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Intensified degradation of pharmaceutical effluents by novel aerobic iron-swarf activated molecular oxygen in the presence of ascorbic acid

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ABSTRACT

An intensified degradation of antibiotics-based pharmaceutical effluent using novel green and clean technology-based process was proposed, in which molecular oxygen was activated by iron swarf in the presence of non-toxic ascorbic acid. In this process, molecular oxygen present in air has been used as oxidant in the place of conventional hydrogen peroxide and an ecofriendly ascorbic acid has been used as reductant to reduce less reactive Fe(III) to desired Fe(II). The degradation was performed in air-lift reactor and purpose of air-lift reactor not only facilitates better mass transfer but also supplies the oxidant for reaction. Three different effluents (having different properties) were collected and named SAM1, SAM2 and SAM3. The various parameters that influencing degradation were studied and the optimal values of reaction time (180 min), dosage of ascorbic acid (600, 500 and 400 mg/L for SAM1, SAM2 and SAM3, respectively), reaction temperature (35°C) and optimal pattern of iron addition (multiple additions) were determined. Under this optimal condition, the proposed treatment produced more promising results (COD reduction of 92.1%, 81.2% and 71.4%, respectively) and the degradation follows second-order kinetics. The ecotoxicity study showed that, the treated effluents were less toxic than the parent pollutant. Thus, this work clearly shows that, the proposed methodology is not only cost-effective but also a green and clean technology, without compromising the rate of degradation.

Keywords: Pharmaceutical effluent; Molecular oxygen; Air-lift reactor; Iron-swarf; Ascorbic acid

1. Introduction

India enjoys a major position in the global pharmaceuticals sector with expected annual growth rate over 15% (years 2015–2020). Currently, more than 80% of antiretroviral drugs consumed across the world to combat acquired immunodeficiency syndrome are supplied by Indian pharmaceutical industries.

The wastewaters produced from pharmaceutical industries contain mainly organic-based pollutants that are often difficult to degrade using conventional wastewater treatment methodologies. This type of effluent is characterized by high chemical oxygen demand (COD) due to the

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presence of biorefractory recalcitrant organic pollutants. The degradation of pharmaceutical effluent is a major challenge for these industries due to lack of homogeneity as well as similar treatment methodologies that cannot be implemented in all cases. Usually, the COD value in these effluents ranges from 1,000 to 10,000 mg/L [1] and in some cases, this value goes beyond high.

Numerous treatment methodologies, such as adsorption, flocculation, precipitation, etc., were employed to treat effluents discharged from pharmaceutical formulation units. These widely used techniques were merely transferred the pollutant from effluent to sludge and subsequent sludge treatment is cumbersome one. The efficacy of membrane distillation was elaborately studied by Baskaran and co-workers [2–4]. Even though membrane distillation was found to be more effective on wastewater treatment, cost involved in procurement of membrane and difficult handling made it less lucrative. Treatment of pharmaceutical effluent is always troublesome due to its complex nature [5,6]. Cost-effective biological methods can be used to degrade these effluents, but the presence of antibiotics and other ingredients resist microbial growth. Thus, biodegradation becomes less effective [7]. In recent decades, effective use of ultrasound irradiation, photocatalysis, microwave, magnetic induction, etc., is tremendously increasing on degrading industrial effluents but these intensified processes are highly restricted to lab-scale operations and implementation in industrial level requires enormous energy thereby huge operating cost would be incurred.

Fenton's process has been widely used by research community for several decades due to its simplicity, cost-effective and oxidizing capability on wide range of substances [8]. During this process, highly reactive radicals (predominantly hydroxyl radicals) were produced and degrade the organic pollutants rapidly. But it has two major disadvantages such as highly acidic condition is required for conducting this process and secondly, sludge generation increases the pollutant load to the environment. In large-scale industrial applications, these two constraints are highly unacceptable as bringing enormous quantity of effluent to highly acidic condition is unbearable.

In recent years, attention of researchers was focused on aerobic ferrous ion process in which highly reactive oxygen species (ROS) produced from molecular oxygen [9–11]. Usually, in Fenton's process ferrous ions were reacted with hydrogen peroxide to produce hydroxyl radicals whereas here, in this process, molecular oxygen from atmospheric air was employed in the place of hydrogen peroxide to produce ROS that includes hydroxyl radicals. Use of molecular oxygen activated by iron instead of Fenton's process does not require highly acidic conditions as well as precipitation of Fe(III) as iron oxide is minimized significantly.

