



A comparative study among different photochemical oxidation processes to enhance the biodegradability of paper mill wastewater

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ABSTRACT

Advanced oxidation processes including UV, UV/H₂O₂, Fenton reaction (Fe(II)/H₂O₂) and photo-Fenton process (Fe(II)/H₂O₂/UV) for the treatment of paper mill wastewater will be investigated. A comparison among these techniques is undertaken with respect to the decrease of chemical oxygen demand (COD) and total suspended solids (TSS) and the evolution of chloride ions. Optimum operating conditions for each process under study revealed the effect of the initial amounts of Fe(II) and hydrogen peroxide. Of the tested processes, photo-Fenton process was found to be the fastest one with respect to COD and TSS reduction of the wastewater within 45 min reaction time under low amounts of Fe(II) and hydrogen peroxide of 0.5 and 1.5 mg/L, respectively, and amounted to 79.6% and 96.6% COD and TSS removal. The initial biodegradability of the organic matter present in the effluent, estimated as the BOD₅/COD, was low 0.21. When the effluent was submitted to the different types of AOPs used in this study, the biodegradability increases significantly. Within 45 min of reaction time, the photo-Fenton process appears as the most efficient process in the enhancement of the biodegradability of the organic matter in the effluent and the BOD₅/COD ratio increased from 0.21 to 0.7.

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1. Introduction

Effluents of the paper and paper industry contain a number of toxic compounds and may cause deleterious environmental impacts if discharged directly to receiving waters. Papering processes utilize large amounts of water, which reappear in the form of an effluent. The most significant sources of pollution in paper and paper industry are wood preparation, papering, paper washing, bleaching and coating operations. Among the various processing steps, papering generates a high-strength wastewater containing toxic chemicals such as phenolics [1]. The wastewater from paper and paper industry contains great amounts of organic matter, with low biodegradability, high colour, AOX and toxicity values.

The main treatment process used in paper mill industry is primary clarification, and then succeeded by secondly treatment, generally of a biological nature. However, these processes do not always achieve the complete removal of toxic organic compounds [2,3]. The effluent after biological treatment still contains appreciable concentrations of COD, colour and toxicity. The COD, which

originates from persistent substances in the wastewater, cannot be further reduced by biological process alone. The colour components are lignin and lignin derivatives, which exist in the form of colloidal particles. The toxicity is related to the amount of chlorinated compounds (AOX), such as dioxins and furans, due to usage of chlorine in paper bleaching. If the treated effluent is discharged into water streams or land mass without further treatment, it will result in severe environmental pollution [4]. In addition, the paper industry is likely to face more stringent regulations on the quality of effluents entering receiving waters. Thus, the use of pre-treatment step prior to the biological process has to be considered in the future.

Advanced oxidation processes (AOPs) as the innovative water treatment technologies, are based on the in situ generation of highly reactive transitory species (i.e. H₂O₂, OH⁻, O₂^{•-}, O₃) for mineralization of refractory organic compounds, water pathogens and disinfection by-products [5,6]. AOPs have been defined broadly as those aqueous phase oxidation processes which are based primarily on the intermediacy of the hydroxyl radical (OH[•]) in the mechanism(s) resulting in the destruction of the target pollutant or xenobiotic or contaminant compound [7]. AOPs have been successfully applied to the complete mineralization of different kinds of organic compounds that come from the lignin degradation. These compounds are responsible for the strong colour of the effluent and are very difficult to degrade.

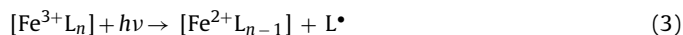
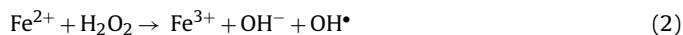
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Generation of the free radicals is commonly accelerated by combining some oxidizing agents such as hydrogen peroxide (H_2O_2), UV radiation and catalyst such as ferrous. Among those methods, UV, hydrogen peroxide and ultraviolet light (UV/ H_2O_2), Fenton's reagent and photo-Fenton process hold the greatest promise for detoxification and mineralization of pollutants. The UV treatment method is based on supplying energy to the chemical compounds as radiation, which is absorbed by reactant molecules that can pass to excited states and have sufficient time to promote reactions [8]. The UV/ H_2O_2 , radiation with a wavelength lower than 400 nm is able to photolyze H_2O_2 molecule. The mechanism accepted for the photolysis of hydrogen peroxide is the cleavage of the molecule into hydroxyl radicals with a quantum yield of two OH^\bullet radicals formed per quantum of radiation absorbed [8], according to Eq. (1).



