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Photocatalytic and photochemical degradation of nitrobenzene using artificial ultraviolet light

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Abstract

Photocatalytic degradation of nitrobenzene has been studied using a semiconductor as photocatalyst and an artificial UV source. The effect of catalyst loading, pH and anions on the photocatalytic degradation of nitrobenzene has been investigated. A kinetic model for the photocatalytic process was investigated. Two types of commercial catalysts Degussa P-25 and Aldrich-TiO_2 (anatase TiO_2 having surface area $250\,m^2\,g^{-1}$) have been compared. Also the degradation has been studied using two different lamps of different λ_{max}. A comparison of photocatalytic degradation of nitrobenzene with phenol showed that nitrobenzene degrades more rapidly than phenol. Further, photochemical degradation of nitrobenzene using hydrogen peroxide and artificial UV lamp has been studied and found to be inferior to the photocatalytic degradation.

Keywords: Nitrobenzene; TiO_2; Phenol; UV light; Photocatalysis; H_2O_2

1. Introduction

Water pollution is a serious problem throughout the world. According to the UN's latest figures, approximately 40% of the world's population of more than two billion people face water shortage. By 2025, this figure is expected to increase to 5.5 billion or more than 2.5 times the present population. Chemical industry is at the forefront of the water management challenge, due to increasing government pressure on effluent discharge, raw water usage, increasing process water costs and in many locations, general lack of available water. For instance, Asian countries and African countries have a serious water shortage. Therefore, treatment of wastewater is a very critical issue for chemicals industries [1].

The treatment of wastewater is being increasingly challenged with the identification of more and more contaminants. Increased knowledge about the consequences from water pollution and the public desire for better quality water has promoted the implementation of much stricter regulations by expanding the scope of regulated contaminants and lowering their maximum contaminant levels (MCLs). The other important factors as mentioned above are the diminishing water resources, rapid population and industrial growth. Therefore the treatment and reuse of municipal and industrial wastewaters is becoming more critical. This is especially true in arid or semiarid areas where potable water and irrigation water has to be imported at great expense.

Advanced oxidation processes (AOPs), hold great promise to provide alternatives for better protection of public health and the environment. In the last decade, these processes have been shown to be effective for the destruction of refractory pollutants [2–4]. They are based on the generation of highly reactive and oxidizing hydroxyl radicals. O_3/UV, H_2O_2/UV, TiO_2/air/UV are the main types of AOPs that have been suggested. Various combinations of them are employed for complete mineralization of pollutants. Ozone is hazardous and has to be generated on site; furthermore, the off gases need strict monitoring. H_2O_2 on the other hand is available as a solution with good shelf life and therefore has an advantage over O_3. Photocatalytic process (TiO_2/air/UV) has significant advantages such as complete mineralization, mild temperature and pressure required and low cost as compared to the conventional processes [5]. Several important studies on photocatalytic degradation of organic compounds in a slurry reactor are reported in the literature [6–11].

Aromatic nitro compounds are commonly used in industrial processes (manufacture of pesticides, dyes and explosives) and as a consequence they appear as contaminant in all kinds of water sources especially in surface water and industrial wastewaters [12]. In the present work, nitroben-

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Nomenclature

C	concentration nitrobenzene after time t (mg l^{-1})
C_0	initial concentration of the nitrobenzene (mg l^{-1})
$C_{t=0}$	concentration of nitrobenzene at time $t = 0$, before the nitrobenzene solution was exposed to UV light (mg l^{-1})
k_{obs}	pseudo-first-order rate constant (l/mg)
K_{c}	second order rate constant (mg/min)
TOC	total organic carbon after time t (mg l^{-1})
$\mathrm{TOC}_{t=0}$	total organic carbon at time t, before the nitrobenzene solution was exposed to UV light (mg l^{-1})

Greek letter

λ	wavelength of light (nm)

zene (NB) is chosen as a model pollutant, because NB is listed as a priority pollutant. It is a very toxic substance and the maximum allowable concentration for NB is 1 mg l^{-1} in wastewaters. It is readily absorbed on contact with the skin and by inhalation of vapours. It affects the central nervous system and produces fatigue, headache, vertigo, vomiting, general weakness, unconsciousness, and coma [13].

This work deals with degradation of NB and is a part of our ongoing study on photocatalytic/photochemical degradation of benzenoid compounds such as phenol [5], *p*-hydroxy benzoic acid [14], benzoic acid [15], aniline [16], benzenesulfonic acid [17] and chlorobenzene [18].

Substantial research work has been reported on the treatment of nitrobenzene by advanced oxidation processes. The details of various literature investigations on destruction of nitrobenzene using AOPs are given below.

