MANAGEMENT OF ORGANIC MATTER IN AQUATIC ENVIRONMENT USING ADVANCED OXIDATION PROCESS (AOP)

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ABSTRACT

The treatment is economic tool to meet the diversity of industrial activities in development country like Egypt. The variety of pollutants is great concern to the deterioration of water reuse, soil performance and quality of agriculture crops in many areas such as the Tenth of Ramadan City. The present study present strength toxic organic matter in industrial wastewater and deal their reduction using advanced oxidation process (AOP) and evaluate oxidative abilities of Fenton H_2O_2/Fe, ultraviolet radiation UV/H_2O_2 and photo-Fenton $UV/H_2O_2/Fe$ reagents. Sampling program was carried out according to standard international methods for many environmental variables such as Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), Oil and Grease (O&G) and Total Dissolved Solids to meet the optimum conditions by AOP process.

The results showed a maximum COD removal reach to 95%, 89% and 50% for Fenton reagent, photo-Fenton and ultraviolet radiation, respectively under optimum conditions. The oxidative ability of photo-Fenton process (85%) was greater than that of the ultraviolet radiation process (50%) for industrial wastewater. The post water quality of treated industrial wastewater under laboratory conditions was achieved by the combinations of UV/ H_2O_2, $UV/ H_2O_2/Fe$ and H_2O_2/Fe process for investigated area. Gas production was more intense when higher reagent concentrations of AOP process were used that can being economic source for energy and achieve more national goals in industrial cities.

1. INTRODUCTION

The removal of organic pollutants involves one or more basic techniques such as chemical oxidation, adsorption and biodegradation. The choice of method depends on process costs and other factors such as type of pollutant, concentration and effluent volume. Advanced oxidation processes (AOPs) are suitable for the degradation of hazardous aqueous pollutants (Zapata *et al*., 2010) and based on the main oxidants involved hydroxyl radicals (OH•), which are able to degrade the most recalcitrant organic molecules into carbon dioxide (CO_2), water (H_2O) and inorganic ions (Navarro *et al*., 2011). Recently, AOP these processes are capable technology as an alternative treatment to conventional wastewater treatment methods, improvement current biological treatment methods and characterized by their capacity for total/partial oxidation of organic content and/or improvement of the biodegradability (Moreira *et al*., 2012).

Hydrogen peroxide has been chosen due to its reasonable cost, high oxidizing power due to highly reactive oxidizing hydroxyl radicals (Carlo *et al*., 2013). It is easily handled, soluble in water and it forms no by-products (Petrovic *et al*., 2011). Fenton's reagent ($H_2O_2/Fe(II)$) technique is widely and routinely used

for industrial wastewater treatment while Fenton and Photo-Fenton oxidation method have been in use successfully, effectively and easily applied to treat different industrial wastewaters (Sawyer *et al*., 2003).

The oxidation method is based on a mixture of special property of ferrous ion (Fe^{+2}) and hydrogen peroxide to generate the hydroxyl radical ($OH^{\cdot}$) at acidic pH in optimum conditions and kinetically the mechanism of the Fenton reaction enhancing the oxidation of the substrate (Liu *et al*., 2012). Both optimal dosage of hydrogen peroxide and ferrous ion must be done to complete oxidation reactions and prevent inhibition of the reaction if either of them is not optimal dosage (Muruganandham *et al*., 2014). Recent studied recommended ratio of ferrous ion to hydrogen peroxide mass ratio to be optimal at 1:10 or 1:5, but it must be optimized for particular wastewater to minimize exploration effects (Torrades *et al.*, 2003, Abd El-Gawad, 2008 and Dincer *et al*., 2008).

The accepted mechanism of the Fenton process proposes is hydroxyl radicals produce by reaction of hydrogen peroxide with ferrous ion which regenerated from the reaction of ferric ion with hydrogen peroxide or intermediate organic radicals (Bautista *et al.*, 2008). This hydroxyl radical attacks organic molecules by abstracting a hydrogen atom or by adding to the double bonds. Organic molecules are then totally mineralized to carbon dioxide and water (Claudia *et al*., 2013).

The photo-Fenton process ($H_2O_2/Fe^{+2}/UV$) keep the hydroxyl radical formation in the reaction mixture through photolysis of hydrogen peroxide (H_2O_2/UV) and Fenton reaction (H_2O_2/Fe^{+2}) (Zapata *et al*., 2010). The H_2O_2/UV or Fenton process alone was successful in removing oxydizable demand from toxic wastewaters. The peroxide dose is important in order to obtain better degradation efficiency, while the iron concentration is important for the reaction kinetics (Claudia *et al*., 2013). The Ultraviolet radiation (UV/H_2O_2) process uses to cleave the O-O bond in hydrogen peroxide and generate the hydroxyl radical. When UV light is absorbed directly by hydrogen peroxide, $OH^{\cdot}$ radicals are generated by photolysis of the peroxidic bond (Carlo *et al*., 2013).

