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Fenton's peroxidation and coagulation processes for the treatment of combined industrial and domestic wastewater

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Abstract

As a consequence of the population growth, major efforts have been made by the Egyptian government to construct new industrial areas. Tenth of Ramadan City is one of the most important industrial cities in Egypt. The wastewater generated from various industrial activities was highly contaminated with organic matters as indicated by COD (1750–3323 mg/L), TSS (900–3000 mg/L) and oil and grease (13.2–95.5 mg/L). All overall appraisals of the analytical data from the industrial wastewater indicate that pretreatment is required for all industrial sectors to achieve compliance with the Egyptian Environmental law which requires effective pretreatment of industrial wastewater prior to its discharge into public sewers. Treatability studies via conventional and Fenton processes have been investigated. The efficiency of conventional treatment methods led to 63% COD and 44% color removal by using $FeCl_3$ as coagulant. Various coagulant aids and powdered activated carbon (PAC) were added to 400 mg/L $FeCl_3$ in order to enhance the removal of color. It was found that polyacrylamide polymer, bentonite and PAC increased the efficiency of the treatments where the color removal increased to 79%, by cationic polymer, 73% by anionic polymer, 84.5% by bentonite and 95% for 0.4 g/L PAC. Fenton process was investigated which under the operating conditions (pH 3.0 ± 0.2, Fe^{2+} dose = 400 mg/L and H_2O_2 = 550 mg/L), color removal up to 100% and more than 90% of COD removal were achieved.

Keywords: Advanced oxidation processes; Coagulation; Fenton; Industrial wastewater

1. Introduction

The Egyptian Government's policy was to establish new industrial areas far from old urban areas to create new job opportunities and to protect the environment of the urban cities. Extended industrialization trends in these new industrial areas and the development of new chemical products are generally associated with the increase in wastewater discharge of effluents loaded with organic and inorganic pollutants [1,2]. Therefore, the aim of the present study is to evaluate the effectiveness of chemical processes in the pretreatment of the combined industrial wastewater (end of pipe) generated from textile, chemical, food and metal finishing industries and domestic wastewater.

Due to the complexity of the combined wastewaters, and in particular the presence of the problematic reactive dyes, color removal is a major concern. The biological processes do not effectively decolorize dyes because most of commercial dyes are refractory compounds; where BOD/COD ratio is less than 0.1 [3] and toxic to organisms used in the biological treatment [4]. Therefore, there is a need for advanced treatment processes to remove color and COD from industrial wastewater. Fenton system Fe^{n+}/H_2O_2 is one of the most interesting promising oxidative techniques for the abatement of refractory and/or toxic organic pollutants in water and wastewater [5,6]. The high removal efficiencies of this technique can be explained by the formation of strong hydroxyl radical ($HO^{\bullet}$) and oxidation of Fe^{2+} to Fe^{3+}. Both Fe^{2+} and Fe^{3+} ions are coagulants, so the Fenton process can, therefore, have dual function, namely oxidation and coagulation, in the treatment processes. Moreover, iron is a highly abundant and non-toxic element, and hydrogen peroxide is easy to handle environmentally.

2. Materials and methods

2.1. Materials used

Powdered activated carbon (PAC) from BDH was washed with distilled water, filtered, dried at 120 °C overnight and

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finally kept in stopper glass bottles. The specific surface area is about 600 m^2/g. BASF Anionic (Sedipur AF100) and Cationic (Sedipur CF304) polyacrylamide polymer was obtained from Chemproha Chemiepartner B.V. Analytical grade ferrous sulfate heptahydrate, ferric chloride, 1 M phosphate buffer solution pH 7.6 and hydrogen peroxide (35%) were supplied by Merck.

Thirteen industrial wastewater samples were collected from four industrial sectors: four samples from textile industry and three samples from each other sector. Three combined industrial and domestic wastewater samples were collected from the manhole of the city.

