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Anomalous behavior of visible light active TiO₂ for photocatalytic degradation of different Reactive dyes

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Abstract

The nanocrystalline undoped, N-doped, N and metal codoped titania having different particle size, surface area, anatase phase content, crystallinity, band gap and zeta potential were synthesized by sol-gel method. The photocatalytic activity of synthesized TiO₂ powders was compared by employing four different Reactive dyes. The order of photocatalytic activity observed for Reactive Red 198 dye (RR 198) was undoped = N,Cu codoped = N-doped > N,Fe codoped TiO₂, Reactive Blue 4 dye (RB 4) was N,Cu codoped > N, Fe codoped > N-doped > undoped TiO₂, Reactive Black 5 dye (RB 5) was N,Cu codoped* > undoped > N-doped > N,Fe codoped TiO₂ and negligible degradation was observed for Reactive Orange 16 dye (RO 16). In this paper, the anomalous trend of the photocatalytic activity of various photocatalysts for the degradation of a particular class of dyes has been observed and accounted for based upon the three parameters; mechanism of degradation, physicochemical properties of the catalyst and adsorption behavior based on the zeta potential. It was concluded that apart from these parameters, substrate-specificity of catalyst is also of equal importance in developing new catalysts for photodegradation of dyes present in textile effluents.

Keywords- photocatalytic degradation, Reactive dyes, doped TiO_2 , substrate-specificity

Introduction

Synthetic dyes are a major part of our life as they are found in various products used by us. However, these dyes are an important source of environmental contamination. The Reactive dyes are a commercially important class of textile dyes and their release into the environment is of great concern due to the coloration of natural waters, toxicity, mutagenicity and carcinogenicity^{1,2} associated with them.

Advanced oxidation processes (AOP's) have been successfully used to degrade and mineralize Reactive dyes into CO_2 and inorganic ions.³ AOP's are based on generation of highly oxidative radicals ($\cdot\text{OH}$, O_2^- or $\text{HO}_2\cdot$), called reactive oxygen species (ROS), which are known to attack almost all pollutants. Among all known AOP's, heterogeneous photocatalytic degradation is most effective because the semiconductor materials used as photocatalysts are inexpensive and can easily mineralize large number of organic compounds.

Titania or titanium dioxide (TiO_2) is one of the most promising semiconductor photocatalyst owing to its long-term stability, non-toxicity and excellent photocatalytic property, however, there are two aspects limiting its application. On the one hand, wide band gap of titania makes it to absorb only ultraviolet (UV) light, which limits the effective usage of solar light. On the other hand, due to its low photo-quantum efficiency it cannot be used in practice in an efficient manner.⁴ Various techniques to overcome the shortcomings of titania include surface modification via organic materials and semiconductor coupling, band gap modification by creating oxygen vacancies and oxygen sub-stoichiometry, doping by non-metals, metals and codoping with various combinations of metals and non-metals.

Doping of semiconductor materials effectively enhance the interfacial charge transfer and lower the electron–hole recombination rate.⁵⁻⁹ Codoping of both metal and non-metal elements into TiO₂ has attracted further considerable interest due to their attractive photocatalytic properties. The advantages of codoping have been demonstrated in several systems^{10,14} but in literature there are many papers that do not support it.¹⁵

In most studies of TiO₂ photocatalysis, the quantification of the photoactivity is an essential part because the comparison of photocatalytic activity among different photocatalysts is not straightforward. The photocatalytic activity of various catalysts using different substrates have reported in the literature and are scattered over thousands of papers and have been measured by different methods under widely varying conditions. Despite the presence of abundant pre-existing data, an activity data set that is obtained under identical experimental conditions is still needed for the systematic comparison of different substrates. It is well known that the photocatalytic activity of a photocatalyst depends on various parameters like phase, band gap, surface area, zeta potential, to mention a few. A generalization however, cannot be made in a manner that a single catalyst is optimized for the degradation of all substrates because of the different adsorption power of catalysts and the different mechanisms involved for degradation of a particular substrate.¹⁶

In view of the above, in the present work, undoped and doped TiO₂ powders were prepared by sol-gel method and characterized by various techniques such as XRD, TEM, FTIR, UV-vis DRS, XPS, BET, zetasizer and their visible light induced photocatalytic activity was examined by using four different Reactive dyes and the obtained results are presented and discussed to reveal the substrate-catalyst relationship.

Materials and methods

Materials

- (a) Sample- RR 198 (Mol. Wt. $984.21 \text{ m}^2\text{g}^{-1}$, CI-18221), RB 4 (Mol. Wt. $681.39 \text{ m}^2\text{g}^{-1}$, CI-61205), RB 5 (Mol. Wt. $991.82 \text{ m}^2\text{g}^{-1}$, CI-20505) and RO 16 (Mol. Wt. $617.54 \text{ m}^2\text{g}^{-1}$, CI-17757) dyes (Fig. 1) were purchased from Sigma Aldrich and were used without any purification.
- (b) Reagents and chemicals- Tetrabutyl titanate (TBT) was purchased from Sigma Aldrich and acetic acid, ethanol, urea, ferric nitrate, copper nitrate were purchased from Merck, India.