The present work focus on the possibility of Fenton's reagent, combination of Fenton's reagent with UV (photo-Fenton process) and combination of UV radiation with hydrogen peroxide to performance AOP method for destruction (in-situ) high concentration of toxic waste from industrial wastewater by studying: (1) wastewater characterization and optimize treatment process for organic wastes, (2) effect of $H2O2/Fe^{+2}$ ratios, (3) wastewater concentration (pollution strength) and (4) oxidation time.

2.   METHOD AND MATERIAL

All environmental measurements that include chemical and microbial parameters measured and performed according to the instructions of international examinations for collection and preservation samples (APHA, 2012). The wastewater quality was compared with water quality standards. The work involved advanced oxidation process (AOPs) including Fenton H_2O_2/Fe, ultraviolet radiation UV/H_2O_2 and photo-Fenton $UV/H_2O_2/Fe$ reagents technique to evaluate their oxidative abilities. These techniques were applied to industrial wastewater that characterized by high load oxidizabile demand, high toxicity waste and low biodegradation.

2.1 Description of Area

Tenth of Ramadan City is being the first new industrial settlement in Egypt (Fig.1). The domestic (≈ 14.000 m3/day) and industrial wastewater collected and disposed in three oxidation ponds that

discharged into Wadi El-Watan (≈15 km northeast of 10th Ramadan City) by artificial and natural canals and collected in low lands.
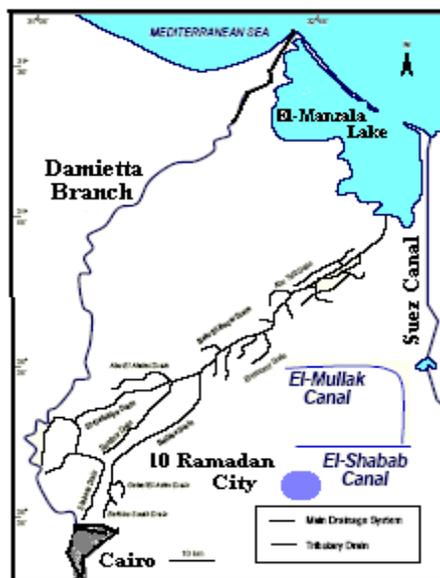

Fig.1: New community of Tenth Ramadan City in Southeast Nile Delta Area

Oxidation pond (No.1) collects ≈14.000 m3/day domestic wastewater and oxidation pond No.2 collects domestic and part of industrial wastewater with an average in flow ≈13.000 m3/day. Oxidation pond (No.3) collects the effluent from heavy industries at an average flow ≈25.000 m3/day. The discharge of industrial wastes into the oxidation ponds is summarized in Table (1).

Table 1: Discharge characterization in oxidation ponds – 10th Ramadan City

No.	Objective	Effect
A- Basin No.1 of oxidation pond No. 3	Collect the industrial wastewater from the third industrial area in the Tenth of Ramadan City.	Industrial waste on the surface of oxidation pond
B- Basin No. 4 of oxidation pond No. 3	solid wastes are observed	Block surface of drainage water
C- Small artificial canal	to carry the drainage water from different factories to low lands	Agricultural and industrial wastewater
D- Natural canals	carry the excess of drainage water from oxidation pond to the low land east of Tenth of Ramadan	Agricultural and industrial wastewater
E- The low lands saturated by waste water from different canals. C- Drainage water in oxidation pond	used for drinking of livestock	Un-health water for animals
D- Seepage of drainage water from oxidation ponds	to adjacent sand soil	Deterioration of economic and animals production
E- Wastewater	The different animals are eaten the natural vegetation which is growing from waste water	Deterioration of economic and animals production

The area of oxidation ponds zones classified as high pollution risk due to infiltration of toxic wastewater that enters to soil and surface water to reuse water for irrigation. In the Tenth of Ramadan City the discharge to the ponds differs according to the days and within the day itself from one hour to another.

2.2   Sampling

The samples were collected and preserved using grab sampler according to international standard environment methods of the American Public Health Association (APHA, 2012) to represent different forms of pollution and compared with Environmental Egyptian standards 92/2013.

