Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2012.698799

Taylor & Francis
Taylor & Francis Group

48 (2012) 89–95
October

Coupled solar photo-fenton process with aerobic sequential batch reactor for treatment of pharmaceutical wastewater

S. Adishkumar*, S. Sivajothi, J. Rajesh Banu

Department of Civil Engineering, Anna University: Chennai, Regional Centre, Tirunelveli, India
Tel. +91 9841339016; email: adishk2002@yahoo.co.in

Received 14 June 2011; Accepted 9 April 2012

ABSTRACT

The pharmaceutical wastewater was treated by coupling solar photo-Fenton process with an aerobic sequential batch reactor (SBR). Pharmaceutical wastewater has high COD and very low BOD and hence it is difficult to treat them biologically. The main purpose is to determine optimal photo-Fenton conditions (i.e., pH, ferrous ion concentration, H_2O_2 dosage and treatment time) for making wastewater biocompatible and suitable for subsequent biological treatment. Solar photo-Fenton process enhances biodegradability and a significant enhancement of biodegradability was found at the optimum conditions of pH = 3, H_2O_2 = 5 g L^{-1}, Fe^{2+} = 1 g L^{-1} and irradiation time = 60 min. At this condition BOD_3/COD ratio increased from 0.015 to 0.54. The coupled solar photo-Fenton with SBR process obtained COD removal of 98% and the effluent COD concentration was found to be 100 mg/L, which meets the requirements of the discharge standard.

Keywords: Pharmaceutical wastewater; Solar photo-Fenton; Aerobic SBR; Coupled treatment; Biodegradability

1. Introduction

Pharmaceuticals, including antibiotics are a new group of man-made chemicals of concern entering our environment. Pharmaceutical and antibiotic residues from human and animal medical care enter the water and soil from many sources [1]. In India, pharmaceutical industries meets around 70% of the country's demand and more than one lakh pharmaceutical products are available in markets. Approximately 30×10^6 kg of human pharmaceuticals and 25×10^5 kg of animal pharmaceuticals are annually used for therapeutic use [2]. US EPA estimated the average daily wastewater generation by the pharmaceutical manufacturing industry to be 1.00681 $\times 10^9$ L [3]. Pharmaceutical wastewater if disposed with insufficient treatment may leads to great damage to the environment and groundwater resources [4].

Many drugs become persist in the environment, enter the food chain, bioaccumulates, biomagnify, and cause harmful effects in wildlife and humans. Because of aquatic contamination by these chemicals, bacteria and other microbes in the aquatic environment can become more resistant to them. This results in the development of more antibiotic resistant and virulent pathogens in the environment. Therefore, the persistence of pharmaceutical chemicals in the environment has become a global problem [5,6]. Hence pharmaceutical wastewater should be treat before allow them into the environment. Since the middle of the 1990s, awareness of pharmaceuticals

*Corresponding author.

in the environment is growing and many studies have been investigated to treat the pharmaceutical wastewater using various treatment methods such as coagulation and granular activated carbon filtration [7], Liquid core microcapsules [8], submerged hollow fiber membrane bioreactor [9], chemical treatment [10], anaerobic treatment [11,12], Fenton's oxidation [5], coupled anaerobic and aerobic treatment [13,14] and coupled advanced oxidation and biological treatment [15].

Even though a lot of treatment methods are available with their own advantages and disadvantages, coupled advanced oxidation process (solar photo-Fenton) and biological treatment (aerobic sequential batch reactor, SBR) is more promising and effective. Lee et al. [16] described the advantages of coupled wastewater treatment as (1) synergistic effects as photocatalytic and biological methods complement with each other, (2) protection of biological culture from inhibitory or toxic compounds by photocatalytic pretreatment, (3) reduction in chemical dosage by the use of cost-effective biological treatment, (4) flexibility in total residence time as a result of different choices that are possible for photocatalytic and biological reactor residence time in a constant efficiency and (5) cost-effective while achieving complete pollutant mineralization.

