Removal of Orange II dye from aqueous solution by adsorption and photodegradation with visible light in presence of nitrogen doped titania nanocatalyst

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The possibility of treating water spiked with an azo dye, Orange II by adsorption and photo-catalytic decolourisation with nitrogen doped TiO_2 has been investigated. The prepared material has been characterised by XRD, BET, TEM, DRS and XPS study. The photocatalytic reaction is carried out after the attainment of adsorption equilibrium between N-TiO_2 and dye. The batch process is chosen to adsorb the dye under different experimental conditions. The photocatalyst dose, initial dye concentration and solution pH have been found to influence both the processes. The percentage decolourisation increases from 73.42% to 91.32% on increasing the N-TiO_2 dose 0.25 to 1.25 g L^{-1}. However, further increase of the catalyst dose to 1.50 g L^{-1} decreases the extent of decolourisation (88.29 %). The lower dye concentration favour decolourisation (decreases from 84.24 to 75.43% for dye concentration of 18.0 to 36.0 µmol L^{-1}). At pH 2.0, N-TiO_2 decolourises almost 84% of the dye within 240 min of irradiation time. COD results reveal ~91% mineralisation of the dye on 360 min of irradiation. The percentage decolourisation of the dye is found to be higher with N-TiO_2 compared to TiO_2 P25. The adsorption process follow the Lagergren first order model while the decolourisation process follow modified Langmuir-Hinshelwood model.

Keywords: Adsorption, COD, Photo-catalytic decolourisation, Orange II, Nitrogen-doped Titania, Nanocatalyst

Azo dyes are a class of synthetic dyes which make up 60-70% of all textile dyestuffs. These water soluble dyes cannot be removed through conventional biological treatments as the electron-deficient character of the azo linkage prevents bacterial mineralization[1]. Most of these dyes are responsible for creating human bladder cancer, splenic sarcomas, hepatocarcinomas and chromosomal abnormality in mammalian cells[2]. The mutagenic, carcinogenic and toxic effects of the azo dyes are either due to the direct action by the compound itself, or the formation of free radicals and aryl amine derivatives generated during the reductive transformation of the azo bond[3-5]. Orange II (also known as acid Orange 7), a molecule with N=N bonds, is widely used in the dyeing of textiles, paper, foodstuff, leather and cosmetics. It is thus found in the wastewater of the related industries[6,7] and therefore has large environmental effects.

During the last few decades, TiO_2 has been widely used as photocatalyst for degradation of dye staff from aqueous system[8-15]. However, the use of TiO_2 as photocatalyst was restricted because of its large band gap that resulted in the use of only UV light for photo excitation. To solve this problem, considerable efforts have been made to modify TiO_2 by reducing the band gap by doping it with various metals and non-metals[16-25]. Asahi *et al.*[26] found that anionic species was better for doping compared to cationic species. Nitrogen doping in TiO_2 is regarded as one of the most effective way to reduce the band gap, because the p state of nitrogen contribute to the narrowing of band gap by mixing with $2p$ state of oxygen of TiO_2[27-29]. The literature reported successful degradation of various water pollutants by N-doped TiO_2[30-36].

In the present study, nano sized ($\leq$ 10 nm) N-doped TiO_2 was synthesized by a very simple method. The material was characterized by XRD, DRS, TEM, XPS and BET measurement. The synthesised material was then used to decolourise Orange II dye in aqueous system under visible light irradiation after attainment of adsorption equilibrium in dark. The adsorption isotherm of the dye was studied due to the importance of adsorption in heterogeneous photocatalysis process[37]. The influence of experimental parameters,

namely, N-TiO$_2$ dose, solution pH and initial dye concentration on both the adsorption and decolourisation processes were also studied.

Experimental Section

Chemicals

All Chemicals were of the highest purity available and were used as received without further purification. TiCl$_3$ (15%, Loba Chemie) and 25% NH$_3$ solution (E Merck) were used as source of titanium and nitrogen respectively. The TiO$_2$ P25 (Aeroxide) was procured from Evonik (Degussa) Industries AG, Germany. Orange II [4-(2-hydroxy-1-naphthylazo) benzenesulfonic acid sodium] (CAS No 633-96-5, molecular formula: C$_{16}$H$_{11}$N$_2$NaO$_4$S, MW 350.33) was procured from Himedia.