The Fenton reagent was first recognised in the 1960s and remains one of the most applied AOPs for its ability to degrade high loading of organic compounds. It consists in a mixture of iron (II) salts and hydrogen peroxide. Although its mechanism of action has not yet been completely elucidated, it may involve decomposition of hydrogen peroxide into hydroxyl radical, catalyzed by the metal cation (Eqs. (2) and (3)). The process can be accelerated by irradiation of the solution. The Fenton reaction is a process that does not involve any light irradiation, whereas the photo-Fenton does react up to a light wavelength of 600 nm. The photo-Fenton reaction is expedited when light source present, causing rapid H_2O_2 decomposition by ferrous or ferric ions and resulting in the formation of radicals. All these soluble iron hydroxyl or iron complexes can absorb not only UV radiation but also visible light. However, the actual oxidizing species responsible for the photo-Fenton reaction is still under discussion [9].



The major objective of this study is to investigate the performance of different advanced oxidation methods and their combinations for chemical oxygen demand (COD), biological oxygen demand (BOD), total suspended solids (TSS) and chloride ions (Cl^-) removal from paper mill effluent. Direct photolysis (UV), hydrogen peroxide with UV, Fenton and photo-Fenton processes treatments were employed at pH 3–3.5, H_2O_2 doses 0–5 g/L, Fe(II) amounts from 0 to 1 g/L, for the treatment of paper mill effluent. The aim of this work was also to evaluate the changes observed on the biodegradability of the paper mill effluent taken in this study, during the advanced oxidation with different combined AOPs. The results are evaluated as BOD_5/COD ratio.

2. Experimental

2.1. Source and the characterization of the wastewater

The original real wastewater used was obtained from Egyptian board paper mill industrial plant and was provided as the material of this study. The plant produces 25 ton/day board paper from recycling wasted paper. Wastewater discharged from the mill amounted to 1000 m^3/day was dumped into a pond nearby the factory without any treatment. The wastewater produced was highly contaminated with suspended solids and organic pollutants as well. The samples are taken from the end-of-pipe and were treated without modifications. These effluents were characterized and analyzed for COD, BOD_5 , (Cl^-) and other physical chemical analysis, according to the procedures described in Standard Methods for the Examination of Water and Wastewater (APHA, AWWA,

Table 1

Composition of the paper mill effluent used in this study.

Parameters	Unit	Concentration
pH	–	8.5
COD	mgO_2/L	10,300
BOD	mgO_2/L	2200
Cl^-	mmol/L	75
TSS	mg/L	5950
BOD_5/COD ratio	–	0.21

2005) [10]. Analysis of the end-of-pipe effluent indicated that it carries significant quantities of TSS, COD and Cl^- . Composition of the paper mill wastewater used in this study is presented in Table 1. Low BOD_5/COD ratio of 0.21 indicated low biodegradability of the organic compounds present in the wastewater requiring advanced treatment.

2.2. Material and analysis

GP grade chemicals namely, ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), hydrogen peroxide (H_2O_2) 30%, sulfuric acid and sodium hydroxide were used without any purification and were provided by Merck.

2.3. Set-up

A laboratory photocatalytic oxidation unit was used for the batch experiments. It consists of a cylindrical photo reactor of 0.85 L volume, made from quartz, with a coaxial and immersed medium pressure UV mercury lamp was used as the UV emitter and light source (Heraeus TQ150, input energy of 150 W) emitting a polychromatic radiation in the range from 100 to 280 nm wavelength. The lamp emitted a power of 6.2 W in the UV-C ($100 < \lambda < 280 \text{ nm}$) range (indication Heraeus), corresponding to $1.32 \times 10^{-5} \text{ Einstein s}^{-1}$. The UV lamp is equipped with a cooling water jacket to maintain the temperature of the reaction of wastewater at room temperature. 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. Mixing was accomplished by means of the magnetic stirring.

2.4. Procedure

The laboratory unit was filled separately with 0.85 L of wastewater under study. The optimum conditions for the different photochemical oxidation as pre-treatment steps for biological treatment were investigated for the paper mill wastewater. The pH of the industrial wastewater was adjusted to the desired value before start-up, and kept at the same value during the reaction. For runs using UV/ H_2O_2 processes, hydrogen peroxide at different amounts was injected in the reactor before the beginning of each run. In the UV/ H_2O_2 process, the variable studied was the influence of the amount of hydrogen peroxide at free pH.