Advanced oxidation processes (AOPs) are used to oxidize complex organic constituents found in wastewater and typically involves the generation and use of the hydroxyl free radicals ($OH^\bullet$) as a strong oxidant to destroy compounds that cannot be oxidized by conventional oxidants. Hence it improves the biodegradability of wastewater [16]. In this process, hydroxyl radicals which are formed react with organic materials breaking them down gradually in a stepwise process. These hydroxyl radicals attack organic molecules by either abstracting a hydrogen atom or adding hydrogen atom to the double bonds. It makes new oxidized intermediates with lower molecular weight or carbon dioxide and water in case of complete mineralization [17]. UV is the most commonly employed light source in photo-assisted oxidation processes, but the high cost of generating artificial UV light leads researchers to the economical light source of the sun. However, H_2O_2 has a low molar extinction coefficient and partly absorbs UV above 320 nm, so the solar photo-Fenton process can only use photons of wavelengths up to 400 nm, which only represent a minority of total solar radiation [18].

Biological processes are the most environmentally compatible and least expensive wastewater treatment methods [19]. SBR is the compatible biological treatment for the pretreated pharmaceutical wastewater. It consists of five discrete time periods such as fill, react, settle, draw and idle. If wastewater contains non-biodegradable organic pollutants, microorganisms cannot degrade the main part of the organics, and hence direct biological processes are not suitable [20]. AOPs are suitable alternatives for the treatment of the wastewater containing toxic or non-degradable pollutants. Although Fenton and photo-Fenton type reactions offer successful pollutant removal with relatively low operational costs and with the possibility of efficient sun radiation exploitation, expenses associated to reagents and energy consumption are the main disadvantages. In order to overcome the economical drawback, and considering that biological treatment is the most desirable wastewater treatment in terms of environmental impact, a two-stage chemical/biological process is being currently proposed by many researchers when working with toxic and/or non-biodegradable waters [21].

This article deals with the use of a solar-driven Fenton process for the treatment of pharmaceutical wastewater. The main purpose is to determine optimal photo-Fenton conditions (i.e., pH, ferrous ion concentration, H_2O_2 dosage and treatment time) for making wastewater biocompatible and suitable for subsequent biological treatment.

2. Materials and methods

2.1. Pharmaceutical wastewater

The wastewater was collected from pharmaceutical industry located in Chennai. The main characteristics as per standard methods [22] were summarized in Table 1.

2.2. Coupled solar photo-Fenton process and aerobic SBR

The treatment was accomplished by coupled treatment of solar photo-Fenton process and SBR.

Table 1
Characteristics of pharmaceutical wastewater

Parameters	Mean values
pH	7.14
TS (mg L^{-1})	4593
TDS (mg L^{-1})	4240
TSS (mg L^{-1})	418
BOD_3@27 °C (mg L^{-1})	85
COD (mg L^{-1})	5750
BOD_3/COD	0.015

2.2.1. Solar photo-Fenton process

All the experiments were carried out in Anna University Campus, Tirunelveli (8°44′N 77°44′E) and the photo-Fenton reactions were carried out in laboratory scale solar photo-Fenton reactors with the working volume of 2 L. It was exposed under strong solar irradiation from the month of January to April (UV intensity 32 ± 2 W/m^2). The tests were started at 12.00 pm and stopped at 1.00 pm. The required pH of wastewater was adjusted using sulphuric acid. The necessary amount of ferrous salt was added to the wastewater and mixed well to enhance the homogeneity of wastewater during the reaction. Thereafter, required amount of hydrogen peroxide was added to the mixture and the mixture was subjected to solar light for irradiation. The time at which hydrogen peroxide was added to the mixture was considered the beginning of the experiment. The reaction was allowed to continue for 60 min. Thereafter, pH was increased for iron precipitation and they were treated with sodium sulfite to remove the remaining hydrogen peroxide from the photo-Fenton reaction. The treated wastewater was left undisturbed for some time to settle the precipitated iron and the supernatant was subjected to treat in the SBR after pH adjusted to 6.8–7.2. The chemical oxygen demand (COD) and biological oxygen demand (BOD_3) of the samples were carried out as per standard methods [22].

