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**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 BOD<sub>5</sub>/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; mixtures 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., Exxon Mobil Co. and Caltex Co., Cairo, Egypt., Sulphuric acid, 95 - 97 % purity, 1.84 g/cm<sup>3</sup> density. used for adjusting pH, FeSO<sub>4</sub>.7H<sub>2</sub>O; 99 % purity, FeCl<sub>3</sub> . 6H<sub>2</sub>O; 99% purity, H<sub>2</sub>O<sub>2</sub> ; 30%, 1.15 g/cm<sup>3</sup> density, Sodium hypochlorite, 15% available chlorine, Sodium bicarbonate, 99% purity, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>; 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 H<sub>2</sub>SO<sub>4</sub>. The amount of reagent (either FeSO<sub>4</sub>.7H<sub>2</sub>O (FP) or FeCl<sub>3</sub>.6H<sub>2</sub>O (FLP)) designed for the experiment is added and homogenized by the stirrer. The designed amount of H<sub>2</sub>O<sub>2</sub> is added. One hour stirring was found by preliminary studies to be sufficient for completion of treatment. Excess H<sub>2</sub>O<sub>2</sub> 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 Shimadzu spectrophotometer (Model UV – 120 – 02), H<sub>2</sub>O<sub>2</sub> 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 BOD<sub>5</sub> 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 H<sub>2</sub>O<sub>2</sub> Concentration

Experiments were thus carried out using real wastewater and up to 32 ml/l H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> of 402 mg/l. The experimental results showed that the remaining amounts of iron and H<sub>2</sub>O<sub>2</sub> 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 H<sub>2</sub>O<sub>2</sub>, which may be attributed to the fact that the high amounts of H<sub>2</sub>O<sub>2</sub> and iron act as scavengers for OH<sup>•</sup> generating during the reaction between H<sub>2</sub>O<sub>2</sub> and iron according to the following reactions [7,8].



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  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (20 mg/l  $\text{Fe}^{2+}$ , FP) as shown in Figure 2 and 100 mg/l  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (20.7 mg/l  $\text{Fe}^{3+}$ , 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 1ml/l which is due to the generation of  $\text{OH}^{\bullet}$  during the reaction of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  with  $\text{H}_2\text{O}_2$ . The removal then decreases, because the excess  $\text{H}_2\text{O}_2$  scavenges the  $\text{OH}^{\bullet}$ . The COD reduction attained 92% while cyanide removal was 73% at 1ml/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  $\text{H}_2\text{O}_2$  concentration of 1ml/l. 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  $25^{\circ}\text{C}$  decreases from 1ml/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  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  very quickly at first and continue to decrease from 0.156ml/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  $45^{\circ}\text{C}$ , decreases within 15 minutes from 1ml/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  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  very quickly at first and decreases to be nil for Fenton and Fenton-like processes after 180 minutes and 120 minutes of reaction, respectively.

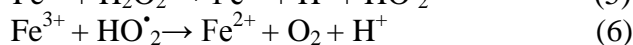
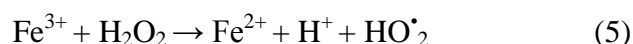
#### 4.3 Effect of $\text{Fe}^{2+}$ or $\text{Fe}^{3+}$ concentration

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

The effect of  $\text{Fe}^{2+}$  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  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (20 mg/l  $\text{Fe}^{2+}$ ) and 1 ml/l  $\text{H}_2\text{O}_2$  where pH and temperature are kept at 3 and  $25^{\circ}\text{C}$ , respectively. At the same time 73% of cyanide content was removed. The effect of the dose of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  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  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (20.7 mg/l  $\text{Fe}^{3+}$ ) and 1 ml/l  $\text{H}_2\text{O}_2$  where pH and temperature are kept at 3 and  $25^{\circ}\text{C}$ , respectively. At the same time 60% of cyanide removal was obtained. The  $\text{Fe}^{3+}$  formed can be expected to react with  $\text{H}_2\text{O}_2$  as well as with hydroperoxy

radicals ( $\text{HO}\cdot_2$ ) with regeneration of  $\text{Fe}^{2+}$  in the solution resulting in a decrease in COD value, as shown in equation 5 and 6 [9] .



Figures 6 and 7 show that the COD value and cyanide removal efficiency started to decrease after a dose of 100 mg/l of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (i.e 20 mg/l  $\text{Fe}^{2+}$  and 20.7 mg/l  $\text{Fe}^{3+}$ ). This may be explained by the redox reactions also since  $\text{OH}\cdot$  may be scavenged by the reaction with the  $\text{H}_2\text{O}_2$  or with another  $\text{Fe}^{2+}$  molecules as shown before<sup>(7,8)</sup> in equations (1 to 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  $\text{H}_2\text{O}_2$  concentration was 1ml/l with 100 mg/l of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ . 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  $\text{H}_2\text{O}_2$  concentration of 1ml/l with  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  at 100 mg/l. The drop in efficiency at high pH values in COD and cyanide removals may be attributed to the precipitation of  $\text{Fe}(\text{OH})_3$ . In this form, iron decomposes  $\text{H}_2\text{O}_2$  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  $\text{OH}\cdot$  is present due to the scavenging effect of the hydrogen ion as shown in equation (7) [8].



#### 4.5 Effect of Temperature

Figure 10, shows the COD and cyanide removal efficiencies for the real wastewater from 20°C to 65°C by the Fenton process where the COD reduction changes from 70% at 20°C to 75% at 65°C. The cyanide removal, on the other hand, changes from 37.5% at 20°C to 51% at 65°C. Figure 11 shows the trend by the Fenton- Like process where the COD reduction changes from 57.5% at 20°C to 80% at 65°C, where the cyanide removal hanges from 25% at 20°C to 34% at 65 °C. It can be concluded that, the removal efficiencies for COD and cyanide is the highest at 45°C but for higher temperatures they are lower. At lower temperatures the reaction rate is expected to be slower and at higher temperatures the  $\text{H}_2\text{O}_2$  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  $\text{OH}\cdot$  during the Fenton's reaction [7,8]. The rapid  $\text{H}_2\text{O}_2$  decomposition at high temperatures is a common behavior in the Fenton process [12].