Preparation of the catalyst

Nitrogen doped TiO$_2$ was prepared from TiCl$_3$ and aqueous NH$_3$ as precursor as given in our previous work[38]. In brief, 100 mL aqueous NH$_3$ solution was added drop wise to 150 mL TiCl$_3$ with constant stirring at 353 K. The mixing required about 2 hr, after which the mixture was stirred for an additional period of 1 hr. The solid precipitate was separated, washed with distilled water and dried in air oven at 343 K. The material was then calcined at 623 K for 4 hrs in a muffle furnace to get a yellowish brown powder.

Characterization methods

The samples were characterised by XRD and DRS using Rigaku Miniflex diffractometer with nickle-filtered CuKα radiation and Hitachi-400 spectrophotometer respectively. BET surface area of the sample was determined with the help of Quantachrome Autosorb-1C surface area analyzer by nitrogen adsorption method at 77 K. XPS and TEM data were collected with ThermoScientifc Escalab 250 instrument with monochromatized Al X-ray source and Jeol JEM 2100 instrument operating at an accelerating voltage of 200 kV, respectively.

Determination of adsorption efficiency

A fixed amount of N-TiO$_2$ (0.50 g L^{-1}) was mixed with a constant volume of aqueous dye solution in 100 mL Erlenmeyer flasks and allowed to agitate in a constant temperature water bath thermostat shaker for a known time interval under dark. It was then centrifuged (Remi R 24) and concentration of Orange II solution remaining unadsorbed in the supernatant liquid was determined with spectrometer (Elico SL 177, India) at λ$_{max}$ 486 nm. The sets of conditions for the different experiments were given in Table 1.

Determination of photocatalytic activity

A glass reactor having water circulation facility was used to carry out the catalytic reaction. The reactor was equipped with a 250 W halogen bulb as the source of visible light and a glass filter was fitted to cut-off short wavelengths (λ < 420 nm).

In a typical reaction 200 ml (18 µmol L^{-1}) of Orange II solution was taken with requisite amount of the catalyst and kept in dark for 60 min under stirring to attain the adsorption-desorption equilibrium. The mixture was then exposed to visible light under constant stirring. The concentration of dye after adsorption (60 min) was considered as the initial concentration for photocatalytic study. Eloquent was collected at a regular interval and the concentration of the dye was measured with the help of spectrometer.

Determination of percentage mineralization

The chemical oxygen demand (COD) is used as a measure of the oxygen equivalent of the organic content in an organic sample, which is susceptible to oxidation by a strong oxidant. The dichromate reflux method was adapted to estimate COD[39]. It was given by[40]:

$$\% \text{ mineralization} = \frac{(COD_o - COD_t) \times 100\%}{COD_o} \quad \dots(1)$$

where, COD$_0$ = COD of original dye, COD$_t$ = COD of degraded dye after time 't' (hour).

Table 1—Experimental conditions for study of dye adsorption and decolourisation

Type of study	Amount of N-TiO$_2$ (g/L)	Dye Concentration (µmol/L)	pH	Temperature (K)	Reaction Time (min)	
					Adsorption	Decolourisation
Effect of N-TiO$_2$ dose	0.25, 0.50, 1.25, 1.50	18	2.0	303	60	240
Effect of initial dye concentration	0.50	18, 27, 36	2.0	303	60	240
Effect of solution pH	0.50	18	2.0, 3.0, 7.0, 9.0, 11.0	303	60	240

Results and Discussion

Characterization of photocatalyst

The results of characterisation were published in our previous work[41]. The results revealed the formation of well crystalline anatase phase having average particle size of about 6.2 nm. The DRS results showed a red shift in the band gap energy of N-TiO$_2$ in comparison to undoped TiO$_2$. The narrower band gap must be due to lower energy gap between the valance band and the conduction band in N-TiO$_2$ compared to undoped TiO$_2$. The decrease in the band gap must have increased the photocatalytic activity of doped TiO$_2$. The TEM images showed formation of crystallites in the range of 6-10 nm which was in agreement with the results obtained from XRD analysis. The BET surface area of N-TiO$_2$ was found to be 176 m^2/g. The binding energy peak at 400 eV in N-TiO$_2$ was attributed to the presence of N1s electron in the sample in O-Ti-N environment.

