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Photocatalytic degradation of 4-nitroaniline using solar and artificial UV radiation

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Abstract

The photocatalytic degradation (PCD) of 4-nitroaniline was studied in the presence of TiO_2 suspensions in a batch and continuous annular reactor. Artificial and solar radiation was employed as sources of UV radiation. The effect of catalyst loading, pH, presence of anions and initial concentration on the rate of photocatalytic degradation was investigated. *p*-Aminophenol, *p*-benzoquinone and hydroquinone were identified as the intermediates during the degradation process. A kinetic expression for PCD of 4-NA is provided.

Keywords: Nitroaniline; Photocatalysis; TiO_2; Kinetics

1. Introduction

Purification of water by semiconductor photocatalysis is a rapidly growing area of interest. Many organic compounds are resistant to conventional chemical and biological treatments, making it necessary to devise new treatment methods which can act as alternative to biological and classical physico-chemical processes. Photocatalytic degradation process can be defined broadly as an aqueous phase oxidation process, which is based primarily on the attack of the hydroxyl radical, resulting in the destruction of the target pollutant or contaminant compound. The distinct advantages of PCD such as complete mineralization, low cost, mild operating conditions and immunity to solution toxicity, over the other destructive and non-destructive technologies has attracted the attention of many researchers [1–2].

p-Nitroaniline (4-NA) is highly toxic with a TLV of $0.001\,kg\,m^{-3}$. 4-NA is found in wastewater discharges from industries where it is either manufactured or used as an intermediate such as in the synthesis of dyes, antioxidants, pharmaceuticals, in gum inhibitors, poultry medicines, and as a corrosion inhibitor. 4-NA has been found to be harmful to aquatic organisms and may cause long-term damage to the environment [3].

The present work deals with photocatalytic degradation of *p*-nitroaniline using solar radiation as well as artificial radiation, in batch and continuous mode. A very limited literature is available on photocatalytic degradation (PCD) of 4-NA. Bauer and Spaeek [4] have compared degradation of 4-NA using photocatalysis and photo Fenton reaction. However, no literature is available with regard to the effect of the various parameters on the rate of photocatalytic degradation. In view of this, batch reactor studies using solar radiations were carried out to study the effect of the various parameters such as catalyst loading, initial 4-NA concentration, pH, presence on anions, and catalyst reusability on the rate of PCD. The kinetics of the photocatalytic degradation was also investigated.

The PCD of 4-NA in a continuous annular reactor was also an integral part of our present study. Notwithstanding the substantial advantages of photocatalytic degradation, the technique of PCD is yet to be implemented on large scale for treatment of industrial wastes. The biggest hurdle has been catalyst filtration/recovery owing to the fine particle size of the TiO_2, the most widely photocata-

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Nomenclature

C_0	initial concentration of 4-nitroaniline (kg m^{-3})
C_ℓ	concentration of intermediates (kg m^{-3})
C_t	concentration of 4-nitroaniline at time t (kg m^{-3})
$C_{t=0}$	concentration of 4-nitroaniline at time $t = 0$, before the 4-nitroaniline solution was exposed to sunlight (kg m^{-3})
I	rate of light absorption
k_1, k_2, k_r	reaction rate constant (s^{-1})
k_{obs}	pseudo-first-order rate constant (m^3 kg^{-1})
K	equilibrium adsorption constant of 4-nitroaniline
K_c	second order rate constant (kg s^{-1})
TOC$_{t=0}$	total organic carbon at time t, before the 4-nitroaniline solution was exposed to sunlight (kg m^{-3})
TOC$_t$	total organic carbon at time t (kg m^{-3})
Greek letters	
λ	wavelength of light (nm)
θ	power term
$\theta_{OH^\bullet}$	fractional site coverage by hydroxyl radicals
θ_C	fraction of sites covered by 4-NA

lyst. In view of this, most investigators have used the catalyst in immobilized forms [5–8]. However, limited surface area and potential losses of catalyst by attrition are main drawbacks. Further, higher catalyst loading leads to solution opacity and poor photon penetration, thereby poor reactor response. One alternative, which can overcome this problem, lies in the use of candle filters relying on surface filtration under conditions such that there is a zone of high shear near the filter surface that prevents solid deposition and plugging of the candle filter [9–10]. The high surface area per unit mass of this catalyst allows low catalyst loading (<0.5 wt%) without affecting the space-time yield. For instance, 0.5 wt% loading of the catalyst affords a surface area of about 200 m^2 m^{-3} of the reactor volume, which is far greater than what can be achieved with an immobilized catalyst. Further, the low photocatalyst loading can allow better penetration of the incident photons. Fig. 1 shows the configuration of the annular reactor used in the present experimental studies. The liquid hydrostatic head in the column serves as the driving force for filtration allowing retention of the catalyst in the reactor. The low particle size and catalyst loading allow ease of solid suspension at relatively low (0.03–0.05 m s^{-1}) air sparging rates. Thus, the energy requirement for air sparging can be kept low.

