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A novel eco-friendly advanced enzymatic Fenton oxidation process for the treatment of ship wastewater

Nagihan Ersoy Korkmaz[a], Abdullah Aksu[a], Omer S. Taskin[a], Ertugrul Aslan[b], Nuray Balkis[a,*]

[a]*Department of Chemical Oceanography, Institute of Marine Science and Management, Istanbul University, Vefa 34134, Istanbul, Turkey, emails: nbal@istanbul.edu.tr (N. Balkis), nagihan.ersoy@istanbul.edu.tr (N.E. Korkmaz), aaksu@istanbul.edu.tr (A. Aksu), omert@istanbul.edu.tr (O.S. Taskin)*

[b]*Environment Institute, Marmara Research Center-TUBITAK, Gebze, Kocaeli, Turkey, email: ertugrul.aslan@tubitak.gov.tr*

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ABSTRACT

The chemical treatment of ship wastewater with high organic content was investigated by an advanced Fenton oxidation process with the addition of a laccase enzyme. In addition, this process was aimed both to reduce the amount of chemicals used in the Fenton process and to minimise the amount of organic matter in the sludge. Ship wastewater was obtained from the Haydarpaşa (Kadıköy/İstanbul/Turkey) waste management facility. This wastewater was treated in the range of pH 3–5 with classic Fenton and a new kind of Fenton method (enzymatic Fenton), and then the treatment results were compared. At a constant mixture speed and temperature, chemical oxygen demand, turbidity, colour and total organic carbon (TOC) values were examined by changing the ratio of Fe^{2+}/H_2O_2, Fe^{2+}/laccase enzyme. In this study, the best treatment efficiency was measured at pH = 5 using the new advanced enzymatic Fenton method. The best treatment efficiency was 98.5%. This higher value was achieved using 200 mg/L H_2O_2 and 200 mg/L laccase. In addition, using this new Fenton method (enzymatic Fenton), TOC concentration is quite low (0.26%) when compared with the classic Fenton method. This advanced eco-friendly method is an alternative to other treatment methods. Thus, ship wastewater containing heavily organic loads can be treated using this new advanced method. Additionally, the residue treatment of mud containing heavy organic carbon loads can also be treated using this new advanced method.

Keywords: Ship; Wastewater; Enzymatic Fenton; Treatment; Eco-friendly

1. Introduction

It is generally established that mainly shipping is chosen for the transportation of goods worldwide, rather than road, rail or airfreight. In other words, it is cheaper than the other means of transport. Nevertheless, all vessels generate pollution such as waste, which is now regulated by the requirements of the International Convention for the Prevention of Pollution from Ships, 1973, as modified by the Protocol of 1978 (MARPOL 73/78) and the International Safety Management Code, both under the auspices of the International Maritime Organisation. Legislation is also in place throughout the European Union relating to the requirements for ports to provide reception facilities for ship-generated waste that cannot be disposed of at sea, in compliance with the MARPOL 73/78 regulations. In other words, shipboard waste is streamed according to MARPOL 73/78 Annexes I–VI, which govern pollution control and disposal of ship-generated waste and prohibit discharges in designated 'Special Areas'. Waste is streamed as oil, hazardous waste, wastewater (black or grey), solid waste and air pollution, falling under MARPOL Annexes I, III, IV, V and VI [1].

Turkey became party to the MARPOL Convention, which is the main international convention concerning the prevention of pollution by ships in the marine environment, in 1990, and the 'Reception of Wastes from Ships and Waste Control Regulation' entered into force on 26 December 2010. The aim

* Corresponding author.

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of the Regulation is to set up procedures and principles on building and operating waste reception ships, for the purpose of collecting waste from ships, storing such wastes and transporting wastes to waste disposal facilities in order to avoid the discharge of wastes originating from ship operations in the maritime areas under the jurisdiction of Turkey [1]. The provisions of this Regulation cover all ships, waste reception facilities, waste reception ships and the transfer of waste to disposal facilities in maritime areas. According to the scope of this regulation, port managers are responsible for the reception of solid and liquid waste (bilge water, sludge, dirty ballast, waste oil, slop, etc.), which includes petroleum or petroleum derivates originating from the normal activities of ships within the context of MARPOL Annex I, toxic liquid substance waste; MARPOL Annex 2, sewage; MARPOL Annex 4, solid waste; MARPOL 73/78 Annex 5 and cargo residues at waste reception facilities.

Ship wastewater is the general term used for bilge water, ballast water, slops, sludge and domestic wastewater (MARPOL 73/78 Annex-I). Bilge water is water leaking from sub-machine tanks, ship warehouse or other similar departments. Ballast water is sea water used to fill ballast tanks to ensure ship stability and is released back into the sea at the harbour. Slop is composed of oil and petroleum-derived oily wastewater and is accumulated in the slop tanks. Sludge consists of residue and oil precipitates in the cargo tanks of oil tankers and the machine compartment of ship fuel tanks. Domestic wastewater is used by passengers and ship staff in the kitchen and the toilets. Several agreements have been signed to avert marine pollution from vessels. One of them is the MARPOL 73/78 Convention. One of the most significant conditions of this agreement is the collection of ship wastewater at waste reception facilities (MARPOL 73/78). Storage locations of ship wastewaters in Turkey are given in Table 1. The first waste reception facilities were founded at Haydarpaşa in order to collect waste from ships. The Haydarpaşa Waste Reception Facility has been collecting waste from ships since 2006, based on the