Adsorption of Orange II under different experimental conditions

Influence of N-TiO$_2$ dose

At the beginning of the adsorbent-adsorbate interactions, the uptake of dye was very fast and attained equilibrium within 60 min. With initial dye concentration of 18.0 μmol L^{-1}, the uptake increased from 14.93 to 23.07% for N-TiO$_2$ dose of 0.25 to 1.25 g L^{-1}. The higher load of N-TiO$_2$ could provide more surfaces for the dye to get adsorbed on it, thereby increasing the adsorption efficiency[42]. Furthermore, it was observed that the increase of adsorbent dose beyond 1.25 g L^{-1} decreased the percentage adsorption (20.02% Orange II adsorption for 1.50 g L^{-1} of N-TiO$_2$). Figure 1a represents C_e/C_0 vs time plots for different doses of N-TiO$_2$.

Influence of initial Orange II concentration

By increasing the initial concentration of Orange II from 18.0 to 36.0 μmol L^{-1}, the percentage of adsorption decreased from 17.30 to 6.25% (Fig. 1b). At low initial dye concentration, the ratio of the number of adsorbate to the number of available adsorption sites was small and consequently the adsorption was independent of the initial concentration, but as the concentration of dye increase, the situation changed and the competition for adsorption sites became fierce[43].

Influence of pH

The uptake of Orange II on N-TiO$_2$ was studied by varying the solution pH from 2.0 to 11.0. The uptake was maximum at pH 2.0 (17.30% at 240 min) and then went down to 0.94% at pH= 11.0. C_e/C_0 vs time plot at different pH was represented by Fig. 1c.

At acidic pH, the adsorption process was favoured by the electrostatic attraction between the positively charged surface of N-TiO$_2$ and anionic dye. At higher pH the surface charge turned towards negative which decrease the adsorption of dye anions. Moreover, the adsorptions of bulky dye anions got suppressed by the preferential adsorption of highly mobile OH$^-$ ions[44].

Decolourisation of Orange II under different experimental conditions

Influence of N-TiO$_2$ dose

The dye decolourisation on different N-TiO$_2$ dose reached equilibrium within 240 min. The decoulorisation process increased from 73.42% (N-TiO$_2$: 0.25 g L^{-1}) to 91.32% (N-TiO$_2$: 1.25 g L^{-1}) for initial dye concentration of 18 μmol L^{-1} at equilibrium, however, further increase of catalyst dose above 1.50 g L^{-1} decreased the decoulorisation to 88.29%. Figure 2a depicted the degradation profile of Orange II on various catalyst doses.
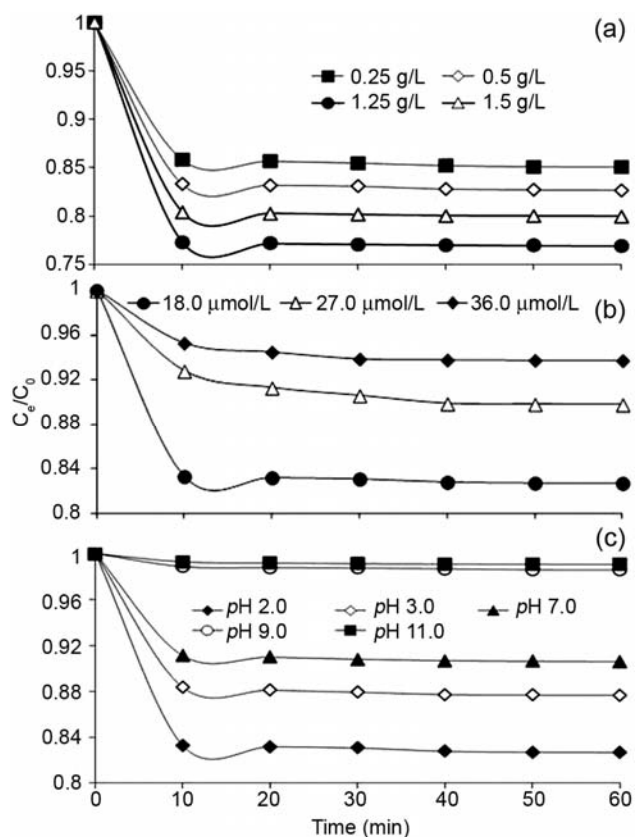

Fig. 1—Influence of N-TiO$_2$ dose (a), initial Orange II concentration (b) and solution pH (c) on the adsorption of dye on N-TiO$_2$ at 303 K.

