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COMBINATION OF PHOTOCATALYTIC AND BIOLOGICAL PROCESSES AS AN INTEGRATED SYSTEM FOR TREATMENT AND RECOVERY OF INDUSTRIAL WASTEWATER CONTAINING PESTISIDES

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Abstract

The combination of chemical oxidation with biological water treatment processes is a promising technique to reduce recalcitrant wastewater loads. As a case study, the treatment of wastewater coming from the HELB Pesticides and Chemical Company wastewater located at New Dammata in the north of Egypt was studied, which was characterized as very biorecalcitrant. Photo-Fenton process was explored as photochemical pre-treatment to improve the biodegradability of such wastewater coming from the pesticides industry. The key to the efficiency of such a system is better understanding of the mechanisms involved during the degradation processes. Wastewater treatment was carried out including a series of bench scale experiments, to identify optimum operating conditions for the treatment pesticides containing wastewater of the end of pipe effluent. The effect of operating parameters as: pH, irradiation time and initial concentrations of both H_2O_2 and Fe^{2+} on the photo-mineralization processes have been studied and the optimal conditions were found.

Experiments were made to obtain information concerning the evolution of the biodegradability of the treated effluent after 82 and 85.6% of TOC (Total Organic compounds) and COD (chemical oxygen demand) respectively of photo-mineralization. The photo-treated effluent is biocompatible and its complete mineralization can be performed by biological means. The results of the present study revealed that the final treated effluent is complying with the environmental regulations set by Law No. 93/1962 and the Ministry of Housing Decree No. 44/2000. The law effectively requires pretreatment of industrial wastewater prior to its discharge into public sewers. The residual values of TSS, BOD, COD, and, oil & grease are 16, 4.5, 28 and 12.8 mg/l, respectively in the case of the treatment with photo-Fenton process accompanied by biological process. Phenols, organic pesticides and heavy metals were not detected in treated the final effluent. The integrated system photocatalytic oxidation followed by biological treatment appears to be feasible for treating recalcitrant compounds, and pesticides wastewater.

KEYWORDS: Pesticides Wastewater, Advanced Oxidation Processes, photo-Fenton Process, and Biological Treatment.

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INTRODUCTION

One of the most alarming phenomena is the growing accumulation of hardly biodegradable anthropogenic substances under the saturated auto-depurative conditions of such perturbed and overloaded cycle. The situation worsens by the lack, or insufficiency, of adequate water treatment systems capable of diminishing the concentration of toxic substances that represent a chronic chemical risk. It can be said that badly-treated wastewaters lead inevitably to a deterioration of water sources quality and consequently, of drinking water. Two strategies of water treatment have to be forced in order to counterbalance these growing environmental problems involve the development of appropriate methods for contaminated drinking, ground, and surface waters, and mainly the development of appropriate methods for wastewaters containing toxic or non biodegradable compounds. The incapability of conventional wastewater treatment methods to effectively remove many biorecalcitrant pollutants evidences that new efficient treatment systems are needed. Besides biological processes, several oxidation systems are currently used or in different stages of development. For the last 25 years the water purification research has been extensively growing. Rigorous pollution control and legislation in many countries have resulted in an intensive search for new and more efficient water treatment technologies.

Chemical treatment methods known as Advanced Oxidation Processes (AOP) are an attractive alternative for the treatment of contaminated ground, surface, and waste waters containing hardly-biodegradable anthropogenic substances as well as for the purification and disinfection of drinking waters [1-5]. These AOP are useful complements to well established techniques like flocculation, precipitation, adsorption on granular activated carbon, air stripping or reverse osmosis, combustion, and aerobic biological oxidation. Some of these latter techniques could transfer pollutants from the aqueous phase to a second one, but they do not destroy the pollutant. Others may be selective but slow to moderate in destruction rate, or rapid but not selective, thus generating appreciable reactor or energy costs. Aerobic biological oxidation is limited when the feeding water contains substances either recalcitrant to biodegradation, or inhibitory or toxic to the bioculture. Other conversion processes can be limited by economic reasons, oxidative potential, effluent characteristics, or tendency to form harmful disinfection by-products as, for example, the case of formation of trihalomethanes (THMs) when a chlorination procedure is used for drinking water treatment [6].

