
Study on the Treatment of Effluents from Paint Industry by Modified Electro-Fenton Process

Ahmed Mostafa Sadek^{1,*}, Riham Ali Hazzaa², Mohamed Hussien Abd-El-Magied¹

¹Chemical Engineering Department, Alexandria University, Alexandria, Egypt

²Petrochemicals Engineering Department, Pharos University, Alexandria, Egypt

Email address:

amsadek@ethyldco-eg.com (A. M. Sadek)

To cite this article:

Ahmed Mostafa Sadek, Riham Ali Hazzaa, Mohamed Hussien Abd-El-Magied. Study on the Treatment of Effluents from Paint Industry by Modified Electro-Fenton Process. *American Journal of Chemical Engineering*. Vol. 4, No. 1, 2016, pp. 1-8.

doi: 10.11648/j.ajche.20160401.11

Abstract: The main goal of this study is to investigate the effectiveness of modified Electro-Fenton process (EF-Fere) involving ferrous ions regeneration coupled with direct oxidation method on COD reduction of paint manufacturing wastewater. The present Electro-Fenton cell consisted of stainless steel porous cathode and lead anode covered by PbO₂ film. The performance was measured through studying the effect of different parameters on the percentage of COD removal such as: ferric ions concentration, initial concentration of wastewater, current density and irradiation of UV light. The parameters showed high COD removal efficiency 99% for highly contaminated wastewater of 13000 mg/l COD in acidic medium pH=2 at continuous H₂O₂ feeding dosage of 1.4 ml/min and current density = 19 mA/cm² in presence of UV light.

Keywords: Paint Manufacturing Wastewater, Fe²⁺ Generation, EF-Fere, COD Removal, Direct Oxidation, UV/EF-Fere

1. Introduction

Water-based paints generally consist of organic and inorganic pigments and dyestuffs, extenders, cellulosic and non-cellulosic thickeners, latexes, emulsifying agents, anti-foaming agents, preservatives, solvents and coalescing agents [1], which, due to their high persistence and toxicity, prove to be difficult to treat effectively. Advanced oxidation processes (AOPs) have been thought as effective routes for treatment of paint manufacturing wastewater. Paint manufacturing wastewater has many kinds of high concentration complex organic constituents, but the conventional method such as coagulation is not useful for removal of total organic carbon (TOC) and chemical oxygen demand (COD) [2]. Alternative technology has been developed to help solving the problem. Advanced oxidation processes (AOPs) are frequently used to oxidize complex organic constituents found in waste-waters which are difficult to be degraded biologically into simpler end products [3]. Fenton reaction is another option for phenol degradation. The classical Fenton reagent, consisting of the reactions between homogeneous Fe²⁺/Fe³⁺ catalysts and hydrogen peroxide (H₂O₂), is highly efficient for the destruction of phenols due to the hydroxyl radicals generated by the Fenton reactions. However, the classic Fenton

processes require a strong acid condition (pH < 3) to avoid the hydrolysis of ferrous and ferric ions, and to achieve optimal removal rate of pollutants. Additionally, non-recyclable soluble iron salts yield large amount of iron oxide sludge, which needs further separation from the treated water [4]. Some AOPs processes based on classic Fenton processes are developed to treat aqueous phenols. Fenton process using zero valence iron [5], Fenton-like reactions [6, 7], photo-Fenton [8, 9], and electro-Fenton (EF) [10-13] have been proven effective for the degradation of phenols. For an electro-Fenton process, either H₂O₂ or ferrous ion is continuously generated or regenerated on the electrode and their accumulative concentrations in aqueous solution depend on a competition between their generation rate and consumption rate [14]. Usually the electro-Fenton processes can be classified into two categories, EF process involving H₂O₂ generation and EF process involving ferrous regeneration, which can be named as EF-Fere. The efficiencies of both processes can be comparable with the conventional chemical dosing methods [15-17]. More importantly, they can decrease the risk of handling H₂O₂ reagents, or decrease the production of ferric hydroxide sludge.

In this study, we propose an improved EF-Fere process coupled with direct oxidation method for the treatment of

concentrated organics-containing paint wastewater. A porous stainless steel cathode, instead of a plate cathode, is adopted in the electrolytic process. The porous cathode is capable of reducing the ferric species (ferric sulfate or ferric hydroxide sludge) to ferrous species more efficiently. Results obtained with synthetic wastewater having COD of 13,000 to 19000 mg/l. Electro Fenton studies were with current density in the range of 12.6 to 21 mA/cm² and H₂O₂ dosage in the range of 1 to 1.6 ml/min and constant pH values of 2. Experiment were carried out in batch reactor using one cylindrical lead anode covered by PbO₂ film and DC power supply. Factors that affected Fe²⁺ generation and chemical oxygen demand (COD) removal efficiency of organics-containing paint wastewater were evaluated in this work. In addition, the UV irradiation is introduced to the electrolytic system to further enhance the efficiency of organics degradation.

2. Experimental

2.1. Chemicals and Materials

The wastewater used was prepared in the laboratory with different COD using high grade chemicals and double distilled water. The preparation of the synthetic wastewater is based on the theoretical oxygen demand of each compound then the COD of the wastewater was measured to get the actual value of COD. The wastewater description is given in Table 1.