The kinetics of reduction of Fe(III) to Fe(II) using L-ascorbic acid (L-AA) was studied by Hsieh and Hsieh [12] in food products and digestive tracts. They reported that, the reduction follows zero-order kinetics with respect to ascorbic acid. Hou et al. [13] demonstrated the potential of ascorbic acid enhanced activation of molecular oxygen on the degradation of rhodamine B explicitly and the intermediates produced as well as possible pathways were analyzed.

In recent years, much focus has been paid toward alternatives for conventional continuous stirred tank reactors (CSTR) in processing low value materials such as wastewaters, etc., in order to minimize the capital as well as operational cost. The pneumatically agitated reactors such as air-lift reactors and bubble column reactors are nowadays employed not only for biological processes but also for abiotic systems wherever contact between liquid and gas are important. Better mixing is happened in both the reactors through the energy generated by gas expansion or up-flowing air bubble buoyancy [14].

Air-lift reactors use draft tube for the betterment of mass transfer through good circulation of fluids whereas the bubble column reactors uses a simple tower. The advantages of using air-lift reactors include: (1) simple design and thus ease in fabrication, (2) better mass and heat transfer, (3) minimal initial and operating cost, as there is no friction due to the absence of any moving part inside the reactor and (4) uniform distribution of shear, not like CSTR in which maximum shear is seen near the shaft and minimal on the wall side.

In this work, real effluent discharged from an industry producing antibiotics of wide range was chosen as target pollutant. An innovative and green technology-based treatment process using molecular oxygen activated by iron swarf in the presence of ascorbic acid was proposed for the degradation of pharmaceutical effluent. The influence of some of the important operating variables was studied and in addition, ecotoxicity of effluent before and after degradation was analyzed.

2. Materials and methods

2.1. Materials

The target pollutant (antibiotic-based pharmaceutical effluent) was obtained from a pharmaceutical formulation unit situated at northern part of Tamil Nadu, India. The effluents were collected simultaneously from three different discharge points (from three plants producing different pharmaceuticals) in the same industry and named as SAM1, SAM2 and SAM3. In each case, effluents were collected thrice at different times (time interval of 8 h) and mixed thoroughly to get homogeneity. The physicochemical properties of all three effluents collected are listed in Table 1. The table illustrates the quantum of hazardousness present in these effluents due to high COD and less biological oxygen demand (BOD_5). The biodegradability index can be determined using Eq. (1) [15]:

Table 1
Physicochemical properties of pharmaceutical effluents

Properties	Values		
	SAM1	SAM2	SAM3
Chemical oxygen demand, mg/L	10,167	8,000	6,667
Biological oxygen demand, mg/L	2,460	2,110	1,990
Biodegradability index	0.242	0.264	0.298
pH	4.1	3.9	4.2
Density, kg/m^3	970	961	949
Total dissolved solids, mg/L	1,080	995	940

$$\text{Biodegradability index} = \frac{\text{BOD}_5}{\text{COD}} \tag{1}$$

Here, the index in all cases was found to be less than 0.3 that indicates the poor biodegradability. These effluents were collected in aseptic and black colored containers, tightly closed and kept in refrigeration unit (4°C) until further use, to prevent aerobic/anaerobic/anoxic degradation as well as photodegradation.

All the chemicals and reagents employed during this study were obtained from Chemspure, India, and are of analytical grade. These chemicals and reagents were used without any pretreatments. The iron swarf was collected from a small-scale industry and it is nothing but the debris generated during operations such as cutting, milling. The collected iron swarf was thoroughly washed with water, dried and sieved. The particle less than the size of 63 μm (230 mesh) was used. The pretreatment of iron swarf was described in previous literature [6].

2.2. Experimental

The degradation experiments were performed in lab-scale and batch mode. All these experiments were conducted in air-lift reactor in which the air has been sparged from the bottom of the reactor, sent through air distributor and lift the liquid up through air-riser section. A draft tube has been kept inside the reactor so that, the difference in gas holdup prevailed inside and outside the draft tube makes the liquid to flow up (in air-riser section) and down (through downcomer). This process totally depends on the presence of oxygen and use of air-lift reactor facilitates the supply of adequate oxygen through air.