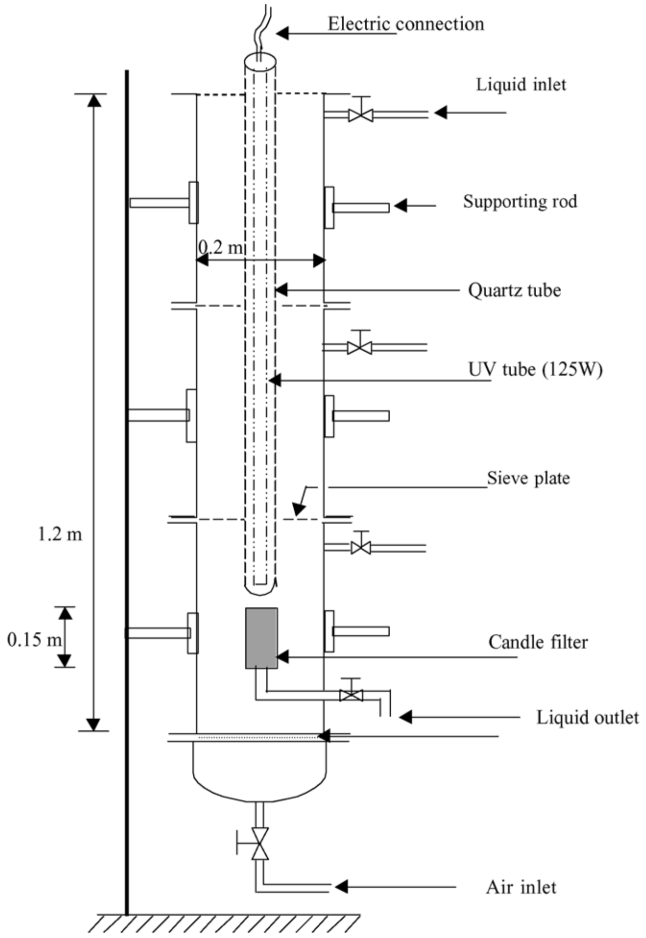

Fig. 1. Novel annular bubble column reactor for continuous photocatalytic degradation of 4-nitroaniline using artificial UV radiations.

2. Experimental

2.1. Materials

All the reagents used for experimental studies were analytical reagent grade. Degussa P-25 TiO_2 was supplied as free sample by Degussa Co., Germany. 4-Nitroaniline, sodium chloride, sodium carbonate, sodium bicarbonate, sodium sulfate of analytical reagent grade were obtained from S.D. Fine Chemicals Ltd., Mumbai, India. All the reaction mixtures and HPLC mobile phase solutions were prepared in deionized water. Plain solar radiation intensity was measured in W m^{-2} by 'Daystar meter' (daystar Inc., Las Cruces, NM, USA) working on photocell principle. Solar radiation intensity at ground level is referred to as plain intensity henceforth.

2.2. Batch experiments

All the experiments were carried out in a quartz cylindrical reactor, similar to that employed by Kamble et al. [9]. 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 4-NA. The temperature of the reaction mixture was maintained at near ambient by passing water through the cooling coil.

Before the start of a batch experiment the 4-NA solution was equilibrated by stirring for 900 s in the dark before exposing the reactor assembly to the concentrated sunlight from a compound parabolic reflector (projected area ≈ 0.14 m^2). The concentration of 4-NA in this filtered sample was treated as the zero time concentration ($C_{t=0}$) in each experiment before exposure to radiation. The reflector was used to concentrate the solar radiation forming a continuous glowing band of concentric light surrounding the wall of the reactor. After every 900 s, the position of the reflector was tracked with respect to the sun so as to maintain the band of light surrounding the reactor wall. Air presaturated with water was bubbled at a sufficiently high velocity ($>0.02\,m\,s^{-1}$) to keep all the TiO_2 in suspension. Samples were taken periodically, centrifuged, filtered, and stored in amber colored bottles. In the case of dark adsorption studies, $50 \times 10^{-6}\,m^3$ aliquots were mixed with TiO_2 and shaken for 24 h to allow equilibration. The glass conical flasks were covered by aluminum foil during shaking. The solutions were then filtered and analyzed using HPLC.

2.3. Continuous experiments

In continuous industrial operation, the effluent generated during night either has to be stored for treatment in the following day or treated during the night. In the former alternative the economics are not favorable since it involves storage tanks and a solar unit sized for treatment of roughly 260–270% of the flow generated during the time sunlight is available. Therefore, a study with artificial UV (alternate to solar radiation) was proposed. Artificial UV has the advantage that it can not only be used in the night but also can be used as a supplement to the solar unit if required. In view of this, continuous experiments were carried out in a SS slurry bubble column reactor of 0.2 m i.d. × 1.2 m length and capacity of $30 \times l0^{-3}\,m^3$, utilizing artificial UV radiation. A schematic of the slurry bubble column reactor is shown in Fig. 1. A low-pressure, 125 W UV lamp ($\lambda = 254\,nm$) having a length of 1 m was used. The UV lamp enclosed within a quartz tube was placed in the center of the reactor. A diaphragm type air compressor (Model HS-2, C.P. Enterprises, Mumbai) was used to sparge air at the bottom of the column through a sintered stainless steel disk. Air was bubbled at sufficiently high velocity ($>0.03\,m\,s^{-1}$) to keep all the TiO_2 in suspension.

2.4. Analysis

In the case of batch experiments, samples were centrifuged and filtered through a membrane filter to separate out TiO_2 particles. However, no such filtration was required in case of continuous reactor studies. Concentrations of 4-NA and its intermediates were measured by HPLC (Knauer) equipped with a C-8 column (5 μm, particle diameter, Merck) and UV–vis detector. The mobile phase was determined from several combinations giving best separation of all the possible intermediates. Water/acetonitrile (70:30%, v/v) was used as the mobile phase with a flow rate of $0.015 \times l0^{-6}\,m^3\,s^{-1}$ at $\lambda = 330\,nm$. Total organic carbon (TOC) was calculated from HPLC analysis and verified using a Total Organic Carbon Analyzer (ANATOC-II, Australia). These values matched within ±2% indicating that the HPLC analysis could detect all the intermediates. The intermediates were further confirmed by spiking the experimental samples with authentic compounds. Increase in concentration on spiking confirmed the presence of the particular compound as an intermediate.

