SOLAR PHOTO FENTON PROCESS WITH AEROBIC SEQUENTIAL BATCH REACTOR FOR TREATMENT OF PHARMACEUTICAL WASTEWATER

Karthik M
PG Scholar, Department of Civil Engineering
Pandian Saraswathi Yadav Engineering College, Sivagangai, Tamil Nadu

M. Appu Sriram
Assistant Professor Department of Civil Engineering
Pandian Saraswathi Yadav Engineering College, Sivagangai, Tamil Nadu

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, Fe2+ = 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*

Introduction

Pharmaceutical Wastewater

Pharmaceutical manufactures use water for process operations, as well as for other non-process purposes. However, the use, discharge practices, the characteristics of the wastewater and treatment techniques (Saleem et al., 2007) will vary depending on the operations conducted at the facility. Process water includes any water that, during manufacturing or processing, comes into direct contact with or results from the use of any raw material or production of an intermediate, finished product, by-product or waste. Process wastewater includes water that was used or formed during the reaction, water used to clean process equipment and floors, and pump seal water. Non-process wastewater includes noncontact cooling water (E.g., used in heat exchangers), non-ancillary water (e.g., boiler blow down, bottle washing), Sanitary wastewater, and wastewater from other sources (e.g., storm water runoff) (Hasmi, 2005)

Environmental Impacts of Pharmaceutical Wastewater

Table 1 Pharmaceutical Wastewater Discharge Standards

Parameters	Permissible Limits
PH	5 – 9
Temperature	40 °C
BOD$_5$ (mg/L)	30
COD (mg/L)	250
TSS	35
Sulphide	0.002
Reactive phosphorus	1.0

Aerobic Sequential Batch Reactor

SBRs are a variation of the activated – sludge process. They differ from activated-sludge plants because they combine all of the treatment steps and processes into a single basin, or tank, whereas conventional facilities rely on multiple basins. EPA reported, an SBR is no more than an activated-

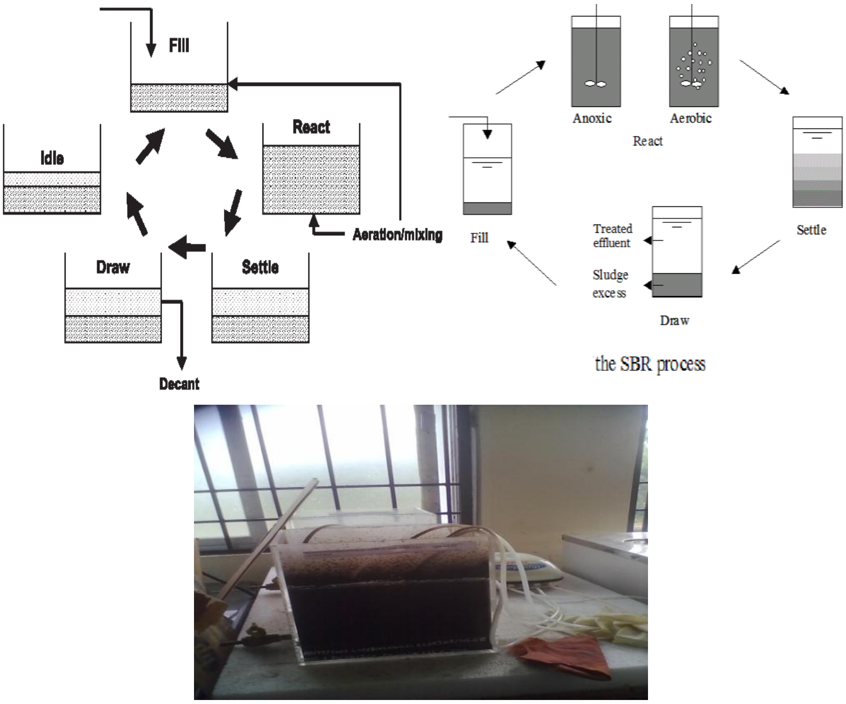

Figure 1 Fabrication of a Sequential Batch Reactor

Characteristic of Different Pharmaceutical Wastewater

Table 1 Characteristic of Different Pharmaceutical Wastewater

Wastewater	Characteristics
Chemical synthesis-based pharmaceutical wastewater	pH:7-8 COD:39000-60000 mg / L TSS:800-1000 mg / L VSS:500-1240 mg / L
Herbal –based pharmaceutical wastewater	pH:4.2-4.5 COD:5000-80000 mg / L TS:4300-74000 mg / L SS:900-18800 mg / L VSS:580-1240 mg / L
pharmaceutical wastewater	pH:7.2 COD:34400 mg / L TS:29150 mg / L TSS:6250 mg / L color:Dark brown

Materials and Methods

Glassware Cleaning

Glassware such as beakers, conical flasks, pipettes, burettes etc. used for experiments were first cleaned with detergent and then soaked in chromic acid cleaning mixture. They were thoroughly rinsed several times in tap water and then in distilled water.