2.3 Analytical Methods

Water sampling for physico-chemical measurements: pH, Dissolved Oxygen (D.O), temperature, turbidity and Electrical conductivity (E.C) were measured in situ using the multi-probe system, model Hydralab-Surveyor according to international standard environment methods of the American Public Health Association (APHA, 2012). On other hand, other environmental parameters: chemical and bacteriology are collected to represent different forms of pollution, analyzed in laboratory according to international standard methods (APHA, 2012) and compared with water quality standards.

Several of chemical measurements determined in laboratory such as cations and anions were analyzed using on chromatography (IC) model DX-500 chromatography systems with CD20 Conductivity Detector that checked using water analyses interpretation computer program, version 6.42-07190, through ion balance as well as analytical checks and comparisons were done. Heavy metal as toxic pollutants in water samples were filtered through Whatman GF/C filters before trace metals analysis. The concentrations of trace elements were determined by using the Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) with Ultra Sonic Nebulizer USN). Many organic measurements are selected to represent organic pollution which are Gross fraction of organic matter include Chemical Oxygen Demand (COD – colorimetric method) using Huch DR – 2010 Spectrophotometer U.S.A), toxicity of wastewater using (Huch DR – 2010 Spectrophotometer U.S.A), Biological Oxygen Demand (BOD) using BOD fast respirometry system model TS 606/2 with a measuring range 0-4000 mg/L at 20 °C incubation in a thermostatic incubator model WTW and Oil and Grease (O&G) gravimetric method. Individual 20 trace organic pollutants are considered to measure: organochlorine (OCP) using Finnigan Gas Chromatograph model 9001 TM with split-splitlessinjector, with ECD detector and column: 30m x 0,25 mm I.D. These pesticides were Alfa-BHC, Gamma-BHC, Beta-BHC, Delta-BHC, Endrin Keton, Endrin, Endrin aldhyde, Dieldrin, Aldrin, Alfa chlorodan, Gamma chlorodan, Heptachlor, Heptachlor epoxid, Methoxychlor, Endosulfan I, Endosul fan II, Endosulfan sulfate, 4,4'-DDD, 4,4'-DDE, and 4,4'-DDT.

For counting total coliforms (T.C), the membrane filter technique was applied using a filtration system completed with stainless steel autoclavable manifold and oil-free "MILLIPORE" vacuum/pressure pump. Water samples were filtered through sterile, surface girded "SARTORIOUS" membrane of pore size 0.45 µm and diameter 47 mm, according to (APHA, 2012). All media used were obtained in a dehydrated form, Difco USA. Results were recorded as Colony Forming Unit (CFU/100 ml).

2.4 Experiment Procedure

All chemical reagents were high quality. The laboratory scale unit (LSU) consisted from two parts that was (1) batch Fenton Reactor process-FRU and (2) UV column-UVU as shown in (Fig.2). All the experiments were done in duplicate for the same set of conditions. The variations were systematically within ±5% of the stated values.
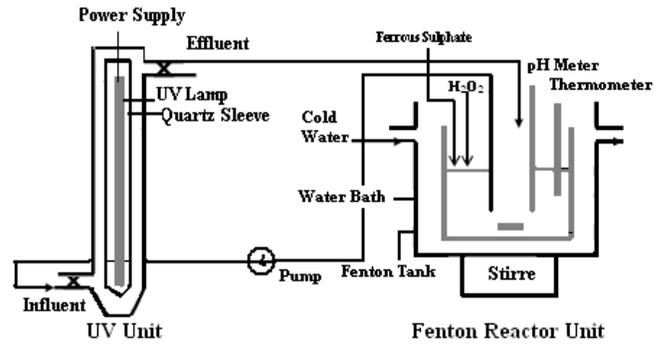
Fig.2: Schematic diagram of laboratory experimental unites

2.4.1   Fenton Process

Batch Fenton reactor process disconnected to UV unit (Fig.2). The reaction solution was stirred with a magnetic stirrer using a constant speed at 240 rpm to maintain a well-mixed solution during the experiment. A 100 ml sample was placed into 500 ml beaker in a water bath for temperature control that is equipped with a magnetic bar, thermometer and pH meter. The reactor container coated with an acid resistant material to avoid corrosion and powerful of Fenton's reagent that can be a serious problem. Reactants are added in the following sequence: wastewater followed by dilute sulphuric acid catalyst (adjustment pH at constant value) and hydrogen peroxide. For many chemicals the ideal pH for the Fenton reaction is 3 ± 0.1 and the optimum catalyst to peroxide ratio is usually 1:5 wt/wt or 1:10 wt/wt (Abd El-Gawad, 2008 and Muruganandham *et al*., 2014). The COD analysis was carried out at 0, 15, 30, 45, 60 minutes.