3. Mechanism for PCD of 4-NA

It is known that the mechanism of PCD is through the attack of $OH^\bullet$ on the substrate. During the photocatalytic reaction process some intermediates can be formed, sometimes these intermediates are more toxic than the original compounds [1–2]. Therefore, the knowledge/identity of the intermediates is a necessity in photocatalytic degradation processes. In aqueous TiO_2 suspensions, aromatic compounds are oxidized through two different mechanisms; either by hydroxylation of the aromatic ring or by direct electron transfer to TiO_2 followed by the addition of a water molecule and loss of a proton. The proposed pathway for PCD of 4-NA in the batch studies is shown in Fig. 2. This pathway is based on the intermediates detected in the samples taken periodically and analyzed with HPLC. The total organic carbon (TOC) calculated from HPLC analysis was tallied with the TOC obtained from TOC analysis and the difference was found to be within ±2% which is acceptable for most experimental results. During the photocatalytic degradation of 4-NA, *p*-aminophenol, *p*-benzoquinone and hydroquinone were observed as intermediates. However, the concentration of these intermediate was very low. It was noted that all the intermediates identified in the process were hydroxylated compounds.

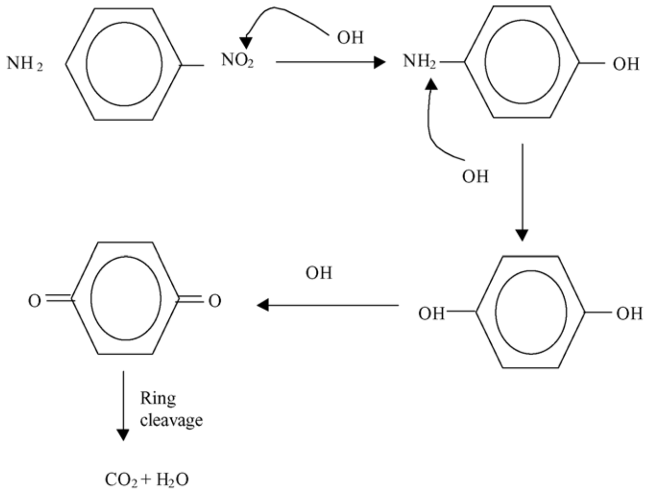

Fig. 2. Suggested pathway for PCD of 4-nitroaniline.

This finding clearly shows that hydroxyl radical plays a crucial role in the degradation of 4-NA and its intermediates. Schemelling et al. [11] have identified a reductive pathway in their studies using CdS–TiO_2/artificial UV and methanol as an electron scavenger. However, because of the different catalyst/radiation combination and electron scavenger used by them a direct comparison of the two mechanisms is difficult.

4. Results and discussions

4.1. Batch photocatalytic degradation with concentrated solar radiation

4.1.1. Effects of the various factors on the adsorption of 4-NA on TiO_2

Adsorption of the substrate on the photocatalyst has a major role in its photocatalytic degradation. Evidence indicates that the attack of $OH^{\bullet}$ radicals take place on the adsorbed substrate [12–13]. Hence, greater the adsorption higher is the rate of degradation. Adsorption is affected by several factors, which may include effluent composition and pH. Industrial effluents commonly contain one or several salts which makes it necessary to study the effect of the presence of these anions on adsorption and therefore on degradation. Studies were carried out to elucidate the effect of chloride, sulfate, carbonate and bicarbonate on the adsorption of 4-NA on the photocatalyst used. Fig. 3 shows that presence of anions did not have any significant effect on the adsorption of 4-NA on the catalyst. Degussa P-25 has a zero point charge (pH_{zpc}), value at pH 6.9. At $pH > pH_{ZPC}$ TiO^- is the predominant species whereas at $pH < pH_{ZPC}$, $TiOH^+$ is the predominant species according to the following equilibria:

$$Ti\cdots OH + OH^- \rightarrow TiO^- + H_2O \quad (1)$$

$$Ti\cdots OH + OH^+ \rightarrow TiH^+ \quad (2)$$

When 4-NA is adsorbed on the surface of TiO_2, it develops a negative charge on TiO_2 surface, since of 4-NA is a weak base. In view of this, the site on which 4-NA is adsorbed develops a negative charge, which probably repels the anionic species also having negative charge and thus the anions have no effect on the adsorption of 4-NA on the photocatalyst. Effect of pH on the adsorption of 4-NA on TiO_2 was studied and it was found that adsorption was more in basic medium than in acidic or neutral medium as shown in Fig. 4. This is probably due to the fact that under basic pH 4-NA is present in the molecular, easy to adsorb form. On the other hand under acidic conditions 4-NA present in the ionized form, which has a relatively weaker attraction for the photocatalyst.

