STUDIES FOR REMOVAL OF CYANIDE AND ORGANIC COMPOUNDS FROM INDUSTRIAL WASTEWATER USING THE FENTON AND FENTON LIKE TECHNIQUES

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ABSTRACT

Removal of the organic load, cyanides and lubricating oils, from liquid effluents of a specific chemical industry is investigated, where the wastewater is characterised by a high value of the chemical oxygen demand (COD) and high content of oils and cyanides. Such an effluent is usually treated by the (coagulation/chlorination) technique which has numerous disadvantages, of which the cyanogen chloride evolution and the possible leakage of chlorine are known to be very dangerous for human being. In the present work the Fenton and Fenton-like processes were employed to remove the majority of organic matters, cyanides and oils. Experimental tests were conducted to determine the effectiveness and the optimum operating conditions for wastewaters. The treatment train was found to be capable of lowering the wastewater (COD) from 16660 mg/l to 333 mg/l by the Fenton process and to 800 mg/l by the Fenton-like one, Cyanides from 9.11 mg/l to 0.18 mg/l and to 1.17 mg/l, and oils from 32910 mg/l to 65.82 mg/l by using both methods. Kinetic studies showed that the reaction is first order for COD measurements and cyanide removal. The ratios of BODs/COD values obtained indicate that both Fenton and Fenton like treatments can enhance the biological treatment since they can convert the pollutants to easily biodegraded compounds. Results proved that the Fenton process is much better than the currently used methods because of its safety, efficiency and low comparative costs.

Keywords

Wastewater, Cyanide Removal, oil Removal, COD, Fenton process.

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1. INTRODUCTION
Many industrial operations produce wastewater which is to be either circulated or drained to the environment. Wastewater from industrial units can be classified as to be either domestic wastewaters or process wastewaters. Within the scope of the present investigation, the process liquid effluents of an electroplating plant was audited due to the lack of efficient treatment procedures to meet with the high organic loads and cyanide content of such an effluent.

In the production sectors of such industry, the electroplating processes for ferrous and non-ferrous metals are carried out. Oils and greases are removed from objects to be electroplated (the tools) using solvent and then tools are put in a detergent. The tools are immersed in hydrochloric acid for a time and then washed by nitric and sulphuric acids (a pickling process). Electroplating can be then carried out where the tools are covered with nickel, copper or chromium, using salts of these metals which contain cyanides. Detergents used for cleaning small tools are mixed with sodium cyanide for some technical reasons. Heat treatments of metals are carried out using sodium cyanide and for quenching purposes oils are used. Sulphuric acid, cyanides, detergents and phosphate compounds are used to phosphatize the ferrous metals. Electroplating of small parts of ferrous metals use nickel salts which contain cyanides. Numerous types of oils and greases are of course generated from the transportation means and maintenance sectors in that industrial factory.

Cyanides are highly toxic, their poisonous effect is rapid in action. When these compounds are inhaled or ingested, their physiological effect involves an inactivation of the respiratory enzymes, preventing tissue utilization of the oxygen carried by the blood. Industrial oils such as lubricating and hydraulic pressure fluids that are used to lubricate steel sheets to reduce rusting are of high level of toxic organic contaminants which cause several environmental pollutions. The effluents from that company, for example, contain industrial and domestic wastewaters, which contain oils, cyanides and traces of heavy metals which are to be treated to meet with the requirements of the environmental. The current treatment method consists of coagulation with ferric chloride as a first step combined with a chlorination step. Analysis of the outlet stream revealed that, the cyanide content was higher than the local Egyptian Environmental requirements, in addition, leakage of chlorine from the chlorination units which is highly dangerous and inevitable, was detected. Chlorine is highly toxic via inhalation, and is of intense irritation of the respiratory system, skin and eyes. Sufficient concentration of the gas irritates the mucous membranes, it can cause pulmonary edema. Liquid chlorine in contact with skin causes frostbite smarting of the skin. Vapors will cause severe irritation of eyes and throat and can cause eye and lung injury, moreover, the chlorination units are very expensive. Another disadvantage of this method is the poisonous effect of cyanogen chloride, which evolves when a waste containing concentrated cyanides is treated directly by this method The Fenton (FP) and Fenton-like (FLP) processes used in the present study proved to be better than the coagulation/chlorination method with respect to its higher efficiency, safe procedures and acceptable results.