The decolourisation process was enhanced by the higher catalyst dose that could produce higher number of photo electrons and thus accelerated the dye decolourisation[13]. On the other hand, agglomeration of catalyst particles was possible beyond the optimum catalyst dose. This could hinder the light absorption and thereby lowering the efficiency of decolourisation, as suggested by Huang *et al.*[45]. Furthermore, the obstruction offered to the incident light by the excess catalyst could decrease the concentration of ˙OH radical. This in turn decreased the efficiency of the dye decolourisation[46].

Influence of initial Orange II concentration

The influence of initial concentration of Orange II on decolourisation process was studied by the variation of dye from 18 to 36 µmol L^{-1} (Fig. 2b). At equilibrium, the % decolourisation decreased from 84.24 to 75.43% on increasing the dye concentration from 18.0 to 36.0 µmol L^{-1}.

At higher concentration, more number of dye molecules covered the active sites of catalyst. This might obstruct the production of ˙OH radicals on the surface which could decrease the decolourisation process, as lesser number of ˙OH radicals were available to oxidize large number of dye molecules[47]. The higher dye concentration supplied more dye molecules that had to be react with the same amount of ˙OH radical, leading to a decrease in the decolourization efficiency[48].

Influence of pH

The extent of decolourisation of dyes on N-TiO$_2$ was studied for the *p*H range 2.0 to 11.0. The decolourisation was favoured by lower *p*H (Fig. 2c). At *p*H 2.0, 0.5 g L^{-1} N-TiO$_2$ could decolourise 84.24% of dye from an initial dye concentration of 18 µmol L^{-1}. On the other hand, only 2.46% decolourisation was observed at *p*H 11.0.

The solution *p*H is an important parameter in the photodegradation process as the generation of hydroxyl radicals is a function of *p*H. The ˙OH radicals were formed by the reaction between OH$^-$ ions and positive holes. At low *p*H, positive holes acted as the major oxidation species, and at neutral or higher *p*H, ˙OH radicals were considered as predominant species. Sleiman *et al.*[49] suggested that in alkaline medium the coulombic repulsion between the negatively charged surface of N-TiO$_2$ and the OH$^-$ ions hinders the formation of ˙OH and thus decrease the photoxidation. Similar observation was reported earlier[38,41,50,51].

Adsorption isotherms

The equilibrium isotherm yields a range of quantitative information about the performance of a solid such as the absorbability, maximum amount that can be removed from solution, etc.[52]. The adsorption of orange II on TiO$_2$ P25 and N-TiO$_2$ was studied by the well known Langmuir isotherm given by[53]:

$$C_e/q_e = (1/bq_m) + (1/q_m) \qquad \ldots(2)$$

where C_e = concentration of Orange II at equilibrium, q_e = amount of dye adsorbed per unit mass of adsorbent at equilibrium, q_m = Langmuir monolayer adsorption capacity. The linear Langmuir plots were obtained by plotting C_e/q_e vs. C_e (r~0.96). The Langmuir capacity for N-TiO$_2$ was higher (1.05×10^{-3} mg g^{-1}) compared to that of TiO$_2$ P25 (2.92×10^{-4} mg g^{-1}), indicating the prepared material is a better adsorbent for the dye.