4.1.2. Influence of catalyst concentration

The effect of catalyst loading on PCD of 4-NA was studied by varying the amount of TiO_2 from 0.1 to 0.3% (w/v of solution). Fig. 5 shows that as the concentration of TiO_2 in-

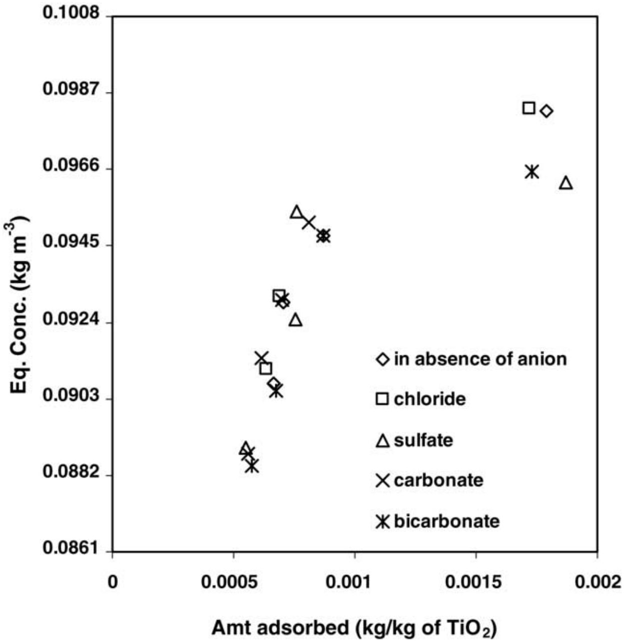

Fig. 3. Effect of the presence of the various anions on the adsorption of 4-nitroaniline on TiO_2. (□) Adsorption isotherm of 4-nitroaniline in the presence of 0.1 M NaCl. (△) Adsorption isotherm of 4-nitroaniline in the presence of 0.1 M Na_2SO_4. (⋇) Adsorption isotherm of 4-nitroaniline in the presence of 0.1 M $NaHCO_3$. (▯) Adsorption isotherm of 4-nitroaniline in the presence of 0.1 M Na_2CO_3. (◇) Adsorption isotherm of 4-nitroaniline in the absence of anion.

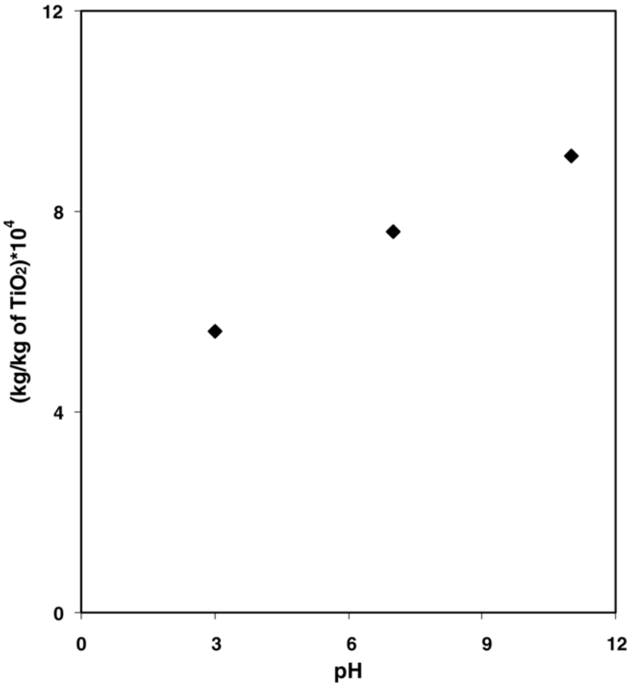

Fig. 4. Effect of pH on adsorption of 4-nitroaniline ($kg\,kg^{-1}$ of TiO_2 vs. pH).

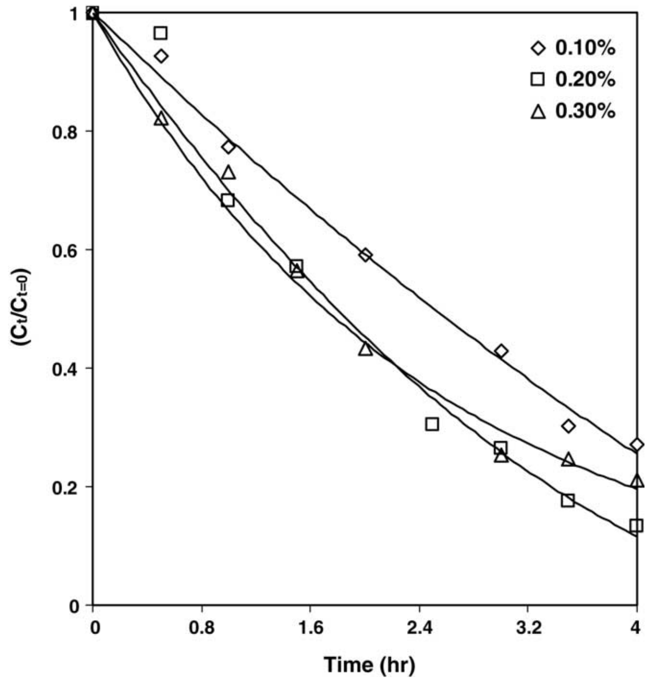

Fig. 5. Influence of catalyst loading on photocatalytic degradation of 4-nitroaniline ($C_t/C_t = 0$ vs. time). (◇) 0.1% (w/v of solution) of catalyst loading; (□) 0.2% (w/v of solution) of catalyst loading; (△) 0.3% (w/v of solution) of catalyst loading.

