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PHOTOCATALYTIC, SONOLYTIC AND SONOPHOTOCATALYTIC
DEGRADATION OF 4-CHLORO-2-NITRO PHENOL

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Abstract: The photocatalytic, sonolytic and sonophotocatalytic degradation of 4-chloro-2-nitrophenol (4C2NP) using heterogeneous (TiO₂) was investigated in this study. Experiments were performed in slurry mode with artificial UV 125 watt medium pressure mercury lamp coupled with ultrasound (100 W, 33+3 KHz) for sonication of the slurry. The degradation of compound was studied in terms of first order kinetics. The catalyst concentration was optimized at 1.5 gL⁻¹, pH at 7 and oxidant concentration at 1.5 gL⁻¹. The results obtained were quite appreciable as 80% degradation was obtained for photocatalytic treatment in 120 minutes whereas, ultrasound imparting synergistic effect as degradation achieved 96% increase in 90 minutes during sonophotocatalysis. The degradation follows the trend sonophotocatalysis > photocatalysis > sonocatalytic > sonolysis. The results of sonophotocatalytic degradation of pharmaceutical compound showed that it could be used as efficient and environmentally friendly technique for the complete degradation of recalcitrant organic pollutants which will increase the chances for the reuse of wastewater.

INTRODUCTION

Pharmaceuticals form a group of substances that are of considerable importance for society as healthcare tools. The risk is directly proportional to the concentration of the chemical substances in various environmental compartments and pharmaceutical waste adds to that risk if it is not managed properly. Several pharmaceutical compounds have been reported to occur in sewage treatment plant effluents as well as in surface waters of many countries [12], and especially of India [1]. The detected compounds included antibiotics, anticonvulsants, painkillers, cytostatic drugs, hormones, lipid regulators, beta-blockers, antihistamines, and X-ray contrast media. The concentrations of these pharmaceuticals were in the range of µg/L to mg/L in sewage treatment plant effluents and surface water. In addition, a number of polar pharmaceutical compounds and metabolites, such as diclofenac, carbamazepine, sulfamethoxazole, and amidotrizoic acid, have been detected in groundwater samples at concentrations of up to 1 mg/L. Wastewater treatment plants usually exceed current discharge standards; the presence of unregulated pollutants in these effluents is of concern. Unregulated contaminants, or emerging pollutants of

concern (EPOCs), are defined as substances that were previously undetected or had not been considered as a risk [10].

Among the various substances that can be categorized as emerging pollutants, pharmaceutical active compounds (PhACs) are of special concern because of the volumes introduced to the environment, their endocrine disrupting activity, and a potential increase of bacterial resistance. It is estimated that hundreds of tons of PhACs are produced and consumed in developed and developing countries each year [17, 26].

4C2NP is pure yellow crystalline powder, has a melting point between 85 and 87°C and is widely used in pharmaceuticals industries, agriculture related industries as an ingredient in pesticides and insecticides, and as a dye intermediate. Conventional wastewater treatment technologies have limitations to treat the wastewater containing these kinds of biorecalcitrant compounds, hence demanding advanced research to tackle complex wastewater treatment [7]. One of the promising technologies could be the use of single chemical oxidants, or the more effective destruction by the use of advanced oxidation processes (AOPs). These advanced processes have been proven to be powerful and efficient treatment methods for degrading recalcitrant materials or mineralizing stable, inhibitory, or toxic contaminants. Advanced oxidation processes are those groups of technologies that lead to hydroxyl radical (OH \cdot) generation as the primary oxidant (second highest powerful oxidant after the fluorine). These radicals are produced by means of oxidizing agent such as H $_2$ O $_2$ and O $_3$, ultraviolet irradiation, ultrasound and homogeneous or heterogeneous catalysts [2]. Hydroxyl radicals are non-selective in nature and they can react without any other additives with a wide range of contaminants whose rate constants are usually in the order of 10 6 to 10 9 L mol $^{-1}$ s $^{-1}$. These hydroxyl radicals attack organic molecules by either abstracting a hydrogen atom or adding the hydroxyl group to the double bonds. It makes new oxidized intermediates with lower molecular weight or carbon dioxide and water in the case of complete mineralization [16].