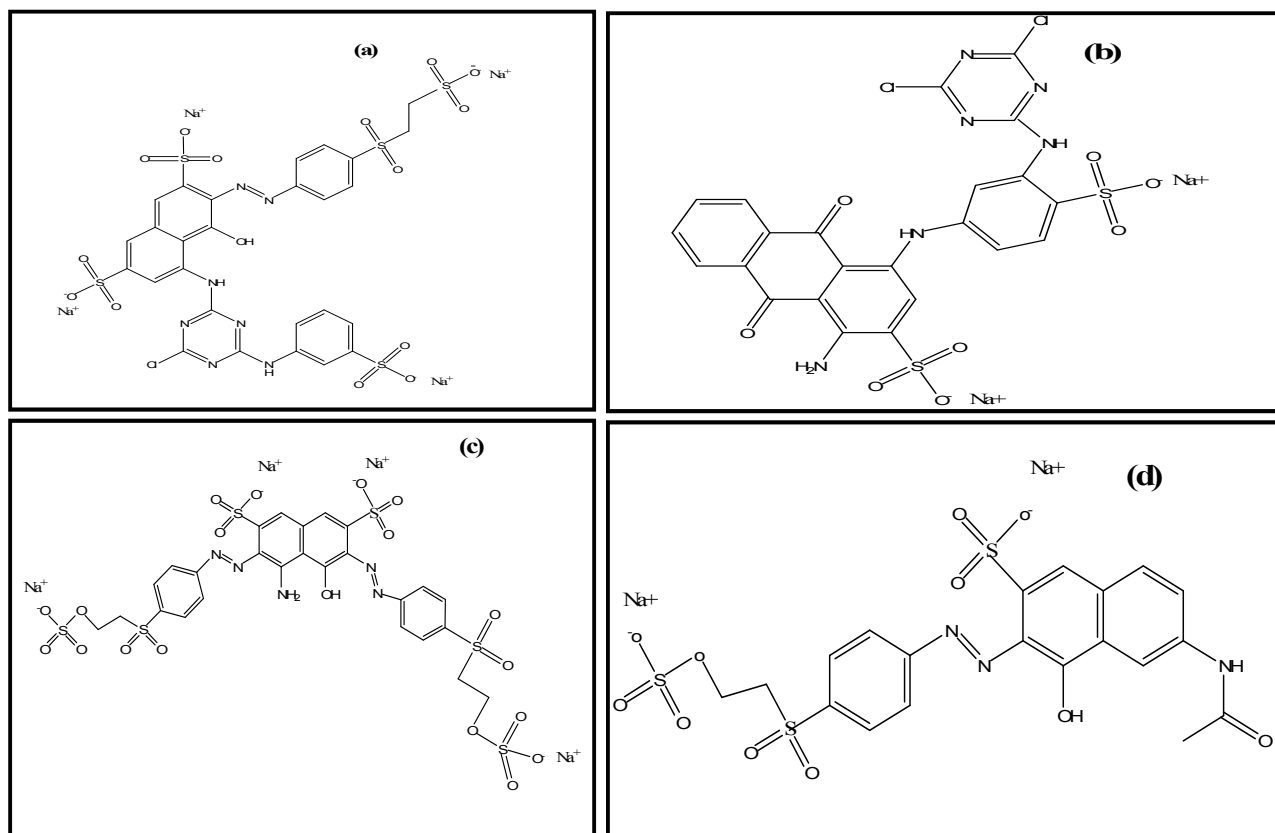


Fig. 1. The chemical structure of Reactive dyes; (a) RR 198, (b) RB 4 (c) RB 5 (d) RO 16 dye.

Preparation method of undoped and doped TiO_2 photocatalysts

The various titania photocatalysts have been synthesized by sol–gel method. Firstly, TBT (5 ml) and acetic acid (5 ml) were added in 25 ml absolute ethanol (solution A). Secondly, acetic acid (2.5 ml) and distilled water (3.25 ml) were added in 12.5 ml absolute ethanol (solution B). Then solution B was added dropwise into solution A with vigorous magnetic agitation. The obtained mixture was stirred for 3 h, and then kept at room temperature in air for 24 h to form an aged homogeneous gel. The as-prepared gel was dried at 100°C in the oven, and then it was porphyzied into a powder and annealed at 500°C at a rate of 3°C per minute in a programmable furnace for 3 h to obtain the undoped TiO₂. The N-doped, N,Fe-codoped and N,Cu-codoped titania were synthesized by the addition of urea (1.8 g, 30 mmol), ferric nitrate (0.1765 g, 0.43 mmol) and copper nitrate (0.1092 g, 0.43 mmol) as nitrogen, iron and copper source in solution B respectively.

Characterisation of nanocrystalline TiO₂

XRD measurements were performed using an X-ray powder diffractometer (XPRT-PRO) operated at 45 kV and 40 mA with Cu-K α radiation ($\lambda=0.15406$ nm) and a scan angle (2θ) of 20-100°. TEM images of samples were studied using transmission electron microscope (TEM) Hitachi (H- 7500) with an accelerating voltage of 120 kV. FTIR spectra in the range 4000-400 cm⁻¹ were taken from Perkin Elmer - Spectrum RX-I. DRS of samples were performed using Perkin Elmer-Lambda 35 instrument using BaSO₄ as reference. X-ray photoelectron spectroscopy (XPS) was recorded with a Shimadzu ESCA-3200 spectrophotometer. The shift of binding energy due to relative surface charging was corrected using the C1s level at 284.6 eV as an internal standard. BET surface areas were calculated by using BET (Brunauer Emmett Teller) equation thermally treated at 180°C for 2 h (Quantachrome Nova Win version 10.01). The pore

size distribution was determined via BJH method. The Zeta potential measurements and hydrodynamic particle size were performed on Malvern Nano ZS equipment

Photocatalytic experiments

The photocatalytic experiments were carried out with 200 ml of dye solution in an immersion well type reactor. The experiments were conducted using a 100 W halogen lamp with the circulation of 2 M NaNO₂ solution for absorption of any irradiation below 400 nm.^{17,18} A vigorous bubbling of oxygen was done to increase dissolved oxygen concentration. An aliquot of 5 ml was taken from the reactor at regular intervals of time with a syringe. The suspension was centrifuged for 5 min at 4000 rpm and subsequently filtered through a Millipore filter (pore size 0.45µm) to remove the catalyst and the filtrate was analyzed by UV-vis spectrophotometer.

Results and discussion

Characterization of synthesized photocatalysts

Fig. 2 shows the XRD spectra of undoped, N-doped, N,Cu codoped and N,Fe codoped TiO₂. It was observed that the undoped and N-doped TiO₂ mainly consisted of the pure anatase phase¹⁹ while in case of N,Fe codoped TiO₂ and N,Cu codoped TiO₂, the rutile phase²⁰ and both rutile and brookite phases²¹ appeared respectively along with the mainly formed anatase phase. The average crystallite size of the samples has been estimated using Debye-Scherrer equation:

$$d = \frac{0.89\lambda}{\beta \cos \theta}$$

where d represents the crystallite size, λ is the wavelength of incident X-ray, β is the full width at half maximum (FWHM) of diffraction formula, and θ represents the scattering angle.