The predetermined quantity of effluent was loaded in the reactor and the reaction time starts when the reactants (ascorbic acid and iron swarf) of predetermined amount were added along with the air supply. The temperature of the reactor is maintained constant at predetermined values using heating/cooling coil. The samples at regular time interval (usually 30 min) were taken from the reactor and centrifuged at 6,000 rpm. The supernatant has been considered for degradation analysis. The COD was analyzed using open reflux method [16] and BOD_5 was estimated by following the outlines framed by APHA [16]. In this work, the effluent degradation was investigated through %COD reduction and it can be estimated by Eq. (2) [15].

$$\%\text{COD reduction} = \left(\frac{C_0 - C}{C_0}\right) \times 100 \tag{2}$$

where C_0 denotes initial COD (mg/L) of the effluent and C denotes residual COD of the effluent at any time, t. The deionized water was used wherever required.

The parameters influencing the degradation such as reaction time, initial pollutant concentration, dosage of ascorbic acid, temperature and pattern of iron addition were studied through COD analyses. The effect of initial pollutant concentration was studied using degradation of SAM1, SAM2 and SAM3 as these effluents are having wide range of initial COD. The effect of ascorbic acid was studied by changing the dosage of ascorbic acid at 300, 400, 500 and 600 mg/L. The optimal dosage was chosen on the basis of maximum degradation and that dosage has been maintained in subsequent studies. The influence of temperature on %COD abatement was studied at 25°C, 35°C and 45°C. The optimal temperature at which maximum COD abatement achieved was determined for each effluent and that temperature were maintained in subsequent studies.

The ecotoxicity test was conducted to study the quantum of effluent toxicity and it has been performed before and after the degradation (at optimal conditions). The study was performed using disc diffusion method in which *E. coli* (MTCC443) was used as test organism and the diameter of inhibition has been estimated by ruler. The detailed study of this analysis has been elaborated in our previous study [17]. All the experiments were performed thrice and the mean values were considered in this work.

3. Results and discussions

3.1. Degradation of effluents

The degradation of three different pharmaceutical effluents was performed in air-lift reactor and the results are shown in Fig. 1. It clearly demonstrates that, reaction time influenced the degradation in significant manner and with increase in reaction time, the %COD reduction was increased in all three cases, but in different proportions. The effluent SAM1 produced maximum COD reduction of about 63.94% and other effluents SAM2 and SAM3 produced 54.17% and 35.0%, respectively. The degradation of these effluents was found to follow second-order kinetics and the rate constant for these effluents are 1×10^{-6} L/(mg min) ($R^2 = 0.951$), 0.9×10^{-6} L/(mg min) ($R^2 = 0.971$) and 0.5×10^{-6} L/(mg min) ($R^2 = 0.954$), respectively.

During this reaction time, the organic pollutants were degraded through the following reactions [6,13,18,19]:

$$\text{Fe}_{(\text{iron-swarf surface})} + 2\text{H}^+ \rightarrow \text{Fe}^{2+} \quad \text{(under acidic conditions)} \tag{3}$$

$$\text{Fe}^{2+} + \text{O}_2 \rightarrow \text{Fe}^{3+} + \text{O}_2^{\circ-} \tag{4}$$

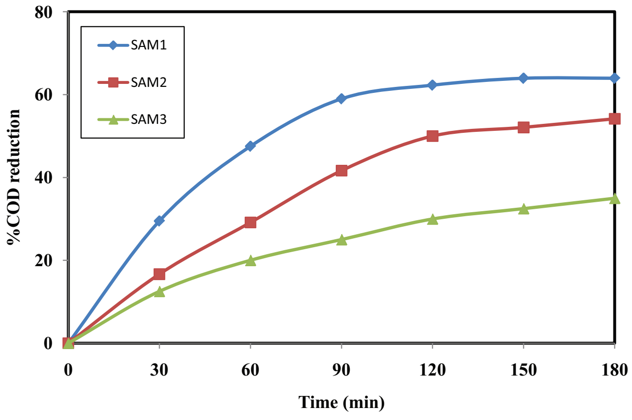

Fig. 1. Influence of reaction time and initial pollutant concentration on %COD reduction (Condition: dosage of ascorbic acid, 400 mg/L; iron swarf, 4 g/L; temperature, 25°C).