When ultrasound is combined with other AOPs, the combination would lead to faster degradation rates when compared to either method alone. If the two modes of irradiations (UV and ultrasound) are operated in combination, a greater number of free radicals will be available for the reaction thereby increasing the rate of reactions [15, 21]. Combining these two modes of irradiations, i.e. US and UV eliminate the drawbacks of individual process and generate a greater number of hydroxyl radicals. Thus the study was undertaken for the degradation of 4C2NP using sonophotocatalytic process. The photocatalytic optimized conditions were used to study the ultrasound treatment to see the viability of synergistic effect due to ultrasound.

REAGENTS, EXPERIMENTAL CONDITIONS, EQUIPMENT DETAILS

4-Chloro-2-nitrophenol 99% pure yellow crystalline powder, was collected as a gift sample from an industry. 4C2NP is highly toxic because it is refractory and hard to remove by conventional biological treatment processes. This compound is known to cause severe pollution problems in aquatic environments (Fig. 1).

The pH adjustment was carried out with H $_2$ SO $_4$ 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 Degussa Company, India branch, Bombay (Evonik).

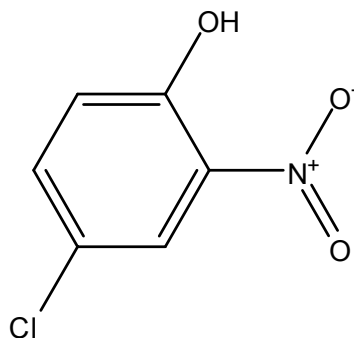


Fig. 1. Structure of 4-chloro-2-nitrophenol

In all experiments Millipore water was used. The spectrum was taken with UV – visible Spectrophotometer (Hitachi V-500 UV/VIS (Japan) double-beam spectrophotometer.

All sonolytic, photocatalytic and sonophotocatalytic experiments were performed using an immersion well photochemical reactor made of Pyrex glass equipped with a 125 watt medium pressure mercury lamp having a wavelength of 365 nm. Short-wavelength UV-radiation and IR-radiation were eliminated by a water circulated glass jacket maintaining a temperature of 25°C. To study the effect of ultrasound the whole photoreactor assembly was immersed into an ultrasonic bath model no. EN 60 US having the capacity 6.5 litre with tank size 12”×6”×6” (100W, 33±3 KHz). Hydrogen peroxide (30% w/v) was obtained from S.D. Fine Chem. Limited having M.W. of 34.01. The aeration was provided using ambient air with flow rate of 1.0 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 the further actual treatment of the 4C2NP.

The stock solution of 0.86 mM 4C2NP was prepared by using Millipore water. An aliquot of 5 ml was taken from the reaction volume of 200 ml at regular intervals of time with help of a syringe and was filtered through syringe filters having pore size of 0.45 µm. The filter was washed every time to ensure that no residual compound remained on the micro filter. These samples were analyzed for COD estimation as well as with UV-Vis spectrophotometer. The (λ)_{max} of 4C2NP was found at 229.5 nm. All experiments were carried out in triplicate for reproducibility of results. Standard closed reflux methods were used for calculating COD [3]. The initial COD of the compound was 980 mgL⁻¹.

PRELIMINARY STUDIES

Blank experiments were carried out in the absence of UV to study the adsorption of the compound 4C2NP. The addition of catalyst in dark showed a very little decrease in concentration, i.e. 9% confirmed spectrophotometrically. The adsorption rate became constant after some time because the adsorption-desorption equilibrium was reached after some time. Thus the results observed from adsorption experiment confirmed that decrease in concentration of compound was due to adsorption, i.e. no degradation of the compound was confirmed. To study the photolytic degradation, the compound was treated in UV

light only. Direct photolysis of the compound yielded only 12–13% degradation after 7 h of irradiations as clear from Fig. 2. Consequently, the photolysis of the compound is negligible and the decomposition that is observed in the presence of the catalyst (TiO_2) is ascribed to the catalyst activity [24].

