DAF-Treated Lube Oil Wastewater (DTLOWW) Treatment: Performance of Bench Scale and Pilot Scale Fenton Process

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Abstract

The lube oil wastewater is produced from Lube Oil Bending Facilities (LOBF) located in Egypt. Currently the lube oil wastewater is treated by oil separator followed by Dissolved Air Flotation (DAF) system. Unfortunately, DAF-Treated Lube Oil Wastewater (DTLOWW) contains high concentration of the soluble COD.

The first part of this work examined the treatability of DAF-Treated Lube Oil Wastewater (DTLOWW) using bench-scale Fenton process. Effects of H_2O_2, Fe^{2+} doses at different reaction time and wastewater strength have been studied. Optimum H_2O_2 dose was 0.8 g/l for normal DTLOWW strength (sCOD<2000 mg/l) and 1.2 g/l for high DTLOWW strength (sCOD>2000 mg/l). Optimum H_2O_2/$FeSO_4$ ratio of 3 was achieved for the normal and high strength DTLOWW at pH 3.5.

The Second part of this work studied the performance of Pilot-scale Fenton process. Pilot scale Fenton reactor was installed in the field and conducted under the optimum H_2O_2/$FeSO_4$ ratio that achieved from the bench scale work. The reactor was operating in batch basis at 8 hour cycle period divided in six phases. The results showed that residual sCOD was 788 ± 56 mg/l with sCOD removal of 53.6% which amply met with the local discharge Standards for discharging the industrial wastewater to the municipal sewage network. The Fenton process could be used for treatment of the DTLOWW with daily chemicals cost of 1.25-1.50 \$/m^3.

Keywords: Bench scale Fenton process; DAF-treated lube oil wastewater; DTLOWW; Pilot scale Fenton process

Introduction

Oily wastewaters is generated during production process of the Petrochemical industries [1,2]. Problems that may be created by the presence of oily wastewater in the Environment are endangering aquatic resources; endangering human health; atmospheric pollution, affecting crop production, destructing the natural landscape [1]. Therefore oily wastewater treatment is an interested area of research.

Different technologies have been reported in the literature for oily wastewater treatment. Some of these technologies are based on separation process such as Flotation [3,4], membrane with different types and materials [5,6]. Other technologies are based on oil degradation either by biological process [7,8], or by chemical oxidation processes [9-12].

Advanced Oxidation Processes (AOPs) have been reported as an emerged technologies in industrial wastewater treatment [13]. Oxidation with Fenton's reagent is based on hydrogen peroxide, ferrous ion and hydroxyl radicals generated by the catalytic decomposition of hydrogen peroxide in acidic solution [14]. Fenton's reagent has been reported to be effective in the treatment of refractory industrial wastewaters – 60% COD removal was achieved for oily wastewater [1].

In our previous work, application of AOPs in degradation of antibiotics in aqueous solution using Fenton [15], photo-Fenton [16],

TiO_2 photocatalysis [17], ZnO photocatalysis [18] were studied. In addition, technical and economic comparisons among different AOPs as well as simulation of Fenton process for treatment of an antibiotic aqueous solution were made [19,20]. However, limited number of pilot Fenton process has been reported; Barbusiński applied the Pilot Fenton scale in textile wastewater treatment [21].

The first part of this study examined the treatability of the DTLOWW using bench scale Fenton process. Effects of H_2O_2, Fe^{2+} doses at different reaction time and wastewater strength have been studied. In the Second part of this study, performance of pilot Fenton scale under specific operating conditions was studied.

Materials and Methods

Chemicals

Hydrogen peroxide (50% w/w) and ferrous sulphate ($FeSO_4 \cdot 7H_2O$) were purchased from local supplier.

DAF-Treated Lube Oil Wastewater (DTLOWW)

The lube oil wastewater is produced from a local Lube Oil Bending Facilities (LOBF). Currently the wastewater is treated by CPI oil separator followed by Dissolved Air Flotation (DAF) system. Unfortunately, DAF-Treated Lube Oil Wastewater (DTLOWW) contains high concentration of the soluble COD.