The pesticide and chemical industries are considered to generate wastewaters containing toxic and non-biodegradable compounds that remain in the environment even after their wastewaters have been subjected to conventional processing [7,8]. Therefore, the human population is exposed to pesticides and other organic micro-pollutants either through drinking water or via the food supply. In addition, there is a formation of mutagenic compounds during conventional oxidation processes [9,10]. Therefore, it is very important to develop water and wastewater treatment technologies for the removal of toxic and refractor organic compounds from water and wastewater. HELB Pesticides and Chemical Company, located at New Dammata in Egypt where agriculture is very intense in this province, is an agrochemical company that manufactures, formulates and packs of wide range of pesticides, fertilizers and the production of some public health chemicals. The factory is considered on of the main suppliers to the local and international markets. Throughout the years the company has undertaken numerous actions regarding emission reduction, waste minimization, effluent management and soil and groundwater protection in order to comply with environmental regulation. The company discharges both industrial and human wastewater into a sewer system containing toxic pollutants such as organic pesticides that would have a serious impact to the environment [11]. Some of these compounds are poorly biodegradable and consequently, they often remain in the effluent from biological treatment processes and depress treatment efficiency [8,9]. Therefore, to enhance the efficiency of conventional processes for industrial wastewater treatment, an effective pretreatment process is always needed to destroy the toxic pollutants [12]. Advanced oxidation processes (AOP) have the potential to treat various organic compounds including pesticides. AOP involve the generation of hydroxyl radical ($OH^{\cdot}$), which has a very high oxidation potential and is able to oxidize almost all-organic pollutants.

Among these AOP, the photocatalytic oxidation system is the most utilized for environmental applications since it uses the UV component of solar light. For detoxification of this water the application of a photocatalytic process was proposed, because conventional biological water treatment is more suitable for high concentrations of biodegradable substances, while photocatalysis is able to deal with effluents containing a low level of highly persistent pollutants. Therefore, photocatalysis appears to be very promising [13]. A wide range of applications have been reported for different compounds using these systems [14]. Like other AOPs (advanced oxidation processes), the iron photoassisted system, the Photo-Fenton reaction has been developed to detoxify non-biodegradable wastewater [15]. The mechanism of the Fenton reaction has been known for a long time [16–17]. The most important improvement, the additional application of light, was based on discoveries in atmospheric chemistry, where ferrous and ferric complexes play a key role in the degradation of organic substances [18-19]. Accordingly the so-called Photo-Fenton reaction was introduced as a very promising water treatment method [20,21]. Previous investigations have shown that the photo-Fenton process is an effective and cheap method, which can promote the photooxidation of pesticides containing wastewaters [22-26].

Although AOPs generally can produce high quality effluent and cheaper than incineration or wet oxidation technologies, the high costs of equipment, chemicals, electricity, and sludge disposal diminish the advantages of these processes. However, their use as a pretreatment step for the enhancement of the biodegradability of wastewater containing recalcitrant or inhibitory compounds can be justified when the intermediates resulting from the reaction can be readily degraded by microorganisms. Furthermore, AOPs alone cannot usually achieve complete treatment of such wastewater. A promising alternative to complete oxidation of biorecalcitrant wastewater is the use of an AOP as a pretreatment step to convert initially biorecalcitrant compounds to more readily biodegradable intermediates, followed by biological oxidation of these intermediates to biomass and water. The solution resulting from the phototreatment stage is considered to be biologically compatible after the elimination of: the initial biorecalcitrant compound, the inhibitory and/or non-biodegradable intermediates. Therefore, combinations of AOP as preliminary treatments with inexpensive biological processes seem very promising from an economical point of view. There are currently a lot of investigations focused in the development of new chemical oxidation technologies that can be potentially applied in this field [27-29]. The chemical processes utilized are based on: ozone [30], ozone/hydrogen peroxide [31], hydrogen peroxide/UV [32], wet air oxidation [33], and artificial sunlight [34], among others. Some results obtained with such kind of methods, mainly at laboratory scale, suggest potential advantages for water treatment.

In the present work, special attention has been given to combining the photoassisted AOP and aerobic biological process to degrade biorecalcitrant, non-biodegradable, and/or toxic pollutants present in pesticides industrial effluent. A combined system is developed using the photoassisted pretreatment as chemical oxidation first step accompanied by biological treatment step using immobilized activated sludge culture.

2. Experimental

2.1. Material & Analysis

GP grad chemicals namely, ferrous sulfate ($FeSO_4$. $7H_2O$), hydrogen peroxide (H_2O_2) 30%, sulfuric acid and sodium hydroxide were used without any purification. The original washing real wastewater used was produced from the industrial plant 'HELB', (Pesticides and Chemical Company, located at New Dammata of Egypt). These effluents were characterized and analyzed for COD, BOD, TOC, other physical chemical analysis, individual organic pesticides and heavy metals according to the procedures described in Standard Methods for the Examination of Water and Wastewater (1998) [35]. The values obtained for the main chemical parameters and compositions were: pH 7.4; COD=9355 mg/L; BOD5=1460 mg/L; total solids concentration =6147 mg/L and Total suspended solids =565 mg/L. The total organic carbon (TOC) was measured using PHENOX TOC analyzer. GC (model HP5880 plus) was used for pesticide analysis. Atomic Absorption (model Varian Spectra 220) was used for heavy metals analysis.

