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Photocatalytic treatment of pharmaceutical industry wastewater over TiO_2 using immersion well reactor: synergistic effect coupling with ultrasound

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ABSTRACT

The sonophotocatalytic degradation of pharmaceutical industry wastewater was studied with a TiO_2 slurry mode process with UV 125 W medium-pressure mercury lamp coupled with ultrasound (100 W, 33 ± 3 kHz). The degradation of wastewater was investigated in terms of reduction in COD that confirmed the apparent first- order degradation kinetics. The rate constant was greatly affected by catalyst dose, variation in pH, and concentration of oxidant (H_2O_2).The catalyst concentration was optimized at $1.0\,g\,L^{-1}$, pH at 4, and the oxidant concentration at $0.075\,g\,L^{-1}$. The first-order rate constants obtained from coupled sonophotocatalysis were two-folds than those obtained from photocatalysis and approximately ten-folds than sonolysis. The COD reduction follows the trend, sonophotocatalysis > photocatalysis > sonocatalytic > sonolysis. The study demonstrates better efficiency of coupled sonophotocatalysis over independent treatment processes.

Keywords: Sonophotocatalysis; Pharmaceutical industry wastewater; Photocatalysis; TiO_2; Sonolysis

1. Introduction

Contamination of soil and groundwater from industrial waste streams and pollutants such as pharmaceuticals, hormones, heavy metals, and pesticides is a serious environmental problem nowadays. The occurrence of emerging organics from several pharmaceutical compounds were reported in sewage treatment plant effluents as well as in surface waters in Germany, Netherlands, Switzerland, Canada, Brazil, Italy, and USA [1]. Pharmaceuticals have been detected in ground and surface water [2], drinking water [3,4], tap water [5], ocean water, sediments and soil [6].

Pharmaceuticals are designed to have a physiological effect on humans and animals in trace concentrations. Persistence against biological degradation and their biological activity are key properties of these pollutants. They retain their chemical structure long enough to do their therapeutic work and because of their continuous input, they could remain in the environment for a long time and their presence is considered dangerous both in low and high concentrations [7]. The detected compounds included antibiotics, anticonvulsants, painkillers, cytostatic drugs, hormones, lipid regulators, beta-blockers, antihistamines,

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and X-ray contrast media that are potentially detrimental to the environment as well as biota. There are several possible sources and routes for the occurrence of pharmaceutical compounds in the aquatic environment [8]. These compounds persist in the environment, enter the food chain, bio accumulate, bio magnify, and cause harmful effects in wildlife and humans. Therefore, the persistence of pharmaceutical chemicals in the environment has become a global problem.

Advanced oxidation processes (AOPs) are considered one of the most attractive methods for the treatment of wastewater because they offer a highly reactive, non-selective oxidant, that is hydroxyl radical ($OH^{\cdot}$) destroying almost every pollutant present in the wastewater. AOPs use combinations of oxidants, ultraviolet irradiation, and catalysts to generate $OH^{\cdot}$ radicals in solutions which oxidize organic pollutants to water, carbon dioxide, and mineral salts. In addition, sonocatalytic treatment is one of the successful techniques for the degradation of pollutants present in wastewater/water [9]. When ultrasound is combined with other AOPs, the combination would lead to faster degradation rates when compared to either method. Actually, the chemical effects of ultrasound basically originate from acoustic cavitation, that is the formation, growth, and collapse of bubbles in liquid resulting from high temperature and pressure conditions locally. So the emerging wastewater treatment methods are increasingly gaining popularity, since they have shown the potential of converting the harmful organic pollutants into innocuous compounds such as carbon dioxide and water [10,11].

There are basically three potential sites for sonochemical activity [12]:

(i) The gaseous region of the cavitation bubble, (ii) the bubble–liquid interface, (iii) the liquid bulk; with series of reactions leading to the formation of more OH radicals.