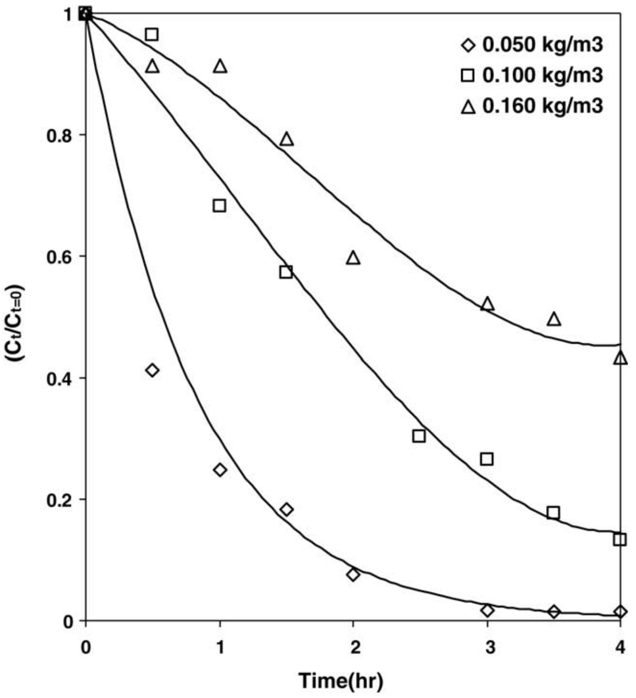

Fig. 6. Effect of the initial concentration on the photocatalytic degradation of 4-nitroaniline ($C_t/C_{t=0}$ vs. time). Catalyst loading = 0.2% (w/v of solution). (◇) Initial concentration 50×10^{-3} kg m^{-3}; (□) initial concentration 100×10^{-3} kg m^{-3}; (△) initial concentration 160×10^{-3} kg m^{-3}.

creases, the rate of degradation increases up to a certain point, and then decreases. Maximum degradation was obtained at a TiO_2 concentration of 0.2% (w/v) of solution. This may be because at high TiO_2 concentrations, an increase in the opacity of the solution reduces the transmission intensity of the radiation significantly decreasing the reaction rate.

4.1.3. Effect of initial 4-NA concentration

The effect of initial concentration of 4-NA on the photocatalytic degradation rate was investigated over the concentration range of (50–160) × 10^{-3} kg m^{-3}, since the pollutant concentration is a very important parameter in water treatment. Experimental results presented in Fig. 6 show that the degradation rate depends on the initial 4-NA concentration. The rate constant *k* decreases with increase in the initial concentration of 4-NA. Wei and Wan [14] explained similar phenomenon observed in photocatalytic degradation of phenol in terms of competitive adsorption between OH^- and ArO^-. More recently, Leng et al. [13] interpreted the decrease in the apparent rate constant with increasing concentration of the substrate, aniline, by assuming that intermediates competed with aniline for the sites on TiO_2. It is likely that competitive adsorption of 4-NA, intermediates and OH^- is responsible for the observed decrease in the rate constant. At high concentration, the concentration of intermediates formed during PCD is high thereby reducing the number of available active sites on TiO_2 for adsorption of H_2O/OH^- (required for $OH^\bullet$ formation) and 4-NA, causing a decrease in the reaction rate constant, k_r. It can be further inferred from the above hypothesis that degradation kinetics of 4-NA follows pseudo order kinetics.

The rate constant, k_r has been found to be a function of I ($k_r \propto I^\theta$), where I is the rate of light absorption and θ is the power term equal to 1/2 or 1 at high and low intensities, respectively [15]. Therefore, a decrease in the intensity of light reaching the TiO_2 surface will cause a decrease in the value of k_r. The solar radiation reaching the earth's surface mostly consists of radiation of 290 nm and above. 4-NA has a high absorbance in the UV spectrum between 300 and 400 nm, therefore an increase in 4-NA concentration causes increased absorbance of UV radiation resulting in a decrease in k_r. 4-NA solution has a yellow color. An increase in concentration intensifies the color of the solution thereby causing a significant reduction in the transmission intensity of the ultraviolet light causing a decrease in the rate constant.

4.1.4. Kinetics of PCD of 4-NA

Fig. 7 shows the kinetics of the disappearance of 4-NA. The semi-logarithmic plots of concentration data gave a straight line indicating that the photocatalytic degradation of 4-NA in aqueous TiO_2 suspensions followed a pseudo first-order kinetic model:

$$\ln C_t = -k_r t + \ln C_{t=0} \qquad (3)$$

where $C_{t=0}$ is the concentration at $t = 0$ and C_t is the concentration of 4-NA at time *t*. The slope of the plots gave the

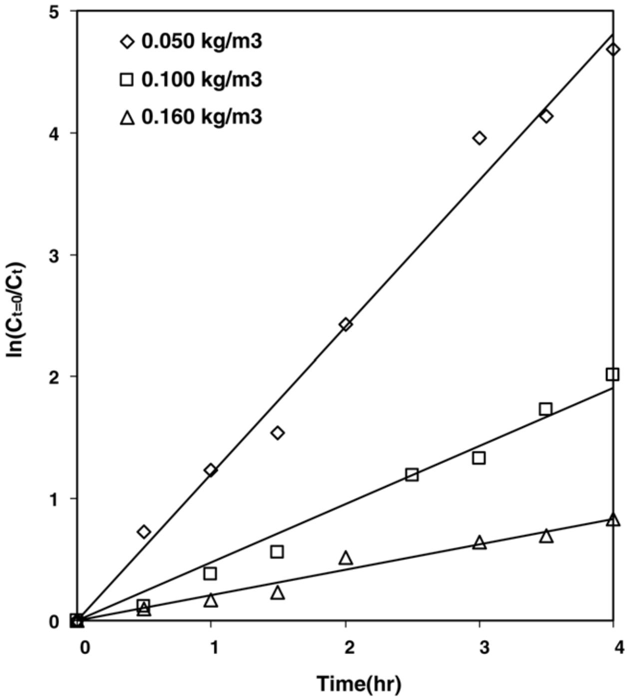

Fig. 7. Kinetics of photocatalytic degradation of 4-nitroaniline. (◇) Initial concentration $50 \times 10^{-3}\,\mathrm{kg\,m^{-3}}$. (□) Initial concentration $100 \times 10^{-3}\,\mathrm{kg\,m^{-3}}$; (△) initial concentration $160 \times 10^{-3}\,\mathrm{kg\,m^{-3}}$.

values of k_r, as listed in Table 1. Decrease in k_r with increase in concentration has already been discussed in Section 4.1.3.