$$2\mathrm{O}_2^{\circ-} + 2\mathrm{H}^+ + \mathrm{H}_2\mathrm{O} \rightarrow \mathrm{H}_2\mathrm{O}_2 + \mathrm{O}_2 \tag{5}$$

$$\mathrm{Fe}_{(\text{iron-swarf surface})} + \mathrm{H}_2\mathrm{O}_2 \rightarrow \mathrm{Fe}^{2+} + 2\mathrm{OH}^- \tag{6}$$

$$\mathrm{Fe}^{2+} + \mathrm{H}_2\mathrm{O}_2 \rightarrow \mathrm{Fe}^{3+} + {}^{\circ}\mathrm{OH} + \mathrm{OH}^- \tag{7}$$

$$\mathrm{Fe}^{3+} + \mathrm{O}_2^{\circ-} \rightarrow \mathrm{Fe}^{2+} + \mathrm{O}_2 \tag{8}$$

$$\mathrm{Fe}^{2+} + \text{L-AA} \rightarrow \mathrm{Fe}^{2+}.\text{L-AA} \tag{9}$$

$$\mathrm{Fe}^{2+}.\text{L-AA} + \mathrm{O}_2 \rightarrow \mathrm{Fe}^{3+}.\text{L-AA} + {}^{\circ}\mathrm{O}_2^- \tag{10}$$

$$\mathrm{Fe}^{2+} + {}^{\circ}\mathrm{O}_2^- + 2\mathrm{H}^+ \rightarrow \mathrm{H}_2\mathrm{O}_2 + \mathrm{Fe}^{3+} \tag{11}$$

$$\mathrm{Fe}^{2+}.\text{L-AA} + {}^{\circ}\mathrm{O}_2^- + 2\mathrm{H}^+ \rightarrow \mathrm{H}_2\mathrm{O}_2 + \mathrm{Fe}^{3+}.\text{L-AA} \tag{12}$$

$$\mathrm{Fe}^{2+}.\text{L-AA} + \mathrm{H}_2\mathrm{O}_2 \rightarrow \mathrm{Fe}^{3+}.\text{L-AA} + {}^{\circ}\mathrm{OH} + \mathrm{OH}^- \tag{13}$$

$$\mathrm{Fe}^{3+} + \text{L-AA} \rightarrow \mathrm{Fe}^{2+} + (\text{oxidative products of L-AA}) \tag{14}$$

$$\mathrm{Fe}^{3+}.\text{L-AA} + \text{L-AA} \rightarrow \mathrm{Fe}^{2+}.\text{L-AA} + (\text{oxidative products of L-AA}) \tag{15}$$

$$\mathrm{Fe}^{3+} + \text{L-AA} \rightarrow \mathrm{Fe}^{3+}.\text{L-AA} \tag{16}$$

$$\text{Organic pollutants} + \text{ROS} \rightarrow \mathrm{CO}_2 + \mathrm{H}_2\mathrm{O} \tag{17}$$

The activation of oxygen was made in the iron-rich water during which the cleavage of bond present in O–O occurred. Superoxide anion radicals ($\mathrm{O}_2^{\circ-}$) (Eq. (4)) were produced from diatomic oxygen by transferring one electron from Fe(II). These superoxide anion radicals generated highly reactive hydroxyl radicals (Eqs. (12) and (13)) without adding hydrogen peroxide and further, hydrogen peroxide was produced by superoxide anion radical. The oxidative degradation was made by the produced ROS and which leads to the formation of carbon dioxide and water (Eq. (17)). This hydroxyl radical was produced in many of the processes reported earlier, but the main attraction of this process is, non-reactive Fe(III) were reduced by ascorbic acid to produce reactive Fe(II) (Eq. (14)) and subsequently the cyclic process was continued. Several additives were tested to reduce Fe(III) to Fe(II) by researchers in recent years. Belanzoni et al. [20] and Laine et al. [21] employed ethylenediaminetetraacetic acid at neutral pH using air and iron to prevent the precipitation of Fe(III). Chen et al. [22] used hydroxyl amine to accelerate the reduction of Fe(III) while Li et al. [23] employed quinone for accelerating ferric and ferrous iron cycles. The above said addictives are either toxic or basically pollutant, in nature. But, in this study, the food addictive L-ascorbic acid, a non-toxic as well as cost-effective material, was employed.

During degradation, the Haber–Weiss reaction [18] was occurred and hydroxyl radicals were produced using hydrogen peroxide and superoxide (${}^{\circ}\mathrm{O}_2^-$) (Eqs. (5) and (7)). Instead of conventional ferrous sulfate salt, iron swarf was employed as the source of iron, which made the system heterogeneous. Purpose of using heterogeneous system is highly favorable for better degradation due to following reasons: (1) broad pH range of operations is feasible using with heterogeneous system, (2) minimal ferric hydroxide formation due to leaching of active components from the surface to the aqueous medium, (3) loss of iron is much reduced on using heterogeneous system because the iron has been anchored in a porous solid medium, (4) easy to recover the iron particles and thus reuse of it is easy and (5) higher catalytic activity that leads to better reaction kinetics. In heterogeneous system, heat and mass transfer were also occurred along chemical reaction. So, it is required not only to keep the chemical reaction rapid but also provide better heat and mass transfer. Use of air-lift reactor in this work facilitates better mass transfer as well as heat transfer that lead to better degradation.