Matthews et al. studied photocatalytic degradation of NB and other compounds in a spiral reactor with immobilized TiO_2. They used initial TOC concentrations between 1.75 and 4.25 mg l^{-1} with various organic solutes such as acetic acid, benzoic acid, nitrobenzene, methanol, etc. They achieved 95–100% degradation using photocatalysis [19]. Makarova et al. used surface modified TiO_2 using specific chelating agents such as arginine, lauryl sulfate and salicylic acid and reduced NB [20]. The photocatalytic degradation of NB, nitrosobenzene, phenylhydroxylamine, aniline, and 4-nitrosophenol was studied in aerated conditions. They showed that in slightly acidic TiO_2 suspensions all these compounds yield quantitative formation of carbon dioxide whereas nitrogen is converted into nitrate and ammonium ions [21]. Pelizzetti et al. studied the degradation of NB and atrazine over TiO_2 and ZnO. They indicated that the detected intermediates disappear with comparable or even faster rates with respect to the initial compound [22]. The photocatalytic degradation of nitrobenzene, chlorobenzene and phenol using concentrated solar radiation in a novel photocatalytic reactor was studied by Kamble et al. [23].

The present work deals with PCD of nitrobenzene using UV radiation and reports the effect of various parameters like presence of anions, pH, wavelength of light, etc. Industrial effluents contain apart from pollutants different salts at different levels of concentration. The presence of anions such as chloride, sulfate, carbonate, and bicarbonates is common in industrial effluents. These ions affect the adsorption of the degrading species, act as hydroxyl ion scavengers and may absorb UV light as well. Therefore, the effects of these salts on photocatalytic degradation of nitrobenzene are important. Generally industrial effluent is neutral, but sometimes it may be acidic or basic. In the case of nitrobenzene the wastewater coming from nitration is likely to be acidic in nature. Hence, it is necessary to study the effect of pH on PCD of nitrobenzene. The effect of these parameters on PCD of nitrobenzene is not available in the published literature. In an earlier study, the PCD of NB using solar radiation has been reported [24]. The purpose of this investigation is to compare the two processes using concentrated solar radiation [24] and artificial UV light. Solar radiation is cost effective but is available during daytime of certain seasons only.

2. Experimental

2.1. Materials

Degussa P-25 TiO_2 (70:30 anatase to rutile % (w/w)) with an average particle size of 30 nm and BET surface area about 55 m^2 g^{-1} was used as the photocatalyst [25]. Aldrich-TiO_2 (pure anatase) having surface area about 250 m^2 g^{-1} was also used in a few experiments. NB was supplied by E. Merck (India) and sodium chloride, sodium carbonate, sodium bicarbonate and sodium sulfate used were supplied by s.d. finechem (India) and were of analytical reagent grade. All the reaction mixtures and HPLC mobile phase solutions were prepared in deionized water.

2.2. Experimental methods

All the experiments were carried out in a quartz cylindrical reactor (i.d. 8 cm) of 465 cm^3 capacity fitted with a centrally mounted sparger surrounded by a cooling coil (i.d. 4 cm), both made of borosilicate glass and a water cooled glass condenser for the outgoing gases/vapours (Fig. 1). The initial temperatures of the reaction mixtures were in the range of 28–32 °C and the final temperature was in the range of 32–35 °C during the PCD of nitrobenzene. The temperature of the reaction mixture was maintained at ambient temperature by passing water through the cooling coil. Further water was passed through the coil inside the reactor, therefore the temperature of the reaction mixtures did not increases at 30 °C. A condenser with chilled water

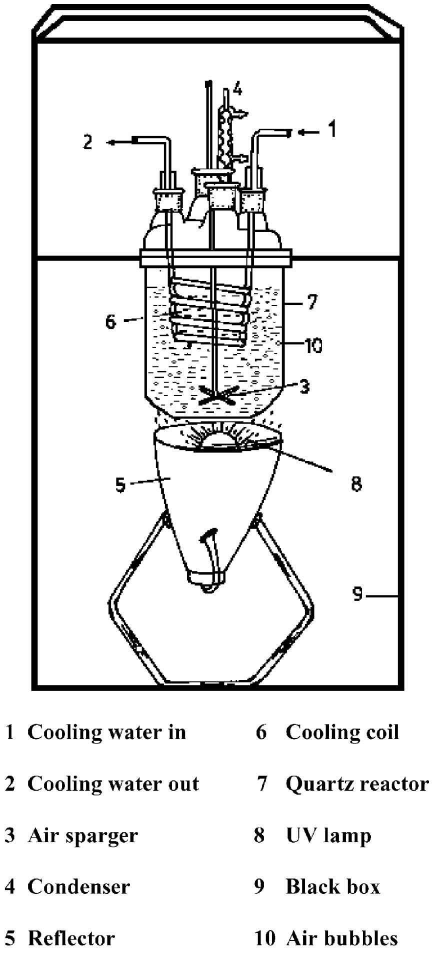

Fig. 1. Experimental setup for photocatalytic and photochemical degradation of NB using UV lamp.

was also provided at the reactor exit to further eliminate the losses of water and pollutants. A sample of the exit gas analyzed by gas chromatography showed no traces of any organic compound. Hence, there was a negligible loss of nitrobenzene/intermediates during the experiment. The whole assembly was enclosed in an acrylic enclosure wrapped externally with black paper. In each experiment 400 ml of solution was charged in the reactor. The reaction mass was irradiated using 125 W Phillips UV lamp from the bottom of the reactor. Lamps with λ_{max} of 365 and 253 nm were used separately.