2.4.2   Ultraviolet Photolysis Process

Batch UV unit disconnected to Fenton reactor process (Fig.2). In UV/H_2O_2 oxidation process, experiments were carried out at different series of H_2O_2 concentrations. These series, hydrogen peroxide was added as following: 1:1, 1:3 and 1:5 (organic matter: H_2O_2 w/w). The organic load in terms of COD represented in sample that added to the reactor and turn UV lamp to start the reaction.

2.4.3   Photo-Fenton Unit

Batch UV reactor was connected to Fenton reactor. Flow of the wastewater between two experiment units was withdrawn by pump at 0, 15, 30, 45, 60, 120, 240 minutes for the COD analysis.   To determine the effect of ferrous concentration on the organic matter removal efficiency, a series of experiments (photo-Fenton) varying the concentration of iron at fixed the other parameters, were carried out. Hydrogen peroxide was in use at the concentration of 5g/l, while different concentrations of iron were tested (0.05, 0.075, 0.15 and 0.25 g/l).

3.   RESULTS AND DISCUSSION

Advanced Oxidation Processes (AOPs) are very efficient compared to conventional treatment methods for degradation and mineralization of recalcitrant organic pollutants present in wastewater **(Wu *et al*., 2011)**. It generates a powerful oxidizing agent, hydroxyl radical, which can react with most of the pollutants present in wastewater.

3.1 Industrial Wastewater Characterization

Environmental problems of discharges industrial processing included a variety of chemicals, depending on the nature of the raw material and product. Some of these chemicals are different enzymes, detergents, dyes, acids, sodas, salts and heavy metal contaminants. The physicochemical and organic characteristic of the wastewater are summarized in Table (1).

Table1: Characteristic of industrial wastewater in treatment processes

Parameter	Unit	Concentration
pH	-----	8.4
D. O	mg/l	2.9
TDS	mg/l	1503
COD	mg/l	572
BOD	mg/l	222
Biodegradability BOD$_5$/ COD	-----	0.38
Oil and Grease	mg/l	0.24
Phenol	mg/l	1.13
Chlorinated Pesticides (OCP)	μg/l	0.125
T. heavy metal	mg/l	1.248
Total Coliform	CFU/100ml	28×10^3

3.1.1　Chemical Characterization

The obtained data recorded D.O as major indicator of water quality (WHO, 2000) that measured the degree of organic pollution, the destruction of organic substances as well as the self purification capacity. The dissolved oxygen observed (1.9 mg/l) was below required standard for aquatic life (5mg/l), while concentration below 2mg/l may lead to death for most fishes (Chapman, 1997) and a concentration below this value adversely affects aquatic biological life. Low concentrations of dissolved oxygen, when combined with the presence of toxic substances may lead to stress responses in aquatic ecosystems because the toxicity of certain elements, such as zinc, lead and copper, is increased by low concentrations of dissolved oxygen (Goyer and Clarkson, 2001). The data showed that TDS (1503 mg/l) and total concentration of heavy metal was (1.248 mg/l) that the industrial effluent is responsible for water contamination above Egyptian Environmental Law (Decision 92/2013) permissible limits.

Organic load of industrial wastewater in term of BOD value was 388mg/l that the amount of dissolved oxygen needed by aerobic biological organisms in water to break down organic material present in the sample at certain temperature over a specific time period. The observed BOD was an effective indicator of organic quality of water, wastewater treatment plants and its value more permissible limits as compared to (EEL, 92/2013). BOD also measures the biodegradable materials in water and helps in the development of bacteria and other organic byproducts (Idris *et al*., 2013). From the results obtained industrial effluents have much effect of non-degradable organic pollution, since the observed values are above the (EEL, 92/2013) maximum standard value of 50 mg/l for discharge of wastewater into stream. The BOD$_5$/COD ratio of industrial wastewater was found to be 0.38 (Table 1). BOD/COD constitutes a good measure of the biodegradability of a wastewater. This wastewater is partially biodegradable according to (Garcia Montano *et al*., 2006). Contaminants with a ratio of BOD$_5$/COD ≥ 0.4 are generally accepted as biodegradable, while those with ratios situated among 0.2 and 0.3 units result partially biodegradable. Therefore, there was a need for advanced treatment processes to decrease pollutions from investigated industrial wastewater. COD value was 572 mg/l that high more permission limits (10mg/l) as compared to (EEL, 92/2013). It represented equality of oxygen required for oxidation of organic matter to produce CO_2 and water in industries wastewater. The data showed toxic waste concentration was represented by

