
Solar Assisted Photocatalytic Degradation of Reactive Azo Dyes in Presence of Anatase Titanium Dioxide

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ABSTRACT: The photocatalytic degradation of two model azo dyes, RemazolOrange and RemazolRed, was investigated using commercial anatase titanium dioxide (TiO₂) as photocatalyst. Direct solar radiation during the duration from 12:00 p.m to 2:30 p.m was applied as an irradiation source. The percent degradation of model dyes in water was measured by UV-Visible spectroscopy. The effects of operational parameters i.e.irradiation time, initial concentration of dye, catalyst loading, and pH of solution on degradation have been investigated. The maximum degradation for Remazol Orange and Remazol Red reached to 91% and 85% respectively for the specific experimental conditions of both dye concentration of 10 mg/L with 200 mg/L anatase titanium dioxide at pH 3.0 and 180 minute irradiation. The presence of anatase phase of TiO₂ was confirmed by x-ray diffraction (XRD). The morphological features of the catalyst were analyzed by Scanning Electron Microscopy (SEM).

Keywords: Photocatalytic degradation, Solar radiation, Reactive azo dyes, anatase TiO₂, XRD,SEM.

1. INTRODUCTION

Worldwide annual productions of organic dyes are 450,000 ton; more than 11% of which are released in effluents during manufacture and application processes[1]. Most of these dyes are toxic and potentially carcinogenic in nature and their removal from the industrial effluents is a major environmental concern[2]. Wastewater released from the textile industries often contains dyestuffs in moderate concentration range of 10-200 ppm[3]. Aesthetically, these colored compounds are not appealing and affect adversely the aquatic ecosystem by preventing the sunlight to enter into the stream and reducing the photosynthetic reactions[4]. Methods such as biodegradation, coagulation, adsorption, advanced oxidation process (AOP) and the membrane process have been used to remove dye from wastewater[5-7]. All of these methods have some advantages or disadvantages over the other methods. Among these methods, the photocatalytic degradation which is an advanced oxidation process appears to be a promising field of study. This method has been reported to be effective for the degradation of dye contaminants from waters because it can provide almost total degradation of dyes and there is no waste disposal problem[8-12]. Titanium dioxide (TiO₂) has emerged as an excellent photocatalyst material for removal of environmental contaminants[13]. Titanium dioxide (TiO₂) by far the most widely employed photocatalyst due to its comparatively higher photocatalytic activity, low toxicity, chemical stability and very low cost. The anatase form of TiO₂ is reported to give the best combination of photoactivity and photostability[14]. The minimum band gap energy required for photon to cause photogeneration of charge carriers over anatase TiO₂ semiconductor is 3.2 eV corresponding to a wavelength of 388 nm[15]. The energy corresponding to this wavelength is available from the solar light; hence solar light is the potential source to generate charge carriers over TiO₂. Photocatalytic oxidation of dye molecules by anatase TiO₂ catalyst is based on the generation of strong oxidizing species, such as hydroxyl radicals (OH•), holes (h⁺), superoxide (O₂⁻) and perhydroxy radicals (HOO•) which are formed in the solution when the catalyst absorb radiation of wavelength 388 nm. These radicals are highly reactive and mineralize the large dye molecule into small products such as carbon dioxide, water and inorganic ions by interacting with chromophores and auxochromes[16]. Since, the numbers of textile industries are increasing day by day around the world, consequently the use of dyes are also increasing; among these the azo dyes are most commonly used. These dyes when come in contact to the nearby water body create environmental problem. So, these dyes must be removed from textile effluent by a cost effective method. In this present study, commercial anatase TiO₂ was used as photocatalyst for the degradation of two model azo dyes, Remazol Red and Remazol Orange.