Chemicals

The chemicals used for the present study were of analytical grade.

Wastewater

Pharmaceutical wastewater which has the COD ranges of 4000 -5000 mg/L.

Seed Materials

Inoculums will be collected from an activated sludge process plant located at Bio plus Bangalore.

Characterization of Wastewater

The wastewater samples are analyses for the following parameters as per the Standard Methods, APHA (2005): pH, Chemical oxygen demand, Total solids, Volatile solids, Volatile fatty acids, Alkalinity.

PH

The pH of the wastewater is determined using a pH meter.

Chemical Oxygen Demand (COD)

10 mL of sample will take in a 500 mL refluxing flask and a pinch of mercuric sulphate will added to it. 5-6 glass beads were also added to it and mixed well. Then 15mL sulphuric acid reagent will be added to it and mixed well and allow cooling. Then 7mL potassium dichromate solution is added to it and mixed well. The mixture is then refluxed for two hours and allows cooling and diluted to twice its volume with distilled water and titrates against 0.25M ferrous ammonium sulphate using ferro in indicator. Appearance of brown colour indicates the end point.

Soluble Chemical Oxygen Demand (SCOD)

The sample is centrifuged at 17500 rpm for 9 min. Then 10mL of centrifuged sample is taken in a 500 ml refluxing flask and a pinch of mercuric sulphate is added to it. 5-6 glass beads were also added to it and mixed well. Then 15mL sulphuric acid reagent is added to it and mixed well and allowed to cool. Then 7mL potassium dichromate solution is added to it and mixed well. The mixture is then refluxed for two hours and allowed to cool and diluted to twice its volume with distilled water and titrated against 0.25M ferrous ammonium sulphate using ferro in indicator. Appearance of brown colour is recognized as the end point.

Total Solids (TS)

20 ml of sample is taken in a pre-weighed evaporating dish and is kept in water bath at 105^0c for 1hr. The dried sample weight is then measured.

Mixed Liquid Suspended Solids (MLSS)

20 mL of sample is filtered in a preweighed filter paper and is kept in oven at 105^0c for 1hr.The dried sample weight is then measured.

Volatile Solids (VS)

A known amount of oven dried wastewater sample is taken in a crucible and burnt in a muffle furnace at 550^0c for 1 hr. After cooling, the weight of the unburned contents is noted.

Alkalinity

A known volume of the sample is titrated against 0.2 N $H_2 SO_4$ using methyl orange as indicator. Appearance of reddish orange colour is taken as end point.

Results and Discussion

Table 2 Characteristics of Pharmaceutical Wastewater

Parameters	Values
pH	7.14
TS (mg/L)	4593
TDS (mg/L)	4240
TSS (mg/L)	418
BOD (mg/L)	85
COD (mg/L)	5500
BOD/COD	0.015

Table 3 Effect of PH on the Removal of COD of Pharmaceutical Wastewater

Time (min)	COD Removal %			
	pH 2	pH 3	pH 4	pH 7
0	0	0	0	0
10	40	7	9	2
20	48	49	15	13
30	55	72	21	13
40	57	95	51	15
50	60	95	73	19
60	61	96	79	21

Effect of Ferrous Dosage

Table 4 Effect of Fe^{2+} Dosage on the Removal of COD of Pharmaceutical Wastewater

Time (min)	COD Removal %				
	Fe^{2+} dosages				
	0 g/L	0.5 g/L	1 g/L	2 g/L	3 g/L
0	0	0	0	0	0
10	17	32	64	58	44
20	33	39	78	59	47
30	40	40	79	63	56
40	48	43	84	73	59
50	53	67	87	76	65
60	57	67	91	79	67

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 operatring cost. The copncentration of H2O H_2O_2 has been varied from 5g/lit to 20 g/lit to study its effect on the COD removal of pharmaceutical wastewater. Fig 4.3 shows the COD removal increased from 81% to 93% with the addition of H_2O_2 from 5 g/lit to 15 g/lit, which resulted from more H_2O_2 radicals produced with the addition of more H_2O_2. However, as H_2O_2 was exceeded 15 g/lit, the COD removal decreased. The reaction rate can be inhibited with an excess of H_2O_2 in this system (Moon et al. 1991). This was probably due to both auto-decomposition of H_2O_2 into oxygen and water (Eq 4), and the recombination of OH. Radical (Eq 5) as follows.

$$2\ H_2O_2 \rightarrow 2H_2O + O_2 \qquad [4]$$

$$H_2O_2 + OH^{\cdot} \rightarrow H_2O + {}^{\cdot}O_2H \qquad [5]$$

The results were agreed with the other studies such as Trizha et al . (2003), Nilesh et al (2006), Fing et al (2003) and Gonzalez et al (2008). For the oxidation of tannery waste water, degradation of azo dyes, discolorization and mineralizarion of reactive dyes and remediation of sulphamethoxoazole respectively. The present study revealed that there was no much variation in Cod removal oercentage with the addition of 5g/lit and 15 g/lit. concentration of H_2O_2 should be three times increased to achieve 93% COD removal from 81%. By considering the operation cost, 5 g/lit of H_2O_2 has been chosen as optimus concentration eventhough 93% of COD removal achieved with 15 g/lit of H_2O_2. The efect of H_2O_2 dosage on COD removal was depicted in table 5