In most of the photocatalytic experiments Degussa P-25 TiO_2 was used as the photocatalyst. Some experiments were conducted using Aldrich-TiO_2 (pure anatase with BET surface area about $250\,m^2\,g^{-1}$). The solution was equilibrated by stirring for 30 min in the dark before exposing the reactor assembly to the concentrated UV light. A sample was removed for analysis. The concentration of NB in this filtered sample was treated as the zero time concentration in each experiment before exposure to radiation. Presaturated air was bubbled at sufficiently high velocity (>$2\,cm\,s^{-1}$) to keep all the TiO_2 in suspension.

2.3. Analysis

In the case of photocatalytic experiments samples were centrifuged and filtered through a membrane filter to separate out TiO_2 particles. Concentrations of NB and its intermediates were measured by HPLC (TOSOH) equipped with a C-18 column (5 μm, particle diameter, Merck) and UV-Vis detector. The best mobile phase was determined for proper separation of possible intermediates from several combinations and used. Methanol:water (50:50%, v/v) was used as the mobile phase with a flow rate of $1\,ml\,min^{-1}$ and $\lambda = 270\,nm$. The elution times for *m*-nitrophenol, 4-nitrocatechol, 2-nitroresorcinol, *p*-nitrophenol, *o*-nitrophenol (intermediates in photocatalytic and photochemical degradation processes) and NB were 1.4, 2.42, 3.1, 6.27, 9.38, 11.33 min, respectively.

Total organic carbon (TOC) was calculated from HPLC analysis and verified using a 915B Total Organic Carbon Analyzer (Beckman Industrial^{TM}, USA). These values matched within ±2% indicating that the HPLC analysis could detect all the intermediates. Pure nitrogen was bubbled through the samples before TOC analysis to remove the dissolved CO_2.

3. Results and discussion

3.1. Effect of catalyst loading

Photocatalytic/photochemical degradation experiments for NB were conducted in the reactor assembly shown in Fig. 1. In each experiment 400 ml aqueous solution of $600\,mg\,l^{-1}$ NB feed was taken. The TiO_2 concentration was varied from 0.05 to 0.3% (w/v) to study its effect on the rate of photocatalytic degradation of nitrobenzene. To study the effect of various parameters like pH, anions, initial concentration, etc. low concentration of TiO_2 (0.05%, w/v) was employed because, the rate of nitrobenzene degradation using artificial UV radiation is relatively high as compared to solar radiation. Each experiment was conducted for 1 h and samples were taken at 15 min interval. As shown in Fig. 2 the optimum catalyst loading is 0.2% (w/v of solution). The percentage degradation increases as the catalyst loading is increased and then after a certain value decreases as the catalyst loading is increased. This is due to the fact that as the loading is increased the light penetration decreases due to increased solution opacity and hence decreases the degradation. A similar effect was observed in the case of photocatalytic degradation of aniline and benzenesulfonic acid using Degussa P-25 TiO_2 and concentrated solar radiations [16,17].

3.2. Kinetic modelling of photocatalytic reaction

The relative decrease of the nitrobenzene concentration, C/C_0, with illumination time for the various initial concentrations is shown in Fig. 3. The initial nitrobenzene

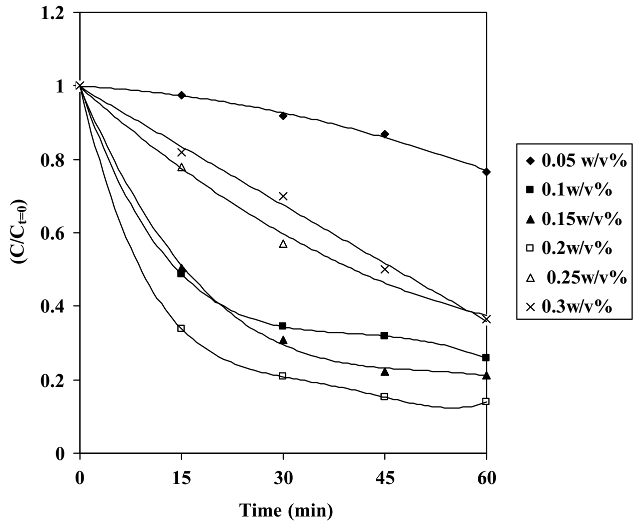

Fig. 2. Optimum catalyst loading for photocatalytic degradation of NB using UV lamp (initial concentration 600 mg l^{-1}, 365 nm UV lamp).

concentration has a pronounced effect on the amount of nitrobenzene degraded. At the same illumination time the percentage of nitrobenzene degraded is smaller if the initial nitrobenzene concentration is higher. It should be noted that the decay function, C/C_0, appears to indicate a pseudo first order kinetics.