2. MATERIALS AND METHODS

Commercial titanium dioxide, lab grade, supplied by Merck, KGaA, 64271 Darmstadt, Germany, was used as received throughout the degradation experiment of dyes. Its molecular weight is 79.90 g/mol and melting point

is 1843°C. It is white color powder and insoluble in water. Remazol Red (RR) & Remazol Orange (RO) dyes were collected from a local textile industry of Bangladesh and used without purification. Fig. 1 shows the structural formula of these dyes [17, 18]. Distilled water was used to prepare experimental solutions of dyes. The pH of the solution was adjusted by using 0.1M NaOH and 0.1M HCl. RO & RR show maximum

absorbance at wavelength 495 nm [18] & 518 nm [19] respectively as determined from the UV-Visible spectra of these dyes (Fig. 2)

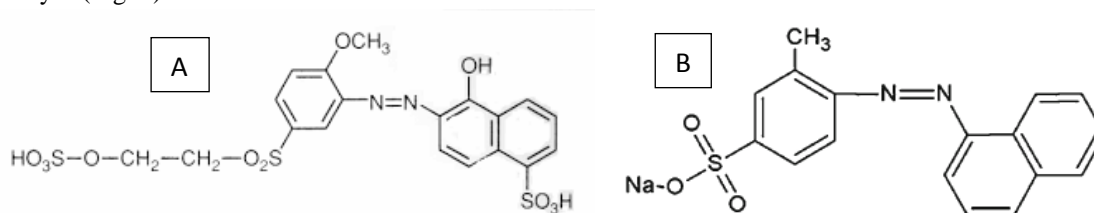


Fig. 1: Structural formula of RR (A) and RO (B)

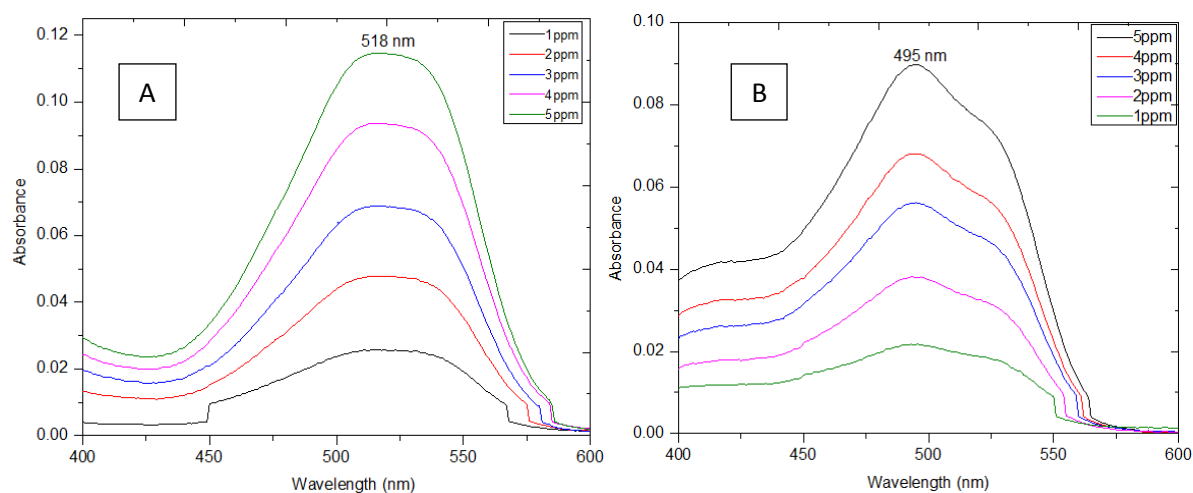


Fig.2: UV-Visible spectra of RR (A) and RO (B)

2.1. Characterization of Titanium dioxide

FT-IR spectrum of TiO_2 was recorded on a FT-IR 8400S spectrophotometer (Shimadzu Corporation, Japan) in the wavenumber range of $4000\text{--}400\text{ cm}^{-1}$. XRD pattern of TiO_2 was recorded by an x-ray diffractometer (Ultima IV, Rigaku Corporation, Japan) at room temperature. $\text{Cu K}\alpha$ radiation ($\lambda=0.154\text{ nm}$), from a broad focus Cu tube operated at 40 kV and 40 mA, was applied to the sample for measurement. The morphology of the sample was analyzed by an analytical scanning electron microscope (JEOL JSM-6490LA, Tokyo, Japan) operated at an accelerating voltage of 20 kV in the back-scattered electron mode.