Table 1. Wastewater description.

| Organic Compound | % of Total COD |
|-----------------------------|---------------------|
| Oleic acid | 50% of Total COD |
| Benzene | 16.66% of Total COD |
| n-heptane | 16.66% of Total COD |
| Tween 80 (emulsifier agent) | 16.66% of Total COD |

All chemicals are analytical grade. All organics were purified by distillation and dissolved into distilled water as stock solution. Before the EF-Fere experiment, ferric sulfates were added and dissolved in the organics-containing solution. The pH of solution was adjusted with sulfuric acid and NaOH solution. The H₂O₂ solution (50 wt.%) was used as amendments without dilution. All the solutions were prepared using double distilled water. In addition, potassium dichromate, silver sulfate and mercury sulfate were of AR grade. Porous stainless steel cylinder used as a cathode while cylindrical lead covered by PbO₂ film act as anode (OD=3 cm) and anode effective electrode area was 118.7 cm², Pb/PbO₂ anode was prepared in our laboratory and the details can be found in the literature [18].

2.2. EF-Fere System

Batch experiments were performed in cylindrical cell (pyrex glass beaker 1 liter) with 800 ml working volume of concentrated organics-containing wastewater equipped with porous stainless steel cathode while cylindrical lead covered by PbO₂ film act as anode (OD=3 cm) and anode effective electrode area was 118.7 cm². The cell was operated in constant current (I) mode 1.5, 1.75, 2.25, 2.5 A, these

corresponding to current densities of 12.6, 14.7, 19, 21 mA/cm², respectively, by using DC power supply. Ferric sulfate was added and dissolved in the organics-containing solution at desired concentration, 1500, 1800, 2000, 2300 mg/l. Hydrogen peroxide was added at desired concentration in continuous feeding mode, 1 mL/min, 1.2 mL/min, 1.4 mL/min, 1.6 mL/min. All the experiments was performed at room temperature 25°C. A magnetic stirrer was used to homogenize the liquid composition. The schematic of the experimental setup is shown in fig. 1. Initial pH was adjusted to a fixed value 2 by using 25 wt.% sulfuric acid. Samples were taken at pre-selected time intervals.

For each run contain 800 mL of the organics containing wastewater. The pH was adjusted by the addition of 25 wt% H₂SO₄ solutions. Hydrogen peroxide (50 wt%) was added at desired concentration in continuous feeding mode. Direct current from the D. C power supply was passed through the solution during the 120 minutes of electrolysis run. Samples were drawn periodically during each experiment. Withdrawn samples were diluted 200 times with distilled water and then COD was measured. The electrodes were washed with H₂SO₄ solution (25 wt%) before each run in order to remove any adhering scales or oxides and then washed with distilled water prior to use.

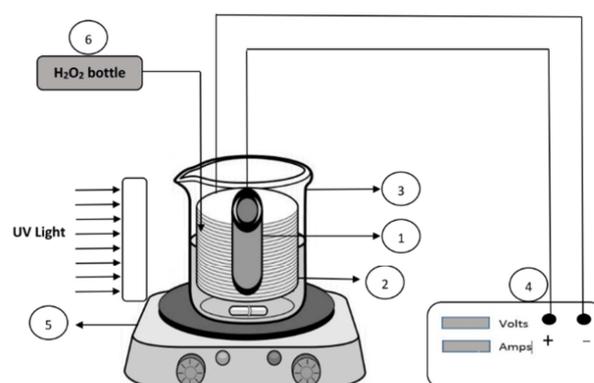


Figure 1. Experimental schematic diagram.

1-Pb/PbO₂ anode, 2-St. steel porous cathode, 3-electrolytic cell, 4-D-C power supply, 5-Magnetic stirrer, 6-H₂O₂ bottle with flow rate regulator.

2.3. Analytical Method

Chemical oxygen demand (COD) of the sample were measured by closed reflux method according to the standard methods for testing material [19]. The samples were tested using COD digestion vials (Hach), where the sample is placed within digestion vials which in turn are heated at 150°C for 2 hours. Digestion vials were then allowed to cool naturally to ambient temperature before having the COD measured.

3. Results and Discussion

3.1. Effect of Ferric Ions Concentration

The initial concentration of Fe⁺³ ions plays an important role in the E-Fenton process. Progress of COD removal with time

for different Fe³⁺ ions (1500, 1800, 2000, 2300 mg/l Fe³⁺) and constant current density, pH and initial COD are shown in figures below. COD removal increases as the concentration of ferric ions and hydrogen peroxide continuous dosage increase, the maximum COD reduction obtained for 2000 mg/l Fe³⁺ and 1.4 ml/min continuous dosage of H₂O₂ was 90%.

