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Treatment of phenolic wastewaters in single baffle reactor by Solar/TiO_2/H_2O_2 process

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ABSTRACT

The treatment of phenolic wastewaters by means of H_2O_2-promoted TiO_2 photocatalysis was investigated in single baffle reactor concerning the effect of major operating factors, namely H_2O_2 dosage and method of addition on process efficiency. Addition of hydrogen peroxide enhances considerably treatment efficiency and its beneficial role is associated with increased production of radicals due to its reaction with conduction band electrons and other reactive species. When compared to rate of degradation, the solar/TiO_2/H_2O_2 process is two to three times faster than the solar/TiO_2 process. For untreated samples of 400 mg/L phenol concentration, from pharmaceutical industry the BOD/COD ratio is 0, while solar photocatalytic treatment of 4 h enhanced the biodegradability values to 0.44. Results of this study open new research window for a more complex approach to photocatalytic experiments where photocatalysis can be combined with hydrogen peroxide.

Keywords: Solar photocatalysis; Phenolic wastewater; Single baffle reactor; Solar/TiO_2/H_2O_2biodegradability

1. Introduction

Optimum wastewater treatment is today's challenge. However, the use of conventional wastewater treatment processes become more challengeable with the identification of more and more pollutants, rapid growth of population and industrial activities, and diminishing availability of water resources. Conventional wastewater treatment methods have been established in removing many chemical and microbial pollutants to public health and the environment from long time ago. However, the effectiveness of these processes has become limited over the last two decades. Industrial wastewaters are known to contain toxic and non-biodegradable organic substances, where biological processes are not efficient in degrading these pollutants. Some of these organics are biorecalcitrant or inhibitory due to enzymatic deficiencies or to their toxicological properties. For the removal of recalcitrant organics, biological processes which are economically beneficial cannot be chosen, but a variety of non-biological processes exist, which can be divided into oxidative and reductive technologies [1].

Among all of them, advanced oxidation processes (AOPs) have become increasingly popular in recent years as alternative or complementary treatment. The

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primary use of AOPs is to degrade organic pollutants in water by oxidation. The advantage of these processes is their destructive and non-selective nature, such that no sludge production is involved. Heterogeneous photocatalysis is an AOP which is successfully used to oxidize many organic pollutants present in aqueous systems. AOPs are all characterized by the same chemical feature: production of radicals ($OH^\bullet$) through a multistep process, although different reaction systems are used. These radicals shows little selectivity of attack and are able to oxidize various organic pollutants due to their high oxidative capacity (reduction potential of $OH^\bullet$ $E_0 = 2.8$ V). Photocatalytic degradation involves the uses of certain semiconductors as catalysts for the production of the above mentioned radicals and has proven to be an effective method for degradation of organic pollutants [2]. The use of titanium dioxide (TiO_2) as a catalyst for the photooxidation of organic compounds has received much interest because TiO_2 is inexpensive, powerful and environmentally friendly [3].

The TiO_2/UV system has been widely studied in the treatment of organic pollutants. Photochemical oxidation by H_2O_2/UV process has also been successfully used, but in this case formation of $OH^\bullet$ species is due to dissociation of the H_2O_2 molecule. On the other hand, the combined H_2O_2/TiO_2/UV process has given good results in the photodegradation of several non-biodegradable organic compounds. In photocatalytic oxidation, oxygen is the most common electron acceptor and it is relatively efficient, but aiming at further inhibiting the electron–hole recombination effect, several studies have investigated the role of hydrogen peroxide as an alternative electron acceptor, because the potential for H_2O_2 reduction (0.72 V) is higher than that for oxygen (−0.13 V) reduction [4]. Hydrogen peroxide can present beneficial or detrimental effects on the photocatalytic degradation of organic pollutants. However, the effect of hydrogen peroxide in most photocatalytic studies have reported an optimal concentration that depends on the characteristics of the wastewater, the concentration of oxygen in the solution, the intensity and wavelength of the UV light. Thus, the hydrogen peroxide concentration should be optimized for each kind of wastewater.

2. Materials and methods

2.1. Titanium dioxide

The photocatalyst employed was commercial titanium dioxide supplied by Degussa P25. According to the manufacturer's specifications, P25 has an elementary particle size of 30 nm, a BET specific surface area of 50 m^2/g and its crystalline mode is 80% anatase and 20% rutile. The catalyst was used as received.