For runs, using Fenton and the photo-Fenton processes, a given weight of iron salt was added. The iron salt was mixed very well with the wastewater before the addition of a given volume of hydrogen peroxide. For photo-Fenton process, the time at which the ultraviolet lamp was turned on was considered time zero or the beginning of the experiment which was taking place simultaneously with the addition of hydrogen peroxide. For Fenton and photo-Fenton processes, the pH varied between 3 and 3.5, the influence of hydrogen peroxide and iron(II) was studied.

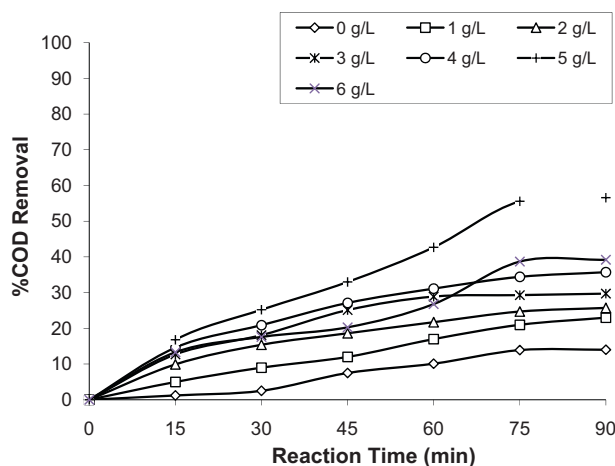


Fig. 1. % COD removal during the treatment of the wastewater by UV/H₂O₂ against reaction time at different doses of hydrogen peroxide [pH = 3].

3. Results and discussion

3.1. Removal of COD of the wastewater

The effect of the initial amounts of hydrogen peroxide in UV/H₂O₂, Fenton and photo-Fenton processes and the amount of Fe(II) in Fenton and photo-Fenton processes were studied in order to select the best conditions for each process, in accordance with the percentage of COD removal.

In the UV process, the runs were carried out at free pH, when pH was increased quantum yield diminished because of secondary reactions. Fig. 1 illustrates the percent removal of COD as a function of the irradiation time at different doses of H₂O₂ input that ranged from 0 to 6 g/L at pH = 3. The direct photolysis of the wastewater in the absence of H₂O₂ gave rather poor results and resulted in a slow removal of COD. By addition of H₂O₂, the COD removal increased when hydrogen peroxide concentration increased however, the effect of peroxide is negative for hydrogen peroxide concentrations higher than 5 g/L. At this concentration, the COD removal reached to 55.6% removal within 75 min reaction time. In this process, hydroxyl radicals generated from the direct photolysis of hydrogen peroxide were the main responsible species of COD removal. However when the addition of excess hydrogen peroxide, coupling of the hydrogen peroxide may occur as given in Eq. (4) or it also reacts with these radicals and hence acts as an inhibiting agent of COD removal and its hydroxyl radical scavenging effect became important according to Eq. (5) as reported by Badawy et al. [12].

In both Fenton and photo-Fenton processes the limiting factors were the amount of hydrogen peroxide and the concentration of Fe(II) ion. The experimental series were carried out at constant pH3. Figs. 2 and 3 illustrate the % COD removals against reaction time at different initial concentrations of hydrogen peroxide for Fenton and photo-Fenton processes, respectively. As shown in Figs. 2 and 3, the % COD removal is demonstrated when H₂O₂ concentration increases for Fenton and photo-Fenton processes, respectively, which is attributed to the effect of the additionally produced OH• radicals. However, above these H₂O₂ concentrations, the % COD removals levels off and becomes negatively affected, by the progressive increase of the hydrogen peroxide. This may be due to auto-decomposition of H₂O₂ to oxygen and water and recombination of OH• radicals (Eqs. (4) and (6)) [11,12]. Excess of H₂O₂ will react with OH• competing with organic pollutants and consequently reducing the efficiency of the treatment, the H₂O₂ itself contributes to the OH• radicals scavenging capacity (Eq. (5)). It is found that, the optimal H₂O₂ concentrations were 2 g/L and

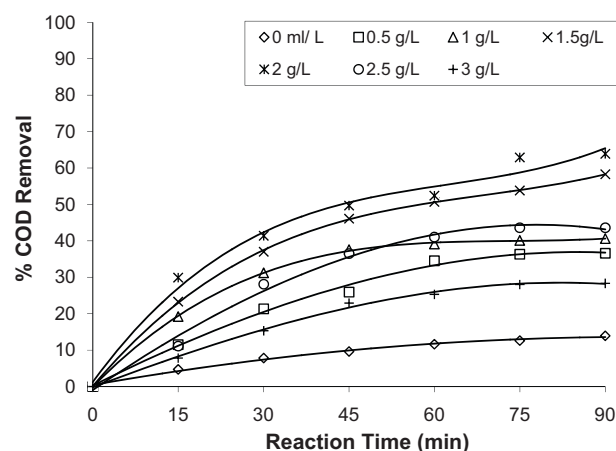


Fig. 2. % COD removal during the treatment of the wastewater by Fenton process against reaction time at different doses of hydrogen peroxide [pH = 3 and Fe(II) = 0.5 g/L].