Table 5 Effect of H_2O_2 Dosage on the Removal of COD of Pharmaceutical Wastewater

Time (min)	COD Removal %				
	H_2O_2 dosages				
	0 g/L	5 g/L	10 g/L	15 g/L	20g/L
0	0	0	0	0	0
10	0	32	33	60	49
20	0	43	44	61	50
30	1	60	47	69	53
40	1	73	70	80	60
50	1	79	82	92	78
60	1	81	89	93	82

Effect of Irradiation Time and Bio Degradability

Table 6 Effect of Irradiation Time and Biodegradability of Pharmaceutical Wastewater

Time (min)	COD Removal %	BOD/COD
0	0	0.015
10	19	0.0138
20	23	0.015
30	42	0.06
40	67	0.14

50	78	0.258
60	84	0.54
70	93	0.625
80	96	
90	96	
100	97	

Table 7 Improvement of Biodegradability by Solar phoTo Fenton Process

Time (min)	COD (mg/L)	BOD (mg/L)	BOD/COD
0	5500	85	0.015
10	5000	69	0.0138
20	4810	72	0.015
30	3200	198	0.06
40	1800	250	0.14
50	1200	310	0.258
60	900	485	0.54

Kinetic Studies

The kinetics has been determined with the COD removal from the pharmaceutical wastewater. The reaction rate constant for pharmaceutical wastewater are shown in table 4.7.

Table 8 Reaction Rate Constant k (min^{-1}) for Pharmaceutical Wastewater

Fenton reactions	K (min^{-1})	R^2
Dark (H_2O_2/**Fe2+)**	0.013	0.989
Solar/ H_2O_2	0.012	0.828
Solar/ H_2O_2/**Fe2+**	0.026	0.974

Aerobic Sequence Batch Reactor

The solar photo-Fenton treated and untreated pharmaceutical wastewater was subjected to treat in the biological reactor. Its results are discussed below.

Table 8 Performance of SBR without Pre-Treated Pharmaceutical Wastewater

Time (hr)	COD Removal %	COD(mg/L)
0	0	5750
24	17	4750
48	37	3650
72	63	2125
96	83	1000
120	95	310

Table 9 Performance of SBR with Pre-Treated Pharmaceutical Wastewater

Time (hr)	COD Removal %	COD(mg/L)
0	0	1560
1	20	1250
2	36	1000
3	49	800
4	81	300
5	95	100

Bio Kinetic Studies

The bio kinetics has been determined with the COD removal by Arabic SBR from the pharmaceutical wastewater. The reaction rate constant for pharmaceutical wastewater are shown in table 10

Table 10 Reaction Rate Constant k (hr^{-1}) for Pharmaceutical Wastewater

Aerobic treatment	k(hr^{-1})	R^2
Treatment of untreated wastewater	0.02	0.77
Treatment of pre-treated wastewater	0.626	0.94

The rate of reaction of pre-treated wastewater is several times higher than the untreated wastewater. It indicates that the solar photo Fenton process converts most of the non-biodegradable organics into simpler compounds and hence the rate of the reaction has been increased several times than raw wastewater.

Performance of Solar Photo-Fenton. Aqerobic SBR and Coupled Process

The overall performance of the present study is summarized in the table 10. It clearly exhibits that coupled solar photo- Fenton and aerobic SBR yields maximum efficiency within a short period of time. The time taken for direct biological treatment of untreated pharmaceutical wastewater was a time consuming process. It took 5 days to attain 95% COD removal whereas 95% COD was reduced within 5 hours of treatment of pre-treated wastewater. Therefore, when coupling the solar photo-Fenton process with aerobic SBR reduces the treatment period and also reduces the cost.

Table 11 Performance of Solar Photo-Fenton, Aerobic SBR and Coupled Process

Parameters	Time	Cod Removal,%
Solar photo Fenton	60 min	84
Aerobic SBR (without pre-treatment)	5 days	95
Aerobic SBR (with pre-treatment)	5 hours	95
Overall	6 hours	98

Conclusion

Better waste management will lead to other environmental benefits such as reduction of surface water and ground water contamination and transformation of organic waste into high quality manure. Since treating effluent a pharmaceutical plant that manufactures drugs and antibiotics is relatively easy, the treatment procedure could be adopted by the pharmaceutical industries as interim measure in cubing their pollution problem in most developing countries. In this study, the pharmaceutical wastewater was treated by aerobic SBR. The hydraulic retention time of 5 h was assessed in the aerobic SBR and 95% COD removal was obtained. The Aerobic SBR in this study 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, Bio treatment of Industrial Effluents, Elsevier, 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. 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. huangandR. 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.