2.2.2. Aerobic sequential batch reactor

The biological treatment was conducted in plexiglass reactor with the size of 21.5 cm × 21.5 cm × 15cm. The reactor was equipped with an air pump and air diffuser to keep dissolved oxygen above 3 mg L^{-1}. Two identical reactors with a total working volume of 7 L were operated in parallel with FILL, REACT, SETTLE and DRAW periods in the ratio of 1:5:1:1 to constitute a cycle time of 8 h. The SBR was inoculated with aerobic sludge from pharmaceutical wastewater treatment plant. Concentration of biomass in the reactor after inoculation was 4000 mg L^{-1}. Mixed liquor suspended solids (MLSS) concentration and COD were analyzed as per standard methods [22].

3. Results and discussion

3.1. Solar photo-Fenton process

3.1.1. Effect of pH

The pH is an important parameter in the solar photo-Fenton process to enhance the generation of hydroxyl radicals and the oxidation efficiency. In order to study its effect, the experiments were conducted with various pH such as 2, 3, 4 and 7. From Fig. 1 it was observed that maximum COD removal efficiency of 96% was obtained at pH 3. But the COD removal efficiency was only 57% and 51% at pH 2 and pH 4, respectively. Hence, pH 3 was found to be the optimum pH in the solar photo-Fenton process. The COD removal efficiency is less at pH 4 is due to the coagulation of Fe^{3+} complex formed in the reaction reduced the catalysis of Fe^{2+}. The low COD removal efficiency at pH 2 is due to the hydroxyl radicals scavenging effects of H^+ ions (Eq. (1)). There was no significant reduction of COD was found in pH 7 because in neutral pH the ferrous salts precipitates and settles down. Huaili et al. [21] reported that photo Fenton process could remove pollutants under acidic condition. The similar results also observed in the degradation of synthetic amoxicillin wastewater [5] and the oxidation of hospital wastewater [23]

$$OH^{\bullet} + H^+ + e^- \rightarrow H_2O \quad (1)$$

3.1.2. Effect of ferrous dosage

The effect of Fe^{2+} concentration on the COD removal of pharmaceutical wastewater has been investigated. To determine the optimal ferrous dosage, experiments were conducted by varying the Fe^{2+} concentrations of 0, 0.5, 1, 2 and 3 g L^{-1}. The results are shown in Fig. 2 the COD removal increased from 67% to 91% at 60 min with the addition of Fe^{2+} from 0.5 g L^{-1} to 1 g L^{-1}. This indicated that Fe^{2+} as a catalyst can significantly accelerate the decomposition of H_2O_2. The increase in COD removal is due to the production of more $OH^{\bullet}$ radicals. Similar results reported in the hetero-bioreactive dye removal [24]. However, COD removal decreased as ferrous concentration increased from 1 g L^{-1} to 3 g L^{-1}. This suggests that excessive Fe^{2+} had negative effect on COD removal of pharmaceutical wastewater. This result might be rationalized by the ferrous ion inhibition that occurred

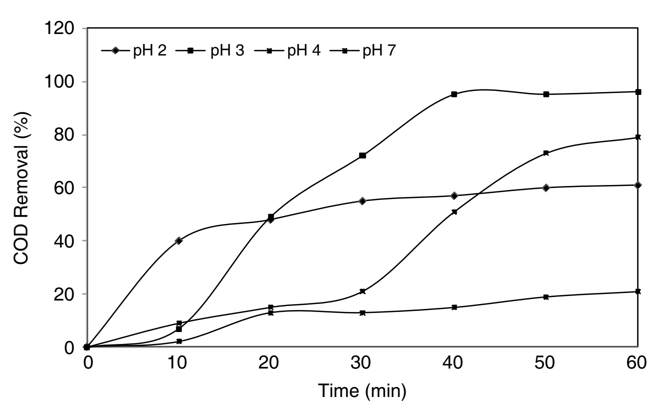

Fig. 1. Effect of pH on the removal of COD (H_2O_2 = 5 g L^{-1}, Fe^{2+} =1 g L^{-1}).

