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Photocatalytic Degradation of Dyes using Rutile TiO_2-Pani Composite Prepared by One Pot Method

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Abstract

Anionic dye (Direct Blue1) and cationic (MethyleneBlue) was subjected to degradation under sunlight with synthesized photocatalysts; via anatase TiO_2 (AT), rutileTiO_2 (RT), and rutile TiO_2-polyaniline (RTP) composite. The composite was synthesized by one pot method using $TiCl_4$ as precursor. The synthesized catalysts were characterized with XRD, FT-IR, UV-Vis and SEM analysis. The dye was degraded and the degree of degradation was calculated. UV-Vis and FT-IR spectra of catalyst loaded with dye were studied with and without sunlight exposure to reveal the photocatalytic action. The %COD removal was also obtained. The results showed that polyaniline can act as sensitizer. A RTP (TiO_2-polyaniline) composition at 1**:** 0.06 ratios was found to degrade the dye better than all other catalysts. Thus rutile TiO_2 that has lower activity can be made more active than anatase itself by proper compositing with polyaniline. The anionic nature of dye makes it to adsorb on the catalysts. The degradation of the dye can be considered as mainly by adsorption in the absence of sunlight and it competes with catalytic process in the presence of sunlight. The % decolourization and the % COD removal were almost equal and found to be at 60%.

Keywords: TiO_2, Polyaniline, Photocatalyst, Dye, Degradation.

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Introduction

TiO_2 is non-toxic, inexpensive, chemically stable, easily available and has excellent photocatalytic performance. Hence, it has received much attention for the detoxification of wastewater. It has emerged as an excellent photocatalyst material for environmental purification. Numerous routes for the synthesis of large and nanosized crystalline TiO_2 particles and films have been developed. These include hydrothermal (Chae et al., 2003), solvothermal (Trentler et al., 1999), sol-gel (Bessekhouad et al., 2003), microwave method (Lin H.Y and Kuo C.Y, 2009), chemical vapor deposition (Chen X and Mao S.S, 2007), electrodeposition (Lei et al., 2001), and other methods (Yu et al., 2001),(Trentler et al., 1999). The formation of anatase is favoured by fast reactions (Wang et al., 2007) and calcination at temperature between 400 and 600°C (Zhao et al 1998). Calcinations at higher temperature or capillary action (Kim et al 2001) will lead to formation of rutile grade. Anatase grade TiO_2 has a band gap of 3.2 eV and indirect band gaps which prevents the electron- hole recombination. In the case of rutile, the band gap is lower (3 eV), but the recombination occurs fast as it has direct and indirect band gaps. This allows anatase grade to act as better photocatalyst than rutile. The main focus of research going around the world is to make the catalyst active at longer wavelength and to prevent the hole–electron recombination. Conducting polymers like polyaniline (Pani) as sensitizer for TiO_2 and enhanced photocatalytic activity of TiO_2 anatase-Polyaniline composites have been reported (Zhang, 2005, Bitao, 2007, Kim,2007, Li, 2003). Sulfonated dyes undergo chemical interactions with the charged backbone of Pani, leading to significant adsorption of the dyes (Mahanta et al., 2008).

In this study, rutile TiO_2 is composited with pani (RTP) using one pot synthesis method and photocatalytic efficiency is compared with anatase grade TiO_2.

Materials and methods

Titanium tetrachloride and Hydrazine hydride were purchased from Loba chemicals. Aniline (CDH) was purified by distillation before use. Ammonium persulfate and hydrochloric acid were obtained from Fisher India Ltd, and used without further purification. The dyes Direct blue 1 (DB1), Methylene blue (MB), was purchased from Nice & Atul Ltd respectively and used as model pollutants.

The Molecular Formula of Direct blue 1 (DB1) dye is $C_{34}H_{24}N_6Na_4O_{16}S_4$, CAS Number is 2610-05-1 and the colour Idex Number is 24410. Its IUPAC name is Tetra sodium (6E)-4amino-6-[[4-[4-[N'-(8-amino-1-oxo-5,7-Disulfonato-2 naphthylidene)hydrazine]-3-methoxy-phenyl]-2-methoxy-phenyl] hydrazono]-5-oxo-naphthalene-1,3-disulfonate.
The Molecular Formula of Methylene blue (MB) dye is $C_{16}H_{18}CN_3S.3H_20$ CAS Number is 61-73-4 and the colour Idex Number is 52015. Its IUPAC name is 3, 7-Bis dimethylamino-phenothiazin -5-iumchloride.