1.5 g/L for the treatment of the wastewater under study using Fenton and photo-Fenton processes, respectively. The corresponding % COD removals were 62.9% and 79.6% after 75 and 45 min reaction time using Fenton and photo-Fenton processes, respectively, at a constant amount of Fe(II) equals 0.5 g/L.

To elucidate the role of Fe(II) concentration in the treatment of the effluent by both Fenton and photo-Fenton process, a series of experiments with various concentrations of iron with the other parameters fixed, were carried out. Fig. 4 shows the % COD removal of the wastewater by Fenton and photo-Fenton process under different initial amounts of Fe(II) after 45 min reaction time. As can be seen, the COD removal was mainly influenced by Fe(II) concentration for the both Fenton and photo-Fenton processes. Nevertheless, an excess of ferrous ions in both systems beyond definite values produced decrease in the COD removal. The possible formation of futile intermediate iron(IV) species (ferryl iron (FeO)²⁺) could be the cause of this negative behavior, producing a possible side reaction that interferes with the formation of hydroxyl radicals that are critical for the oxidation of organic matter (Eqs. (7)–(9)) [13].

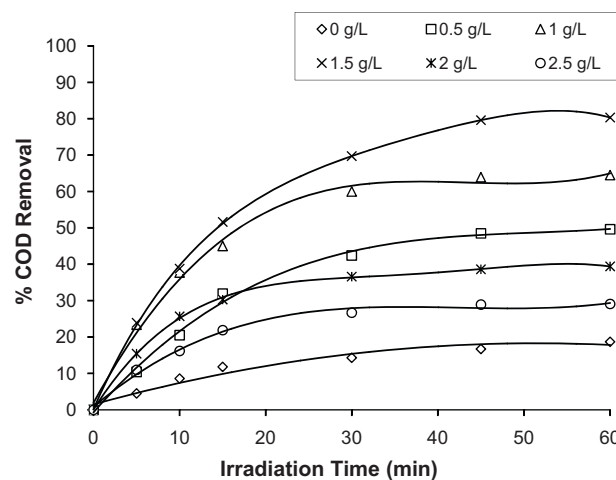
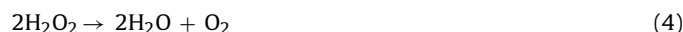


Fig. 3. % COD removal during the treatment of the wastewater by photo-Fenton process against reaction time at different doses of hydrogen peroxide [pH = 3 and Fe(II) = 0.5 g/L].

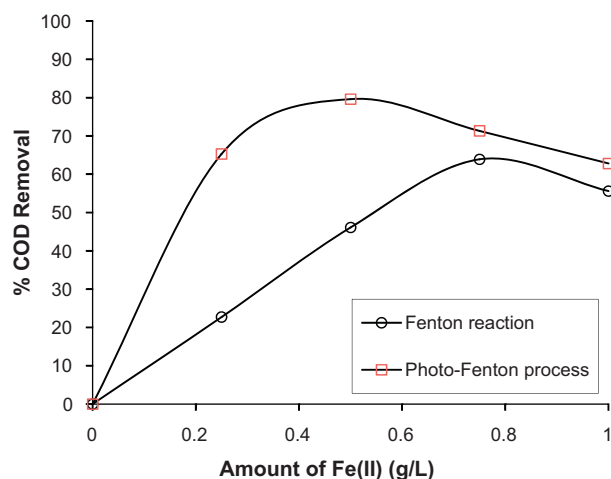
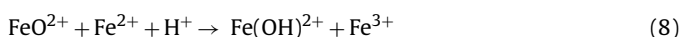


Fig. 4. % COD removal during the treatment of the wastewater by Fenton and photo-Fenton process at different amounts of Fe(II) [H_2O_2 (1.5 g/L), pH = 3, reaction time 45 min].



In photo-Fenton process, a higher addition of iron salt by using photo-Fenton treatment resulted in brown turbidity of nanocrystalline iron(III) hydroxide that hinders the absorption of the UV light required for photolysis and caused the recombination of OH radicals. In this case, Fe^{2+} reacted with OH radicals as a scavenger according to Eq. (10) [14].

