenton oxidation followed by activated carbon adsorption.

Therefore, this study was aimed to investigate the treatability of bilge water by granular activated carbon adsorption after using Fenton oxidation as a pre-treatment method, as recommended by Oz and Cetin [23]. The effects of different adsorption periods, adsorbents dosages, temperatures, and pH conditions were tested to identify the optimum operational conditions in terms of the removal efficiency of organic materials. In addition, Freundlich and Langmuir isotherms were applied in order to determine which isotherm presents a better fit for adsorption isotherm studies.

2. Materials and Methods

2.1. Bilge Water

The bilge water used in this project was collected from the influent of chemical treatment unit in Haydarpaşa Waste Collection Plant in Haydarpaşa Port, Istanbul [25]. The sampling point is presented in Figure S1. The characterization of the bilge water is presented in Table 1.

Table 1. Bilge water characterization.

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. Synthetic Bilge Water

Synthetic bilge water containing 5 g of COD L⁻¹ was prepared in order to adjust the amount of organic compound for the adsorption isotherm studies. The oil and sea water contents in artificial bilge water were adjusted as recommended by Peng et al. [6] and Körbahti and Artut [14], respectively. The synthetic bilge water consisted of diesel fuel, lubricating oil, hydraulic oil, detergents and surface-active reagents, NaCl, Na₂SO₄, KCl, and CaCl₂. The composition of the synthetic wastewater is summarized in Table 2.

Table 2. The composition of synthetic bilge water.

Contents	Concentration (mg L ⁻¹)
Diesel fuel	1000
Lubricating oil	800
Hydraulic oil	200
Detergents and surfactants	500
NaCl	11,000
Na ₂ SO ₄	2000
KCl	400
CaCl ₂	600

2.3. Experimental Setup and Operational Conditions

2.3.1. Fenton Oxidation

Fenton oxidation was applied as a pre-treatment method in this study. Temperature and pH were set to 20 °C and 3, respectively. Ferrous sulphate and hydrogen peroxide were added. A jar test setup with 6 stirrers was used, and the agitation rate was adjusted to 200 rpm for half an hour. The oxidation was completed in 2 h. The upper phase was transferred in a beaker for the sedimentation. The pH was set to 7.5. The settlement was maintained for 2 h. The supernatant phase of samples was collected for the adsorption process.

2.3.2. Granular Active Carbon Adsorption

We transferred 200 mL of effluent of Fenton oxidation samples to 250 mL volumetric flasks. Granular active carbon (GAC) with a pore diameter of 1.5 mm was added to the flasks. GAC was weighed on a balance. pH was adjusted with a pH meter (WTW Inolab*7110). The flasks were placed in a temperature-controlled shaker at 170 rpm (Gallenkamp) and fixed by clamps. Samples were collected after 1, 3, 5, 7, 24, 48, and 72 h at 25 °C by using 1 g of GAC L⁻¹ in order to determine the equilibrium time. In the experiments for the optimum GAC concentration and temperature, 1, 1.5, 2, 2.5, and 3 g of GAC L⁻¹ were added to the volumetric flasks at 15, 20, 25, and 30 °C; pH was adjusted to be 2, 4, 6, 8, and 10 using 0.5 N NaOH and 1 N H₂SO₄ at 20 °C in order to identify the effect of pH on granular activated carbon adsorption. Table 3 summarizes the experimental plan to identify optimum adsorption conditions for the treatment of bilge water.

Samples were collected after reaching the equilibrium time at all adsorption experiments. We used 0.45 µm syringe filters for filtration, and sCOD was analyzed following SM 5220-D [26].