#### 4.6 Effect of presence of Excess $\text{H}_2\text{O}_2$

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  $\text{H}_2\text{O}_2$  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  $\text{Fe}(\text{OH})_3$  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 process 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  $\text{Fe}_2(\text{SO}_4)_3 = \text{FeSO}_4 > \text{FeCl}_3$  and that it is the same for the cyanide removal efficiency. From literature<sup>(16)</sup>, 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  $\text{Fe}^{3+}$  react with  $\text{H}_2\text{O}_2$  producing  $\text{HO}_2^\bullet$  with regeneration of  $\text{Fe}^{2+}$  in the solution. The  $\text{HO}_2^\bullet$  formed is relatively non-reactive with organic matter, being of lower oxidation capability than the  $\text{OH}^\bullet$  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  $\text{HCO}_3^-$  ions due to the  $\text{OH}^\bullet$  scavenging characteristics of  $\text{HCO}_3^-$  by reacting with the free  $\text{OH}^\bullet$  as in reaction (8). The carbonate radicals ( $\text{CO}_3^{\bullet-}$ ) formed could then react with  $\text{H}_2\text{O}_2$  to form  $\text{HO}_2^\bullet$  (reaction 9). Both  $\text{H}_2\text{O}_2$  and  $\text{HO}_2^\bullet$  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.



#### BIODEGRADIBILITY OF THE TREATED WASTEWATER:

The ratio of  $\text{BOD}_5/\text{COD}$  in wastewater is normally used to express the biodegradability of the wastewater. When the ratio of  $\text{BOD}_5/\text{COD}$  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  $\text{BOD}_5/\text{COD}$  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  $\text{BOD}_5/\text{COD}$  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 BOD<sub>5</sub>/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)

$$\ln C_t / C_0 = - K_0 t \quad (10)$$

applies thus to both COD and Cyanide treatments, where C<sub>0</sub> and C<sub>t</sub> are the ratios (mg/l) at zero and (t) time intervals and K<sub>0</sub> is a first-order rate constant (min<sup>-1</sup>). Figure 20 shows the relation between log K<sub>0</sub> and log (agitation speed) for COD treatments by the Fenton and Fenton-like processes. It can be seen that log K<sub>0</sub> 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 K<sub>0</sub> 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 K<sub>0</sub> 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 H<sub>2</sub>O<sub>2</sub> = 1ml/l. and ferrous sulphate was 100 mg/l. The average value of COD<sub>0</sub> 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, H<sub>2</sub>O<sub>2</sub> needed was 0.12 ml/l (138 mg/l), FeSO<sub>4</sub>·7H<sub>2</sub>O is 12 mg/l, H<sub>2</sub>SO<sub>4</sub> is 300 mg/l and Na<sub>2</sub>CO<sub>3</sub> 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/m<sup>3</sup> real wastewater in comparison to 0.981 LE/m<sup>3</sup> 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 (BOD<sub>5</sub>/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.

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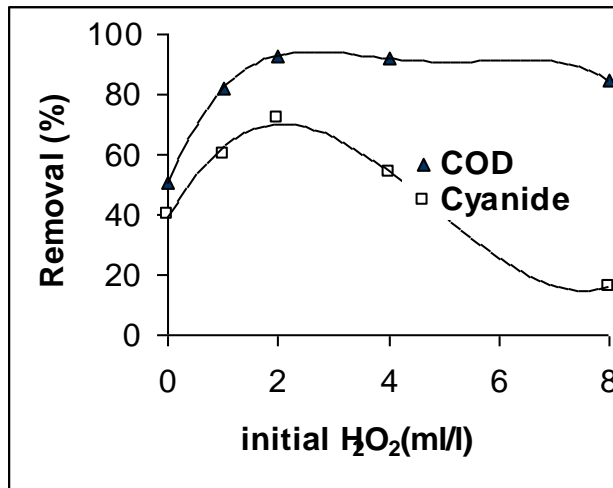


Figure 1: Effect of different H<sub>2</sub>O<sub>2</sub> concentrations on removal efficiency  
 ( COD<sub>0</sub> = 16660 mg/l, CN<sub>0</sub> = 9.11 mg/l, Time = 60 min, Temp = 25<sup>o</sup>C, pH = 3  
 Fe<sup>2+</sup> = 402 mg/l)

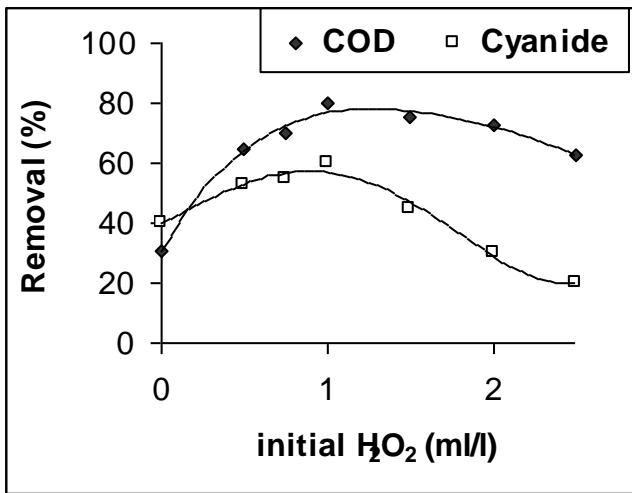


Figure 3: Effect of H<sub>2</sub>O<sub>2</sub> concentration on removal efficiency (FLP, RW)

(COD<sub>0</sub> = 16660 mg/l, CN<sub>0</sub> = 9.11 mg/l  
 pH = 3, Time = 60 min, Fe<sup>3+</sup> = 20.7 mg/l  
 Temp = 25<sup>o</sup>C)