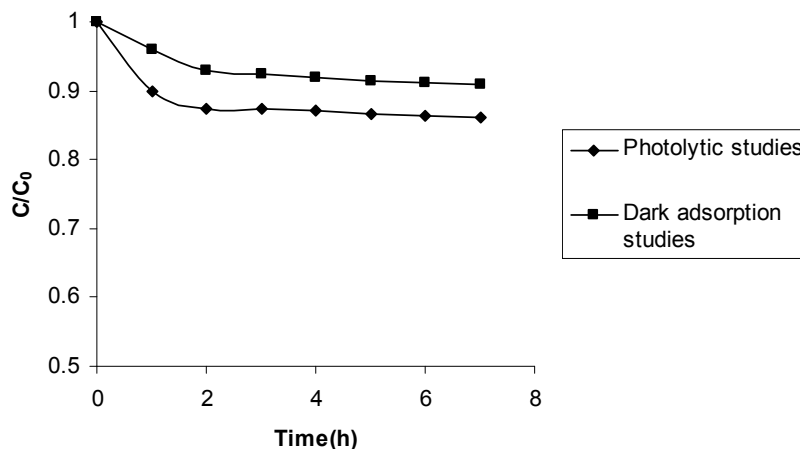


Fig. 2. 4C2NP concentration-time profiles during dark adsorption and photolysis under UV irradiations ($C_0=0.86$ mM, pH= 5.8)

PHOTOCATALYTIC TREATMENT AND PROCESS OPTIMIZATION

The photocatalytic oxidation of various organic contaminants over illuminated TiO_2 fitted the pseudo-first order kinetics model, i.e.

$$-dC/dt = kC$$

$$\text{or } \ln C_0/C = kt$$

A plot of $\ln C_0/C$ versus time represents a straight line, the slope of which upon linear regression equals the first-order rate constant k . Generally first-order kinetics is appropriate for the entire concentration range of ppb or few ppm [13].

Effect of photocatalyst amount

To study the effect of catalyst dose on the degradation of compound, TiO_2 dose was varied from 0.5 to 4.0 gL^{-1} during the photocatalytic treatment process. It was observed that the rate of photocatalytic process increased with the increase in concentration of the catalyst up-to 1.5 gL^{-1} and then decreased. As discussed that initial reduction may be due to the adsorption of the compound but after adsorption-desorption equilibrium is reached, the actual degradation of the compound is observed. As the concentration of TiO_2 is increased, the number of photons absorbed from UV light and the number of compound molecules adsorbed on the surface of catalyst are increased owing to an increase in photocatalytic reaction rate. The addition of excess of TiO_2 above 1.5 gL^{-1} did not significantly enhance the degradation. The reason for this is clustering of catalyst

particles at higher concentrations and thus causing a decrease in the number of active sites on its free surface. Above a certain level, the compound molecules available are not sufficient for the adsorption by the increased number of TiO_2 particles. Hence the increased catalyst amount is not involved in the catalytic activity and the rate does not increase together with an increase in the amount of catalyst beyond a certain limit [23]. Other reasons may be an increase in the opacity and light scattering by the particles. Fig. 3 depicts that the maximum degradation was achieved with 1.5 gL^{-1} of photocatalyst.

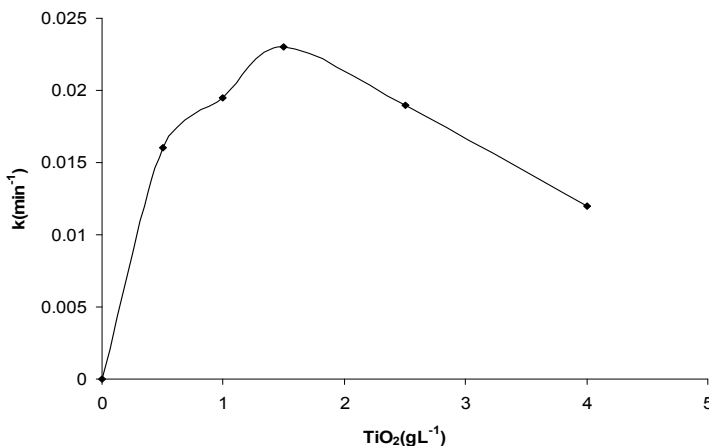
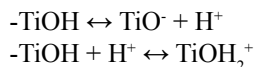


Fig. 3. TiO_2 dose effect on rate constant of 4C2NP photocatalytic degradation, (k was calculated in terms of first order kinetic, $C_0=0.86 \text{ mM}$, $\text{pH}=5.8$)

Influence of pH

The effect of initial pH on the photocatalytic degradation of 4C-2-NP is presented in Fig. 4 with the optimum amount of catalyst. By comparison with experiments performed at natural pH, a considerable influence of pH upon the degradation is observed. The generation of the hydroxyl radicals in AOP's is effected by pH of the solution which is a powerful oxidizing agent.