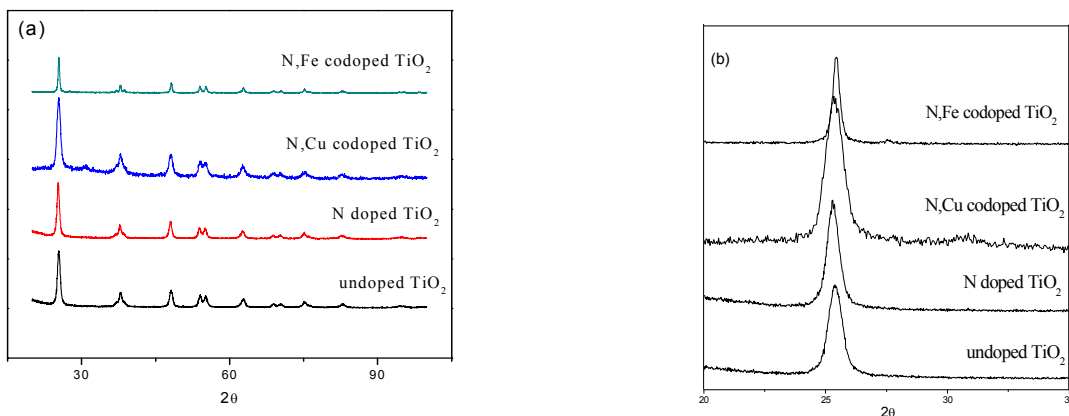


Fig. 2. (a) XRD spectra of all synthesized photocatalysts (b) enlarged spectra from 20-35°

The phase content of anatase:rutile in N,Fe codoped TiO₂ was found to be 95.55:4.45 respectively by using the following equation:

$$F_A = 100 - \frac{1}{1 + \frac{0.8I_A}{I_R}} 100$$

where I_A is the intensity of the 101 peak of anatase at $2\theta = 25.5^\circ$ and I_R is the intensity of the 110 peak of rutile at $2\theta = 27.5^\circ$.

The phase contents of anatase:rutile:brookite in the N,Cu codoped TiO₂ has been calculated from the integrated intensities of the anatase (101), rutile (110), and brookite (121) peaks as given in **Table 1** with the following formulas²² and was found to be 83.8:2.4:13.8.

$$W_A = \frac{K_A A_A}{K_A A_A + A_R + K_B A_B}$$

$$W_R = \frac{A_R}{K_A A_A + A_R + K_B A_B}$$

$$W_B = \frac{K_B A_B}{K_A A_A + A_R + K_B A_B}$$

where W_A , W_R and W_B represent the weight fractions of the anatase, rutile, and brookite phases, respectively. A_A , A_R and A_B are the integrated intensities of the anatase (101), rutile (110), and brookite (121) peaks, respectively. The variables K_A and K_B are coefficients with values 0.886 and 2.721, respectively.

From the present work, the results of XRD analysis showed that the particle size and crystallinity remains almost similar on incorporation of nitrogen in TiO_2 . It has been observed that when Cu accompanies nitrogen in the lattice structure of TiO_2 , the crystallite size and crystallinity increases while in case of N,Fe codoped TiO_2 the crystallite size and crystallinity decreases. It can therefore, be concluded that use of different dopants leads to the synthesis of TiO_2 materials with different crystallinity, particle size and different anatase phase content.

The particle size distribution (PSD) for all the synthesized TiO_2 samples, calcined at 500°C was determined. The average hydrodynamic particle size for undoped, N-doped, N,Fe-codoped and N,Cu-codoped TiO_2 was found to be 2388.4, 1327.6, 252.5 and 405.4nm respectively. The hydrodynamic size of photocatalysts was considerably different from the crystallite size calculated by Scherer equation which is due to their tendency to aggregate in an aqueous medium and generate larger particles.

The results of the structural characterization of these synthesized catalysts are summarized in Table 1.

Table1. Physicochemical properties of all synthesized catalysts

	Undoped TiO ₂	N-doped TiO ₂	N,Cu codoped TiO ₂	N,Fe codoped TiO ₂
Anatase phase content	100.00	100.00	83.80	95.55
Crystallite size(nm) from XRD	14.2	13.6	21.3	10.0
Particle size (nm) from TEM	8-15	12-18	20-25	9-12
Hydrodynamic particle size (nm)	2388.4	1327.6	405.4	252.5
BET surface area (m ² g ⁻¹)	103.8	83.4	83.4	98.0
Pore diameter (Å)	7.5	8.9	7.9	6.5
Band gap (eV)	3.00	2.57	2.51	2.41

The TEM images in Fig. 3 showed that the samples of the synthesized undoped, N,Cu codoped and N,Fe codoped TiO₂ have cubic shape while N-doped TiO₂ showed rectangular shape with low aggregation of particles.²³ The particle size from TEM as shown in Table 1, are consistent with the results that were observed from the size calculated using XRD analysis by Debye-Scherrer equation.

