

Comparative Study for Photodegradation of Remazol Red R by Different TiO₂ Samples

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Abstract

Potassium dichromate modified TiO₂ photocatalyst (MD-TiO₂) was prepared and its photocatalytic activity was compared with that of ordinary commercial TiO₂ (C-TiO₂) and special Degussa P25 TiO₂ (D-TiO₂). An organic dye, remazol red R(RRR) was used as a substrate for photodegradation from aqueous solution into environmentally safe products such as water, carbon dioxide and mineral ions. The photodegradation of RRR was carried out by varying the concentration of different types of TiO₂ suspension, initial concentrations of dyes between 0.5×10^{-4} M and 2.5×10^{-4} M, pH between 2.0 and 6.0 and light sources which are UV, artificial visible and sunlight. With increasing the catalyst concentration, percent degradation was found to increase up to a concentration of 1.2 g/100 mL of C-TiO₂, 0.12 g/100 mL of D-TiO₂ and 0.10 g/100 mL of modified MD-TiO₂ for a definite concentration of RRR. However, RRR shows adsorption on TiO₂ samples except C-TiO₂. Again, the photodegradation efficiency is inversely affected by the dye concentration. Thus, the removal efficiency was found to be influenced by all of the above parameters. The maximum removal efficiency is found at pH 3.0 under sunlight in the presence of modified MD-TiO₂, which suggests that MD-TiO₂ can be used as an effective material for the removal of RRR instead of C-TiO₂ and D-TiO₂.

I. Introduction

Textile and leather industries are discharging effluents containing a large volume of carcinogenic and non-biodegradable dyes directly into waterstreams¹. The azo dyes constitute the largest and the most important class of commercial dyes^{2,3}. Azo dyes typically contain the chromophoric -N=N- group unit in their molecular structures⁴. Usually azo dyes are non-degradable under sunlight and their stability is proportional to their structural complexity^{4,5}. These non-degradable azo dyes are mainly present in textile wastewater exhaust. Remazol red R (RRR), (Fig. 1) is an important azo dye which is commonly used in textile industries and mixed with the wastewater during dyeing process.

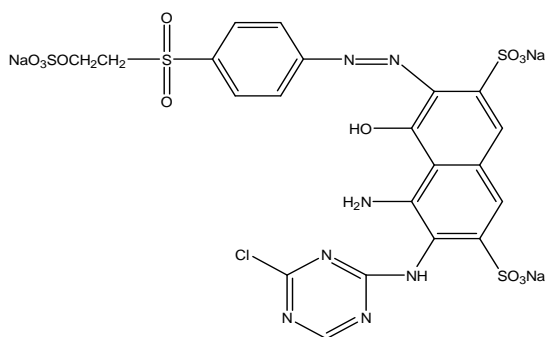


Fig. 1. Molecular structure of Remazol Red R (RRR)

For the treatment of wastewater from textile dyeing industries, various physical and chemical methods have been developed. Physical method such as adsorption using activated carbon is very efficient in removing organic pollutants including dyes. However reactivation of the adsorbent for reuse is not economically favourable in large scale applications. Membrane filtration techniques have the potential to produce reusable water and to remove the dyes completely. But all physical methods terminate in secondary waste generation⁶. Chemical degradation processes like ozonation, sodium hypochlorite treatment and electrochemical destruction are used for the decolorization of some classes of dyes⁷. But ozonation needs on-site preparation of

ozone. Hypochlorite treatment leaves water with high chloride content and electrochemical destruction requires very high power supply which is not economically feasible⁸.