2.2. Degradation Study

All photocatalytic experiments were carried out under similar conditions on sunny days of November–December 2015 between BST (Bangladesh Standard Time) 12:00 p.m. to 2:30 p.m. An open borosilicate glass beaker of 250 mL capacity was used as the reaction vessel. Irradiation was carried out in an open air condition. During the irradiation time no volatility of the solvent was observed. After addition of 5, 10, 15 and 20 mg of TiO_2 in 50 mL of each of 5, 10, 15 and 20 ppm solutions of RR and RO respectively, each of the solution was irradiated under direct solar radiation during the above mentioned time with occasional stirring. Before addition of catalyst to the dye solutions, the initial absorbance was recorded by a UV-Vis spectrophotometer (UV-2100PC Human Lab Instrument Co., Korea). Absorbance of each of the solutions after irradiation was measured

at an interval of 30 minute up to total time period of 180 minute. In each 30 minute interval 2.0 mL irradiated sample was taken and centrifuged to obtain clear solution and absorbance was recorded. Using this absorbance the final concentrations of these dyes weremeasured from the calibration curve of RR and RO. Then the percent degradation of dye was measured by the following equation:

$$\% \text{ Degradation} = \frac{\text{Initial concentration} - \text{Final concentrtrion}}{\text{Initial concentration}} \times 100$$

3. RESULTS AND DISCUSSION

3.1. Characterization

The XRD pattern ofcommercial TiO₂ as shown in Fig. 3 revealed well-defined reflections at 2θ values of 25.36°, 37.84° and 48.09°which are the typical characteristic peaks of anatase TiO₂[20, 21].

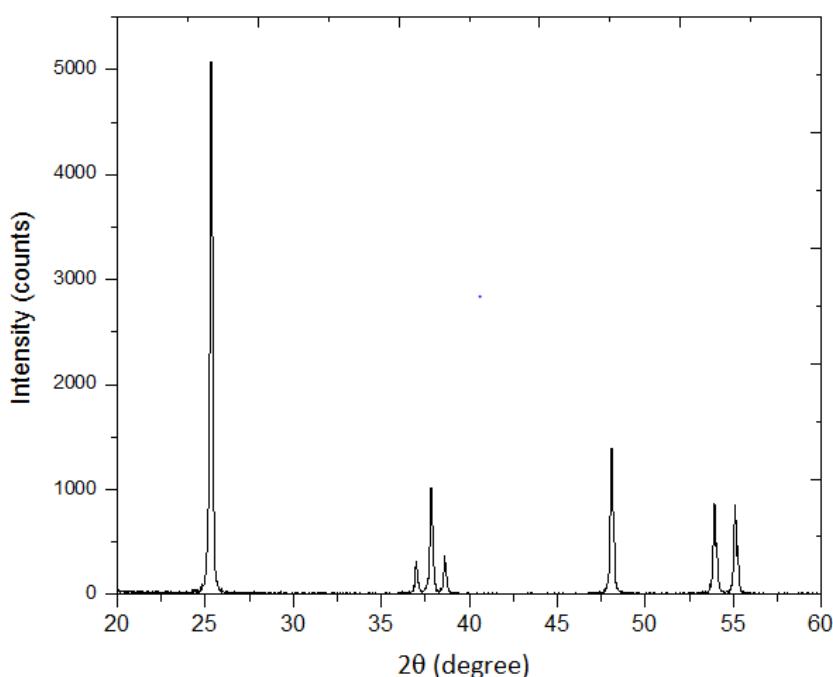


Fig.3: XRD pattern of titanium dioxide

The FT-IR spectrum of TiO₂ showed various characteristic peaks as shown in Fig. 4. In this spectrum, the absorption band at 3454.51cm⁻¹ is related to stretching and 1631.78 cm⁻¹ to bending vibration of O-H, representing the water as moisture. The intense peak at 690.52 cm⁻¹ is assigned to the Ti-O stretching band which is the characteristic peak of TiO₂[21].