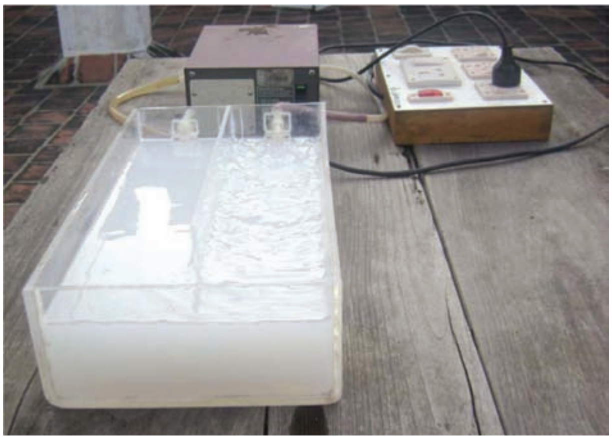

Fig. 1. Photographic view of single baffle reactor.

2.2. Solar photocatalytic reactor

Single baffle reactor was made from an extruded double skinned acrylic panel with built in flow channels of cross-section of 0.4 m × 0.1 m. The size of reactor was 0.4 m × 0.2 m × 0.1 m. The irradiated surface area and volume of reactor was 0.08 m^2 and 5 L, respectively. The set up consisted of a flow-through reactor placed on a platform under solar irradiation. The wastewater was continuously recycled with the help of circulating pump. Fig. 1 depicts the photographic view of single baffle reactor.

2.3. Solar photocatalytic oxidation (SPCO)

All photocatalytic experiments were carried out at Anna University campus in Chennai, (13°00.57"N; 80°14.12"E), Tamil Nadu. The degradation of phenolic wastewaters was carried out by solar/TiO_2/H_2O_2 system, in a single baffle reactor with volume of wastewater 5 L and recycle flow rate at 500 mL/min. All experiments were conducted using solar light on clear sunny days in the month of April and May (UV intensity 32 ± 2 W/m^2). The tests were started at 10 a.m and stopped at 4 p.m. At specific time intervals, required amount was withdrawn and filtered to separate the catalyst.

2.4. Analysis

Phenol was monitored spectrophotometrically by the aminoantipyrine method using visible spectrophotometer (Spectronic) with an optical path length of 1 cm. The method is based on the reaction of phenol with 4-aminoantipyrine in the presence of potassium

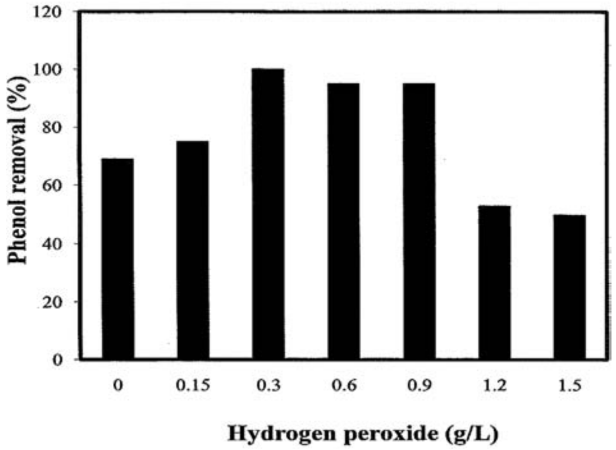

Fig. 2. Effect of Hydrogen peroxide on SPCO of phenol (pH = 6, phenol = 50 mg/L, TiO_2 = 0.25 g/L, contact time = 5 h).

ferricyanide at pH 7.9 to form a colored antipyrine complex (AMPH). COD and BOD of the samples were carried out as per standard methods (APHA, 2003).

2.5. Wastewater composition

The wastewaters were collected from pharmaceutical industry near Chennai. The main chemical parameters and compositions were pH = 8.0 ± 0.4, phenol = 360 ± 40 mg/L, chlorides = 182 ± 17 mg/L, sulphates = 163 ± 16 mg/L, COD = 1080 ± 87 mg/L, BOD = 162 ± 27 mg/L and BOD/COD ratio = 0.15 ± 0.01

3. Results and discussion

3.1. Effect of H_2O_2 concentration

In order to keep the efficiency of the added H_2O_2, it is necessary to choose the optimum concentration of H_2O_2 according to the type and concentration of the pollutants. The effect of addition of H_2O_2 (0.15–1.5 g/L) on the phenol removal is shown in Fig. 2. The addition of H_2O_2 from 0.15 to 0.3 g/L increases the phenol removal from 75% to 99%. When the H_2O_2 concentration is higher than 0.3 g/L, the phenol removal efficiency was decreased. Similar results have been reported by [5–7] for degradation of azo dye, sulfamethazine and eosin Y respectively. Hence, 0.3 g/L concentration appears to be optimum for the removal of phenol.

