

Use of amorphous TiO₂ deposited on cotton by sol-gel process for de-colorization of direct dye solutions in presence of UV radiation

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In this investigation, decolorization of a direct dye solution catalysed by TiO₂ coated on a cotton fabric by sol-gel route in presence of UV radiation has been studied. Effect of various process and material parameters like initial dye solution concentration, treatment time and temperature, stirring rate and construction of fabric on dye decolorization extent has been studied. It is observed that with a starting dye solution concentration of 0.1 g/L, almost 80% dye removal can be achieved. It is not possible to improve the decolorization extent beyond 80% by any combination of parameters. X-ray diffraction studies reveal that the form of TiO₂ deposited on cotton fabric is not crystalline but amorphous in nature. While the UV radiation intensity and the fabric construction influence the dye decolorization, the treatment temperature and stirring rate do not have much bearing on decolorizing efficiency.

Keywords: Anatase, Cotton, Dye decolorization, Rutile, Sol-gel process, Titanium dioxide, UV radiation

1 Introduction

The textile dyehouse effluent contains various synthetic dyes, having complex aromatic molecular structure, many types of acidic and basic auxiliary chemicals, a variety of finishing chemicals, surfactants, etc. Such effluent cannot be discharged without appropriate treatment. The color in effluent is highly visible and is something that needs to be removed for aesthetic reasons. As different dyes have different characteristics, methods of treatment used are also different.

The primary issue with the effluent is its disposal, which has led to high contamination of water and soil in many countries worldwide¹⁻³. It is known that the fresh water available for drinking and other purposes is less than 0.5 % of all the water on the earth, so effluent treatment is inevitable⁴. Another issue with the dye water de-colorization is that dyes might produce hazardous amines when treated through conventional biological methods⁵. Many textile houses use adsorption and coagulation techniques to treat the waste water, but end up making the situation even worse by secondary pollution^{6,7}.

Since 1970, a lot of research has focused on advanced oxidation processes (AOP) through which a lot of organic dyes can be oxidized and removed⁸. Many oxide semiconductor photocatalysts have been

exhaustively tested and titanium dioxide has appeared to be the most promising due to its strong oxidizing power, non-toxicity and long term photostability⁹. The use of titanium dioxide for the remediation of organic substances of dye is well known and it is used in powder form inside the treatment chamber.

Though crystalline TiO₂ is known to exist in three different forms, namely anatase, rutile and brookite, most of the work has centred on anatase and rutile forms. Anatase form has been described as being more photo-catalytic than rutile, probably due to its higher affinity for organic compounds^{10, 11}.

In semiconductor TiO₂, an energy gap exists between the occupied valence and conduction bands. The band gap energy is 3.2 eV for anatase and 3.0 for rutile form¹². In presence of UV radiation having energy equivalent to or higher than the band gap energy, the electrons are transferred from the valence band to the conduction band. This causes formation of photo generated charge carriers, i.e. negatively charged electrons in the conduction band and positively charged holes in the valence band. The electrons are strongly reducing while the holes are strongly oxidizing in nature. These charged carriers can migrate to the surface of TiO₂ particles and may interact with adsorbed organic molecules. The electrons can reduce the atmospheric oxygen into superoxide anions and the holes can convert water into hydroxyl radicals. These are highly reactive

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transient species and can react with adsorbed organic compounds to degrade them into simpler volatile molecules like CO₂, etc^{13,14}.

In the present work, the decolorization of the textile dyehouse waste water was carried out by TiO₂ catalysed oxidation in presence of UV radiation. A titanium dioxide coated form of a fabric was used for the photocatalytic decomposition of the dye solution instead of dispersing titanium dioxide in the treatment chamber. The dispersion of TiO₂ in reaction chamber requires filtration or extraction of TiO₂, which again is a complex procedure. In the present study, the effluent was circulated for a few hours in a reaction chamber while being exposed to UV radiation in presence of a TiO₂ coated cotton fabric. TiO₂ was coated on a rectangular fabric strip which was placed at the center of the cylindrical reaction chamber. As TiO₂ acts as a photocatalyst, it is not consumed up during the reaction and can be easily reused. The sol-gel process is able to create deposition of TiO₂ on cotton which is quite durable to washing.