2.2. Analytical measurements

The physical and chemical characteristics of the wastewater were analyzed according to APHA [7]. The total organic carbon (TOC) was measured using Phoenix TOC. Atomic absorption (Varian Spectra 220) was used for heavy metals analysis. Meanwhile Jasco-V-530 spectrophotometer was used for color measurements. The color measurement was run by the spectrophotometric method at wave length ranged from 400 to 650 at pH 7.6 with 10 ordinates wave length and using distilled water as a blank according to APHA [7]. Percentage of decolorization was calculated by comparing the absorbance values of wastewater after treatment to the absorbance value of the raw sample.

2.3. Chemical coagulation process

Chemical coagulation experiments were conducted with the Jar test method. The coagulation processes proceeded with rapid mixing of wastewater samples at 400 rpm for 3 min, slow mixing of 40 rpm for 30 min and then standstill for 30 min. Anionic and cationic polymers, powdered activated carbon and bentonite were added as coagulant aids during the slow mixing step. The supernatant was withdrawn and filtered through 0.45 μm. The COD and DOC were measured according to procedures described in [7]. Prior to the color measurement the pH of the sample was adjusted at 7.6 by adding 1 M phosphate buffer solution.

2.4. Fenton-coagulation process

Fenton process was carried out at room temperature by adding various doses of $FeSO_4\cdot 7H_2O$. The pH was adjusted at 3.0 ± 0.2 and kept at the same value during the reaction. The required amount of H_2O_2 was fed by dosing pump during a period of 15 min, and then the coagulation experiments were conducted with the Jar test method. This method was preceded with rapid mixing of the Fenton treated effluent at 100 rpm for 5 min, slow mixing at 40 rpm for 30 min and then standstill for 30 min. After 30 min settling time, the supernatant was withdrawn, filtered through 0.45 μm, treated with 1N NaOH and heated at 40 °C to remove residual H_2O_2. Physical and chemical characteristics of the treated wastewater were analyzed according to APHA [7]. The pH for oxidation and coagulation experiments was controlled at 3.0 ± 0.2 and 8.5 ± 0.2, respectively, with 0.1N sulfuric acid or sodium hydroxide.

3. Results and discussion

3.1. Physical and chemical characteristics of the industrial wastewater

A monitoring program was prepared and implemented to determine the quantity and the quality of the effluents arising from the various industrial activities and to characterize waste-streams up to the final discharge point. Thirteen composite wastewater samples were collected from the effluents of various manufacturing industries.

Results in Table 1 revealed that the textile industry produced wastewater characterized by a remarkable content of hazardous materials and their concentration ranged from 189 to 798 mg/L with the mean value of 525 mg/L, which have environmental impacts and may cause problems in biological wastewater treatment. For example, such compounds may not respond to the biological process due to their refractory or toxic properties. Saquib and Muneer [8] revealed that wastewater from the textile industry is highly colored and of a complex and variable nature. The large amounts of dyestuffs used in the dyeing processes represent an increasing environmental danger due to their refractory nature.

Table 1
The physical and chemical characteristics of the raw industrial wastewater (mg/L)

Parameter	Textile		Chemical		Metals		Food	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean
pH	7.1–12.9	9.6	7.5–13.4	9.5	8.2–9.1	8.5	7.3–9.1	8
TSS	162–704	532	127–371	272	229–634	431	280–1580	802
TS at 105 °C	900–7554	2575	1216–4448	3761	1010–1492	1267	816–9970	5664
COD	660–2660	1750	960–4280	2921	970–5040	2373	1400–6300	3323
BOD	180–550	313	315–942	699	250–330	317	400–2700	1400
Oil and grease	11–16	13.2	8.4–670	359.5	225–290	257	180–500	293
Dyes	198–550	525	<1		<1		<1	
Heavy metals[a]	0.14–0.46	0.29	NA		15.63–21.7	20.73	<0.1	

NA: not analyzed.
[a] Means the sum of Pb, Cu, Cr, Ni, Zn and As.

Chemical industry is considered one of the most industrial activities that generate wastewaters highly contaminated with organic matters as indicated by COD (960–4280 mg/L), BOD ranged from 315 to 942 mg/L with the mean value of 669 mg/L and TSS (845–4129 mg/L). Previous studies carried out by [9,10] indicated that the wastewater generated from chemical industry contains toxic and non-biodegradable compounds, which can damage the sewers and interfere with the treatment facilities. Moreover, refractory or toxic pollutants influence the quality of drinking water resources and the efficiency of water and wastewater conventional treatment techniques. Therefore, human population can be possibly exposed to organic micropollutants either through drinking water or via the food supply [11–13].