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 4-NA may be written in terms of Langmuir–Hinshelwood kinetics as [16]:

$$r = k''\theta_{OH}\theta_{C} \tag{4}$$

where k'' is the surface second order rate constant, $\theta_{OH^{\bullet}}$ the fractional site coverage by hydroxyl radicals and θ_C is the fraction of sites covered by 4-NA. These two last variables can be written as:

$$\theta_{OH^{\bullet}} = \frac{K_{O_2} p_{O_2}}{1 + K_{O_2} p_{O_2}} \tag{5}$$

$$\theta_{C_\ell} = \frac{KC}{1 + KC + \sum_i K_i C_{\ell_i}} \tag{6}$$

where K_{O_2}, K and K_i are the equilibrium adsorption constant and ‘C_ℓ’ refers to the intermediate products of 4-NA degradation. Eq. (6) can be modified by making the following assumption:

$$KC + \sum_i K_i C_{\ell_i} = KC_0 \tag{7}$$

A further assumption that the adsorption coefficients for all organic molecules present in the reacting mixture are effectively equal is made. Substituting Eq. (7) into Eq. (6) gives the following expression:

$$r = k''\frac{K_{O_2}P_{O_2}}{1 + K_{O_2}P_{O_2}} \times \frac{KC}{1 + KC_0} \tag{8}$$

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,

$$k''\frac{K_{O_2}P_{O_2}}{1 + K_{O_2}P_{O_2}} = \text{constant} = k_c \tag{9}$$

Eq. (9) can therefore be written as:

$$r = k_c\frac{KC}{1 + KC_0} = k_{\text{obs}}C \tag{10}$$

Eq. (10) is a typical Langmuir–Hinshelwood kinetics equation. The relationship between k_{obs} and C_0 can be expressed by a linear Eq. (11):

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k_c K} + \frac{C_0}{k_c} \tag{11}$$

The value of k_{obs} and k_c were obtained by fitting the experimental data to Eq. (11) and are $k_{\text{obs}} = 438.35\,\mathrm{m^3\,kg^{-1}}$ and $k_c = 4.91 \times 10^{-6}\,\mathrm{kg\,s^{-1}}$ ($R^2 = 0.98$). 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.

4.1.5. *Effect of pH*

The dependence of the rate of PCD of 4-NA on pH is shown in Fig. 8. It was observed that highest degradation rates were obtained at pH 11. The higher rates of degradation at high pH values can also be attributed to the higher adsorption of 4-NA at high pH values as discussed in Section 4.1.1. Higher rates of adsorption lead to higher rates of degradation. Studies show that the concentration of intermediates of 4-NA was pH dependent. High concentrations of intermediates were detected at pH 11 while low concentrations were detected at pH 3 suggesting that photocatalytic degradation of 4-NA at lower pH favored direct ring cleavage. A similar result was observed during the PCD of 2-chlorophenol by Doong et al. [17].

4.1.6. *Effect of anions*

The adsorption of the substrate on the photocatalyst plays an important role in its photocatalytic degradation. Adsorption is affected by several factors, such as the effluent composition and pH of the aqueous solution. Industrial effluents

Table 1
The reaction rate constant at different initial concentration of 4-NA

Concentration of 4-NA ($\mathrm{kg\,m^{-3}}$)	k_r ($\mathrm{h^{-1}}$)
0.050	1.25
0.100	0.47
0.160	0.21

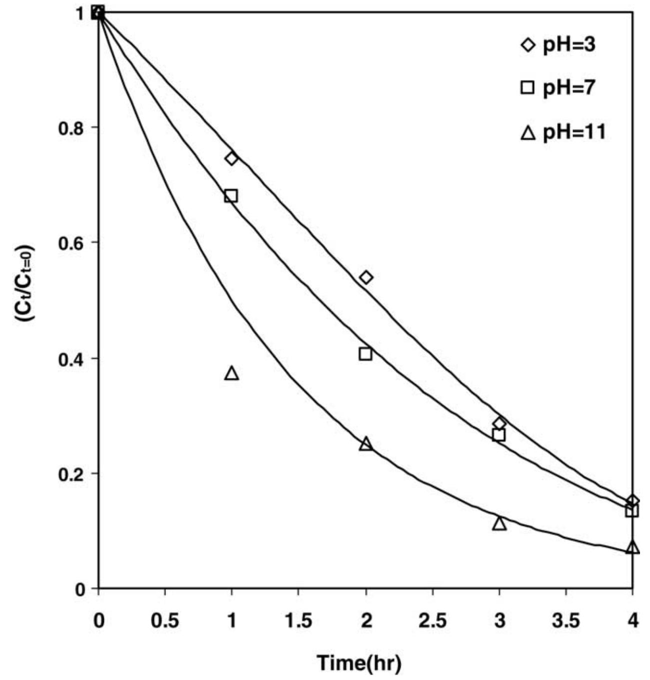

Fig. 8. Effect of pH on the photocatalytic degradation of 4-nitroaniline on TiO_2 ($C_t/C_{t=0}$ vs. time). Catalyst loading = 0.2% (w/v of solution). (◇) pH 3.0, (□) pH 7.0 and (△) pH 11.0.