The effect of the solution pH on the degradation rate can be explained mainly by adsorption of compound on TiO_2 surface. TiO_2 shows an amphoteric character so that either a positive or a negative charge can be developed on its surface. The point of zero charge of the used TiO_2 (Degussa P-25) is widely reported at $\text{pH}\approx 6.5$ [6, 25]. The TiO_2 surface is negatively or positively charged above and below this value according to the following equations:



Hence, employing TiO_2 as photocatalyst the degradation of compound in the aqueous suspensions was studied in the pH range between 4 and 9. It is interesting to note that the degradation rate of phenol was better at neutral pH than in acidic and alkaline conditions. In our study the degradation rate was maximum at pH 7.0 but decreased after 7.0 and

continues to decrease in alkaline conditions. Thus the pH 7.0 was selected as optimum pH. Moreover, the final pH after photo catalytic treatment was 6.5 which is suitable for biological treatment as well as discharge of compound into the water bodies [20.]

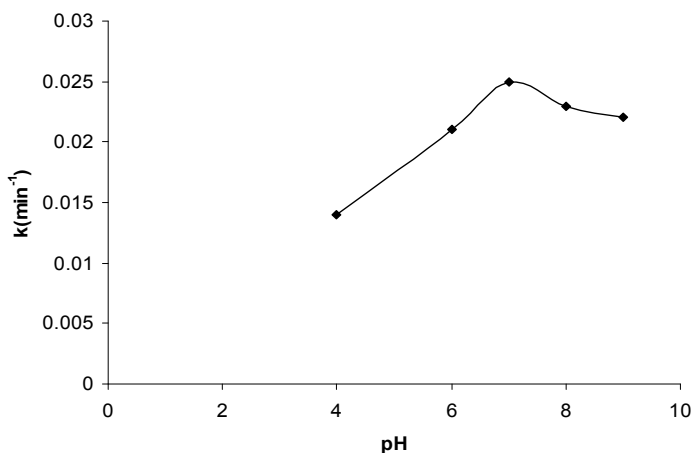
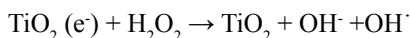


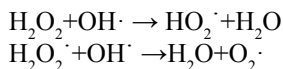
Fig. 4. pH effect on the rate constant, k , of 4C2NP photocatalytic degradation
{ $C_0=0.86$ mM, $TiO_2 = 1.5$ gL⁻¹}

Effect of Oxidant addition

One of the major reasons for decrease in the required quantum yield thus reaction rate is the undesired electron/hole recombination which represents the major energy-wasting step. One possible way to increase the reaction rate is to increase the concentration of OH radicals because these species are promoters of photocatalytic degradation. The addition of hydrogen peroxide/electron acceptors to the photocatalytic treatment process increases the concentration of OH radical, since it impairs the electron-hole recombination, according to the following equation:



It accepts the photo generated electron from the conduction band and thus promotes the charge separation, and it also forms OH radicals. However at high concentrations of H_2O_2 it also acts as scavenger as shown in the following equation [5].



With this view, we have studied the effect of oxidant dose (H_2O_2) concentrations on the photocatalytic treatment from 0.75 to 4.5 gL⁻¹ at constant pH of 7 and catalyst dose of 1.5 gL⁻¹. It has been observed that best results were obtained when oxidant addition came out to be 1.5 gL⁻¹ of the sample and has been taken as the optimum amount required for maximum effective treatment of compound and the results are depicted in Fig 5.

The effect of H_2O_2 has been reported in various studies and it shows that the degradation rate increases together with increases in addition of H_2O_2 , becomes maximum

at certain level and then starts decreasing with further increase in the concentration of H_2O_2 due to the reasons cited above. S.K.Kavitha and P.N.Palanisamy have reported a similar behavior during photocatalytic and sonophotocatalytic degradation of Reactive Red 120 using Dye sensitized TiO_2 under visible Light [11].