The pseudo-first-order rate expression is given by

$$-\frac{\mathrm{d}C}{\mathrm{d}t} = k_{\mathrm{obs}}C \tag{1}$$

Integration of Eq. (1) form $C = C_0$ to $C = C$ yield the following equation:

$$-\ln\frac{C}{C_0} = k_{\mathrm{obs}}t \tag{2}$$

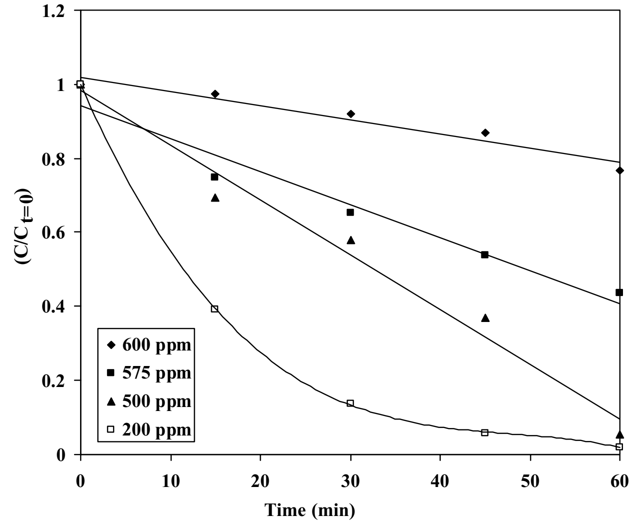

Fig. 3. Effect of initial concentration on photocatalytic degradation of NB using UV lamp: (□) initial concentration 200 mg l^{-1}; (▲) initial concentration 500 mg l^{-1}; (■) initial concentration 575 mg l^{-1}; (◆) initial concentration 600 mg l^{-1}.

where C is the concentration nitrobenzene at time t, C_0 the initial concentration of nitrobenzene and k_{obs} the pseudo-first-order rate constant.

It is well known that the rate of photocatalytic reaction depends upon the concentration of OH$^{\bullet}$ radicals [23,25,26]. The rate determining step of the catalyzed reaction (photocatalytic reaction) is considered to be the reaction between OH$^{\bullet}$ radicals and organic molecules on the catalyst surface. Therefore the reaction rate for second order surface decomposition of nitrobenzene may be written in terms of Langmuir–Hinshelwood kinetics as [27]:

$$r = k''\theta_{\mathrm{OH}}\theta_{\mathrm{C}} \tag{3}$$

where k'' is the surface second order rate constant, $\theta_{\mathrm{OH}^{\bullet}}$ the fractional site coverage by hydroxyl radicals and θ_{C} the fraction of sites covered by nitrobenzene. These two last variables can be written as

$$\theta_{\mathrm{OH}^{\bullet}} = \frac{K_{\mathrm{O}_2}P_{\mathrm{O}_2}}{1 + K_{\mathrm{O}_2}P_{\mathrm{O}_2}} \tag{4}$$

$$\theta_{\mathrm{C}} = \frac{KC}{1 + KC + \sum_i K_i I_i} \tag{5}$$

where K_{O_2}, K and K_i are equilibrium adsorption constant and I the intermediate products of nitrobenzene degradation. Eq. (5) can be modified by making the following assumption:

$$KC + \sum_i K_i I_i = KC_0 \tag{6}$$

A further assumption that the adsorption coefficients for all organic molecules present in the reacting mixture are effectively equal is made. Substituting Eq. (6) into Eq. (5) gives the following expression:

$$r = k''\frac{K_{\mathrm{O}_2}P_{\mathrm{O}_2}}{1 + K_{\mathrm{O}_2}P_{\mathrm{O}_2}}\frac{KC}{1 + KC_0} \tag{7}$$

Owing to the fact that the oxygen partial pressure remained constant for all photocatalytic runs, the fractional sites coverage by hydroxyl radicals could be considered to be constant. Thus,

$$k''\frac{K_{\mathrm{O}_2}P_{\mathrm{O}_2}}{1 + K_{\mathrm{O}_2}P_{\mathrm{O}_2}} = \text{constant} = k_{\mathrm{c}} \tag{8}$$

Eq. (7) can therefore be written as

$$r = k_{\mathrm{c}}\frac{KC}{1 + KC_0} = k_{\mathrm{obs}}C \tag{9}$$

Eq. (9) is a first order kinetics equation with respect to the organic concentration. The relationship between k_{obs} and C_0 can be expressed by a linear equation:

$$\frac{1}{k_{\mathrm{obs}}} = \frac{1}{k_{\mathrm{c}}K} + \frac{C_0}{k_{\mathrm{c}}} \tag{10}$$