Bilge water and synthetic bilge water were mixed in different ratios for adsorption isotherm experiments to adjust organic material concentrations, as shown in Table 4. We added 1.5 g of GAC L⁻¹ to the volumetric flasks. The temperature of shaker was set to 20 °C, and the pH was adjusted to 6. Freundlich and Langmuir isotherms were performed via Equations (1) and (2), respectively.

$$\log q_e = \log K_F + (1/n) \log C_e \quad (1)$$

where C_e : COD concentration measured following adsorption (mg L⁻¹); q_e : amount of adsorbate in the adsorbent at equilibrium (mg g⁻¹); K_F : Freundlich constant (mg g⁻¹) (dm³ g⁻¹)^{1/n}; and n : adsorption intensity.

$$(C_e/q_e) = (C_e/Q_0) + (1/(Q_0 * K_L)) \quad (2)$$

where C_e : COD concentration measured following adsorption (mg L^{-1}); q_e : amount of adsorbate in the adsorbent at equilibrium (mg g^{-1}); Q_0 : maximum monolayer adsorption capacity (mg g^{-1}); and K_L : adsorption energy coefficient (L mg^{-1}).

Table 3. Experimental plan.

Experiment Number	Equilibrium Time (h)	Adsorbent Dosage (g GAC L^{-1})	Temperature ($^{\circ}\text{C}$)	pH
1	1			
2	3			
3	5			
4	7	1	25	7.5
5	24			
6	48			
7	72			
8		1		
9		1.5		
10	24	2	25	7.5
11		2.5		
12		3		
13		1		
14		1.5		
15	24	2	15	7.5
16		2.5		
17		3		
18		1		
19		1.5		
20	24	2	20	7.5
21		2.5		
22		3		
23		1		
24		1.5		
25	24	2	30	7.5
26		2.5		
27		3		
28				2
29				4
30	24	2	20	6
31				8
32				10

Table 4. Mixing ratio of bilge water and synthetic bilge water for adsorption isotherm experiments.

Ratio of Bilge Water (%)	Ratio of Synthetic Bilge Water (%)
100	0
90	10
80	20
70	30
60	40
50	50

2.4. Analytical Procedures and Chemicals

COD, Total Suspended Solids (TSS), Volatile Suspended Solids (VSS), and Oil–Grease were analyzed following standard methods (SM 5220 D, SM 2540 D, SM 2540 E, and

SM 5520 D, respectively) [26]. Chloride was analyzed via the Mohr Method. All of the chemicals used in this study were purchased from MERCK (Burlington, Massachusetts, ABD) or similar manufacturers at an equivalent purity; the granular activated carbon with a pore size of 1.5 mm was also purchased from MERCK.

2.5. Statistical Analysis

All analyses were conducted in duplicate. Data are reported as average \pm standard deviation. Statistical analysis was performed by using one-way analysis of variance (ANOVA) in IBM SPSS Statistics version 23. *p*-Values of less than 0.05 indicate significant differences. *Post hoc* Tukey tests were conducted to compare the different means.

3. Results and Discussion

3.1. Fenton Oxidation

In our previous research, the optimum operational conditions for Fenton oxidation to remove organic materials from bilge water were identified to be $[\text{Fe}^{2+}]$: 6 mM; $[\text{H}_2\text{O}_2]$: 30 mM; and the ratio of $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$: 1/5 [23]. COD removal efficiency was reported to be $59.0 \pm 0.2\%$, corresponding to the concentration of organic materials in the effluent was $450.8 \pm 2.5 \text{ mg O}_2 \text{ L}^{-1}$. The discharge standard set in Su Kirliliği Kontrol Yönetmeliği (SKKY) [11] could not be met, so Fenton oxidation was proposed as a pre-treatment method to treat bilge water.

3.2. Adsorption

3.2.1. Equilibrium Time

The adsorption process was applied to the effluent sample of Fenton oxidation. Samples were collected at 1, 3, 5, 7, 24, 48, and 72 h to determine equilibrium time by dosing 1 g of GAC L^{-1} at pH = 7.5, 25 °C, and a 170 rpm agitation rate (Figure 1). COD removal efficiencies fluctuated in the range between $3.1 \pm 1.3\%$ and $10.7 \pm 3.6\%$ for adsorption between the equilibrium time of 1 and 5 h. There were significant increases in COD removal efficiencies from $10.7 \pm 3.7\%$ and $54.5 \pm 1.8\%$ to $26.3 \pm 2.2\%$ and $62.5 \pm 1.1\%$ for adsorption and total, respectively, with the increase in the equilibrium time from 5 to 24 h, which corresponded to the decrease in COD concentration from 500.0 ± 28.3 to $410 \pm 18 \text{ mg L}^{-1}$ ($p = 0.008$ and 0.012 for COD removal efficiencies and COD concentrations for 5 and 24 h, respectively). COD removal increases until reaching equilibrium time due to the formation of monolayer cover of organic materials on the outer surface of GAC [27]. Further increases in the equilibrium time did not show any statistical differences ($p > 0.05$); therefore, 24 h was used as the equilibrium time for further experiments. Mohammad-Pajooch et al. [28] reported over 50% COD removal from raw leachate by GAC after 24 h of contact time as their preliminary results.