phenol-1.13mg/l, oil&grease-0.24mg/l and OCP pesticides-0.123μg/l that their concentration were within permission limits of (EEL, 92/2013) except phenol.
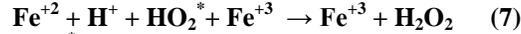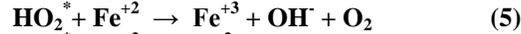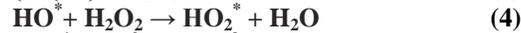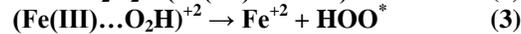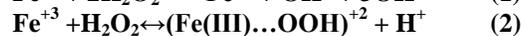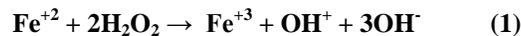
3.1.2   Microbiology Quality

Microbiological pollution in terms of T.C as microbial quality indicator was $28x10^3$ CFU/ml to reflect contamination of water resources that was above the (EEL, 92/2013) limits. Therefore, this wastewater can cause serious damage to the environment when discharged directly without proper treatment.

3.2   Experiments Procedure

3.2.1   Fenton Process (FP)

Fenton's oxidation process is composed of four stages including pH adjustment, oxidation reaction, neutralization and coagulation, and precipitation. The organic substances are removed at two stages of oxidation and coagulation (Zhou *et al*., 2010). $^{\bullet}$OH radicals are responsible for oxidation, and coagulation is attributed to the formation of ferric hydroxo complexes (Eq.1-9). The relative importance of oxidation and coagulation depends primarily on the H_2O_2/Fe^{2+} ratio that optimum at 1:5 wt/wt (Abd El-Gawad, 2008) at pH=3 or 1:10 wt/wt at pH=3 (Dincer *et al*., 2008).

$$Fe^{+2} + 2H_2O_2 \rightarrow Fe^{+3} + OH^+ + 3OH^- \qquad (1)$$
$$Fe^{+3} + H_2O_2 \leftrightarrow (Fe(III)\ldots OOH)^{+2} + H^+ \qquad (2)$$
$$(Fe(III)\ldots O_2H)^{+2} \rightarrow Fe^{+2} + HOO^* \qquad (3)$$
$$HO^* + H_2O_2 \rightarrow HO_2^* + H_2O \qquad (4)$$
$$HO_2^* + Fe^{+2} \rightarrow Fe^{+3} + OH^- + O_2 \qquad (5)$$
$$HO_2^* + Fe^{+3} \rightarrow Fe^{+2} + H^+ + O_2 \qquad (6)$$
$$Fe^{+2} + H^+ + HO_2^* + Fe^{+3} \rightarrow Fe^{+3} + H_2O_2 \qquad (7)$$
$$2HO^* + \rightarrow H_2O_2 + O_2 \qquad (8)$$
$$2H_2O_2 \rightarrow 2H_2O + O_2^{\cdot} \qquad (9)$$

The study clarified Fenton oxidation process resulting significant reductions of organic load for industrial wastewater, improvement of biodegradability and removal of colour and odour. Figure (3) demonstrated COD removal in Fenton oxidation experiment at 60 minutes at different ratios that reached to EEL, 2013 limits (COD 0-10mg/l). The increase on H_2O_2 concentration improved the removal of organic matter but the extended H_2O_2 concentration could not extended COD removal efficiency (Abd El-Gawad, 2008). This is probably due to both the auto-decomposition of H_2O_2 into oxygen and water (Zhou *et al*., 2010). Increasing the Fe^{+2} concentrations to H_2O_2 concentration in parallel produced a higher degree of degradation. The experimental results suggest that optimal H_2O_2/Fe^{+2} ratios has to be preserved to achieve the maximal degradation efficient. Many recent studies suggested Fe^{+2} to H_2O_2 mass ratio to be optimal at 1:10 (Zhou *et al*., 2010), 1:5 (Abd El-Gawad, 2008) but it must be optimized for particular wastewater. The COD removal as a function of the dosage of Fe^{+2} is illustrated in Fig.3.
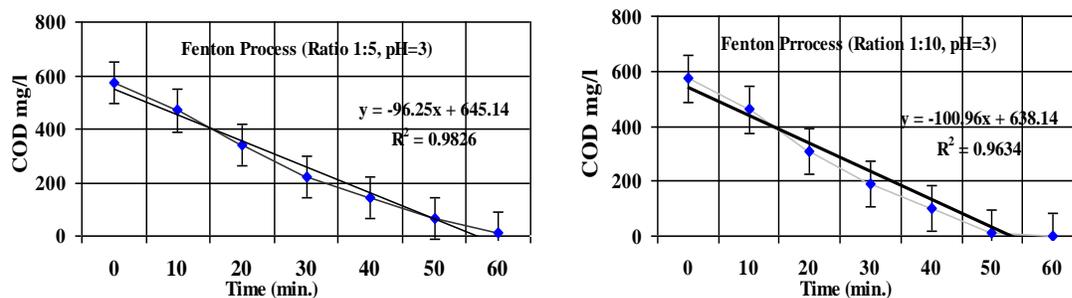