The enhancement of degradation by addition of H_2O_2 is due to increase in the hydroxyl radical concentration by the following ways. (i) Oxygen is the primary acceptor of the conduction band electron with formation of super oxide radical anion (Eq. (1)). H_2O_2 can compensate for the O_2 lack and play a role as an external electron scavenger according to (Eq. (2)). It can trap the photogenerated conduction band electron and thus inhibiting the electron–hole recombination and producing hydroxyl radicals as shown by the (Eq. (2)) [8].

$$TiO_2e^-_{(CB)} + O_2 \rightarrow O_2^{\bullet -} \quad (1)$$

$$e^-_{(CB)} + H_2O_2 \rightarrow {}^{\bullet}OH + OH^- \quad (2)$$

(ii) H_2O_2 may also be photolysed to produce hydroxyl radicals directly (Eq. (3)).

$$H_2O_2 \rightarrow 2{}^{\bullet}OH \quad (3)$$

(iii) H_2O_2 also reacts with superoxide anion to form ${}^{\bullet}OH$ radical (Eq. (4))

$$H_2O_2 + O_2^{\bullet -} \rightarrow {}^{\bullet}OH + H^+ + O_2 \quad (4)$$

At high H_2O_2 dosage (0.6 g/L) the degradation rate decreases due to (i) Hydroxyl radical scavenging effect of H_2O_2. The reaction between excess hydrogen peroxide and hydroxyl radical (${}^{\bullet}OH$) forms hydroperoxy radical. These hydroperoxy radicals are much less reactive and do not contribute to oxidative degradation of organics (Eqs. (5) and (6)) [9]

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \quad (5)$$

$$HO_2^{\bullet} + {}^{\bullet}OH \rightarrow H_2O^{\bullet} + O_2 \quad (6)$$

(ii) H_2O_2 is also a powerful hole scavenger. In excess it may react with holes to produce oxygen and hydrogen ion (Eq. (7)). In photocatalyic degradation, hole oxidises the organic directly and with water produce hydroxyl radical [10]. Hence, the removal of holes decreases the phenol removal rate.

$$H_2O_2 + h_{vB}{}^+ \rightarrow O_2 + 2H^+ \quad (7)$$

3.2. Effect of method of H_2O_2 addition

In order to study the effect of method of H_2O_2 addition, studies were conducted on initial phenol concentration of 50 and 500 mg/L by one time addition of H_2O_2 and stepwise addition of H_2O_2 at regular intervals. In stepwise addition, instead of adding the entire amount of H_2O_2 in the beginning of the reaction, it was added by increments of 25% of their total amount added to the reaction. The addition was made every 30 min. up to 2 h. The results of the experimental studies are depicted in Figs. 3 and 4. At 50 mg/L phenol concentration, the phenol removal efficiency of 98% and 94% was observed for entire amount of H_2O_2

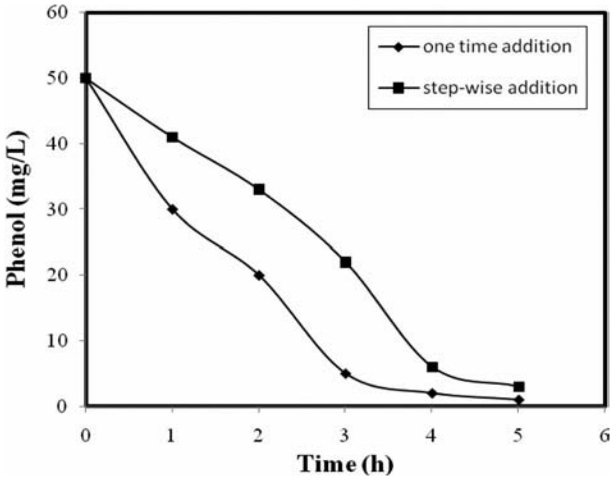

Fig. 3. Effect of stepwise addition of H_2O_2 on SPCO of phenol (50 mg/L) (pH = 6, phenol = 50 mg/L, TiO_2 = 0.25 g/L, H_2O_2 = 0.3 g/L).