2. Materials
Due to the real industrial nature of the present investigation, all experimental procedures were carried by laboratory means and the results were actually tested on an industrial scale using an already operating system. Preliminary experiments were carried out to choose the best laboratory operating conditions. The materials used for testing were: Sodium cyanide; 98.5% purity, Sodium hydroxide; 99% purity, Copper ion samples; mixture of copper cyanide,
sodium cyanide and sodium hydroxide, Chromium ion samples; mixture of potassium dichromate and sodium hydroxide, Nickel ion samples; mixture of nickel sulphate, boric acid and sodium hydroxide. (Where Cu, Cr and Ni mixtures represent the heavy metals in the real wastewater); Simulating oils (Lubricant oils, hydraulic oils, cooling oils, cut oils and quenching oils were obtained from Misr Co., Co - operation, Co., Exon Mobil Co. and Caltex Co., Cairo, Egypt., Sulphuric acid, 95 - 97 % purity, 1.84 g/cm³ density. used for adjusting pH, FeSO₄.7H₂O; 99 % purity, FeCl₃ . 6H₂O; 99% purity, H₂O₂ ; 30%, 1.15 g/cm³ density. Sodium hypochlorite, 15% available chlorine, Sodium bicarbonate, 99% purity, Fe₂(SO₄)₃; 65 to 75% purity.

The diversity of the wastewater obtained from that industry considered, due – of course – to the diverse operations and treatments, samples of the wastewater were carefully followed – up and collected over chosen periodical periods of times conforming with the diversity of industrial operations carried out. Table 1 shows the average characteristics of the real industrial wastewater collected at different periods of times aiming to attain representatives annual averages for the whole operations.

3. Experimental
To begin an experiment, 250 ml of the real wastewater is put in a 400 ml beaker fitted with a magnetic stirrer, where the pH is adjusted to 3 by H₂SO₄. The amount of reagent (either FeSO₄.7H₂O (FP) or FeCl₃.6H₂O (FLP)) designed for the experiment is added and homogenized by the stirrer. The designed amount of H₂O₂ is added. One hour stirring was found by preliminary studies to be sufficient for completion of treatment. Excess H₂O₂ is then removed by adding drops of sodium hydroxide for neutralization and to prevent interference with the results of sample analysis for the COD content and absorbance measurements. The pH of the sample is adjusted at 7 to 10 and allowed to settle overnight [1]. After filtration, the filtrate is tested for its COD and cyanide values.

ANALYSIS
COD and cyanide were analyzed according to standard examination methods of water and wastewater (1995) [2] by a calibrated Shimadzue spectrophotometer (Model UV – 120 – 02), H₂O₂ was determined by iodometric titration [3,4], pH measurements were carried out by pH meter CG 810 GMBH D 6238 HOFHEIM/TS – POSTFACH 1130, Heavy metals (Ni,Cr,Cu.) were determined with Nanocolor meter MACHEREY-NAGAL.GmbH & Co.KE Postfach 101352 D – 52313 DUEREN. Total suspended solids (T.S.S), oils and greases and BOD₅ analyses were determined according to standard methods of examinations. The total organic carbon (TOC) was determined by the potassium permanganate method [5,6].

4. Results and discussion
4.1 Effect of H₂O₂ Concentration
Experiments were thus carried out using real wastewater and up to 32 ml/l H₂O₂ and Fe²⁺ of 402 mg/l. The experimental results showed that the remaining amounts of iron and H₂O₂ by Fenton process were high. As can be seen from Figure 1 the removal of cyanide decreased and the values of COD were nearly constant for values after 2 ml/l H₂O₂, which may be attributed to the fact that the high amounts of H₂O₂ and iron act as scavengers for OH⁻ generating during the reaction between H₂O₂ and iron according to the following reactions [7,8].
\[ \text{Fe}^{2+} + \text{OH}^* \rightarrow \text{Fe}^{3+} + \text{OH}^- \]  \hspace{1cm} (1)
\[ \text{H}_2\text{O}_2 + \text{OH}^* \rightarrow \text{HO}_2^- + \text{H}_2\text{O} \]  \hspace{1cm} (2)
\[ \text{HO}_2^- + \text{OH}^* \rightarrow \text{H}_2\text{O} + \text{O}_2 \]  \hspace{1cm} (3)
\[ \text{OH}^* + \text{OH}^* \rightarrow \text{H}_2\text{O}_2 \]  \hspace{1cm} (4)