2 Materials and Methods

2.1 Materials

The chemicals such as rutile (99.9%) and anatase (99%) forms of TiO₂, nitric acid and titanium (iv) isopropoxide (97%), all of AR grade, were obtained from Aldrich. Laboratory grade ethanol was supplied by Thomas Baker. Deionized water was always used for making dye solutions and dilutions. A direct dye (Direct Orange BDC) was used for decolorization studies. For performing decolorization studies, TiO₂ was coated on cotton fabric. A plain woven cotton fabric with GSM 100, EPI 125 and PPI 65 was used in the study. A nonwoven cotton fabric of thickness 0.11 cm and GSM 100 was used for conducting the control experiments.

2.2 Coating of TiO₂ on Fabrics

Sol-gel technique was employed to coat titanium dioxide on a woven cotton fabric. The following procedure was followed¹⁵.

Firstly, 200 mL ethanol was taken in a 500 mL beaker to which 60 mL of titanium isopropoxide was added. Few drops of nitric acid were added to the mixture to maintain the pH of the solution to 2.4. The solution was stirred for 20 min on a magnetic stirrer (500 rpm) at room temperature.

Now, an oven dried fabric (10 × 10 cm²) size was taken and inserted into the beaker containing the solution and allowed to soak for 5 min with gentle

stirring. The soaked samples were then padded on a lab scale padding mangle (R B Electronics, Mumbai, India) at a nip pressure of 2.75 kg/cm² and speed of 3 m/min. The padded substrate was dried at 80°C for 4 min followed by curing at 120°C for 3 min in a hot air oven. The add-on % of TiO₂ on fabrics was calculated using the following formula:

$$\text{Add on (\%)} = \frac{W_{(T)} - W_{(UT)}}{W_{(UT)}}$$

where $W_{(T)}$ and $W_{(UT)}$ are the weight of treated and untreated fabric samples after drying.

2.3 Instrument Set up for Decolorization Studies

A simple set-up was prepared for carrying out waste-water decolorization. It consisted of a two litre cylindrical glass beaker with 16 cm diameter and 24 cm height, a UVA lamp and a metallic (aluminium) rectangular frame connected to a shaft to hold the fabric in a vertically hanging position. The beaker contained the dye solution and the rectangular metallic frame was hung in the centre of the beaker and kept submerged in the dye solution. The fabric strip was held in the solution by fixing it on the metallic frame, which, in turn, was fixed in its position by a stand. The beaker containing the dye solution was mounted on a magnetic stirrer (IKA, Germany). The exposed size of the fabric was 10 × 10 cm². The UV lamp was fixed at a distance of 20 cm from the beaker.

2.4 Color Measurement of Decolorized Dye Solution

For assessment of decolorization efficiency of the process, a direct dye (Direct Orange BDC) was selected. A stock solution of 0.2 g/L concentration of this dye was prepared and then 5 more solutions (0.02, 0.04, 0.06, 0.08 and 0.1 g/L) were made from it by diluting it with water. The absorbance of the solutions was measured on a Shimadzu UV-Vis spectrophotometer at λ_{max} of 410 nm and a calibration curve was prepared.

2.5 Dye Decolorization Procedure

One litre solution of Direct Orange BDC dye (0.1 g/L) was taken in the beaker. The beaker was set atop the magnetic stirrer and a TiO₂ treated fabric was attached in the frame and then placed in the centre of the beaker in a vertical position. The assembly was covered with a black box and left for 9 h under UV radiation with the solution allowed to be stirred at a desired rpm.

After fixed time intervals of 3 h, 2 mL of the dye solution was taken from the beaker and its absorbance was measured. The concentration of the dye solution was determined from the calibration curve.