Instruments used: UV-Vis spectra were recorded using JASCO-V-530 spectrophotometer. FT-IR spectra were recorded using SHIMADZU 8400S spectrophotometer. XRD analysis was performed using XPERT PANALYTIC. The particle size and morphology of the composite were examined by scanning electron microscope (SEM) HITACHI S300H. Dye degradation percentage was analyzed using MERCK Thermoreactor COD analyzer.

Preparation of catalysts

- **Preparation of anatase TiO_2 (AT):** 5 ml of titanium tetrachloride was dissolved in 10 ml of hydrochloric acid with constant stirring for 2 hours at cooling condition. 40 ml of distilled water was added drop wise. Then 3M hydrazine hydride was added drop wise under vigorous stirring for 1 hour. The precipitate thus obtained was filtered and dried over night and then calcination was carried out at 500°C for 2 hours.
- **Preparation of rutile TiO_2 (RT):** 2 ml of titanium tetrachloride was dissolved in 10 ml of alcohol and 34 ml of 1M hydrochloric acid was added. Yellow gel was obtained which turned colorless on addition of hydrochloric acid and heated with constant stirring for 4 hours. White precipitate was obtained. It was filtered and washed with distilled water and dried.
- **Preparation of Pani:** Pani was prepared by chemical polymerization of aniline. About 5 ml of aniline was dissolved in 34 ml of 1M hydrochloric acid with constant stirring at ice-cold condition. Then 10 g of ammonium persulfate was dissolved in 5 ml of hydrochloric acid and added drop wise to the above solution at 0°C. The solution was stirred vigorously. The Green precipitate thus obtained was washed with hot water, ethanol and then dried.
- **Preparation of rutile TiO_2 - Pani (RTP):** 4 ml of titanium tetrachloride was dissolved in 10 ml of alcohol taken in a beaker. 5 ml of aniline dissolved in 34 ml of 1M hydrochloric acid was added drop wise with constant stirring. Yellow gel was obtained which turned colorless on addition of hydrochloric acid. Stirring was continued for 4 hours. Then nitrogen gas was passed for 5 minutes, sealed to make the inert atmosphere of Nitrogen inside. Then 1.6 g of ammonium persulfate dissolved in 5 ml of hydrochloric acid was injected at ice-cold condition. The system was stirred vigorously for 2 hours and kept overnight for the completion of reaction. The Green precipitate thus obtained was then filtered. This process was repeated with 0.5, 0.1 and 0.03 ml of aniline to get TiO_2-Pani composites at different ratios such as 1:0.1, 1:0.06 and 1:0.02 respectively.

Dye degradation

Known amount of the dye was added with different catalyst separately and subjected to direct sunlight exposure for 30 min in noon time. Similar control system was kept in dark for 30 min to study the effect of adsorption. Then all test solutions were centrifuged and catalyst was removed. The optical density of dye solution before and after catalytic treatment was noted and compared. The results obtained with polyaniline, pure TiO_2 (both anatase and rutile) and different polyaniline/TiO_2 ratio were compared. The effects of dye concentration, catalyst loading and pH were studied.

COD analysis

The chemical oxygen demand (COD) of the test sample was measured using thermoreactor TR 200 (Merck) with COD solution A and COD solution B. In this analysis, 0.03 ml of COD solution A (Art.no1.14538) and 2.30 ml of COD solution B (Art.no1.14680) were taken in a cell and mixed. Then 3 ml of solution to be tested was added to the cell and the lid was closed. The cell content was digested using thermoreactor at 148^{o}C for 2 hours. In another cell, 0.30 ml of COD solution A and 2.30 ml of COD solution B were taken, 3ml of pure distilled water was added to it and the lid was closed and digested, which was considered as blank sample. Then the cells were cooled down to ambient temperature and the absorbance of this solution was measured at a wavelength of 585 nm against the blank and multiplied with a factor 1636 to get the COD value in ppm.

Result and Discussion

XRD analysis

The average particle size of the composites synthesized was calculated from Scherrer`s formula. The average particle sizes were found to be 14 and 22 nm respectively for anatase and rutile forms respectively. The hydrolysis reaction of $TiCl_4$ in HCl and ethanol may be in two different routes. The mechanisms proposed in the literature explain that $TiCl_4$ in HCl undergo hydrolysis yielding $TiO_2.nH_2O$, which on calcination gives anatase TiO_2 depending upon calcinating temperature and time, whereas $TiCl_4$ in ethanol yields TiO_2 on reacting in the following path way.