2.2. Set-up

It is clear that conventional treatment processes are unable to consistently meet the current standards for pesticides, and the additional treatment processes will be required. This work presents an integrated system by applying photocatalytic oxidation by using photo-Fenton process accompanied by biological process as an advanced alternative treatment option. A photo reactor as shown in Figure (1) was used for the photo-oxidation process as the pre-treatment step. It consists of an external stirred vessel (1.0) liter with a variable speed stirrer, combined with a cylindrical photo reactor (0.95L) with a coaxial medium pressure UV mercury lamp (Heraeus TQ150, input energy of 150 w) emitting a polychromatic radiation in the range from 200 to 280nm wavelength. The lamp emitted a power of 6.2 W in the UV-C ($100<\lambda<280$nm) range, corresponding to $1.32*10^{-5}$ Einsteins^{-1}. The UV lamp is equipped with a cooling water jacket to maintain the temperature of the reaction solution at room temperature (25°C). There is one cooling circle for cooling UV lamp. The UV system is placed positioned coaxial inside the reactor vessel. The UV system is made from quartz glass, which is available for the transfer of UV irradiation. The reaction chamber is filled with the wastewater, which is between the reactor walls and UV lamp system. The reactor was designed for different flow rates, organic loads, recalculation rates, and oxidant addition rates.

2.3. Procedure

Prior to any experiment, the wastewater were centrifuged and filtered to remove suspended solids. The optimum conditions for photo-Fenton treatment as a pre-treatment for biological treatment were investigated for wastewater containing pesticides. In the photochemical oxidation, the pH of the industrial wastewater was adjusted to the desired value with sulfuric acid or sodium hydroxide addition and kept at the same value during the reaction. Then appropriate amount of ferrous sulfate was added into the mixing-vessel. After 10 min, the solution is re-circulated in batch mode at 22 L/hr through the illuminated part of the photo-reactor by means of peristaltic pump. The UV lamp is turned on for 10 min prior to reaction to obtain a constant light intensity output and to eliminate variations in temperature. Finally, the desired volume of H_2O_2 was injected to the solution by using a dosing pump during a period of 5 min. After 45 min reaction time the lamp was turned off. The pH of the photo-Fenton treated effluent was adjusted to 3 and the photo-oxidation effluent was settled and directed to the biological treatment step. Several samples were taken periodically to analyze the TOC in all experiments.

The pre-photo-treated solution is subjected to the biological treatment which, is developed in an agitated tank charged with two- liter plexiglass laboratory columns of pre photo-oxidized wastewater into which air was fed continuously to ensure an excess of dissolved oxygen and facilitate respiration of microorganisms. Biomass was taken from an activated sludge process of a municipal wastewater treatment plant (concretely from recirculating line between the secondary sedimentation unit and a biological oxidation tank). Collected activated sludge samples were acclimated to photo-Fenton treated effluent Acclimatization consisted of mixing given amounts of activated sludge with pre-photo-oxidized wastewater for periods of four weeks. Air supply was adjusted to maintain a minimum concentration of 2.0 mg O_2/l. Air supply to the columns were turned off once a day and the sludge was allowed to settle for 60 minutes, then the supernatant was drained. The columns were refilled with various ratios from Photo-Fenton treated effluent/sewage. Since the Photo-Fenton treated effluent did not contain enough nitrogen and phosphorus, it was added to the Photo-Fenton treated effluent to reach the ratio COD: N: P = 100: 5:1. After acclimation period of almost three weeks, considerable amount of sludge was produced. In order to study the effect of aeration time and the sludge loads on the treatment process, an appropriate volume of mixed liquor suspended solids (MLSS) was transferred to different columns followed by the addition of Photo-Fenton treated effluent/sewage (6/4). Air supply was adjusted to maintain a minimum dissolved oxygen concentration of 2.0 mg/l. The system was allowed to operate 24 hrs and the experiment was carried out using MLSS of 3-4mg/l.

The same procedure was carried out for other two days by using fresh treated Photo-Fenton treated effluent/sewage at the rate of (8/2) and detention time of 6 hours. The specific parameters were analyzed after 6hrs (optimum detention time).Samples were withdrawn at regular intervals to follow COD and TOC. Sludge volume and sludge analyses were also determined. Also, parameters like BOD, pH, TSS, heavy metals and temperature were followed during the course of both photo-Fenton oxidation and biological treatment.