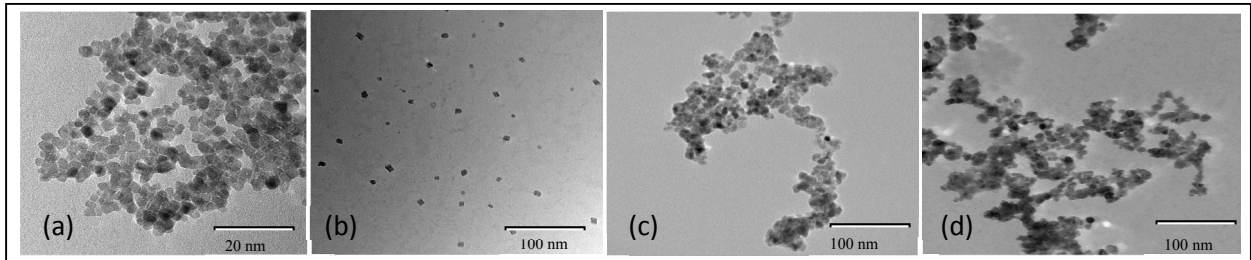


Fig. 3. TEM images of TiO₂ samples (a) undoped, (b) N-doped, (c) N,Cu codoped (d) N,Fe codoped TiO₂

Fig. 4 shows the FTIR spectra of all photocatalysts wherein the peak at 3400 cm⁻¹ (stretching vibration) and the peak around 1640 cm⁻¹ (bending vibration) corresponds to the absorbed water molecules over the samples. The peak around 742 cm⁻¹ is due to the stretching vibration of Ti–O bond. The peak in between 1250 to 1500 cm⁻¹ could be attributed to the doped nitrogen species in TiO₂ network^{24,25} in N-doped TiO₂. The peak of Fe-O-Ti and Cu-O-Ti were not observed, which may be ascribed to their low doping content in the corresponding samples.

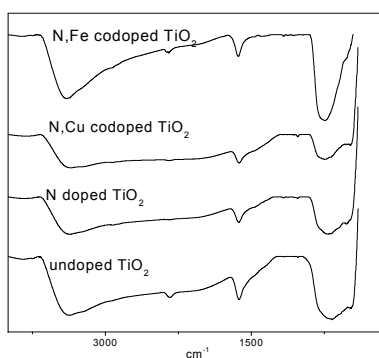


Fig. 4. FTIR spectra of all synthesized photocatalysts

The dopants in TiO₂ significantly affect the electronic structure, which then affects the visible light absorbance and photocatalytic activity. Fig. 5 shows the UV-vis DRS (Diffuse Reflectance Spectra) and Tauc plot for calculation of band gap of photocatalysts. The undoped TiO₂ has a band gap of 3.0 eV indicating that it can absorb only UV light. In N-doped TiO₂, the band gap shifts from 3.0 eV to 2.57 eV because of hybridization of N 2p with O 2p orbitals.²⁶ In N,Cu and N,Fe codoped TiO₂, the band gap energy further decreases because Fe and Cu partly replace Ti⁴⁺ in the TiO₂ crystal lattice.

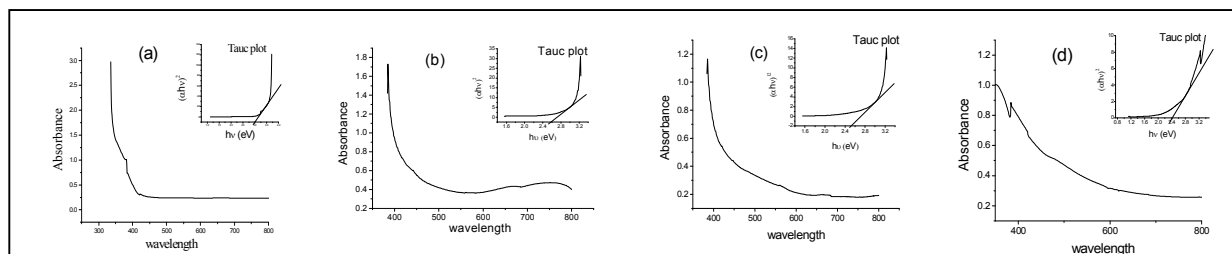


Fig. 5. UV-vis DRS spectra of all synthesized photocatalysts (a) undoped, (b) N-doped (c) N,Cu codoped (d) N,Fe codoped TiO_2 .

The XPS spectra of doped samples as represented in Fig. 6, showed a clear N 1s binding energy around 400 eV, which indicates that N has been incorporated into the titanium oxide lattice.²⁷ In case of N,Cu codoped TiO_2 , the peaks observed at 951.95 and 932.51 eV were associated to Cu 2p_{3/2} and Cu 2p_{1/2}. The band at 932.2 eV also indicates the possible presence of both Cu_2O and metallic Cu phase.^{28,29} The N,Fe codoped TiO_2 sample showed peaks for the binding energies of Fe 2p located at 722.6 and 709.7 eV indicating the existence of Fe-O bond on the surface of the sample.