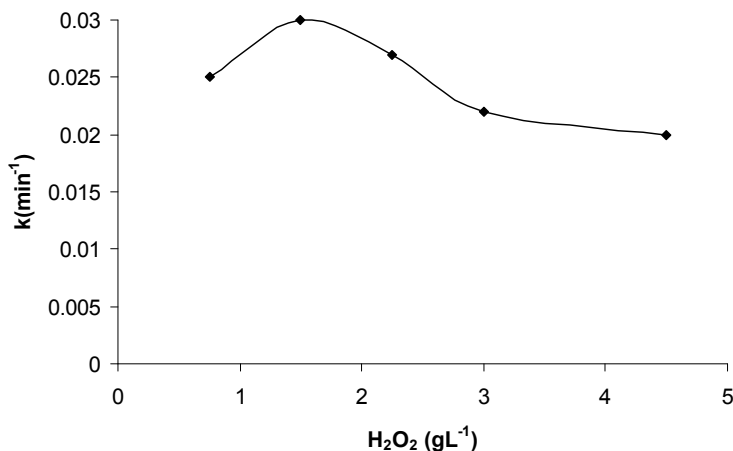


Fig. 5. H_2O_2 dose effect on the rate constant, k , of 4C2NP photocatalytic degradation ($C_0=0.86$ mM, $TiO_2=1.5$ gL⁻¹, pH =7)

EFFECT OF ULTRASOUND

Comparison of Sonolytic (US) and Sonocatalytic (US+TiO₂) and (US+ TiO₂+H₂O₂)

Sonolysis is the breaking of chemical bonds or formation of radicals using ultrasound. The action of ultrasound allows for the creation of micro bubbles in water at high temperature and pressure, leading to localize transient supercritical conditions. This leads to the production of active radicals (H^\cdot and OH^\cdot) 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 the following figure that maximum degradation was achieved with US+ TiO_2 + H_2O_2 then US + TiO_2 and then US. Fig. 6 shows Sonolysis with all optimum parameters (i.e. i. US+ TiO_2 + H_2O_2 , ii. US+ TiO_2) shows better results than alone Sonolysis because ultrasound plays a profound role due to substantial increase in the number of active sites. 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 [8].

Photocatalytic and Sonophotocatalytic degradations

In order to check the synergistic effect provided by ultrasound, photocatalytic treatment (UV+ TiO_2 + H_2O_2) with all optimized parameters was compared with sonophotocatalytic treatment (UV+US+ TiO_2 + H_2O_2) shown in Fig 7. The studies revealed that sonophotocatalytic degradation resulted in faster degradation rates of the contaminants than that during the individual treatment under similar conditions. This is because in heterogeneous catalytic systems, the use of ultrasound creates conditions of increased

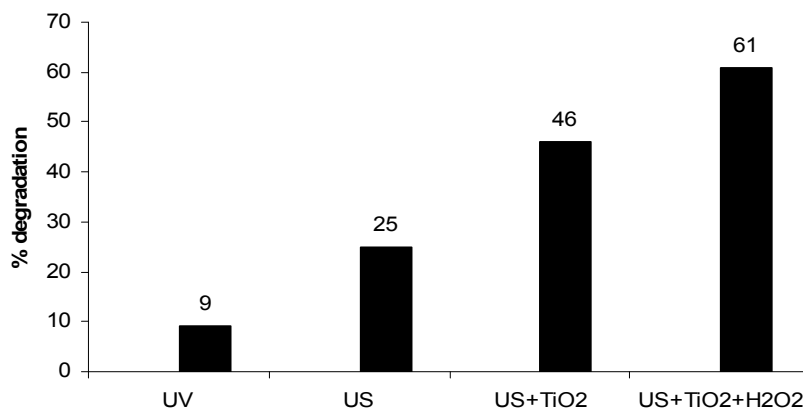


Fig. 6. Degradation of 4C2NP using various processes ($C_0=0.86$ mM, $\text{pH}=7$, $\text{H}_2\text{O}_2=1.5$ gL⁻¹, $\text{TiO}_2=1.5$ gL⁻¹)

turbulence in the liquid, thus decreasing mass transfer limitation and increasing the surface area available due to catalyst fragmentation and de-agglomeration. The reason for this is that the basic mechanism for both ultrasound and photocatalytic oxidation is generation of free radicals. If these modes of irradiations are operated in combination, a greater number of radicals will be available for the reaction. Under the optimized conditions for sonophotocatalytic there was 18% increase in the degradation rate in comparison to photocatalytic and it was almost 58% when compared to sonocatalytic after one hour of treatment. A.S. González and S.S. Martínez have shown similar results on the degradation of basic blue 9 industrial textile dyes [9].