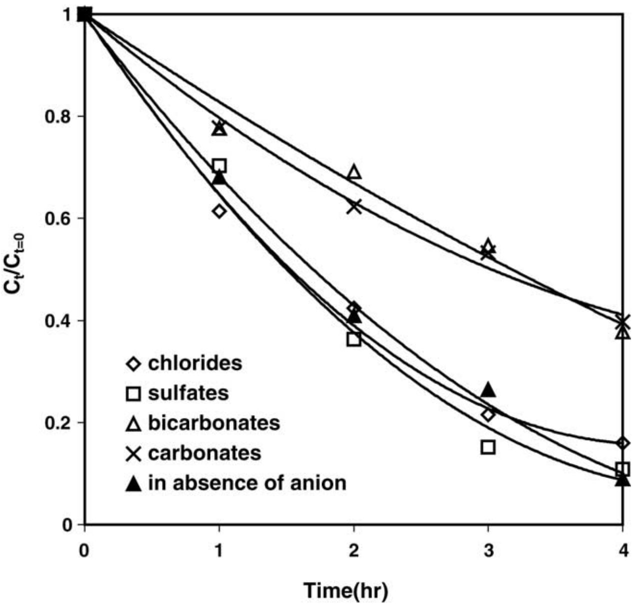

Fig. 9. Effect of the presence of the various anions on photocatalytic degradation of 4-nitroaniline on TiO_2 ($C_t/C_{t=0}$ vs. time). Catalyst loading = 0.2% (w/v of solution). (▲) PCD of 4-nitroaniline in the absence of anions. (◇) PCD of 4-nitroaniline in the presence of 0.1 M NaCl. (□) PCD of 4-nitroaniline in the presence of 0.1 M Na_2SO_4. (△) PCD of 4-nitroaniline in the presence of 0.1 M $NaHCO_3$. (×) PCD of 4-nitroaniline in the presence of 0.1 M Na_2CO_3.

commonly contain one or several salts and these salts have a deleterious effect on adsorption of substrate on TiO_2 and hence on photocatalytic degradation [18–19]. Studies were carried out to determine the effect of the presence of anions on the rate of degradation of 4-NA. Fig. 9 shows the effect of chlorides, sulfates, carbonate and bicarbonates on PCD of 4-NA. It was observed that the presence of anions had negligible effect on adsorption (Section 4.1.1). However, the presence of carbonates and bicarbonates significantly affected the degradation rate. This can be attributed to the scavenging of hydroxyl radical by carbonates and bicarbonates as per the following reactions:

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

$$HCO_3{}^{2-} + HO^{\bullet} \rightarrow CO^{\bullet}{}_3 + H_2O \qquad (13)$$

The presence of sulfates and chlorides has negligible effect on the rate of photocatalytic degradation of 4-NA. Chloride is also $OH^{\bullet}$ scavenger but its effect is pronounced at low pH [20] whereas in the present study the anion effect was studied at self-pH of 4-NA (pH 7).

4.1.7. Catalyst reusability

An experiment was performed with used catalyst to determine its reusability. An experiment was conducted with $l00 \times 10^{-3}$ kg m^{-3} concentration of 4-NA and 0.2% (w/v of solution) catalyst loading. The used catalyst was filtered and then used for the next similar experiment. As can be seen from Fig. 10, 87% degradation of 4-NA occurred in its first use. However, only 38% degradation of 4-NA was observed in the second experiment. This can be attributed to the deposition of 4-NA and the intermediates, formed during PCD, on the catalyst surface. Further support for this conclusion could be obtained from the color (light purple) of the catalyst after first use. This color was obviously due to the intermediates

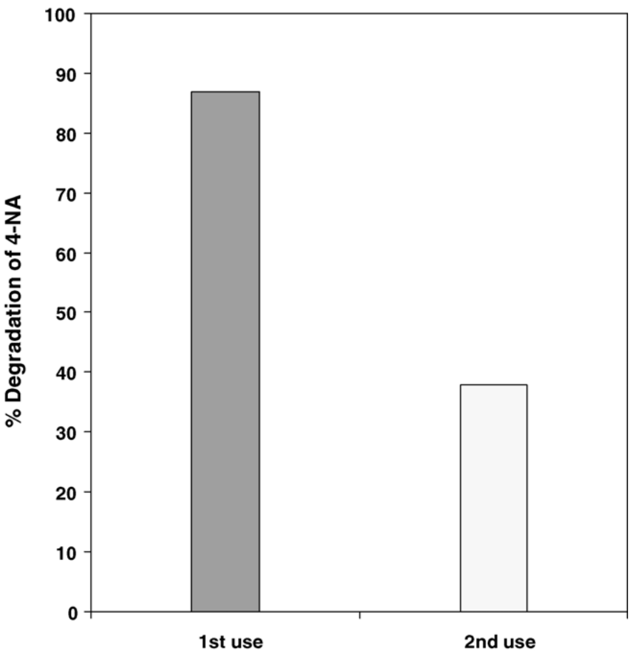

Fig. 10. Effect of reused catalyst in the slurry batch reactor on the photocatalytic degradation of 4-NA.