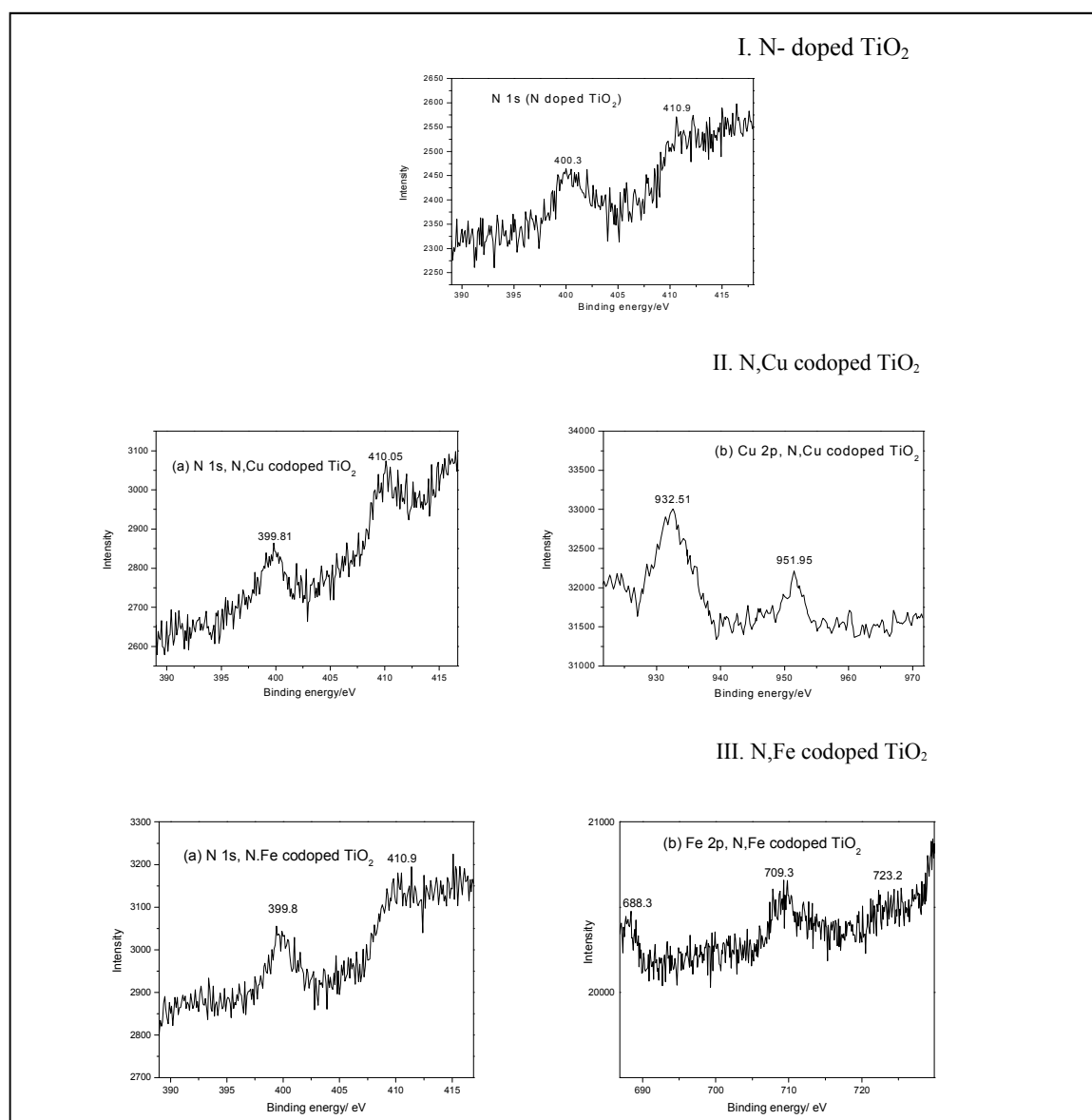


Fig. 6. XPS spectra of dopants present in doped TiO₂; (a) N-doped TiO₂, (b) N,Cu-codoped TiO₂, (c) N,Fe codoped TiO₂

Fig. 7 shows the surface zeta potential versus pH for doped and undoped TiO₂ photocatalysts. The pH at the isoelectric point (IEP) for the undoped, N-doped, N,Cu codoped and N,Fe codoped TiO₂ was found to be 5.1, 4.2, 3.0 and 2.2 respectively and were consistent with those reported in literature.²⁰⁻³⁵ The determination of zeta potential is of importance to know the surface charge of the catalyst and thus adsorption of substrate over the surface of catalyst.

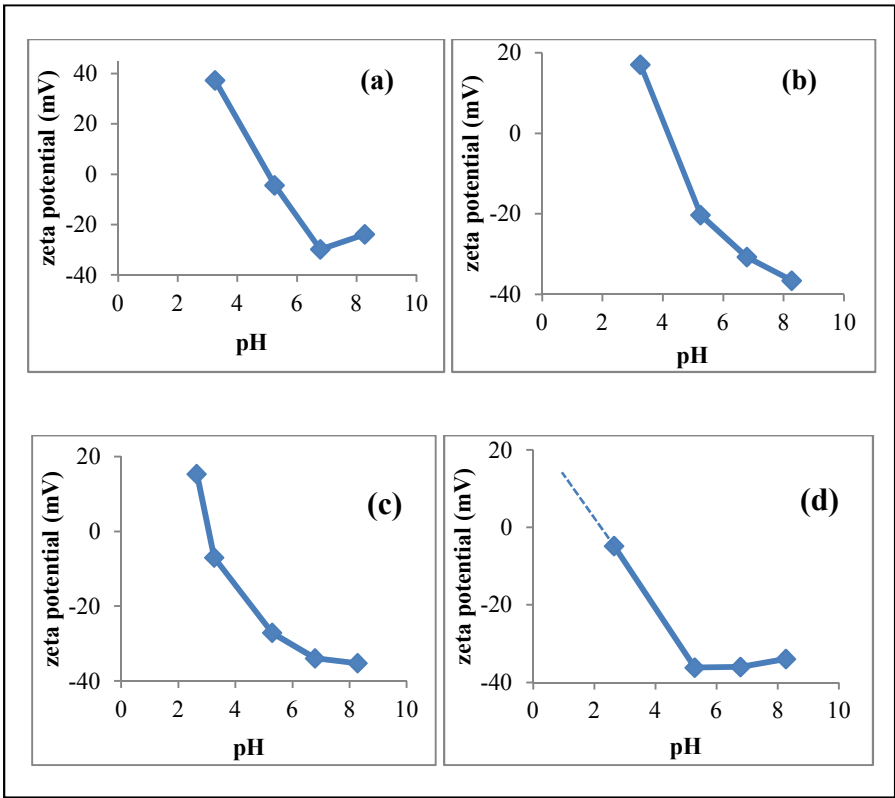


Fig. 7. Zeta potential of (a) undoped TiO₂, (b) N-doped TiO₂, (c) N,Cu codoped TiO₂ and (d) N,Fe codoped TiO₂ at different pH.

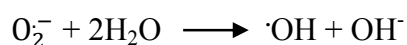
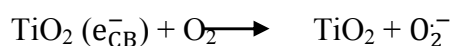
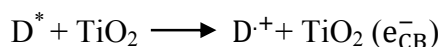
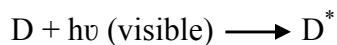
Photocatalytic degradation experiments

Photocatalytic activity of various synthesized TiO₂ was determined with four different Reactive dyes under identical experimental conditions and is summarized in Fig. 8.

Each catalyst was found to have a different activity for a different substrate. The explanation for anomalous behaviour towards photocatalytic activity of each photocatalyst for a particular dye has been explained based on three parameters; firstly the mechanism involved for degradation, secondly the physicochemical properties of the catalyst while the third factor is the adsorption of substrate over the surface of catalyst.