2.6 Source of UV Radiation

Two UV lamps of different irradiation power (8 and 125 watt) were used in the decolorization studies. The lamps were of Phillips make and the maximum emission band for both was 365 nm, making them UVA radiation source.

2.7 Scanning Electron Microscopy

The surface characteristics of untreated and TiO₂ coated cotton fabric samples were studied with the help of scanning electron microscope (ZEISS, model: EVO 50). The samples were first coated with a silver layer to provide surface conductivity.

2.8 X-Ray Diffraction Studies

The wide angle X-ray diffraction (WAXD) studies were carried out on a Philips X-ray diffractometer with Nickel-filtered CuK α (1.54 Å) as radiation source. Additionally, XRD was also performed on neat rutile and anatase forms of TiO₂. The diffractometer was operated at 40 kV and 30 mA in reflection mode with angle 2 θ range from 10° to 35° at a scanning rate of 2°/min. The objective of these studies was to determine the nature of crystal type of TiO₂ deposits on textile fabrics.

2.9 Control Experiments

One litre solution of the dye of initial concentration (0.0375g/L) was taken in a beaker. The pH of the solution was maintained at 7. The beaker was put under the reactor assembly without any TiO₂ treated fabric. The assembly was covered with a black box and was left for 9 h under UV radiation.

The same study was performed in presence of a TiO₂ treated fabric but without a UV radiation source. Two milliliter (2 mL) dye solution was taken after every 3 h interval and the concentration of the solution was determined through the calibration curve. In both the cases, no decolorization of the dye solution was observed. Therefore, the results clearly establish that the presence of only one out of two necessary conditions, i.e. UV radiation and TiO₂, cannot cause decolorization of dye solutions.

3 Results and Discussion

3.1 Add-on% and SEM Study

The add-on % of TiO₂ on woven cotton fabric is found to be 19.5%. Figure 1 shows the SEM images of untreated and treated cotton samples. It can be clearly seen in Fig. 1(a) that while the surface of untreated cotton sample is free of any deposition, the deposits of the size < 1 micron are clearly visible on treated cotton sample [Fig. 1(b)]. The deposition is rather uniformly distributed over the surface of the fibres.

3.2 X-Ray Diffraction Studies

The XRD patterns of rutile and anatase crystalline forms of TiO₂ show characteristic dominant crystalline peaks at 27.56° and 25.43° respectively. Figure 2 shows XRD of untreated and treated cotton woven fabrics. XRD was done for treated fabrics both before and after the use. It is clear that there is not much difference in peaks of treated and untreated cotton fabrics. The peak of TiO₂ corresponding to anatase and rutile forms are absent in the XRD patterns of treated cotton fabric.

To confirm the nature of the deposits, an XRD was performed on the TiO₂ formed by sol-gel technique described above. TiO₂ powder was synthesized as per the procedure outlined in section 2.2 but in absence of fabric, collected and used for XRD studies. The XRD