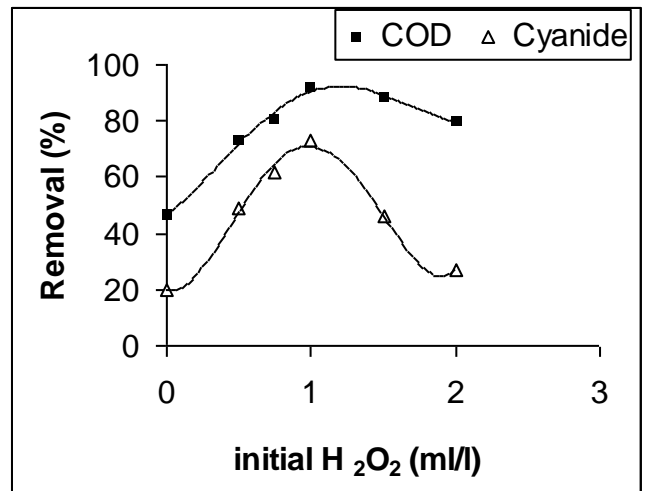


Figure (2): Effect of low H<sub>2</sub>O<sub>2</sub> concentration on removal efficiency (FP, RW) (Temp = 25<sup>o</sup>C,  
 (COD<sub>0</sub> = 16660 mg/l, Fe<sup>2+</sup> = 20 mg/l)  
 CN<sub>0</sub> = 9.11 mg/l, Time = 60 min)

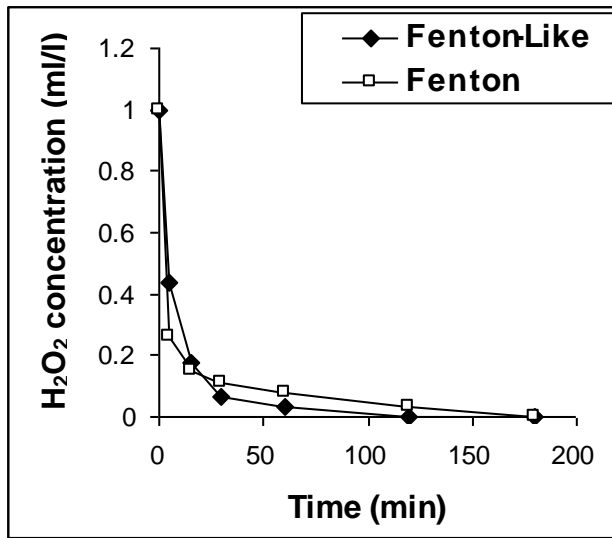


Figure 5: Comparative consumption of  $H_2O_2$  by time at  $45^\circ C$  by both (FP and FLP) ( $COD_0 = 16660 \text{ mg/l}$ ,  $CN_0 = 9.11 \text{ mg/l}$ ,  $pH = 3$ ,  $Fe^{2+} = 20 \text{ mg/l}$ ,  $Fe^{3+} = 20.7 \text{ mg/l}$ )

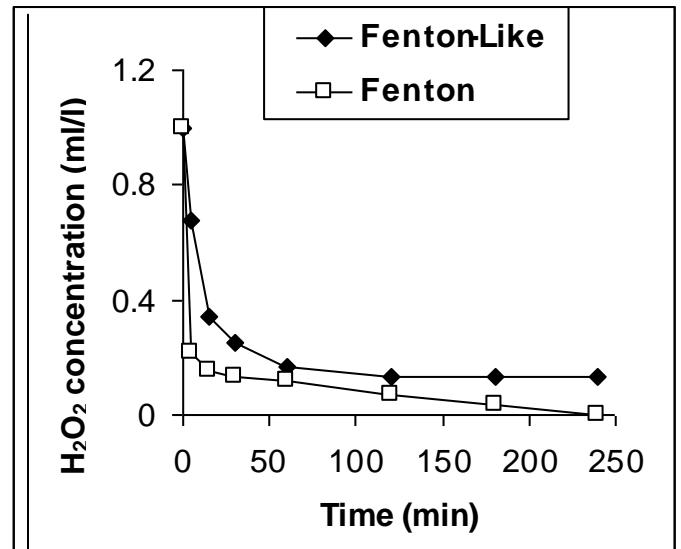


Figure 4: Comparative consumption of  $H_2O_2$  by time at  $25^\circ C$  by both (FP and FLP). ( $CN_0 = 9.11 \text{ mg/l}$ ,  $pH = 3$ ,  $Fe^{2+} = 20 \text{ mg/l}$ ,  $COD_0 = 16660 \text{ mg/l}$ ,  $Fe^{3+} = 20.7 \text{ mg/l}$ )

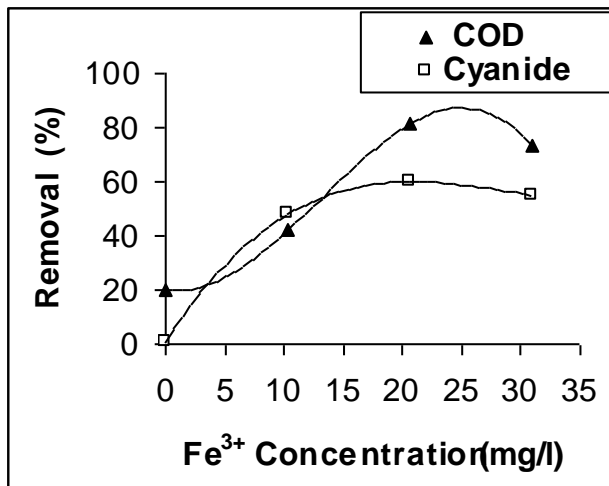


Figure 7: Effect of  $Fe^{3+}$  dose on removal Efficiency (FLP) ( $COD_0 = 16660 \text{ mg/l}$ ,  $pH = 3$ ,  $CN_0 = 9.11 \text{ mg/l}$ ,  $Temp. = 25^\circ C$ ,  $H_2O_2 = 1 \text{ ml/l}$ ,  $Time = 60 \text{ min}$ )