In recent years, semiconductor oxide mediated photodegradation of textile dyes are drawing attention of the scientists all over the world. Titanium dioxide represents one of the most efficient photocatalyst⁹⁻¹³, although the effective photo-excitation of TiO₂ semiconductor particles requires the application of light with energy higher than their band gap energy (3.2 eV). This is an advanced oxidation process based on the generation of reactive species such as hydroxyl radicals that oxidizes the organic dyes quickly and non-selectively^{14,15}. Photosensitization of titanium dioxide involving doping or surface modification with p-block elements (N, C, S, Cl, Br, I, Pb)¹⁶⁻²⁵ and with d-block elements (V, Cr, Au, Rh, Ni, Pt)²⁶⁻³⁰ are well studied in very recent years. In this work, we have attempted to prepare Cr₂O₇²⁻ ion modified Degussa P25 TiO₂ (MD-TiO₂) and we have applied it as a photocatalyst for photodegradation of RRR dye. A comparative study of photodegradation of RRR dye by different TiO₂ samples, which are MD-TiO₂, ordinary commercial TiO₂ (C-TiO₂) and unmodified Degussa P25 TiO₂ (D-TiO₂), has been discussed.

I. Experimental

Three different types of TiO₂ which are C-TiO₂, D-TiO₂ and MD-TiO₂ were used as photocatalysts. C-TiO₂ and D-TiO₂ were obtained from Fluka, Switzerland and MD-TiO₂ was prepared by modifying D-TiO₂ with K₂Cr₂O₇. Double distilled water was used throughout the present study.

The surface modified material was obtained from D-TiO₂ by 4 hours sonication with aqueous solution of K₂Cr₂O₇ at room temperature. Where Cr₂O₇²⁻ were at the titanium dioxide surface from acidic solution. Modification of white D-TiO₂ resulted into light yellow MD-TiO₂ photocatalyst³¹.

All the aqueous solutions were prepared with deionized water. The C-TiO₂, D-TiO₂ and MD-TiO₂ suspensions were prepared separately by taking the required amount of TiO₂ in a beaker. Exactly 20 mL deionized water was added to it. The TiO₂ was soaked overnight to achieve the smoothness

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of the surface. This suspension was then used for either adsorption or photodegradation study.

The dye, RRR was obtained from Dyester (Germany) and used here without further purification. 10 well stoppered reagent bottles each of which contains 1.0×10^{-4} M dye solution in 100 mL suspension containing 0.10 g of TiO_2 were taken. Then the reagent bottles were placed in a thermostatic shaker maintained at 30°C temperature and shaken continuously. The reagent bottles were successively withdrawn after 10, 20, 30, 50, 70 and 90 minutes. 5 mL of supernatant liquid from each bottle was centrifuged. The absorbance of the clear solution was measured using UV-visible spectrophotometer (UV-1610A, Shimadzu, Japan) at $\lambda_{\text{max}} = 520$ nm of the aqueous dye solution and the concentrations of the RRR solutions were calculated. The initial concentration in the absence of TiO_2 was determined. The time taken for centrifuge and subsequent analysis was kept constant. Similar procedure was followed for other RRR solution of concentrations 0.5×10^{-4} M, 1.5×10^{-4} M, 2.0×10^{-4} M and 2.5×10^{-4} M.

A beaker of 100 mL was taken as the reactor to perform photodegradation of RRR in the presence of different forms of TiO_2 . The source of radiation was comprised of a lamp emitting monochromatic radiation of 254 nm. The reactor was placed on a magnetically stirred plate and the distance of the solution surface from the lower part of the lamp was fixed at 5.0 cm. The total system was enclosed in a wooden box called lamp house. Inner surfaces of the lamp house were covered with aluminium foil. To study the photodegradation of RRR molecules, a solution of 1.0×10^{-4} M in 100 mL suspension containing 0.10 g of TiO_2 was taken in the beaker. A magnetic bar was placed to the reaction mixture. Then the solution was irradiated with constant stirring (magnetically) and the degradation time was monitored using a stopwatch. After a definite interval of time certain portion of the irradiated solution was taken out and then the absorbance of the irradiated solution was measured.

The percent degradation (%) has been calculated as-

$$\% \text{ photodegradation} = \frac{(A_0 - A_t)100}{A_0}$$

Where, A_0 is the absorbance at $t = 0$ and A_t is absorbance at time t .

This experiment was repeated to study the effect of catalyst dosage, effect of initial concentration of RRR, effect of pH and effect of light source on photodegradation of RRR.