3.2.2. Granular Active Carbon Concentration

Figure 2 presents the effects of different adsorbent dosages on COD removal for 24 h at 25 °C, pH = 7.5, and an agitation rate of 170 rpm. We tested 1.0, 1.5, 2.0, 2.5, and 3.0 g of GAC L^{-1} to identify optimum adsorbent dosage. A gradual increase in COD removal was observed from $50.0 \pm 5.1\%$ and $74.5 \pm 2.6\%$ to $68.3 \pm 1.9\%$ and $83.9 \pm 1.0\%$ for adsorption and total, respectively, with increases granular activated carbon concentration from 1 to 3 g L^{-1} . Regarding COD concentration, there was a slight decrease from 280.0 ± 28.3 to $177.5 \pm 10.6 \text{ mg O}_2 \text{ L}^{-1}$. Increases in the removal of organic material with increases in adsorbent dosage have been reported in many studies [28,29], and it could be explained by the total specific surface area and active sites on the adsorbents [30].

The change in COD removal for adsorption was statistically different between 1 and 2 g of GAC L^{-1} ($p = 0.033$). Further increases in adsorbent concentration did not show any significant influence on COD removal ($p > 0.05$). This situation could be attributed to the fact that the adsorption capacity could not be further increased once equilibrium was reached [26]. The increase in total COD removal was not significantly different at all

tested adsorbent concentrations, except between 1 and 3 g of GAC L⁻¹ ($p > 0.05$). A similar statistical trend was observed in COD concentrations. The p -values obtained for COD removal and COD concentration between 1 and 3 g of GAC L⁻¹ were 0.029 and 0.027, respectively. Therefore, from the statistical perspective, the optimum considered granular activated carbon concentration was 2 g of GAC L⁻¹.

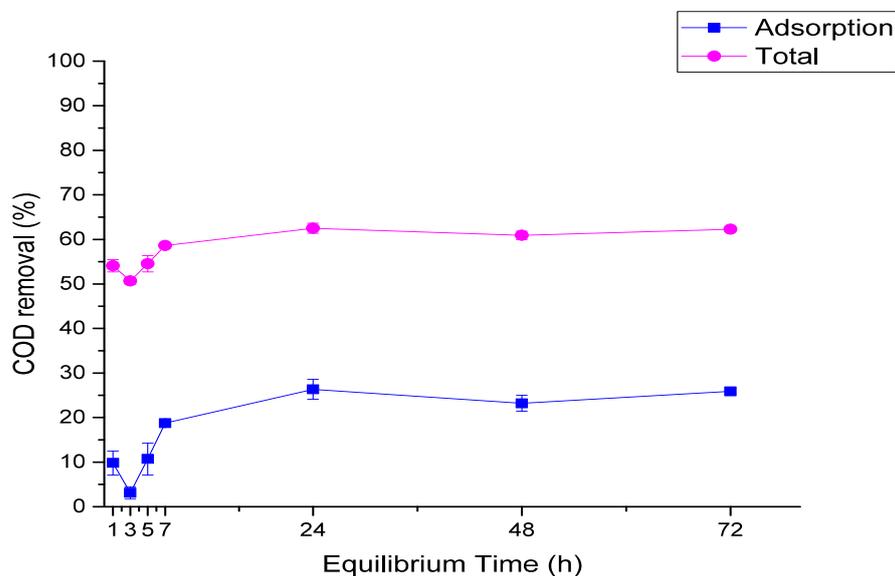


Figure 1. Effect of equilibrium time on COD removal.