3. Results and discussion

3.1. Wastewater characterization and non biodegradability indicators

The composition and physicochemical characteristic of the wastewater under study are summarized in Tables (1). The results of analysis indicated that wastewater generated from the company contained toxic pollutants such as organic pesticides, which have a serious impact to the environment. Results in Table (1) revealed that the pesticides concentration ranged between 20.6 and 38.98 mg/l with a mean value of 27.38 mg/l, which may cause problems in biological wastewater treatment. For example the toxic compounds in such waste may inhabit the process or pass through biological application because of their refractory and toxic properties [36]. Moreover, refractory and toxic pollutants influence the quality of water resources. Therefore, human population is exposed to organic micro-pollutants either through drinking water or via the food supply [7,37]. The mean concentrations of COD, BOD, TOC, oil and grease (extractable organic matter), total Kjeldahl nitrogen (TKN) and phosphorus are 3058 mg/l, 389 mg/l, 586 mg/l, 710.75 mg/l, 55.85 and 26 mg/l, respectively (Table 1). These data indicated that the industrial wastewater is highly loaded with organic matter. Some of these compounds are poorly biodegradable and consequently, they often remain in the effluent from biological treatment processes and depress treatment efficiency of city treatment plant. The ratio of BOD/COD in wastewater is normally used to express the biodegradability of the wastewater. When the ratio of BOD/COD is more than 0.3, the wastewater has a better biodegradability. Whereas the BOD/COD is less than 0.3, indicating that the wastewater generated from these activities inhibits the respiratory activity of bacterial seed due to their toxicity or refractory properties and it is difficult to be biodegraded [38,39]. Results in Table (1) showed that the values of BOD/COD ratios of the collected samples are less than 0.3, which indicated that the industrial wastewater contains organic pesticides which are poorly biodegradable and the wastewater required chemical pretreatment before discharged into the sewer system. The non-biodegradability of a wastewater was then confirmed before apply a photochemical treatment, since classical biological treatments are, at the present, the cheapest and most environmentally compatible.

The obtained results indicate that the wastewater generated from HELB Company does not comply with the environmental law 93/1962 and the Ministry of Housing, Decree No. 44/2000. The law effectively requires pretreatment of industrial wastewater prior to its discharge into public sewers. Therefore, an effective waste minimization program includes pollution prevention control and end of pipe treatment has to be conducted to reduce the amount of hazardous wastewater.

3.2. The photo-Fenton reaction as end of pipe pre-treatment process

Industrial wastewater from pesticides processing is characterized by a remarkable content of organic substances. Biological processes alone are not always able to reach effluent standards for the discharge into municipal sewer or into surface waters, so a pretreatment is required. Therefore, the treatment processes were designed to cover two main objectives: detoxification of the toxic pesticides and removal of other pollutants. The treatment system was carefully investigated using advanced oxidation processes, (Photo-Fenton), followed by biological treatment as activated sludge. Photo-Fenton system $UV/Fe^{2+}/H_2O_2$ is one of the most interesting promising oxidative techniques for the abatement of refractory and toxic organic pollutants in water and wastewater [20]. In this technique, the strong oxidizing agent $OH^{\bullet}$ radical is produced. The formation of $OH^{\bullet}$ radical depends on several parameters such as pH, initial amount of Fe^{2+}, initial concentration of H_2O_2, the organic loads and the irradiation time. Because these parameters are the most influential variables and determine the oxidation efficiency, it is important to optimize the initial amounts and conditions of these reagents and the operating conditions. One of the aims of this study was mainly to reach the optimum operating conditions such as: irradiation time, optimum pH (acidity), optimum initial amounts of both H_2O_2 and Fe^{2+} respectively for the best TOC removals of the pesticides effluent by photo-Fenton process. Experimental design was applied.

3.2.1. Effect of irradiation time

The phototreatment time must be as short as possible to avoid a high electricity consumption, which represents about 60% of the total operational cost when using electric light sources [40]. However, if the fixed pretreatment time is too short, the intermediates remaining in solution could still be structurally similar to initial biorecalcitrant compounds and therefore, nonbiodegradable. Furthermore, at short phototreatment times, the residual H_2O_2 concentration may be high enough to inhibit the biological stage of the coupled reactor. This oxidant is not required for all the photochemical processes but, whenever utilized it has to be eliminated before the biological stage. Figure (2) indicate that the optimum irradiation time was 45min.

3.2.2. Effect of the pH

The photo-Fenton systems have a maximum catalytic activity at pH of about 2.8-3. The pH value influences the generation of $OH^{\bullet}$ radicals and thus the oxidation efficiency. For pH values above 4 the degradation strongly decreases since iron precipitates as hydroxide derivate, reducing the Fe^{2+} availability and the radiation transmission [19,41,42]. Therefore, the all experiments of this work are performed at pH 3.

3.2.3. Effect of the initial hydrogen peroxide concentration

To elucidate the role of H_2O_2 concentration on the photodegradation of these pesticides wastewater in the photo-Fenton system, some experiments are carried out by varying the initial H_2O_2 concentrations at constant COD and initial Fe^{2+}. As shown in Figure (3), the degradation efficiency represented by %TOC removal is demonstrated when H_2O_2 concentration increases from 0.5 to $4x10^{-4}$ M/L, which is explained by the effect of the additionally produced $OH^{\bullet}$ radicals [40-42]. However, above this H_2O_2 concentration, the reaction rate levels off and sometimes is negatively affected, by the progressive increase of the hydrogen peroxide. This may be due to auto-decomposition of H_2O_2 to oxygen and water and recombination of $OH^{\bullet}$ radicals (Reactions 1,2). Excess of H_2O_2 will react with $OH^{\bullet}$ competing with organic pollutants and consequently reducing the efficiency of the treatment, the H_2O_2 itself contributes to the $OH\bullet$ radicals scavenging capacity. It is found that, the optimal H_2O_2 concentration is $4x10^{-4}$ M/L for the degradation of pesticides with 82% TOC removal after 45 min irradiation time as shown in Figure (3).Therefore, H_2O_2 should be added at an optimal concentration to achieve the best degradation. This optimal H_2O_2 concentration depends on the nature and concentration of the compound to treat and on the iron concentration.