$$H_2O+))) \rightarrow H^{\cdot} + OH^{\cdot} \tag{1}$$

$$H^{\cdot} + O_2 \rightarrow {}^{\cdot}OOH \tag{2}$$

$$OH^{\cdot} + OH^{\cdot} \rightarrow H_2O_2 \tag{3}$$

$${}^{\cdot}OOH + {}^{\cdot}OOH \rightarrow H_2O_2 \tag{4}$$

$$H_2O_2 + H^{\cdot} \rightarrow H_2O + OH^{\cdot} \tag{5}$$

Organics of low solubility and/or high volatility are likely to undergo fast sonochemical degradation as they tend to accumulate inside or around the gas–liquid interface [13]; in this respect, the process may be well suited to tackle the pharmaceutical micro-pollutants. Various studies have demonstrated the degradation of organic compounds like dyes, pesticides, and pharmaceutical compounds [14–16], but the degradation of real pharmaceutical effluent using photocatalysis in combination with ultrasound has not been reported. In an attempt to increase the efficiency of degradation, the work was carried out using heterogeneous sonophotocatalytic (sonolysis + photocatalysis) treatment. Combining these two modes of irradiations, that is US and UV, eliminate the drawbacks of the individual process and generate more hydroxyl radicals. In this work, sono-photocatalysis was used for the degradation of industrial wastewater of pharmaceutical origin which is characterized by its extremely high value of COD and a low value of BOD, that is very low biodegradability, probably due to the presence of toxic/refractory compounds, which restrict direct biological treatment.

2. Reagents

Raw effluent was collected from a, nearby pharmaceutical industry, flow equalization stage of the treatment plant and used as received. The raw sample was diluted with distilled water to get the COD values within a range, that is $2,500 \pm 500\,\text{mg}\,\text{L}^{-1}$. BOD values of the pharmaceutical wastewater were relatively low. The amount of total suspended solids, total dissolved solids, sulfate and chloride was $2,390\,\text{mg}\,\text{L}^{-1}$, $3,820\,\text{mg}\,\text{L}^{-1}$, $1,750\,\text{mg}\,\text{L}^{-1}$, and $3,750\,\text{mg}\,\text{L}^{-1}$, respectively. Standard APHA methods were followed for analyzing the above mentioned parameters. The initial pH of the effluent was 3.75 and further adjustment in pH was carried out with concentrated solutions of HCl and NaOH (obtained from Merck). The photo catalyst was TiO_2 P-25 (a mixture of anatase and rutile form of titanium dioxide in the ratio of 70:30, procured from Evonik Industries India Pvt. Ltd; Mumbai Branch, as a gift sample with a BET surface area of $50\,\text{m}^2\text{g}^{-1}$ and average particle size of 30 nm. Hydrogen peroxide (Ranbaxy, India) was used as an oxidant.

3. Experimental conditions

About 200 mL solution of wastewater was maintained in dark for at least 1 h to reach complete adsorption equilibrium. The solution was then irradiated for about 7–8 h under 125 W UV lamps in the reactor. The aeration provided the required degree of stirring to the solution. The aeration was provided using ambient air with a flow rate of $4.5\,\text{Lh}^{-1}$. The process was optimized by varying the catalyst dose, operating pH, addition of oxidant, and the reaction kinetics was studied. These optimized conditions were used for further actual treatment of the wastewater. An aliquot of 3 mL was taken from the reaction volume of 200 mL at regular intervals (1 h) of time with the help of a syringe. The catalyst was filtered from the sample by a millipore filter (0.45 µm). These samples were analyzed for COD estimation as well as scanned with a UV-vis spectrophotometer (HITACHI model no (U-2800)). Standard APHA method was used for calculating COD [17]. The filter was washed every time to ensure that no residual compound remain on the micro filter. All experiments were carried out in triplicate for the reproducibility of results.

4. Equipment detail

An immersion well photochemical reactor made of Pyrex glass equipped with a 125 W medium pressure mercury lamp was used in the study. Short-wavelength UV-radiation and IR-radiation were eliminated by a water circulated glass jacket. The temperature was maintained at 25℃ and an opening for the supply of oxygen was used. To study the effect of ultrasound, the whole photoreactor assembly was immersed into an ultrasonic bath (100 W, 33 ± 3 kHz) having the capacity 6.5 L with the tank size 12´´x6´´ x6´´. All sonolytic, photocatalytic, and sonophotocatalytic experiments were performed using same immersion well reactor. The average intensity during the experiments was 25 $\mathrm{Wm^{-2}}$ measured with a Eppley (model no. 33013) radiometer.