For the purpose of treatability study, two composite samples at different days have been collected from the DAF outlet. The sample

collection started from 11 am to 5 pm which covered the working day of the lube oil bending facilities. The sampling bottle of 2 l was filled every one hour throughout the working day. The collected sampling bottles were mixed together in a big container and kept in icebox. Thereafter, big container was sent to the National Research Center laboratory for analysis. The wastewater sample has been kept at 4°C throughout the treatability study period. The DTLOWW wastewater characteristics are summarized in Table 1.

Parameter	Unit	Normal strength (Sample 1)	High strength (Sample 2)
pH	-	6.3	7.6
Total suspended Solids (TSS)	mg/l	56 ± 10	225 ± 17
Soluble Chemical Oxygen Demand (sCOD)	mg/l	1500 ± 50	4800 ± 75
Biological Oxygen demand (BOD)	mg/l	865 ± 42	2150 ± 61
Total Nitrogen	mg/l	14.6	16.2
Phosphate (PO$_4$-P)	mg/l	1.2	5.6

Table 1: DTLOWW wastewater characteristics.

Analytical methods

Physico-chemical analysis of the samples and the treated effluent were carried out. The wastewater samples were analyzed for pH, soluble Chemical Oxygen Demand (sCOD), Biological Oxygen Demand (BOD), Total Suspended Solids (TSS), Total Phosphate (T.P), unless otherwise specified, were conducted according to the Standard Methods for water and wastewater [22].

Experimental setup and procedure

The experimental setup and procedures of Bench scale Fenton process and on-site pilot scale Fenton process are detailed as the followings sub-sections.

Stage 1: Lab scale Fenton process: Batch bench scale Fenton process experiments were conducted in a 600 ml Pyrex reactor with 500 ml of the DTLOWW. The pH of the solution was adjusted to the required value using H_2SO_4. The required amount of iron in the form of $FeSO_4.7H_2O$ was added to the DTLOWW and mixed by a magnetic stirrer. Thereafter, necessary amount of hydrogen peroxide was added gradually to the mixture and the time of the hydrogen peroxide addition was considered the beginning of the experiment. Samples were taken at pre-selected time intervals for studying the effect of reaction time. Thereafter, pH of the withdrawn samples was raised above 9 for iron precipitation and decomposing residual H_2O_2 [23]. Precipitated iron was separated from the reactor and the supernatant was used for measurement of soluble Chemical Oxygen Demand (sCOD).

On-site pilot scale Fenton process: On-Site pilot scale Fenton process reactor with volume of 1.0 m^3 was installed in the field. The pilot was equipped with suitable mixer. The mixer paddle was located at the three quarters of the reactor depth. The pilot was equipped with hydrogen peroxide, acid and alkaline dosing pumps. Figure 1 shows photo and schematic of the on-Site pilot scale Fenton process reactor. The DTLOWW feeding pumps was used to fill the reactor. The pH of the solution was adjusted to the required value using H_2SO_4. The required amount of iron in the form of $FeSO_4.7H_2O$ was added in solid form to the DTLOWW and the mixer was switched-on. Thereafter, the necessary amount of hydrogen peroxide was added to the mixture and the time of the hydrogen peroxide addition was considered the beginning of the reaction. The reaction continued for the predetermined time. At the end of the reaction time, pH of the solution was raised above 9 by operating the sodium hydroxide dosing pump. For achieving mixer neutralization, mixing continued for 30 min. Thereafter, mixing was stopped for iron precipitation and decomposing residual H_2O_2 [23]. The supernatant was used for the measurement of soluble Chemical Oxygen Demand (sCOD).
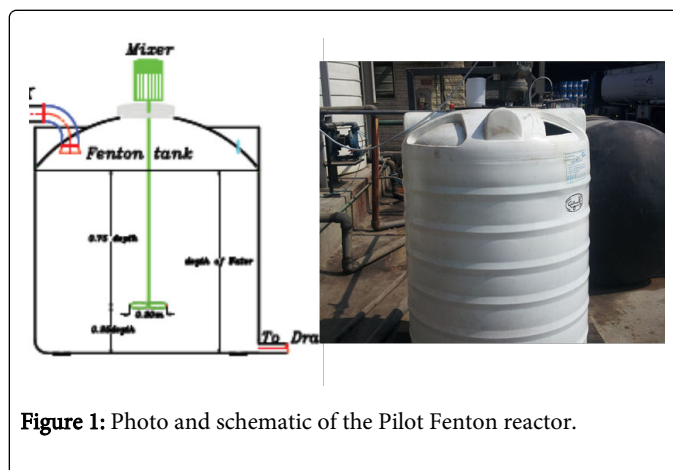