$$2H_2O_2 \rightarrow 2H_2O + O_2 \quad \text{[Reaction 1]}$$
$$OH^{\cdot} + H_2O_2 \rightarrow HO_2^{\cdot} + H_2O \quad \text{[Reaction 2]}$$

3.2.4. Effect of the initial Fe^{2+} concentration

Iron in its ferrous form acts as photo-catalyst and requires a working pH below 4. To further elucidate the role of Fe^{2+} concentration on the mineralization of the effluent, a series of experiments varying the concentration of iron and keeping fixed the other parameters, were carried out. Figure (4) shows a plot the efficiency of TOC removal as a function of initial Fe^{2+} concentrations for a reaction time 45 min. The Figure shows that the addition of Fe^{2+} enhances the efficiency of TOC removal. The results indicate that increasing initial quantities of iron in solution produce increasing rates of TOC removal. The best TOC removal (82%) was obtained with initial Fe^{2+} concentration $2x10^{-5}$ M/L. Lower initial concentrations of Fe^{2+} would cause fewer $OH^{\bullet}$ free radicals to be available for oxidation. When further increase of initial Fe^{2+} concentration H_2O_2 ratio ($Fe^{2+} > 2x10^{-5}$ M/L), it can also be observed that the efficiency of the TOC removal actually decreases attains a plateau. This may be due to: (a) the increase of formation of a brown turbidity in the solutions during the photo-treatment, which hinders the absorption of the UV light required for the photo-Fenton process and promoted the recombination of hydroxyl radicals (Reaction 3) [40-42]; (b) the redox reactions since OH radicals may be scavenged by the reaction with another Fe^{2+} molecule as indicated below (Reaction 4) [41,42,44] ; (c) the Fe^{3+} formed can react with H_2O_2 (Reaction 5) as well as with hydroperoxy radicals with regeneration of Fe^{2+} in the solution resulting in decrease in degradation rate [41,42]. It is desirable that the ratio of H_2O_2 to Fe^{2+} should be as small as possible, so that the recombination can be avoided and the sludge production from iron complex is also reduced.

$$OH^{\cdot} + OH^{\cdot} \rightarrow H_2O_2 \quad \text{[Reaction 3]}$$
$$Fe^{2+} + OH^{\cdot} \rightarrow Fe^{3+} + OH^{\cdot} \quad \text{[Reaction 4]}$$
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\cdot} + H^{+} \quad \text{[Reaction 5]}$$

The results presented in Figures 2, 3 & 4 indicated that the optimum operating conditions for photo Fenton applications are 45 min, $4x10^{-4}$ and $2x10^{-5}$ M/L for the irradiation time, pH, initial amounts H_2O_2 and Fe^{2+} concentrations respectively. Results in Table (2) show that the quality of the Photo Fenton effluents and the efficiency of treatment. The decrease of COD of the wastewater is more significant after photocatalytic oxidation pretreatment by photo-Fenton. It was found that the residues of TSS, COD, BOD, Oil & grease, phenol and total organic pesticides are 3, 519, 162, 3.1, 1.6 and 0.3 mg/l respectively. These data indicated that Photo-Fenton treated effluent is complying with Ministerial Degree 44/2000 except for two items, namely phenols and pesticides and these values are exceeded the limits set by the Ministerial Degree. Therefore, the biological techniques are examined to remove the organic pesticides and phenolic derivatives from the photo-Fenton oxidation effluent as post-treatment processes to reach the limit values of their presence in the final effluent

3.3. Post step biological treatment

The photo-treated effluent of the photo-Fenton process is subjected to a post biological treatment by using activated sludge. It was found that, after two-hour detention time the total organic carbon (TOC) removal was 78%. By increasing the period of aeration to four hours, the TOC removal values increased to 82%. After six hours the TOC, TSS, COD and BOD removal values are 86.3%, 87%, 93% and 96% respectively. It can be seen that the reduction in the COD and TOC values of the treated effluent was significantly obtained during the first 6 hours. Further increase in the detention time exerted no significant effect on the efficiency of the system. The analysis of the sludge showed that the sludge index ranged from 86 to 97, which is an indication of a good settable sludge. Also, microscopic investigation showed the presence of many colonies of protozoa, especially Paramecium, Pelomyxa, and Gamphonema.