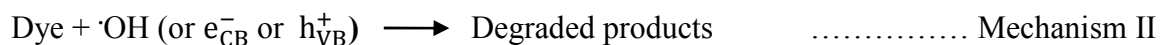
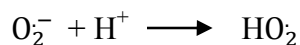
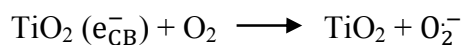
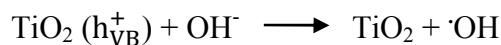
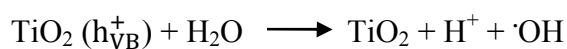
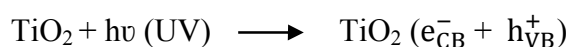
According to the first parameter, two mechanisms, mechanism I and II namely dye sensitized photocatalytic and photocatalytic respectively, are involved for degradation of dyes

under visible light. The band gap of the catalyst decides which mechanism will play a major role for degradation. As the band gap of undoped TiO_2 was found to be 3.0eV indicating that under visible light, the mechanism I must be dominantly involved. In this mechanism I, the excitation of adsorbed dye takes place by absorption of visible light where an excited dye (D^*) scavenged by O_2 to form active oxygen radicals^{36,37} as shown below:



The photodegradation rate via mechanism I largely depends on the nature of dye and its ability to promote the photosensitization of the catalyst.

While other doped catalysts, which are visible light active because of the appreciable red shift in absorption edge, follows both the mechanisms I and II. The relevant reactions of mechanism II at the surface of photocatalyst can be expressed as follows:



The second parameter also plays an important role whereby the photocatalytic behavior of a photocatalyst varies with the physicochemical properties of a photocatalyst such as particle size, surface area, anatase phase content and zeta potential.

The third parameter which accounts for the photodegradation rate is the adsorption of substrate on the surface of catalyst due to different substrate-catalyst interaction. The chosen Reactive dyes as substrates are anionic dyes (-vely charged), due to which the catalyst having a positive zeta potential (or least negative zeta potential) will adsorb the dye efficiently and assist in increasing the degradation rate. To understand this adsorption and interaction behavior of various dyes, the zeta potential of the various photocatalysts at the natural pH of corresponding dyes was also determined and is summarized in Table 2.

Table 2. Zeta potential of synthesized photocatalysts of all dyes at natural pH.

Zeta potential(mV) of TiO ₂ catalysts				
Dyes ; natural pH	Undoped TiO ₂	N-doped TiO ₂	N,Cu codoped TiO ₂	N,Fe codoped TiO ₂
RR 198; 4.9	2.59	-13.92	-23.44	-31.69
RB 4; 5.0	1.34	-15.30	-24.10	-32.50
RB 5; 5.7	-11.85	-23.39	-28.92	-36.15
RO 16; 5.5	-8.18	-21.85	-28.23	-36.17

Photocatalytic activity of catalysts on RR 198 dye degradation

The results in Fig. 8(a) illustrate that the undoped, N-doped and N,Cu codoped TiO₂ showed 100% degradation of RR 198 dye with similar rate of reaction. The activity of undoped titania can be attributed to the presence of pure anatase phase³⁸, large surface area, positive zeta potential (at the natural pH of dye) which is responsible for the higher adsorption and also the

mechanism I is followed with effective photosensitisation by RR 198 dye.³⁶ In case of doped titania both the mechanisms I and II are followed due to their ability to absorb visible light also and result in effective degradation with the better results for N-doped and N,Cu codoped TiO₂. The lower photocatalytic activity of N, Fe codoped TiO₂ can be due to the higher negative zeta potential leading to lower adsorption of the dye over the catalyst.