Figure 1: Photo and schematic of the Pilot Fenton reactor.

Results and Discussion

Lab scale Fenton process

Effect of H_2O_2/COD molar ratio: To study the effect of H_2O_2 dose on soluble COD (sCOD) removal, initial H_2O_2 dose was varied in the range of 0.8–2.4 g/l. Other operating conditions were; pH 3.5, initial sCOD 1500 mg/l, ferrous sulphate heptahydrate ($FeSO_4.7H_2O$) 0.70 mg/l and reaction time 150 min. The effect of H_2O_2 dose and Fenton reaction time on sCOD removal at initial sCOD of 1500 mg/l and 4800 mg/l in the form of residual sCOD are shown in Figure (2a) and (b), respectively. As shown in the figure, both H_2O_2 concentration and reaction time significantly affect the sCOD reduction. After 150 min reaction time, the residual sCOD was 300, 266, 391 and 637 mg/l for initial sCOD of 1500 mg/l; and 1641, 1366, 1508 and 2142 mg/l for initial sCOD of 4800 mg/l at H_2O_2 dose of 0.8, 1.2, 1.6 and 2.4 g/l, respectively. The achieved sCOD removal was 80.0, 82.30, 74.0 and 57.6% for initial sCOD of 1500 mg/l; and 65.3, 71.1, 68.1 and 54.7% for initial sCOD of 4800 mg/l at H_2O_2 dose of 0.8, 1.2, 1.6 and 2.4 g/l, respectively. The minimum residual sCOD concentration was 1366 mg/l at initial sCOD of 4800 mg/l which did not complying with the required local Standard. However, it was 266 mg/l at initial sCOD of 1500 mg/l which complied with the local Standard.
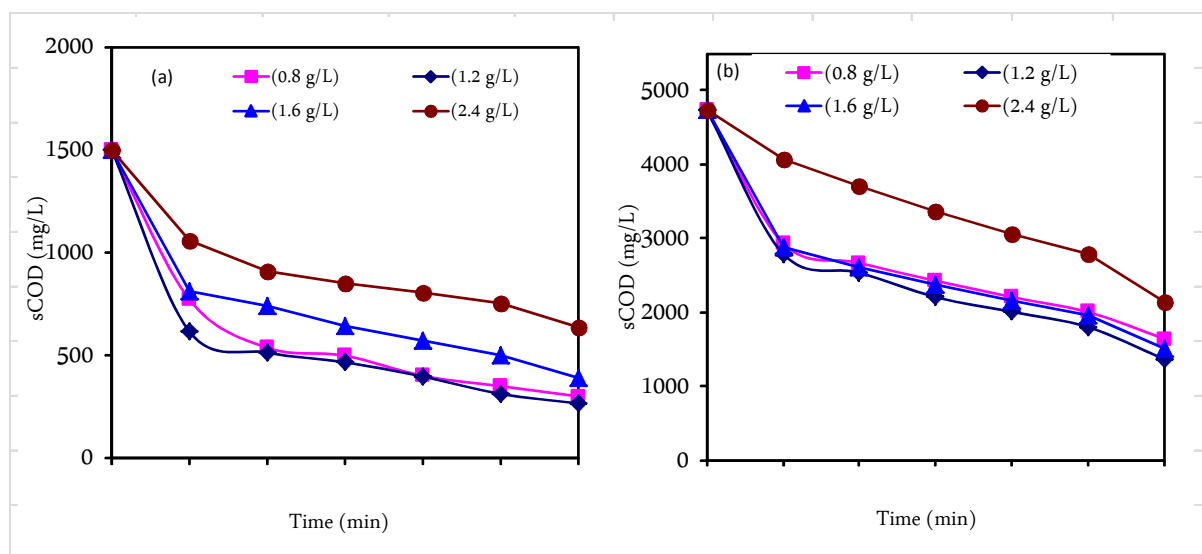
Figure 2: Effect of H_2O_2 dose on residual sCOD at pH 3.5, Fe dose 0.70 mg/l for: (a) initial sCOD of 1500 mg/l; (b) 4800 mg/l.

