



Photocatalytic degradation of textile dyes by hydrogel supported titanium dioxide nanoparticles

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Abstract

Background: Textile industry has been condemned as one of the world's worst offenders in terms of pollution because 10-15% of all the dyes used in the industry are lost within wastewater during processing. The presence of even very low concentrations of dyes in effluent is highly visible and degradation products of these textile dyes are often carcinogenic. Owing to the complex nature of synthetic dyes, conventional biological treatment methods are ineffective. Hence there exist needs for developing treatment techniques that can lead to the complete destruction of the dye molecules from waste stream. The current study focused to develop a new photocatalytic reactor using immobilized TiO₂ capacity to decolourise and degrade textile industry effluent in an effective way.

Methods: TiO₂ nanoparticles synthesized by simple precipitation method at pH 5 was successfully entrapped in biopolymer calcium (Ca)-alginate and used as heterogeneous photocatalyst for the degradation of various textile dyes using UV radiations. Photocatalyst was characterized by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The influence of previous operational parameters on the photodegradation has been studied by setting up a laboratory scale photocatalytic reactor.

Results: The scanning electron microscopic images indicate that, the alginate gel acts as a bridge that binds the nanoparticles together. The experimental results showed that the rate of degradation depends on the chemical structure of different dyes as well as adsorption of dyes by TiO₂ which is directly proportional to the surface area and dispersion of the catalyst, the adsorption of light by the dye. The kinetics of COD disappearance was slower than the discoloration of the solution. The supported TiO₂ can be used several times without lose of efficiency

Conclusions: The results of this study have shown that the degradation of different textile dyes was successfully carried out in laboratory scale photoreactor containing coated TiO₂ as photo catalyst. Calcium alginate can be used as a green support for immobilizing TiO₂ nanoparticles and can be used for developing a new environment friendly immobilization system for large scale water treatment.

Keywords: Immobilized TiO₂ nanoparticles, photocatalytic degradation, textile dyes

Background

Wastewater from textile industries poses a threat to the environment as large amount of chemically different dyes are used for various industrial applications and a significant proportion of these dyes enter the environment via wastewater. Around 10-15% of all the dyes used in the industry are lost within wastewater during synthesis and processing [1]. Due to its complex chemical structure, dye is one of the most difficult constituents in textile wastewater to treat [2]. The presence of even very low concentrations of dyes in effluent is highly visible and degradation products of these textile dyes are often carcinogenic [3]. Many dyes are visible in water at concentrations as low as 1 mgL⁻¹. Textile processing wastewaters, typically with dye content in the range 10-200mgL⁻¹ [4] are therefore usually highly coloured and discharge in open waters presents an aesthetic problem. The treatment of textile effluents is of interest due to their toxic and aesthetical

impacts on receiving waters. Treating wastewater before it is discharged to the natural water bodies reduces the risks posed to human and environmental health [5].

There are more than 10,000 commercially available dyes with over 7x10⁵ tones of dyestuff produced annually across the world [6]. With the increased use of a wide variety of dyes, pollution by dye's wastewater is becoming increasingly alarming. Most of the dyes used in the textiles industries are stable to light and non biodegradable [7]. In order to reduce the risk of environmental pollution from such wastewater, it is necessary to treat them before discharging it into the environment [8]. Physical and chemical processes has been usually used to treat the wastewater. However these processes are costly and cannot be used effectively to treat the wide range of dye wastewater [9,10]. Adsorption is a useful and simple technique which has gain considerable attention in the recent few years [11]. However, these systems merely

transfer the dye from one form of waste to another (e.g., liquid to solid), and, therefore, cannot be considered to be a complete treatment of the waste [12]. In recent years great efforts have been made using widely called advance oxidation technologies (AOT) for treatment of these recalcitrant pollutants to more biodegradable molecules. The generation of reactive species like hydroxyl radicals is the basis for AOPs. These radicals can attack most of the organic molecules with rate constant usually in the range of 10^6 - 10^9 $M^{-1} S^{-1}$ [13]. Among the many processes proposed and being developed to destroy water soluble organic pollutants in water and wastewater one of the most important oxidation processes is heterogeneous photocatalysts via combination of TiO_2 and light [14]. TiO_2 is a commonly used photo-catalyst because of its stability in UV light and water. TiO_2 can function as both an oxidative and reductive catalyst. TiO_2 is considered very close to an ideal semiconductor for photocatalysis because of its high strong oxidizing power, non toxicity and long term photostability [15]. Some challenges in TiO_2 photocatalysis, including enhancement of the catalytic activity, controllability of the structural properties, immobilization to form films and membranes and narrowing of the band gap energy, could be solved by introducing nanotechnological synthesis routes, noble material processing approaches, and new reactor design and concepts. Nanoscale particles are promising in this area because of their unique properties such as small particle sizes, large surface to volume ratio and the ease with which they can be anchored onto the solid matrices for enhanced treatment of water, wastewater [16]. TiO_2 nanoparticles have unique properties of small size, larger special surface area, stronger magnetism, photocatalyst, well-UV absorption, surface activity, heat-conductance, disperse property. However, the obligation to separate the small TiO_2 particles from the suspension after treatment limits the process development.