The values of k_{c} and K can be calculated by plotting $1/k_{\mathrm{obs}}$ versus C_0. The values of k_{obs} and k_{c} were obtained by regressing the data according to Eq. (10) and found to be

Table 1
Comparison of UV lamps of different wavelength in case of photocatalytic degradation of NB

Catalyst loading (% (w/v) of solution)	0.2	0.05	0.2
Initial NB concentration (mg l^{-1})	300	400	500
% degradation using 365 nm lamp	99.6	91.6	94.9
% degradation using 253 nm lamp	99.22	92.2	95.4

0.0103 l/mg and 7.36 mg/min, respectively. The objective of this kinetic modeling is to determine the reaction rate constants for photocatalytic reaction. These reaction rate constants may be useful for comparison with other processes like photolysis. The regression coefficient for the fit equation (10) is $R^2 = 0.96$.

3.3. *Effect of wavelength*

Photocatalytic degradation experiments were conducted using Degussa P-25 as the catalyst and using UV lamps emitting lights at λ_{max} 253 and 365 nm, respectively. Both lamps gave almost similar degradation as can be seen from Table 1. This may be due to the fact that the generated $OH^{\bullet}$ concentration must be nearly the same in both the cases. This is in agreement with the results of Hofstadler et al. [28]. Using pulsed photocatalysis they found negligible difference in TOC removal with the shorter and longer wavelength in the case of 4-chlorophenol degradation. It may be noted that λ_{min} for anatase TiO_2 is 387 nm [25]. Thus, it appears that a wavelength below 387 nm is sufficient.

3.4. *Effect of presence of anions on photocatalytic degradation*

The presence of inorganic ions has been shown to influence the kinetics and mechanism of the transformation processes of organic compounds. It is well known that photocatalytic reactions occur at the surface of the semiconductor particle, so that specific adsorption of ions may affect the system performance [29]. Specific adsorption of ions can give surficial coordination reactions at the oxide–water interface [30]. The adsorption degree is dependent on the value of pH and on the exchange reactions with the surface hydroxyl groups. The surface occupation by anions may be competitive with the adsorption of organic molecules, this effect being directly related to their coverage fraction.

The effect of presence of common anions, chloride, carbonate, bicarbonate, sulfate and nitrate was studied using the corresponding sodium (Na^+ as cation). All the experiments were carried out using 0.1 M solutions of the anions with initial NB concentration of 500 mg l^{-1} and 0.05% (w/v) of catalyst loading, and 365 nm UV lamp. The effect of presence of these anions on photocatalytic degradation of NB showed the following trend (Fig. 4):

$$HCO_3^{-} > Cl^{-} > CO_3^{2-} > SO_4^{2-} > NO_3^{-}$$

The pronounced effect of chloride, bicarbonate and carbonate is due to their effect on adsorption of NB on the

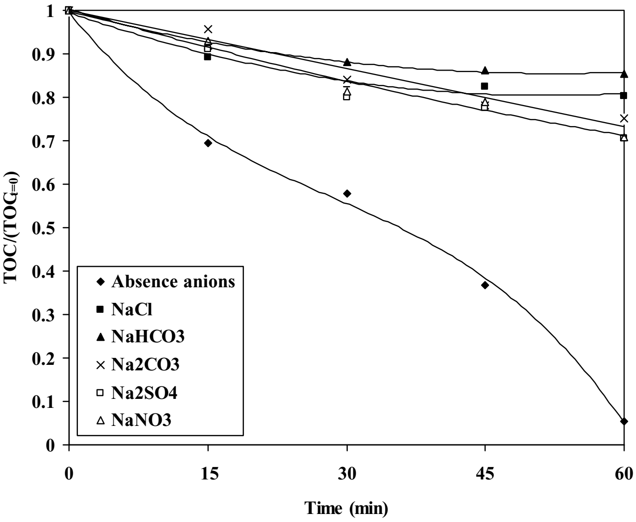

Fig. 4. Effect of presence of anions on photocatalytic degradation of NB (initial concentration 500 mg l^{-1}, catalyst loading 0.05 w/v of solution, 365 nm UV lamp): (◆) photocatalytic degradation of NB in the absence of anions; (■) photocatalytic degradation of NB in the presence of 0.1 M NaCl; (▲) photocatalytic degradation of NB in the presence of 0.1 M $NaHCO_3$; (×) photocatalytic degradation of NB in the presence of 0.1 M Na_2CO_3; (□) photocatalytic degradation of NB in the presence of 0.1 M Na_2SO_4; (△) photocatalytic degradation of NB in the presence of 0.1 M $NaNO_3$.

photocatalyst and their ability to act as hydroxyl radical scavengers by the following reactions:

$$OH^{\bullet} + Cl^{-} \rightarrow Cl^{\bullet} + OH^{-} \quad (11)$$

$$CO_3^{2-} + HO^{\bullet} \rightarrow CO_3^{\bullet -} + H_2O \quad (12)$$

$$HCO_3^{2-} + HO^{\bullet} \rightarrow CO_3^{\bullet} + H_2O \quad (13)$$

These ions might also block the active sites of the catalyst surface thus deactivating the catalyst towards the organic molecules [31].