Table (3) listed the characterization of the final treated effluent after biological process by using activated sludge as a post treatment for the previously phototreated effluent by photo-Fenton process. The concentration of TSS, COD, BOD, Oil & grease, TPO4, TKN, Heavy Metals, Phenol and Total Pesticides are 16, 28, 8.5, 0, 4.8, 26.8, <0.1, <0.005 and <0.005 mg/l. The results show that the biodegradability tendency can be enhanced by the photocatalytic oxidation converting the non-biodegradable organic substrates into more biodegradable compounds. Also, these results indicated that the treated effluent is free from pesticides and comply with standards given by Ministry decree No. 44/2000, which regulate the disposal of industrial wastewater into the sewage system. The treated final effluent can be used also for water reuse according to the environmental law No. 93/1962. The obtained results indicate that a coupled photoassisted-biological treatment system is a possible way to achieve the complete mineralization of biorecalcitrant pollutants.

3.4. Economic analysis

The economic assessment will be based on the expected capital cost for each alternative considering the operation and maintenance costs required for different components. The expected benefits will be quantified and evaluated in terms of money to perform the cost benefit analysis. The costs for the treatment of 20 m^3/day of the pesticides wastewater was estimated to be 300000 LE as capital costs and to be 60000 LE/year for the annual maintenance and operating costs for the treatment by using photo-Fenton process as a pretreatment accompanied by biological treatment.

3.5. Conclusions

This study demonstrates the usefulness of the photo-Fenton process as a pretreatment method preceding a biological treatment for the complete mineralization of non-biodegradable organic substances. The results from this study showed that the rate of percentage of TOC degradation was strongly accelerated by photoassisted chemical oxidation processes. The oxidation rate was influenced by many factors such as irradiation time, initial amounts of both H_2O_2, Fe^{2+}. The optimum operating conditions obtained for the best degradation treatment for 82 and 85.5% TOC and COD removal respectively were pH 3, $4x10^{-4}$ and $2x10^{-5}$ M/L initial amounts of H_2O_2, Fe^{2+} respectively within 45 minutes reaction time. The analysis of the photo-treated effluent after the photo-Fenton process showed that the residues of TSS, COD, BOD, Oil & grease, phenol and organic pesticides are 3, 519, 142, 3.1, 1.6 and 0.3 mg/l respectively.

Analysis assured that the photochemical pretreatment induces a beneficial effect on the biocompatibility of the treated effluent. The characterization of the final treated effluent after biological process by using activated sludge as a post treatment for the previously phototreated effluent by photo-Fenton process show that the concentration of TSS, COD, BOD, Oil & grease, T.PO4, TKN and Phenol are 16, 28, 4.5, 12.8, 4.8, <0.001and 0.005 mg/l. The results show that the biodegradability tendency can be enhanced by the photocatalytic oxidation converting the non-biodegradable organic substrates into more biodegradable compounds. Also, these results indicated that the treated effluent is free from pesticides and comply with standards given by Ministry decree No. 44/2000, which regulates the disposal of industrial wastewater into the sewage system and the treated final effluent, can be used for water reuse purposes according to the environmental law 93/1962.