$TiCl_4 + 4ROH \rightarrow Ti(OR)_4 + HCl$

$TiCl_4 + Ti(OR)_4 \rightarrow 2TiO_2 + 4RCl$

$TiCl_4 + 2ROR \rightarrow TiO_2 + 4RCl$

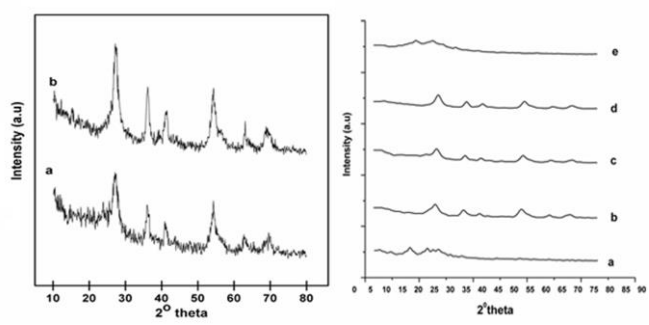

Fig.1

XRD pattern of TiO_2. (a = AT, b = RT).

XRD patterns of RTP composites at different ratios (a = 1:1, b = 1:0.1, c = 1:0.06, d = 1:0.02, e = pristine Pani)

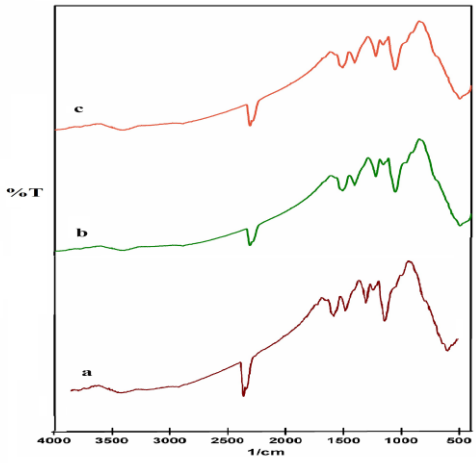

Fig.3

a. FT-IR spectrum of RTP composite
b. RTP composite after treating with dye in sunlight
c. RTP composite after treating with dye in dark

FT-IR analysis

The FT-IR spectra of Pani and Pani-TiO_2 clearly show the formation of composite. In the latter, the characteristic bands of PANI appeared and obviously shifted to the lower wavenumber. The main characteristic bands of Pani are assigned as follows: The peak at 3419 cm^{-1} is attributed to N−H stretching mode. Peaks at 1562 cm^{-1} and 1 479 cm^{-1} are associated for C=N and C=C stretching mode for the quinonoid and benzenoid rings.

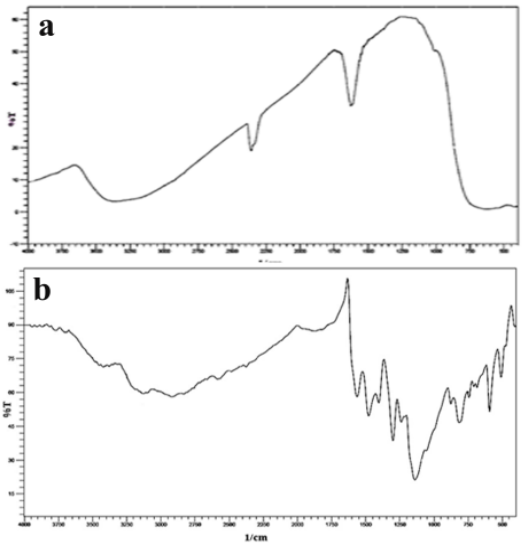

Fig.2

a. FT-IR spectrum of TiO_2 (RT)
b. FT-IR spectrum of Pani

Peaks at 1300 cm^{-1} and 1240 cm^{-1} can be attributed to C−N stretching mode for benzenoid ring. Peak at 1141 cm^{-1} is due to quinonoid unit of doped Pani. Peak at 815 cm^{-1} is usually assigned to an out-of-plane bending vibration of C−H of 1, 4 substituted benzenoid rings, which confirmed the formation of Pani. The intensities of some peaks, for example 3419, 1562, 1058 and 815cm^{-1} are affected by the presence of TiO_2 in Pani synthesis. These differences in the IR spectra can be explained on the basis of constrained growth and restricted modes of vibrations in Pani grown in the presence of TiO_2. In such case, aniline monomer gets adsorbed onto the oxide particles, which were dispersed in the reaction mixture and polymerization proceeds initially on the surface of these oxide particles when ammonium persulfate was added to the solution. This leads to adhesion of the polymer to the TiO_2 particles and the constrained growth around these particles. Such adsorption and constrained motion of the chains lead to the differences. The finer size of the particles can also give rise to sharpness of the peaks in the IR spectra giving better resolution of the bands.