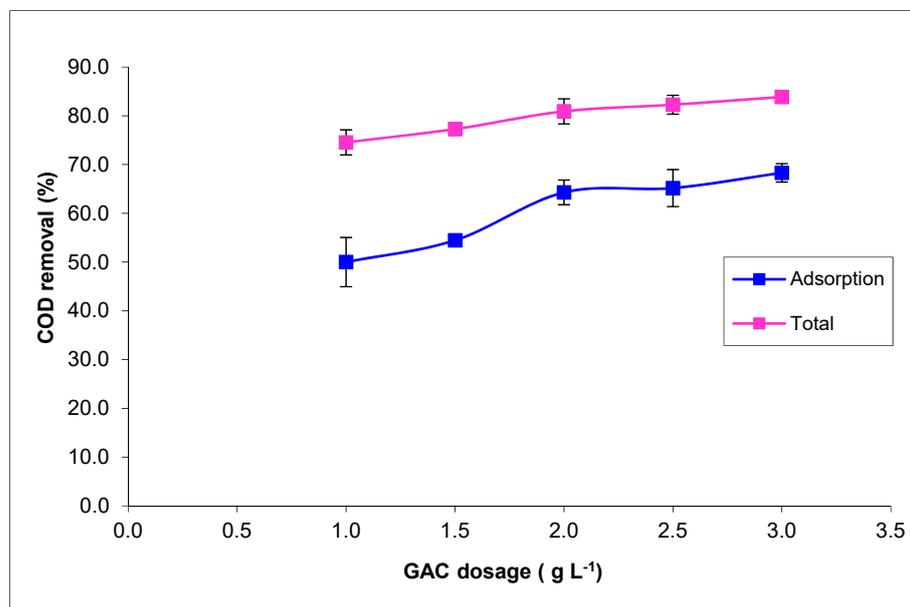


Figure 2. Effect of granular activated carbon dosage on COD removal.

3.2.3. Temperature

The effects of temperature on COD removal are depicted in Figure 3. To determine optimum temperature at all granular activated carbon dosages, the shaker was set to four different temperatures of 15, 20, 25, and 30 °C, as well as pH = 7.5 with a 170 rpm agitation rate, for 24 h. There was a significant increase in COD removal between 15 and 20 °C for adsorption and total ($p = 0.007$). This situation could be attributed to the fact that pore size could become larger with increases in temperature, which could increase the adsorption capacity by activating the surface of the adsorbent [31]. However, further increases in

temperature did not present any statistical differences in COD removal, regardless of the tested adsorbent concentrations ($p > 0.05$ for all experiments). Larous et al. [32] reported that desorption could occur beyond a certain temperature limit via the enlargement of pore size with the increase in temperature and thus decrease the adsorption rate. As such, the optimum temperature was designated as 20 °C because it led to the greatest removal efficiencies of COD for adsorption and total achieved— $70.5 \pm 3.6\%$ and $85.0 \pm 1.8\%$, respectively—at 20 °C and 2 g of GAC L⁻¹, which corresponded to a concentration of $165.0 \pm 20 \text{ mg L}^{-1}$ COD.