As shown from Fig. 4, the optimum amounts of ferrous ions were 0.75 and 0.5 g/L for Fenton and photo-Fenton processes, respectively. The corresponding values of % COD removals were 63.9 and 79.6 within 45 min reaction time. Fig. 5 summarizes the optimum results obtained from each process at the optimum operating conditions. It shows the relationship between the % COD removal of the wastewater against reaction time at the optimum operating conditions of each process.

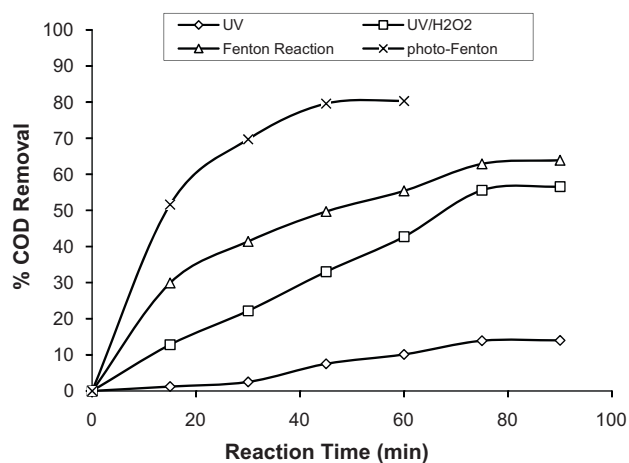


Fig. 5. Comparison of the % COD removal of the wastewater after the treatment of different AOPs [UV/ H_2O_2 , H_2O_2 (5 g/L); Fenton reaction, H_2O_2 (2 g/L), Fe(II) (0.75 g/L); photo-Fenton process, H_2O_2 (1.5 g/L), Fe(II) (0.5 g/L), pH = 3 for the all processes].

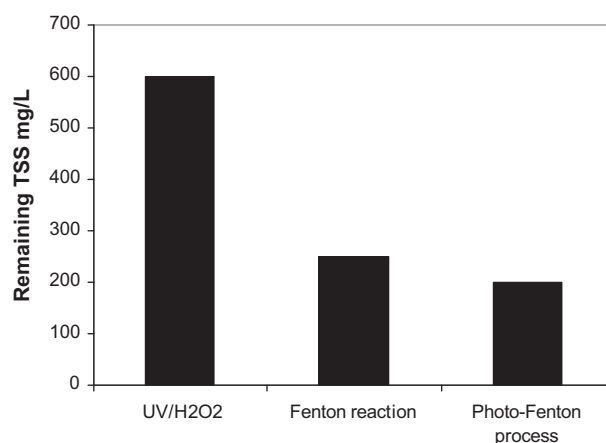


Fig. 6. Remaining of TSS in the wastewater after the treatment of different AOPs [UV/ H_2O_2 , H_2O_2 (5 g/L); Fenton reaction, H_2O_2 (2 g/L), Fe(II) (0.75 g/L); photo-Fenton process, H_2O_2 (1.5 g/L), Fe(II) (0.5 g/L), pH = 3 for the all processes].

3.2. Removal of TSS of the wastewater

The wastewater produced was highly contaminated with suspended solids (TSS) with a value of 5950 mg/L. It is noteworthy that the concentration of TSS in the final effluent discharged from any paper mill varies based on the first pass retention time, white water system design, clarification equipment, equipment arrangement and system constraints in terms of water reuse [15]. Fig. 6 shows the remaining of TSS in the final effluents treated with different types of AOPs tested in this study, the final values ranges from 600 to 200 mg/L according to the type of the advanced oxidation process within 45 min reaction time. The residual values of TSS within 45 min reaction time from the final effluents treated with the different types of AOPs used in this study, except the direct photolysis (UV alone) process (TSS, 2500 mg/L) comply with the National regulatory standards for wastewater discharge into the public sewage network (Egyptian Ministerial decree 4/2000, Ministerial decree for discharge into public sewerage system, this value is 800 mg/L according to this law). The photo-Fenton process causes a decrease of TSS values from 5950 mg/L in the wastewater before the treatment to 200 mg/L within 45 min of the reaction time.