SEM analysis

SEM results show that pristine TiO_2 is of nanometer in size with two dimensional branched structures. The SEM image of Pani is given below. The SEM image of the TiO2-Pani composite prepared has flake like structures arranged one above the other. The polymer growth is above the semiconductor particles giving TiO_2 fully embedded in polymer matrix. The EDAX results show the presence of titanium in TiO_2 - Pani.

UV-Visible spectral analysis

The UV-visible spectra of pristine TiO_2 (RT) and RTP composite are given. It is clear from the spectra that the absorption range of TiO_2 is red shifted in the composite. Hence the Pani sensitizes TiO_2 to the visible region and influence the activation under the visible light.

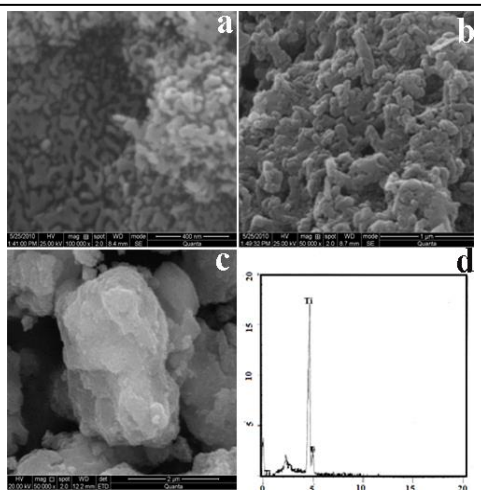

Fig.4

a. TiO_2 (RT)
b. Pani
c. RTP composite
d. EDAX of Pani TiO_2 composite

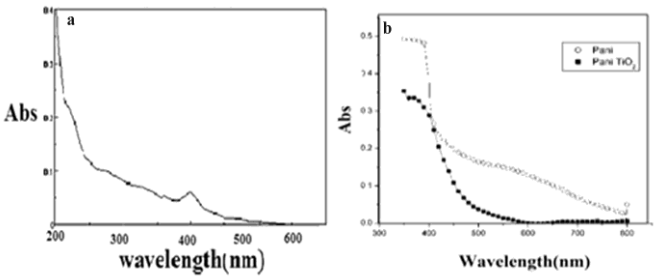

Fig.5

a. pristine TiO_2
b. RTP composite and pristine Pani

Catalytic degradation of DB1 dye

It can be inferred from the table that MB is not adsorbed while DB1 is greatly adsorbed to the catalyst. The degradation of DB1 can be considered as adsorption only and on sunlight exposure, it competes with catalytic process. The decrease in degradation percentage with 1:1 ratio of TiO_2-PANI may be explained as the result of desorption due to the competition.

Catalyst (grams)	% Dye degradation			
	With sunlight exposure		Without sunlight exposure	
	MB	DB1	MB	DB1
TiO_2 anatase	61.14	33.31	15.28	12.87
TiO_2 Rutile	50.29	23.25	3.85	19.02
1:1 (TiO_2-PANI)	18.61	35.25	8.85	93.45
1:0.1 (TiO_2-PANI)	50.81	85.19	37.35	89.19
1:0.06 (TiO_2-PANI)	69.29	89.34	14.54	88.03
1:0.02 (TiO_2-PANI)	29.83	59.03	15.54	40.94

The mechanism of adsorption of anionic dyes on PANI explained by (D.Mahantha et al., 2008) also supports this observation. The SO_3^- group on the dye could lead to chemical interactions with the positively charged backbone of PANI emeraldine salt, and Na^+ ions interact with the chloride ions that are invariably present in doped PANI. This will lead to the adsorption of various sulfonated dyes on the emeraldine salt of PANI. In basic aqueous solutions (dispersion of emeraldine base in water), the dissociation of the functional group of the dye would be inhibited, and no chemical interaction with the PANI backbone would be expected. But in the case of composites, the TiO_2 core acts as negative centre and so when activated by sunlight, the electrons will be provided by TiO_2. At lower concentration of PANI, the adsorption takes places in the dark and catalysis exceeds it in presence of sunlight.

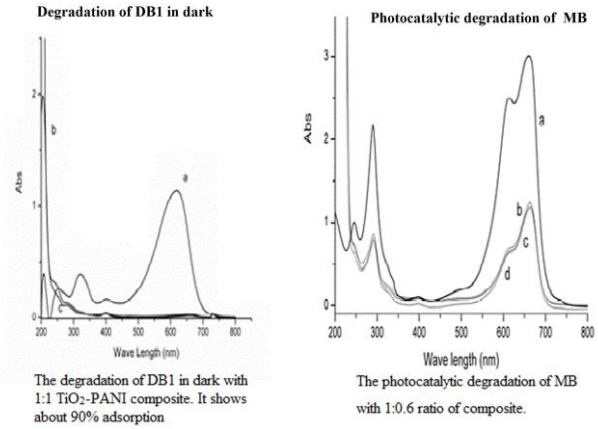

Fig.6

The curves a b, c, d represents the time of irradiation for degradation at 15, 30, 45 and 60 minutes respectively. The prolonged irradiation has no effect. This may be due to the catalytic action may come to equilibrium after a period of time.