The achieved sCOD removal percent at initial sCOD of 4800 mg/l is quite lower than that of 1500 mg/l. There is small improvement in sCOD removal due to increase H_2O_2 dose from 0.80 to 1.2 mg/l; however increasing H_2O_2 dose more than 1.2 did not improve the sCOD removal. This may be due to scavenging of $OH^{\bullet}$ by H_2O_2 as in Reaction 1 [24].

$$OH^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \qquad \text{Reaction 1}$$

Based on the results, it may be considered that optimal H_2O_2 dose of 0.8 g/l for initial sCOD of 1500 mg/l and 1.2 g/l for initial sCOD of 4800 mg/l. This agrees well with reported study in the literature [21].

Effect of $H_2O_2/FeSO_4$ ratio: In Fenton process, iron and hydrogen peroxide are two major chemicals determining the operation cost as well as efficiency [16]. As much as we can reduce the required chemicals, the operation cost of the treatment process will be decreased. To study the effect of iron dose on the sCOD removal, experiments were conducted at H_2O_2 dose of 0.8 mg/l for initial sCOD of 1500 mg/l and 1.2 g/l for initial sCOD of 4800 mg/l; and varying $FeSO_4$ dose in the range 0.2-1.4 g/l. The corresponding $H_2O_2/FeSO_4$ ratio (w/w) were 0.6, 1.2, 3 and 4 for initial sCOD of 1500 mg/l and 1.2, 2.4, 3 and 4 for initial sCOD of 4800 mg/l. Other operating conditions were pH 3.5 and reaction time up to 150 min.

The effect of $FeSO_4$ dose and Fenton reaction time on sCOD removal at initial sCOD of 1500 mg/l and 4800 mg/l in the form of residual sCOD are shown in Figure (3a) and (b), respectively. As shown in the Figure both $FeSO_4$ dose and reaction time significantly affect the sCOD removal. After 150 min reaction time, residual sCOD was 490, 312, 263 and 290 mg/l for initial sCOD of 1500 mg/l at $H_2O_2/FeSO_4$ ratio 0.6, 1.2, 3 and 4; and 1642, 1392, 1050 and 1201 mg/l for initial sCOD of 4800 mg/l at $H_2O_2/FeSO_4$ ratio 1.2, 2.4, 3 and 4, respectively. The achieved sCOD removal was 67.8, 79.5, 82.7 and 81.0% for initial sCOD of 1500 mg/l at $H_2O_2/FeSO_4$ ratio 0.6, 1.2, 3 and 4; and 65.5, 70.7, 77.9 and 74.4% for initial sCOD of 4800 mg/l at $H_2O_2/FeSO_4$ ratio 1.2, 2.4, 3 and 4, respectively.