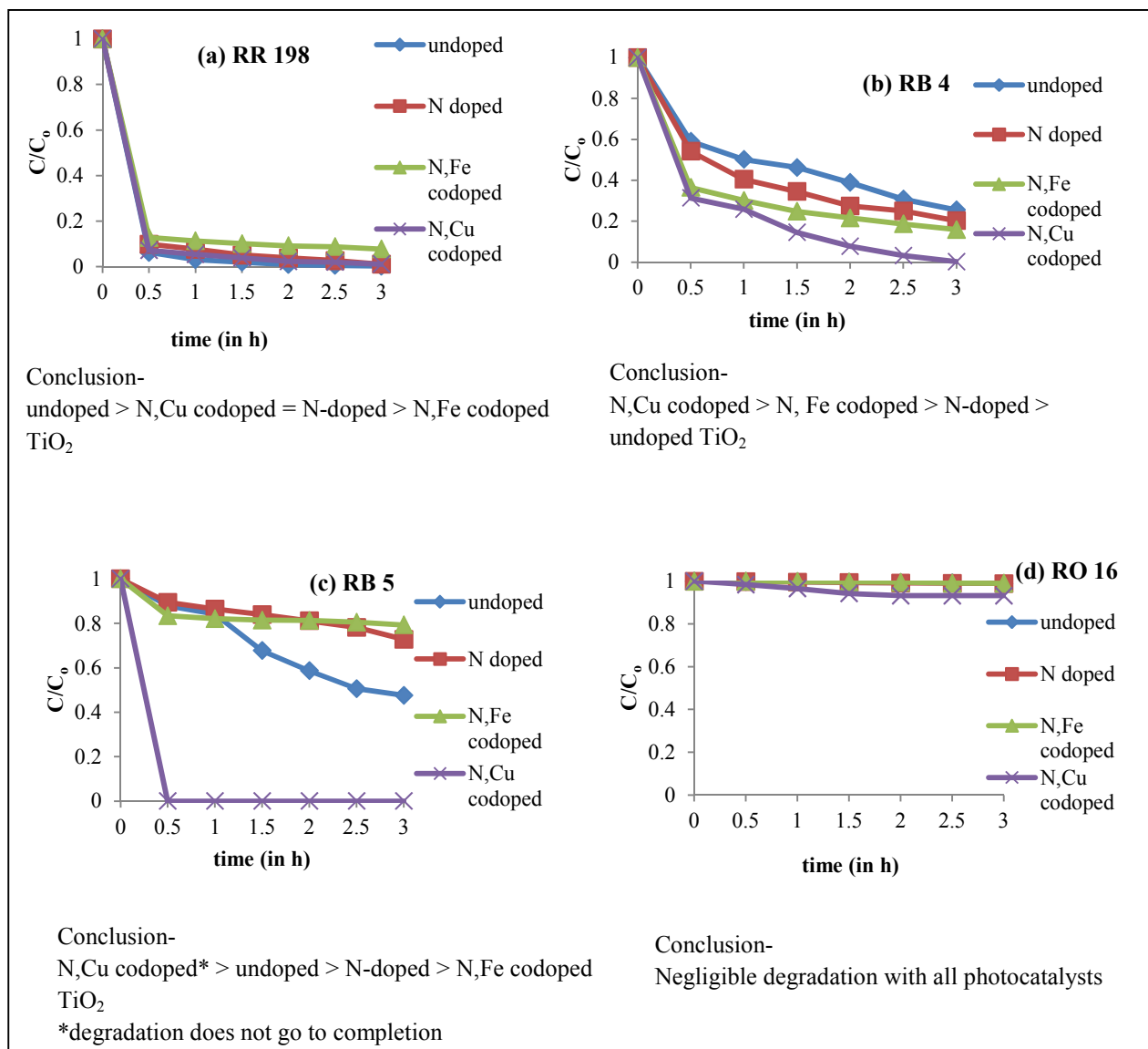


Fig. 8. Photocatalytic degradation of Reactive dyes; (a) RB 5, (b) RB 4, (c) RR 198, (d) RO 16 ; C₀ = 10 ppm, catalyst loading = 0.24gm/200ml at the natural pH of dyes.

Photo catalytic activity of catalysts on RB 4 dye degradation

Fig. 8(b) showed the photocatalytic decomposition of RB 4 dye under visible light with all synthesized catalysts wherein the activity order followed was N,Cu codoped > N, Fe codoped > N-doped > undoped TiO₂ with 100, 84, 80 and 75% of degradation respectively which is different from RR198 dye. This different activity order of catalysts can be explained based on the effectiveness of the mechanism followed in the various catalysts and in this case the mechanism II is predominant. Besides this, the higher photocatalytic activity of N,Cu codoped TiO₂ can also be due to the synergistic effect of coupling of anatase, rutile and brookite phase. The undoped TiO₂ showed lower photocatalytic activity which can be accounted for based on lower effectiveness of mechanism I although the adsorption parameter and physicochemical properties were favorable in this case.

Photocatalytic activity of catalysts on RB 5 dye degradation

As shown in Fig. 8(c), the photocatalytic degradation of black colored RB 5 dye showed incomplete degradation with undoped, N-doped and N,Fe codoped TiO₂ upto 52.4, 27.23 and 20.7% respectively. In case of N,Cu codoped TiO₂, degradation of the dye also does not undergo to completion, however the black color disappeared rapidly with the formation of a pink colored residual solution which might be due to the formation of some new intermediates. The higher photoactivity of undoped TiO₂ correlates to the high surface area, pure anatase phase, efficient sensitization of the dye and the least negative zeta potential while the low activity of N-doped and N,Fe codoped TiO₂ is probably due to the highly negative zeta potential as shown in Table 2 which lowers the adsorption and thus degradation of the dye.

Photocatalytic activity of catalysts on RO 16 dye degradation

The RO 16 dye undergoes negligible degradation with all synthesized photocatalysts despite having favorable conditions as shown in Fig. 8(d). Although the dye belongs to the same group and is structurally similar, this anomalous behavior of various catalysts towards degradation of RO 16 dye could not be accounted for which further indicates that some substrate-specificity of catalyst exists and is also an important factor in the photodegradation studies. The adsorption of dye over catalyst is one of the deciding factor for the efficiency of a catalyst. There was almost negligible adsorption of RO 16 dye over all catalysts which might be a strong reason for the dye to remain rigid towards photocatalytic degradation.

Fig. 9 shows a comparison of photoactivity of all catalysts for degradation of the different dyes. In light of above observations, it can be concluded that one single catalyst cannot be effective for degradation of even structurally similar class of dyes.

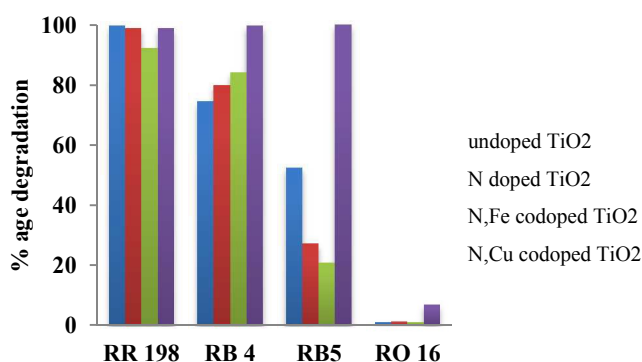


Fig. 9. % age degradation of dyes with synthesized photocatalysts.

Identification of major reactive species involved for degradation using radical quenchers.

The different dyes undergo photocatalytic degradation to different extent using undoped, N-doped, N,Fe and N,Cu codoped TiO₂ catalysts. This might be attributed to the different mechanistic pathway chosen by a catalyst for the degradation of a dye using reactive oxygen species. As we know, singlet oxygen, hydroxyl radical and superoxide ions are three major

active species involved for the degradation of dye and to understand the role of each reactive species in the degradation three radical quenchers, NaN_3 , DABCO and 1,4-benzoquinone were added under identical conditions. Among these, NaN_3 is quencher of $^1\text{O}_2$ and $\cdot\text{OH}$ radical, DABCO is quencher of $^1\text{O}_2$ and 1,4-benzoquinone is of superoxide ion.