added in the beginning of reaction and stepwise added during reaction, respectively. Similarly, for 500 mg/L phenol concentration, the phenol removal efficiency of 45% and 44% was observed for entire amount added in the beginning of reaction and stepwise added during reaction, respectively. In 50 and 500 mg/L phenol concentrations, it shows no substantial difference between the two cases, i.e., one time addition of H_2O_2 and stepwise addition of H_2O_2. Also it was observed that the process is very fast in the beginning of the reaction and afterwards the phenol removal is leveling off, and it might be due to the exhaustion of H_2O_2 [11].

In order to study the effect of second time addition of H_2O_2 after exhaustion, the H_2O_2 was added again after 1 h of treatment irrespective of first time addition.

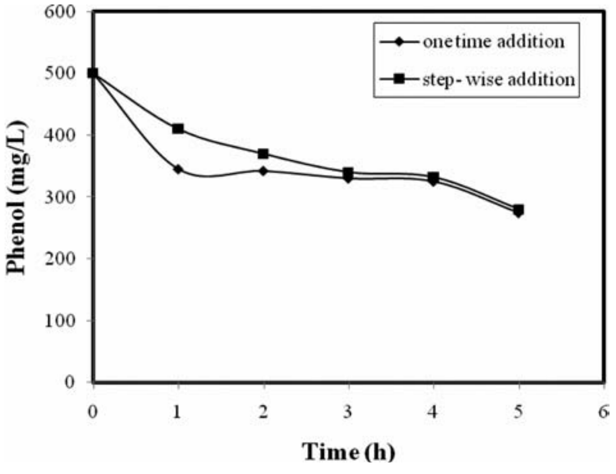

Fig. 4. Effect of stepwise addition of H_2O_2 on SPCO of phenol (500 mg/L) (pH = 6, phenol = 500 mg/L, TiO_2 = 0.25 g/L, H_2O_2 = 0.3 g/L).

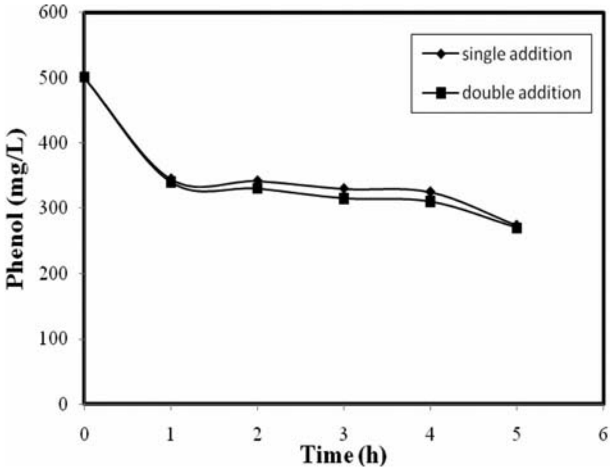

Fig. 5. Effect of double addition of H_2O_2 on SPCO of phenol (500 mg/L) (pH = 6, phenol = 500 mg/L, TiO_2 = 0.25 g/L, H_2O_2 = 0.3 g/L).

The results of the experimental studies are depicted in Fig. 5. Phenol removal efficiency of 45% and 46% was observed for single addition and double addition of H_2O_2, respectively. In some cases H_2O_2 acted simply as an alternate electron acceptor and could not be sustained. The rate enhancement in solutions that had received H_2O_2 addition persisted long after all of the initial H_2O_2 was exhausted and an addition of more H_2O_2 at that time had no accelerating effect [12]. It appears that H_2O_2 plays a role in initiation of radical chain reactions that persist after the initial dose of H_2O_2 has been consumed.