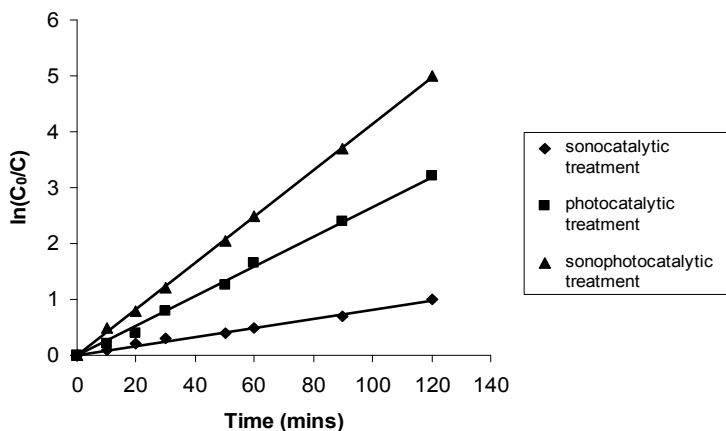


Fig. 7. Degradation as a function of irradiation time for sonocatalytic, photocatalytic and sonophotocatalytic processes ($C_0=0.86$ mM, $\text{TiO}_2 = 1.5$ gL⁻¹, $\text{H}_2\text{O}_2 = 1.5$ gL⁻¹, $\text{pH}=7$)

Mineralization studies

The disappearance of parent compound peaks from UV spectrum confirms the degradation of the compound under study (Fig. 8). Total mineralization of the compound

should be considered since the intermediate products of some compounds can sometimes be more toxic than the original compound itself. COD reflects the degree to which the mineralization of an organic species has occurred. Therefore, the reduction of COD is also monitored along with 4C-2-NP concentration (Silva et. al., 2007). Percentage reduction of COD after the sonophotocatalytic treatment is shown in Fig 9. Neither sonocatalytic nor photocatalytic alone totally remove COD. But both in combination that is sonophotocatalytic process showed a considerable reduction in COD (96%).

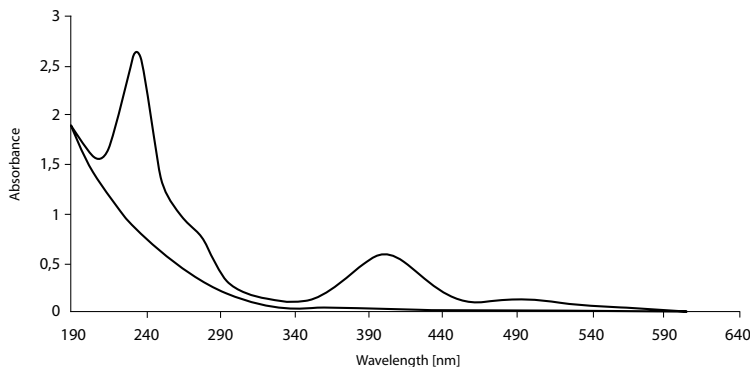


Fig. 8. Absorption spectra of 4C2NP solution ($C_0=0.86$ mM) recorded before and after 1.5 h of the sonophotocatalytic treatment ($\text{pH}=7$, $[\text{H}_2\text{O}_2]=1.5$ gL $^{-1}$, $[\text{TiO}_2]=1.5$ gL $^{-1}$, optical length = 10 mm)