when too high concentration of ferrous was presented. Ferrous ion themselves may react with hydroxyl radicals resulting in the retardation of the reaction as shown in Eq. (2).

$$OH^{\bullet} + Fe^{+} \rightarrow OH^{-} + Fe^{3+} \quad (2)$$

Similar results reported for the treatment of hospital wastewater [23], oxidation of acidic acid dye Eosin Y [21] and the degradation of synthetic amoxicillin wastewater [5]. Hence, 1 g $L^{-1}$of Fe^{2+} can be used as optimum dosage for the treatment of pharmaceutical wastewater by solar photo-Fenton process.

3.1.3. Effect of H_2O_2 dosage

In solar photo-Fenton reaction, H_2O_2 concentration affects the COD removal of pharmaceutical wastewater and its optimal concentration may also reduce the operating cost. The concentration of H_2O_2 has been varied from 5 g L^{-1} to 20 g L^{-1} to study its effect on the COD removal of pharmaceutical wastewater. From Fig. 3 it was observed that the COD removal increased from 81% to 93% with the addition of H_2O_2 from 5 g $L^{-1}$to 15 g L^{-1}, which resulted from more H_2O_2 radicals produced with the addition of more H_2O_2. However, as H_2O_2 concentration was exceeded 15 g L^{-1}, the COD removal decreased. The reaction rate can be inhibited with an excess of hydrogen peroxide in the system [23]. This was probably due to both auto-decomposition of H_2O_2 into oxygen and water (Eq. (3)), and the recombination of OH? radical (Eq. (4)) as follows:

$$2H_2O_2 \rightarrow 2H_2O + O_2 \quad (3)$$

$$H_2O_2 + OH^{\bullet} \rightarrow H_2O + O_2H^{\bullet} \quad (4)$$

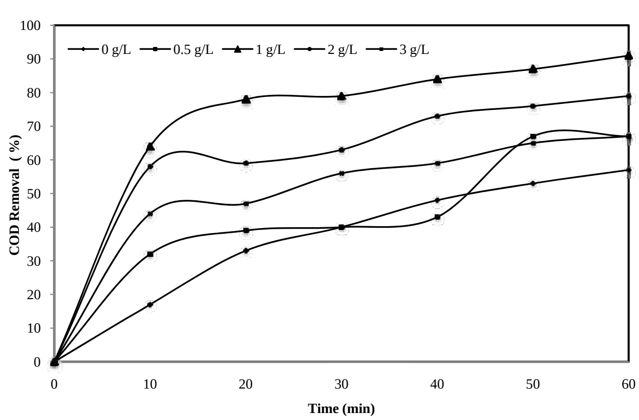

Fig. 2. Effect of ferrous on the removal of COD (pH = 3, H_2O_2= 5 g L^{-1}).

The present study revealed that there was no much variation in COD removal percentage with the addition of 5 g $L^{-1}$and 15 g L^{-1}. Concentration of H_2O_2 should be three times increased to achieve 93% of COD removal from 81%. By considering the operation cost, 5 g L^{-1} of H_2O_2 has been chosen as optimum concentration even though 93% COD removal achieved with 15 g L^{-1} of H_2O_2.