Table 1
Storage locations of ship wastewater in Turkey [3]

Location[a]	Tank capacity (m^3/day)	Treatment capacity (m^3/day)
TCDD Haydarpaşa Harbor	107	240
TCDD Mersin Harbor	275	720
TCDD İskenderun Harbor	80	240
TCDD Samsun Harbor	80	240
TCDD Derince Harbor	51	240
TCDD Bandirma Harbor	155	480
TCDD İzmir Harbor	400	648
TCDD İstanbul Harbor	100	120
TCDD Giresun Harbor	100	120
TCDD Trabzon Harbor	100	120
TCDD Hopa Harbor	100	120

[a]TCDD: Turkish State Railways.

International Convention for the Prevention of Pollution from Ships (MARPOL 73/78) [1,2].

Various technologies are available for wastewater treatment, such as physical, biological and chemical processes. Chemical oxidation is a process used to degrade pollutant organic molecules into carbon dioxide and water (full mineralization) [4–13]. Fenton's oxidation process is one of the most influential advanced oxidation processes used for the treatment of organic pollution in wastewater [8,14–18]. This process is based on the formation of hydroxyl radicals as a result of ferric ions and hydrogen peroxide reaction at acidic pH. Highly reactive hydroxyl radicals react with organic compounds in order to treat wastewater pollutants [15]. The advantages of the Fenton method include very fast oxidation, low cost and applicability in different processes, but the disadvantages comprise the cost of disposal of produced sludge, continuation of the normal chemical reactions and a potential polymerization reaction [17,18,19–21].

Laccase enzymes (EC 1.10.3.2, benzenediol: oxygen oxidoreductase), which are isolated from certain plants, insects and mainly fungi, are a group of oxidative enzymes [19]. Laccase oxidation is an environmentally friendly method used for the treatment of pollution [22].

Lately, laccase enzymes have been studied increasingly in scientific research projects owing to their implementation in various industrial sectors [19]. Laccase enzymes have been used for catalysis of the oxidation of aminophenol, ortho and paradifenols, polyamines and polyphenols, [23] the fragmentation of environmental pollution, bleaching of pulp in the paper industry, the improvement of food industry wastewater, biosensor, [19] denim washing and textile dye decolourization [24].

In this study, we investigated the chemical treatment of ship wastewater using an eco-friendly advanced Fenton oxidation process to reduce the disadvantages of the classic Fenton process. This process is based on the addition of a laccase enzyme to Fenton oxidation reagents. The aim of this study was first to achieve the best treatment efficiency using an alternative newly developed treatment method. Second, the study aimed at the amount of organic matter in sludge. The most important result of this new method is minimisation of the amount of H_2O_2. For this reason, the new method is considered an eco-friendly method.

2. Materials and methods

2.1. Ship wastewater

The ship wastewater samples were obtained from Haydarpaşa waste management facility in Istanbul, Turkey. In this study, we analysed the wastewater remaining after the physical separation of ship wastewater at waste reception facilities. The ship wastewater samples were preserved at room temperature. The wastewater was a dark brown mixture and its main characteristics are presented in Table 2.

2.2. Chemicals

Hydrogen peroxide [(Merck (Darmstadt/Germany), 35% (w/v)], ferrous(II) sulphate heptahydrate (Sigma-Aldrich (Overijse/Belgium), 99.5%), Laccase from *Pleurotus ostreatus*

Table 2
Characteristics of the tested ship wastewater

Parameter (unit)	Mean
COD (mg/L)	2,393
Turbidity (NTU)	64.6
Colour 680[a]	0.15

[a]Absorbance at 680 nm.

(mushroom) (Sigma-Aldrich), sodium hydroxide (Merck, 99%) and sulphuric acid (Merck, 96.5%) were used as received.

2.3. Analytical procedures

The closed reflux titrimetric method (5220 C) was used to determine chemical oxygen demand (COD) [20]. The quantity of hydrogen peroxide consumed was measured by the iodometric titration method using a molybdate catalyst. In this study, the correction was carried out according to the following formula of Kang et al. [7]:

$$\text{COD (mg/L)} = \text{COD}_m - f\,[H_2O_2]$$

$$f = 0.4706 - (4.06 \times 10^{-5})\,[H_2O_2]$$

In this formula:

f = correction factor

COD_m = measured COD concentration with H_2O_2 interference (mg/L) [7].

Turbidity of the solution was measured with a nephelometric turbidimeter (2100P IS Hach).

A spectrophotometer (SHIMADZU UV-1800) was used for the determination of colour at 680 nm. The colour removal ratio was calculated by dividing the difference between initial and final absorbance with initial absorbance at 680 nm [25].

Total organic carbon (TOC) was determined by PerkinElmer CHNS element analyzer.

2.4. Experiments

We performed four different alternative wastewater treatment experiments.