The optimum amount of \( \text{H}_2\text{O}_2 \) is thus about 2 ml/l as shown in Figure 1 where the removal of COD and cyanide was 93 and 71%, respectively. Thus experiments were carried out using up to 2.5 ml/l \( \text{H}_2\text{O}_2 \) for both FP and FLP and 100 mg/l of FeSO\(_4\).7H\(_2\)O (20 mg/l Fe\(^{2+}\), FP) as shown in Figure 2 and 100 mg/l FeCl\(_3\).6H\(_2\)O (20.7 mg/l Fe\(^{3+}\), FLP) as shown in Figure 3. Figure 2 shows that the COD and cyanide removals increase with increasing \( \text{H}_2\text{O}_2 \) until 1 ml/l which is due to the generation of OH\(^*\) during the reaction of FeSO\(_4\).7H\(_2\)O with \( \text{H}_2\text{O}_2 \). The removal then decreases, because the excess \( \text{H}_2\text{O}_2 \) scavenges the OH\(^*\). The COD reduction attained 92% while cyanide removal was 73% at 1 ml/l \( \text{H}_2\text{O}_2 \). Figure 3 on the other hand shows a COD reduction of 80% and a cyanide removal of 60% at 1 ml/l \( \text{H}_2\text{O}_2 \) concentration. The optimum operating \( \text{H}_2\text{O}_2 \) concentration is thus about 1 ml/l for the wastewater by both methods, FP and FLP.

### 4.2 Rate of \( \text{H}_2\text{O}_2 \) Consumption

Figure 4 shows that the concentration of \( \text{H}_2\text{O}_2 \) at 25\(^\circ\)C decreases from 1 ml/l to 0.156 ml/l by the Fenton process and to 0.34 ml/l by the Fenton-like (after 7 minutes), where \( \text{H}_2\text{O}_2 \) reacts with Fe\(^{2+}\) or Fe\(^{3+}\) very quickly at first and continue to decrease from 0.156 ml/l to nearly nil for Fenton and to 0.156 ml/l for Fenton-like process at the end of the reaction (after 240 minutes). Figure 5 on the other hand shows that the concentration of \( \text{H}_2\text{O}_2 \) at 45\(^\circ\)C, decreases within 15 minutes from 1 ml/l to 0.15 ml/l by the Fenton process and to 0.17 ml/l by the Fenton-like, where \( \text{H}_2\text{O}_2 \) reacts with Fe\(^{2+}\) or Fe\(^{3+}\) very quickly at first and decreases to be nil for Fenton and Fenton-like processes after 180 minutes and 120 minutes of reaction, respectively.

### 4.3 Effect of Fe\(^{2+}\) or Fe\(^{3+}\) concentration

Oxidation by \( \text{H}_2\text{O}_2 \) alone is not effective for high concentrations of certain refractory contaminants, such as highly chlorinated aromatic compounds and inorganic compounds such as cyanides, because of the low rates of reaction at reasonable \( \text{H}_2\text{O}_2 \) concentrations. Transition metal salts (e.g. iron salts), ozone and UV-light can activate \( \text{H}_2\text{O}_2 \) to form hydroxyl radicals which are strong oxidants [9].

When the added amount of Fe\(^{2+}\) increases, the elimination rate of pollutants increases as well [10]. However, when Fe\(^{2+}\) is overdosed, the hydroxyl radicals are scavenged as shown in the mechanism by equation (1)[7].

The effect of Fe\(^{2+}\) concentration on removal efficiencies for real wastewater by Fenton process is given in Figure 6 which shows that the maximum COD reduction is 92% by using 100 mg/l FeSO\(_4\).7H\(_2\)O (20 mg/l Fe\(^{2+}\)) and 1 ml/l \( \text{H}_2\text{O}_2 \) where pH and temperature are kept at 3 and 25\(^\circ\)C, respectively. At the same time 73% of cyanide content was removed. The effect of the dose of FeCl\(_3\).6H\(_2\)O on the COD value and cyanide removal efficiency by Fenton-like process has been studied and the results are shown in Figure 7. The maximum COD reduction is 80% by using 100 mg/l FeCl\(_3\).6H\(_2\)O (20.7 mg/l Fe\(^{3+}\)) and 1 ml/l \( \text{H}_2\text{O}_2 \) where pH and temperature are kept at 3 and 25\(^\circ\)C, respectively. At the same time 60% of cyanide removal was obtained. The Fe\(^{3+}\) formed can be expected to react with \( \text{H}_2\text{O}_2 \) as well as with hydroperoxy.
radicals (HO\textsubscript{2}\textsuperscript{-}) with regeneration of Fe\textsuperscript{2+} in the solution resulting in a decrease in COD value, as shown in equation 5 and 6 [9].