3.1.4. Effect of irradiation time and biodegradability

In order to study the effect of irradiation time, the experiment was carried out under optimized pH, hydrogen peroxide and ferrous concentration for 120 min. Fig. 4 shows the effect of irradiation time on COD removal of pharmaceutical wastewater. The results showed that almost 96% of COD was depleted at 100 min. Since partial oxidation is enough in the present study and moreover BOD_3/COD ratio increased to 0.54 at 60 min itself, hence the optimum irradiation time has been chosen to be 60 min. Similar results are obtained in the work of Emad et al. [5] and Huaili et al. [20]. When increasing the irradiation time, the COD removal also increased because the maximum time of exposure of reaction mixture to the solar light allows them to utilize more energy from sunlight and hence it leads to the generation of more hydroxyl radicals. In the photo-Fenton process, the rate of contaminant degradation can be considerably increased via photochemical reaction as shown in Eq. (5)–(7).

$$H_2O_2 + hv \rightarrow 2OH^{\bullet} \quad (5)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{-} + O_2H^{\bullet} \quad (6)$$

$$Fe^{3+} + H_2O + hv \rightarrow OH^{\bullet} + Fe^{2+} + H \quad (7)$$

3.1.5. Improvement of biodegradability of pharmaceutical wastewater by solar photo-Fenton

As the pharmaceutical wastewater is non-biodegradable in nature, the feasibility of enhancement of biodegradability of wastewater was carried out by solar photo-Fenton process. The biodegradability of the pharmaceutical wastewater was evaluated with BOD_3/COD ratio. The results of the experimental studies are depicted in Fig. 5. The BOD_3/COD ratio is 0.015 for untreated wastewater but 60 min solar photo-Fenton treatment enhanced the biodegradability values to 0.54. The results indicated that solar photo-Fenton process could break down or rearrange molecular structures of organic matters and convert the non-biodegradable organics to more biodegradable forms. Similar results

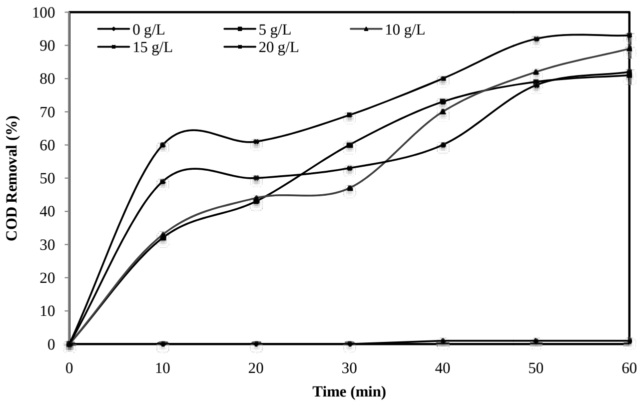

Fig. 3. Effect of H_2O_2 on the removal of COD (pH = 3, Fe^{2+} = 1 g L^{-1}).

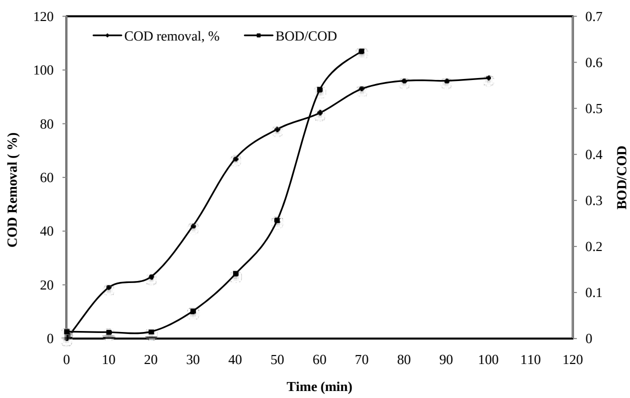

Fig. 4. Effect of irradiation time and biodegradability of pharmaceutical wastewater (pH = 3, Fe^{2+} = 1 g L^{-1}, H_2O_2= 5 g L^{-1}).