3.2. *Effect of initial pollutant concentration*

The effect of initial pollutant concentration on %COD abatement can be observed using Fig. 1 in which three different effluent samples (of different initial CODs) were taken into consideration. Highly concentrated effluent (SAM1) produced maximum degradation than other effluents as minimal degradation (35%) was achieved with SAM3. This clearly shows that degradation is rapid at higher concentration and it might be attributed due to several reasons which are as follows: it is well known fact that, the rate of chemical reaction is proportional to reactant concentration as better interaction between the reactants possible. Further, in this work, the oxidative degradation was made mainly through highly reactive ROS and the life span of these radicals is very less. The life span of hydroxyl radical is about few nanoseconds [24] and after which the radicals will be degraded through self-quenching. So, the probability of collisions between the pollutants and hydroxyl radicals are very high in SAM1 due to high pollutant concentration. High probability favors better degradation and in the case of less concentrated effluent (SAM3), the potential of hydroxyl radials was not utilized properly and due to this, these radicals were destroyed without serving its purpose.

The initial degradation rate was studied for the first 30 min and observed that, the initial degradation rate was 0.7×10^{-6} and 0.8×10^{-6} mg/(L min) for SAM3 and SAM2, respectively. The initial degradation rate of SAM1 was found to be higher (1×10^{-6} mg/(L min)) than other two cases. This is because, during initial time, the presence of high strength reactants (here, iron swarf and L-AA) as well as concentrated pollutants maximized the probability of collisions, there by maximum degradation was achieved with SAM1.

On the other hand, at 180 min, no further degradation is possible in SAM1 and no drastic decrement in rate of degradation was seen in other two cases. This is attributed to the fact that, at 180 min, the reactants such as iron swarf as well as L-AA might be exhausted that leads to nullify the degradation in the case of SAM1. This trend was not seen in other two effluents as the rate of degradation was less all times that leads to the presence of reactants even after 180 min, thus the rate of degradation was not decreased significantly, and thus further degradation is possible in SAM2 as well as SAM3.

3.3. *Effect of dosage of ascorbic acid*

The influence of ascorbic acid dosage was studied on the degradation of three samples of effluent and the results are

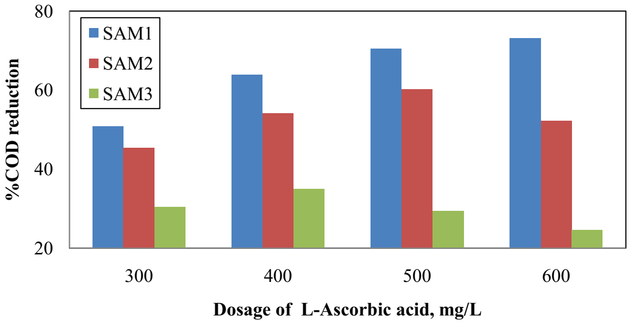

Fig. 2. Influence of dosage of L-ascorbic acid on %COD reduction (Conditions: reaction time, 180 min; iron swarf, 4 g/L; temperature, 25°C).

shown in Fig. 2. Increase in ascorbic acid dosage enhanced the degradation in all the cases, because it acts as a reactant (Eqs. (12)–(16)) on the production of ROS that oxidize the organic pollutants. In SAM1 degradation, a significant increase in %COD reduction (from 50.82 to 70.49) was observed from 300 to 500 mg/L of ascorbic acid and beyond that, a moderate increase in degradation (70.49%–73.2% at 600 mg/L) was found. This trend was not seen in other cases. With respect to SAM2, degradation was found to increase (from 45.4% to 60.2%) with the increase in ascorbic acid dosage from 300 to 500 mg/L. Further increase in ascorbic acid dosage does not fetch any positive result; rather it produced detrimental effect as the %COD abatement was reduced from 60.2 to 52.2. This is because of self-quenching of hydroxyl radicals due to its rapid generation:

$$^{o}OH + {}^{o}OH \rightarrow H_2O_2 \qquad (18)$$

Hence, the optimal dosage of ascorbic acid for the degradation of SAM2 effluent was found to be 500 mg/L. On the other hand, in SAM3 degradation, increase in ascorbic acid dosage from 300 to 400 mg/L increased the degradation from 30.4% to 35.0%. Beyond 400 mg/L, the detrimental effect was prevailed as mentioned above and the %COD reduction was reduced to 29.4 at 500 mg/L and 24.6 at 600 mg/L. The decrease in degradation at higher concentrations of ascorbic acid was due to enhanced coalescence caused because of enormous collisions between bubbles, which lead to generation of large sized bubbles. Generation of large bubbles will reduce the interfacial area [25]. Here, maximum degradation was achieved at 400 mg/L. Thus, it can be concluded that, optimal dosage of ascorbic acid was not same for all cases and it depends mainly on concentration of pollutants. The subsequent experiments were conducted with the optimal dosage of ascorbic acid (600, 500 and 400 mg/L for SAM1, SAM2 and SAM3, respectively).

3.4. Effect of temperature

Increase in temperature enhanced the %COD abatement in all the cases as shown in Fig. 3 and this trend was observed from 25°C to 35°C. The positive effect of temperature was due to several reasons such as: (1) increase in temperature reduces the viscosity and surface tension of the fluid that results in the generation of small but stable bubbles, (2) decrease in viscosity leads to decrease in film thickness of the stagnant film present at liquid–gas interface, thus increase in mass transfer coefficient, (3) increase in temperature might enhance turbulence that leads to better mass as well as heat transfer and (4) enhanced gas holdup at elevated temperatures [26]. Thus, changes in diffusivity, viscosity and interfacial tension due to enhancement of temperature caused positive results. Further increase in temperature (beyond 35°C), in all the three cases, %COD abatement was reduced significantly. This is because increase in temperature may promote coalescence of smaller bubbles that leads to development of larger bubbles [27]. Due to this, interfacial area will drastically reduce results in less degradation.

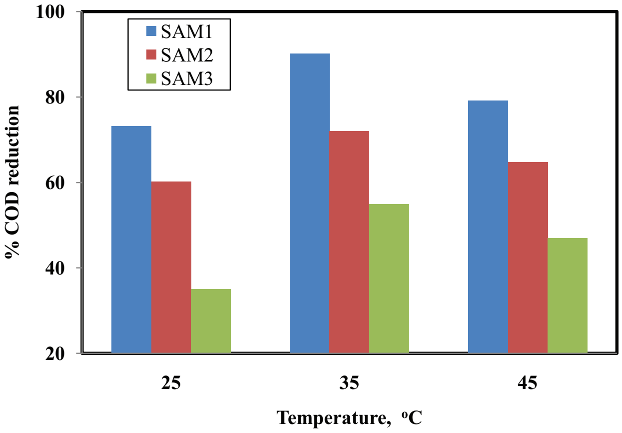

Fig. 3. Influence of reaction temperature on %COD reduction (Conditions: reaction time, 180 min; dosage of ascorbic acid, 600, 500 and 400 mg/L for SAM1, SAM2 and SAM3, respectively; iron swarf, 4 g/L).

3.5. Effect of addition pattern of iron swarf

Iron swarf was added in the degradation of three effluents in two different patterns such as (1) predetermined amount of iron swarf was added in single dose, just before starting the degradation, (2) predetermined amount of iron swarf was divided into equal amounts and added the fraction of iron swarf in regular interval of time from starting of degradation till 180 min of process (Fig. 4). In SAM1 degradation, single dose iron addition produced 90.2 %COD abatement while multiple additions of equally divided dose during the entire period produced 92.1%. With respect to SAM2, improved %COD reduction was observed (from 72.0% to 81.2%) due to multiple additions. Under the similar conditions, SAM3 degradation produced the enhanced degradation from 55% to 71.4%. The pattern change fetched excellent result (29.82% enhancement) in SAM3 degradation, because multiple additions in minimal dosages made the system iron-rich in all times which are very much required for molecular oxygen activation and thus this favorite condition accelerated the degradation. The moderate impact on SAM2 degradation (12.77% enhancement) and minimal effect on SAM1 (just 2.1%) were observed. Insignificant enhancement in SAM1 might be due to the following reasons: one time addition made the system iron-rich and enormous hydroxyl and other radicals (ROS) were produced. These radicals were