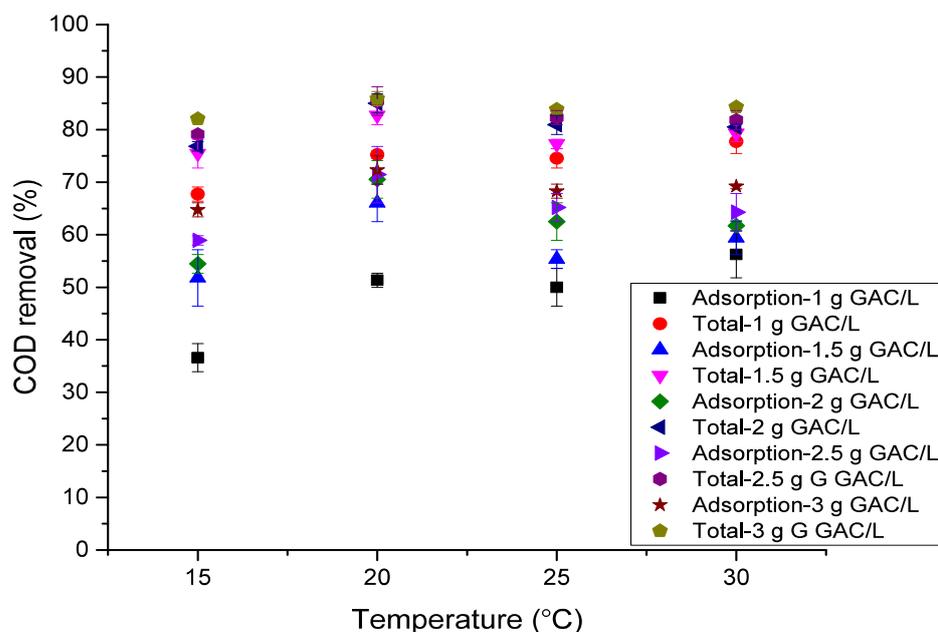


Figure 3. Effect of temperature on COD removal at different granular activated carbon dosages.

3.2.4. pH

To identify the optimum pH, it was adjusted to represent both acidic and alkaline conditions at 20 °C, 2 g of GAC L⁻¹, and an agitation speed of 170 rpm for 24 h (Figure 4). COD removal efficiency significantly increased from $54.0 \pm 5.7\%$ and $76.6 \pm 2.9\%$ to $79.5 \pm 3.8\%$ and $89.5 \pm 1.9\%$ between pH = 2 and 6 for adsorption and total, respectively ($p = 0.033$), which corresponded to a decrease in COD concentration from 257.5 ± 31.8 to $115.0 \pm 21.2 \text{ mg O}_2 \text{ L}^{-1}$. With a further increase in pH, COD removal efficiency did not present any significant changes ($p > 0.05$). Therefore, the optimum pH was found to be 6 for Fenton oxidation followed by adsorption for the treatment of bilge water. The greatest COD removal rate from bilge water achieved under optimum operational conditions was higher than the rates reported in previous studies with different treatment processes [4,15–17].

Nayl et al. [29] also reported that the highest COD removal was achieved at pH = 6 by using activated carbon. This situation could be related to the fact that the surface of activated carbon becomes positively charged by the presence of larger number of H⁺ at lower pH values, so adsorption is triggered with high electronegative charge of oxygen. Furthermore, the abundance of OH⁻¹ at higher pH values reduces the adsorption capacity [33,34]. On the other hand, opposite effects of pH on adsorption has been observed when using positively and negatively surface-charged adsorbates and adsorbents, respectively [35].

3.2.5. Adsorption Isotherm Studies

Adsorption isotherm studies are essential to establish the relationship between an adsorbate and adsorbent. Freundlich and Langmuir isotherm models were created in this study by using Equations (1) and (2), respectively. Adsorption isotherms for the Freundlich and Langmuir models are presented in Figures 5 and 6, respectively.