RR 198 dye was taken as a model compound and effect of various quenchers was examined. It has observed that with undoped, N-doped and N,Cu codoped TiO_2 catalysts, the degradation was below 10% in the presence of all quenchers indicating that all three reactive species $^1\text{O}_2$, $\cdot\text{OH}$ and superoxide radicals are playing a significant role in the degradation process (Fig. 10). However, in the case of N,Fe codoped TiO_2 , a variation was observed where the $^1\text{O}_2$ is the major degrading species while $\cdot\text{OH}$ and superoxide radicals are less significant.

These results are further supported by photocatalytic degradation experiments wherein undoped, N-doped and N,Cu codoped TiO_2 catalysts showed equally high degradation because of the participation of all three reactive species while in case of N,Fe codoped TiO_2 only the $^1\text{O}_2$ is the major active species resulting in lower degradation rate.

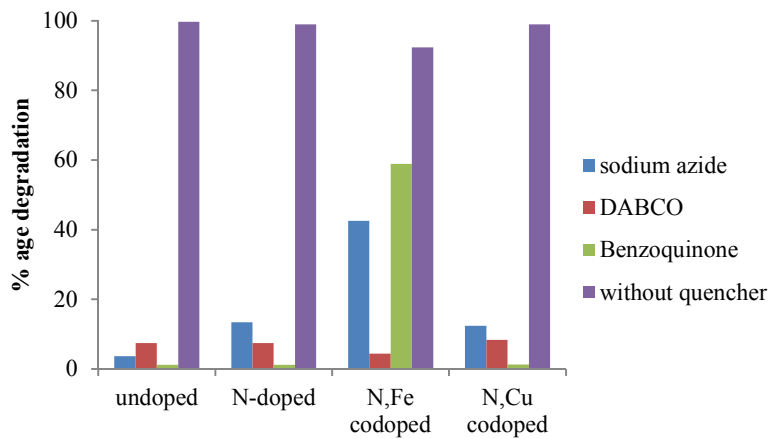


Fig. 10. The effect of radical quenchers on the photocatalytic degradation rate of RR 198 dye; $C_0 = 10$ ppm, catalyst = 0.24 gm/ 200ml, quencher = 0.02 gm/ 200ml

Correlation of photocatalytic activity and structure of the dye

The chemical structure of the dyes have a considerable effect on the reactivity towards photodegradation. The appropriate photocatalytic material has to be chosen depending on the functional groups in the chemical structure of the dye.³⁹⁻⁴² In general, photodegradation of dye molecule occur by undergoing various cleavages such as a) cleavage of C-S bond between the aromatic ring and sulfonate group, b) cleavage of the aromatic ring, c) cleavage of C-N and C-C bonds and d) cleavage of azo bond.

RR 198 dye undergo rapid degradation with all catalysts probably be due to presence of number of labile groups especially chloro and diamino substituted 1,3,5-triazine. RB 4 dye also showed good degradation which might be attributed to naphthaquinone and dichloro and amino substituted 1,3,5-triazine group and other C-S labile groups. Collectively, it can be concluded that substituted triazine type structure facilitates the degradation of RR 198 and RB 4 dyes.

RB 5 dye undergoes comparatively slow degradation which can be explained by the large steric strain due to aromatic ensembles as observed by Lachheb et al in case of Congo Red dye.⁴³ An anomalous behavior in case of RO 16 dye was observed which showed negligible degradation even in the presence of labile groups and can be probably because of the amide group present in the ring which might be causing some interference in the photodegradation process.

Conclusion

This work entails the photocatalytic degradation of four structurally similar Reactive dyes (RR 198, RB 4, RB 5 and RO 16) with synthesized undoped, N-doped, N,Cu codoped and N,Fe

codoped titania. The photocatalytic behavior of the various photocatalysts has been compared and found to follow an anomalous trend for each dye. The rate of degradation of a dye is not only dependent on the mechanism involved for degradation, nature of the catalyst in terms of its physicochemical properties, adsorption behavior based on zeta potential but also an additional effect of substrate-specificity of catalyst has been found to play an important role. It can be concluded that the detailed study with different dyes needs to be conducted for the optimization of a photocatalyst before being used for any industrial application.

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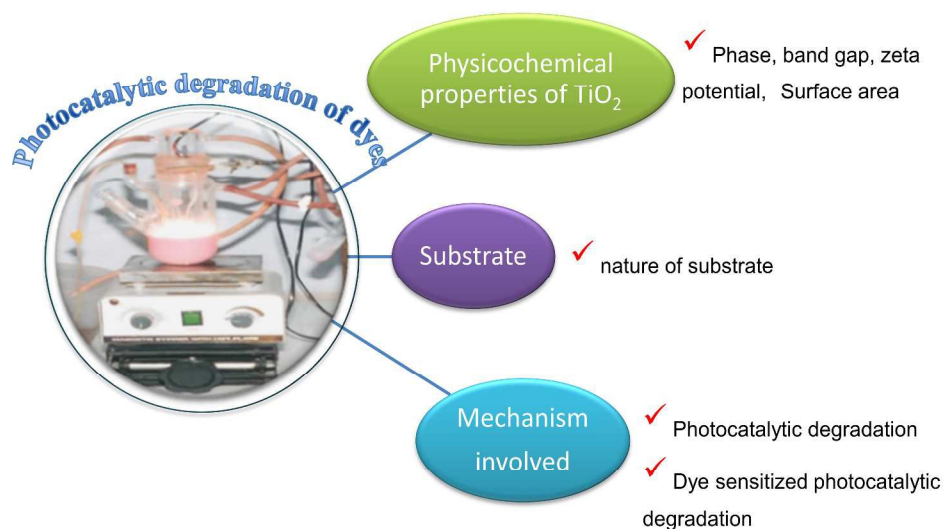
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Anomalous behavior of visible light active TiO₂ for photocatalytic degradation of different reactive dyes

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Statement of novelty

This article illustrates the important substrate-catalyst interaction studies with reactive dyes and various modified TiO₂ under visible light irradiation and demonstrates the need for developing new catalysts for degradation of dyes having different structural features present in textile effluents.