The key problem of industrializing the technology seems to be its time consuming and expensive process of separation and recycling. The above problems can be avoided by immobilization of the photocatalyst over suitable supports. Systems which incorporate immobilization on a solid surface are most popular due to their relative ease implementation [17]. Although entrapment is one of the simplest methods used for cells and enzymes immobilization that can be adapted for TiO_2 immobilization also. This method consists in the inclusion of these species within polymeric matrices [18]. Biodegradable polymer materials will reduce the need for synthetic polymer and will results in production at a low cost, thereby producing a positive effect both environmentally and economically. Calcium alginate is a biocompatible and mechanically stable gel. Moreover, alginate is nontoxic, biodegradable, and non immunogenic, and produces thermally irreversible and water insoluble

gels [19]. Therefore Calcium alginate can be used as a green support for TiO_2 immobilization that can be used for developing a new environmentally friendly immobilization system for large scale water treatment. The main objective of this work is to develop a photocatalytic reactor using immobilized TiO_2 nanoparticles with high photocatalytic activity in the removal of contaminants from textile industry. In the present work, the photocatalytic degradation of some dyes having different chemical structures (azo, anthraquinone and reactive dye) on laboratory scale photocatalytic reactor with immobilized TiO_2 nanoparticles as photocatalyst has been investigated.

Methods

Synthesis of TiO_2 Nanoparticles

Chemical precipitation method was adopted to synthesize TiO_2 nanoparticles in this work. $TiCl_3$ (MERCK 15%) solution in HCl (10–15%) was introduced under vigorous stirring in deionized water ($[Ti^{3+}] = 0.15$ mol L^{-1}). A blue-violet solution was obtained at room temperature. The pH was adjusted between 2.5 and 5.0 with sodium hydroxide (NaOH) solution. The solutions were then heated at $60^\circ C$ in an oven for 24 h. The white suspension obtained were then centrifuged, washed with an acidic solution (pH =1) and distilled water in order to remove salts. Solid nano TiO_2 was prepared by drying the suspension in an oven at a temperature of $120^\circ C$ for 12 hour and calcined in a muffle furnace at $450^\circ C$ for 3 hour.

Immobilization on biopolymer-Calcium Alginate

In the present work, we attempted to use a new support for immobilization of nanoparticles for the purpose of water treatment. We used one step encapsulation method for immobilization of nanoparticles in semi permeable alginate beads. Sodium-Alginate manufactured by Hi-Media Laboratories Pvt. Ltd was used for this study. A solution containing TiO_2 nanoparticles (2.0 wt %) and sodium alginate (2.0 wt %) was prepared with distilled water, and stirred for 30 min at $85^\circ C$. Afterwards, the solution was extruded as small drops by means of syringe into a stirred solution of calcium chloride (8.0 wt %), where spherical gel beads were formed with a size of 2-3 mm. The gel beads were retained in the $CaCl_2$ solution for 12 h for hardening and then washed with distilled water. The excess water in the beads was removed by blotting with filter paper [20]. Stability of alginate beads were studied using concentrated and diluted solutions of hydrochloric, nitric and sulphuric acids and sodium and potassium hydroxides. Stability of beads depends on pH values of the aqueous solutions and the initial physical state of the beads. These beads were used for further photocatalytic studies.

Characterization of Photo-catalyst

The characterization of nanoparticles was done using UV-spectrophotometer and SEM/EDS.



Figure 1. Experimental set up.

UV-Visible spectrophotometer

Evolution 201 UV-Visible Spectrophotometer (Thermo Scientific, USA) was used for the characterization of TiO_2 nano particles. The instrument has a scanning speed up to 6000 nm/min and has a wavelength range between 190 –1100 nm.