X-ray diffraction (XRD) data of MD- TiO_2 were recorded (Philips PW-1380 X-ray generator operating at 40 kV-30 mA) on image plate using an XDC-700 Guinier-Hägg focusing camera. The radiation used was Cu $\text{K}\alpha 1$ and the sample was exposed for 15 minutes. The image plate was then scanned using HD-CR 35 NDT/ CR 35 NDT scanner. The recorded X-ray data were plotted as Intensity vs. 2θ

III. Results and Discussion

Spectral changes of the dye during photodegradation

RRR is a strongly absorbing dye in the UV-visible region with distinct bands at 290 nm and in the visible region at 520 nm. The latter band is responsible for the colour arising from aromatic rings connected by azo groups and the former is associated with benzene like structures in the molecule. Fig. 2 shows time dependent absorption spectra of RRR. The topmost spectrum is the original spectrum of the aqueous solution of 1.0×10^{-4} M dye and the next one is for the same solution after adsorption leading to the equilibrium. All other subsequent spectra were recorded during photodegradation at different time intervals. It is clear from the figure that the intensities of both the peaks decrease during adsorption. However, the intensities of both the peaks decreased sharply during photodegradation and this peak almost disappeared after 90 minutes of photodegradation. The disappearance of the peak at 520 nm is related to the removal of the azo group leading to the decolourisation of the dye. However, decrease in the intensity near 200 nm is related with the complete mineralization of the benzene ring. The appearance of the peak at the lower wavelength region predicts that benzene ring like structures still exist even after 90 minutes degradation, although the solution is colourless.

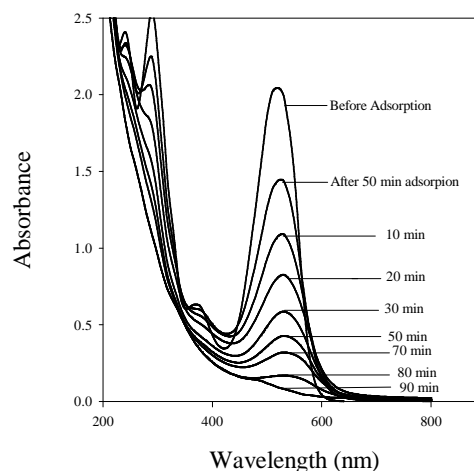


Fig. 2. Absorption spectra of 1.0×10^{-4} M RRR during adsorption and photodegradation by UV light in the presence of 0.10 g/100.0 mL MD- TiO_2 suspension at different time intervals.

Characterization of the prepared sample by XRD

X-Ray Diffraction (XRD) phase analysis of the prepared MD- TiO_2 sample shows the characteristic peaks of MD- TiO_2 (Fig. 3). All the characteristics peaks are consistent with those reported by Macyk et al³¹ indicating the chemisorption of dichromate ion on the TiO_2 . The physical appearance of the coloured materials as well as the persistence of the colour even after sonication of these materials in presence of water indicates strong bonding between dichromate ions and TiO_2 .

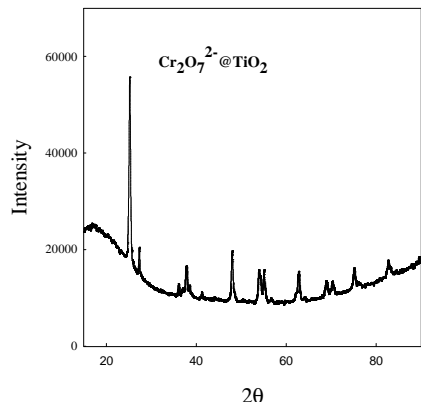


Fig. 3. XRD spectrum of MD-TiO₂ photocatalyst.