2.4.1. Enzymatic Fenton treatment

The oxidation of 300 mL ship wastewater samples was carried out in 1 L glass beakers at ambient temperature. 0.1 M H_2SO_4 or 1 N NaOH was added to the wastewater in order to adjust the pH values in the range of 3–5 [14]. $FeSO_4.7H_2O$ was added to obtain the intended Fe^{2+} concentration. A 300 mg/L ferric ion dose was used. In this newly developed method, H_2O_2 and laccase were used at different concentrations in order to determine the best treatment efficiency. The treatment efficiency value was also calculated per reagent amount. Seven different concentrations of catalyst, H_2O_2 and laccase enzyme were applied at 200, 400, 600, 700, 800, 900 and 1,000 mg/L (1/1 w/w). When all reagents were incorporated, the wastewater was stirred at a mixing speed of 100 rpm for 30 min [26]. After the oxidation process, the pH value was adjusted to the 7–8 range using sodium hydroxide. Then we waited for precipitation to occur for 1 h [14]. At the end of treatment, COD, turbidity and colour analyses were performed in the water. Finally, TOC analyses were carried out in the sludge.

2.4.2. Classic Fenton treatment

The oxidation of 300 mL ship wastewater samples was carried out in 1 L glass beakers at ambient temperature. 0.1 M H_2SO_4 or 1 N NaOH was added to the wastewater in order to obtain pH values in the range of 3–5 [14]. $FeSO_4.7H_2O$ was added to obtain the intended Fe^{2+} concentration. A 300 mg/L ferric ion dose was used. A different dosage of H_2O_2 was used. Three different concentrations of H_2O_2 were applied at 200, 700 and 1,000 mg/L. When all reagents were incorporated, the wastewater was stirred at a mixing speed of 100 rpm for 30 min [26]. After the oxidation process, the pH value was adjusted to the 7–8 range using sodium hydroxide. Then we waited for precipitation to occur for 1 h. At the end of treatment, COD, turbidity and colour analyses were performed in the water. Finally, TOC analyses were carried out in the sludge.

2.4.3. Treatment of wastewater using iron ions and laccase enzyme without hydrogen peroxide

The oxidation of 300 mL ship wastewater samples was carried out in 1 L glass beakers at ambient temperature. 0.1 M H_2SO_4 or 1 N NaOH was added to the wastewater in order to obtain pH values in the range of 3–5. $FeSO_4.7H_2O$ was added to obtain the intended Fe^{2+} concentration. A 300 mg/L ferric ion dose was used. A different dosage of laccase enzyme was used. Three different concentrations of laccase enzyme were applied at 200, 700 and 1,000 mg/L. When all reagents were incorporated, the wastewater was stirred at a mixing speed of 100 rpm for 30 min. After the oxidation process, the pH value was adjusted to the 7–8 range using sodium hydroxide. Then we waited for precipitation to occur for 1 h. At the end of treatment, COD, turbidity and colour analyses were performed in the water. Finally, TOC analyses were carried out in the sludge.

2.4.4. Treatment of wastewater using iron ions without hydrogen peroxide and laccase enzyme

The oxidation of 300 mL ship wastewater samples was carried out in 1 L glass beakers at ambient temperature. 0.1 M H_2SO_4 or 1 N NaOH was added to the wastewater in order to obtain pH values between 3 and 5. $FeSO_4.7H_2O$ was added to obtain the intended Fe^{2+} concentration. A 300 mg/L ferric ion dose was used. Then the wastewater was stirred at a mixing speed of 100 rpm for 30 min. After the oxidation process, the pH value was adjusted to the 7–8 range using sodium hydroxide. Then we waited for precipitation to occur 1 h. At the end of treatment, COD, turbidity and colour analyses were performed in the water. Finally, TOC analyses were carried out in the sludge.

3. Results and discussion

The results of this research are given under four main subheadings, namely, enzymatic Fenton treatment, classic Fenton treatment, treatment of wastewater using iron ions and laccase enzyme without hydrogen peroxide and treatment of wastewater using iron ions without hydrogen peroxide and laccase enzyme. In this study, we examined the changes of certain parameters. These parameters are pH, amount of laccase enzyme and H_2O_2. Optimum H_2O_2 and laccase enzyme amounts were determined using the enzymatic Fenton method at pH = 3, 4 and 5, respectively. We investigated optimum H_2O_2 and laccase enzyme amounts, which reached the highest yield in the enzymatic Fenton treatment method. The classic Fenton experiment was carried out using these optimum quantities. Then, the productivity of the advanced oxidation method using the laccase enzyme without hydrogen peroxide method was investigated. Finally, the effect of the use of iron ions without hydrogen peroxide and laccase enzyme on the efficiency of the advanced oxidation method was investigated.

3.1. Enzymatic Fenton treatment

Fig. 1(a) shows that the highest COD values were 414.74, 334.4 and 436 mg/L at pH = 3, 4 and 5, and 800, 400 and 600 mg/L H_2O_2 and laccase enzyme, respectively. The lowest COD values were 0, 104.6 and 36.64 mg/L at pH = 3, 4 and 5, and 1,000, 600 and 200 mg/L (1/1 w/w) H_2O_2 and laccase enzyme, respectively. As shown in Fig. 1(b), enzymatic Fenton treatment at pH = 3, 4 and 5 (1,000, 600 and 200 mg/L 1/1 w/w H_2O_2, and laccase enzyme) resulted in maximum COD removal from ship wastewater efficiencies (100%, 95.63% and 98.46%), respectively. Minimum COD removal efficiencies (82.7%, 86% and 81.8%) were also obtained using 800, 400 and 600 mg/L H_2O_2 and laccase enzyme at pH = 3, 4 and 5, respectively.