3.3. Dechlorination

In AOPs, the produced hydroxyl radical will attack the aromatic ring of the organic matter and the radical mechanism can be distinguished by the direct dechlorination [16]. Previous results indicated that some organochlorine compounds are found in the paper mill effluent during the bleaching process of cellulose by chlorine dioxide [17]. Partial mineralization of the organic matter was confirmed by measuring the formation of chloride ions. Fig. 7 shows the concentrations of the free chloride produced during the treatment of the paper mill effluent at different AOPs. As shown from the figure, when the paper mill effluent was submitted to one of the AOPs investigated in this study, chloride ions are released into the solution reaching maximum values after 40 min for all systems, and then remain unchanged. It is reported by Tang and Huang [18] that in the reaction with hydroxyl radicals, the aromatic chlorinated compounds are first degraded to aliphatic chlorinated compounds and then irreversibly oxidized to CO_2 and chloride ions, which in turn can react with hydroxyl radicals produced by the AOPs, forming HOCl and inhibiting further oxidation reaction. The best degradation represented with a maximum value of chloride ions generated, was obtained by photo-Fenton process comparing with the other types of AOPs.

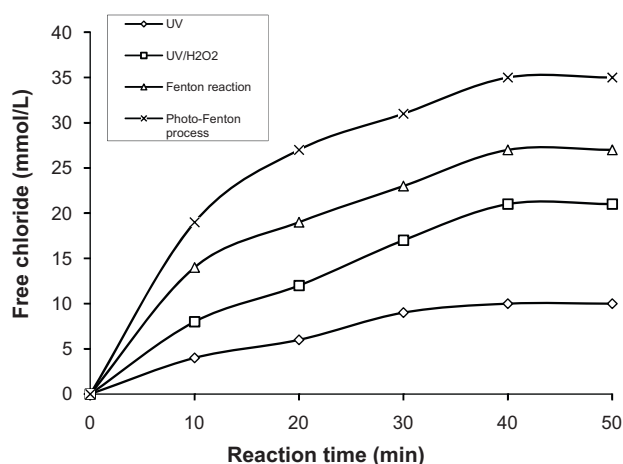


Fig. 7. Resulting free chloride during the treatment of the wastewater with different AOPs [UV/H₂O₂, H₂O₂ (5 g/L); Fenton reaction, H₂O₂ (2 g/L), Fe(II) (0.75 g/L); photo-Fenton process, H₂O₂ (1.5 g/L), Fe(II) (0.5 g/L), pH = 3 for all the processes].

3.4. Biodegradability enhancement

One interesting alternative that is gaining importance among the potential techniques for non-biodegradable or toxic wastewater treatment is the combination of one of the AOPs with a subsequent biological step. In this way the use of the AOPs, the expensive part of the global procedure is reduced to the attainment of a non-toxic and/or biodegradable solution, being the rest of the organic matter removed in the biological step.

The biodegradability of the pretreated wastewater by different AOPs investigated in this study is followed or assessed by means of: (i) analyzing global parameters, such as biological oxygen demand (BOD₅), chemical oxygen demand (COD); (ii) estimating the ratio BOD₅/COD, this ratio considers the most used parameter to quantify the biodegradability of a contaminated effluent. The initial ratio of BOD₅/COD in wastewater before treatment as shown in Table 1 was low (0.21). This indicates that, the wastewater is poorly biodegradable and cannot be biodegraded by activated sludge. These results reveal that the biorecalcitrance of this effluent, in the tested conditions, is associated with the structural stability of compounds towards microbiological attack with no with the toxicity of the solution. Furthermore the value of BOD₅ of the raw wastewater is very low; indicating that wastewater containing chlorinated phenols inhibits the respiratory activity of bacterial seed. Therefore, they not only cannot be biodegraded but also decrease the efficiency of biological treatment. The obtained results indicate that the wastewater generated from the industry does not comply with the environmental laws. The biodegradability is related to the ratio of BOD₅/COD, when BOD₅/COD ratio > 0.5, the wastewater has a good biodegradability as reported by Ghaly et al. [19]. When the ratio is less than 0.3, the wastewater is difficult to be biodegraded [20–23]. The non-biodegradability of a wastewater has to be confirmed before the AOPs treatment, since classical biological treatments are, at the present, the cheapest and most environmentally compatible. As found by Preis et al. [24] and reported by Stasinakis [25] that the biodegradability of phenolic compounds increases only slightly after the photochemical treatment and they recommended a subsequent biological treatment if the effluent BOD₅/COD ratio is equal to or exceeds the value 0.6. The key question concerning the combined use of one of the AOPs as a pretreatment step and a biological treatment is to prove that the biodegradability of the pre-treated effluent and, particularly, the BOD₅/COD ratio increases during the AOPs, approaching the value higher than 0.3 that is considered the quantitative index for organic matter complete biodegradability. Thus, BOD₅ and COD analysis of the treated wastewater were car-