As can be observed, when the dose of ferric ions increased from 1500 mg/L to 2000 mg/L, the COD removal efficiency after 2 hours electrolysis increases from 55% to 69% at 1 ml/min H₂O₂ dose, from 76% to 84% at 1.2 ml/min H₂O₂ dose and from 80.3% to 90% at 1.4 ml/min H₂O₂ dose. The increase of initial ferric ions concentration and hydrogen peroxide continuous dosage was beneficial for the Fe³⁺ - H₂O₂ complexes formation (Eq. 1 and Eq. 2), which would be enhanced and consequently accelerated the formation of Fe²⁺ and OH. Thus, organics degradation in the wastewater is enhanced. However, when initial ferric ions concentration and H₂O₂ dosage further increased to 2300 mg/L Fe³⁺ ions and 1.6 ml/min H₂O₂ dose, respectively, COD removal efficiency instead declined to 83.5%. This observation probably can be explained by the negative effects of the presence of large amount of ferric ions: 1) H₂O₂ consumption by the Fenton-like reactions is also enhanced, resulting in lower utilization of H₂O₂; 2) higher ferric ions concentration causes the presence of more ferrous ions, which may quench hydroxyl radicals (Eq.3), leading the COD removal efficiency of organics because of less available hydroxyl radicals, also COD removal decreased to 86% as the concentration of hydrogen peroxide increases at 1.6 ml/min, this is due to the side reaction between hydrogen peroxide and hydroxyl radical (Eq.4), this reaction result in the consumption of hydrogen peroxide as well hydroxyl radical and the production hydroperoxyl radical, a species with much weaker oxidizing power compared with hydroxyl radical, and these are consistent with previous research deals with degradation of phenol-containing wastewater using an improved Electro-Fenton processes[20].

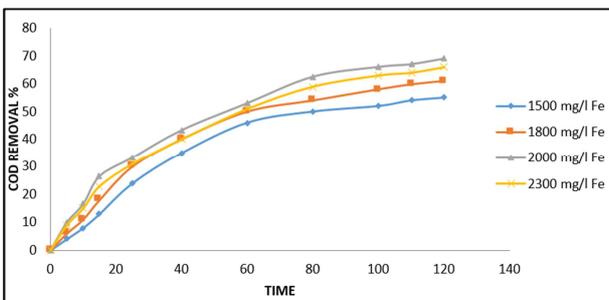
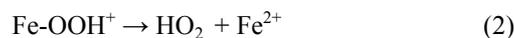


Figure 2. Effect of different ferric ions concentration on the percentage of COD removal (pH =2, C. D =14.7 mA/cm², initial COD = 19000 mg/l, time = 120 min, H₂O₂ dosage= 1ml/min).

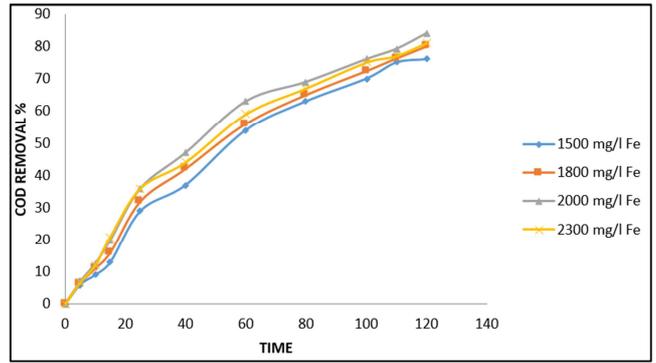


Figure 3. Effect of different ferric ions concentration on the percentage of COD removal (pH =2, C. D =14.7 mA/cm², initial COD = 19000 mg/l, time = 120 min H₂O₂ dosage= 1.2 ml/min).

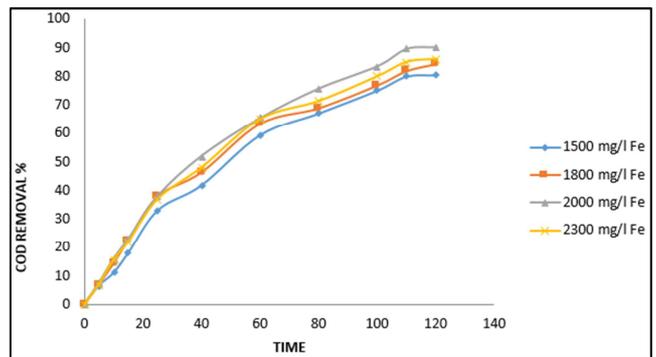


Figure 4. Effect of different ferric ions concentration on the percentage of COD removal (pH =2, C. D =14.7 mA/cm², initial COD = 19000 mg/l, time = 120 min H₂O₂ dosage= 1.4 ml/min).

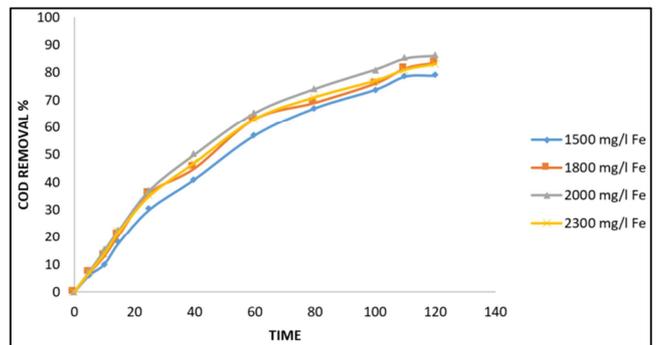


Figure 5. Effect of different ferric ions concentration on the percentage of COD removal (pH =2, C. D =14.7 mA/cm², initial COD = 19000 mg/l, time = 120 min H₂O₂ dosage= 1.6 ml/min).