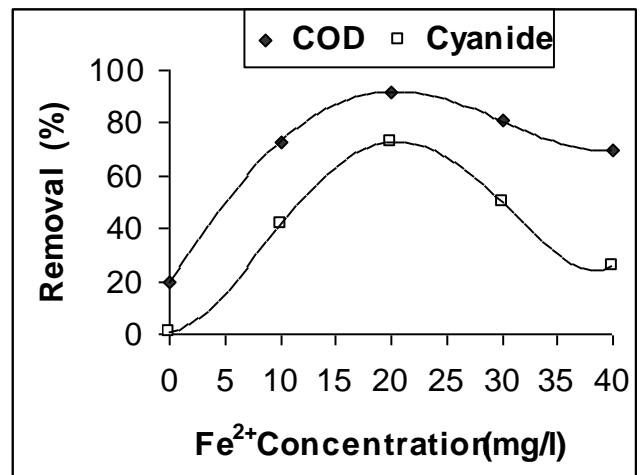


Figure 6: Effect of  $Fe^{2+}$  dose on removal efficiency, ( $Fe^{2+} = 20 \text{ mg/l}$ ,  $CN_0 = 9.11 \text{ mg/l}$ ,  $pH = 3$ ,  $Temp. = 25^\circ C$ ,  $COD_0 = 16660 \text{ mg/l}$ ,  $H_2O_2 = 1 \text{ ml/l}$ ,  $Time = 60 \text{ min}$ )

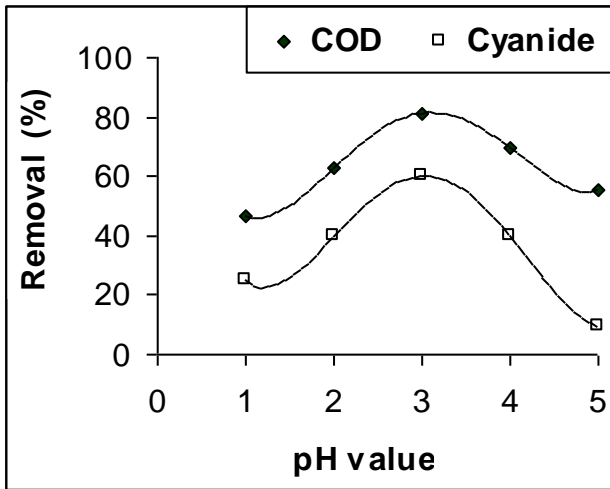


Figure 9: Effect of pH values on removal efficiency (FLP) ( $H_2O_2 = 1\text{ml/l}$ , Time = 60 min Temp =  $25^\circ\text{C}$ ,  $COD_0 = 16660\text{ mg/l}$ ,  $CN^-_0 = 9.11\text{ mg/l}$ ,  $Fe^{3+} = 20.7\text{ mg/l}$ )

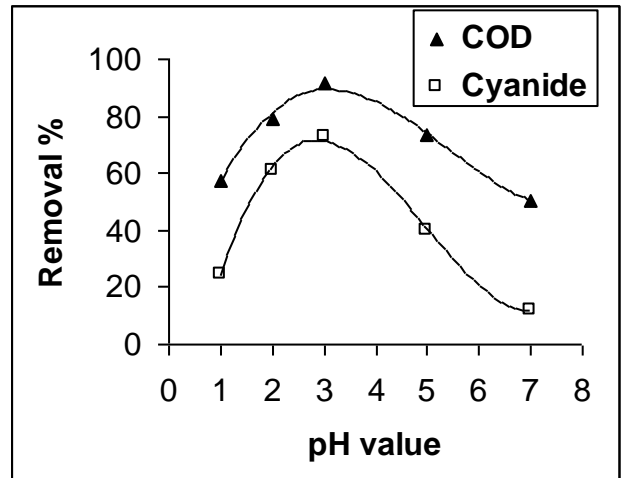


Figure 8: Effect of pH values on removal efficiency (FP) ( $COD_0 = 16660\text{ mg/l}$ ,  $CN^-_0 = 9.11\text{ mg/l}$ ,  $Fe^{2+} = 20\text{ mg/l}$ , Time = 60 min Temp. =  $25^\circ\text{C}$ ,  $H_2O_2 = 1\text{ml/l}$ )

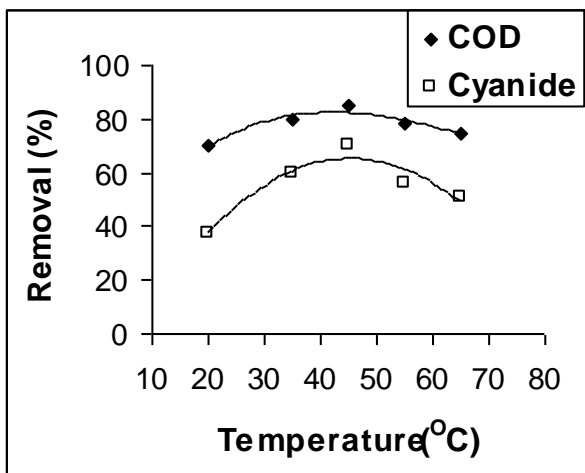


Figure 10: Effect of temperature on COD depression and cyanide removal efficiency for (FP) ( $COD_0 = 16660\text{ mg/l}$ ,  $CN^-_0 = 9.11\text{ mg/l}$ ,  $Fe^{2+} = 20\text{ mg/l}$ ,  $H_2O_2 = 1\text{ ml/l}$ , pH = 3, Time = 60 min)