\[
\begin{align*}
\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{HO}_2^- \quad (5) \\
\text{Fe}^{3+} + \text{HO}_2^- & \rightarrow \text{Fe}^{2+} + \text{O}_2 + \text{H}^+ \quad (6)
\end{align*}
\]

Figures 6 and 7 show that the COD value and cyanide removal efficiency started to decrease after a dose of 100 mg/l of FeSO\textsubscript{4}.7H\textsubscript{2}O and FeCl\textsubscript{3}.6H\textsubscript{2}O (i.e 20 mg/l Fe\textsuperscript{2+} and 20.7 mg/l Fe\textsuperscript{3+}). This may be explained by the redox reactions also since OH\textsuperscript{-} may be scavenged by the reaction with the H\textsubscript{2}O\textsubscript{2} or with another Fe\textsuperscript{2+} molecules as shown before\textsuperscript{(7,8)} in equations (1to 4).

4.4 Effect of acidity of the medium

Real wastewater was treated by the Fenton process to determine the optimum pH as illustrated in Figure 8. About 92% COD decrease and 73% cyanide removal were obtained at pH 3 whereas the H\textsubscript{2}O\textsubscript{2} concentration was 1ml/l with 100 mg/l of FeSO\textsubscript{4}.7H\textsubscript{2}O. By the Fenton-like process the optimum pH was determined, by changing pH value between 1 and 5 as illustrated in Figure 9. About 80% COD and 60% cyanide removals were obtained at pH = 3 and at H\textsubscript{2}O\textsubscript{2} concentration of 1ml/l with FeCl\textsubscript{3}.6 H\textsubscript{2}O at 100 mg/l. The drop in efficiency at high pH values in COD and cyanide removals may be attributed to the precipitation of Fe(OH)\textsubscript{3}. In this form, iron decomposes H\textsubscript{2}O\textsubscript{2} into oxygen and water and consequently the oxidation rate decreases because less hydroxyl radicals are available [11]. On the other hand, at very low pH values the reaction may be inhibited where less amount of OH\textsuperscript{-} is present due to the scavenging effect of the hydrogen ion as shown in equation (7) [8].

\[
\text{OH}^- + \text{H}^+ + \text{e}^- \rightarrow \text{H}_2\text{O} \quad (7)
\]

4.5 Effect of Temperature

Figure 10, shows the COD and cyanide removal efficiencies for the real wastewater from 20\textdegree C to 65\textdegree C by the Fenton process where the COD reduction changes from 70% at 20\textdegree C to 75% at 65\textdegree C. The cyanide removal, on the other hand, changes from 37.5% at 20\textdegree C to 51% at 65\textdegree C. Figure 11 shows the trend by the Fenton- Like process where the COD reduction changes from 57.5% at 20\textdegree C to 80% at 65\textdegree C, where the cyanide removal hanges from 25% at 20\textdegree C to 34% at 65\textdegree C. It can be concluded that, the removal efficiencies for COD and cyanide is the highest at 45\textdegree C but for higher temperatures they are lower. At lower temperatures the reaction rate is expected to be slower and at higher temperatures the H\textsubscript{2}O\textsubscript{2} decomposes into oxygen and water. This agrees with some findings in literature [1,11], where the destabilization of flocs results in an increase in ferrous ions, which scavenges the OH\textsuperscript{-} during the Fenton’s reaction [7,8]. The rapid H\textsubscript{2}O\textsubscript{2} decomposition at high temperatures is a common behavior in the Fenton process [12].