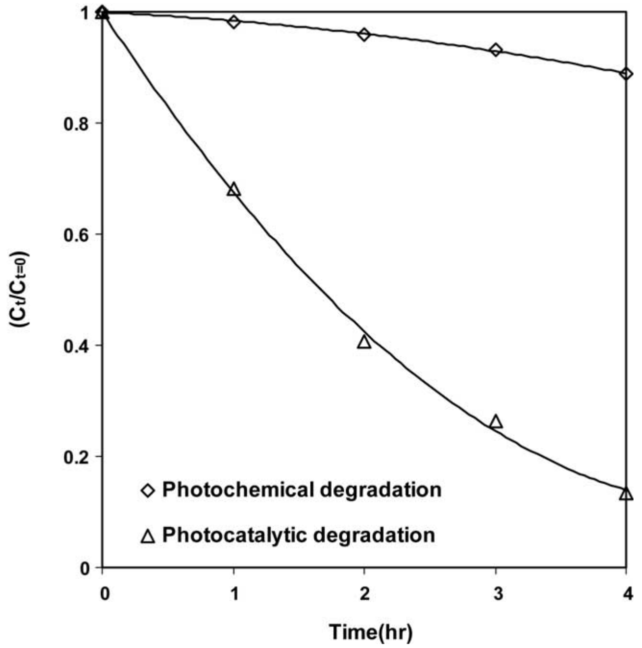

Fig. 11. Comparison of photochemical and photocatalytic degradation of 4-nitroaniline. Initial concentration = 100 × 10^{-3} kg m^{-3}. (△) Photocatalytic degradation of 4-nitroaniline and (◇) photochemical degradation of 4-nitroaniline.

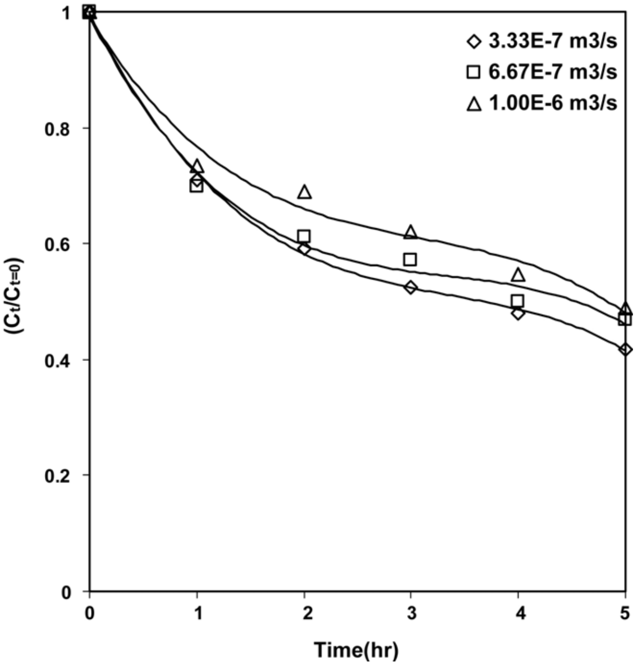

Fig. 12. Variation in the extent of PCD of 4-nitroaniline with flow rate in the continuous annular reactor. Initial concentration = 100 × 10^{-3} kg m^{-3}, catalyst loading = 0.2% (w/v of the solution). (◇) 3.33 × 10^{-7} m^3 s^{-1}, (□) 6.66 × 10^{-7} m^3 s^{-1} and (△) 1 × 10^{-6} m^3 s^{-1}.

adsorbed on the surface of the catalyst. As mentioned earlier, 4-NA has a high UV absorbance and hence the substrate itself can act as a UV shield, significantly reducing the intensity of light reaching the catalyst surface. An increase in the catalyst particle size was also observed after the first experiment. Aggregation of particles resulted in a decrease in the reaction surface area leading to a decrease in the degradation rate.

4.1.8. Comparison between photochemical and photocatalytic degradation

Photocatalytic and photochemical degradation studies were carried out using 100 × 10^{-3} kg m^{-3} initial concentration of 4-NA. In the photocatalytic degradation experiments, Degussa P-25 TiO_2/concentrated solar radiation/air were used, while for the photochemical degradation experiment stoichiometric amount of hydrogen peroxide with concentrated solar radiation was used. Fig. 11 shows the course of, photocatalytic and photochemical degradation of 4-NA using concentrated solar radiation. In the case of photochemical degradation, a decrease of 12% in 4-NA concentration was observed whereas 87% decrease in 4-NA concentration occurred during PCD reactions. Similar observations have been reported for phenol [21], aniline [22] and 2,4-dichlorophenoxyacetic acid [23].

4.1.9. Continuous reactor study

Experiments were carried out at three different flow rates to study for the effect of residence time on the rate of PCD. Results of the experiments are shown in Fig. 12. A decrease in degradation with increase in flow rates was observed which is a natural consequence of lower exposure time. In view of the shielding of the photocatalyst by the intermediates it will be desirable to employ a relatively higher residence time than the maximum used in this work to ensure that complete degradation of all the species involved is achieved.

5. Conclusions

Batch photocatalytic degradation studies indicate that 4-NA is best degraded under basic pH. If complete degradation is not achieved, the intermediates of the degradation process adsorbed on the photo catalyst hinder its reuse.

The results obtained in the continuous flow studies demonstrate the potential of photocatalytic degradation as a promising technology for treating aqueous streams containing 4-nitroaniline. In view of shielding of the photocatalyst by the intermediates it will be desirable to employ a relatively higher residence time than used in this work to ensure that complete degradation of all the species involved is achieved. Further, it will be desirable to have a higher and distributed UV dosage to ensure complete degradation. Further work directed at optimizing the reactor efficiency in terms of utilization of the UV energy input is in progress.

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