Efficiency of the photocatalyst on removal of RRR

The efficiency of C-TiO₂, D-TiO₂ and MD-TiO₂ on removal of RRR by both adsorption and photodegradation was investigated and the result is shown in Fig. 4. It is seen that RRR molecule does not adsorb on the C-TiO₂ while considerable extent of adsorption of RRR has occurred for 0.10 g of D-TiO₂ and MD-TiO₂. The initial rapid degradation for the latter two samples is due to adsorption together with photodegradation. In addition to these results, RRR does not undergo degradation in absence of any photocatalyst.

However, the dye molecules undergo photodegradation in presence of all forms of TiO₂ under UV irradiation. Percent removal of RRR comprising adsorption and photodegradation was found 11%, 35% and 45% during 90 minutes of irradiation with 0.10 g of C-TiO₂, D-TiO₂ and MD-TiO₂ as photocatalyst respectively. The chemisorption of chromate (VI) species on the surface of D-TiO₂ photosensitizes TiO₂, which enhances the photocatalytic activity of MD-TiO₂. Hence MD-TiO₂ becomes the most active photocatalyst³¹.

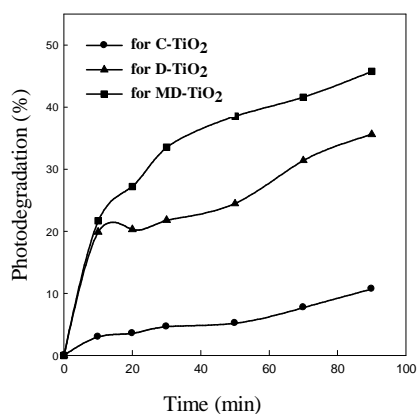


Fig. 4. Percentage of photodegradation of 1×10^{-4} M RRR solution in presence of 0.10 g of different types of TiO₂ photocatalysts. Initial pH = 5.0.

Effect of catalyst dosage on removal of RRR

The amount of catalyst affects the rate as well as the extent of photocatalytic degradation. The effect of catalyst dosages was investigated by carrying out the experiments with different amount of TiO₂ for each type catalyst used (Fig.5(a) and 5(b)). For C-TiO₂ the catalyst dosages were between 0.05 g and 1.6 g/100 mL in 1.0×10^{-4} M RRR, but for D-TiO₂ and MD-TiO₂ these dosages were from 0.02 g to 0.14 g/100 mL solution. It is seen that, as the concentration of catalyst increases, the percent degradation increases and reaches a maximum value, after that decreases with a further increase in the concentration. The optimum dosage is found to be different for different samples. The optimum dosages for C-TiO₂, D-TiO₂ and MD-TiO₂ are 1.20 g, 0.12 g and 0.10 g per 100 mL solution, respectively. Increase in the rate of degradation with increase in the amount of catalyst is due to availability of greater catalyst surface area for absorption of quanta and interaction of molecules in the reaction mixture with catalyst. As a result, the number of holes, hydroxyl radicals and super oxide anions (O₂⁻) are increased. These are principal oxidizing intermediate in advance oxidation process and increases the rate of degradation³².

It is expected that after certain amount of TiO₂, the surface area does not change anymore. Accordingly, the percentage degradation should show a constant value after a certain amount of TiO₂. However, increased amount of TiO₂ makes the suspension more cloudy. As a result, the light can't penetrate thus can't reach the bulk of the suspension. Thus, most particles of the TiO₂ in the bulk remain ineffective in producing radicals for photodegradation. It is interesting to note that the optimum degradation capacity changes to lower dosage region with D-TiO₂ and MD-TiO₂. This phenomenon can be correlated with the smaller particle size of these two samples compared with those of the C-TiO₂.

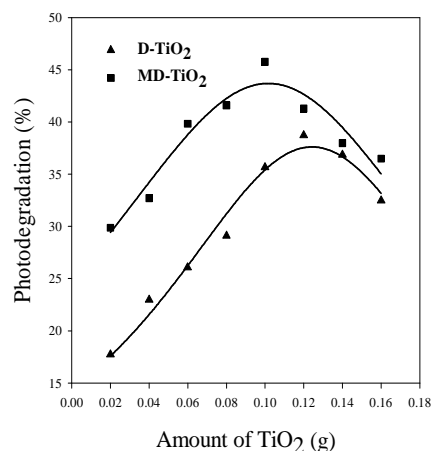


Fig. 5(a). Percent photodegradation of 1×10^{-4} M RRR solution in 90 min in presence of different amount of D-TiO₂ and MD-TiO₂ in suspension.