As shown in Fig. 1(c), the highest colour removal efficiency of 98.6% was achieved by enzymatic Fenton treatment at pH = 3 using 200, 400 and 800 mg/L H_2O_2 and laccase enzyme (1/1 w/w), respectively. The highest colour removal efficiency of 100% was achieved using 1,000 mg/L H_2O_2 and laccase enzyme (1/1 w/w) at pH = 4. The highest colour removal efficiency of 100% was also found using 200, 400, 900 and 1,000 mg/L H_2O_2 and laccase enzyme (1/1 w/w) at pH = 5. In contrast, the lowest colour removal efficiencies of 90%, 94.66% and 96.66% were determined at pH = 3, 4 and 5 using 700, 900 and 600 mg/L H_2O_2 and laccase enzyme (1/1 w/w), respectively. As shown in Fig. 1(d), the highest turbidity values were 5.8, 39.6 and 51.3 NTU at pH = 3, 4 and 5 using 700, 800 and 1,000 mg/L H_2O_2 and laccase enzyme, respectively. The lowest turbidity values were 1.18, 4.81 and 1.77 NTU at pH = 3, 4 and 5, and 1,000, 400 and 400 mg/L (1/1 w/w) H_2O_2 and laccase enzyme, respectively. Fig. 1(e) shows that the maximum TOC removal efficiencies in the waste sludge (3.28%, 1.98% and 0.98%) were obtained using 900, 700 and 1,000 mg/L (1/1 w/w) H_2O_2 and laccase enzyme at pH = 3, 4 and 5, respectively. Minimum TOC removal efficiency (0%) was determined using 600, 800 and 1,000 mg/L (1/1 w/w) H_2O_2 and laccase enzyme at pH = 3. The lowest TOC removal efficiency (0%) was found using 800 and 900 mg/L (1/1 w/w) H_2O_2 and laccase enzyme at pH = 4. Finally, the lowest TOC removal efficiency (0.26%) was obtained using 200 mg/L (1/1 w/w) H_2O_2 and laccase enzyme at pH = 5. As shown in Fig. 1(f), the highest residual H_2O_2 values were 16.32 and 70.4 mg/L at pH = 3 and 5 using 800 and 1,000 mg/L (1/1 w/w) H_2O_2 and laccase enzyme, respectively. The highest residual H_2O_2 value of 25.16 mg/L was measured using 900 and 1,000 mg/L (1/1 w/w) H_2O_2 and laccase enzyme at pH = 4. The lowest residual H_2O_2 values of 0 mg/L were also achieved using 200 and 400 mg/L (1/1 w/w) H_2O_2 and laccase enzyme at pH = 3. The lowest residual H_2O_2 values of 0 mg/L were found using 200, 400 and 600 mg/L (1/1 w/w) H_2O_2 and laccase enzyme at pH = 4. Similarly, the lowest residual H_2O_2 values of 0 mg/L were also determined using 200 and 400 mg/L (1/1 w/w) H_2O_2 and laccase enzyme at pH = 5.

3.2. Classic Fenton treatment

Fig. 2(a) shows that the highest COD values were 1,912, 1,486 and 1,533 mg/L at pH = 3, 4 and 5, and 200 mg/L H_2O_2, respectively. The lowest COD values were 377.7, 294.4 and 912.8 mg/L at pH = 3, 4, 5, and 1,000, 700 and 1,000 mg/L H_2O_2, respectively. As shown in Fig. 2(a), Fenton treatment at pH = 3, 4 and 5 (1,000, 700 and 1,000 mg/L H_2O_2) resulted in the maximum COD removal from ship wastewater efficiencies (85%, 87% and 61%), respectively. Minimum COD removal efficiencies (20.99%, 37.8% and 35.9%) were obtained using 200 mg/L H_2O_2 at pH = 3, 4 and 5, respectively. As shown in Fig. 2(b), the highest turbidity values were 9.87, 8.23 and 5.44 NTU at pH = 3, 4 and 5 using 200, 700 and 200 mg/L H_2O_2, respectively. In contrast, the lowest turbidity values were 0.81, 8.22 and 5.04 NTU at pH = 3, 4 and 5, and 1,000, 200 and 1,000 mg/L H_2O_2, respectively.

As shown in Fig. 2(b), the highest colour removal efficiencies of 93.33%, 100% and 100% were achieved by the Fenton treatment at pH = 3, 4 and 5 using 700, 200 and 1,000 mg/L H_2O_2, respectively. The lowest colour removal efficiencies of 98%, 95.33% and 95.33% were achieved at pH = 3, 4 and 5 using 1,000, 700 and 200 mg/L H_2O_2, respectively. Fig. 2(c) shows that the maximum TOC removal efficiencies in the waste sludge (10.54%, 9.54% and 9.04%) were obtained using 200 mg/L H_2O_2 at pH = 3, 4 and 5, respectively. Minimum TOC removal efficiency (0.032%, 6.35% and 4.07%) was found using 1,000, 700 and 1,000 mg/L H_2O_2 at pH = 3, 4 and 5, respectively. As shown in Fig. 2(c), the highest residual H_2O_2 values were 34.68, 2.72 and 13.6 mg/L at pH = 3, 4 and 5 using 1,000, 700 and 1,000 mg/L H_2O_2, respectively. On the contrary, the lowest residual H_2O_2 values of 1.36, 0.68 and 0 mg/L were also measured using 200 mg/L H_2O_2 at pH =3, 4 and 5.