3.3. Comparison of solar/H_2O_2, solar/TiO_2 and solar/TiO_2/H_2O_2 on initial phenol concentration

Solar photocatalytic experiments were carried out to define effectiveness of the optimized experimental conditions for different initial concentrations 100, 200, 300, 400 and 500 mg/L. To compare the efficiency of phenol removal, studies were conducted in three processes viz. solar/H_2O_2, solar/TiO_2 and solar/TiO_2/H_2O_2. The results of the experimental studies are depicted in Figs. 6–10. Table 1 shows reaction rate constant (*k*) for initial phenol concentration. In solar/H_2O_2 process, it was observed that only 20%, 12%, 5%, 4% and 3% phenol removal was obtained for the initial phenol concentration of 100, 200, 300, 400 and 500 mg/L, respectively. It was observed that, the phenol removal in solar/H_2O_2 is low in a homogeneous system. Although hydroxyl radicals are claimed to exist in such system, the reaction rate is relatively small due to the probability of collision as follows (Eqs. (8) and (9)) [4]

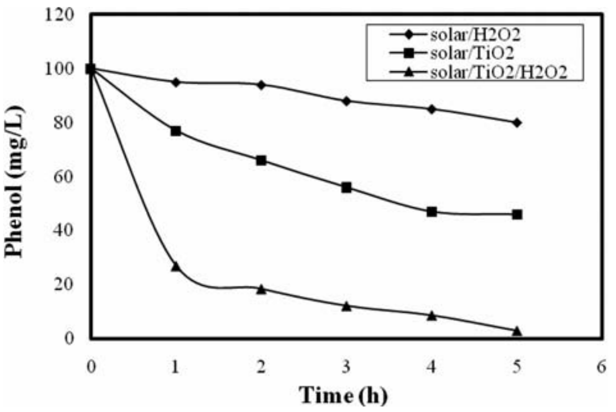

Fig. 6. Effect of solar/TiO_2/H_2O_2 on phenol (100 mg/L) (pH = 6, TiO_2 = 0.25 g/L, H_2O_2 = 0.3 g/L).

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \tag{8}$$

$$H_2O_2 + HO_2^{\bullet} \rightarrow {}^{\bullet}OH + H_2O + O_2 \tag{9}$$

In solar/TiO_2 processes, 54%, 35%, 23%, 22% and 22% phenol removal was obtained for the initial phenol concentration of 100, 200, 300, 400 and 500 mg/L, respectively. According to photocatalytic processes, the electrons and holes are separated by photoexcitation of semiconductors (e.g., TiO_2). The holes migrate to the surface and react with adsorbed species while the electrons react with O_2 to form hydroxyl radicals. It has been known that O_2 plays an important role in trapping electrons in this process [13].

In solar/TiO_2/H_2O_2 process, it was observed that 97%, 70%, 54%, 47% and 45% phenol removal were obtained for the initial phenol concentration of 100, 200, 300, 400 and 500 mg/L, respectively. The addition of hydrogen peroxide to heterogeneous photocatalytic system was expected to increase the oxidation, because it acts as an electron acceptor and the photolysis of H_2O_2 can produce higher amounts of $OH^{\bullet}$ radicals (Eqs. (10)–(11)) [13].

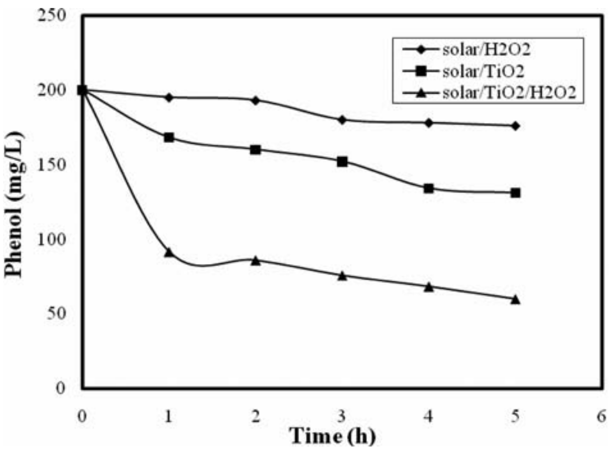

Fig. 7. Effect of solar/TiO_2/H_2O_2 on phenol (200 mg/L) (pH = 6, TiO_2 = 0.25 g/L, H_2O_2 = 0.3 g/L).