SEM/EDS: Scanning Electron Microscopy with X-ray microanalysis

The size and shape of the nano- and submicro-particles was examined with a Field Emission scanning electron microscope equipped with Horiba EDX analyser, made by Hitachi (SU-6600). It utilizes advanced Variable Pressure (VP) technology and an improved Schottky field emission electron source that provides exceptional imaging and high probe current with great stability in both high vacuum and variable pressure operation. SEM images were observed with a magnification of 2.00 μm with an accelerating voltage of 15.0kV.

Experimental Set Up

The experimental set up consists of an ultraviolet light source, electronic ballast and an aluminum column of length 20 cm and diameter 15 cm. The ultraviolet light source used was mercury vapor lamp of predominant wavelength 292.3 nm developed by Philips Lighting. The UV source can be described as tube light reactor (TLR) operated at 60V, and produced 9 W. This lamp is placed inside the reactor. Electrical wires were connected to the lamp through copper holders that are screwed around the lamps end. The TiO_2 nanoparticle immobilized in calcium alginate which was

in the form of spherical beads, were used as the catalyst. 100gm beads containing TiO_2 2 % wt were used in this experiment. It was filled uniformly on the outer surface of the low wattage lamp so as to provide a higher illuminated specific catalyst surface area than even a slurry reactor. The photocatalytic reactor was fixed as vertical hung. The experimental set up of the photocatalytic reactor is as shown in Figure 1. The photocatalytic reactor is vertically hung on the stand. The initial dye solutions were passed through the inlet port of the photocatalytic reactor and the treated solutions were taken out through the outlet port of the photocatalytic reactor.

Photo catalytic Studies

The photocatalytic activity of TiO_2 nanoparticles on the degradation of the synthetically prepared effluents and industrial effluent was evaluated in laboratory conditions under illumination of UV light in the photoreactor. Stock solutions of anthraquinone dye and azo dye were prepared by dissolving the requisite quantity of each dye in distilled water without further purification. The dyes used were Methyl Orange, Methyl Red from MERCK and Alizarin Red S from LOBA chemicals. Real time effluents from the field were collected from two local dyeing industries. Methyl orange is a stable azo dye, hence it was used for the experiments. Effluent collected from ACR textiles, Kannur consists of a mixture of three reactive dyes namely Red SB, Blue SG, Yellow S3R, NaCl and Soda ash. Similarly effluent collected from Co-operative weaver's society, Kozhikode consisted of vat dyes. The dye solutions were introduced to the inlet of the photoreactor and at different time intervals the treated effluent was withdrawn from the outlet of the reactor. All experiments were carried out under ambient conditions *i.e.*, at room temperature and 1 atm.

Degradation studies of the dye solutions

The photocatalytic activity of TiO_2 nanoparticles on the dye solutions were determined by measuring the absorbance of the dye solutions before and after the treatment, determining the COD of the dye solutions before and after the treatment, FTIR analysis of the dye solutions before and after the treatment.

UV Spectra

The absorbance of the prepared dye solutions and the effluents collected were measured before and after degradation at different degradation times. Measurements were carried out using Evolution 201 UV-Visible Spectrophotometer in the photon energy range of wavelength from 200 to 600 nm. The colour removal of the dye solution was measured at the λ maximum of the absorption spectrum of each dye. Decolorization efficiency was calculated from a mathematical equation adapted from measurements of decolorization. From the respective absorbances obtained, percentage color

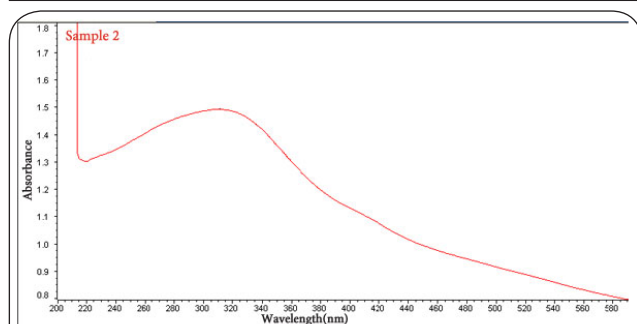


Figure 2. UV-Visible spectra of the solution with TiO₂ nano particles.