Kinetic study

Kinetics study provides the knowledge of the factors that influence the rates of a chemical process. Study of chemical kinetics includes careful monitoring of the experimental conditions that influence the speed of a chemical reaction and help to attain equilibrium in a reasonable length of time[54].
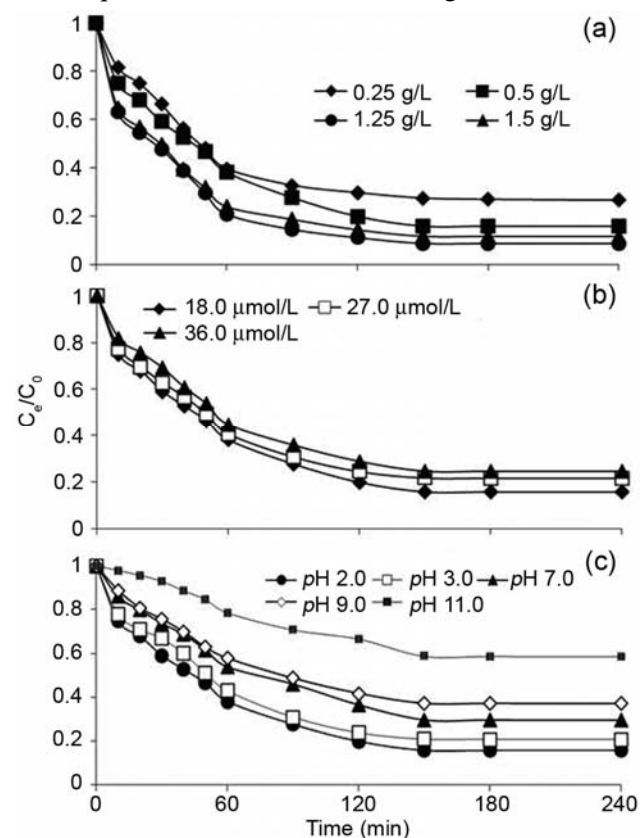

Fig. 2—Influence of N-TiO$_2$ dose (a), initial Orange II concentration (b) and solution *p*H (c) on the degradation of dye on N-TiO$_2$ at 303 K.

Kinetics of adsorption

The Lagergren pseudo-first order model was applied to study the dye adsorption on N-TiO$_2$[55,56].

$$\log(q_e - q_t) = \log q_e - k_1 t \qquad \ldots(3)$$

where, q_e and q_t are the amounts adsorbed per unit mass at equilibrium and at any time t, respectively. k_1 is the first order adsorption rate constant. The log $(q_e - q_t)$ vs t plots (Fig. 3) are linear (r~ -0.90 to -0.99) for all the experimental variables.

The first order rate constants varied in accordance with the variation of the experimental parameters. Thus, by increasing the N-TiO$_2$ dose from 0.25 g L^{-1} to 1.25 g L^{-1}, k_1 increased from 7.8×10^{-2} to 8.7×10^{-2} min^{-1} and then decreased to 8.5×10^{-2} min^{-1} for 1.5 g L^{-1} of N-TiO$_2$. The increase in dye concentration from 18 to 36.0 µmol L^{-1} decreased the rate constant from 8.4×10^{-2} to 6.4×10^{-2} min^{-1}. Similarly, a steady decrease of the k_1 values was observed from 8.4×10^{-2} to 5.9×10^{-2} min^{-1} for the increase in solution pH (pH 2.0 to 11.0 (Table 2).
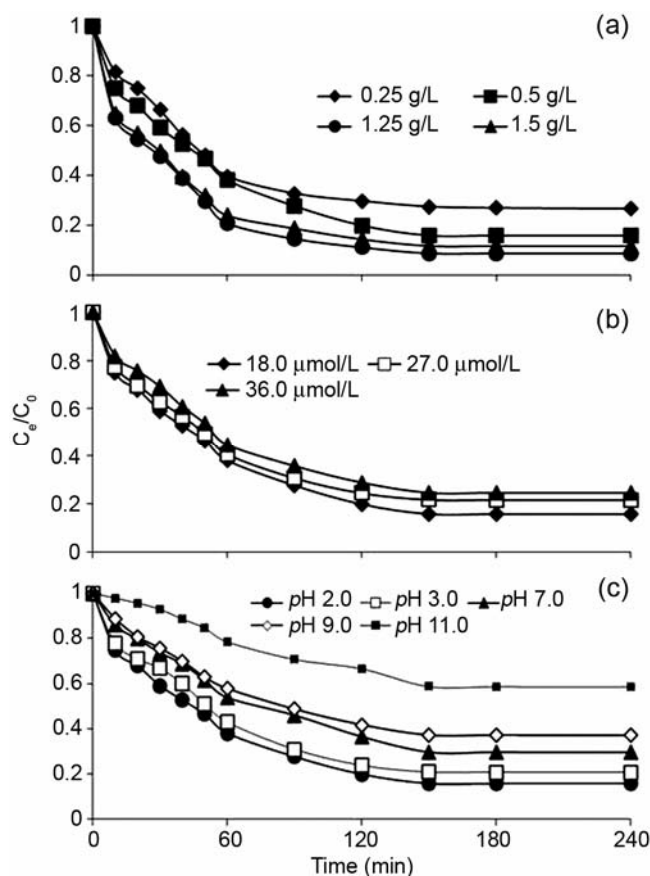

Fig. 3—Lagergren plots for adsorption of Orange II for variation of (a), N-TiO$_2$ dose (b) initial dye concentration and (c) solution pH.

Kinetics of decolourisation

The modified Langmuir-Hinshelwood (L-H) kinetic model was applied to study the rate of the dye decolorisation on N-TiO$_2$. The model is given by:

$$-dc/dt = (kK_eC)/(1 + K_eC) \qquad \ldots(4)$$

where, C is the concentration of Orange II, k is the apparent reaction rate constant (min^{-1}), K_e is the apparent equilibrium constant for the adsorption of the dye on the catalyst surface.

The equation (3) can be written as:

$$t = 1/(K_e k)\ln(C_0/C_t) + (1/k)(C_0 - C_t) \qquad \ldots(5)$$

where, C_0 and C_t are the concentration of dye at initial and at any time t, respectively.

For the sufficient low concentration of dye, the equation (4) can be expressed as:
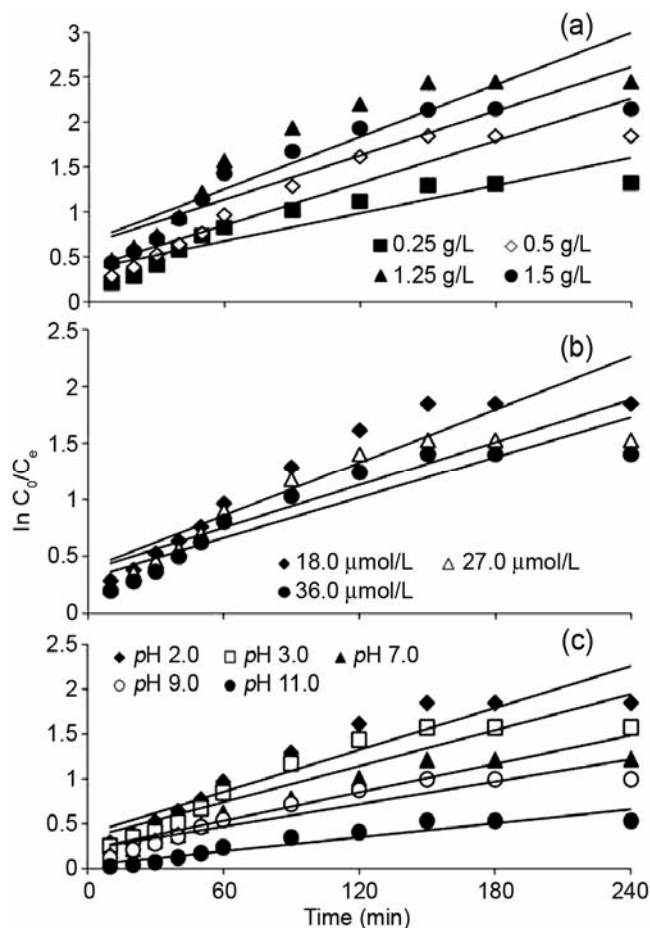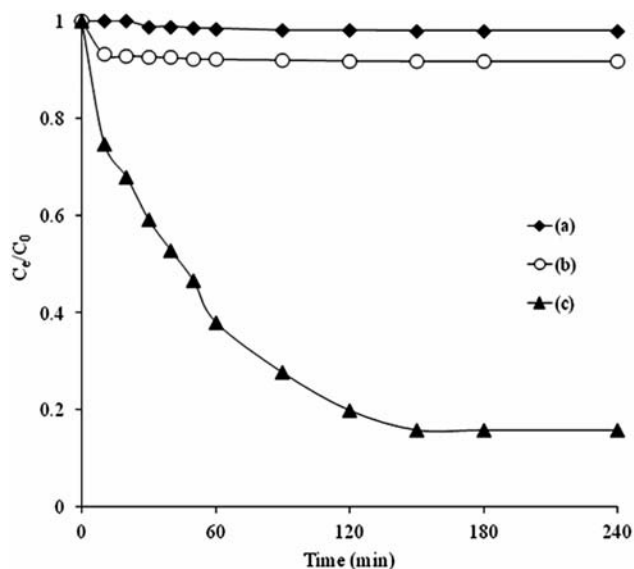
$$\ln(C_0/C_t) = kK_e t = kt' \qquad \ldots(6)$$

where, k' is the overall rate constant (min^{-1}). By plotting $\ln(C_0/C_t)$ as a function of irradiation time through regression, we obtained for each catalyst sample the k'(min^{-1}) constant from the slopes.

The overall rate constant for dye-N-TiO$_2$ interactions was studied for variation different experimental parameters, namely change of catalyst load, initial dye concentration and solution pH. Although the curves did not pass through the origin as required by the model, the intercepts were close to zero (varied from + 0.041 to + 0.675) (Fig. 4).

The Langmuir-Hinshelwood rate constants showed a steady increase from 5.2×10^{-3} min^{-1} (catalyst load 0.25 g L^{-1}) to 9.7×10^{-3} min^{-1} (catalyst load 1.25 g L^{-1}) decreased further (8.2×10^{-3} min^{-1}) for catalyst load 1.5 g L^{-1}. The decrease in initial dye concentration had a positive influence on the rate constant (7.8×10^{-3} min^{-1} to 5.9×10^{-3} min^{-1} for 18.0 µmol L^{-1} to 36.0 µmol L^{-1}). In terms of solution pH, the rate of decolourisation favoured lower pH (7.8×10^{-3} min^{-1} at pH 2.0 to 2.6×10^{-3} min^{-1} at pH 11.0). All the k' values are given in the Table 2. These results were consistent with the influence of experimental parameters on photocatalytic decolourisation. Orange II degradation by active TiO$_2$ layers, immobilized on aluminium sheets[57] possessed a rate constant of 2.2×10^{-3} min^{-1} and TiO$_2$ active layers screen printed on ceramic tiles[58] showed a rate constant of 2.9×10^{-3} min^{-1}.

Table 2—Lagergren first order rate constants (for dye adsorption) and Langmuir-Hinshelwood first order rate constants (for dye decolourisation) on N-TiO$_2$

Parameters		Lagergren rate constants $k_1 \times 10^2$ (min^{-1})	L-H rate constants $k' \times 10^3$ (min^{-1})
N-TiO$_2$ dose (g L^{-1}) (Initial dye concentration 18 µmol L^{-1}, *p*H 2.0)	0.25	7.8	5.2
	0.50	8.4	7.8
	1.25	8.7	9.7
	1.50	8.5	8.2
Initial dye concentration (µmol L^{-1}) (N-TiO$_2$ dose 0.50 g L^{-1}, *p*H 2.0)	18.0	8.4	7.8
	27.0	7.8	6.3
	36.0	6.4	5.9
*p*H (N-TiO$_2$ dose 0.50 g L^{-1}, Initial dye concentration 18 µmol L^{-1})	2.0	8.4	7.8
	3.0	8.1	6.7
	7.0	7.2	5.3
	9.0	6.0	4.2
	11.0	5.9	2.6

Fig. 4—Langmuir-Hinselwood plots for Orange II degradation for variation of (a) N-TiO$_2$ dose (b) initial dye concentration and (c) solution *p*H.

Fig. 5—Comparison of the photocatalytic decolourisation of Orange II (a) blank (b) TiO$_2$ P25 (c) N-TiO$_2$ (N-TiO$_2$ dose 0.5 g L^{-1}, initial dye concentration 18.0 µmol L^{-1}, temperature 303 K).

Comparison of Orange II decolourisation on N-TiO$_2$ and pure TiO$_2$ P25

In a blank experiment (carried out with 18 µmol L^{-1} dye for 240 min in absence of catalyst under visible light), only 1.99% decolourisation was observed (Fig. 5). A comparative study was carried for the decolourisation of Orange II by N-TiO$_2$ and pure TiO$_2$ P25. It was observed that from an initial dye concentration of 18 µmol L^{-1} (irradiation time 240 min), 0.5 g L^{-1} of N-TiO$_2$ could decolourise ~84.24% of dye, while only 8.21% decolourisation
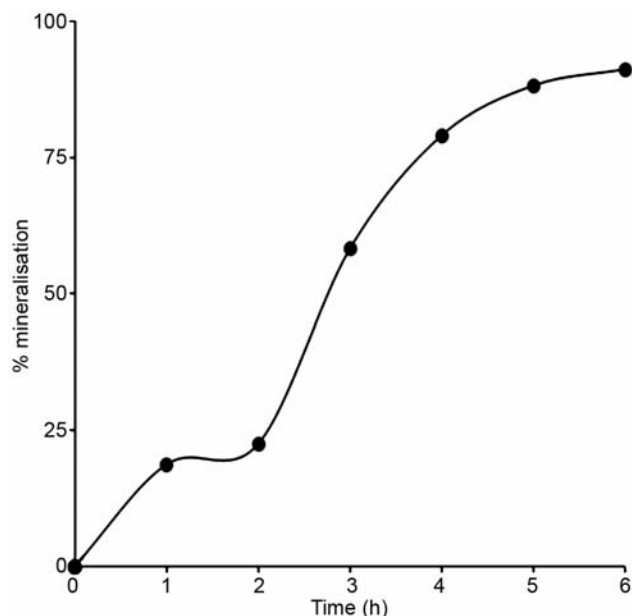
Fig. 6—Variation of percentage mineralisation with irradiation time (N-TiO$_2$ dose 0.5 g L^{-1}, Initial dye concentration 18.0 µmol L^{-1}, pH 2.0, temperature 303 K)

was noticed by TiO$_2$ P25. The study revealed that N-TiO$_2$ could more efficiently decolourise the dye by ~10 times more than undoped TiO$_2$. The Langmuir-Hinshelwood rate constant of the dye decolourisation by N-TiO$_2$ and TiO$_2$ P25 was 7.8 × 10^{-3} and 2.0 × 10^{-4} min^{-1}, respectively indicating that the rate constant of nitrogen doped TiO$_2$ was ~39 times higher compared to the pure catalyst.

Mineralization of dyes

The extent of degradation/mineralization of an organic species is often understood by the reduction of Chemical Oxygen Demand (COD). With initial Orange II concentration of 18.0 µmol L^{-1} and catalyst load 0.5 g L^{-1}, a steady decrease in COD with the increase in the irradiation time was observed (Fig. 6). The percentage mineralisation of the dye increased from 18.71 to 91.14% as the photocatalytic reaction was carried out at 1 to 6 h. Moreover, the percentage mineralization was less (79.02%) compared to percentage decolourisation (84.24%). The production of smaller uncoloured products during the decolourisation process might be responsible for comparatively higher values of COD, which could not impart any colour, showing higher percentage of decolourisation.

Conclusion

The N doped TiO$_2$ has been synthesized by a very simple method using TiCl$_3$ and aqueous NH$_3$ and the material is found to be active for the decolourisation of Orange II from aqueous solution. The variation of N-TiO$_2$ load, initial dye concentration and solution pH influence the adsorption of dye as well as decolourisation process. The higher catalyst amount favour decolorisation of the dye. However, the efficiency of the process decreases after a certain N-TiO$_2$ load. The decrease in initial Orange II concentration as well as low solution pH favour dye decolourisation.

Adsorption of dye follow Lagergren first order kinetic model while the photo-catalytic decolourisation follow modified Langmuir-Hinshelwood model. N-TiO$_2$ is comparatively a better adsorbent than TiO$_2$ P25 as depicted by the Langmuir monolayer capacities. Modification of TiO$_2$ improves the decolourisation compared to TiO$_2$ P25. The percentage mineralization of the dye increases form 18.71 to 91.14 % for the increase of irradiation time 1 to 6 hr.

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