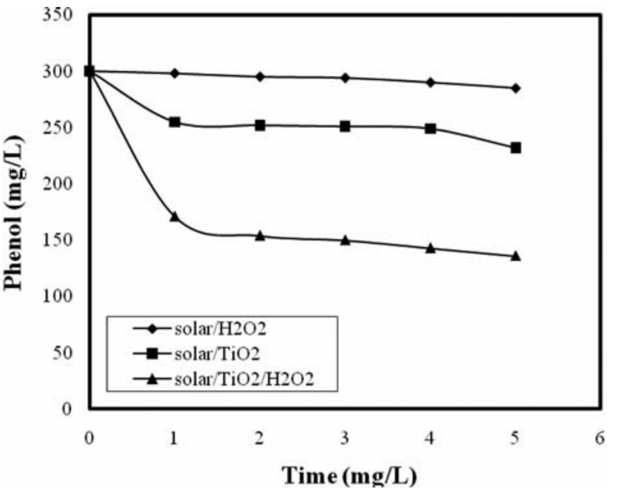

Fig. 8. Effect of solar/TiO_2/H_2O_2 on phenol (300 mg/L) (pH = 6, TiO_2 = 0.25 g/L, H_2O_2 = 0.3 g/L).

$$TiO_2(e^-) + H_2O_2 \rightarrow TiO_2(h^+) + OH^{\bullet} + OH^- \tag{10}$$

$$H_2O_2 + e^-_{(CB)} \rightarrow OH^{\bullet} + OH^- \tag{11}$$

It also reported that the highest degradation of tannery wastewater was obtained by addition of hydrogen peroxide to heterogeneous photocatalytic system [9]. Similar results were also observed for degradation of reactive dye bath wastewater [10]. One practical problem in using TiO_2 as a photocatalyst is the undesirable electron/hole recombination, which, in the absence of proper electron acceptor or donor, is extremely

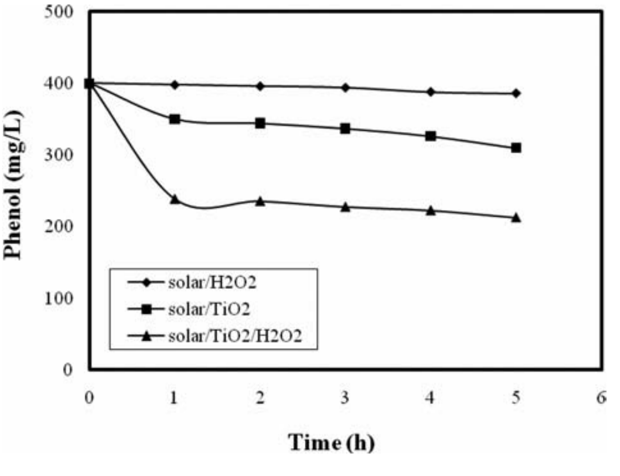

Fig. 9. Effect of solar/TiO_2/H_2O_2 on phenol (400 mg/L) (pH = 6, TiO_2 = 0.25 g/L, H_2O_2 = 0.3 g/L).

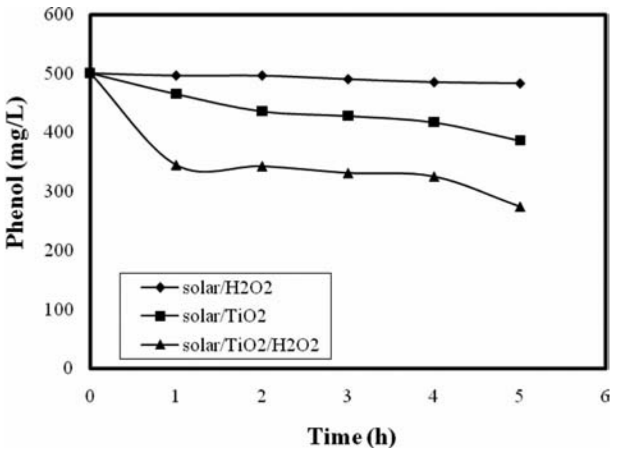

Fig. 10. Effect of solar/TiO_2/H_2O_2 on phenol (500 mg/L) (pH = 6, TiO_2 = 0.25 g/L, H_2O_2 = 0.3 g/L).

efficient and thus represent the major energy-wasting step, hence limiting the achievable quantum yield. The electron acceptor like H_2O_2 inhibit the electron–hole pair recombination process along with the additional effects of increasing the number of trapped electrons, to generate more OH radicals and other oxidizing species, increases oxidation rate of intermediate compounds and avoid problems caused by low oxygen concentration.