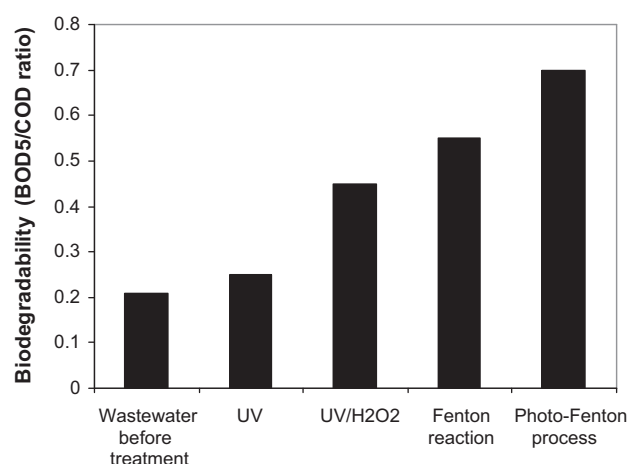


Fig. 8. Biodegradability of the wastewater after the treatment of different AOPs [UV/H₂O₂, H₂O₂ (5 g/L); Fenton reaction, H₂O₂ (2 g/L), Fe(II) (0.75 g/L); photo-Fenton process, H₂O₂ (1.5 g/L), Fe(II) (0.5 g/L), pH = 3 for all the processes].

ried out in order to characterize the evolution of the BOD₅/COD ratio.

Fig. 8 shows the biodegradability enhancement of the effluents treated with the different AOPs investigated in this study within 45 min reaction time. After 45 min reaction time, the BOD₅/COD values were varied from 0.25 to 0.7 according the type of the advanced oxidation process.

These results show that the biodegradability can be enhanced by the all oxidation processes, except the direct photolysis (UV alone), converting the non-biodegradable organic substrates into more biodegradable compounds. The ratio of BOD₅/COD of the pre-treated effluent with photo-Fenton process gives the higher values with 0.7 and 0.8 within 45 and 60 min reaction time, respectively, comparing with the other AOPs. Therefore, the more appropriate photo-Fenton time was 45 min for practical wastewater treatment. The results show that there is a relationship between the removal of COD and the biodegradability of the wastewater selected as case study; results show that the removal of COD during the all AOPs is accompanied by the enhancement of the pretreated wastewater. When the removals of COD for the wastewater treated with UV, UV/H₂O₂, Fenton reaction and photo-Fenton process were 10.9, 33, 49.7 and 79.6%, respectively, the corresponding ratios of the biodegradability of the wastewater were 0.22, 0.25, 0.45, 0.55 and 0.7.

4. Conclusion

COD and TSS removals from a paper mill effluent were investigated by using different advanced oxidation processes (AOPs). The effect of the amount of the initial hydrogen peroxide in the UV/H₂O₂, Fenton and photo-Fenton processes and Fe(II) in the Fenton and photo-Fenton processes were investigated and the most suitable operating conditions were determined. Peak performances of each treatment method were compared for COD and TSS. The advanced oxidation processes used in this study show significantly reduction in both of COD and TSS of the paper mill wastewater. The results show significant dechlorination of the treated wastewater represented by the evolution of free chloride proving the efficiency of the AOPs used in this study. Photo-Fenton treatment process seems to be more advantageous yielding higher COD and TSS removals as compared with UV/H₂O₂ and Fenton reaction. Treatment by photo-Fenton process yielded high COD (79.6%) and TSS (96.6%) removals at a pH 3 with 0.5 g/L Fe(II) and 1.5 g/L H₂O₂ after 45 min of treatment.

AOPs (UV/H₂O₂, Fenton and photo-Fenton processes) used in this study were also efficient in improving the biodegradability measured as BOD₅/COD. The photo-Fenton process shows a significant enhancement in biodegradability of the wastewater with a BOD₅/COD ratio of 0.7 after 45 min reaction time comparing with the other AOPs.