4.6 Effect of presence of Excess H\textsubscript{2}O\textsubscript{2}

Figure (12) shows the effect of neutralization of a sample of wastewater after treatment by the Fenton and the Fenton–like processes on the COD and cyanide analysis. Sodium hydroxide was added to remove the residual H\textsubscript{2}O\textsubscript{2} which may interfere with wastewater analyses till neutralization. Results show that the neutralization gave better results for removals. The COD reduction percentage has increased by about 13.15% while the cyanide removal by about 36% for the Fenton process, by the Fenton - like process, on the other hand, an increase of 23.8% for COD reduction analysis and about 35% increase for the cyanide analysis was attained.
These findings can be interpreted by the fact that after treatment by the Fenton or the Fenton–like processes, highly insoluble Fe(OH)$_3$ forms in equilibrium with iron salts in solution, to give a flocculent precipitate which facilitates the separation of suspended materials such as domestic wastes and oils in effluent and so reducing the COD. Also, this treatment can reduce the dissolved compounds by adsorption onto the ferric gel [13]. As a result, both the COD reduction and cyanide removal will gain higher values.

4.7 Effect of Stirring
Figure 13 shows the effect of stirring speeds on COD and cyanide removals for real wastewater. The COD reduction efficiency by the Fenton process at (70 rpm) is 92%, at (170 rpm) is 60.16% and at (300 rpm) is 58%. The cyanide removal efficiency at (70 rpm) on the other hand is 73%, at (170 rpm) is 62%, at (300 rpm) is 37%. By the Fenton – like processes COD reduction efficiency at (70 rpm) is 80%, at (170 rpm) is 62.8% and at (300 rpm) is 49.5%. From these results it can be concluded that the low speed (70 rpm) is the best for the reaction results in between the three speeds tested, these results agree with literature findings [14,15]. This is perhaps due to the better steady state conditions given by low speed agitation and thus the resulting stream line actions far from turbulence which may accelerate the deterioration of some of the hydrogen peroxide reactant.

4.8 Effect of Catalyst Type
Figure 14 shows that the COD reduction efficiency is in the order Fe$_2$(SO$_4$)$_3$ = FeSO$_4$ > FeCl$_3$ and that it is the same for the cyanide removal efficiency. From literature [16], it was sited that, the presence of chloride ions in wastewater might act as a scavenger for hydroxyl radicals, thus decreasing the organic matter degradation. Also the Fe$^{3+}$ react with H$_2$O$_2$ producing HO$_2^*$ with regeneration of Fe$^{2+}$ in the solution. The HO$_2^*$ formed is relatively non-reactive with organic matter, being of lower oxidation capability than the OH$^*$ resulting in decrease in COD reduction.

4.9 Effect of Scavenging Elements
Figures 15 shows that the COD and cyanide removals decreased in presence of HCO$_3^-$ ions due to the OH$^*$ scavenging characteristics of HCO$_3^-$ by reacting with the free OH$^*$ as in reaction (8). The carbonate radicals (CO$_3^{2-}$*) formed could then react with H$_2$O$_2$ to form HO$_2^*$ (reaction 9). Both H$_2$O$_2$ and HO$_2^*$ are intermediate species with less oxidation potentials compared to the free hydroxyl radical. The presence of bicarbonate ions in water, thus, consumes the radicals and consequently decreases the oxidation rate of organics and cyanide.

\[ \text{OH}^* + \text{HCO}_3^- \rightarrow \text{CO}_3^{2-}^* + \text{H}_2\text{O} \]  
\[ \text{CO}_3^{2-}^* + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^* + \text{HCO}_3^- \]  

BIODEGRADIBILITY OF THE TREATED WASTEWATER:
The ratio of BOD$_5$/COD in wastewater is normally used to express the biodegradability of the wastewater. When the ratio of BOD$_5$/COD is more than 0.3, the wastewater has a better biodegradability, whereas if that ratio is less than 0.3, the wastewater is considered as difficult to be biodegraded [1,17,18].

The ratio of BOD$_5$/COD of the wastewater under study is 0.15 before treatments and thus it can’t be treated biologically, indicating that, wastewater containing cyanide and organic compounds (in the form of oils) inhibits the respiratory activity of bacterial seed due to their toxicity. After Fenton and Fenton – like treatments, the ratio of BOD$_5$/COD became 0.6 and
0.3, respectively. These ratios indicate that both Fenton and Fenton-like treatments can enhance the biological treatment since they can convert the pollutants present in the wastewater to be easily biodegraded, they can be used as pretreatment steps accompanied by biological treatments, since the values of the ratios of BOD₅/COD are equal to or higher than 0.3. A decrease in treatment costs can also be achieved by short reaction times and by using fewer chemicals.