3.4. Biodegradability improvement of phenolic wastewaters by solar/TiO_2/H_2O_2 process

As the phenolic wastewaters are non-biodegradable in nature, the feasibility of enhancement of biodegradability of wastewater was carried out by solar/TiO_2/H_2O_2 system, in a single baffle reactor with volume of wastewater 5 L and recycle flow rate at 500 mL/min. The phenolic wastewater samples were collected from the pharmaceutical industry. The biodegradability of the phenolic wastewaters was evaluated through the evolution of the BOD_3/COD ratio. The results of the experimental studies are depicted in Fig. 11. As a reference, this parameter for biodegradable municipal wastewater is of around 0.4. It should be noticed that BOD_3/COD ratio higher than 0.4 indicate a readily and rapidly degradable solution while ratio below 0.4 involve the presence of slowly biodegradable compounds [2]. For untreated samples of 400 mg/L phenol concentration, the BOD/COD ratio is 0, while solar photocatalytic treatment of 4 h enhanced the biodegradability values to 0.44. The results indicated that the solar photocatalytic process could break down or rearrange molecular structures of organic matters and convert the non-biodegradable organics to more biodegradable forms. Similar results were observed for degradation of humic acid of 100 mg/L [14]. And it was reported that, the BOD/TOC ratio raised from 0.02 to 0.53 after 3.5 h of photocatalysis. Also, it was demonstrated that photo-Fenton reaction can be successfully used as a pre-treatment process to bio-compatibilize Procion Red H-E7B reactive dye solutions [15]. With partial oxidation run under mild conditions, dye solution became decolourised and more biodegradable, as well as non toxic. This is a fact of remarkable importance for the application of photocatalytic-biological integrated systems to wastewater treatment. Photocatalytic process could transform organic recalcitrant compounds into easily biodegradable products, improving the efficiency and reducing the cost of further biological steps.

Table 1
Reaction rate constant k (h^{-1}) for initial phenol concentration

	Solar/TiO_2		Solar/TiO_2/H_2O_2	
Phenol (mg/L)	k (h^{-1})	R^2	k (h^{-1})	R^2
100	0.176	0.94	0.35	0.95
200	0.093	0.91	0.20	0.75
300	0.055	0.87	0.13	0.75
400	0.040	0.87	0.09	0.75
500	0.040	0.95	0.09	0.75

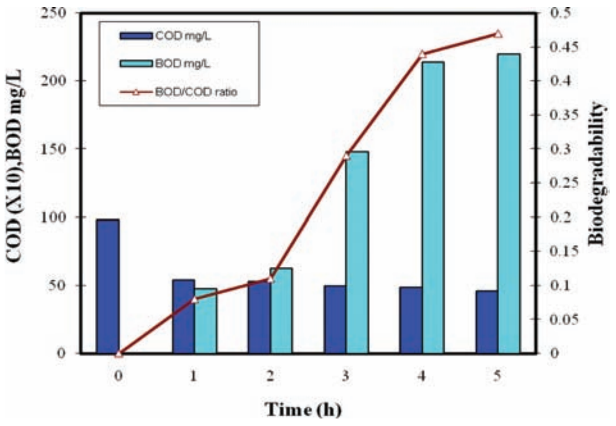

Fig. 11. Biodegradability of phenolic wastewater from pharmaceutical industry.

4. Conclusions

- In solar/TiO_2/H_2O_2 system, the addition of H_2O_2 from 0.15 to 0.3 g/L increases the degradation from 75% to 99%. When the H_2O_2 concentration is higher than 0.3 g/L the degradation rate decreases.
- For phenol concentration of 500 mg/L, the phenol removal efficiency of 45% and 44% was observed for entire amount added in the beginning of reaction and stepwise added during reaction, respectively. It shows that, no substantial difference between the two cases.

- When compared to rate of degradation, the solar/TiO_2/H_2O_2 process is two to three times faster than the solar/TiO_2 process.
- Overall, it was found that addition of hydrogen peroxide to the photocatalytic system was beneficial and it was demonstrated that the desired enhancement can be achieved with small doses of hydrogen peroxide, which is promising from economic perspective since it requires miniscule consumption of the non-recyclable agent, H_2O_2.
- For untreated samples of 400 mg/L phenol concentration, from pharmaceutical industry, the BOD/COD ratio is 0, while solar photocatalytic treatment of 4 hours enhanced the biodegradability values to 0.44.

Acknowledgement

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