3.2. Effect of Initial Concentration of Waste Water

The process for the removal efficiencies of COD of oxidation reaction at different initial concentrations of wastewater is illustrated in Figures below, four different initial concentration including 19000, 17000, 15000 and 13000 mg/l COD were tested with fixed current density and pH value of 14.7 mA/cm² and 2, respectively; the removal efficiency increased with decreasing initial COD concentration from 19000 mg/l COD to 13000 mg/l COD and increasing ferric ions concentration from 1500 mg/l Fe³⁺ to 2000 mg/l Fe³⁺ however, when initial ferric ions

concentration increased to 2300 mg/l, the COD removal percentage is decreased to 86, 86.5, 88 and 89% at 19000, 17000, 15000 and 13000 mg/l COD, respectively. This is due to the negative effects of the presence of large amount of ferric ions as discussed before in 3.1. Effect of ferric ions concentration.

The maximum COD removal observed was 95.6% at initial concentration of wastewater 13000 mg/l COD, current density 14.7 mA/cm², pH value 2 and initial ferric ions concentration 2000 mg/l Fe⁺³. This effect has been previously discussed in a research deals with Removal of 17β-Estradiol by Electro-Fenton Process [21].

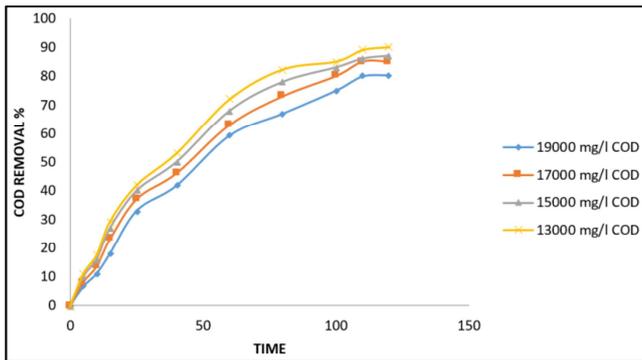


Figure 6. Effect of initial concentration of waste water on the percentage of COD removal (pH =2, C. D =14.7 mA/cm², H₂O₂ = 1.4 ml/min, time = 120 min, Fe⁺³ = 1500 mg/l).

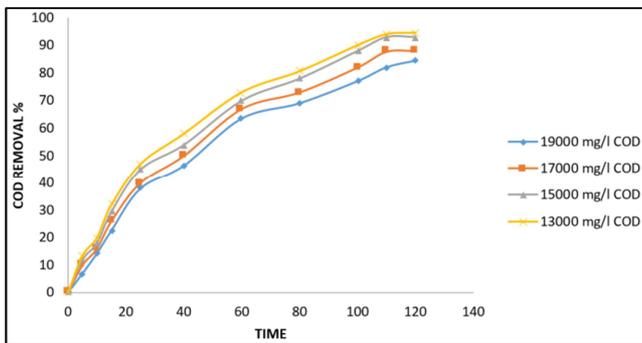


Figure 7. Effect of initial concentration of waste water on the percentage of COD removal (pH =2, C. D =14.7 mA/cm², H₂O₂ = 1.4 ml/min, time = 120 min, Fe⁺³ = 1800 mg/l).

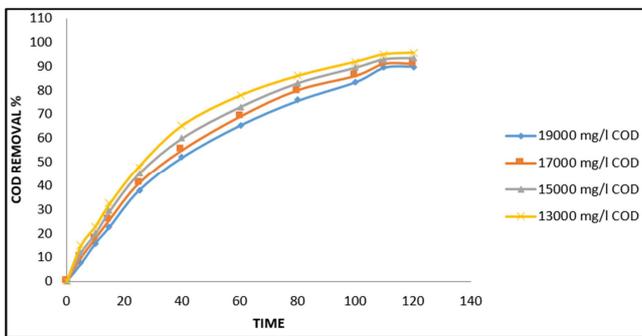


Figure 8. Effect of initial concentration of waste water on the percentage of COD removal (pH =2, C. D =14.7 mA/cm², H₂O₂ = 1.4 ml/min, time = 120 min, Fe⁺³ = 2000 mg/l).

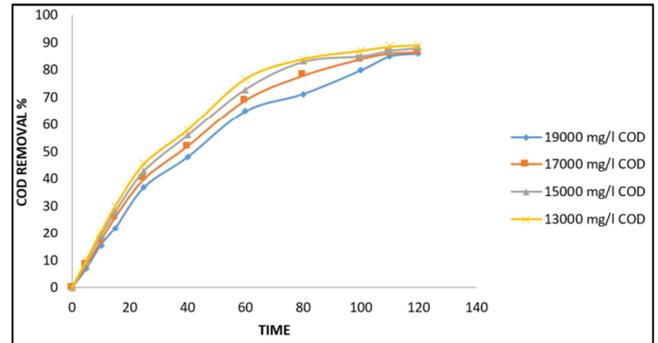


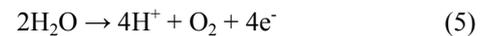
Figure 9. Effect of initial concentration of waste water on the percentage of COD removal (pH =2, C. D =14.7 mA/cm², H₂O₂ = 1.4 ml/min, time = 120 min, Fe⁺³ = 2300 mg/L).

3.3. Effect of Current Density

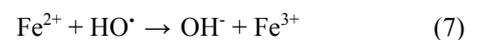
One of the critical parameters in the EF-Fere processes is the electrical current which is responsible for the generation of ferrous ions within the electrochemical cell.