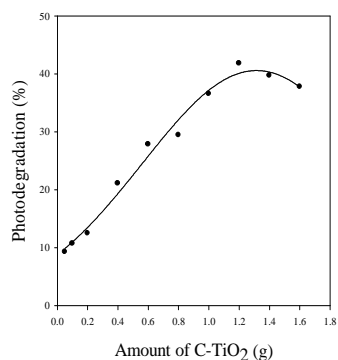


Fig. 5(b). Percent photodegradation of 1×10^{-4} M RRR solution in 90 min in presence of different amount of C-TiO₂ in suspension.

Effect of pH on photodegradation of RRR

pH value of the solution has an influence on the rate of photodegradation of some organic compounds in photocatalytic processes³³. To study the effect of pH on the photodegradation efficiency, experiments were carried out at various pH values, ranging from 2.0 to 6.0 at a constant dye concentration of 1×10^{-4} M. The results show that the percent degradation is very high at high acidic pH~3.0 for both C-TiO₂ and MD-TiO₂ and ~4.0 for D-TiO₂ (Fig.6). It is well established that upon hydration, the TiO₂ surface develops hydroxyl groups, which can undergo a proton association or dissociation reaction³³.



The pH_{zpc} of TiO₂ is within 6 to 7. So in the acidic solution of $\text{pH} < \text{pH}_{\text{zpc}}$, the surface of TiO₂, is presumably positively charged. Since the dye has a negatively charged sulfate group, the acidic solution favors degradation of dye onto photocatalyst surface. The photogenerated electron transfer becomes easier from the bulk to the interface due to electrostatic attraction, which is probably due to close approach of the negatively charged dye to a positive oxide surface. Hence the photodegradation efficiency increases. At a pH lower than 3.0, the suspension of TiO₂ is coagulated and settled down into the beaker. The net result is the lowering of the rate of degradation.

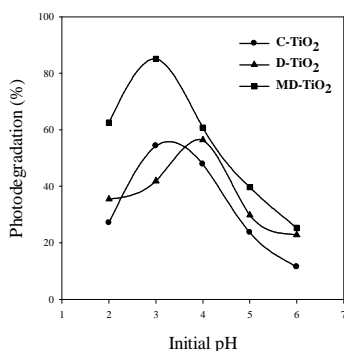


Fig. 6. Plots of percent photodegradation of RRR in 90 min against initial pH of the solution for different types of TiO₂ photocatalysts. Amount of the catalysts are C-TiO₂ = 1.20 g/100 mL, D-TiO₂ = 0.12 g/100 mL, MD-TiO₂ = 0.10 g/100 mL.

Effect of initial concentration of RRR on photodegradation

The photocatalytic degradation of RRR solution was carried out by varying the initial concentration of RRR from 0.5×10^{-4} M to 2.0×10^{-4} M in order to assess the appropriate concentration required for maximum degradation. For these experiments, MD-TiO₂ was used as the photocatalyst.

The results show that with the increase of initial concentration of RRR, the percentage of photodegradation decreases (Fig. 7). As the dye concentration is increased, the light can penetrate less on the surface of the catalyst because most of the light is absorbed by the dye. Moreover, the higher value of the denominator lowers the value of the percentage degradation³⁴.

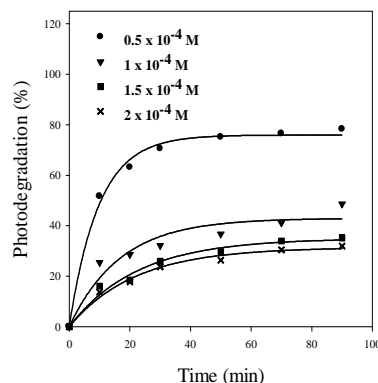


Fig. 7. Percent photodegradation of different concentrations of RRR solution with time. Amount of MD-TiO₂ = 0.10 g/100 mL. Initial pH = 3.0.