The obtained results in Table 1 showed that the mean concentration of TSS, COD, BOD and heavy metals were 1267, 237, 317 and 20.73 mg/L, respectively. These results indicated that wastewater produced from metal and engineering industries is mainly containing high load of TSS, COD and heavy metals. Therefore, industrial wastewater can cause serious damage to the aquatic environment when discharged directly without proper treatment.

Food industry is an important industrial sector that represents 8% of the manufacturing industries in the studied area. It is, however, an important consumer of water and a major contribution of loads discharged into the water resources. Data presented in Table 1 revealed that the ends of pipe effluents from food industry are characterized by high values of organic matter. The mean values of BOD, COD, TSS and oil and grease are 1400, 3323, 802 and 293.3 mg/L, respectively.

The obtained results indicate that the industrial effluents generated from textile, chemical, metals and foods industries do not comply with the Egyptian Environmental law 93/1962 and its amendments No. 9/1989 and the Ministry of Housing Decree No. 44/2000, which govern the discharge of industrial effluents to sewer system, in order to protect the biological treatment plants and aquatic environment. Therefore, an effective wastewater pretreatment has to be conducted for treatment of the final effluent. The ratio of BOD/COD in wastewater is normally used to express the biodegradability of the wastewater. When the ratio of BOD/COD is greater than 0.3, the wastewater has a better biodegradability. Whereas the BOD/COD less than 0.3 indicates that the wastewater generated from these activities inhibits the metabolic activity of bacterial seed due to their toxicity or refractory properties and it is difficult to be biodegraded [14]. Data in Table 1 showed that the ratio of BOD/COD for textile, chemical and metal wastewaters is less than 0.3. However, in the case of wastewater from food industry BOD/COD value is more than 0.3. Therefore, all industrial wastewaters required chemical pretreatment before being discharged into the sewer system except food industry which can be biologically treated.

3.2. Physical and chemical characteristics of the combined wastewater

To insure the proper selection of wastewater treatment operations, it was necessary to characterize the nature of wastewater generated by the existing industries. This is especially true for industries that exhibit significant differences in their line of activity, generating effluents of varying and complex mixture. Obtained results presented in Table 2 show the physicochemical characteristics of samples collected from the manhole of the city. The results showed a significant difference in the characteristics of the wastewater. This is attributed to the variation flow and concentration of pollutants discharged from various industrial activities. The mean concentrations of COD, BOD and TSS are 2284, 525.7 and 372.0 mg/L, respectively. These results indicate that wastewaters contain high load of organic matter. The COD/BOD ratio is 4.3, which is considered relatively high and indicates the presence of persistence and/or toxic compounds. Persistent untreated pollutants may contaminate receiving water bodies and increase the environmental risks and cost of sludge treatment and disposal [1,11,13].

Table 2
Physical and chemical characteristics of wastewater samples collected from manhole of the city

Parameter (unit)	Range	Mean
pH	7.3–9.8	–
TDS at 105 °C (mg/L)	2200–3320	2874.3
TSS at 105 °C (mg/L)	320–476	372
COD (mg/L O_2)	1596–2598	2284
BOD (mg/L O_2)	297–780	525.7
NH_4 (mg/L)	10.6–18.2	14.2
TKN (mg/L)	28.7–46.5	38.1
CN (mg/L)	0.2–3.4	2
PO_4 (mg/L)	12.6–22.7	16.7
Cr (mg/L)	0.2–3.5	1.8
Cu (mg/L)	1.5–5	3.2
Ni (mg/L)	1.5–3.4	2.4
Zn (mg/L)	3.5–6.4	4.7
As (mg/L)	<0.05	<0.05