3.3. Treatment of wastewater using iron ions and laccase enzyme without hydrogen peroxide

Fig. 3(a) shows that COD values were 153.8 and 105.6 mg/L at pH = 3 and 4, and 700 mg/L laccase enzyme, respectively. The highest and lowest COD values were 273.68 and 119.68 mg/L at pH = 5, and 200 and 1,000 mg/L laccase enzyme, respectively. As shown in Fig. 3(b), laccase enzyme treatment at pH = 3 and 4 (700 mg/L laccase enzyme) resulted in COD removal efficiencies of 93.5% and 95.58% from

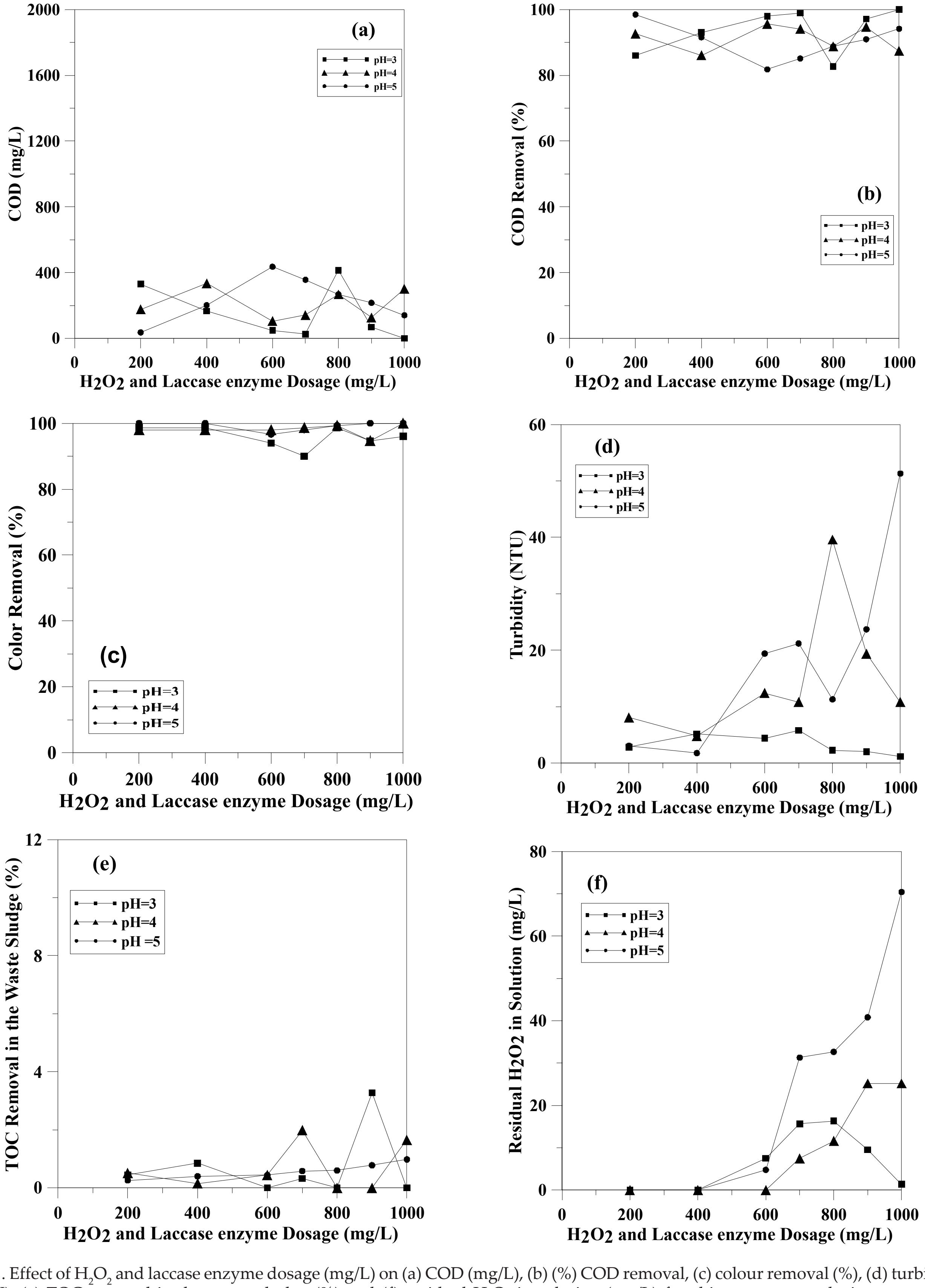

Fig. 1. Effect of H_2O_2 and laccase enzyme dosage (mg/L) on (a) COD (mg/L), (b) (%) COD removal, (c) colour removal (%), (d) turbidity (NTU), (e) TOC removal in the waste sludge (%) and (f) residual H_2O_2 in solution (mg/L) for ship wastewater during enzymatic Fenton treatment at pH values 3, 4 and 5 (iron powder 300 mg/L), respectively.