The carbonate radical anion is a weak oxidizing agent that hardly reacts with other molecules [32]. The detrimental effect showed by chloride is due to its strong effect on adsorption. Sulfate and nitrate have comparatively smaller effect on adsorption and consequently on the photocatalytic degradation [4]. The trend of effect of anions is the same as that in the case of photocatalytic degradation of NB using solar radiation [24]. The catalyst loading used for studying the anion effect was much smaller than the optimum. Thus, the degradation can be improved by increasing the catalyst loading. The amounts of intermediates formed were negligible even in the presence of anions; as against appreciable amount of intermediates, observed in the case of solar assisted degradation in presence of anions [24]. This may be attributed to higher concentration of $OH^{\bullet}$ due to greater supply of the photons in the UV range in the case of photocatalytic degradation using UV lamp.

3.5. Effect of pH

The pH of the aqueous solution significantly affects titanium dioxide (TiO_2), in term of the surface charge on the photocatalyst, the size of the aggregates it forms and also the state of ionization of the substrate and hence its adsorption. The pH at which the surface of an oxide is uncharged is defined as the zero point charge (pH_{zpc}), which for TiO_2 is around 7.

Above and below this value, the catalyst is negatively or positively charged according to the following equations:

$$–TiO_2^- \leftrightarrow TiOH + H^+ \tag{14}$$

$$–TiOH \leftrightarrow TiO^- + H^+ \tag{15}$$

The photocatalytic degradation of the ionisable organic compounds is affected by the pH. In many cases, a very important feature of photocatalysis is not taken into account when it is to be used for decontamination of water, is that during the reaction, a multitude of intermediate products are produced that may behave differently depending on the pH of the solution [33].

Effect of pH on the photocatalytic degradation of NB was studied using initial concentration of $500\,mg\,l^{-1}$ and catalyst loading of 0.05% (w/v of solution). The pH was adjusted using NaOH in the case of alkaline solutions and using $HClO_4$ in the case of acidic solutions. From Fig. 5 it can be clearly observed that pH has a negligible effect on the photocatalytic degradation of NB. NB does not have a group (e.g. OH, NH_2), which can react with acid/base and ionize under different pH. In such cases pH is expected to play a negligible role in the PCD [4,24].

3.6. Comparison of Degussa P-25 and Aldrich-TiO_2

Photocatalytic degradation experiments were conducted using initial concentration of $500\,mg\,l^{-1}$ of NB and 0.05% (w/v of solution) catalyst loading and using 365 and 253 nm UV lamps. The results are shown in Fig. 6. Clearly Degussa P-25 is a better catalyst than Aldrich-TiO_2. The surface area of Aldrich-TiO_2 is $250\,m^2\,g^{-1}$ whereas for Degussa P-25 the same is $55\,m^2\,g^{-1}$. Although the surface area of Aldrich-TiO_2 is five times that of Degussa P-25; the degradation is greater using Degussa P-25. Anatase is more active crystalline form of TiO_2 as compared to rutile. However, the presence of rutile in Degussa P-25 decreases the recombination of the generated $OH^\bullet$ radicals which is responsible for the greater activity of Degussa P-25 [34]. The better performance of Degussa P-25 which is partly anatase (70%) and rutile (30%) is an indication that the rutile part is helpful in preventing the recombination of positive holes in the valence band and electrons in the conduction band.

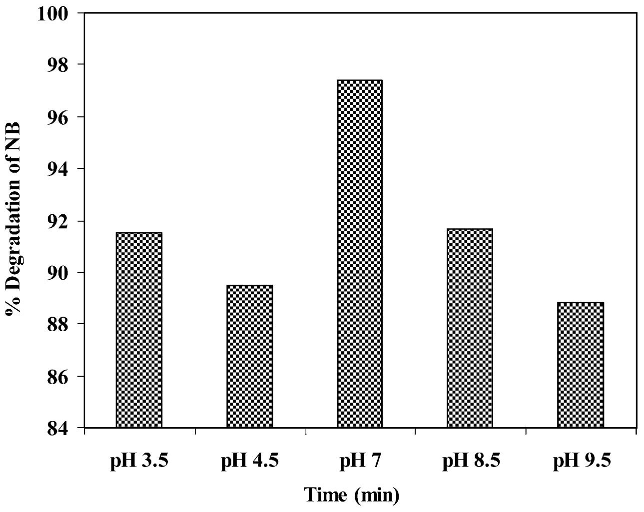

Fig. 5. Effect of pH on photocatalytic degradation of NB (initial concentration $500\,mg\,l^{-1}$, catalyst loading 0.05 (w/v) of solution, 365 nm UV lamp).