The results show that sCOD removal increased with increase of $H_2O_2/FeSO_4$ ratio up to 3.0. Increasing $H_2O_2/FeSO_4$ ratio more than 3 did not significantly improve sCOD removal. This may be ascribed to direct reaction of $OH\bullet$ radical with metal ions at high concentration of Fe^{2+} as in Reaction 2 [24].

$$Fe^{2+} + OH^{\bullet} \rightarrow Fe^{3+} + HO^{-} \qquad \text{Reaction 2}$$

Based on the results, it may be considered that optimal $H_2O_2/FeSO_4$ ratio is 3 for sCOD removal.

On-site pilot scale Fenton process

The On-Site pilot scale Fenton process reactor is operated in batch basis at 8 hour cycles divided in six phases: 0.50 hr filling, 0.25 hr adding reagents, 5 hr reaction, 0.50 hr neutralisation, 1.5 hr chemical sludge settling and 0.25 hr decanting. The reagents doses were: 1000 mg/l for H_2O_2 and 330 mg/l for Fe^{2+} in the form of ferrous sulphate (the weight ratio between H_2O_2 to Fe^{2+} was 3:1) and pH 3.5. The sCOD of DTLOWW which has been used in the pilot study was 1700 ± 150 mg/l. Fenton reactor is filled with DTLOWW and then pH is adjusted (with H_2SO_4) to value of 3.5. The next step was addition of ferrous sulphate. Thereafter, hydrogen peroxide was added to the mixture. When addition of the required amount of H_2O_2 is completed, the pumps are shut off and Fenton reaction started. All the experimental time, the DTLOWW and reagent are mixed by means of mixer. At the end of the reaction time, pH of the solution was raised to above 9 by operating the sodium hydroxide dosing pump and the mixing continued for 30 min for neutralization. The pilot study was repeated three times and the standard deviation is presented in Figure 4. The Figure shows the effect of reaction time on residual sCOD and sCOD removal percent. After 5 hours reaction time with overall cycle period of 8 hours, residual sCOD was 788 ± 56 mg/l with sCOD removal of 53.6% which amply met with the local discharge Standards for discharging the industrial wastewater to the municipal sewage network [25]. Excessive heating was noted during the reaction time this could be ascribed to the exothermic phenomena of the Fenton reaction [21]. It is noted that the mixing is a crucial factor in the

performance of the pilot scale Fenton process. In the preliminary works (data not shown), the Fenton process performance was bad when the mixing was conducted using circulation pumps.
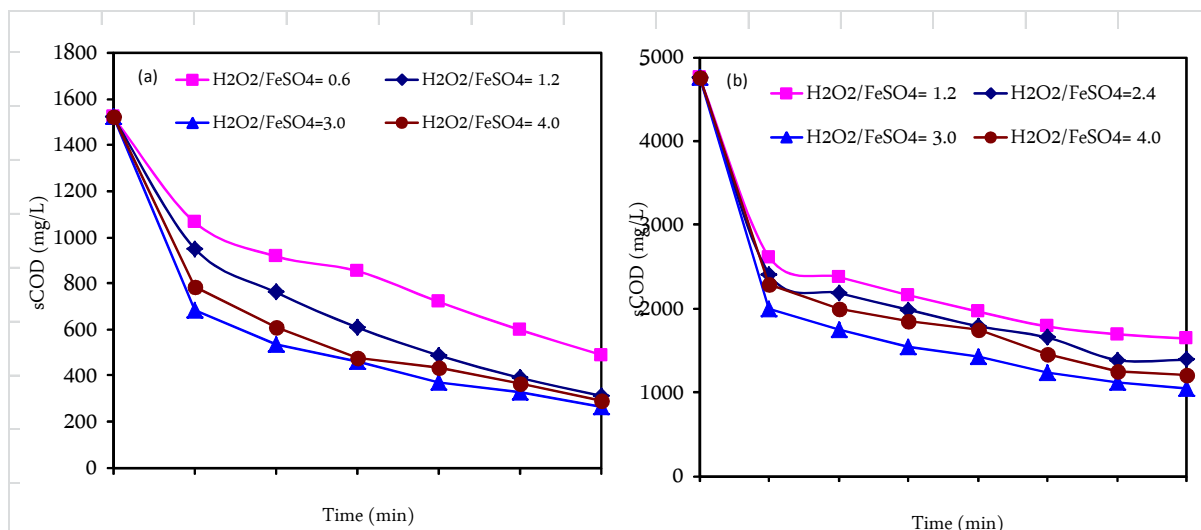