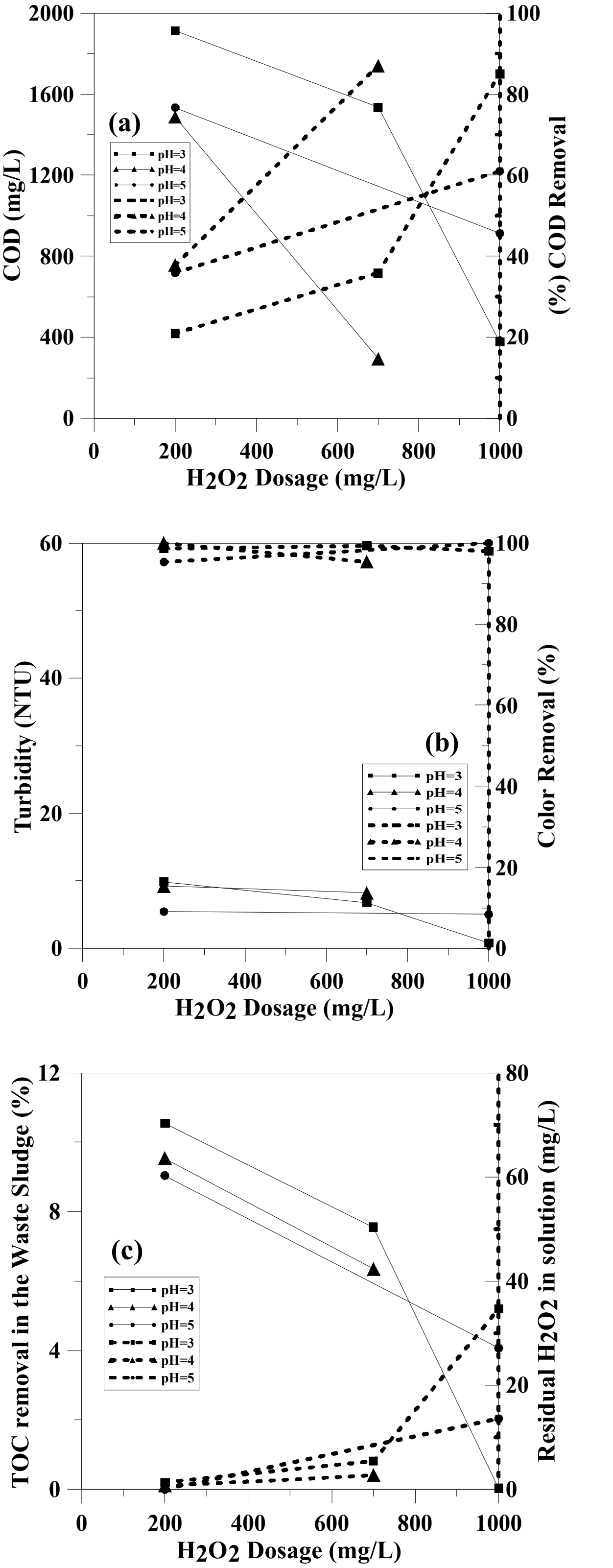

Fig. 2. Effect of H_2O_2 dosage (mg/L) on (a) COD (mg/L) and (%) COD removal, (b) turbidity (NTU) and colour removal (%) and (c) TOC removal in the waste sludge (%) and residual H_2O_2 in solution (mg/L) for ship wastewater during enzymatic Fenton treatment at pH values 3, 4 and 5 (iron power 300 mg/L).

ship wastewater, respectively. The highest and lowest COD removal efficiencies (95% and 88.56%) were obtained using 1,000 and 200 mg/L laccase enzyme at pH = 5, respectively. As shown in Fig. 3(c), colour removal efficiencies of 98.66% and 99.33% were obtained by the laccase enzyme treatment method at pH = 3 and 4 using 700 mg/L laccase enzyme, respectively.

The highest and lowest colour removal efficiencies of 100% and 99.33% were determined at pH = 5 using 1,000 and 200 mg/L laccase enzyme, respectively. As shown in Fig. 3(d), turbidity values were 4.79 and 7.78 NTU at pH = 3 and 4 using 700 mg/L laccase enzyme, respectively. The highest and lowest turbidity values were found as 15.4 and 10.9 NTU at pH = 5, and 1,000 and 200 mg/L laccase enzyme, respectively. Fig. 3(e) shows that TOC removal efficiencies in the waste sludge (3.94% and 3.4%) were obtained using 700 mg/L laccase enzyme at pH = 3 and 4, respectively. The maximum and minimum TOC removal efficiencies (3.8% and 1.8%) were found using 200 and 1,000 mg/L laccase enzyme at pH = 5.

In this study, first, we achieved chemical treatment of ship wastewater containing heavy organic matter using the eco-friendly advanced enzymatic Fenton process, based on the addition of a laccase enzyme to the classic Fenton oxidation method. Second, ship wastewater obtained from Haydarpaşa Harbor was also treated using classic Fenton oxidation processes. Then, the results of both these methods were compared and discussed with respect to COD removal, colour, turbidity of wastewater and TOC residue in sludge. The advantages and disadvantages of these methods are given in Table 3.

