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Hydrothermal preparation of neodymium oxide coated titania composite designer particulates and its application in the photocatalytic degradation of procion red dye

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Nd_2O_3 coated onto titania composite designer particulates using 1M NaOH at 250°C and P∼80 bars with an experimental duration of 5–72 h were obtained under hydrothermal conditions. Different weight % of Nd_2O_3 (1–9%) was used for coating in order to reveal the role of Nd_2O_3. Characterization of the Nd_2O_3 coated titania composite designer particulates obtained was carried out using XRD and FTIR spectroscopy techniques. Photocatalytic reactivity of Nd_2O_3 coated titania composite designer particulates was evaluated by studying the degradation of procion red dye. The effect of various kinetic parameters like initial dye concentration, catalyst amount, pH of the medium, temperature of the medium, light source and catalyst reusability on the photodegradation of procion red dye has been discussed in detail. The thermodynamic parameters like energy of activation, enthalpy of activation, entropy of activation and free energy of activation were estimated. *© 2006 Springer Science + Business Media, Inc.*

1. Introduction

Color in industrial wastewater is often objectionable and is sometime regulated in the effluent discharge. The color of wastes is the most apparent indicator of waste pollution and it should be reduced before it enters into the environment. More recently the degradation of colored wastewater in environmental protection studies has gained importance. The disadvantage of commonly used traditional methods of wastewater purification is the fact that they are not destructive but only transfer the contamination from one phase to another.

New technologies of wastewater purification leading to the complete mineralization of organic pollutants are now considered as the most suitable solution. Recently, the

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advanced oxidation processes (AOP) have been proposed as the alternative methods for water purification [1–3]. Many organic compounds in aqueous solution can be decomposed in the presence of TiO_2 illuminated with UV light or sunlight [4].

Coating with metal complexes has been proved to be a potential option for the improvement of photocatalytic activity of titanium dioxide. Enhanced photoactivity by coating titania with rare earth metal oxides was envisaged as a good tool to improve photocatalytic properties. Rare earth ions are known for their ability to form complexes with various Lewis bases (e.g., acids, amines, aldehydes, alcohols, thiols, etc.) in the interaction of these functional groups with the *f*-orbitals of the lanthanides. It is expected that the incorporation of rare earth oxides into TiO_2 matrix could provide a means to concentrate the organic pollutant at the semiconductor surface thereby enhancing the photoactivity of titania [5]. The reason for the increased interest in photocatalytic processes is the fact that the process is carried out under ambient conditions. It does not require expensive oxidants (atmospheric oxygen is an oxidant) and catalyst is inexpensive, nontoxic and can be activated by UV light. The photocatalytic oxidation of dyes is a specific type of photocatalysis, namely sensitized photocatalysis [6, 7]. The particles of dye adsorbed onto the photocatalyst surface are excited during the process of sensitized photocatalysis and after that electron injection from excited dye particle to the conduction band of semiconductor takes place. The advantage of sensitized photocatalysis is the fact that it extends the range of excitation energy into visible range and thus gives full use of solar energy.

The aim of the present study is to synthesize Nd_2O_3 coated titania composite designer particulates and to investigate the photocatalytic degradation of procion red dye using the catalyst.

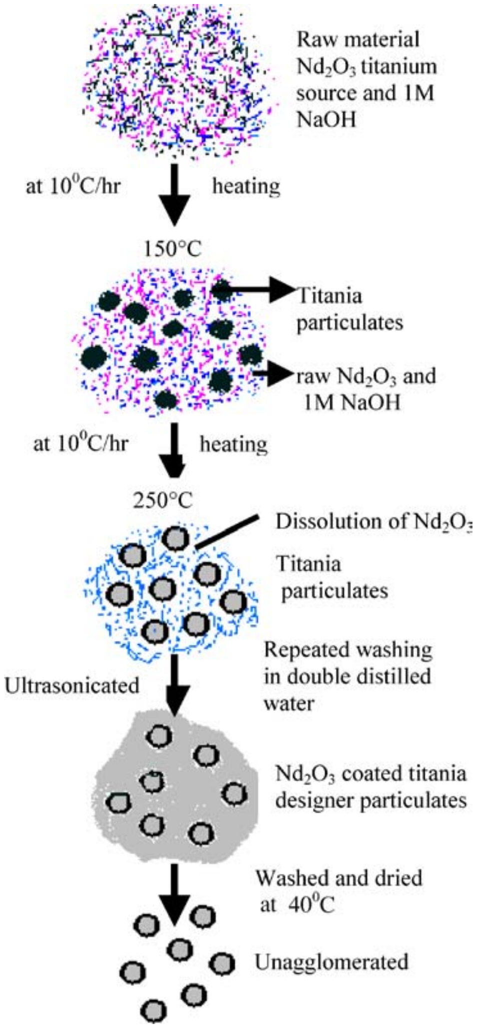


Figure 2 The schematic representation of the formation of Nd_2O_3 coated titania designer composite particulates.

2. Experimental

In the preparation of Nd_2O_3 coated titania composite designer particulates, titanium (IV) oxide-325mesh, 99 + % (M/s Aldrich, India) and neodymium oxide (Loba Chemie, India) were taken in a Teflon liner. A required amount of an effective mineralizer was added into this mixture in the teflon liner, which was later placed inside an autoclave.

Figure 1 Schematic diagram of hydrothermal autoclave.

A schematic representation of the hydrothermal autoclave used in the present work is given in Fig. 1. The autoclave was then placed inside the furnace and the temperature was raised by 10°C per hour up to 150°C held for 36–40 h at 150°C that results in the formation of titania particulates. Then the temperature of the furnace was raised by 10°C per hour up to 250°C and held for 24 h. The pressure inside the reactor was measured in the initial runs using a Bourdon gauge and the volume was maintained for subsequent experiments.

As the temperature was raised from 150 to 250°C in the presence of a strong mineralizer, the Nd_2O_3 begins to crystallize. The already formed titania particulates form the nucleation centers for the crystallization of Nd_2O_3, which starts forming a coating around titania particulates. The Nd_2O_3 coating is strong at the interface surface with titania and they are held firmly by a chemical bonding, which does not break even after repeated ultrasonication after the experiments. Fig. 2 shows the schematic representation of the formation of Nd_2O_3 coated titania designer composite particulates under the present experimental conditions. In the present work, different wt% of Nd_2O_3 like 1, 3, 5, and 9% were tested.

The mineralizer used was 1M NaOH. In some experiments acid mineralizers like HNO_3 and HCl were tried, but the TiO_2 formation and Nd_2O_3 coating on TiO_2 were not satisfactory. Thus NaOH was found to be very effective as a mineralizer. The experimental temperature, molarity, type of the mineralizer and % fill controls the size and morphology of the final product [8, 9]. The precursors were prepared using double distilled water. After the experimental run, the autoclave was quenched and the liner was taken out. The resultant product inside the liner was thoroughly washed with double distilled water repeatedly and ultrasonicated. The product was dried at 40°C in an oven.

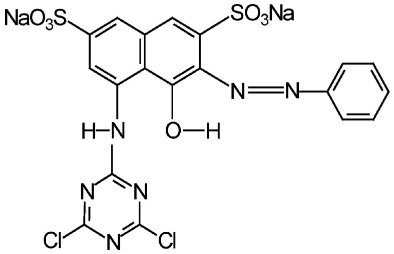
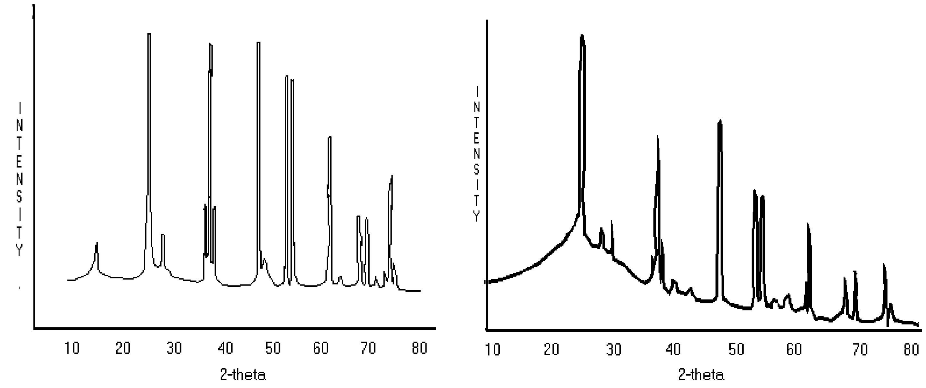


Figure 3 Molecular structure of procion red dye.

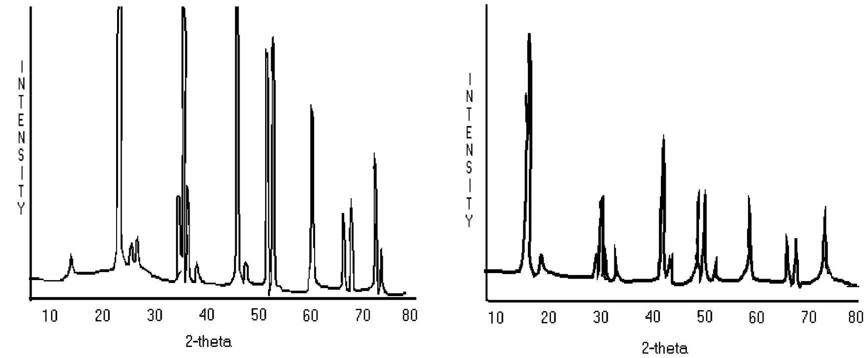
The Nd_2O_3 coated titania designer particulates prepared were characterized using X-ray powder diffractometer (Rigaku Miniflix, Model IGC2, Rigaku Denki Co. Ltd, Japan). The scanning range was 10–80°(2θ). The surface functional groups of the Nd_2O_3- TiO_2 were analyzed using FTIR spectroscopy (Jasco, FTIR-460 plus, Japan). The FTIR Spectra were recorded in the range of 4000–400 cm^{-1}. Further, the authors have carried out the XPS, EDAX and high resolution SEM studies to confirm the formation of the Nd_2O_3 coated titania particulates. The results will be published separately elsewhere. In the present work, the title compounds were used in the photodegradation of procion red dye.

In the photocatalytic treatment of procion red dye (the structure of procion red dye is shown in Fig. 3), a known molar concentration of the dye solution (50 ml) was taken in a 500 ml dry beaker. A required amount of as prepared catalyst was added into this dye solution. Then the beaker was placed in a closed chamber with a UV source



(a) 1% Nd_2O_3

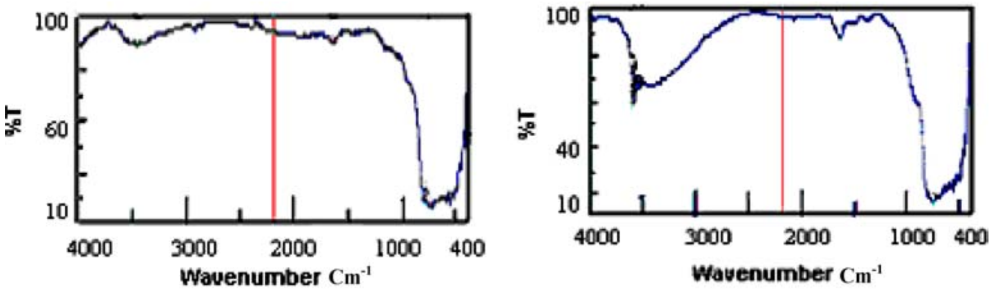
(c) 5% Nd_2O_3



(b) 3% Nd_2O_3

(d) 9% Nd_2O_3

Figure 4 XRD patterns of Nd_2O_3 coated titania.



(a) (b)

Figure 5 FTIR spectra of titanium oxide and Nd_2O_3 coated titania: (a) Pure titanium oxide (b) Nd_2O_3 (9%) coated titania.

(Sankyo Denki, Japan, 8W). The intensity of the UV light was estimated by photolysis of uranil oxalate [10] and it was found to be 2.3775×10^{15} quanta/sec. Dye samples were taken out at a regular interval from the test solution, centrifuged for 4 to 5 min at 950–1000 rpm and then used in the measurement of %T at 538nm using a Spectrophotometer (Model: Minispec, Systronics, India). Chemical oxygen demand (COD) was estimated before and after the treatment (using $K_2Cr_2O_7$ oxidation method). For all the photocatalytic experiments in the present work 5×10^{-5} M procion red dye, and 150 mg Nd_2O_3 coated titania were taken as an optimum concentration and UV light was used as the source of illumination unless specified.

3. Results and discussion

X-ray powder diffraction patterns of different percents of Nd_2O_3 coated titania designer particulates are shown in Fig. 4a–d. The identification of crystalline phases of Nd_2O_3 coated titania was accomplished by comparison with JCPDS FILES, (PDF 330942). It can be observed that as the Nd_2O_3 coating thickness was increased the Nd_2O_3 peaks become stronger and more intense as seen in Fig. 4 (a–d).

The Fig. 5a shows the FTIR spectrum for uncoated pure TiO_2, and Fig. 5b shows the FTIR spectrum for the Nd_2O_3 coated TiO_2. The presence of Nd_2O_3 is distinctly seen in the Fig. 5b with the appearance of absorption bands in the range 1041 cm^{-1}. Further with the presence of Nd_2O_3 the absorption bands in the range 1040 cm^{-1} to 400 cm^{-1} becomes narrower with more splitting.

4. Photocatalytic degradation of procion red dye

In order to study the role of Nd_2O_3 in the Nd_2O_3 coated TiO_2 systems, Nd_2O_3 coated TiO_2 prepared with 1 to 9 wt% of Nd_2O_3 was tested for their photodegradation efficiency. Nd_2O_3 coated TiO_2 prepared with 3% Nd_2O_3 was found to be more efficient, because it shows maximum photodegradation efficiency, which can be noticed from Fig. 6. In all the subsequent experiments $Nd_2O_3-TiO_2$ prepared with 3% Nd_2O_3 has been considered.

The efficiency of prepared $Nd_2O_3-TiO_2$ over untreated TiO_2 was compared by degrading procion red dye (5×10^{-5}M). It was found that the Nd_2O_3-TiO_2 shows very high efficiency; when compared with the untreated TiO_2. Fig. 7 shows plot of log (C_0/C) Vs irradiation time for untreated TiO_2 and Nd_2O_3 coated titania.

5. Kinetic and thermodynamic studies

The rate of photomineralization of an organic substrate sensitized by a semiconductor, not only depends on the nature of the semiconductor photocatalyst but also on the nature and concentration of the organic substrate, light intensity, concentration of the semiconductor, COD, pH, etc. The influence of various kinetic parameters on the efficiency of photodegradation of procion red dye has been presented in the subsequent section.

The photodegradation reaction follows the pseudo-first order reaction kinetics with respect to procion red concentration. Fig. 8 shows the first order plot (log

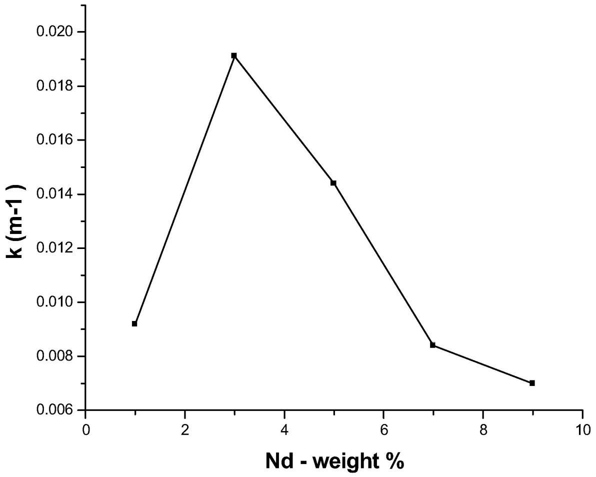


Figure 6 Rate constant plot for Nd_2O_3- titania prepared with different % Nd_2O_3

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TABLE I COD values of initial and treated procion red dye solution

Dye concentration (M)	Initial COD (mg/l)	Final COD (mg/l)	Photodegradation efficiency (%)
9×10^{-4}	352	32.1	90.8
5×10^{-4}	144	9.2	93.6
9×10^{-5}	124	13.6	89
5×10^{-5}	80	24	70

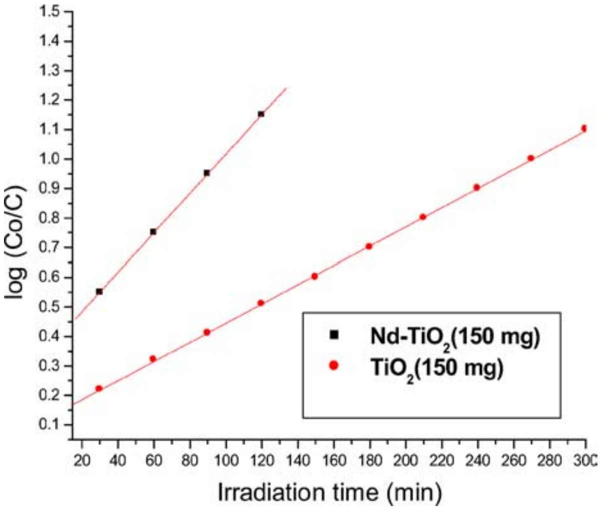

Figure 7 Photoefficiency comparison of untreated titania and Nd_2O_3 coated titania.

C_0 / C Vs time). Table I gives the rate constant and $t_{1/2}$ values for the reaction. It is clear that the rate constant k (m^{-1}) and the half-life ($t_{1/2}$) are independent of the initial concentration of the dye.

The Fig. 8 shows the plot of log (C_0/C) Vs time with respect to different initial concentrations of the dye. It shows a high efficiency at mere low initial concentration of the dye (1×10^{-5} M) with fast degradation. As the dye concentration increases, the quantity of intermediates increases as well, competing through side reactions with the parent dye decomposition [10, 11]. Since illumination time and amount of catalyst are constant, the OH radical (primary oxidant) formed on the surface of catalyst is also constant. So the relative number of free radicals attacking the dye molecules decreases with increasing amount of the catalyst [12]. The major portion of degradation occurs in the region nearer to the irradiated side, since the irradiation intensity in this region is much higher than that at the other side [13]. Hence at higher concentration, degradation decreases at sufficiently longer distances from the light source or reaction zone due to the retardation of penetration of light. Thus, the rate of degradation decreases with increase in concentration of dyes.

The Fig. 9 illustrates the effect of different amounts (50–250 mg) of Nd_2O_3 coated TiO_2 on the rate constant of the photodegradation reaction and the rate constant increases up to 150 mg/50 ml of the dye, beyond which it shows a gradual reduction in the rate constant. The reduction in the rate constant may be due to the reduction in the penetration of light with surplus amount of Nd_2O_3 coated TiO_2. Hence, an optimum catalyst 150 mg is added in the study in order to avoid unnecessary excess catalyst and also to ensure total adsorption of light photons [14].

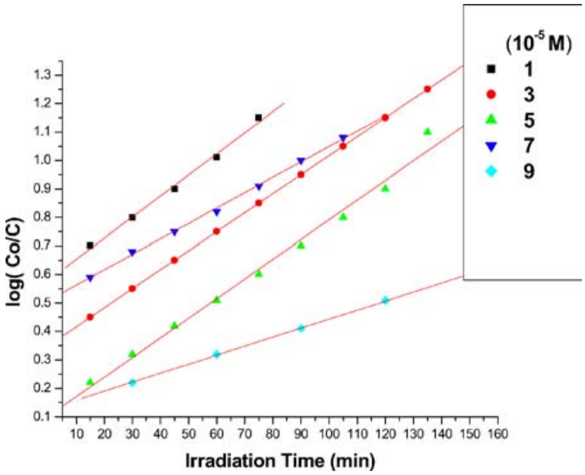

Figure 8 First order plot for varying concentrations of dye.

The wastewaters from textile industries usually have a wide range of pH values. Hence, attempts have been made to study the influence of pH in the degradation of procion red dye using UV light. It is clear from Fig. 10 that both acidic and basic media influences the efficiency of photodegradation reaction. Under acidic conditions, the perhydroxyl radical is formed by the protonation of the superoxide radical. Consequently the perhydroxyl radical can form hydrogen peroxide, which in turn dissociates to give hydroxyl radical, which results in the

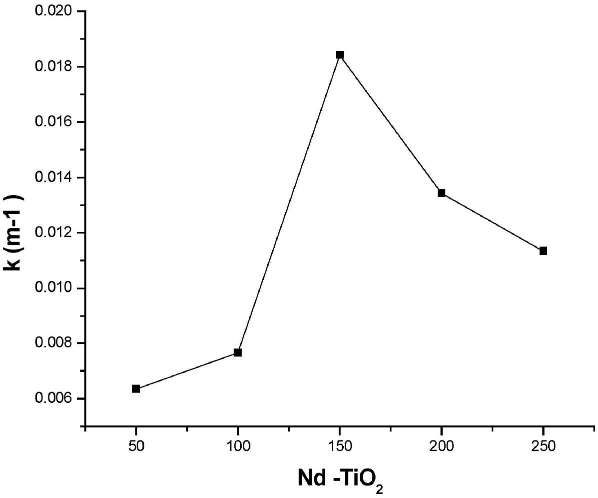

Figure 9 Effect of Nd_2O_3 coated TiO_2 weight on the rate constant of the photodegradation reaction.

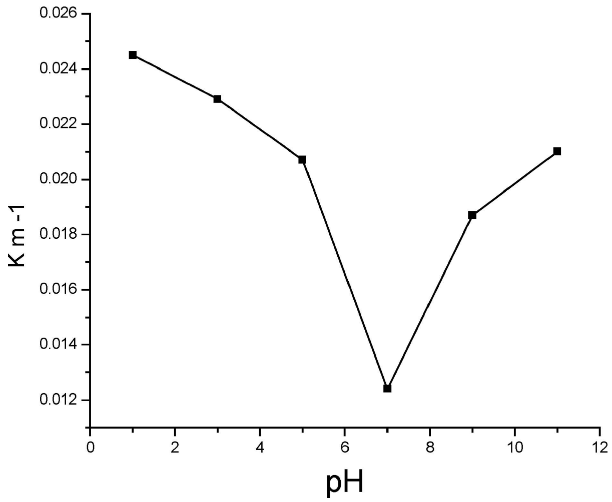

Figure 10 Effect of pH on the rate constant of the photodegradation reaction.

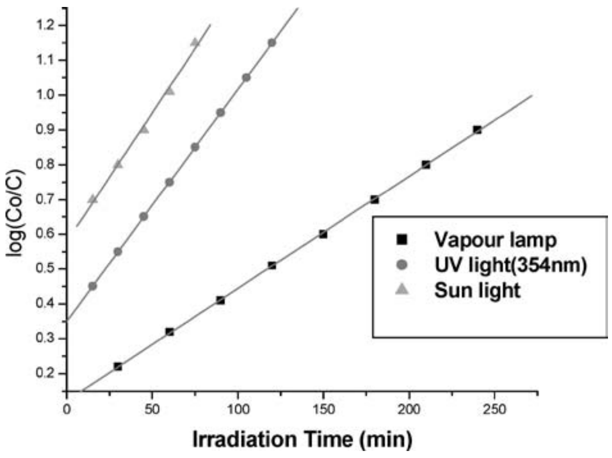

Figure 11 Effect of light source on the photodegradation efficiency.

degradation of the dye. An increase in the concentration of hydroxyl ion increases the rate of reaction, which in turn increases the concentration of OH radicals with time. Even though there is an increase in efficiency at higher acidic and alkaline pH, it is not suggested to use in waste treatment, popularly because it may cause corrosion of the entire waste treatment system.

The photodegradation experiments were carried out with UV light, sunlight and Mercury vapor lamp. It was found that the sunlight is more favorable and it takes 90 min for the complete degradation of procion red dye (Fig. 11). The intensity of sunlight was measured and it was found to be 8.425×10^{16} quanta/s (between 2 pm to 3 pm on a sunny day), and the intensity of UV light was found to be less when compared to that of sunlight (2.3775×10^{15} quanta/s). This increase in the light intensity may facilitate the electron-hole formation and retards the electron-hole recombination, which enhances the photodegradation efficiency. The chemical oxygen demand test is widely used as an effective technique to measure the organic strength of wastewater. The test allows measurement of waste in terms of the total quantity of oxygen required for oxidation of organic matter to CO_2 and water. The COD of the dye solution before and after the treatment has been estimated. The reduction in the COD values of the treated dye solution indicates the mineralization of dye molecules along with the color removal. The Table I gives the COD values of blank and treated dye solutions. The photodegradation efficiency is calculated from the equation given below

$$Photodegradationefficiency = \frac{Initials_{COD} - Final_{COD}}{Initials_{COD}} \times 100$$

6. Conclusion

Preparation of photocatalytic Nd_2O_3 coated titania was carried out under hydrothermal conditions (T = 250°C, P∼80 bars). Nd_2O_3 coating was done in order to enhance the photocatalytic activity. The photocatalytic degradation of dyes using Nd_2O_3 coated titania composite designer particulates may be an efficient and environmentally benign technique, because it facilitates the complete mineralization of the complex dye molecules into simpler non-toxic substances. More over, the use of sunlight as the source of illumination in the photodegradation reaction could be a safe and cost effective source.

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