Effect of electrical current on COD removal efficiency is shown in figures below at different initial concentration of wastewater. Experiments were applied to current density from 12.6 to 21 mA/cm² at constant pH, Fe⁺³ concentration and H₂O₂ continuous dosage. Apparently, the COD removal efficiency goes up when applied current density increases from 12.6 to 19 mA/cm², indicating an enhancement on the degradation capacity. At higher current, the electro-regeneration of Fe²⁺ is enhanced with the increasing of current, as a result, the efficiency of Fenton reactions and degradations of organics are improved. However, further increase of the electrical current density to higher than 19 mA/cm², causes lower COD removal efficiency, as we can see from figures below.

The maximum COD removal observed at 19 mA/cm² was 97, 95, 93.5, and 92.5% at initial concentration of wastewater 13000, 15000, 17000, and 19000 mg/l COD, respectively. The efficiency of E-Fenton will be less at higher current density 21 mA/cm², this is due to the competitive electrode reactions in electrolytic cell which are the evolution of oxygen at anode as shown in Eq. (5) and the evolution of hydrogen at cathode as shown in Eq. (6). These reactions reduce E-Fenton reaction efficiency. And these are consistent with previous research deals with degradation of phenol-containing wastewater using an improved Electro-Fenton processes [20].



Also at higher current density COD removal decreased. This decrease in COD removal happens to the scavenging effect of ferrous ion eq. (5.7). In this reaction ferrous ions consume hydroxyl radicals.



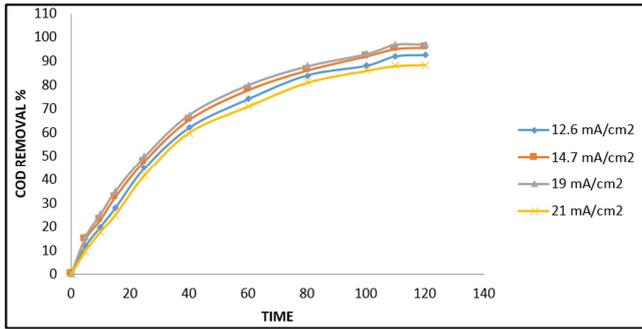


Figure 10. Effect of different current densities on the percentage of COD removal ($\text{pH} = 2$, $\text{Fe}^{+3} = 2000 \text{ mg/l}$, $\text{H}_2\text{O}_2 = 1.4 \text{ ml/min}$, time = 120 min, COD initial = 13000 mg/l).

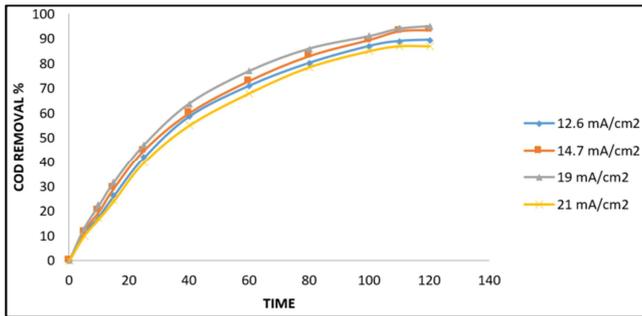


Figure 11. Effect of different current densities on the percentage of COD removal ($\text{pH} = 2$, $\text{Fe}^{+3} = 2000 \text{ mg/l}$, $\text{H}_2\text{O}_2 = 1.4 \text{ ml/min}$, time = 120 min, COD initial = 15000 mg/l).

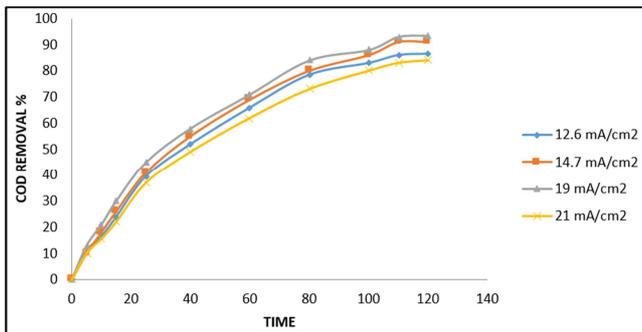


Figure 12. Effect of different current densities on the percentage of COD removal ($\text{pH} = 2$, $\text{Fe}^{+3} = 2000 \text{ mg/l}$, $\text{H}_2\text{O}_2 = 1.4 \text{ ml/min}$, time = 120 min, COD initial = 17000 mg/l).

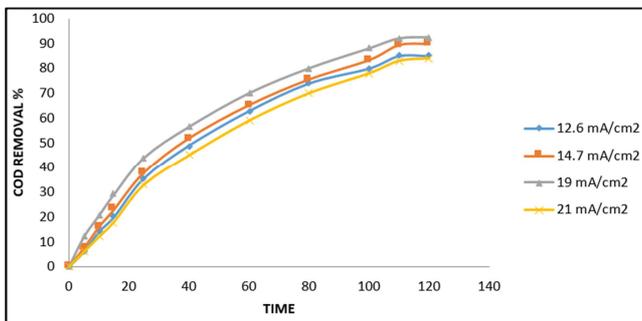
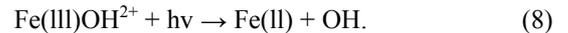


Figure 13. Effect of different current densities on the percentage of COD removal ($\text{pH} = 2$, $\text{Fe}^{+3} = 2000 \text{ mg/l}$, $\text{H}_2\text{O}_2 = 1.4 \text{ ml/min}$, time = 120 min, COD initial = 19000 mg/l).