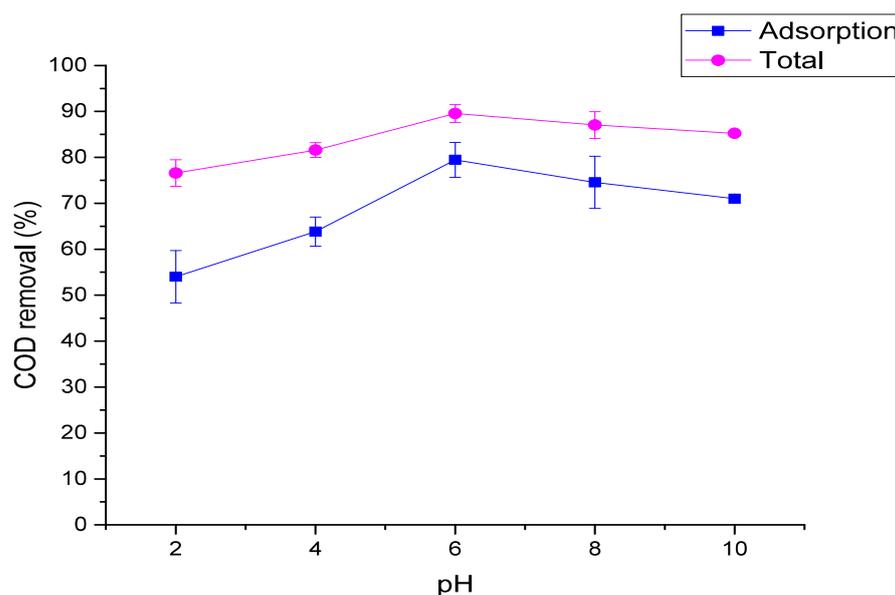


Figure 4. Effect of pH on COD removal.

The constants K_F and n for the Freundlich isotherm model were calculated from the intercept and slope of the linear plots in Figure 5, respectively. K_F and n were found to be 17.68 mg g^{-1} and 2.27, respectively. $n > 1$ indicates favorable multiple adsorption conditions for organic materials on granular activated carbon. The regression coefficient for the Freundlich isotherm model was 0.78. Regarding the constants of the Langmuir isotherm model, Q_0 and b were calculated from the slope and intercept of the linear plots in Figure 6, respectively, to be 523.26 mg g^{-1} and 0.0026 L mg^{-1} . The regression coefficient was determined to be 0.90. The parameters for the Freundlich and Langmuir isotherm models are summarized in Table 5.

Table 5. Freundlich and Langmuir isotherm constants for the adsorption of COD in GAC.

Freundlich Isotherm Constants			Langmuir Isotherm Constants		
$K_F \text{ (mg g}^{-1}\text{)}$	n	R^2	$Q_0 \text{ (mg g}^{-1}\text{)}$	$K_L \text{ (L mg}^{-1}\text{)}$	R^2
17.68	2.27	0.78	523.26	0.0026	0.90

The feasibility of the Langmuir isotherm was determined with a dimensionless constant separation factor or equilibrium parameter, R_L , which was calculated using Equation (3). R_L values fluctuated between 0.19 and 0.67, which evidences favorable adsorption of organic materials onto granular activated carbon due to the fact that the system is suitable at R_L values in the range of 0–1.

$$R_L = \{1/[1 + (K_L * C_0)]\} \quad (3)$$

where K_L is the Langmuir constant (L mg^{-1}) and C_0 is the initial COD concentration.

The Freundlich isotherm model performed well in heterogeneous and multilayer adsorption systems, whereas the Langmuir isotherm model performed well in monolayer adsorption with uniform and homogenous adsorbent surfaces. Although the isotherm studies conducted in this study showed that both the Freundlich and Langmuir isotherm models fit the adsorption of COD on GAC, the Langmuir isotherm model was more appropriate than the Freundlich isotherm model due to its greater regression coefficient.