5. Results and Discussion

5.1. Preliminary studies

Preliminary runs demonstrated that the wastewater is perfectly stable, that is resistance to the degradation in the absence of titanium dioxide. Treatment under UV light, that is photolysis of the effluent yielded only 10% reduction in COD after 7 h of irradiation (Fig. 2). Consequently, the photolysis of the effluent is negligible and the decomposition that is observed in the presence of the catalyst (TiO_2) is ascribed to the catalyst activity. Moreover, blank experiments in the absence of UV light exhibited negligible adsorbance of the pharmaceutical pollutants on the catalyst's surface [18]. The results observed from the adsorption experiment confirmed 14% reduction in COD values. The reduction in COD values is mainly due to the formation of a pollutant monolayer on the catalyst surface. The pollutants present in the waste water gets adsorbed on the catalyst surface as soon as it is being added to irradiated waste water resulting in the formation of a pollutant monolayer. After monolayer formation, no free active sites would be available and, therefore, no further reduction in COD was observed (Fig. 1). The degradation of the waste water using TiO_2 with UV light showed 85% reduction in COD, thus assuming that adsorption–desorption of the substrate and the reaction intermediate is relatively slow as compared to the formation of electron/hole pairs.

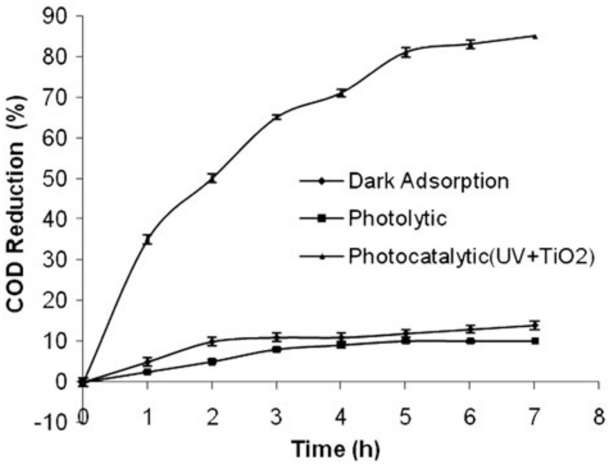

Fig. 1. Comparison between photolysis and percentage of COD reduction of wastewater in the presence and absence of UV irradiations.

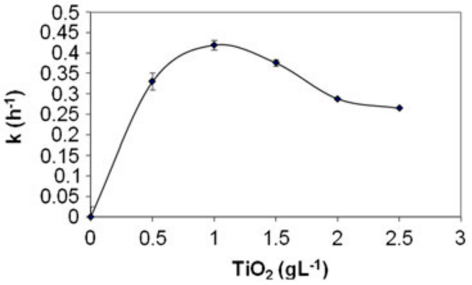

Fig. 2. Effect of catalyst concentration on the photodegradation of wastewater (reaction volume 0.200 L, initial COD = 2,500 ± 500 $\mathrm{mg\,L^{-1}}$, pH = 3.75, and UV intensity 28 $\mathrm{Wm^{-2}}$).

5.2. Effect of photocatalyst concentration

Photocatalytic degradation studies were performed in the immersion well reactor to study the first-order degradation rate constant by varying the concentration of titanium dioxide.

Photocatalytic reactions can usually be described by a pseudo-first-order kinetic expression, that is

$$-\mathrm{d}C/\mathrm{d}t = kC$$

or $\ln C_0/C = kt$

where k is an apparent first-order reaction rate constant, and C_0 and C are the initial and the final concentration of pollutants in waste water, respectively. TiO_2 concentrations were varied from 0.5 to $2.5\,\mathrm{g\,L^{-1}}$ during the photocatalytic treatment process and the experiment was conducted for 7–8 h. As shown in Fig. 2 the optimum catalyst loading was $1.0\,\mathrm{g\,L^{-1}}$. With the increasing concentration of TiO_2, the number of photons absorbed in the UV light and the number of pollutant molecules adsorbed on the surface of catalyst are increased owing to an increase in the rate of photocatalytic reaction. Above a certain level, the pollutant molecules available are not sufficient for the adsorption by the increased number of TiO_2 particles. The other reason for this is the decrease in surface area of catalyst due to aggregation of TiO_2 causing a decrease in the number of active sites on its free surface. A similar effect was studied in the case of photocatalytic and photochemical degradation of nitrobenzene using TiO_2 catalyst and artificial ultraviolet light [19].

5.3. Effect of pH

The photocatalytic degradation of the ionizable organic compounds in wastewater is affected by the pH. The initial pH values varied from 2 to 10 (i.e. acidic to basic) to study the influence of pH on the kinetics of COD reduction. The effect of the pH on the degradation rate can be explained mainly by the adsorption of wastewater pollutant on TiO_2 surface. In acidic suspensions, the adsorption of a pollutant on the TiO_2 particles increased significantly comparing to the extent of adsorption in alkaline suspensions. This is attributed to the fact that TiO_2 shows an amphoteric character so that either a positive or a negative charge can be developed on its surface [20]. The point of zero charge of the used TiO_2 (Degussa P-25) is widely reported at pH ≈ 6.5. The TiO_2 surface is positively charged in acidic solution and negatively charged in basic solution. Fig. 3 confirms that the degradation rate is better at acidic pH and decreased towards alkaline conditions. The maximum degradation was observed at pH 4.0 and the final pH after photocatalytic treatment was 7.1 which is suitable for biological treatment as well as discharge of wastewater into the water bodies [21].