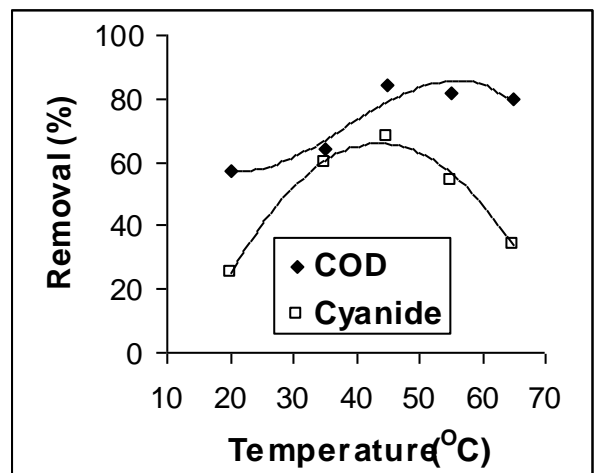


Figure 11: Effect of temperature on COD depression and cyanide removal efficiency for (FLP) ( $COD_0 = 16660\text{ mg/l}$ ,  $CN^-_0 = 9.11\text{ mg/l}$ ,  $Fe^{3+} = 20.7\text{ mg/l}$ ,  $H_2O_2 = 1\text{ ml/l}$ , pH = 3, Time = 60 min)

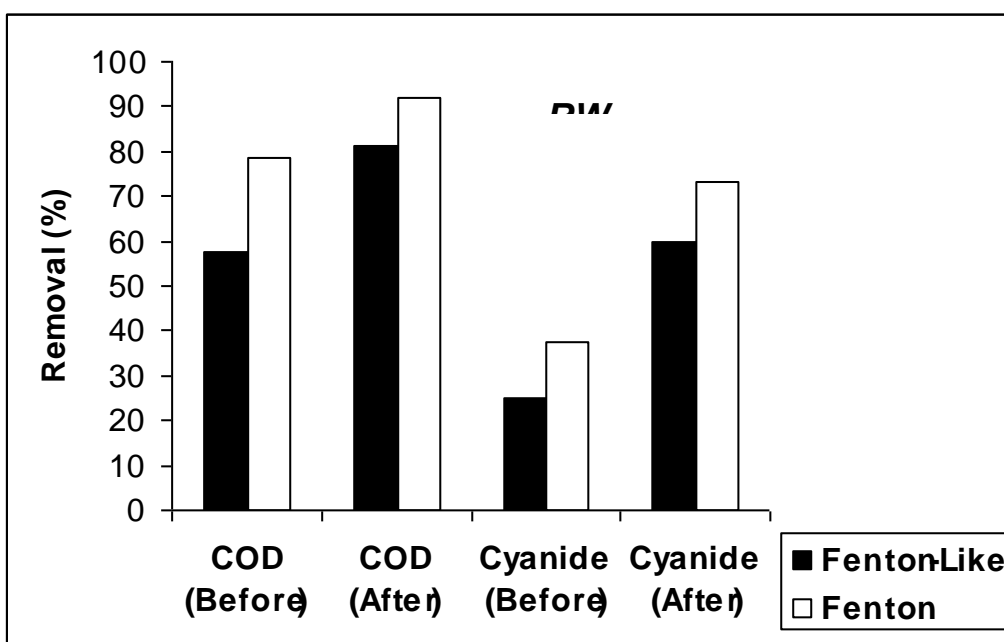


Figure 12: Effect of presence of free H<sub>2</sub>O<sub>2</sub> after treatment ( Fe<sup>3+</sup> =20.7mg/l H<sub>2</sub>O<sub>2</sub> = 1ml/l, Fe<sup>2+</sup> = 20 mg/l , pH = 3, Time = 60 min, COD<sub>O</sub>= 16660 mg/l CN<sub>O</sub> = 9.11 mg/l)

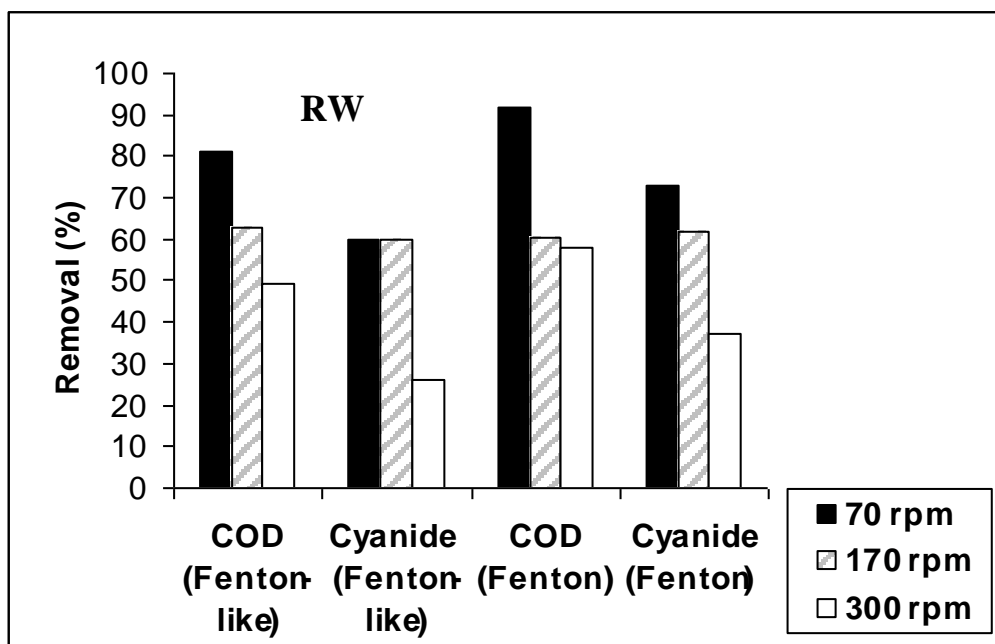


Figure 13: Effect of stirring on COD and cyanide removals ( Fe<sup>3+</sup> =20.7mg/l H<sub>2</sub>O<sub>2</sub> = 1ml/l, Fe<sup>2+</sup> = 20 mg/l , pH = 3, Time = 60 min, COD<sub>O</sub>= 16660 mg/l CN<sub>O</sub> = 9.11 mg/l)