3.3. Treatment of combined wastewater (end of pipe of the city)

3.3.1. Efficiency of conventional process

Treatment of wastewater by coagulation is a well-established technology which is suitable for wastewater that contains large amount of colloids and suspended matters. Ferric salts have been found to be economically preferable in wastewater treatment [15]. The results presented in Fig. 1 showed that the 400 mg/L of $FeCl_3$ removed 63% of COD and 44% of color. Various coagulant aids and powdered activated carbon were added to 400 mg/L $FeCl_3$ in order to enhance the removal of color. It was found that polyacrylamide polymer, bentonite and PAC increased the efficiency of the treatment and the color removal increased to 79%, by cationic polymer (2 mg/L), 73% by anionic polymer (2 mg/L), 84.5% by bentonite (0.4 g/L) and 95% for 0.4 g/L PAC. However, high amount of sludge was produced by using bentonite (0.84–1.493 g/L) and PAC (0.784–1.187 g/L); see Fig. 2. Therefore, $FeCl_3$ with polymer can be used as a pretreatment in order to enhance the biodegradability of wastewater during the biological treatment.

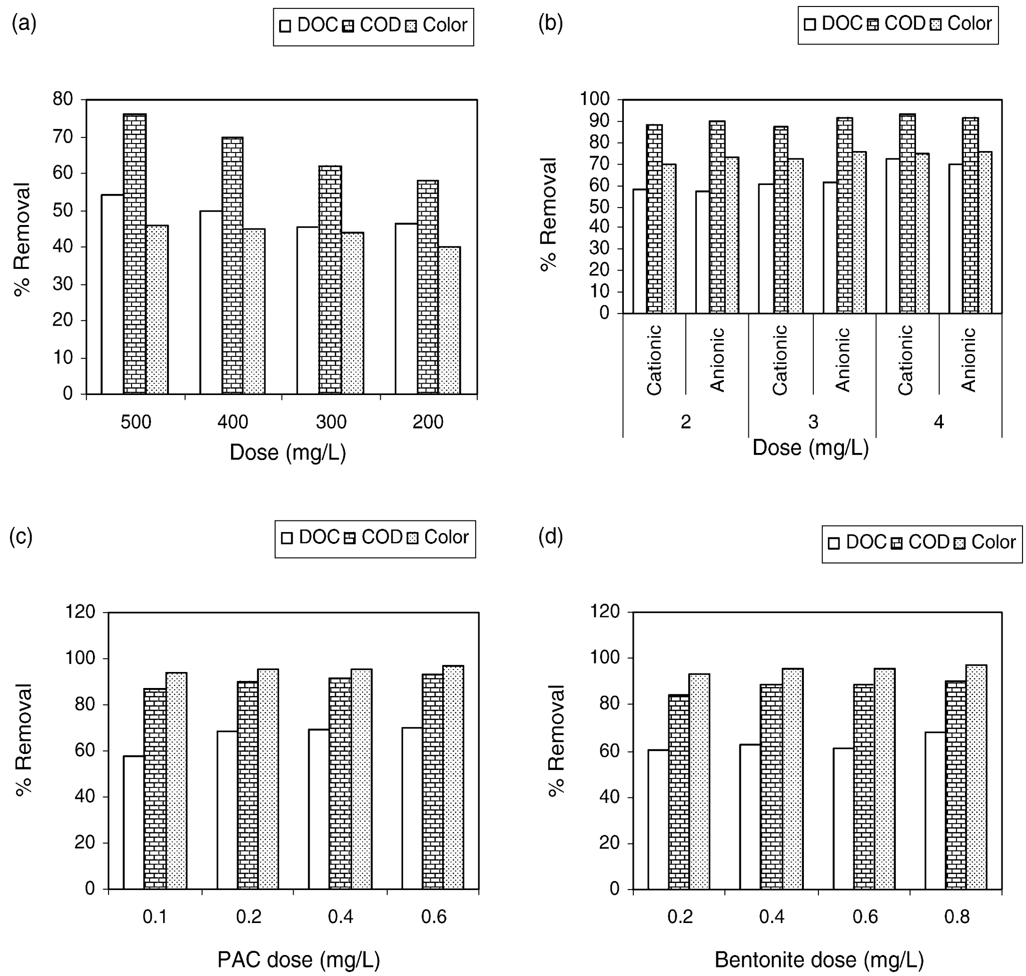

Fig. 1. Efficiency of coagulation processes in the treatment: (a) $FeCl_3$; (b) 400 mg/L $FeCl_3$ + polymer;(c) 400 mg/L $FeCl_3$ + PAC;(d) 400 mg/L $FeCl_3$ + bentonite.