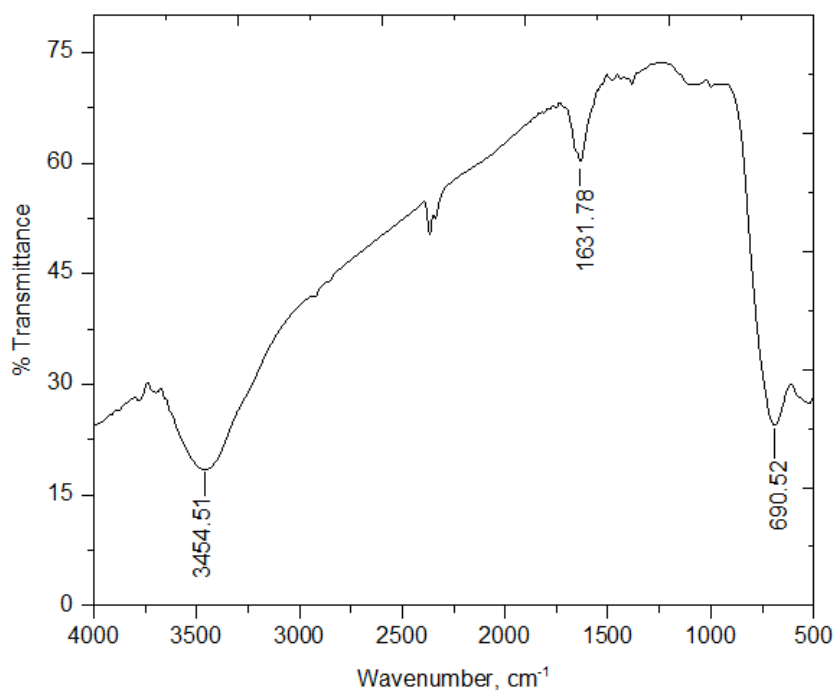


Fig.4: FT-IR spectrum of titanium dioxide

The SEM micrograph as illustrated in Fig. 5 revealed that the particle size of TiO_2 was in the nanometer range. This small particle size provides large surface area for hydroxyl ions (OH^-) of the solution to come in contact with TiO_2 surface to form hydroxyl radical (OH^\bullet), which is a strong oxidizing agent and oxidize large amount of dye molecules adsorbed on the surface of TiO_2 . It was also observed from the image that the particles were spherical shaped, smooth, uniformly distributed and the shape of the catalyst was in homogeneous structure and no odd structures were detected on the surface [20, 21].