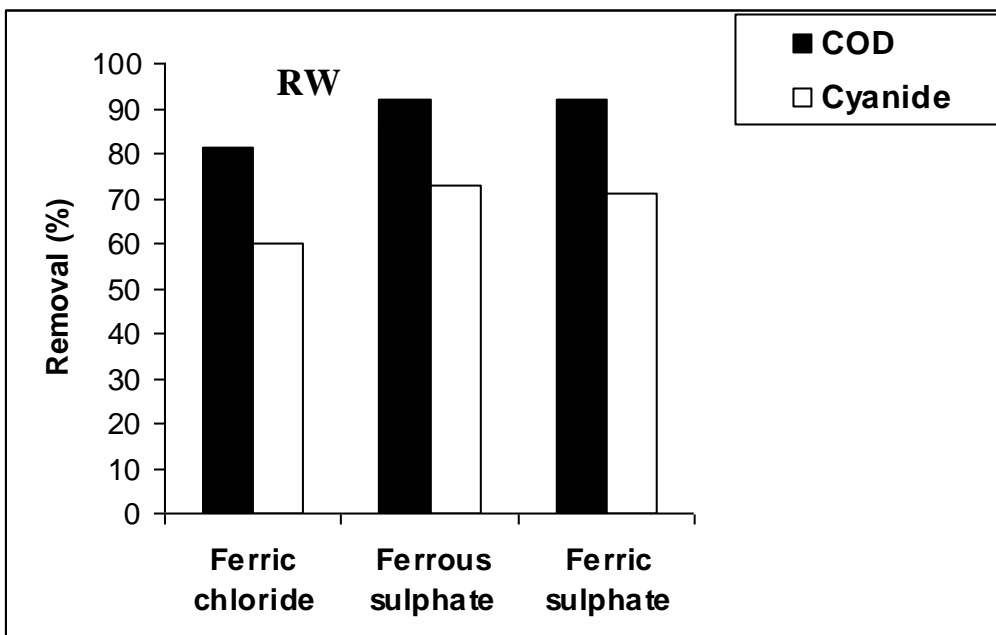


Figure 14: Effect of the type of catalyst on COD and cyanide removals. (  $COD_0 = 16660 \text{ mg/l}$ ,  $CN^-_0 = 9.11 \text{ mg/l}$ ,  $pH = 3$ ,  $H_2O_2 = 1 \text{ ml/l}$ ,  $Fe^{2+} = 20 \text{ mg/l}$ ,  $Fe^{3+} = 20.7 \text{ mg/l}$ , Time = 60 min)

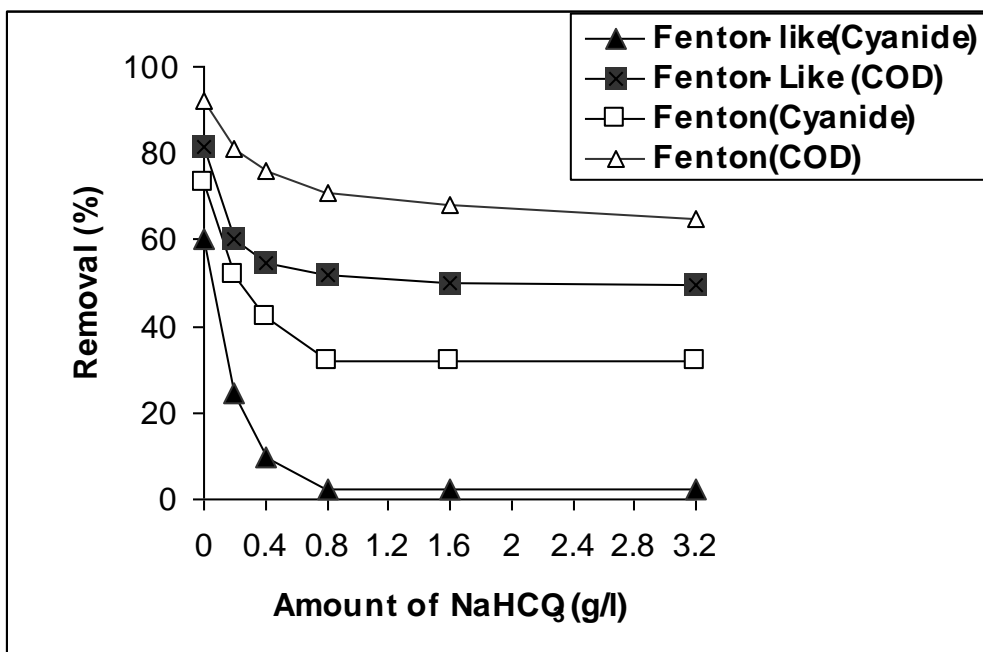


Figure 15: Effect of (OH•) scavengers on COD and cyanide removals ( $H_2O_2 = 1 \text{ ml/l}$ ,  $Fe^{2+} = 20 \text{ mg/l}$ ,  $pH = 3$ , Time = 60 min,  $Fe^{3+} = 20.7 \text{ mg/l}$ ,  $CN^-_0 = 9.11 \text{ mg/l}$ ,  $COD_0 = 16660 \text{ mg/l}$ )