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Figures

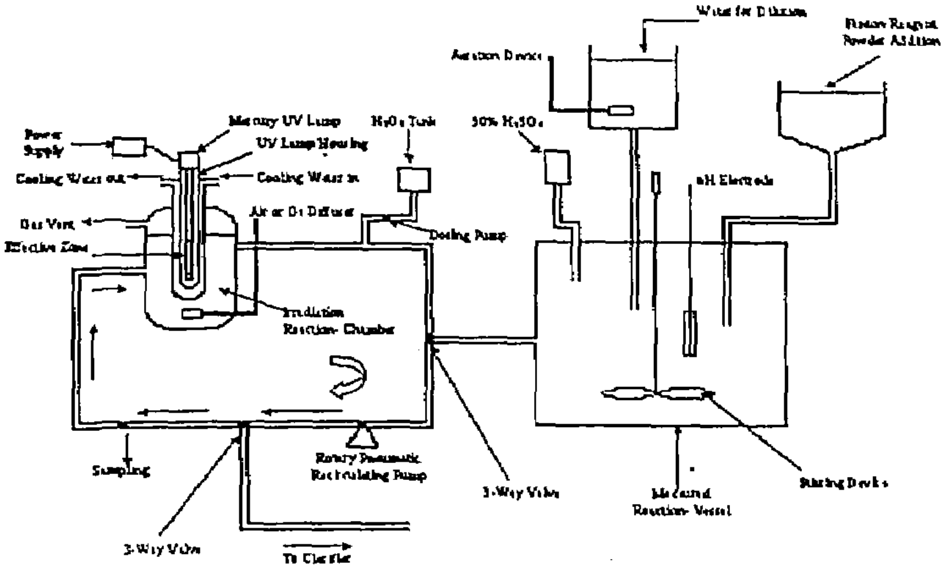

Figure (1): Photo reactor system

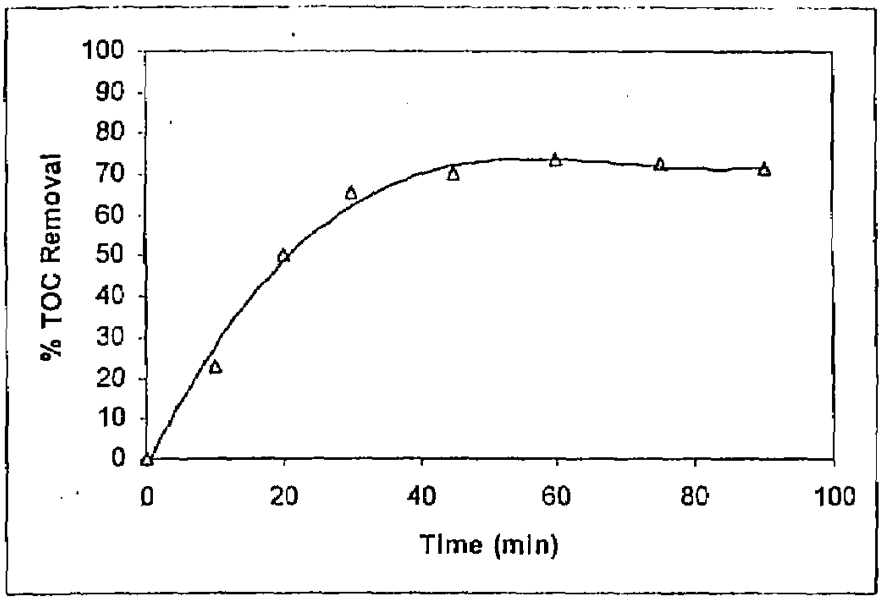

Figure (2): Effect of irradiation time on the treatment efficiency of the photo-Fenton treatment. *[pH=3, H_2O_2= $4x10^{-4}$M/L, Fe^{2+}= Fe^{2+}=$2x10^{-5}$M/L].*

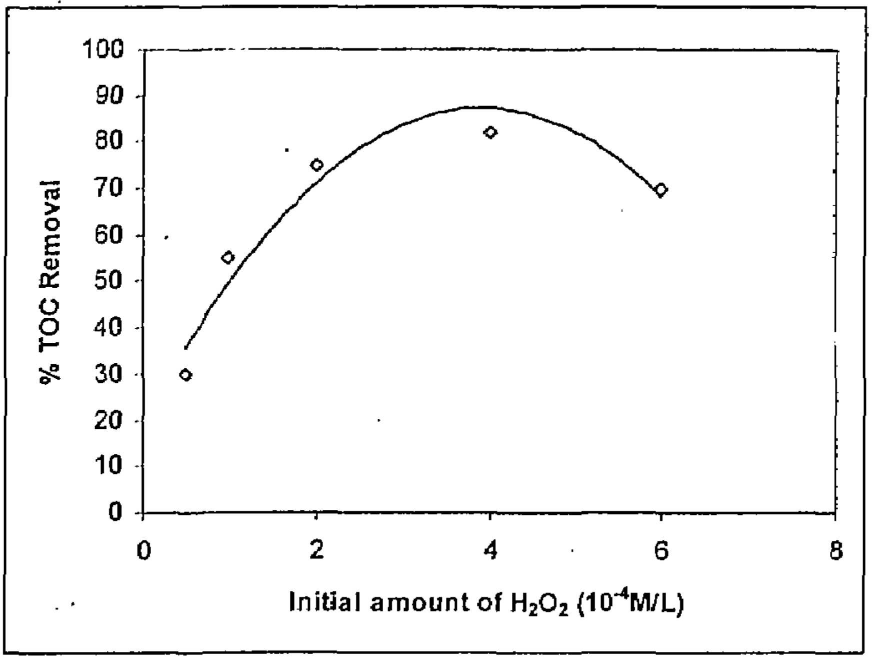

Figure (3): Effect of initial amount of H_2O_2 on the efficiency of the photo-Fenton treatment. *[Irradiation time=45min; pH=3.0; $Fe^{2+}=2x10^{-5}$M/L]*