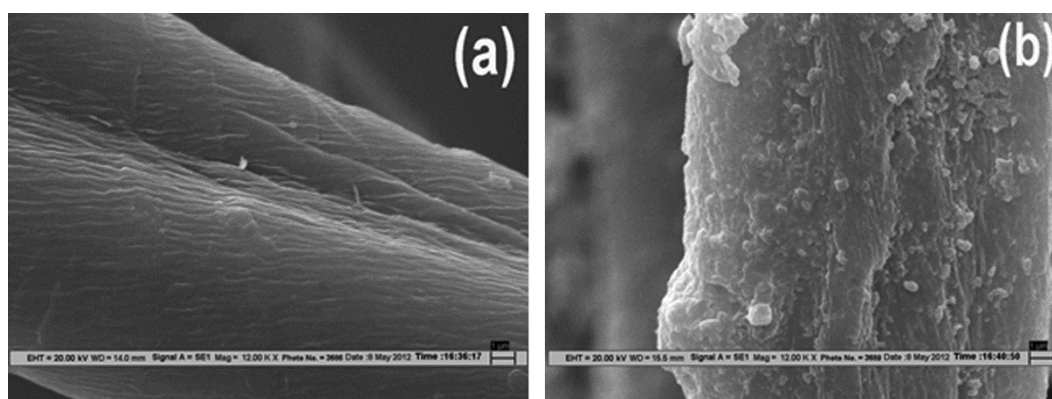


Fig. 1 — SEM of (a) untreated cotton, and (b) treated cotton showing deposition of TiO₂

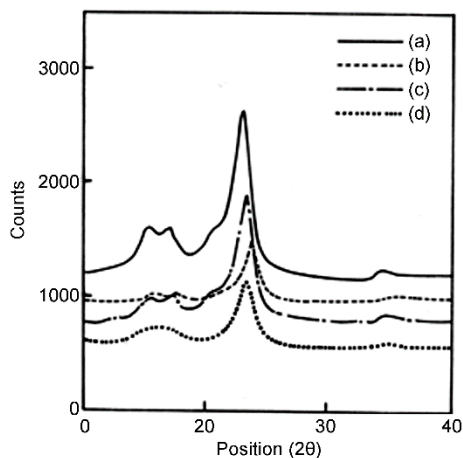


Fig. 2 — XRD of cotton fabrics (a) neat woven cotton, (b) treated woven cotton (unused), (c) treated woven cotton (after use), and (d) treated nonwoven cotton (after use)

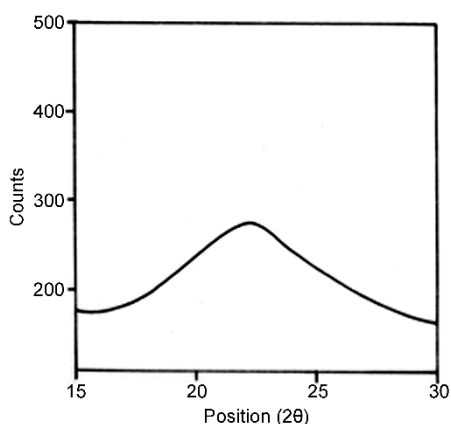


Fig. 3 — XRD of TiO₂ formed by sol-gel process in absence of cotton fabric

pattern of the TiO₂ thus formed is shown in Fig. 3. As can be seen, the XRD of the TiO₂ formed in the sol-gel process shows only a broad diffused peak at 22.4°, which in all probability is due to the amorphous nature of TiO₂ deposits. Hence, it can be inferred that the sol-gel process described above and used in this study results in the deposition of amorphous forms of TiO₂ on the fabrics under study. Some continuing work in this area by authors has shown that TiO₂ can be crystallized to some extent, if the fabric is given a hydrothermal treatment at 120°C for an extended time (> 3 h). Since it facilitates recombination of photo-generated electrons and holes under UV irradiation¹⁶, amorphous TiO₂ is generally considered to have poor photocatalytic activity. However, it has recently been reported that much higher specific surface area of amorphous TiO₂ can work in its favour. The ability of amorphous TiO₂ to act as good electron transfer

mediator for photosensitized decolorization of the Rhodamine B dye has been reported¹⁷. The amorphous TiO₂ has good adsorptivity for dye. The dye molecules are adsorbed by the surface of amorphous TiO₂ and subsequently the exposure of ultraviolet irradiation helps in degrading them¹⁸.

3.3 Decolorization Studies

3.3.1 Effect of Time

Preliminary studies indicate that the extent of decolorization of the dye solution depends on treatment time. Hence, an attempt has been made to optimize the treatment time by exposing 1 litre of 0.1 g/L dye solution for 30 h in presence of a treated cotton nonwoven fabric and UV radiation from a 125 watt UV lamp. A mild agitation of the dye solution was maintained by agitating it at 100 rpm with the help of a magnetic stirrer. Two millilitre dye solution was taken after every 3 h and its concentration was determined. The temperature of the bath was maintained at 30 °C. The results obtained are shown in Fig. 4 (a).