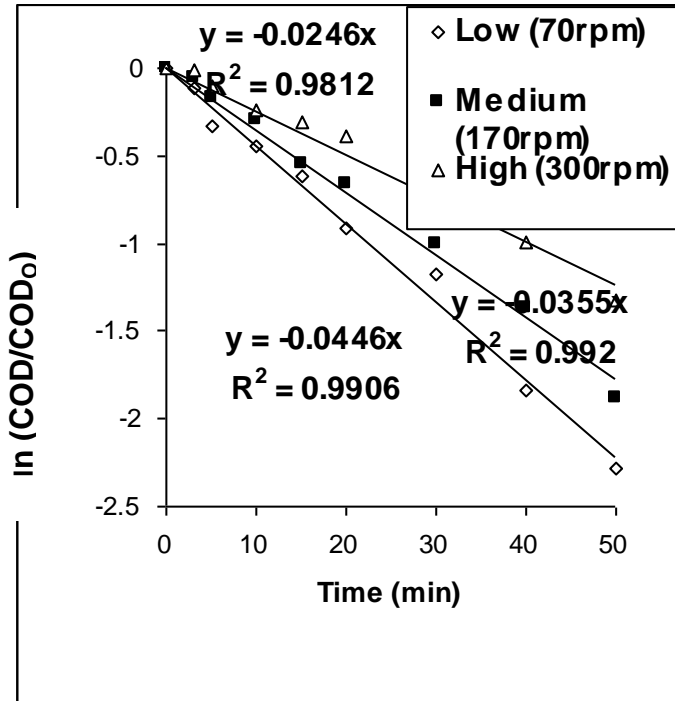


Figure 16: COD – Logarithmic dimensionless concentration change (FP) (  $COD_0 = 2640$  mg/l, pH=3,  $CN_0 = 120$ mg/l,,  $Fe^{2+} = 60$ mg/l., Temp. =  $25^{\circ}C$  ,  $H_2O_2 = 4$ ml/l)

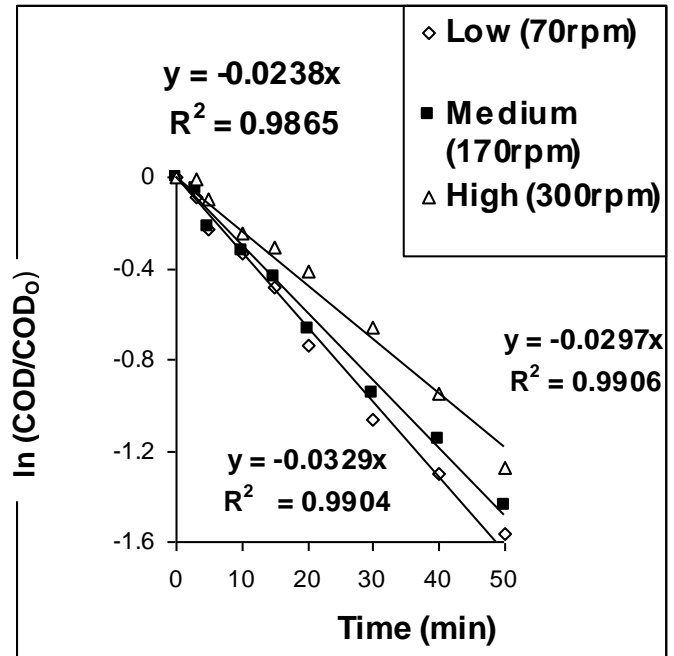


Figure (17): COD – Logarithmic dimensionless concentration change (FLP) ( $COD_0 = 2640$  mg/l, pH=3,  $CN_0 = 120$ mg/l.,  $Fe^{3+} = 62$ mg/l.,  $H_2O_2 = 4$ ml/l, Temp. =  $25^{\circ}C$ )

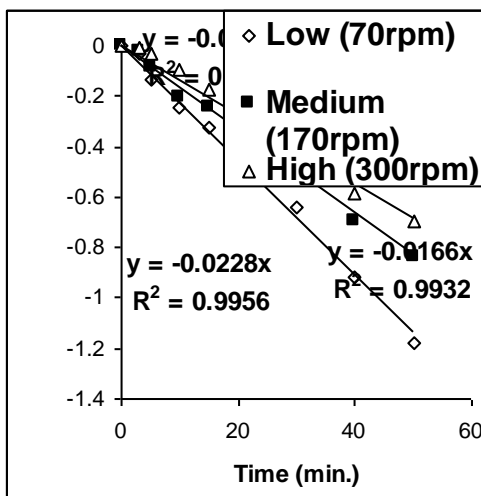


Figure18)Cyanide – Logarithmic dimensionless concentration change (FP) ( $COD_0 = 2640$  mg/l,  $CN_0 = 120$  mg/l,  $H_2O_2 = 4$ ml/l, Temp.=  $25^{\circ}C$ ,  $Fe^{2+} = 60$  mg/l)

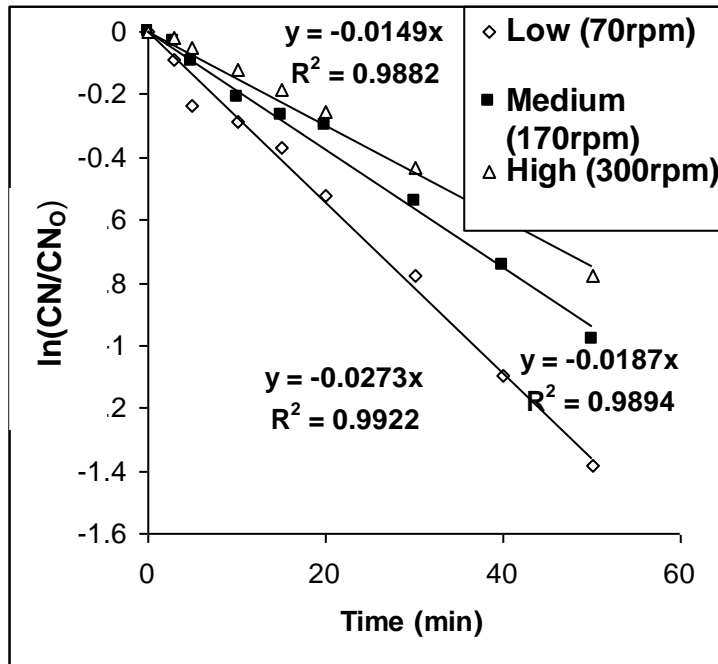


Figure19 Cyanide – Logarithmic dimensionless concentration change (FLP)  
 $COD_0 = 2640 \text{ mg/l}$ ,  $CN_0^- = 120 \text{ mg/l}$ ,  
 $H_2O_2 = 4 \text{ ml/l}$ . Temp. =  $25^\circ\text{C}$ .  $Fe^{3+} = 62 \text{ mg/l}$