Fig.3: Effect of Fenton Reagent Ratio (1: 5 and 1:10 wt/wt)) for COD Removal
Fenton process (pH=3, T=40-80ºC, t=60 min)

The reaction is fast and exothermic (40-80ºC) that was practically no difference in the rate and extent of degradation of the reaction in the temperature between 40-75ºC (Dutta *et al*., 2001). The favorable H_2O_2 to Fe^{+2} mass ratios was found to be 1:7 (w/w) but the economic cost found to be 1:5 as shown in Figs. (3&4).The results confirmed the recent studies that showed Fenton process (homogeneous nature) is the best compromise because it is industrially simple, there is no mass transfer limitation, and both iron and hydrogen peroxide are cheap and nontoxic (Claudia *et al*., 2013). From the economic point of view, using the Fenton process as a pretreatment can lower the cost and improve biological treatment efficiency (Zhou *et al*., 2010).
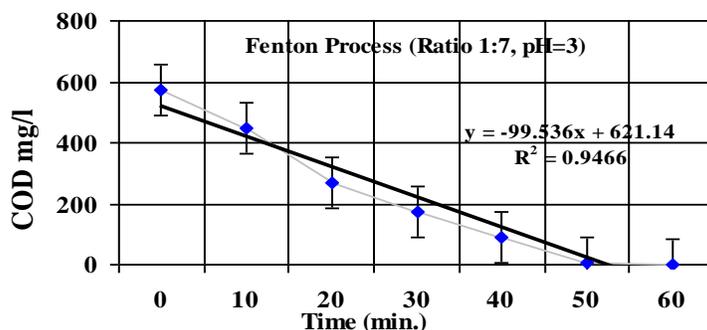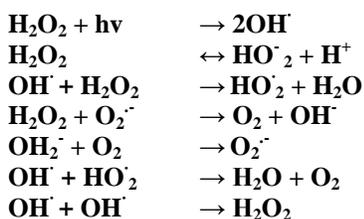

Fig.4: Effect of Fenton Reagent at Optimum Ratio (1: 7wt/wt) for COD Removal Fenton process (pH=3, T=40-80ºC, t=60 min)

3.2.2   UV/H_2O_2 Process

The UV/H_2O_2 process is a homogeneous advanced oxidation process using hydrogen peroxide with UV light. Hydrogen peroxide requires activation by an external source such as UV light and the photolysis of hydrogen peroxide generates the effective oxidizing species hydroxyl radical ($^\cdot$OH). The rate of photolysis of H_2O_2 depends directly on the incident power or intensity. Ultraviolet photolysis combined with hydrogen peroxide (the main absorber) found appropriate oxidation process for treatment of low organic pollution strength wastewater (Dincer *et al*., 2008).

$$H_2O_2 + h\nu \rightarrow 2OH^\cdot$$
$$H_2O_2 \leftrightarrow HO^\cdot_2 + H^+$$
$$OH^\cdot + H_2O_2 \rightarrow HO^\cdot_2 + H_2O$$
$$H_2O_2 + O_2^{\cdot -} \rightarrow O_2 + OH^-$$
$$OH_2^\cdot + O_2 \rightarrow O_2^{\cdot -}$$
$$OH^\cdot + HO^\cdot_2 \rightarrow H_2O + O_2$$
$$OH^\cdot + OH^\cdot \rightarrow H_2O_2$$