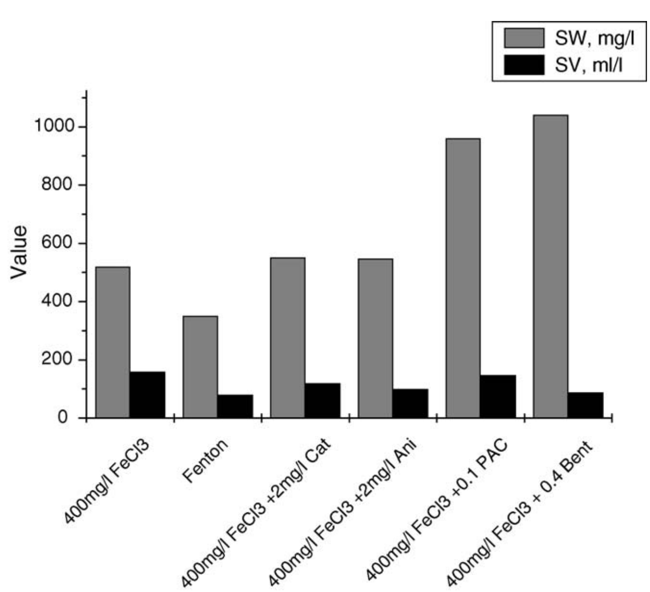

Fig. 2. Sludge production from various processes. SW: sludge weight; SV: sludge volume.

The obtained results (see Table 3) indicated that the chemically treated effluents by $FeCl_3$ contained 173 mg/L dyes which creates environmental problems due to the reduction of the light penetration, interfere with photosynthetic activity of aquatic algae and may also be toxic to some aquatic life due to the presence of aromatics, metals, chlorides, sulfate, bicarbonate, etc., in dyes [3,15]. Therefore, the wastewater required further treatment.

3.3.2. *Efficiency of Fenton oxidation*

The efficiency of Fenton process as a pretreatment step of wastewater was investigated. The effects of pH and dose of hydrogen peroxide were studied. Previous study carried out by Badawy and Ghaly [16] indicated that pH value has a significant effect on the oxidation potential of HO radicals. The maximum degradation of wastewaters using Fenton's reagent as well as color removal up to 90% was achieved at pH 3.0 ± 0.2. Previous studies carried out by [17] revealed that more $Fe(OH)^+$ is formed at pH in the range from 2 to 4. The activity of $Fe(OH)^+$ in Fenton and photo Fenton reaction and the decomposition of H_2O_2 in acidic medium was very fast in producing HO radicals. The amount of H_2O_2 is considered one of the most important factors which should be considered in the Fenton oxidation. The

Table 3
Efficiency of the treatment of the combined wastewater

Parameter (unit)	Raw	Treated effluent[a]	Treated effluent[b]	Limits[c]
pH	9.5	6	8.2	6–9
TDS at 105 °C (mg/L)	2200	1829	1400	1500
TSS at 105 °C (mg/L)	320	20	5	50
COD (mg/L O_2)	1596	702	80	300
BOD (mg/L O_2)	500	310	50	150
BOD/COD	0.313	0.441	0.625	–
Phenol (mg/L)	1.7	0.65	<0.001	<0.01
Oil and grease (mg/L)	5.8	2.6	0.4	5
NH_4 (mg/L)	18.2	11.8	2.8	3
PO_4 (mg/L)	22.7	4.8	3.5	20
SAR		5.3	5.8	9
Heavy metals (mg/L)	18.32	8.7	2.5	10
CN (mg/L)	2.5	2.2	<0.1	0.1
Dyes (mg/L)	315	173	<1	–
Sludge volume (m^3)		0.124	0.084	–
Sludge weight at 105 °C (mg/L)		520	350	–