Figure 3: Effect of $FeSO_4$ dose on residual sCOD at pH 3.5, for: (a) initial sCOD of 1500 mg/l; (b) 4800 mg/l.
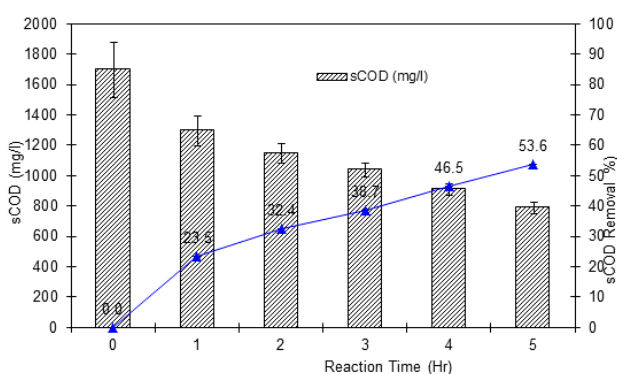

Figure 4: Effect of reaction time on residual sCOD at pH 3.5, H_2O_2 1000 g/l and Fe^{2+} 330 g/l.

Estimated chemical costs for pilot scale Fenton process

The estimated chemical consumption and its cost are based sCOD strength of less than 2000 mg/l. The main cost contributors for Fenton process are hydrogen peroxide (H_2O_2) and ferrous sulphate ($FeSO_4.7H_2O$). The average price in the local market of 1.0 kg of ferrous sulphate is 0.6 $/kg; however, the average price of hydrogen peroxide 1.0 $/kg. Considering that hydrogen peroxide and ferrous sulphate are the main consumed chemicals in the Fenton process so, the daily cost of chemicals is 1.25-1.50 $/m^3.

Conclusions

- In bench scale Fenton process, optimum H_2O_2 dose is 0.8 g/l for normal DTLOWW strength (sCOD<2000 mg/l) and 1.2 g/l for high strength DTLOWW strength (sCOD>2000 mg/l) with optimum $H_2O_2/FeSO_4$ ratio of 3 for the normal and high strength DTLOWW and pH 3.5.

- The On-Site pilot scale Fenton process achieved residual sCOD of 788 ± 56 mg/l with sCOD removal of 53.6% which amply met with the local discharge Standards for discharging the industrial wastewater to the municipal sewage network.

- The Fenton process could be used for treatment of the DAF-Treated lube oil wastewater (DTLOWW) with daily chemicals cost of 1.25-1.50 $/m^3.

Acknowledgement

References

1. Chen GH, He GH (2003) Separation of water and oil from waterin-oil emulsion by freeze/thaw method. Sep Purif Technol 31: 83–89.

2. Wenhu Z, Dejin W, Ruoyu F, Feng L (2013) Studies on affecting factors and mechanism of oily wastewater by wet hydrogen peroxide oxidation. Arab J Chem (In press).

3. Yu L, Han M, He F (2013) A review of treating oily wastewater. Arab J Chem (In press).

4. Painmanakul P, Sastaravet P, Lersjintanakarn S, Khaodhiar S (2010) Effect of bubble hydrodynamic and chemical dosage on treatment of oily wastewater by Induced Air Flotation (IAF) process. Chem Eng Res Design 88: 693–702.

5. Salahi A, Noshadi I, Badrnezhad R, Kanjilal B, Mohammadi T (2013) Nano-porous membrane process for oily wastewater treatment: Optimization using response surface methodology. J Environ Chem Eng 1: 218–225.