The fig.6 a and 6 b show the absorption spectra of composite catalyst used for DB1 and MB in sunlight and dark. In the case of DB1, the adsorption takes place in dark (Abs at 600-700nm region is 0.05 a.u) and photocatalytic activity and desorption in light leaving behind sensitized catalyst over the entire visible area (Abs at UV region increases to maximum showing degradation of adsorbed materials and revealing the property of catalyst). In the case of MB, the adsorption is not taking place and in the sunlight and the degraded product of MB is adsorbing on the catalyst.

Catalyst loading

The catalyst loading effect in sunlight and dark reactions work in similar manner. The initial increase and then decrease may be due to the decrease in available surface area at higher concentration

Effect of pH

The effect of pH is similar in the case of MB for dark and sunlight reaction but reverse with DB1. This may be due to the fact that in DB1, the mechanism of sunlight and dark reaction is different.

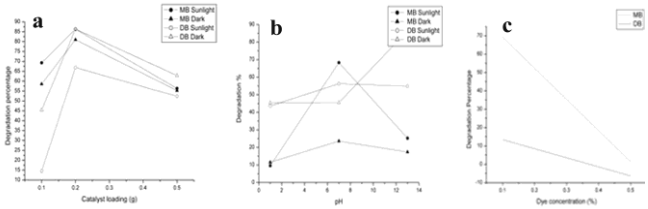

Fig.9

a. **0.1M dye concentration, 30 min interval at pH 7**
b. **0.1g of catalyst with 0.1 M dye concentration at 30 min interval**
c. **0.1 to 0.5 dye concentration**

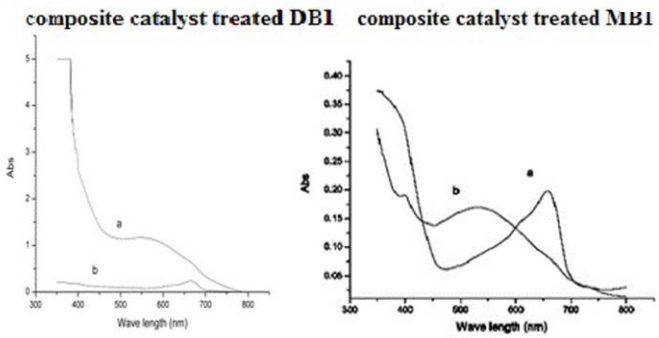

Fig.7

a. In sunlight b. In dark

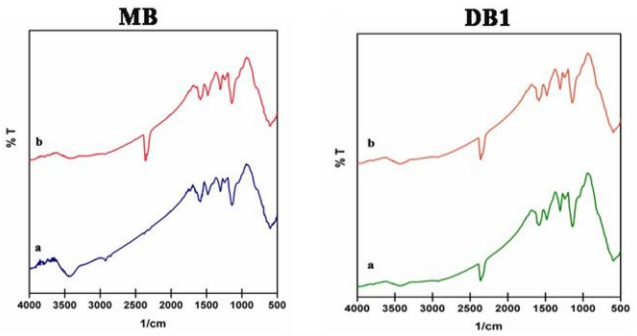

Fig.8

The following FT-IR results of the catalysts used for DB1 and MB in dark and sunlight (figures 8) also supports the adsorption and photocatalytic mechanism explained above.

Parameter studies

Dye concentration

Increase in dye concentration from 0.1 to 0.5 % decreases the dye degradation. This may be due to the lower availability of catalytic at those concentrations

COD analysis

The COD analysis shows the degradation efficiency (ppm removal) of MB and DB1 as 62 and 60% respectively, which supports the conclusion that photocatalysis occurred for DB1 in the presence of sunlight.

Conclusion

RTP composite acted as better photocatalyst than all other catalyst studied. RTP at ratio 1: 0.6 showed better dye degradation efficiency than other ratios. In our study, it is concluded that the process is adsorption in dark and photocatalysis in the presence of light. The anionic dye adsorbs in dark and undergoes photocatalytic reaction in presence of sunlight. The percentage degradation was higher with cationic dye (MB) than with anionic dye (DB1).

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