AN APPROACH TO KINETIC STUDIES:

1. Time – Temperature Relations:
   At 25°C, 98.77% for COD and 97.8% for cyanide were obtained by the Fenton process while by the Fenton-like, the results were 95.5% for COD and 85.86% for cyanide removals. At 45°C the values were 99.3% for COD and 97.8% for cyanide by the Fenton process, while being 97% for COD and 84.8% for cyanide by the Fenton-like process.

   At the beginning of the reaction the results obtained at 45°C were better than the results at 25°C, while at the end of the reaction the removal efficiency for both two temperatures are nearly the same. Thus, operation at room temperature will be much more acceptable from an economic and operating point of views, for a maximum time of 300 minutes.

2. Kinetic Estimations:
   Figures 16 to 19 show the relation between time and logarithmic concentration ratios at different agitation speeds. The plots show straight line relations and the results agree with a first order reaction kinetics for both COD and cyanide treatments by both techniques; Fenton and Fenton–like processes. The following relation (10)
   \[ \ln \frac{C_t}{C_0} = -K_0t \]
   applies thus to both COD and Cyanide treatments, where C₀ and Cₜ are the ratios (mg/l) at zero and (t) time intervals and K₀ is a first–order rate stant (min⁻¹). Figure 20 shows the relation between log K₀ and log (agitation speed) for COD treatments by the Fenton and Fenton–like processes. It can be seen that log K₀ decreases with increasing log rpm and that the straight line corresponding to the Fenton process is higher than that for the Fenton–like process. Figure 21, on the other hand, shows the relation between log K₀ and log (agitation speed) for the removal of cyanide by both the Fenton and the Fenton-like processes. It can be observed also that log K₀ decreases with increasing of log (rpm); thus the same discussion above can be applied.

AN APPROXIMATE COMPARATIVE LOCAL COST ESTIMATION:

From experiments it was known that the initial COD was 16660 mg/l, the amount of H₂O₂ = 1ml/l. and ferrous sulphate was 100 mg/l. The average value of CODo wastewater for 6 months was calculated to be 2000 mg/l.

Chemicals were used in wastewater treatment according to COD values. If COD is 2000 mg/l, H₂O₂ needed was 0.12 ml/l (138 mg/l), FeSO₄.7H₂O is 12 mg/l, H₂SO₄ is 300 mg/l and Na₂CO₃ is 200 mg/l.

For achieving 99% COD reduction and 98 % cyanide removal by the Fenton process the total cost estimated was about 0.741 LE/m³ real wastewater in comparison to 0.981 LE/m³ real
wastewater for achieving 93% COD measurement and 94 % cyanide removal by the traditional method which shows an economic benefit besides the other technical and safety advantages discussed before.

5. Conclusion
As discussed before the efficiency and safety of the Fenton process are higher than those for the coagulation / chlorination method, also the costs of the novel processes are estimated to be lower than that for the coagulation / chlorination method. It is thus of importance to consider the Fenton process as the better treatment method for the real industrially produced cyanide wastewater. This is encouraged by two points of view; the first of which is the simplicity of its application accompanied by its lower costs, and the second, is its sustainable friendship to environmental impacts. The chemicals and operating conditions of the Fenton process have the least (or no) corrosion behavior; this elongates the life operating time of equipment, as compared to the conditions of the traditional methods using chlorine and chlorides. Kinetic studies proved that both the Fenton and Fenton-like processes can be expressed by the simple first-order reaction for both COD changes and cyanide removals. The ratio (BOD₅/COD) were found to be of about 0.6 and 0.3 maximum values for real effluent by novel methods Fenton and Fenton – Like treatments compare to 0.12 and 0.15 values before treatments. These ratios indicate that both Fenton and Fenton – Like treatment can enhance the biological treatment since they can convert the pollutants present in the wastewater to be easily biodegraded, which gives an additional benefit for these novel techniques.