6. Mittal P, Jana S, Mohanty K (2011) Synthesis of low-cost hydrophilic ceramic–polymeric composite membrane for treatment of oily wastewater. Desalination 282: 54–62.

7. Scholz W, Fuchs W (2000) Treatment of oil contaminated wastewater in a membrane bioreactor. Water Res 34: 3621–3629.

8. Liu GH, Ye ZF, Tong K, Zhang YH (2013) Biotreatment of heavy oil wastewater by combined upflow anaerobic sludge blanket and immobilized biological aerated filter in a pilot-scale test. Biochem Eng J 72: 48–53.

9. Santos MRG, Goulart MOF, Tonholo J, Zanta CLPS (2006) The application of electrochemical technology to the remediation of oily wastewater. Chemosphere 64: 393–399.

10. Ma HZ, Wang B (2006) Electrochemical pilot-scale plant for oil field produced wastewater by M/C/Fe electrodes for injection. J Hazard Mater 132: 237–243.

11. Kang J, Lu L, Zhan W, Li B, Li D, et al. (2011) Photocatalytic pretreatment of oily wastewater from the restaurant by a vacuum ultraviolet/TiO2 system. J Hazard Mater 186: 849-854.

12. Ong CS, Lau WJ, Goh PS, Ng BC, Ismail AF (2014) Investigation of submerged membrane photocatalytic reactor (sMPR) operating parameters during oily wastewater treatment. Desalination 353: 48-56.

13. Pera-Titus M, Garcıa-Molina V, Banos MA, Giménez J, Esplugas S (2004) Degradation of Chlorophenols by means of advanced oxidation processes: a general review. Appl Cataly B: Environ 47: 219–256.

14. Chamarro E, Marco A, Esplugas S (2001) Use of Fenton reagent to improve organic chemical biodegradability. Water Res 35: 1047–1051.

15. Elmolla E, Chaudhuri M (2009) Optimization of Fenton process for treatment of amoxicillin, ampicillin and cloxacillin antibiotics in aqueous solution. J Hazard Mater 170: 666-672.

16. Elmolla ES, Chaudhuri M (2009) Degradation of the antibiotics amoxicillin, ampicillin and cloxacillin in aqueous solution by the photo-Fenton process. J Hazard Mater 172: 1476-1481.

17. Elmolla ES, Chaudhuri M (2010) Photocatalytic degradation of amoxicillin, ampicillin and cloxacillin antibiotics in aqueous solution using UV/TiO2 and UV/H2O2/TiO2 photocatalysis. Desalination 252: 46-52.

18. Elmolla ES, Chaudhuri M (2010) Degradation of amoxicillin, ampicillin and cloxacillin antibiotics in aqueous solution by the UV/ZnO photocatalytic process. J Hazard Mater 173: 445-449.

19. Elmolla ES, Chaudhuri M (2010) Comparison of different advanced oxidation processes for treatment of antibiotic aqueous solution. Desalination 256: 43-47.

20. Elmolla ES, Chaudhuri M, Eltoukhy MM (2010) The use of artificial neural network (ANN) for modeling of COD removal from antibiotics aqueous solution by Fenton process. J Hazard Mater 179: 127-134.

21. Barbusiński K (2009) The Full-Scale Treatment Plant For Decolourisation Of Dye Wastewater. Archit Civil Eng Environ 35: 89–95.

22. APHA, AWWA, WPCF (1992) Standard Methods for the Examination of Water and Wastewater. [18th edn], American Public Health Association, American Water Works Association, Water Pollution Control Federation, Washington, DC, USA.

23. Talinli I, Anderson GK (1992) Interference of hydrogen peroxide on the standard COD test. Water Res 26: 107–110.

24. Kavitha V, Palanivelu K (2005) Destruction of cresols by Fenton oxidation process. Water Res 39: 3062–3072.

25. EEAA (1994) Law 4/1994 for the Protection of the Environment, disposal of the industrial wastewater to the public sewerage system, the Egyptian Environmental Affairs Agency (EEAA).