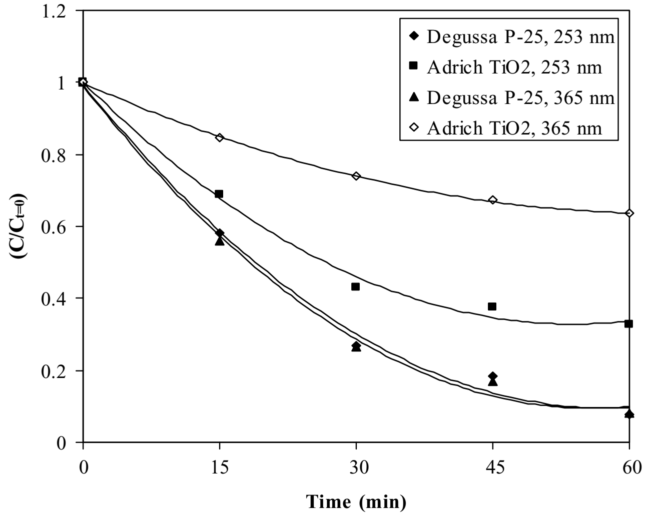

Fig. 6. Comparison of Degussa P-25 and Aldrich-TiO_2 as photocatalysts for photocatalytic degradation of NB (initial concentration $500\,mg\,l^{-1}$, catalyst loading 0.05 (w/v) of solution): (◆) photocatalytic degradation of NB using Degussa P-25 and 253 nm UV lamp; (☐) photocatalytic degradation of NB using Aldrich-TiO_2 and 253 nm UV lamp; (△) photocatalytic degradation of NB using Degussa P-25 and 365 nm UV lamp; (○) photocatalytic degradation of NB using Aldrich-TiO_2 and 365 nm UV lamp.

3.7. Comparison of photocatalytic and photochemical degradation of nitrobenzene in presence of artificial UV radiations

Photochemical degradation of NB in the presence of artificial UV radiations (365 nm, λ_{max}) was studied using stoichiometric amount of hydrogen peroxide and $200\,mg\,l^{-1}$ of initial nitrobenzene concentration. Fig. 7 shows that photochemical degradation is much slower as compared to photocatalytic degradation. Only 35.5% degradation of $200\,mg\,l^{-1}$ initial concentration of NB was possible in 2 h with the photochemical route, whereas 99.5% nitrobenzene was degraded in the same time for the photocatalytic route. The decomposition of H_2O_2 and generation of $OH^\bullet$ species is dependent on the overall intensity of light and even pho-

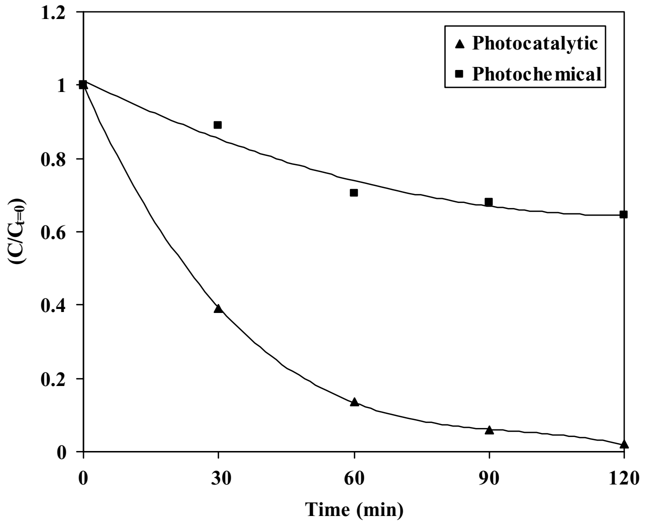

Fig. 7. Comparison of photocatalytic and photochemical degradation of NB using 365 nm UV lamp (initial NB concentration 200 mg l^{-1}): (■) photochemical degradation of NB using H_2O_2 and 365 nm UV lamp; (▲) photocatalytic degradation of NB using Degussa P-25 and 365 nm UV lamp.

tons having wavelength in the visible region are also useful for the decomposition. In the case of photocatalytic degradation, the amount of UV radiation having $\lambda \leq 389$ nm reaching the catalyst is more important than the overall intensity. Thus UV/H_2O_2 is a poor alternative for UV/TiO_2/air.