3.4. Effect of UV on Organic Removal

The optimal operation conditions of EF-Fere system were adopted for the comparison of EF-Fere and UV/EF-Fere process. Fig. 14 presents the degradation of organics in wastewater by these processes as a function of time. The 2 hours COD removal efficiencies with UV light are 99, 96.5, 95.5 and 94% at initial concentration of wastewater 13000, 15000, 17000 and 19000 mg/l COD, respectively.

Irradiation of UV on EF-Fere process may have two aspects of effects. One is the direct destruction of organics due to the photolysis of organic molecules under UV, and another effect is the enhancement of OH· by the following reactions eq. (8).



Under the irradiation of UV light (254nm), ferric species can be reduced and hydroxyl radicals are produced for the organics oxidation process. In other words, in addition to the reactions proceeding in the EF-Fere process, the light irradiation can further catalyze the production of hydroxyl radicals and degrade the organics. Enhancing the Fenton process by UV light was discussed in a previous research has title of Enhancing the Fenton process by UV light applied in textile wastewater treatment [22].

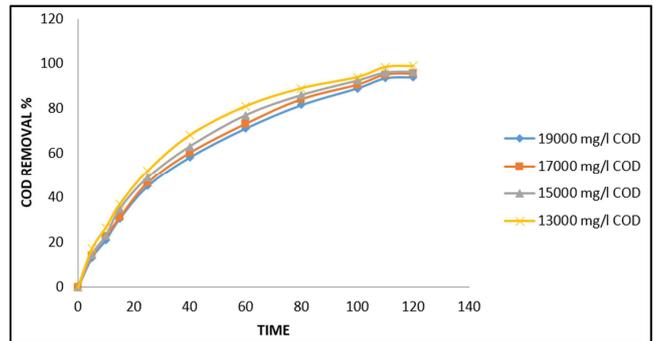


Figure 14. Effect of UV on the percentage of COD removal ($\text{pH} = 2$, $\text{Fe}^{+3} = 2000 \text{ mg/l}$, $\text{H}_2\text{O}_2 = 1.4 \text{ ml/min}$, time = 120 min, C. D = 19 mA/cm²).

4. Electrical Energy Consumption and Electrode Consumption

It is clear that a technically efficient process must also be feasible economically. The major operating cost of EF is associated with electrical energy consumption during process. According to the results presented energy consumption values ranged from 0.0046777 to 0.0097783 kWh/g COD removed and Pb consumption from 3.34795E-07 to 5.83211E-07 g Pb / g COD removed at different current density, It can be concluded that the higher voltage of the system applied, the weight of the electrode consumed in the process has been increased and also the higher the concentration of the Fe^{2+} in the solution which is responsible for H_2O_2 activation. Also it is noticed that the most economic concentration of ferric ions is 2000 mg/l which achieves about 0.004784357 kWh/g COD (energy consumption) and

$2.74672E-07$ g Pb/g COD removed (Pb consumption) quench hydroxyl radicals (Eq.3).
 because of the presence of more ferrous ions, which may

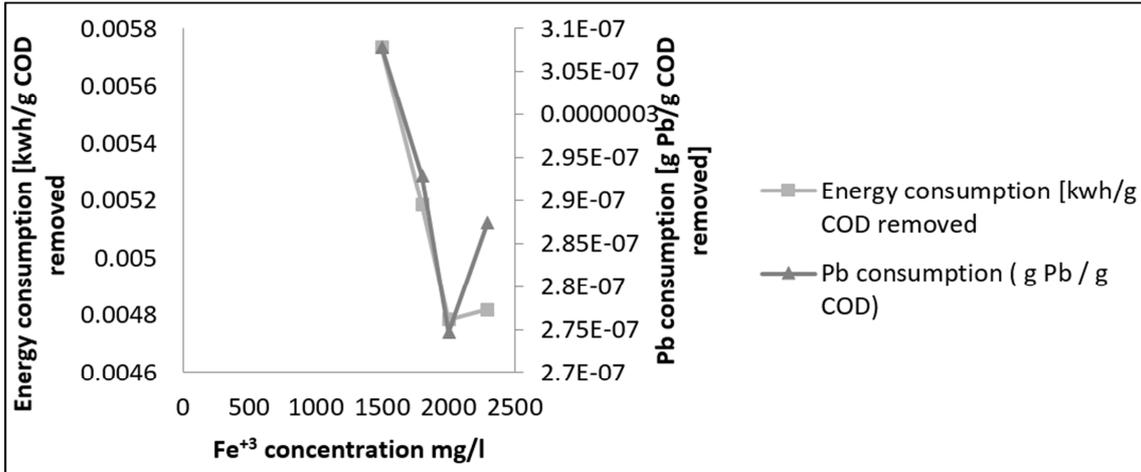


Figure 15. Effect of ferric ions concentration on the energy consumption and Pb consumption ($H_2O_2 = 1.4$ ml/min, Current = 1.75A, pH= 2, initial COD = 19000 mg/l).