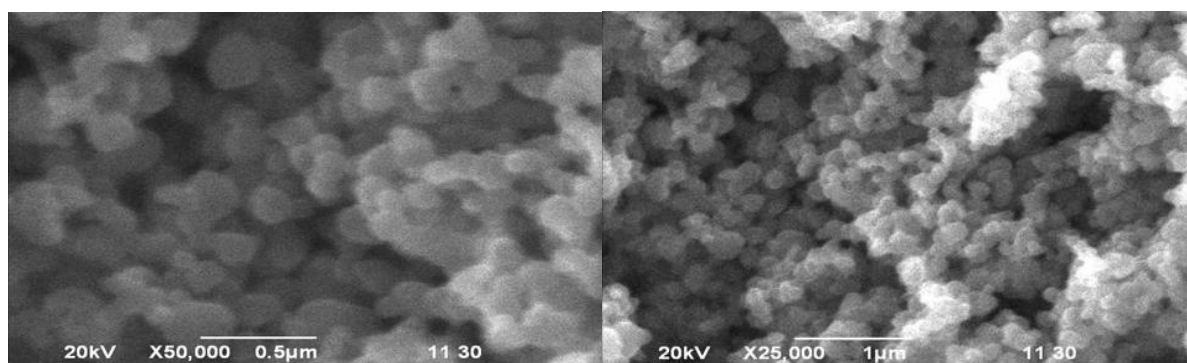


Fig.5: SEM images of titanium dioxide

3.2. Photocatalytic degradation of RR and RO in presence of TiO_2

3.2.1. Effect of irradiation time on degradation of RR & RO

Initially, the percent degradation of both dyes increased with the increase of irradiation time as depicted in Fig. 6. This is because when the dyes were allowed to remain in contact with the catalyst for more times more amount of dyes got adsorbed by the catalyst surface and consequently, more amount of dyes were degraded due to the generation of increased amount of hydroxyl radicals by the catalyst. But after 150 minute of irradiation time, reaction rate for both dyes decreased because of the competition for degradation occur between the reactant and the intermediate products formed during degradation. The slow degradation after 150 minute is due

to the slow reaction of short chain aliphaticity with $\text{OH}\cdot$ radicals and short life-time of photocatalyst because of active sites deactivation by strong by-products deposition[22, 23].

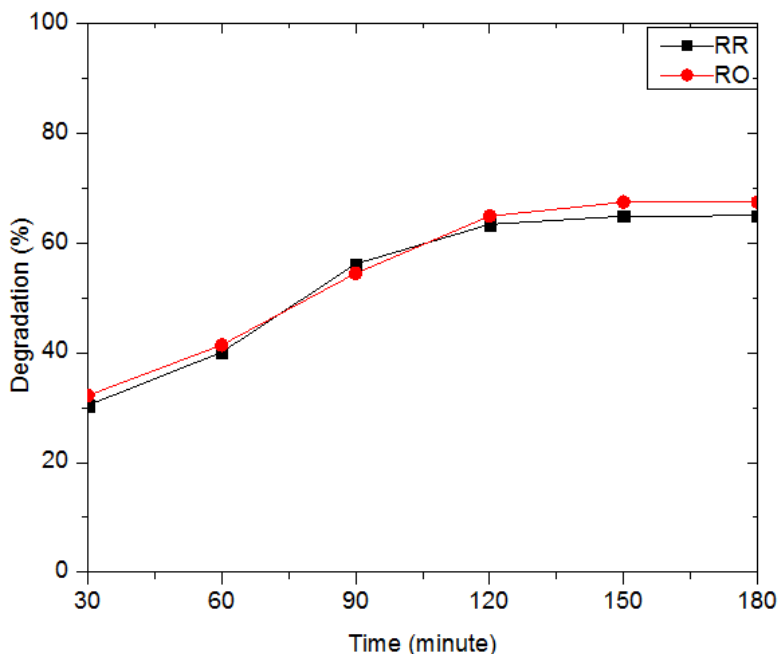


Fig.6: Effect of irradiation time on degradation of RR & RO (RR concentration: 10 mg/L, RO concentration: 10 mg/L, catalyst amount: 200 mg/L, pH: 5.2,).

On the onset of 120 minutes the degradation of RO was found higher than RR. This is because of the presence of more bulky degraded products produced from RR compared to RO which inhibit the approachment of parent RR towards the activated TiO_2 surfaces. It was also observed from the figure that after 150 minute the percent degradation almost reached equilibrium. But, irradiation was carried out for 180 minute to ensure the equilibrium time and similar degradation result as of 150 minute was obtained both for RR and RO. Thus, 180 minute was taken optimum irradiation time for the maximum degradation of RR & RO.

3.2.2. Effect of initial dye concentration on degradation of RR & RO

Initially, the percent degradation of both dyes increased up to 10 ppm as depicted in Fig. 7. This is because more amount of dye molecules come in contact to the catalyst surface, so the degradation amount is also high. But when the dye concentration increased above 10 ppm, percent degradation of dyes gradually decreased, because less number of photons are available to reach the catalyst surface and therefore less $\text{OH}\cdot$ are formed. At dye concentration higher than 10 ppm, a significant amount of solar light may be absorbed by the dye molecules rather than the catalyst which reduced the catalyst efficiency, thus causing an inhibition in percent degradation[24]. The figure showed that the maximum degradation of both dyes was obtained for 10 ppm dye solutions for 180 minute exposure to sunlight. Thus, 10 ppm concentration of dyes was taken optimum for the measurement of other effects on the catalytic process.