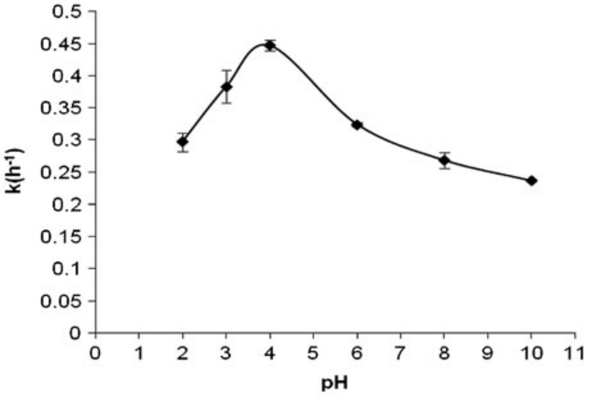

Fig. 3. Effect of pH on rate constant k (reaction volume 0.200 L, initial COD = 2,500 ± 500 mg $\mathrm{L^{-1}}$, $TiO_2 = 1.0\,\mathrm{g\,L^{-1}}$, and UV intensity 28 $\mathrm{W m^{-2}}$).

5.4. Effect of electron acceptor

The electron acceptor hydrogen peroxide (H_2O_2) increases the concentration of OH radicals which play an important role in the photocatalytic degradation. It facilitates the electron-hole recombination, according to the following equation:

$$TiO_2(e^-) + H_2O_2 \rightarrow TiO_2 + OH^- + OH^{\cdot}$$

H_2O_2 accepts the photo-generated electron from the conduction band and thus promotes the charge separation, and thereby forming OH radicals.

However, at a high concentration of H_2O_2, it also acts as a scavenger as shown in the following equations [22].

$$H_2O_2 + OH^{\cdot} \rightarrow HO_2^{\cdot} + H_2O$$

$$H_2O_2 + OH^{\cdot} \rightarrow H_2O + O_2$$

With this view, we studied the effect of an electron acceptor, that is H_2O_2 in the range of 0.0375–0.450 $\mathrm{g\,L^{-1}}$ at a constant pH 4 and catalyst dose of $1\,\mathrm{g\,L^{-1}}$ (Fig. 4). As expected, the H_2O_2 addition enhanced the degradation rate of the pollutants present in the wastewater at an optimum amount of H_2O_2 addition at $0.075\,\mathrm{g\,L^{-1}}$ of the sample [23].

5.5. Comparison of Sonolytic (US) and Sonocatalytic (US +TiO_2) degradation of waste water

Sonolysis is the breaking of chemical bonds or the formation of radicals using ultrasound. The use of

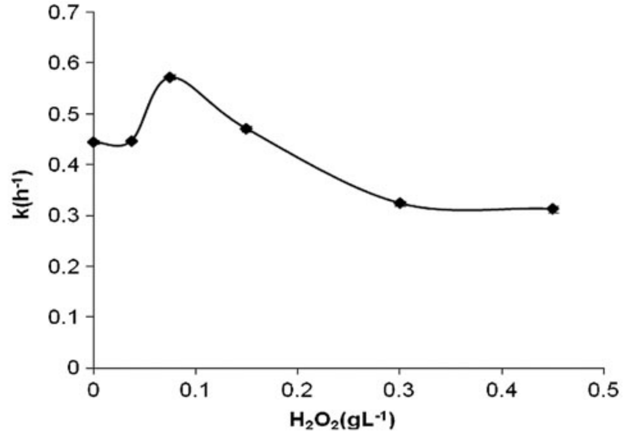

Fig. 4. Showing the effect of oxidant dose on rate constant k (reaction volume 0.200 L, $TiO_2 = 1.0\,g\,L^{-1}$, pH = 4, initial COD = 2,500 ± 500 $mg\,L^{-1}$, and UV intensity 28 Wm^{-2}).

ultrasound has recently been an attraction as an emerging advanced oxidation process for wastewater treatment [24]. The action of ultrasound allows for the creation of micro bubbles in water at high temperature and pressure, leading to localize transient supercritical conditions [25]. This leads to the production of active radicals ($H^{\cdot}$ and $^{\cdot}OH$) that take part in the degradation of organic matter. The use of photocatalyst and oxidant addition further raises the degradation level, and it is clear from Fig. 6 that the maximum degradation was achieved with $US + TiO_2 + H_2O_2$ than $US + TiO_2$ and US all under UV. Dai et al. [26] confirmed similar kind of results for the degradation of 4-chlorophenol.