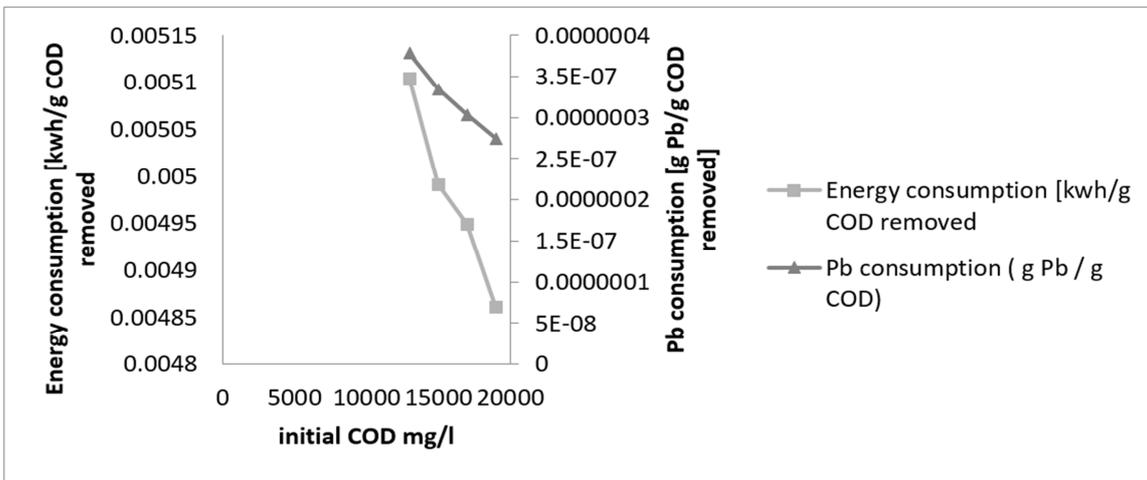


Figure 16. Effect of initial concentration of waste water on the energy consumption and Pb consumption ($H_2O_2 = 1.4$ ml/min, Current = 1.75A, pH= 2, $Fe^{+3} = 2000$ mg/l).

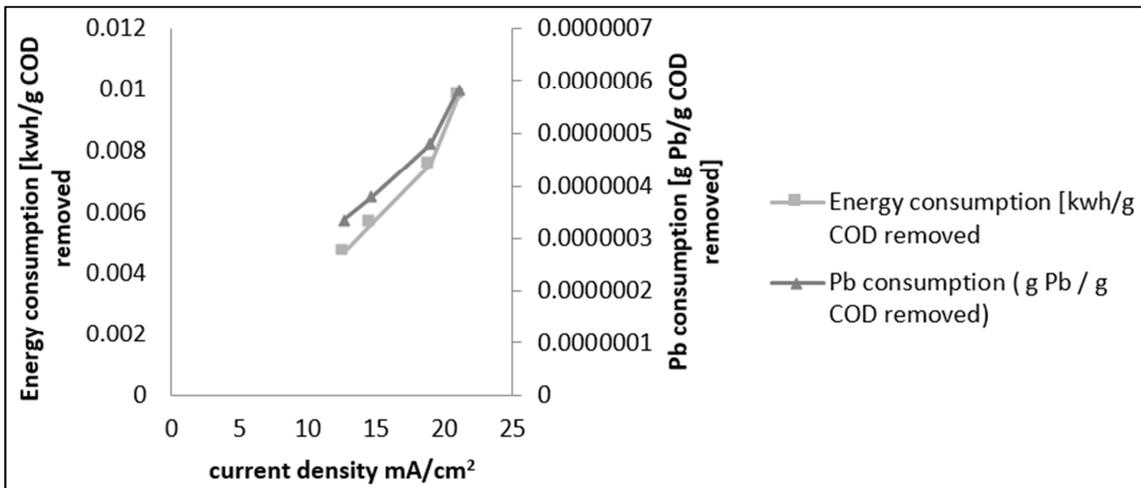


Figure 17. Effect of current density on the energy consumption and Pb consumption ($H_2O_2 = 1.4$ ml/min, initial COD = 13000 mg/l, pH= 2, $Fe^{+3} = 2000$ mg/l).

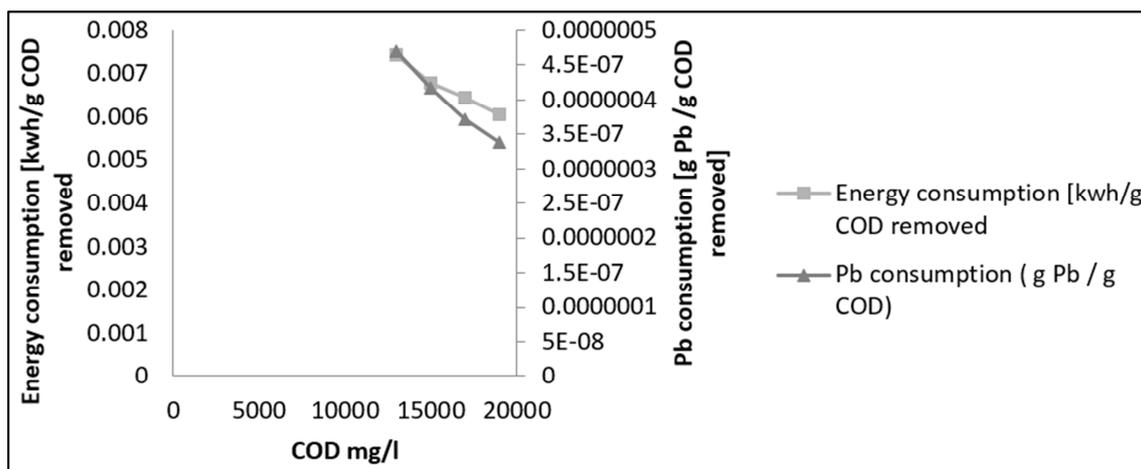


Figure 18. Effect of UV on the energy consumption and Pb consumption ($H_2O_2 = 1.4$ ml/min, current = 2.25 A, pH = 2, $Fe^{+3} = 2000$ mg/l).