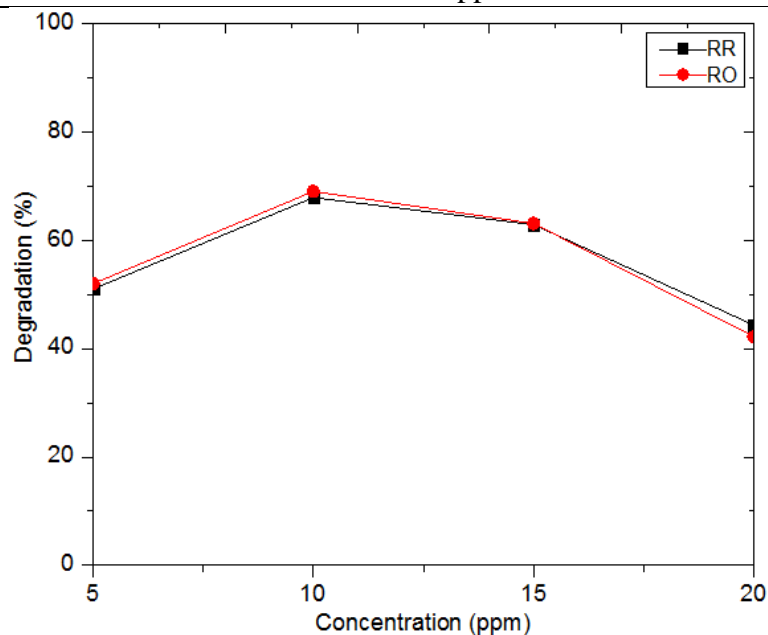


Fig.7: Effect of initial dye concentration on degradation of RR & RO (irradiation time: 180 minute, Catalyst amount: 200 mg/L, pH: 5.2,)

3.2.3. Effect of catalyst amount on degradation of RR & RO

Initially, the percent degradation of both dyes increased up to catalyst amount 200 mg/L, then the degradation decreased with the increases of catalyst amount as depicted in Fig. 8. The increase in the degradation with an increase in the catalyst amount is due to an increase in the available active sites on the catalyst surface for the reaction, which in turn increases the rate of radical formation. At catalyst loading more than 200 mg/L the percent degradation decreased due to the scattering of light by excess of catalyst particles[25, 26]. At the same time, the penetration of light to the active site of the catalyst through the solution becomes difficult due to agglomeration of particles, which reduce the degradation rate[27]. Maximum degradation was found to be 64.9% for RR and 67.44% for RO with optimized catalyst amount of 200mg/L.

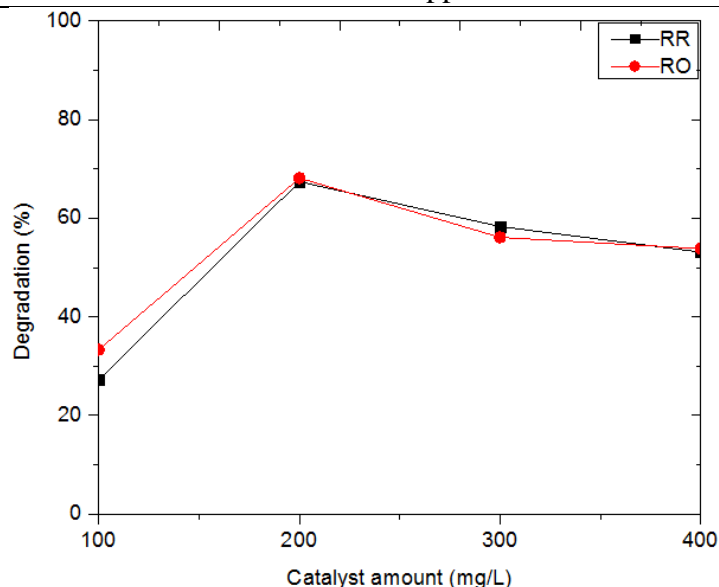
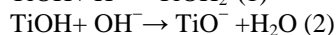
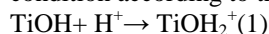