Our study shows that sonocatalysis with all optimum parameters shows better results than sonolysis alone (Fig. 5), because ultrasound plays a profound role due to the substantial increase in the number of active sites and also the surface area available due to the defragmentation of the catalyst agglomerates under the action of turbulence by acoustic streaming along with an increase in the diffusion rates of contaminants.

5.6. Comparisons of Sonocatalytic, Photocatalytic and Sonophotocatalytic treatment

Fig. 6 shows that the sonophotocatalytic treatment (i.e. Sonolysis + photo catalysis), with all the optimized conditions degraded 99% after 4 h of treatment followed by photocatalytic treatment (90% after 4 h) and sonocatalytic process (45% after 4 h) because the use of ultrasound creates conditions of increased turbulence in the liquid, thus decreasing the mass transfer limitation and increasing the surface area available due to catalyst fragmentation and de-agglomeration. Thus, by combining these two modes of irradiations (US + UV), more hydroxyl radicals are produced.

Literature studies have shown the similar kind of results on the degradation of basic blue 9 industrial textile dyes [27].

5.7. Biodegradability studies

The ratio of BOD to COD, an established representative of the solution biocompatibility, defined as biodegradability ratio. The BOD values were obtained after 5 days of incubation period, that is BOD_5. It should be noticed that BOD_5/COD ratio higher than

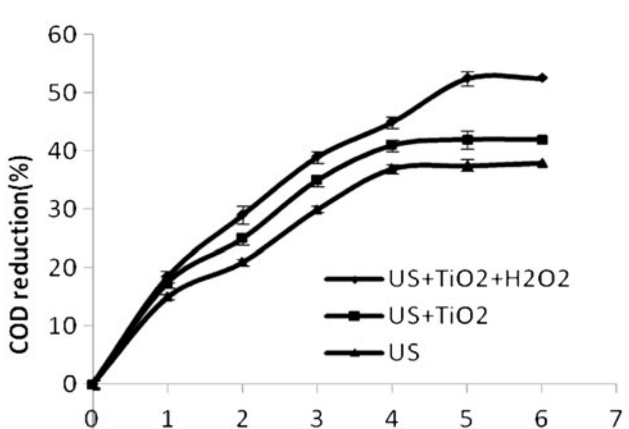

Fig. 5. % COD reduction due to Sonolytic [US] and Sonocatalytic [$US + TiO_2$] and Sonocatalytic + oxidant [$US + TiO_2 + H_2O_2$] [pH = 4, $TiO_2 = 1.0\,g\,L^{-1}$, initial COD = 2,500 ± 500 $mg\,L^{-1}$, $H_2O_2 = 0.075\,g\,L^{-1}$].

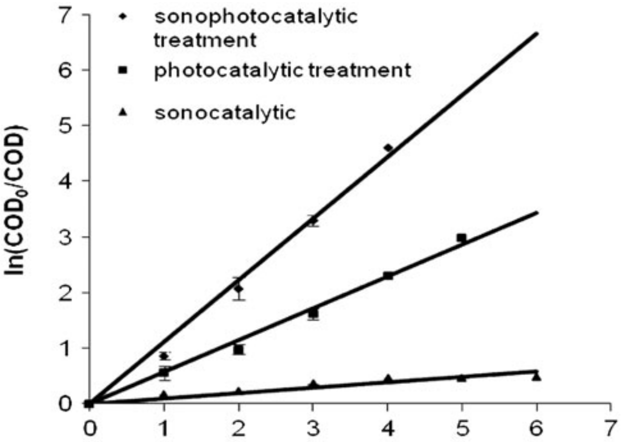

Fig. 6. First order kinetic plot with $TiO_2 = 1.0\,g\,L^{-1}$, $H_2O_2 = 0.075\,g\,L^{-1}$and pH = 4, initial COD = 2,500 ± 500 $mg\,L^{-1}$ under Sonophotocatalysis, photocatalysis and Sonocatalysis as a function of time.