3.8. Comparison of solar and artificial UV radiation in photocatalytic degradation

The photocatalytic degradation of NB using concentrated solar radiations in the same reactor has been studied previously [24]. Using artificial UV light the degradation was found to be much faster as compared to solar radiation. Complete destruction of NB at the same catalyst loading which took place in 4 h required only 1 h using artificial UV lamps even though in experiments with solar radiations concentrated sunlight was used. This is due to the fact that in the artificial light the percent useful component (UV) is substantially higher. The intermediates generated in the case of solar radiation were smaller in amount and were in the range of 5–10 mg l^{-1} whereas in the case of artificial radiation the intermediates were negligible. The optimum catalyst loading required in the case of artificial light is also less as compared to solar radiation.

3.9. Comparison of photocatalytic and photochemical degradation of NB and phenol

The comparison of photocatalytic degradation of NB and phenol is shown in Fig. 8. Initial concentrations of 200 mg l^{-1} and catalyst loading of 0.05% (w/v) of solution were used. The degradation of phenol is slower than that of NB. NB is a much strongly adsorbing species than phenol and hence its degradation rates are also higher [4]. Phenol lies in the middle position in the group with unshared pair of electrons arranged in the descending order. (+I effect) NO_2 is at the 2nd position in the group that lack unshared pair on the atom bound to the ring arranged in the descending order (−I effect). Species containing functional groups which show either stronger +I or stronger −I effect degrade faster [4]. Hence NB degrades at a faster rate than phenol. In the case of photochemical degradation 200 mg l^{-1} of initial concentration and stoichiometric amount of hydrogen peroxide was used. Photochemical degradation of phenol using artificial UV radiations is also slower than that of NB as shown in Fig. 9.

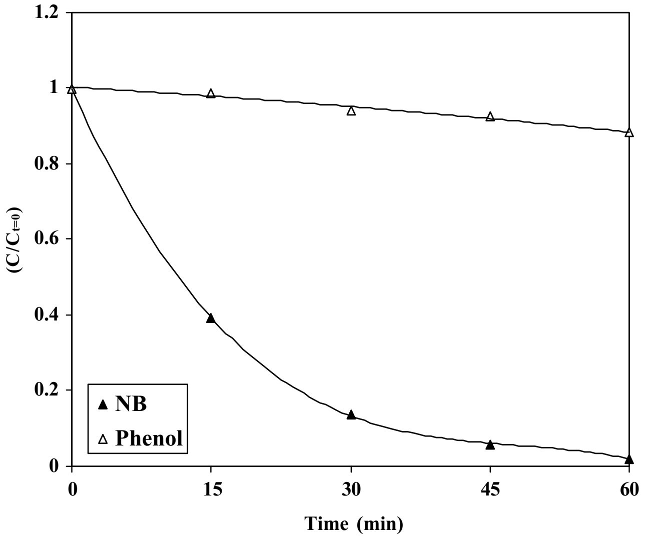

Fig. 8. Comparison of photocatalytic degradation of NB and phenol (initial NB and phenol concentration 200 mg l^{-1}, catalyst loading 0.05 (w/v) of solution): (▲) photocatalytic degradation of phenol using Degussa P-25 and 365 nm UV lamp; (△) photocatalytic degradation of NB using Degussa P-25 and 365 nm UV lamp.

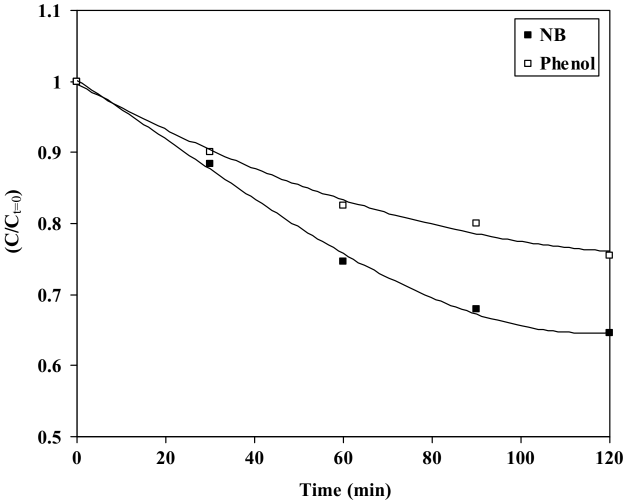

Fig. 9. Comparison of photochemical degradation of NB and phenol (initial NB and phenol concentration 200 mg l^{-1}): (■) photochemical degradation of phenol using 365 nm UV lamp; (□) photochemical degradation of NB using 365 nm UV lamp.

4. Conclusions

(1) Use of artificial UV lamps can substitute solar energy for photocatalytic degradation (UV+TiO_2^-+air) whenever required.
(2) Artificial UV radiation gives faster photocatalytic degradation of NB than concentrated solar radiation.
(3) The photocatalytic (UV+TiO_2+air) route yields higher degradation rates than the photochemical (UV + H_2O_2) route.
(4) For photochemical route the use of solar radiation is favourable as a large spectrum of the solar radiation is useful for the decomposition of H_2O_2.

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