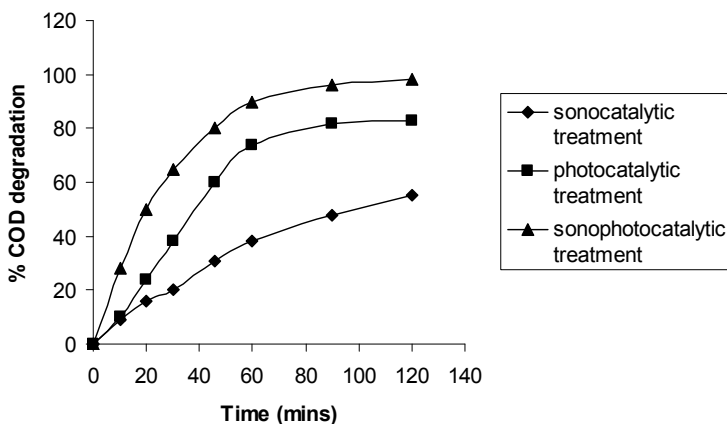
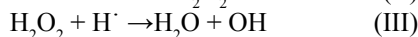
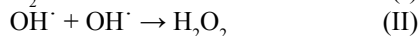
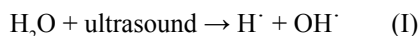


Fig. 9. Reduction in COD using various processes ($C_0=0.86$ mM, $\text{pH}=7$, $\text{H}_2\text{O}_2=1.5$ gL $^{-1}$, $\text{TiO}_2=1.5$ gL $^{-1}$)

Synergistic effect with ultrasound

Several studies have proposed the concept of synergy between photocatalysis and sonophotocatalysis (Selli, 2002). Actually the ultrasound promoted reactions increased the catalytic activity of TiO_2 by de-aggregating the catalyst particles, thus increasing the surface area for the reaction. Secondly, the increased production of hydroxyl radicals as per the following reactions [22]:



Also the mass transport enhancement between liquid and the solid catalyst surface induces synergy to the reaction. This synergistic effect was studied between ultrasound and ultraviolet irradiation in our study since rate constants of the combined process ($k_{\text{US+UV+TiO}_2+\text{H}_2\text{O}_2}$) are greater than the sum of the rate constants of the individual processes ($k_{\text{UV+TiO}_2+\text{H}_2\text{O}_2} + k_{\text{US+TiO}_2+\text{H}_2\text{O}_2}$). The synergy can be quantified as the normalized difference between the rate constants obtained under sonophotocatalysis and the sum of those obtained under separate photocatalysis and sonocatalysis [14].

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

In our study the rate constant of combined process ($k_{\text{US+UV+TiO}_2+\text{H}_2\text{O}_2}$) is $.0411 \text{ hr}^{-1}$ and the rate constant of $k_{\text{UV+TiO}_2+\text{H}_2\text{O}_2}$ is 0.0279 hr^{-1} and for $k_{\text{US+TiO}_2+\text{H}_2\text{O}_2}$ is 0.0077 hr^{-1}

$$k_{\text{UV+TiO}_2+\text{H}_2\text{O}_2} + k_{\text{US+TiO}_2+\text{H}_2\text{O}_2} = .0279 + .0077 = .0356 \text{ hr}^{-1}$$

$$k_{\text{US+UV+TiO}_2+\text{H}_2\text{O}_2} = 0.0411 \text{ hr}^{-1}$$

So it is clear that the rate constants of the combined process are greater than the sum of the rate constants of the individual processes.

Therefore, synergy is 13.3%

Berberidou C. et al. have shown a similar synergistic effect on the degradation of Malachite green in aqueous solution [4].

CONCLUSION

- 4-chloro-2-nitrophenol has been successfully degraded in the presence of TiO_2 photocatalyst. In the case of stock solution of 0.86 mM concentration, degradation was found to be 80% in 2 hours of UV light exposure at the optimized reaction conditions like pH of 7, catalyst dose of 1.5 gL^{-1} and oxidant concentration of 1.5 gL^{-1} . Hence, it is deduced that UV can be effectively used for the compound degradation.
- Sonophotocatalytic treatment has synergy effect on the degradation of pollutants as confirmed by the percentage degradation in this case reaches up to 96% in 90 minutes. The addition of ultrasound treatment with AOP's can have synergetic effect on the degradation of most priority pollutants.
- The mineralization studies were done in terms of COD reduction and 96% reduction in COD value shows that organic compounds are converted into simpler ones. Hence, it can be concluded from the observations that sonophotocatalysis can be suitably and effectively employed for the degradation of 4-chloro-2-nitrophenols.

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