It can be seen that the concentration of dye solution keeps on decreasing continuously with time. However, the rate of change in dye concentration becomes very low after 9 h. Hence, the remaining studies have been carried out for 9 h exposure times only.

3.3.2 Effect of Initial Dye Solution Concentration

To find out whether initial dye concentration has any effect on the decolorization process, two dye solutions (0.1 and 0.05 g/L) were treated in the presence of TiO₂ coated cotton nonwoven fabric and UV radiation from a 125 watt UV lamp for 9 h. The results are shown in Fig. 4 (b).

As can be seen from the figure, the dye concentration in the bath decreases continuously with treatment time. However, the rate of decolorization is rather low for dye solution of lower concentration. Ultimately, at the end of 9 h, the concentration of both the solutions becomes almost same (0.02 g/L). This seems to be the lower limit, which might be difficult to lower further with any combination of parameters. The reason may lie in the fact that with reduction in the number of dye molecules in solution, the probability of a dye molecule coming in contact with TiO₂ and a UV photon at the same time becomes low.

3.3.3 Effect of Agitation

The decrease in dye concentration in dye solution takes place due to oxidative destruction of dye molecules when they come in contact with TiO₂ in the

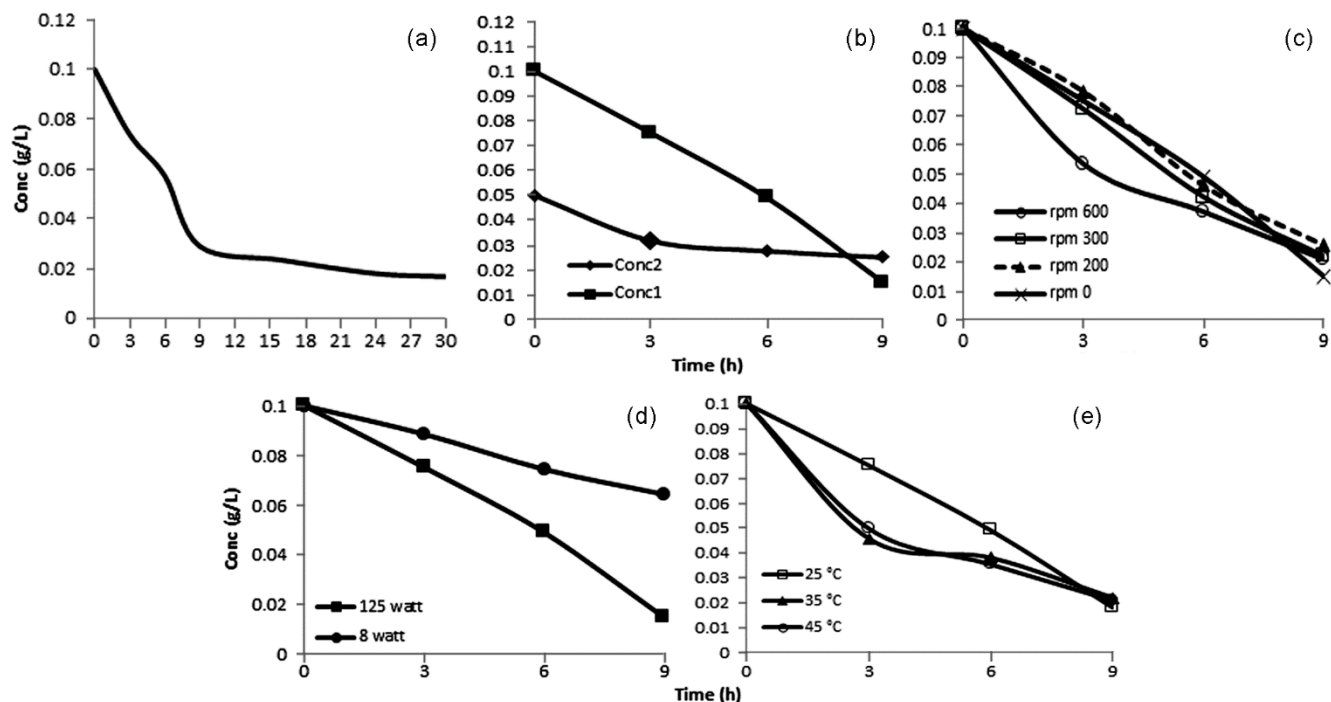


Fig. 4 — Dye decolorization as a function of (a) time, (b) initial dye concentration, (c) stirring rate, (d) UV radiation intensity, and (e) initial dye solution temperature

presence of UV radiation. Since the position of the TiO_2 coated fabric in dye solution remains static, it is postulated that any parameter which might increase the contact between dye molecules and TiO_2 may affect the decolorization process. Hence, agitation or circulation is assumed to play an important role. Therefore, to study the role of agitation on decolorization dynamics, the experiments are conducted in a similar manner as discussed above with different agitation rates. A magnetic stirrer is used to agitate the dye solutions at rpm varying between 0 and 600. The results are shown in Fig. 4 (c).

The results are a little surprising in the sense that up to the rpm of 300, there does not seem to be much effect of agitation on decolorization process. The decolorization rate increases, however, at least for the first half of treatment when an rpm of 600 is used, although by the end of 9 h treatment time all solutions end with almost same dye concentration. This experiment again affirms that there is indeed a lower limit to which the dye concentration by decolorization can be lowered for the dye in question. Overall, the experiment establishes that the agitation does not affect the dynamics of dye decolorization significantly.