Fig.8: Effect of catalyst amount on degradation of RR & RO (irradiation time: 180 minute ,RR concentration: 10 mg/L, RO concentration: 10 mg/L, pH: 5.2)

3.2.4. Effect of pH on degradation of RR & RO

The percent degradation of both dyes were maximum at pH 3.0 as depicted in Fig. 9 and it was also observed that with further increase of pH, the percent degradation decreased and it was minimum at pH 11.0. This was because, the surface of titania becomes protonated or deprotonated respectively under acidic or alkaline condition according to the following reactions:



Thus, titania surface remains positively charged in acidic medium and negatively charged in alkaline medium. Titanium dioxide is reported to have higher oxidizing activity at lower pH, but excess H^+ at very low pH causes decrease in reaction rate, thus the percent degradation also decreases [28].

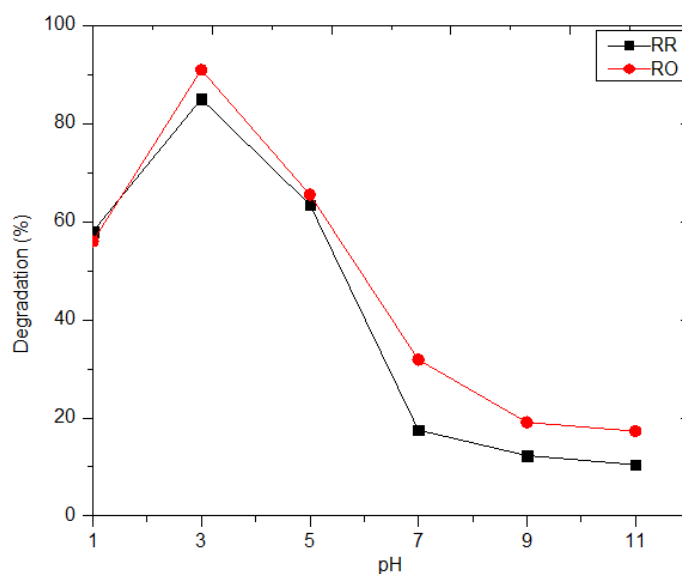


Fig.9: Effect of pH on degradation of RR & RO (irradiation time: 180 minute, RR concentration: 10 mg/L, RO concentration: 10 mg/L, catalyst amount: 200 mg/L)

Theazo linkage ($-N=N-$) is particularly susceptible to electrophilic attack by OH^\bullet radical, but at pH below 3.0 the H^+ ions interact with the azo linkage decreasing the electron densities at the azo group. Consequently, the reactivity of OH^\bullet radical by the electrophilic mechanism decreased, thus the degradation decreased. Above pH 3.0 the degradation was continually decreased due to the decreased concentration of $TiOH_2^+$. At pH above 7.0 the approach of the dye anions to the catalyst surface is minimum due to the competition between hydroxyl ions and dye anions[29].

Finally, the percent degradation estimated at optimized conditions observed for RR and RO are summarized in table 1.

Table 1 - Maximum RR and RO degradation at optimum conditions: Irradiation time = 180 minute, Initial dye concentration = 10ppm, Catalyst amount = 200mg/L and pH = 3.0

Concentration of dyes before degradation (ppm)		Concentration of dyes after degradation (ppm)		Degradation (%)	
RR	RO	RR	RO	RR	RO
10	10	1.49	0.89	85	91

4. CONCLUSION

In this present study, the azo dyes Remazol Red and Remazol Orange were successfully degraded by anatase TiO_2 in aqueous solution under direct solar radiation. The degradation of both dyes was studied by changing various parameters. The remarkable percent of degradation of RR and RO in the presence of TiO_2 nanoparticle at pH 3.0 suggests that the textile effluents having stated azo dyes could successfully be treated for maintaining the sustainable green environment. This process can also be applicable for degrading other azo dyes.

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