The lowest COD value of 36.64 mg/L was measured by the enzymatic Fenton treatment at pH = 3 and 5 using 1,000 and 200 mg/L H_2O_2 and laccase enzyme, respectively. In contrast, the lowest COD value was 294.401 mg/L at pH = 4, and 700 mg/L H_2O_2 in the classic Fenton treatment. Besides, the lowest COD value (105.6 mg/L) was also obtained using 700 mg/L laccase enzyme at pH = 4 – treatment of wastewater using laccase enzyme without hydrogen peroxide. These results indicate that the enzymatic Fenton process lowered the COD value compared with other treatments. On the other hand, the lowest COD value of the enzymatic Fenton treatment was determined at pH = 3. The basic aim of this study was to obtain maximum treatment using the minimum amount of chemical. Therefore, the most effective enzymatic Fenton treatment was achieved with a low COD value of 36.64 mg/L using minimum chemical (200 mg/L H_2O_2 and laccase enzyme) at pH = 5.

Maximum COD removal efficiencies were 100% and 98.46% at pH = 3 and 5, and 1,000 and 200 mg/L H_2O_2 and laccase enzyme, respectively. At pH = 4, the treatment efficiency of the COD value was higher than 80% when using the enzymatic Fenton and classic Fenton method, separately. Additionally, at the same pH value, the treatment efficiency of COD was calculated without H_2O_2 being higher than 85%. The best treatment result was obtained using the enzymatic Fenton process with the minimum amount of chemical reagents (200 mg/L H_2O_2 and laccase enzyme). We compared enzymatic (eco-friendly method) treatment efficiency with classic Fenton treatment efficiency. For this comparison, we also used treatment without H_2O_2. As a result, treatment efficiency changed as follows: enzymatic Fenton treatment > laccase enzyme without hydrogen peroxide treatment > classic Fenton treatment.

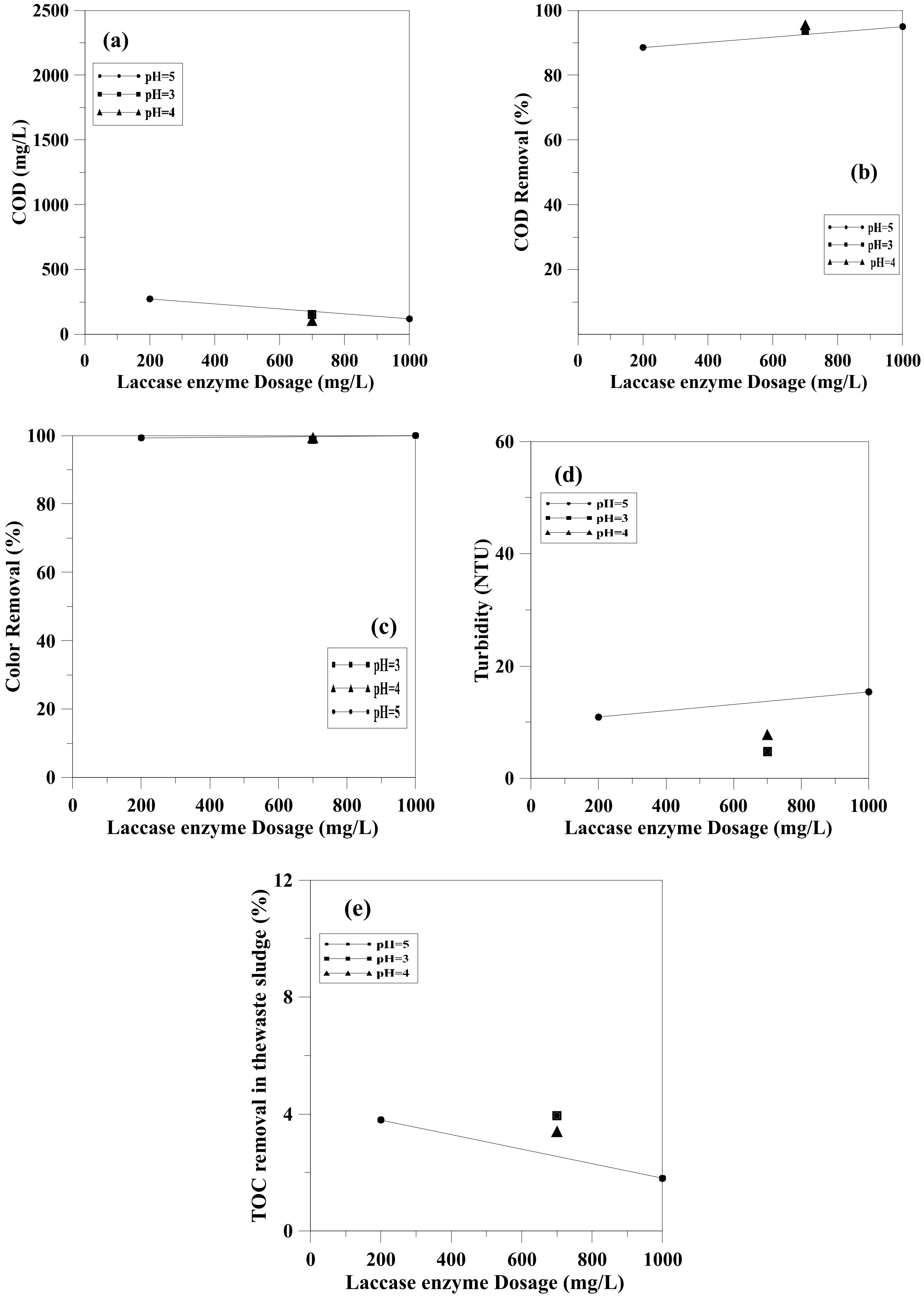

Fig. 3. Effect of laccase enzyme dosage (mg/L) on (a) COD (mg/L), (b) (%) COD removal, (c) colour, (d) turbidity (NTU) and (e) TOC removal in the waste sludge (%) for ship wastewater during enzymatic Fenton treatment at pH values 3, 4 and 5 (iron powder 300 mg/L), respectively.