The UV/H_2O_2 process requires a long UV exposure time with a powerful at a wide range of wavelengths that this treatment is more economically attractive due to its lower energy consumption (Sillanpää *et al*., 2011). The efficiencies of the UV/H_2O_2 process in the different dosage ratios of organic matter/H_2O_2 (1:1, 1:2 and 1:5 w/w) are illustrated in Fig.5.
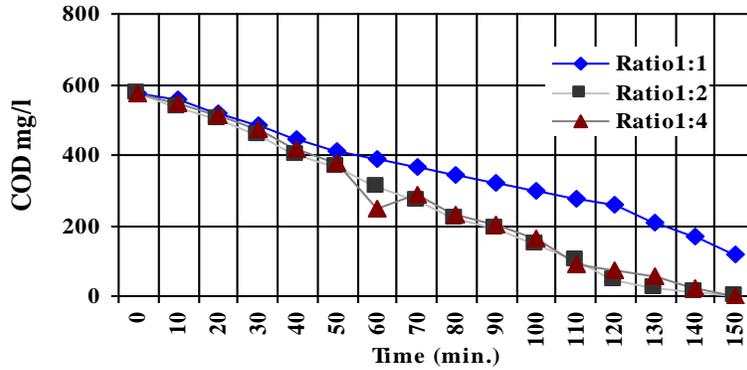
**Fig.5: Variation ratio of COD/H2O2 by UV/H$_2$O$_2$ process
(pH=3, T=40-45ºC, COD=572mg/l)**

Fig. 5 illustrates variations of COD removal with the different COD/H$_2$O$_2$ ratios at COD-572mg/l during reaction time (120 min.). No development on COD reduction was obtained with increase H$_2$O$_2$ concentration as shown in Fig.6. The contribution of COD/ H$_2$O$_2$ ratio to COD removal reached 55%, 92% and 85% for the dosage ratios of COD/ H$_2$O$_2$ as 1:1, 1:2 and 1:4, respectively. The study clarified COD reduction was 55% and it increased to 92% due to increase in the formation of OH˙. Further, increase in H$_2$O$_2$ dosage (1:4) lead to the decrease of COD removal efficiency (85%) that more amounts of H$_2$O$_2$ led to formation of much less powerful HO$_2$˙ radicals. The results confirmed with recent studies that efficiency of the UV/ H$_2$O$_2$ process for COD reduction is dependent on wastewater pollution strength or dilution of wastewater, hydrogen peroxide concentration and reaction time (Muruganandham *et al*., 2014).

3.2.3   Photo-Fenton Unit

Batch UV reactor was connected to Fenton reactor as shown in Fig.(1). In this process, the photolytic decomposition of Fe(OH)$^{2+}$ is accelerated, providing an additional source of highly oxidative hydroxyl radicals compared to Fenton process (Ramirez *et al*., 2010). The photo-Fenton process produces more hydroxyl radicals than the conventional Fenton method (Fe(II) with hydrogen peroxide) or photolysis, thus promoting organic pollutant degradation rates. This process consists of a combination of Fenton reagents (Fe^{2+}/H$_2$O$_2$) and light energy and oxidation-reduction reactions frequently and completely mineralize organic pollutants to CO$_2$ and H2O (Nachiappan and Karuppan, 2013):
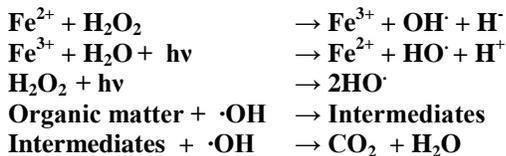
$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \qquad\qquad \rightarrow \text{Fe}^{3+} + \text{OH}^\cdot + \text{H}^-$$
$$\text{Fe}^{3+} + \text{H}_2\text{O} + \text{h}\nu \qquad \rightarrow \text{Fe}^{2+} + \text{HO}^\cdot + \text{H}^+$$
$$\text{H}_2\text{O}_2 + \text{h}\nu \qquad\qquad \rightarrow 2\text{HO}^\cdot$$
$$\text{Organic matter} + \cdot\text{OH} \quad \rightarrow \text{Intermediates}$$
$$\text{Intermediates} + \cdot\text{OH} \quad \rightarrow \text{CO}_2 + \text{H}_2\text{O}$$