0.4 indicates a readily and rapidly degradable solution, while ratios below 0.4 involve the presence of slowly degradable compounds. The relationship between the structure and the biodegradability of the organic compounds makes possible the evaluation of the biological treatment of wastewater and the removal of organic compound by the treatment process. In the present study, the initial BOD_5/COD of pre-treated effluent was approx. 0.34, which clearly indicates that the effluent is nonbiodegradable; while the biodegradability reached up to 0.58, which is an indication of the positive effect of the applied sonophotocatalytic treatment (Fig. 7). Thus, the results presented agree with those recorded in literature [28]. The amount of total suspended solids, total dissolved solids, sulfate and chloride was reduced up to 96, 99.5, 93.7, and 98.7%, respectively.

5.8. Synergistic effect of ultrasonic treatment

Many studies reported the possible outcomes for the combination of sonolysis and photocatalysis. Actually, increase in surface area of the catalyst by the disaggregation of the catalyst with the help of sonolysis is reported. This will increase the rate of the reaction causing synergistic effect over photocatalysis. In our study, combined effect of ultrasonic and photocatalytic treatment showed synergic results than individual treatment of ultrasound and irradiations with optimized parameters, that is the degradation rate constant for the combined effect was greater than the sum of the degradation rate constants for the individual treatment as clear from the following formula [29]:

$$\%\,\text{synergy} = 100 \times \{(k_{\text{US+UV+TiO}_2\text{+H}_2\text{O}_2}) - (k_{\text{UV+TiO}_2\text{+H}_2\text{O}_2} + k_{\text{US+TiO}_2\text{+H}_2\text{O}_2}) / (k_{\text{US+UV+TiO}_2\text{+H}_2\text{O}_2})\}$$

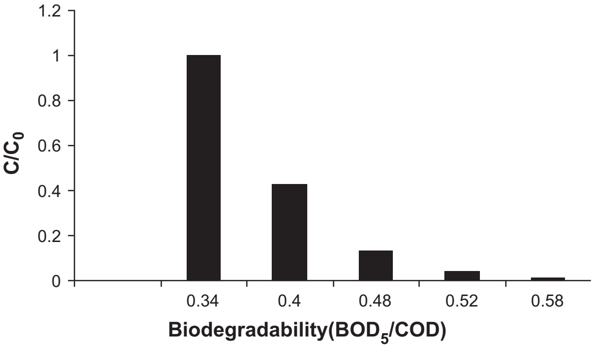

Fig. 7. Biodegradability enhancement during sonophotocatalytic treatment.

In our study, the rate constant of the combined process ($k_{\text{US+UV+TiO}_2\text{+H}_2\text{O}_2}$) is $1.1\,\text{h}^{-1}$ and rate constant of $k_{\text{UV+TiO}_2\text{+H}_2\text{O}_2}$ is $0.57\,\text{h}^{-1}$ and for $k_{\text{US+TiO}_2\text{+H}_2\text{O}_2}$ is $0.15\,\text{h}^{-1.}$

$$k_{\text{UV+TiO}_2\text{+H}_2\text{O}_2} + k_{\text{US+TiO}_2\text{+H}_2\text{O}_2} = 0.57 + 0.15 = 0.72\ \text{h}^{-1}$$

$$k_{\text{US+UV+TiO}_2\text{+H}_2\text{O}_2} = 1.1\ \text{h}^{-1}$$

So, clearly the rate constants of the combined process are greater than the sum of the rate constants of the individual processes.

$$\%\,\text{synergy} = 100 \times \{(1.1) - (0.57 + 0.15)\}/1.1$$

Therefore, synergy percent is 34.5.

The similar kinds of studies have shown the same synergistic effect on the degradation of malachite green in aqueous solution [30].

6. Conclusion

The sonolytic, photocatalytic, and sonophotocatalytic degradation of wastewater was studied in the presence of heterogeneous photocatalyst TiO_2. The following observations can be made based on our experimental investigations.

(1) Ninety-nine percent degradation of pharmaceutical wastewater was achieved using sonophotocatalysis after 4 h of reaction time followed by photocatalytic treatment, that is 90% after 4 h and 45% under sonocatalytic process after same duration.
(2) The 34.5% synergy was quantified as the normalized difference between the rate constants obtained under sonophotocatalysis and the sum of those obtained under separate photocatalysis and sonocatalysis.
(3) The complete degradation of recalcitrant organic pollutants will increase the chances for the reuse of wastewater. Because secondary waste materials are not generated, there is no need to dispose materials. So, we can say that sonophotocatalytic process has large capability for the water treatment.

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