3.3.4 Effect of UV Radiation Intensity

The decrease in dye concentration is dependent on the intensity of UV light used for de-colorization.

To study the effect, two UV bulbs of 8 and 125 watt power were used. All other conditions were maintained as above, with a moderate agitation of 100 rpm. The results are shown in Fig. 4 (d).

As expected, the results do show that the rate of dye decolorization is higher when higher intensity of UV radiation is used, which is maintained through the entire period of treatment time. It is also clear that with lower radiation intensity, it would take a much longer time for the dye solution to reach the lower limit of 0.02 g/L.

3.3.5 Effect of Dye-bath Temperature

The effect of dye solution temperature on the decolorization dynamics has also been studied. The experiment was conducted by maintaining 3 different dye solution temperatures of 25, 35 and 45°C. All other conditions were maintained as above. The results are shown in Fig. 4 (e).

It can be seen from the results that at temperatures higher than the room temperature (25°C), the decrease is steeper for the initial 3 h and then it flattens out. However, at 25°C, a slow and steady rate is maintained throughout. At the end of 9 h, the residual dye concentration is again almost same, i.e. around 0.02 g/L. This shows that for longer treatment durations, the temperature does not affect the extent of decolorization.

4 Conclusion

The decolorization of a direct dye solution catalysed by TiO₂ deposited on a fabric by sol-gel route in the presence of UV radiation is possible. Most of the decolorization occurs in initial 9 h of treatment after which there is only marginal decrease in dye concentration. The decolorization seems to be taking place at a higher rate for dye solutions of higher concentrations; however, there seems to be a lower limit of approximately 0.02 g/L, below which it is difficult to reduce the dye concentration.

The temperature and agitation of the dye solution affect the decolorization rate in the initial phase of the treatment, but the overall effect is not significant when the entire treatment time is taken into consideration. Decolorization rate is higher when higher intensity of UV radiation is used. The decolorization is also higher for cotton fabric as compared to polyester fabric which may be attributed to higher add-on% of TiO₂ on cotton than that on polyester. The fabric structure also seems to affect the decolorization rate with woven cotton fabrics showing better results in comparison to nonwoven fabric.

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