References

- [1] D. Pokhrel, T. Viraraghavan, Treatment of pulp and paper mill wastewater: a review, *Sci. Total Environ.* 333 (2004) 37–58.
- [2] K.A. Kahmark, J.P. Unwin, Pulp and paper effluent management, *Water Environ. Res.* 70 (1998) 667–690.
- [3] K.T. Das, A.K. Jain, Pollution prevention advances in pulp and paper processing, *Environ. Prog.* 20 (2001) 87–92.
- [4] R. Yuan, R. Guan, P. Liu, J. Zheng, Photocatalytic treatment of wastewater from paper mill by TiO₂ loaded on activated carbon fibers, *Colloids Surf. A: Physicochem. Eng. Aspects* 293 (2007) 80–86.
- [5] S. Esplugas, J. Giménez, S. Contreras, E. Pascual, M. Rodríguez, Comparison of different advanced oxidation processes for phenol degradation, *Water Res.* 36 (2002) 1034–1042.
- [6] M. Pera-Titus, V. García-Molina, M.A. Baños, J. Giménez, S. Esplugas, Degradation of chlorophenols by means of advanced oxidation processes: a general review, *Appl. Catal. B: Environ.* 47 (2004) 219–256.
- [7] D. Ollis, Comparative aspects of advanced oxidation processes, *Emerging Technologies in Waste Management II*, ACS Symposium Series 518, Washington, DC, 1993, pp. 18–34.
- [8] O. Legrini, E. Oliveros, A.M. Braun, Photochemical processes for water treatment, *Chem. Rev.* 93 (1993) 671–698.
- [9] J.J. Pignatello, D. Liu, P. Huston, Evidence for an additional oxidant in the photoassisted Fenton reaction, *Environ. Sci. Technol.* 33 (1999) 1832–1839.
- [10] APHA, AWWA, Standard Methods for the Examination of Water and Waste Water, 20th ed., WPCF, New York, 1998.
- [11] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical review of rate constants for reaction of hydrated electrons, hydrogen atoms and hydroxyl radicals (OH•/O•-) in aqueous solution, *J. Phys. Chem. Ref. Data* 17 (1988) 513–886.
- [12] M.I. Badawy, M.Y. Ghaly, T.A. Gad-Allaha, Advanced oxidation processes for the removal of organo-phosphorus pesticides from wastewater, *Desalination* 194 (2006) 166–175.
- [13] K.H. Chan, W. Chu, The dose and ratio effects of Fe(II) and H₂O₂ in Fenton's process on the removal of atrazine, *Environ. Technol.* 24 (2003) 703–710.
- [14] M. Yang, J. Hu, K. Ito, Characteristics of Fe₂C/H₂O₂/UV oxidation process, *Environ. Technol.* 19 (1998) 183–191.
- [15] B. Panchapakesan, White water reuse and save alls Pulp and Paper Manufacture, vol. 6, Joint Textbook Committee of the Paper Industry, Tappi, CPPA, 1992.
- [16] M.Y. Ghaly, G. Härtel, R. Mayer, R. Haseneder, Photochemical oxidation of p-chlorophenol by UV/H₂O₂ and photo-Fenton process. A comparative study, *Waste Manage.* 21 (2001) 41–47.
- [17] J. Freer, E. Gonzales, J. Rodrriguez, J. Baeza, A. Pacheco, H.D. Mansilla, Ozone degradation of the bleaching effluents in the paper and paper industry, in: *Proceedings of the 12th World Congress of the International Ozone Association*, Lille, France, vol. 2, 1995, pp. 653–656.
- [18] W.Z. Tang, C.P. Huang, 2,4-Dichlorophenol oxidation kinetics by Fenton's reagent, *Environ. Technol.* 17 (1996) 1371–1378.
- [19] M.Y. Ghaly, G. Härtel, R. Haseneder, Integrated coupled systems as biodegradability enhancement of textile wastewater by photo-Fenton process, in: *Afinidad LXVI*, vol. 543, 2009, pp. 421–428.
- [20] C. Hu, W. Yizhong, Decolorization and biodegradability of photocatalytic treated azodyes and wool textile wastewater, *Chemosphere* 39 (1999) 2107–2115.
- [21] V. Sarria, S. Parra, M. Invernizzi, P. Peringer, C. Pulgarin, Photochemical-biological treatment of a real industrial biorecalcitrant wastewater containing 5-amino-6-methyl-2-benzimidazolone, *Water Sci. Technol.* 44 (2001) 93–101.
- [22] M.I. Badawy, T.A. Gad-Allah, M.Y. Ghaly, A. Lopez, Combination of photocatalytic and biological processes as an integrated system for treatment and recovery of industrial wastewater containing pesticides, in: *Afinidad*, vol. 63, 2006, pp. 478–487.
- [23] M.I. Badawy, F.El. Gohary, M.Y. Ghaly, M.E.M. Ali, Enhancement of olive mill wastewater biodegradation by homogeneous and heterogeneous photocatalytic oxidation, *J. Hazard. Mater.* 169 (2009) 673–679.
- [24] S. Preis, S. Kamenev, J. Kallas, R. Munter, Advanced oxidation processes against phenolic compounds in wastewater treatment, *Ozone Sci. Eng.* 17 (1995) 399–418.
- [25] A.S. Stasinakis, Use of selected advanced oxidation process (AOPs) for wastewater treatment – a mini review, *Global NEST J.* 10 (2008) 376–385.