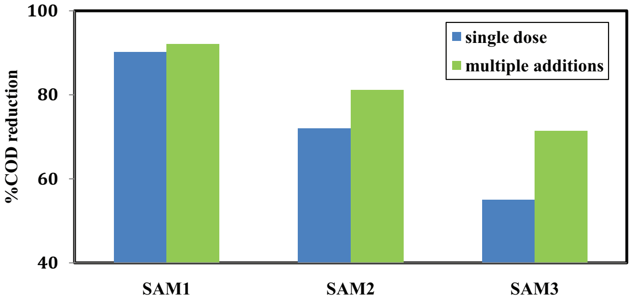

Fig. 4. Influence of pattern of iron addition on %COD reduction (Conditions: reaction time, 180 min; dosage of ascorbic acid, 600, 500 and 400 mg/L for SAM1, SAM2 and SAM3, respectively; iron swarf, 4 g/L; temperature, 35°C).

consumed by highly dense pollutants and thus better degradation was achieved in single dose. When minimal dose was added, the presence of less iron-rich condition produced minimal radicals that lead to decrement in rate of degradation. Usually, it is difficult to produce complete degradation of industrial effluents, especially pharmaceutical effluents as it might contain recalcitrant biorefractory pollutants.

3.6. Ecotoxicity test

The pharmaceutical effluent contains numerous ingredients and during oxidative degradation, these reactants were converted to carbon dioxide and water under ideal conditions. Under non-ideal situations, the intermediates and products might be toxic than the untreated effluent. In this study, the zone of inhibition was 27 mm for untreated effluent, which illustrates the acute toxic nature of effluent discharged from the industry. The proposed treatment methodology reduced the zone of inhibition to 9 mm with respect to SAM1, while the values were found to be 7 and 11 mm for SAM2 and SAM3, respectively. It should be noted here that, disc diameter of 6 mm is included in these values. The obtained data in this study show that the level of toxicity in effluent decreased considerably after the proposed degradation methodology. In comparison of three effluents after treatment, toxicity was found to be more for SAM3 than other two effluent samples and it might be due to the presence of recalcitrants in treated effluent (SAM3). The observed results were in line with the previous study [28], in which pharmaceutical effluent was degraded using sono-Fenton-sorption.

4. Conclusions

This study illustrates the potential of no-cost waste material – iron swarf in activating molecular oxygen for the degradation of three different pharmaceutical effluents in the presence of food additive – L-ascorbic acid. Use of air-lift reactor and heterogeneous system using iron swarf facilitated the degradation in better way. Degradation follows second-order kinetics and all the parameters considered here influenced the degradation in positive way with different magnitude. Ecotoxicity studies clearly showed that the treated effluents are less toxic than the parent pollutants. The clean and green technology-based degradation produced promising results on all the three cases.

References

[1] Y. Guo, P.S. Qi, Y.Z. Liu, A review on advanced treatment of pharmaceutical wastewater, IOP Conf. Ser. Earth Environ. Sci., 63 (2017) 012025.

[2] R. Baskaran, S.R. Selvi, Desalination of well water solar power membrane distillation and reverse osmosis and its effective analysis, Int. J. Chemtech. Res., 6 (2014) 2628–2636.

[3] R. Baskaran, S.R. Selvi, Solar photo voltaic powered membrane distillation as sustainable clean energy technology in desalination, Curr. Sci. India, 109 (2015) 1247–1254.

[4] R. Baskaran, S.R. Selvi, Application of regression modelling techniques in desalination by membrane distillation, Int. J. Eng. Sci. Technol., 7 (2015) 267–278.

[5] H. Tekin, O. Bilkay, S.S. Ataberk, T.H. Balta, I.H. Ceribasi, F.D. Sanin, F.B. Dilek, U. Yetis, Use of Fenton oxidation to improve the biodegradability of a pharmaceutical wastewater, J. Hazard. Mater., 136 (2006) 258–265.

[6] S. Nachiappan, K. Muthukumar, Treatment of pharmaceutical effluent by ultrasound coupled with dual oxidant system, Environ. Technol., 34 (2013) 209–217.

[7] M.I. Badawy, R.A. Wahaab, A.S. El-Kalliny, Fenton biological treatment processes for the removal of some pharmaceuticals from industrial wastewater, J. Hazard. Mater., 167 (2009) 567–574.

[8] S. Ishak, A. Malakahmad, Optimization of Fenton process for refinery wastewater biodegradability augmentation, Korean J. Chem. Eng., 30 (2013) 1083–1090.