Effect of light sources on photodegradation of RRR

To study the effect of light sources on photodegradation of RRR several experiments were carried out in sunlight, artificial visible light and UV light (Fig. 8). The results show that percent photodegradation with MD-TiO₂ was found to be 85.1%, 54.5% and 95.9% under UV, artificial visible and sunlight, respectively under 90 min irradiation. Again, for C-TiO₂ photocatalyst, 54.3%, 24.6% and 52.3% photodegradation of RRR were found under UV, artificial visible and sunlight, respectively. Finally, for D-TiO₂ photocatalyst 41.9%, 42.3% and 59.9% photodegradation of RRR were found by UV, visible and sun light, respectively.

The degradation by the sun light is about 10.8 % higher than the artificial UV and 41.4 % higher than the artificial visible light after 90 min irradiation for MD-TiO₂. The intensity of the UV light source was measured previously which was $0.14 \text{ mW cm}^{-2} \text{ s}^{-1}$ ³⁵. Although the intensity of the sunlight was not measured, this value is higher than the value measured for UV³⁶. It is well known that the photocatalyst, TiO₂ is a semiconductor having a band gap energy of 3.2 eV which corresponds to 387 nm of the wavelength of the radiation. Thus, any light having wavelength less than 387nm will be capable of producing electron-hole pairs and causes photodegradation. Visible light can cause photodegradation by different mechanism, where dye molecules become excited by absorbing the light photon.

These excited molecules transfer electrons to the conduction band of TiO₂. However, a higher rate of degradation by the sunlight than the artificial visible light could be related to the very high intensity of this light.

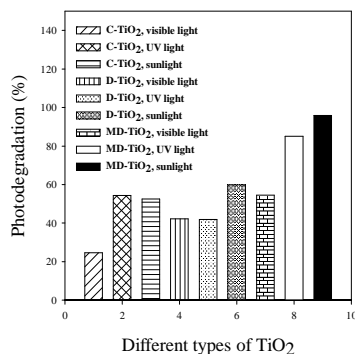


Fig. 8. Percent photodegradation of 1×10^{-4} M RRR solution in presence of C-TiO₂, D-TiO₂ and MD-TiO₂ under artificial visible, UV and sun light. Amount of catalysts are C-TiO₂ = 1.20 g/100 mL, D-TiO₂ = 0.12 g/100 mL, MD-TiO₂ = 0.10 g/100 mL. Initial optimum pH = 3.0 for C-TiO₂ and MD-TiO₂ and pH = 4.0 for D-TiO₂.

IV. Conclusion

The effectiveness of different photocatalysts like commercial, C-TiO₂, Degussa P25, D-TiO₂ and prepared surface modified, MD-TiO₂ has been investigated for the photodegradation of a textile dye RRR. Among these three catalysts, D-TiO₂ shows better adsorption efficiency but MD-TiO₂ yields a net higher photocatalytic efficiency than the other two catalysts. The optimum concentration of MD-TiO₂ for the photodegradation of RRR was found to be 0.10g/100 mL whereas those of D-TiO₂ and C-TiO₂ were 0.12 g/100 mL and 1.20 g/100 mL, respectively. Photodegradation decreases with the increase of initial concentration of RRR. Increased concentration of RRR might make the light difficult to penetrate the solution to reach the surface of the oxides to generate photoholes and electrons. Maximum photodegradation was found at pH 3.0 for both C-TiO₂ and MD-TiO₂ but 4.0 for D-TiO₂. It has been observed that almost 96.0% of 1.0×10^{-4} M of RRR was photodegraded when irradiated 90 min under sunlight in the presence of 0.10 g/100 mL of MD-TiO₂. Photodegradation was much higher in sunlight than in UV and visible light because of the greater intensity of light.

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