Table 3
Comparison of enzymatic Fenton treatment and Fenton treatment

Fenton treatment [26,27]		Enzymatic Fenton treatment [19,24]
Advantages	Disadvantages	Advantages
Initial investment cost is low	High chemical cost	Low chemical cost
Reduces toxicity for biological treatment	The cost of disposal of the resulting sludge	The organic carbon of the resulting sludge is low
Applicability to different processes	Formation of the polymerization reactions	Low treatment cost for sludge
Removal of toxic and durable compounds	Continuation of the chemical reactions	No residual hydrogen peroxide in the solution
The oxidation speed is very high	Corrosion problems	Laccase enzyme is an environmentally friendly chemical which reduces the use of hydrogen peroxide
Oxidation waiting time is low	Removal of foam formation	Less foam formation

Good turbidity removal was achieved at different pH and concentrations in the enzymatic Fenton treatment. The best removal result (3.07 NTU) was determined when using the enzymatic Fenton treatment with 200 mg/L H_2O_2 and laccase enzyme at pH = 5. In the classic Fenton treatment, the best turbidity removal was obtained at pH = 3 using 1,000 mg/L H_2O_2. Nevertheless, the amount of hydrogen peroxide used in this treatment is higher than the value of enzymatic Fenton treatment. For this reason, enzymatic Fenton [Fe^{2+}/H_2O_2/laccase enzyme] has more advantages than classic Fenton [Fe^{2+}/H_2O_2] as regards turbidity removal in wastewater. Additionally, good turbidity removal was also found when the use of a laccase enzyme without hydrogen peroxide in a treatment process. According to this result, laccase enzyme without hydrogen peroxide treatment can be used as an alternative method for turbidity removal in wastewater.

The best (100%) colour removal was achieved using the minimum amount of chemical substance (200 mg/L H_2O_2 and laccase enzyme) in all treatments: enzymatic Fenton, classic Fenton and laccase enzyme without hydrogen peroxide. The experimental results indicate that all three methods are very effective for colour removal in ship wastewater.

TOC content of the waste sludge is generally quite high and reduction requires additional treatment methods. This leads to high costs. For this reason, minimised TOC content is very important in waste sludge and especially ship waste. In this study, good TOC removal was achieved at different pH values and concentrations in the enzymatic Fenton treatment. The best removal result (0.26%) was also obtained using the enzymatic Fenton oxidation process with 200 mg/L H_2O_2 and laccase enzyme at pH = 5. In other words, the TOC content of waste sludge after chemical treatment using classic Fenton treatment and laccase enzyme without hydrogen peroxide treatment was higher than for the enzymatic Fenton process. It is concluded that enzymatic Fenton is the most effective method as it does not generate excess waste in wastewater treatment.

The analysis of the results of the enzymatic Fenton treatment at pH values of 3, 4 and 5 indicates that hydrogen peroxide was completely consumed during the treatment process, respectively. This result was found when H_2O_2 and laccase enzyme were used; 200 and 400 mg/L, respectively. In addition, the cost was also reduced because of the small quantity of chemicals used in the enzymatic Fenton process. However, extra waste, especially hydrogen peroxide, was generated during the classic Fenton treatment. For this reason, enzymatic Fenton treatment is more advantageous than classic Fenton treatment.

Additionally, ship wastewater treatment was also carried out using iron(II) ions without hydrogen peroxide and laccase enzyme. In this case, all water quality parameters such as COD, turbidity, colour and residual TOC and the amount of hydrogen peroxide in the waste sludge were found to be quite higher than in both the enzymatic Fenton and classic Fenton oxidation process. In other words, physical treatment occurred with coagulations by using iron(II) ions only. The high percentage of TOC in the waste sludge also supports this result.

4. Conclusion

Chemical treatment of ship wastewater, containing large quantities of both organic matter and COD, using an advanced oxidation process with the addition of a laccase enzyme to a classic Fenton method was accomplished successfully. The main findings can be summarised as follows:

- This method is an eco-friendly and low-cost treatment method;
- Most of the chemicals used in the enzymatic Fenton treatment, especially hydrogen peroxide, were completely consumed in the reaction;
- The amount of hazardous waste released as a result of enzymatic Fenton treatment was lower than for the classic Fenton treatment;
- TOC content of the waste sludge of enzymatic Fenton treatment was also quite lower than that of classic Fenton treatment;
- No additional pollution after treatment of wastewater with high COD content such as ship wastewater and
- No extra cost for sludge disposal associated with this treatment method and the equipment will be built as a prototype on ships and in harbours.

In conclusion, it is clear that the enzymatic Fenton oxidation method has more advantages than the classic Fenton process.

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