[9] R.K. Tewari, F. Hadacek, S. Sassmann, I. Lang, Iron deprivation-induced reactive oxygen species generation leads to non-autolytic PCD in *Brassica napus* leaves, Environ. Exp. Bot., 91 (2013) 74–83.

[10] J.M. Burns, P.S. Craig, T.J. Shaw, J.L. Ferry, Multivariate examination of Fe(II)/Fe(III) cycling and consequent hydroxyl radical generation, Environ. Sci. Technol., 44 (2010) 7226–7231.

[11] J.L. Pierre, M. Fontecave, Iron and activated oxygen species in biology: the basic chemistry, Biometals, 12 (1999) 195–199.

[12] Y.H.P. Hsieh, Y.P. Hsieh, Kinetics of Fe(III) reduction by ascorbic acid in aqueous solutions, J. Agric. Food Chem., 48 (2000) 1569–1573.

[13] X. Hou, W. Shen, X. Huang, Z. Ai, L. Zhan, Ascorbic acid enhanced activation of oxygen by ferrous iron: a case of aerobic degradation of rhodamine B, J. Hazard. Mater., 308 (2016) 67–74.

[14] H. Nakajima, A.M.M. Martínez, E.M.E. Silva, Mass Transfer – Advances in Sustainable Energy and Environment Oriented Numerical Modeling, InTech Chapters, 2013, pp. 387–388.

[15] S. Nachiappan, K.P. Gopinath, Treatment of pharmaceutical effluent using novel heterogeneous fly ash activated persulfate system, J. Environ. Chem. Eng., 3 (2015) 2229–2235.

[16] APHA, American Public Health Association, American Water Works Association, Water Pollution Control Federation, Standard Methods for the Examination of Water and Wastewater 20, 1998.

[17] S. Nachiappan, K. Muthukumar, Intensification of textile effluent chemical oxygen demand reduction by innovative hybrid methods, Chem. Eng. J., 163 (2010) 344–354.

[18] F. Haber, J. Weiss, Uber die Katalyse des Hydroperoxydes (On the catalysis of hydroperoxide Naturwissenschaften), Die Naturwissenschaften, 20 (1932) 948–950.

[19] M.D. Paciolla, S. Kolla, S.A. Jansen, The reduction of dissolved iron species by humic acid and subsequent production of reactive oxygen species, Adv. Environ. Res., 1 (2002) 169–178.

[20] P. Belanzoni, L. Bernasconi, E.J. Baerends, O_2 activation in a dinuclear Fe(II)/EDTA complex: spin surface crossing as a route to highly reactive Fe(IV)oxo species, J. Phys. Chem. A, 113 (2009) 11926–11937.

[21] D.F. Laine, A. Blumenfeld, I.F. Cheng, Mechanistic study of the ZEA organic pollutant degradation system: evidence for H_2O_2, HO°, and the homogeneous activation of O_2 by Fe^{II}EDTA, Ind. Eng. Chem. Res., 47 (2008) 6502–6508.

[22] L. Chen, J. Ma, X. Li, J. Zhang, J. Fang, Y. Guan, P. Xie, Strong enhancement on Fenton oxidation by addition of hydroxylamine

to accelerate the ferric and ferrous iron cycles, Environ. Sci. Technol., 45 (2011) 3925–3930.

[23] Y. Li, T. Zhu, J. Zhao, B. Xu, Interactive enhancements of ascorbic acid and iron in hydroxyl radical generation in quinone redox cycling, Environ. Sci. Technol., 46 (2012) 10302–10309.

[24] N.K. Daud, B.H. Hameed, Decolorization of acid red 1 by Fenton-like process using rice husk ash-based catalyst, J. Hazard. Mater., 176 (2010) 938–944.

[25] N.C. Panja, R.D. Phaneswara, Measurement of gas–liquid parameters in a mechanically agitated contactor, Chem. Eng. J., 52 (1993) 121–129.

[26] T.J. Lin, K. Tsuchiya, L.S. Fan, Bubble flow characteristics in bubble columns at elevated pressure and temperature, AIChE J., 44 (1998) 545–560.

[27] Y. Weiguo, W. Jinfu, J. Yong, Gas-liquid mass transfer in a slurry bubble column reactor under high temperature and high pressure, Chin. J. Chem. Eng., 9 (2001) 253–257.

[28] S. Nachiappan, K. Muthukumar, Treatment of pharmaceutical effluent by sono-Fenton-sorption, Clean Soil Air Water, 42 (2014) 1526–1533.