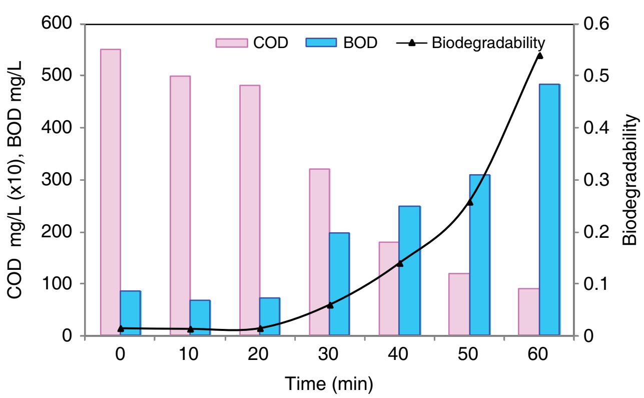

Fig. 5. Biodegradability of solar photo-Fenton treated pharmaceutical wastewater (pH = 3, Fe^{2+} = 1 g L^{-1}, H_2O_2 = 5 g L^{-1}).

were observed in degradation of phenolic compounds of 400 mg/L [25]. It was reported that, BOD_3/COD ratio increased from 0 to 0.4 after 4 h of photo-catalytic reaction. And also observed in the oxidation of hospital wastewater. It was evaluated that BOD_5/COD ratio increased from 0.3 to 0.52 after the photo-Fenton treatment [23]. Thus this process could transform organic recalcitrant compounds into easily biodegradable products, improving the efficiency and reducing the cost of further biological steps.

3.2. Coupled solar photo-Fenton and aerobic sequencing batch reactor

The biological treatment process was studied to determine the treatability of photo-Fenton treated pharmaceutical wastewater in comparison with raw wastewater and to determine the improvement in bio-kinetics. Raw and pre-treated wastewater effluent was allowed to a biological degradation process using aerobic SBR in a batch experiment. Initially, the raw pharmaceutical wastewater was treated in aerobic SBR. Fig. 6 shows that 95% of COD has been removed after 120 h of biological treatment and it shows that the pharmaceutical wastewater possessed low biodegradable organics.

On the other hand, the photo-Fenton treated wastewater under the optimized conditions (pH = 3, Fe^{2+} = 1 g L^{-1}, H_2O_2 = 5 g $L^{-1}$and irradiation time 60 min) was submitted to aerobic SBR. The biodegradability of wastewater increased to 0.54. The result which is depicted in Fig. 7 shows that the photo-Fenton treated wastewater attains 95 % of COD removal at the end of 5 h treatment period. And the improvement in the first-order rate constant (k) value from 0.02 h^{-1} to 0.63 h^{-1} in biological treatment was also observed. The results obtained are clearly shown that photo-Fenton process can be the effective pretreatment process to enhance the biodegradability of the pharmaceutical wastewater. Similar results have been reported for the treatment of antibiotic wastewater [4] and hospital wastewater [23].

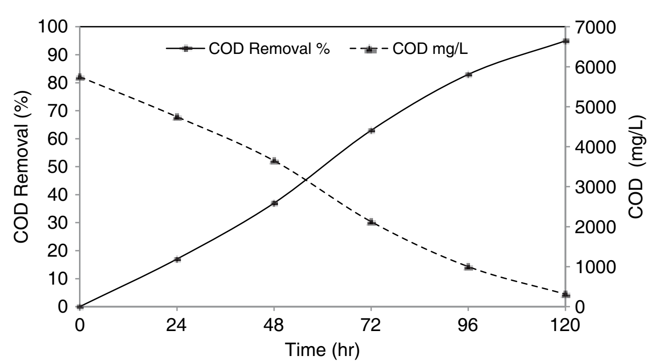

Fig. 6. Performance of SBR without pretreated pharmaceutical wastewater.

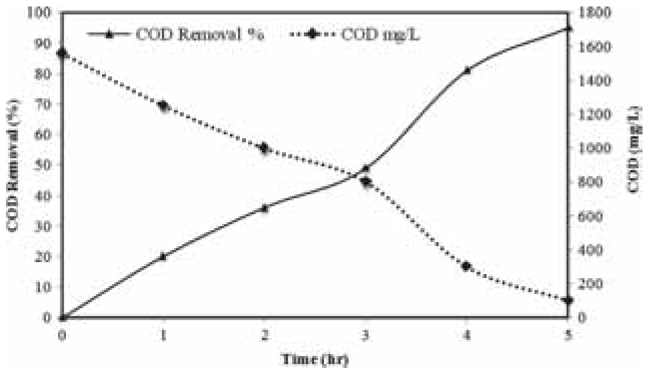

Fig.7. Performance of SBR with solar photo-Fenton treated pharmaceutical wastewater.