SAR: sodium absorption ratio.
[a] Treated with 400 mg/L $FeCl_3$.
[b] Fenton's reagent.
[c] Limits for water reuse.

effect of hydrogen peroxide dose on the efficiency of the oxidation process was investigated under the operating conditions (pH 3, Fe^{2+} = 1.465 mM and the concentration of H_2O_2 varied from 5 to 17.6 mM). It was found that color and COD removal efficiency increases with increasing peroxide dose. Maximum removal efficiency was attained at 16.17 mM. Further addition of H_2O_2 did not improve the treatment efficiency. The COD degradation decreased from 95 to 82% as the H_2O_2 dose increased from 16.17 to 17.6 mM (see Table 4). The negative COD removal may be due to residual H_2O_2, which consumes $K_2Cr_2O_7$. Kang et al. [18] reported that the COD removal decreased from 22 to 17%, as the H_2O_2 dosage increased from 10 to 100 mg/L, respectively.

The Fenton treatment of wastewater collected from the end of pipe of the city was carried out at the treatment operating conditions (pH 3.0 ± 0.2, Fe^{2+} dose = 400 mg/L and H_2O_2 = 550 mg/L). Under these conditions, the color was completely removed and the degradation of COD was more than 90%. The results presented in Table 2 showed that the quality of treated effluent is quite satisfactory. Residual values of COD, BOD, oil and grease, ammonia and heavy metals are 80, 50, 0.4, 2.8 and 2.5 mg/L, respectively. These results indicated that Fenton process could be used for treatment of such industrial wastewater without further treatment and the treated effluent complied with the Egyptian law for water reuse under restriction category.

Table 4
Effect of H_2O_2 concentrations on the efficiency of Fenton oxidation

	Concentration of H_2O_2 (mg/L)					
	170	340	400	510	550	600
Color removal (%)	35	50	76	95	100	100
COD removal (%)	25	42	64	87	92	80
TOC removal (%)	25.8	45.4	70.4	91.6	88.5	92.7

pH 3.0 ± 0.2; Fe^{2+} = 1.465 mM.

The BOD/COD ratio of treated wastewater reached 0.625 as compared to 0.313 of the raw wastewater. This result indicates that the biodegradability of the wastewater has been enhanced and is comparable to BOD/COD ratio of domestic wastewater which ranges from 0.5 to 0.7 [19]. Hence, the Fenton process appears to be useful in increasing the biodegradability of wastewater that contains refractory or toxic compounds.

Data presented in Fig. 2 showed that the Fenton process generates lower amount and volume of sludge compared to coagulation processes. Therefore, Fenton process has the advantage in terms of the operation costs. Duran et al. [20] mentioned that Fenton's reagent has two important advantages compared to the coagulation–flocculation processes namely a disinfecting action, since the fecal coliforms and *Salmonela* sp. contents were completely eliminated in treated wastewater, and the sludge production was 10% lower than the one found for coagulation–flocculation process. Ramirez-Zamora et al. [21] studied the characteristics of the coagulation and Fenton's reagent sludge yielded by the treatment of a municipal wastewater. They found that the Fenton sludge presented preferable characteristics such as the specific resistance to filtration (SRF), metals and pathogen content.

4. Conclusion

Coagulation–flocculation was effective in the removal of suspended and insoluble matter. Nevertheless, this process had poor effect on the removal of soluble organic compounds such as reactive dyes. The best treatment results were obtained with the Fenton process, which under the given operating conditions (pH 3, Fe^{2+} dose = 400 mg/L and H_2O = 550 mg/L). Under these conditions, 100% color removal and more than 90% decrease in COD was achieved. In the case of pretreatment, lower dose of Fenton's reagents can be used. Fenton process attains higher costs, if compared to those of coagulant and flocculent agents. These costs could be compensated by lower consumption of disinfecting agents and by the lower costs of sludge handling and disposal. The treated effluent by Fenton reagent can be used for irrigation of ungrouping plants.