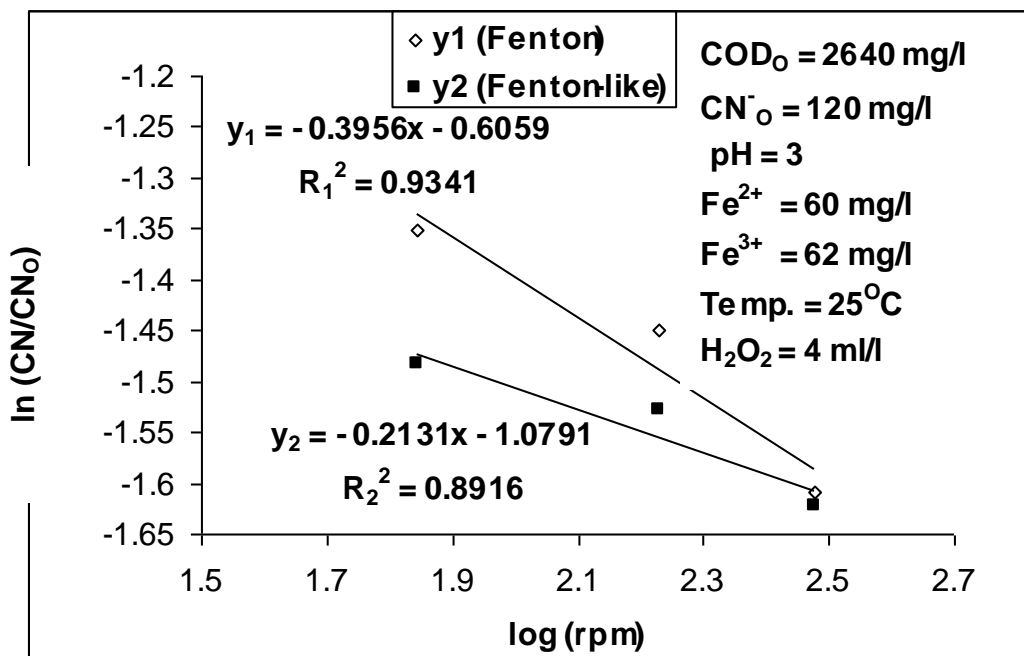


Figure 20: Log  $K_o$  versus log rpm for COD changes



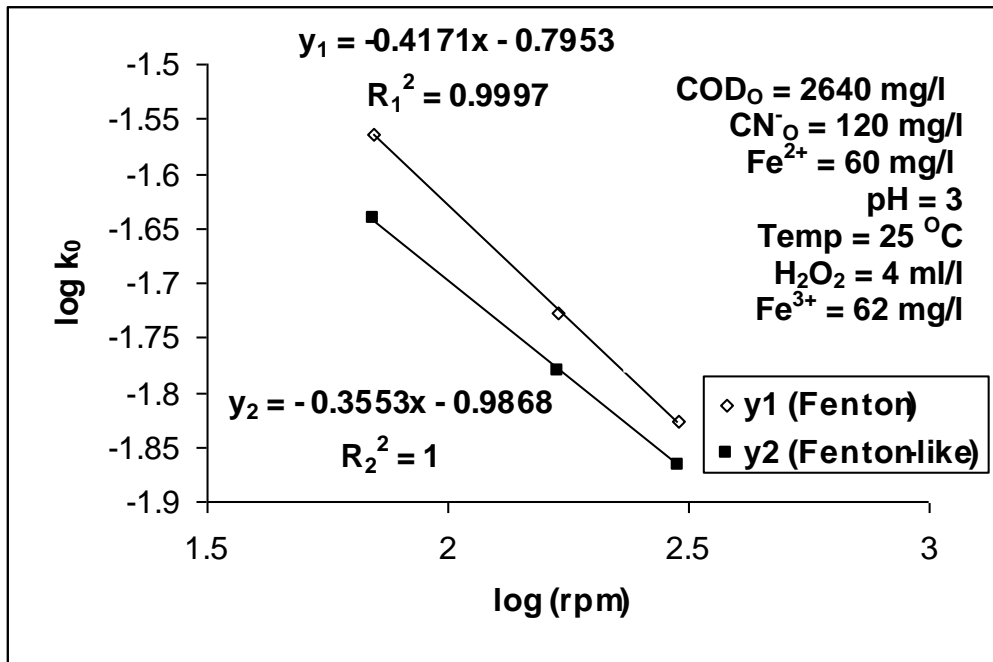


Figure 21: Log  $K_o$  versus log rpm for cyanide removal

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

Parameter (ppm)	Periodical effluent types (Averages)		
	(6 months)	(15 days + heavy oils)	(15 days + light oils)
COD	2000	16660	6634
CN <sup>-</sup>	8.7	9.11	9
Oils	4000	32910	23000
pH	6.6	6.6	6.6
T.S.S	400	6910	4208
BOD <sub>5</sub>	450	2500	800
TOC	700	6000	2600
Cu <sup>++</sup>	0.114	0.11	0.2
Cr (VI) <sup>+</sup>	0.3	0.13	0.215
Ni <sup>++</sup>	0.85	0.4	0.6

Table 2: Optimum operating conditions for realwastewater treatments

Parameters	Values
H <sub>2</sub> O <sub>2</sub>	1150 mg/l
FeSO <sub>4</sub> .7H <sub>2</sub> O	100 mg/l
Reaction time	300 min
PH	3
Temperature	45 °C
Speed of Agitator	70 rpm
COD	16660 mg/l

Table 3: Total cost for treating one m<sup>3</sup> by the Fenton process

Chemicals costs, Na <sub>2</sub> CO <sub>3</sub> is used	0.73 LE
Equipments costs	11 × 10 <sup>-3</sup> LE
Construction costs	2.14 × 10 <sup>-4</sup> LE
Total costs, Na <sub>2</sub> CO <sub>3</sub> is used	0.741 LE

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