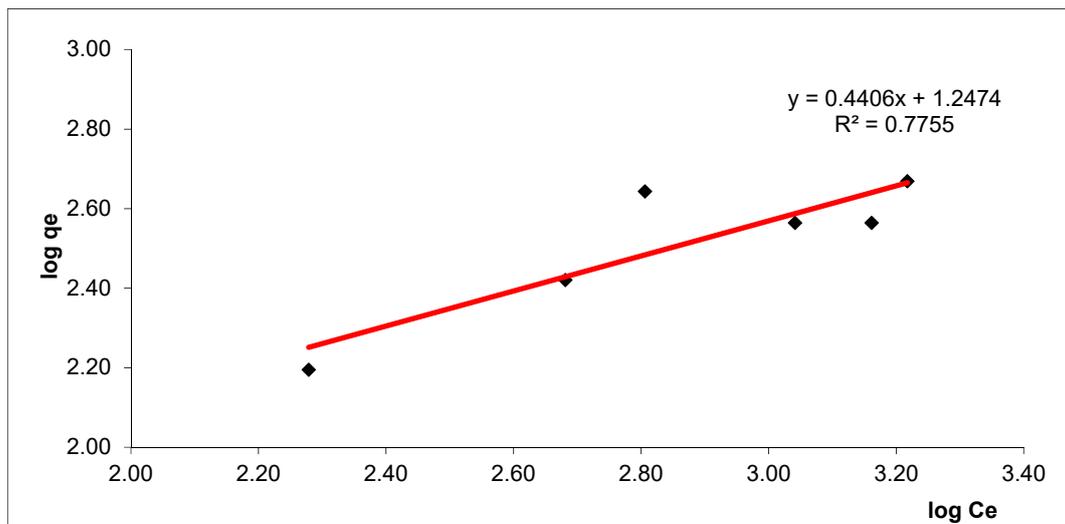


Figure 5. Freundlich adsorption isotherm.

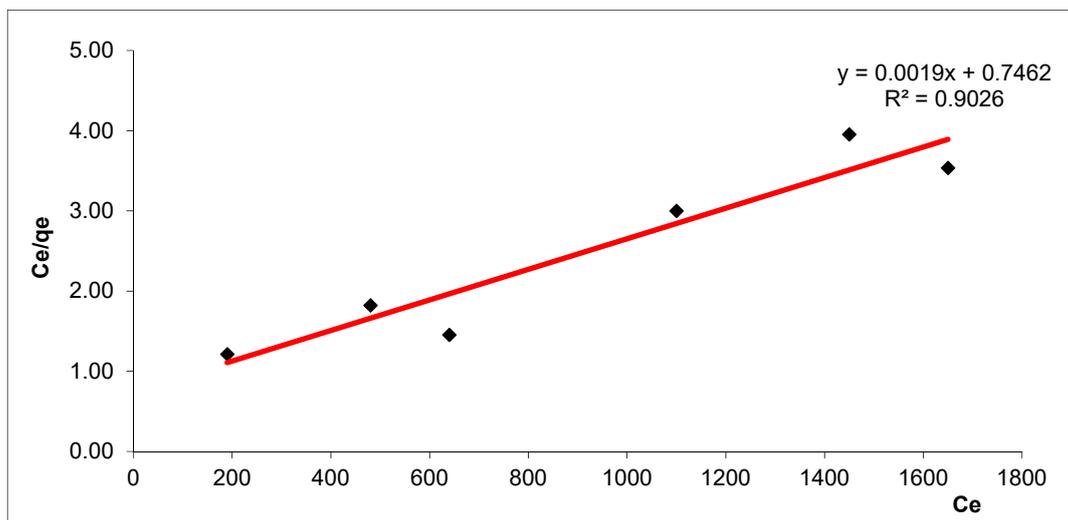


Figure 6. Langmuir adsorption isotherm.

4. Conclusions

In this study, the treatability of bilge water by Fenton oxidation followed by adsorption was investigated. The optimum operational conditions for adsorption, which resulted in a total COD removal efficiency of $89.5 \pm 1.9\%$ (corresponding to $115.0 \pm 21.2 \text{ mg O}_2 \text{ L}^{-1}$ organic matter concentration), were identified to as follows: an equilibrium time of 24 h, an adsorbent dosage of 2 GAC L^{-1} , a temperature of $20 \text{ }^\circ\text{C}$, and $\text{pH} = 6$. Freundlich and Langmuir isotherm models were compared in order to determine their applicability. Both isotherm models presented a good fits for the adsorption of organic materials on granular activated carbon. The Langmuir isotherm model was considered more suitable than the Freundlich isotherm model due to its greater regression coefficient. Fenton oxidation followed by granular activated carbon has shown promising potential for the treatment of bilge water from an economical perspective.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/w13192792/s1>: Figure S1: Process flow diagram of Haydarpassa Waste Reception Plant.

Author Contributions: Ç.Ö. carried out the laboratory analyses, analyzed the data, conducted the literature research, and wrote and submitted the manuscript. E.Ç. contributed to identifying the research problem and research gap. Both authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Istanbul University Scientific Research Funds, grant number 27466.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors also would like to thank Ömür Temizel for her help at the laboratory studies.

Conflicts of Interest: The authors declare no conflict of interest.

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