References

[1] J. Pierce, Colour in textile effluents-the origins of problem, J. Soc. Dyers Color 110 (1994) 131–133.
[2] F. El-Gohary, R. Abdel Wahaab, F. Nasr, H.I. Ali, Development industrial wastewater management programme, in: Proceedings of the 2nd Specialized Conference on Pretreatment of Industrial Wastewaters, Greece, 1996, pp. 148–155.
[3] T. Robinson, G. Memullan, R. Marchant, P. Nigam, Remediation of dyes in textile effluents: a critical review on current review, Bioresour. Technol. 77 (2001) 247–255.
[4] L.W. Little, Acute toxicity of selected commercial dyes to the fathead minnow and evaluation of biological treatment for reduction of toxicity, in: Proceedings of the Purdue Industrial Wastes Conference, 1977.

[5] S.F. Kang, C.H. Liao, S.T. Po, Decolorization of textile wastewater by photo-Fenton oxidation technology, Chemosphere 41 (2000) 1287–1297.
[6] V. Kavitha, K. Palanivelu, Destruction of cresols by Fenton oxidation process, Water Res. 39 (2005) 3062–3072.
[7] APHA, AWWA, Standard Methods for the Examination of Water and Waste water, 20th ed., WPCF, New York, 1998.
[8] M. Saquib, M. Muneer, TiO_2-mediated photocatalytic degradation of a triphenylmethane dye (gentian violet), in aqueous suspensions, Dyes Pigments 56 (2003) 37–49.
[9] S. Mukhi, X. Pan, G.P. Cobb, R. Patino, Toxicity of hexahydro-1,3,5-trinitro-1,3,5-triazine to larval zebrafish (*Danio rerio*), Chemosphere 61 (2005) 178–185.
[10] G. Bertanza, C. Collivignarelli, I.R. Pedrazzan, The role of chemical oxidation in combined chemical–physical and biological processes: experience of industrial wastewater treatment, Water Sci. Technol. 44 (2001) 109–116.
[11] M.I. Badawy, Use and impact of pesticides in Egypt, Int. J. Environ. Health Res. 8 (1998) 223–240.
[12] M.A. El-Dib, F.A. Hoda, M.A. Azza, Impact of pentachlorophenol on growth and community structure of Nile River water. Microalgae, Int. J. Environ. Health Res. 10 (2000) 239–250.
[13] M.I. Badawy, RA. Wahaab, Environmental impact of some chemical pollutants on Lake Manzala, Int. J. Environ. Health Res. 7 (1997) 161–170.
[14] H. Chun, Y. Wang, Decolorization and biodegradability of photocatalytic treated azo dyes and wool textile wastewater, Chemosphere 39 (1999) 2107–2115.
[15] W. Chen, N.J. Horan, The treatment of a high strength pulp and paper mill effluent for wastewater re-use, Environ. Technol. 19 (1998) 173–182.
[16] M.I. Badawy, M.Y. Ghaly, Advanced oxidation processes for the removal of organo-phosphours pesticides from wastewater, Desalination 1xx, (2006), in press.
[17] I.A. Alaton, I.A. Balciglu, D.W. Bahnemann, Advanced oxidation of a reactive dye bath effluent, Water Res. 36 (2002) 1143–1145.
[18] S.F. Kang, L. Chih-Hsaing, C. Mon-Chun, Pre-oxidation and coagulation of textile wastewater by the Fenton process, Chemosphere 46 (2002) 923–928.
[19] W.G. Kuo, Decolorizing dye wastewater with Fenton's reagent, Water Res. 26 (7) (1992) 881–886.
[20] A. Duran-Moreno, E.G. Lorenzo, C.D. De Baza, J. Malpica de la Torre, R.M. Ramirez-Zamora, Fenton's reagent and coagulation-flocculation as pre treatments of combined wastewater for reuse, Water Sci. Technol. 47 (2003) 145–151.
[21] R.M. Ramirez-Zamora, M.T. Orta de Velazquez, A. Duran-Moreno, J. Malpica de la Torre, Characterization of Fenton sludges issued from wastewater treatment, Water Sci. Technol. 46 (2002) 40–43.