REFERENCES
Figure 1: Effect of different H$_2$O$_2$ concentrations on removal efficiency
(COD$_0$ = 16660 mg/l, CN$^-_0$ = 9.11 mg/l, Time = 60 min, Temp = 25$^\circ$C, pH = 3,
Fe$^{2+}$ = 402 mg/l)

Figure 2: Effect of low H$_2$O$_2$ concentration on removal efficiency (FP, RW) (Temp = 25$^\circ$C,
(COD$_0$ = 16660 mg/l, Fe$^{3+}$ = 20 mg/l)
CN$^-_0$ = 9.11 mg/l, Time = 60 min)

Figure 3: Effect of H$_2$O$_2$ concentration on removal efficiency (FLP, RW)
(COD$_0$ = 16660 mg/l, CN$^-_0$ = 9.11 mg/l
pH = 3, Time = 60 min, Fe$^{3+}$ = 20.7 mg/l
Temp = 25 $^\circ$C)
Figure 5: Comparative consumption of H$_2$O$_2$ by time at 45°C by both (FP and FLP) (COD$_0$ = 16660 mg/l, CN$_0$ = 9.11 mg/l pH = 3, Fe$^{2+}$ = 20 mg/l, Fe$^{3+}$ = 20.7 mg/l)

Figure 4: Comparative consumption of H$_2$O$_2$ by time at 25°C by both (FP and FLP). CN$_0$ = 9.11 mg/l, pH =3, Fe$^{2+}$ = 20 mg/l COD$_0$ =16660 mg/l, Fe$^{3+}$ = 20.7 mg/l

Figure 7: Effect of Fe$^{3+}$ dose on removal efficiency (FLP) (COD$_0$=16660 mg/l, pH=3 CN$_0$ = 9.11 mg/l, Temp. = 25°C, H$_2$O$_2$ = 1ml/l Time = 60 min)

Figure 6: Effect of Fe$^{2+}$ dose on removal efficiency, (Fe$^{2+}$=20 mg/l, CN$_0$ = 9.11mg/l, pH = 3, Temp.=25°C, COD$_0$=16660mg/l, H$_2$O$_2$ = 1ml/l,Time = 60min)
Figure 8: Effect of pH values on removal efficiency (FP)
(COD$_0$ = 16660 mg/l, CN$^-$_0 = 9.11 mg/l, Fe$^{2+}$ = 20 mg/l, Time = 60 min, Temp. = 25°C, H$_2$O$_2$ = 1 ml/l)

Figure 9: Effect of pH values on removal efficiency (FLP) (H$_2$O$_2$ = 1 ml/l, Time = 60 min, Temp = 25°C, COD$_0$=16660 mg/l, CN$^-$_0 = 9.11 mg/l, Fe$^{3+}$ = 20.7 mg/l)

Figure 10: Effect of temperature on COD depression and cyanide removal efficiency for (FP) (COD$_0$ = 16660 mg/l, CN$^-$_0 = 9.11 mg/l, Fe$^{2+}$ = 20 mg/l, H$_2$O$_2$ = 1 ml/l, pH = 3, Time = 60 min)

Figure 11: Effect of temperature on COD depression and cyanide removal efficiency for (FLP) (COD$_0$ = 16660 mg/l, CN$^-$_0 = 9.11 mg/l, Fe$^{3+}$ = 20.7 mg/l, H$_2$O$_2$ = 1 ml/l, pH = 3, Time = 60 min)
Figure 12: Effect of presence of free H₂O₂ after treatment (Fe³⁺ = 20.7 mg/l, H₂O₂ = 1 ml/l, Fe²⁺ = 20 mg/l, pH = 3, Time = 60 min, COD₀ = 16660 mg/l, CN₋₀ = 9.11 mg/l).

Figure 13: Effect of stirring on COD and cyanide removals (Fe³⁺ = 20.7 mg/l, H₂O₂ = 1 ml/l, Fe²⁺ = 20 mg/l, pH = 3, Time = 60 min, COD₀ = 16660 mg/l, CN₋₀ = 9.11 mg/l).
Figure 14: Effect of the type of catalyst on COD and cyanide removals.
(COD₀ = 16660 mg/l, CN₀ = 9.11 mg/l, pH = 3, H₂O₂ = 1 ml/l, Fe²⁺ = 20 mg/l, Fe³⁺ = 20.7 mg/l, Time = 60 min)

Figure 15: Effect of (OH⁻) scavengers on COD and cyanide removals
(H₂O₂ = 1 ml/l, Fe²⁺ = 20 mg/l, pH = 3, Time = 60 min, Fe³⁺ = 20.7 mg/l, CN₀ = 9.11 mg/l, COD₀ = 16660 mg/l)
Figure 16: COD – Logarithmic dimensionless concentration change (FP) ($\text{COD}_0 = 2640 \text{ mg/l}$, pH=3, $\text{CN}^{-} = 120 \text{ mg/l}$, $\text{Fe}^{2+} = 60 \text{ mg/l}$, Temp. = 25°C, $\text{H}_2\text{O}_2 = 4 \text{ ml/l}$)