5. Conclusion

The COD removal of highly contaminated paint manufacturing wastewater has been studied. It has shown that modified Electro-Fenton method could effectively reduce COD of paint industry wastewater.

We are able to remove about 97% of initial COD at initial pH=2, initial concentration of wastewater = 13000 mg/l COD, initial ferric ions concentration = 2000 mg/l, H_2O_2 continuous dosage = 1.4 ml/min and current density = 19 mA/cm² after 120 min, while COD removal increased to about 99% with irradiation of UV light. The results show that Electro Fenton is an effective technology for COD reduction in industrial wastes with low capital cost. The application of Electro Fenton has received increase attention in the last decade to treat paint manufacturing wastewater. Overall, UV/EF-Fere process is promising technology for application in wastewater treatment.

References

- [1] Dey, Hashim M, Hassan S (2004) Micro filtration of water-based paint effluents, *Adv. in Environ. Res.* 8, p. 455-466.
- [2] Huang Y, Chang P, Chen C (2008) Comparative study of oxidation of dye-Reactive Black B by different advanced oxidation processes. *Jr. of Haz. Mat.* 154, p. 655-662.
- [3] Torrades F, García-Hortal J, Domènech X (2002) Removal of organic contaminants in paper pulp treatment effluents under Fenton and photo-Fenton conditions. *Applied Catalysis B: Environmental* 36 (1), p. 63-74.
- [4] Xia M, Long M, Yang Y, Chen C, Cai W, Zhou B (2011) a highly active bimetallic oxides catalyst supported on Al-containing MCM-41 for Fenton oxidation of phenol solution, *Appl. Catal. B: Environ.* 110, p. 118-125.
- [5] Bremmer D, Burgess A, Houllemare D, Namkung K (2006) *Appl. Catal. B: Environ.* 63, pp. 15.
- [6] Zhang A, Wang N, Zhou J (2012) Heterogeneous Fenton-like catalytic removal of p-nitrophenol in water using acid-activated fly ash, *J. Hazard. Mater.* 201, p. 68.
- [7] Luis A, Miguel A, Antonio G (2011) *Chem. Eng. J.* 178, P. 146.
- [8] Ayodele O, Lim J, Hameed B (2012) Pillared montmorillonite supported ferric oxalate as heterogeneous photo-Fenton catalyst for degradation of amoxicillin, *Appl. Catal. A-Gen.* 413, P. 301.
- [9] Youssef S, Ines W, Ridha A, Kinetic degradation of the pollutant guaiacol by dark Fenton and solar photo Fenton processes (2001), *Environ. Sci. pollut. Res.* 18, p. 1497.
- [10] Lypczynska-Kochany E (1993) Hydrogen peroxide mediated photodegradation of phenol as studied by a flash photolysis/HPLC technique, *Environ. Pollut.* 80, P. 147-152.
- [11] Maciel R, Sant-Anna G, Dezotti M (2004) Phenol removal from high salinity effluents using Fenton's reagent and photo-Fenton reactions, *Chemosphere*, 57, P. 711.
- [12] Wang W, Kalck P, Faria J (2005) visible light photo degradation of phenol on MWCNT TiO₂ composite catalysts prepared by a modified sol-gel method *Mol. Catal. A Chem.*, 235, P. 194.
- [13] Herrmann J (1999) Fundamentals and applications to the removal various types of aqueous pollutants, *Catal. Today*, 53, p. 115.
- [14] Boye B, Dieng M, Brillas E (2002) Degradation of herbicide 4-chlorophenoxyacetic acid by advanced electrochemical oxidation methods, *Environ. Sci. Technol.*, 36, p. 3030.
- [15] Brillas E, Calpe J, Casado J (2000) Mineralization of 2, 4-D by advanced electrochemical oxidation, *Water Res.*, 34, p. 2253.
- [16] Qiang Z, Chang J, Huang C (2002) Electrochemical generation of hydrogen peroxide from dissolved oxygen in acidic solution, *Water Res.*, 36, P. 85.
- [17] Gozmen B, Oturan M, Oturan N (2003), *Environ. Sci. Technol.*, 37, P. 3716.
- [18] Fernandes A, Morao A, Magrinho M, Lopes A, Goncalves I (2004) Electrochemical degradation of C. I. Acid orange 7, *Dyes Pigments.*, 61, p. 287-296.
- [19] Clesceri L, Greenberg A, Andrew D (1998) Standard methods for the examination of water and wastewater. 20, p. 312.

- [20] Li J, Xuhui M (2012) Degradation of Phenol-containing Wastewater Using an Improved Electro-Fenton Process, *Int. J. Electrochem. Sci.* 7, P. 4078 – 4088.
- [21] Naimi I, Bellakhal N (2012) Removal of 17 β -Estradiol by Electro-Fenton Process, *Materials Sciences and Applications*, 3, P. 880-886.
- [22] Vasilica A, Igor C, Doina L, Constantin L, Ioannis P (2015) enhancing the fenton process by UV light applied in textile wastewater treatment., *Environmental Engineering and Management Journal.* 14, P. 595-600.