Table 2
Performance of coupled solar photo-Fenton – SBR process for degradation of pharmaceutical wastewater

Parameter	Solar photo-Fenton process	SBR process	Coupled processes
Volume of wastewater (L)	7	7	7
Treatment time (h)	2	120	6
Influent COD concentration (mg L^{-1})	5750	5750	5750
Effluent COD concentration (mg L^{-1})	1560	310	100
COD removal efficiency (%)	73	95	98

4. Conclusion

In this study, the pharmaceutical wastewater treated by coupled solar photo-Fenton process and aerobic SBR. Based on the above-mentioned results, the following conclusion has been drawn.

- Solar photo-Fenton process is an effective pretreatment for the removal of high COD from pharmaceutical wastewater. It utilized maximum amount of sunlight hence it is more suitable for tropical country like India.
- Pharmaceutical wastewater contains several organic substances which are highly resist biodegradation and hence direct biological treatment is difficult. In this study, solar photo-Fenton process enhances biodegradability and a significant enhancement of biodegradability was found at the optimum conditions of pH = 3, H_2O_2 = 5 g L^{-1}, Fe^{2+} = 1 g L^{-1} and irradiation time 60 min. At this condition BOD_3/COD ratio increased from 0.015 to 0.54.
- In biological process, the solar photo-Fenton pretreated wastewater attains 95% of COD removal at the end of 5 h treatment period. And the improvement in the first-order rate constant (k) value from 0.02 h^{-1} to 0.63 h^{-1} in biological treatment was also observed.The overall COD removal efficiency of 98% was obtained in the coupled solar photo-Fenton and aerobic SBR process.
- The coupled solar photo-Fenton and aerobic SBR represents a suitable solution for the treatment of pharmaceutical wastewater with an efficient remediation of major characteristics (BOD, COD) of the wastewater.

References

[1] Mukesh Doble and Anil kumar, Biotreatment of Industrial Effluents, Elsiever, 2005, 1st ed., pp. 217–224.
[2] N.E. Alder, J. Koschorreck and B. Rechenberg , Environmental impact assessment and control of pharmaceuticals: the role of environmental agencies. J. Water Sci. Technol., 57 (1) (2008) 91–97.
[3] EPA Office of Compliance, Profile of the Pharmaceutical Industry, 1997, pp. 48–50.
[4] M. Saleem, Pharmaceutical wastewater treatment: a physicochemical study. J. Res. (Sci.), 18 (2) (2007) 125–134.
[5] E. Emad and C. Malay, Improvement of biodegradability of synthetic amoxicillin wastewater by photo Fenton process. J. World Appl. Sci., 5 (2009) 53–58.
[6] T. Okuda, Y. Kobayashi, R. Nagao, N. Yamashita, H. Tanaka, S. Tanaka, S. Fuiji, C. Konishi and I. Houwa, Removal efficiency of 66 pharmaceuticals during wastewater process in Japan. J. Water Sci. Technol., 57 (1) (2008) 65–97.
[7] J.C. Keun, G.K. Sang and H.K. Seung, Removal of antibiotics by coagulation and granular activated carbon filtration. J. Hazard. Mater., 151 (1) (2008) 38–43.
[8] W. Michael, Urs von Stockar and I.W. Marison, Removal of pharmaceuticals from water: using liquid-core microcapsules as a novel approach. J. Water Res., 44 (2010) 2314–2324.
[9] X. Wen, H. Ding, X. huang andR. Liu, Treatment of hospital wastewater using a submerged membrane bioreactor. Process Biochem. 39 (2004) 1427–1431.
[10] A.P. Vanerkar, S. Shanta and Dharmadhikari, Herbal pharmaceutical wastewater treatment by conventional coagulants and synthetic polyelectrolytes, J. Poll. Res., 24 (2) (2005) 341–346.
[11] B. Kasapgil Ince, A. Selcuk and O. Ince, Effect fof a chemical synthesis-based pharmaceutical wastewater on performance, acetoclastic methanogenic activity and microbial population in an upflow anaerobic filter. J. Chem. Technol. Biotechnol., 77 (2002) 711–719.
[12] M.E. Anne, Sharon McHugh, C. Gavin and O.F. Vincent , Low-temperature anaerobic biological treatment of solvent containing pharmaceutical wastewater. J. Water Res. 39 (19) (2005) 4587–4596.
[13] S.M. Nora San, F.F. Joseph, S. Xavier Font and S.F. Antoni, Preoxidation of an extremely polluted industrial wastewater by the Fenton's reagent. J. Hazard. Mater., (2003) 315–322.
[14] Ping Zhou, Chengyi Su, Binwei Li and Yi qian, Treatment of high-strength pharmaceutical wastewater and removal of antibiotics in anaerobic and aerobic biological treatment processes. J. Environmental Engineering, ASCE, 2006.
[15] S. Delia Terese and D. Pinar, Treatability of sulfamerazine in sequential upflow anaerobic sludge blanket reactor (UASB)/ completely stirred tank reactor (CSTR) Processes. J. Separ. Pur. Technol., 56(1) (2007) 108–117.
[16] H.H.W. Lee, G. Chen and P.L. Yue, Integration of chemical and biological treatments for textile industry wastewater: a pos-