$y = -0.0446x$
$R^2 = 0.9906$

$y = -0.0355x$
$R^2 = 0.992$

$y = -0.0246x$
$R^2 = 0.9812$

Figure 17: COD – Logarithmic dimensionless concentration change (FLP) ($\text{COD}_0 = 2640 \text{ mg/l}$, pH=3, $\text{CN}^{-} = 120 \text{ mg/l}$, $\text{Fe}^{3+} = 62 \text{ mg/l}$, $\text{H}_2\text{O}_2 = 4 \text{ ml/l}$, Temp. = 25°C)

$y = -0.0297x$
$R^2 = 0.9906$

Figure 18: Cyanide – Logarithmic dimensionless concentration change (FP) ($\text{COD}_0 = 2640 \text{ mg/l}$, $\text{CN}^{-} = 120 \text{ mg/l}$, $\text{H}_2\text{O}_2 = 4 \text{ ml/l}$, Temp. = 25°C, $\text{Fe}^{2+} = 60 \text{ mg/l}$)

$y = -0.0228x$
$R^2 = 0.9956$

$y = -0.0166x$
$R^2 = 0.9932$

$y = -0.0136x$
$R^2 = 0.9858$
Figure 19: Cyanide – Logarithmic dimensionless concentration change (FLP)
COD₀ = 2640 mg/l, CN₀ = 120 mg/l, H₂O₂ = 4 ml/l, Temp. = 25°C, Fe²⁺ = 62 mg/l

Figure 20: Log Ko versus log rpm for COD changes
\[ y_1 = -0.4171x - 0.7953 \]
\[ R_1^2 = 0.9997 \]
\[ y_2 = -0.355x - 0.9868 \]
\[ R_2^2 = 1 \]

**Figure 21:** Log \( K_o \) versus log rpm for cyanide removal

**Table 1:** Characteristics of the investigated real wastewater (RW)

<table>
<thead>
<tr>
<th>Parameter (ppm)</th>
<th>Periodical effluent types (Averages)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(6 months)</td>
</tr>
<tr>
<td></td>
<td>(15 days + heavy oils)</td>
</tr>
<tr>
<td></td>
<td>(15 days + light oils)</td>
</tr>
<tr>
<td>COD</td>
<td>2000</td>
</tr>
<tr>
<td>CN</td>
<td>8.7</td>
</tr>
<tr>
<td>Oils</td>
<td>4000</td>
</tr>
<tr>
<td>pH</td>
<td>6.6</td>
</tr>
<tr>
<td>T.S.S</td>
<td>400</td>
</tr>
<tr>
<td>BOD₅</td>
<td>450</td>
</tr>
<tr>
<td>TOC</td>
<td>700</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>0.114</td>
</tr>
<tr>
<td>Cr (VI)⁺</td>
<td>0.3</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>0.85</td>
</tr>
</tbody>
</table>

**Table 2:** Optimum operating conditions for real wastewater treatments

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2\text{O}_2 )</td>
<td>1150 mg/l</td>
</tr>
<tr>
<td>( \text{FeSO}_4\cdot7\text{H}_2\text{O} )</td>
<td>100 mg/l</td>
</tr>
<tr>
<td>Reaction time</td>
<td>300 min</td>
</tr>
<tr>
<td>PH</td>
<td>3</td>
</tr>
<tr>
<td>Temperature</td>
<td>45°C</td>
</tr>
<tr>
<td>Speed of Agitator</td>
<td>70 rpm</td>
</tr>
<tr>
<td>COD</td>
<td>16660 mg/l</td>
</tr>
</tbody>
</table>
Table 3: Total cost for treating one m³ by the Fenton process

<table>
<thead>
<tr>
<th>Description</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemicals costs, Na₂CO₃ is used</td>
<td>0.73 LE</td>
</tr>
<tr>
<td>Equipments costs</td>
<td>11 × 10⁻³ LE</td>
</tr>
<tr>
<td>Construction costs</td>
<td>2.14 × 10⁻⁴ LE</td>
</tr>
<tr>
<td>Total costs, Na₂CO₃ is used</td>
<td>0.741 LE</td>
</tr>
</tbody>
</table>
Military Technical College
Kobry El-Kobbah,
Cairo, Egypt

5th International Conference on
Chemical & Environmental Engineering