Figure (6) depicted reduction of COD by photo-Fenton process at 7g/l of H$_2$O$_2$ and Fe^{+2} concentration was increased in sequence from 25, 50, 75, 150 and 250 mg/l mass (w/w) ratios for a reaction time of 30, 60, 90, 120, and 150 min. The removal efficiency increased from 65% to 95% and then decreased to 76%, 68% and 55%, respectively. This increasing development is as a result of higher ferrous dosage; the more the OH˙ can be formed through reaction led to high COD reduction. The best COD reduction performance was obtained with Fe^{+2} concentrations of 50 mg/1. The highest percent COD reduction was 95% after 120 min of oxidation.
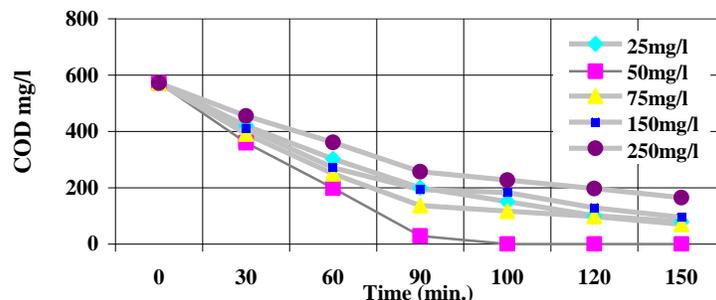
Fig.6: Variation of COD Concentration in different Time and Fe by Photo-Fenton Process
(pH=3, T=40-45ºC, COD=572mg/l, H_2O_2=7 mg/l)

The dosage of ferrous ions more 50 mg/1 does not increase the COD reduction due to increase brown turbidity in the wastewater during the photo-treatment led to hind the absorption of the UV light. Excessive formation of Fe^{+2} which can challenge with the organic carbon for $OH^{\cdot}$ radical and also fixed H_2O_2 concentration must be removed after treatment. Therefore, wastewater was diluted (1:2) and used in photo Fenton and UV/ H_2O_2 experiments. The overall degradation rate of organic compounds is considerably increased in the Photo-Fenton process, even at lower concentration of iron salts present in the system (Idil and Tugba, 2011). It was found that the oxidative ability of UV/H2O2 (92%) is less than that of the UV/Fe^{+2}/H_2O_2 (95%) process although both processes destroy 1:2 diluted wastewater (COD/H_2O_2=1/2 w/w).

The results showed the toxicity of wastewater included organic pollutants and advanced oxidation intermediates was negative that the key factor to evaluate the applicability of the AOPs, improve the biocompatibility of the effluent and to apply a biological treatment (Abd El-Gawad, 2008). Advanced oxidation may form inert and/or toxic degradation products, since free radical chain reaction-based treatment methods are difficult to control thus requiring the toxicity assessment of the formed advanced oxidation intermediates (González *et al.*, 2007).

Bubbling was observed in all testing and a rapid boil was observed for tests using higher reagent concentrations. Gas production was more powerful when higher reagent concentrations were used that can be used in indusial production to meet more national goals and decrease industrial cost.

4. CONCLUSIONS

The characterization and degradation of industrial wastewater was investigated by the Fenton, UV/H_2O_2 and photo Fenton processes. Organic load of industrial wastewater in term of BOD and COD values was 388mg/l and 572mg/l that were effective indicators of organic water quality. From the results obtained industrial effluents have much effect of non-degradable organic pollution and more permission limits of Egyptian Environmental Law. The biodegradability BOD_5/COD ratio of industrial wastewater was found to be 0.38 that was partially biodegradable.

The COD reduction performance was strongly affected by many factors included the concentration of H_2O_2, Fe^{+2} and the ratio of organic materials to the Fenton reagents. The COD reduction performance reached to 100 % under the optimum operating conditions economically: pH=3, 1:5 of H_2O_2/Fe^{+2} and 60 min of treatment time. The study clarified high COD reduction performance (1:2-COD/2 H_2O_2) was found for the photo process.

In addition, the optimum operating conditions for the photo Fenton oxidation of wastewater was carried out at the given operating conditions (pH=3, Fe^{+2}: 50 mg/1 and H_2O_2: 7 mg/1, T: 40-45ºC) to produced a COD reduction of 95% for diluted wastewater 1:2 (COD: 572mg/1). The results showed the toxicity of wastewater was negative that depicted the applicability of the AOPs, to improve the biocompatibility of the effluent and to apply a biological treatment **.**

5. RECOMMENDATIONS

The wastewater of oxidation ponds in the Tenth of Ramadan is highly polluted with different variables that must be treated to increase their efficiency and utilization in water reuse. Then, the environmental studies must be focused on:

- Renew and develop factories in-situ treatment plant that has pretreatment unit before discharge its effluents into oxidation ponds.
- Environmental monitoring along new cities to check their water quality, avoid pollution sources and their wastes must not be used for irrigation
- Environmental monitoring for groundwater quality to avoid pollution sources
- Separation for agricultural and domestic drainage water from industrial wastewater to construct suitable domestic sewage facilities to avoid their effluents into agricultural drains.

6. ACKNOWLEDGMENT

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