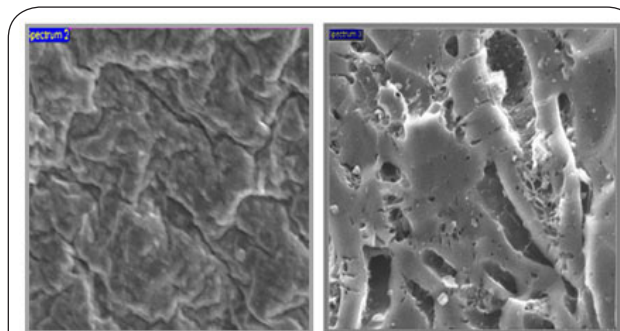


Figure 3. SEM image of 2%TiO₂ nanoparticles entrapped Alginate beads at different magnification.

disappearance was calculated using the following:

$$\text{Decolorization \%} = \frac{(\text{Absorbance})_0 - (\text{Absorbance})_t}{(\text{Absorbance})_0} \times 100$$

Where (Absorbance)₀ is the absorbance before irradiation and (Absorbance)_t is the absorbance at time t.

Chemical Oxygen Demand (COD)

To investigate the biodegradability of the dye solutions, COD analysis was done by the standard acid dichromate method. COD measurement before the treatment and after the treatment with the photocatalyst is used as a measure of mineralization of the dye solutions. The photodegradation efficiency of the different dye solutions were calculated .

FTIR analysis

Degradation of the dye solutions was confirmed with IR spectroscopy which involves collecting absorption information and analyzing it in the form of a spectrum. FTIR spectrum was used as a measure to confirm the degradation of textile effluent. Measurements were carried out using Bruker Alpha Spectrophotometer, utilizing the ATR (Attenuated Total Reflection) FT-IR sampling technique.

Effect of pH and ions

In the real effluents, the dyes are present with many organic and inorganic species that can affect the photocatalytic degradation. The effluent pH may vary according to the

type of dyes used. Therefore study of pH is an important parameter in the degradation of dyes. The effect of pH was studied by adjusting the pH value to different range by addition of HNO₃(1N) and NaOH (1N). Similarly, the effects of various ions were investigated using (100ppm) solutions of chloride, sulphate, nitrate and phosphate prepared using NaCl, KNO₃, NaH₂PO₄ and K₂SO₄ respectively. All chemicals used were purchased from E MERCK India.

Recycling of Photocatalyst

The catalyst's lifetime is an important parameter of the photocatalytic process, due to the fact that its use for a longer period of time leads to a significant cost reduction of the treatment. For this reason, the catalyst was recycled four times. After the optimized conditions for the degradation of the effluent were determined, the catalyst was recovered by giving acid wash using dil. HCl and hot water and again used to study its recyclability.

Results and discussion

Preparation and Characterisation of Photocatalyst

Chemical precipitation method was adopted to synthesize TiO₂ nanoparticles. In the precipitation method, the first product precipitated at pH 3 was a mixture of anatase and rutile. By increasing the pH of the solution, the formation of anatase was favored and at pH 5, only anatase TiO₂ could be formed [21]. The formation of nanoscale TiO₂ at pH 5 was confirmed by UV and EDAX examination of the product. The room temperature absorption spectrum of the TiO₂ nanoparticles is shown in **Figure 3**. TiO₂ exhibited larger absorption in the visible light region with an onset absorption band at 280–400 nm The absorption spectrum of TiO₂ at 400 nm is due to the charge transfer from the valence band (mainly formed by 2p orbitals of the oxide anions) to the conduction band (mainly formed by 3d t_{2g} orbitals of the Ti⁴⁺ cations) [22]. The obtained result showed a strong, but broad peak located at a range 290-400 nm (**Figure 2**).

TiO₂ nanoparticles were then entrapped in a biopolymer for studying its photo catalytic degradation of textile dyes. Ca-Alginate was used as the solid support in this work. Calcium alginate beads in diluted acidic and alkaline solutions were mechanically stable. But gel beads in strong acidic solutions, tends to shrink and completely dissolve in concentrated solutions of sodium and potassium hydroxides after 3 days. This may be due to the ion-exchange process taking place between Na⁺/K⁺ ions in solution and Ca²⁺ ions in the beads. SEM study was carried out to confirm the size of the particles, and its distribution pattern in polymeric matrix. A representative SEM image in **Figure 3** shows that most of the particles are well distributed. The particle size of the samples estimated from the SEM micrographs was below 50 nm. The quantitative compositional analysis of the TiO₂ nanoparticle entrapped beads was carried

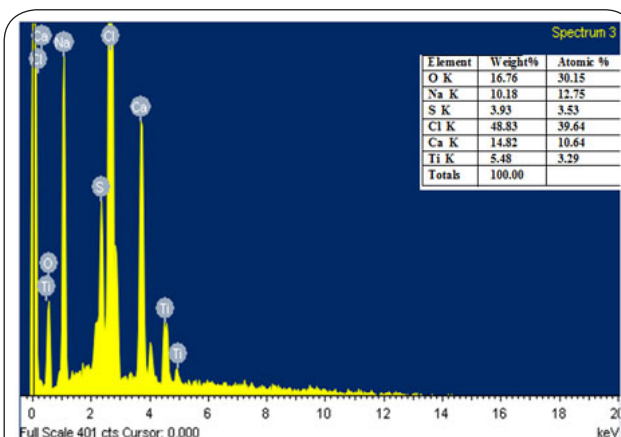


Figure 4. EDX spectrum of TiO₂ nanoparticles entrapped Calcium Alginate beads.

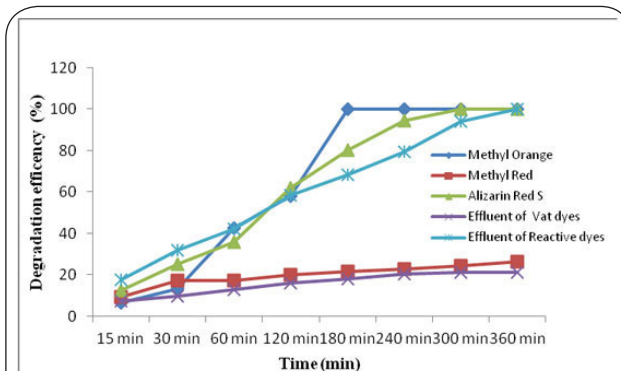


Figure 5. Kinetics curves of colour disappearance for the five dyes.

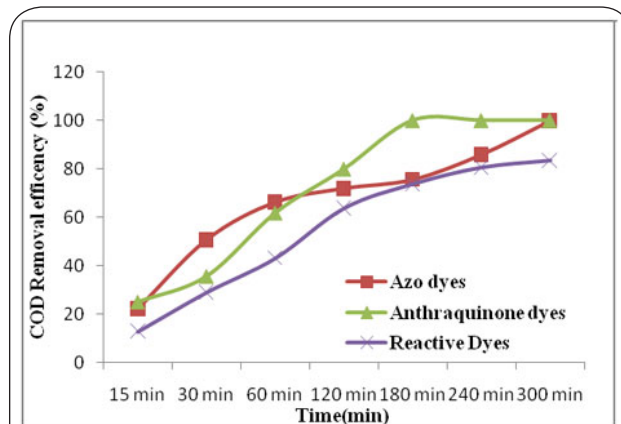


Figure 6. Kinetics curves of COD disappearance for the three dyes.

out using energy dispersive X-ray (EDAX) spectroscopy measurements. The spectra confirm the presence of TiO₂ in the structure, as shown in **Figure 4**. The spectra were recorded from a single bead. From the measurements, it is enumerated that the each bead consist of an average

5.48% Ti, 16.76% O₂, 14.82% Ca, 10.18% Na and 48.83% Cl₂. EDS analysis showed no significant levels of impurities which could have originated from the process.

Photocatalytic studies

An understanding of reaction rates and how the reaction rate is influenced by different parameters is important for the design and optimization of an industrial system. The rate of photocatalytic degradation depends on several factors including illumination intensity, catalyst type, oxygen concentration, pH, presence of inorganic ions and the concentration of the organic reactant. The efficiency of photocatalytic activity of TiO₂ nanoparticles on the dye solutions were determined by measuring the absorbance of the dye solutions before and after the treatment, determining the COD of the dye solutions before and after the treatment, FTIR analysis of the dye solutions before and after the treatment.

Absorbance Measurements

Figure 5 shows the trend of gradual decomposition of the five dyes which was monitored by measuring the absorbance at regular intervals. It was noticed that among these 5 dyes, Methyl orange, suffers degradation with the higher rate than the others. The efficiency reached only around 25.5% after 5 hours in the case of methyl red and vat dyes. