

Nano TiO₂ Assisted Degradation of Textile Dyes in H₂O₂ Aqueous Solution: Kinetic Studies with pH and Mass Effects

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Abstract: In order to exploit the efficiency of the photocatalyst TiO₂ nano crystallites were prepared by a combination of hydrothermal and sol gel method. XRD, SEM, UV- visible spectroscopy measurements were used for characterization. The catalytic efficiency of the nano crystalline TiO₂ was investigated under visible light irradiation for the oxidative degradation of four different intensely coloured dyes containing H₂O₂ in aqueous medium. Also these dyes act as potential aqueous pollutants. Reactive yellow 1(RY), acid blue ffs(BFA), methyl orange(MO) and acid green 3GM(AG) are the dyes studied. The catalytic coefficient (ϕ) measured on comparison with the rate constant values in the absence of catalyst were found to be predominantly high for the nano TiO₂ catalyst with the values: 14.7, 33.1, 11.6 and 11.5 respectively for AG, MO, BFA and RY systems. Such photo catalytic degradations have much significance in organic pollutants and colourants, bleaching processes.

Keywords: Nano TiO₂, Photo catalytic degradation, Textile dyes, Catalytic coefficient

Introduction

Synthetic dyes are used extensively in numerous industrial processes. During various dyeing and finishing process, it is found that considerable amount of waste is generated^{1,2}. The discharge wastes containing dyes are toxic to micro organisms, aquatic organisms and human beings. These coloured dyes when discharged into rivers or lakes they cause non-aesthetic pollution, biological magnification eutrophication, toxicity and perturbation in aquatic life³. These dye pollutant are chemically stable, so traditional water treatment methods are ineffective. Combination of UV radiation and hydrogen peroxide oxidation has been applied for the advanced oxidation degradation of dyes in waste water⁴. UV/H₂O₂ process destroys the chromophore structure of these dyes and leads to complete decolourisation of dyes. In the advanced oxidation process, the hydroxyl radical is formed which can oxidize the wide range of organic compounds and there is no sludge formation during different stages of treatment⁵.

In the photo catalytic reactions, the semi conducting material absorbs light energy more than or equal to energy gap, which generates the holes and electrons, which further give rise to efficient oxidizers of organic dyes. For the degradation of organic dyes, nano crystalline TiO_2 used as a photo catalyst in aqueous medium which is a much needed process for the current issue⁶. Smaller the particle size of the catalyst, especially in nano meters, better photo catalytic activity is imparted due to high surface area and high surface area to volume ratio values.

We have focused our study on the oxidative degradation of four commercially used organic dyes Acid green 3GM (AG), Blue Ffs acid (BFA), Methyl orange(MO) and Reactive yellow 1(RY) in aqueous medium in the presence of nano crystalline TiO_2 as synthesized and characterized in the laboratory. UV-visible spectroscopy is employed to study the kinetic and reaction pathway of photo catalytic degradation of the dyes. In the Figure 1 the molecular structure of the four dyes (AG, BFA, MO and RY) are given. The size characterizations on TiO_2 are measured using FE-SEM, TEM and EDX. The catalyst particle size and poly dispersity index are studied. A combination method of sol-gel and hydrothermal method is utilized in the preparation of nano crystalline TiO_2 ⁷. The efficiency of H_2O_2 and nano TiO_2 catalyst for the degradation of the four organic dyes are graded⁸. The effect of variation in pH, solvent and ionic strength are carried out to optimize the oxidation rates in aqueous medium⁹⁻¹².

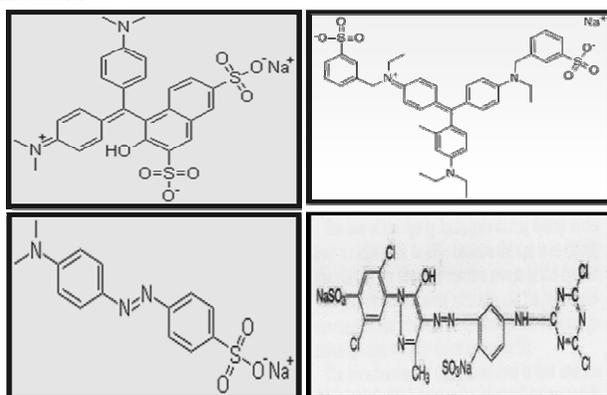


Figure 1. The molecular structure of the organic dyes a) AGM b) BFA c) MO d) RY

Experimental

Titanium tetra isopropoxide was used as the precursor in the synthesis of nano TiO_2 and was purchased from S.D.Fine chemicals Ltd, India with 99.9% purity. Triple distilled water was used in all solution preparations. The organic solvents used were purchased from Merck (Germany). The textile dyes are purchased from S.D fine chemicals India Ltd.

Preparation of nano crystalline TiO_2

Nano particles of TiO_2 were synthesized by hydrolyzing titanium tetra isopropoxide in a mixture of 1:1 anhydrous ethanol and water. 9 mL of titanium tetra isopropoxide is mixed with 41 mL of anhydrous ethanol (A). 1:1 ethanol and water mixture is prepared (B). Solution A is added in drop wise to solution B and stirred vigorously for 2 h. At room temperature hydrolysis and condensation are performed, using 1 M sulphuric acid and stirred for 2 h. Then the ageing was undertaken for 12 h.

The gel was transferred into an autoclave and tightly closed and the mixture was subjected to hydrothermal treatment at 353 K for 24 h. After filtration the solid residue was washed thoroughly with water and ethanol mixture, dried at 373 K in an oven and calcined at 773 K.

Characterization of nanocrystalline TiO₂

The white nano crystalline powders of TiO₂ are characterized by powder x-ray diffraction (XRD) with Philips X'pert PAN analytical model using Cu-K_α radiation. Figure 2, XRD patterns are obtained for 20-80° (2θ) by step scanning with a step size of 0.02°. UV-Visible diffused spectra of the samples were recorded with Shimadzu UV 2450 model using BaSO₄ white plate as reference. Scanning Electron microscope (SEM) photos of catalysts are taken by JEOL - SEM instrument Figure 3.

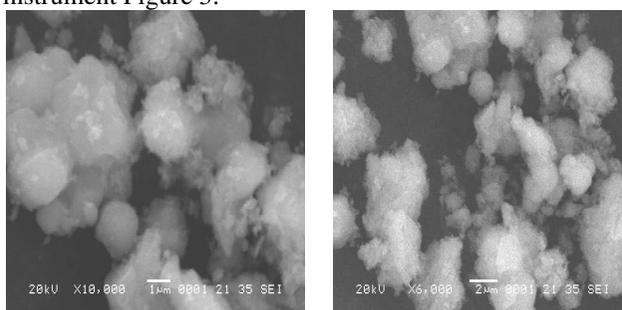


Figure 2. SEM Photograph of nanoTiO₂

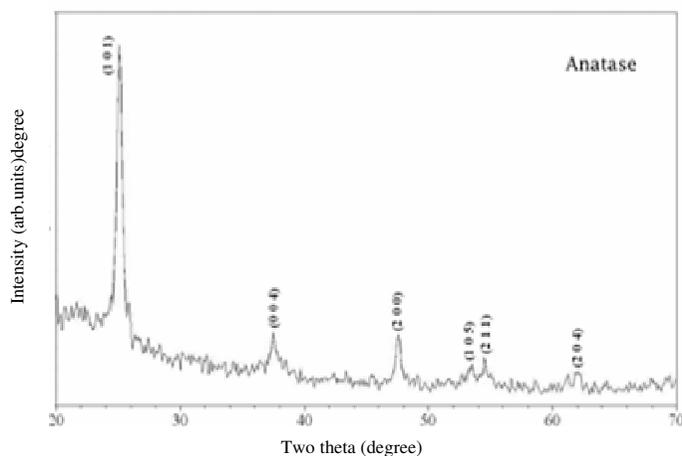


Figure 3. XRD analysis of nano TiO₂ particles

Reaction catalysis

The catalytic degradation of the four organic dyes was performed in a glass three necked round bottomed flask considered as the reactor. 100 watt tungsten lamp was lit placing above the reactor. For every 10 mL of the aqueous solution of the 1 mL of 0.01 M H₂O₂ and 1 mg of catalyst were fed into the reactor and stirred continuously under visible light illumination. Small aliquots of the sample was collected at regular intervals of time and filtered before the UV – visible spectra scan.

Results and Discussion

Kinetic studies

The aqueous solutions of organic dyes with known concentration are irradiated with, visible light using tungsten lamp which is compatible with solar radiation both in the presence of hydrogen peroxide¹² and nanocrystalline TiO₂. After the start of the irradiation at regular intervals of time 5 mL aliquots of the solution are subjected to UV-spectral scan. The completion of the oxidative degradation of the dyes is known from the gradual decrease of the absorbance value approaching the base line. The time of completion of oxidative degradation varies with the chemical structure of the organic dyes. From the time dependence UV-spectra profiles, OD vs. time plots is drawn. Figure 5(a, b). The limiting regions in the exponential plots indicate the completion of reactions. It was found that in the presence hydrogen peroxide the oxidative degradation was detected on the substrates and the rate of oxidative degradation is enhanced in the presence of nano crystalline TiO₂ in the present work. The photo catalytic disappearances of dyes are found initiated only upon the incorporation of hydrogen peroxide and nano TiO₂ particles. From the OD vs. time plots, the kinetic plots consisting of $\log OD_0/OD_t$ vs. time are generated. (Figure 6a, 6b) The first order rate coefficient (k) values are obtained from the slope values of the kinetic plots, multiplied with 2.303. The best fit linear plots are found in the kinetic analysis for the first order reaction under pseudo conditions only.

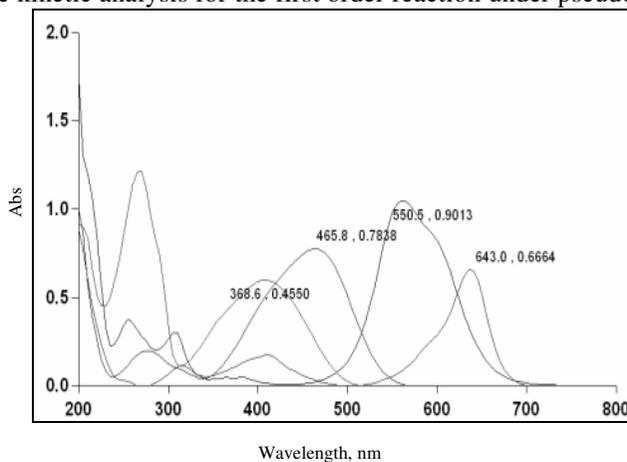


Figure 4. UV –visible spectrum for the four organic dyes (AG, BFA, MO and RY)

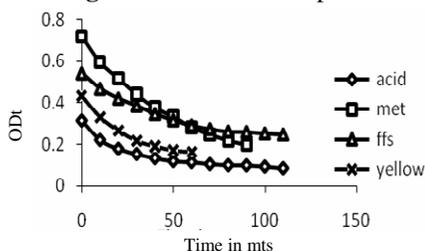


Figure 5a. OD_t vs. time plots for the dyes with H₂O₂

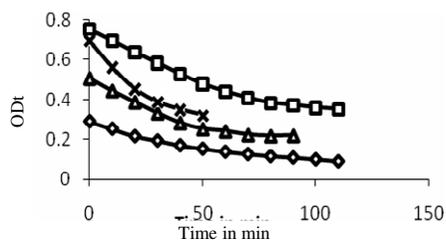


Figure 5b. OD_t vs. time plots for the dyes with nano TiO₂

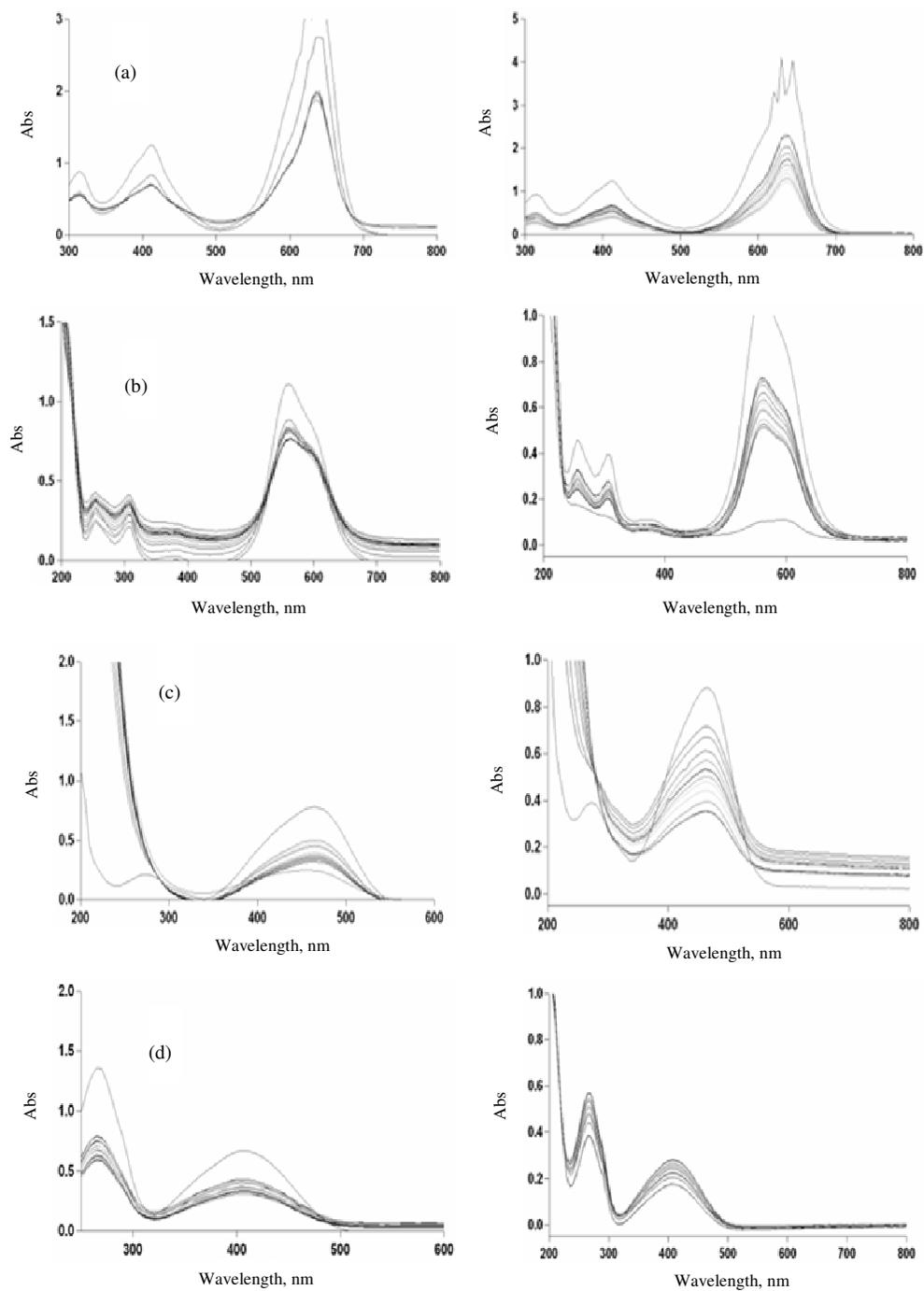


Figure 6. Time dependent UV visible spectra of (a) AG, (b) BFA, (c) MO and (d) RY 2, in the absence and in the presence of nano TiO₂

Spectral studies

In most cases the peak present in the visible region (more than 400 nm) are chosen for the time dependence study on the spectra. In Figure 6 time dependent UV-spectra for the four organic dyes are presented. When the visible light was switched off, no variation in the UV-spectra with time was recorded. Therefore presence of visible light seems to trigger oxidative degradation soon after the visible light irradiation. Using these time dependent spectra absorbance vs. time plots were prepared. Figure 5a, b. The kinetic plots for the rate co-efficient determination was successfully generated using $\log OD_0/OD_t$ vs. Time data. Such kinetic plots are given in the Figure 7a,7b.

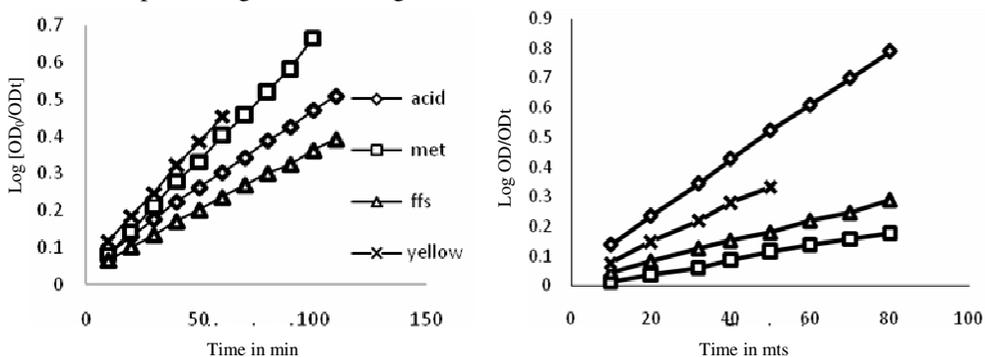


Figure 7a,7b. Log OD_0/OD_t vs. time plots for the four organic dyes

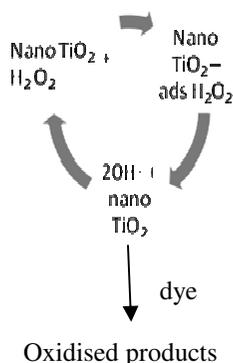
In Table 1 the pseudo first order rate coefficient values determined from the Figure 5a,5b are given for the four organic dyes. It was found that, among the organic dyes used, the rate coefficient value of was found to be the highest for RY and least value is for MO in the presence of hydrogen peroxide. In the presence of nano crystalline TiO_2 the rate coefficient value was found to be the highest for RY and the least value for the BFA.

Table 1. Pseudo first order rate coefficient values of the organic dyes

| Name of the dye | k_1 in sec^{-1} with $H_2O_2 \times 10^{-4}$ | k_2 in sec^{-1} with $TiO_2 \times 10^{-3}$ | Catalytic coefficient (ϕ) = k_1/k_2 |
|-------------------|---|--|--|
| Acid green 3GM | 2.17 | 3.19 | 14.7 |
| Methyl Orange | 0.796 | 2.64 | 33.16 |
| Blue Ffs acid | 1.4 | 1.62 | 11.57 |
| Reactive yellow 1 | 2.906 | 3.35 | 11.52 |

Oxidation mechanism

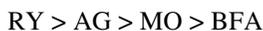
In the TiO_2 aided degradation of reactant dyes in aqueous medium the ionization state of the surface of the TiO_2 nano particles is an important step in producing hydroxyl radicals (OH^\cdot) from hydrogen peroxide in aqueous phase. OH^\cdot Radicals can be produced by the reaction between positive holes H_2O_2 in water. At low pH the positive holes are considered as as the major oxidation species. However in the presence of H_2O_2 the in situ reaction with the positive holes generates OH^\cdot Radicals which triggers the degradation of the dyes. The plausible sequence of steps is as follows.



According to the mechanistic approach H_2O_2 adsorbs on to TiO_2 surface will be in the hydrated form. In the acidic pH less than 6.8 dye degradation occurs rapidly. This is because of the first step depicted for the generation of h^+ (hole) has the optimum pH 6.8. When TiO_2 surface catalysis is considered if the pH exceeds 6.8 the medium produces alkalinity. When the medium of pH is below 6.8 the catalytic reaction is acidic according to the conditions. pH 6.8 happens to be near the point of zero charge of TiO_2 . Regarding the variation in the optimum pH values, for different dyes used in the present work, the acid and basic equilibrium on the TiO_2 surface determines the overall catalysis. In the Table 1 the rate constants for the four organic dyes in the presence and in the absence of nano TiO_2 catalysis are given.

Conclusion

Among the four intensely coloured dyes investigated in this work, it is found that the nano crystalline TiO_2 also induces, oxidative degradation of dyes in the visible light wavelength range, in aqueous medium. The overall trend among the dyes responsive towards nano TiO_2 particles follows as,



Therefore the visible light catalytic reaction took place mainly by the in-situ degradation of nano adsorbed H_2O_2 with subsequent reaction between the OH and dye molecules.

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