sible zero-discharge system. Water Sci. Technol., 44 (5) (2001) 75–83.

[17] S. Emad, Elmolla and Malay Chaudhuri, Effect of photo-Fenton operating conditions on the performance of Photo-Fenton–SBR process for recalcitrant wastewater treatment. J. Appl. Sci. 10 (24) (2010) 3236–3242.

[18] M. Mohajerani, M. Mehrvar and F. Ein-Mozaffare, An overview of the integration of advanced oxidation technologies and other processes for water and wastewater treatment. Int. J. Eng., 3 (2) (2001) 120–146.

[19] Metcalf & Eddy, Inc., George Tchobanoglous., in: L.B. Franklin and H. David Stensel (Eds.), Wastewater Engineering, Treatment and Reuse, Tata McGraw Hill, 2003, 4th ed.

[20] C. Marta, O. Francisco, M.L. Juan, L. Maria, G.J. Carmen, R. Isaac, G. Mariano and T. Thomas, Behaviour of pharmaceuticals, cosmetics and hormones in a sewage treatment plant. J. Water Res., 38 (2004) 2918–2926.

[21] Huaili Zheng, Yunxia Pan and Xinyi Xiang, Oxidation of acidic dye Eosin Y by the solar photo-Fenton processes. J. Hazard. Mater.,141 (3) (2007) 458–464.

[22] APHA-AWWA-WEF, Standard Methods for the Examination of Water and Wastewater. American Public Health Association, Washington, D.C. Applications, McGraw-Hill, 2005.

[23] K. Puangrat and S. Nattapol, Evaluation of biodegradability and oxidation degree of hospital wastewater using photo-Fenton process as the pretreatment method. J. Hazard. Mater., 138 (2) (2006) 384–391.

[24] H. Tekin, I. Gulkaya, O. Bilkay, S. Ataberk, H. Balta Tolga, I.H. Ceribasin and U. Yetis, Treatment of pharmaceutical wastewaters by Fenton's oxidation by activated sludge: A case study. J. Water Environ., 20 (2002) 290–309.

[25] S. Adishkumar and S. Kanmani, Treatment of phenolic wastewaters in single baffle reactor by Solar/TiO_2/H_2O_2 process. J. Desalination and Water Treatment, 24 (2010) 67–73.