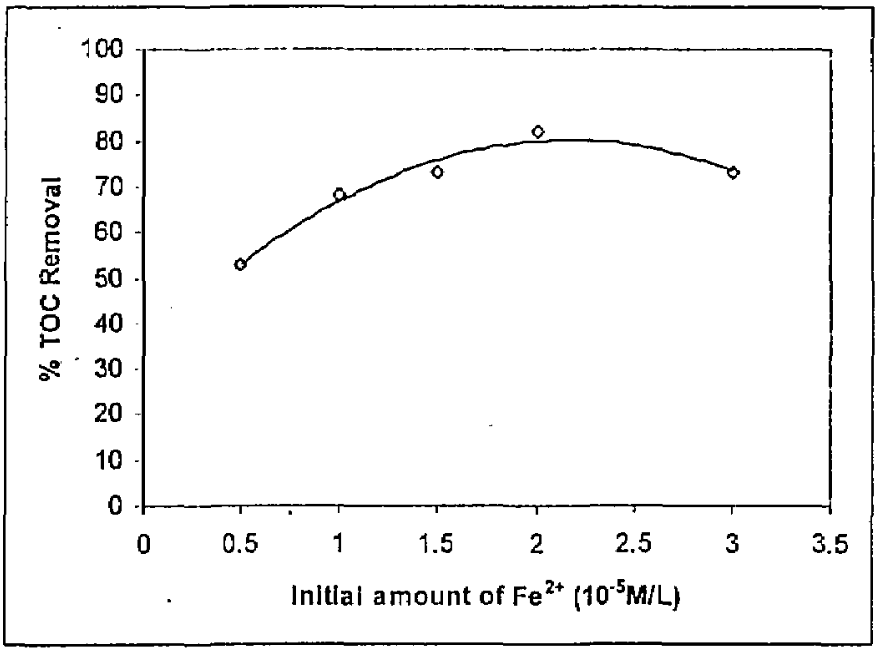

Figure (4): Effect of initial amount of Fe^{2+} on the efficiency of the photo-Fenton treatment. *[Irradiation time=45min; pH=3.0; $H_2O_2=4x10^{-4}$M/L]*

Tables

Table (1): Physico-chemical characteristic of the industrial wastewater samples collected from end of pipe effluent

Parameter	**Unit**	**Sample (1)**	**Sample (2)**	**Sample (3)**	**Sample (4)**	**Limits***
pH		7.4	7.2	7.0	7.1	6-10
TSS at 105C°	Mg/l	324	242	239	517	50
COD	mg/l	2164	2270	5640	2130	1100
BOD	Mg/l	280	180	600	495	600
BOD:COD		0.13	0.08	0.10	0.23	**
TOC	Mg/l	459	253	1383	249	**
Oil& grease***	Mg/l	731	480	1383	464.7	100
Pesticides	Mg/l	23.4	20.6	38.98	25.54	free
Phenol	Mg/l	0.21	0.36	1.6	0.25	0.005
TKN as N_2	Mg/l	53.2	92.4	56.0	21.8	100
$T.PO_4^{3-}$	Mg/l	12.0	40.0	20.0	32.0	5.0
Sulfide as S^{2-}	Mg/l	<0.1	<0.1	<0.1	<0.1	1.0
Heavy metals:						10
Cr^{+6}	Mg/l	<0.02	<0.02	<0.02	<0.02	**
Cu	Mg/l	<0.01	<0.01	<0.01	34.67	**
Ni	Mg/l	<0.02	<0.02	<0.02	<0.02	**
Zn	Mg/l	<0.01	<0.01	<0.01	<0.01	**

Table (2): Characterization of the treated effluent of photo-Fenton process as a pretreatment step of industrial pesticides wastewater

Parameter	**Unit**	**Raw wastewater**	**Treated effluent**	**% of Removal**	**Limits***
pH value	-	7.0	4.0	42	6-10
TSS at 105C°	mg/L	600	3	99.5	50
COD	mg/L	3618	519	85.6	1100
BOD	mg/L	345	162	59	600
BOD: COD	-	0.1	0.3	-	-
TOC	mg/l	677	120	82	**
$T.\ PO_4^{3-}$	mg/l	22	3.2	85	**
TKN as N_2	mg/l	263.2	3.1	99	100
Oil and grease***	mg/l	613	3.1	99.5	100
Phenol	mg/l	0.5	1.6	-73	0.005
Total pesticides	mg/l	20.20	0.30	96	Free
Heavy metals	mg/l	<0.1	<0.1	-	10

*Ministerial Degree No. 44/2000

** Not applicable

*** Total extractable organic matter

Table (3): characterization of the final treated effluent after biological process by using activated sludge as a post treatment of industrial pesticides wastewater

Parameter	Unit	Raw Wastewater	Treated Effluent	% of Removal	Limits*
PH value		7	7.8	-	6-10
TSS	mg/l	600	16	97.33	20
COD	mg/l	3617	27.7	99.23	40
BOD	mg/l	645	8.5	98.7	20
BOD: COD		0.18	0.31		-
TOC	mg/l	676.6	18	97.34	**
Total PO_4	mg/l	22	4.8	78.18	**
TKN as N_2	mg/l	263.2	26.88	89.79	100
Oil and grease***	mg/l	612.5	0	100	5
Phenol	mg/l	0.045	<0.005	100	0.005
Total pesticides	mg/l	20.2	<0.005	100	Free
Heavy metals	mg/l	<0.1	<0.1	-	10

* Environmental law No. 93/1962 for water reuse after tertiary treatment.

** Not applicable

*** Total extractable organic matter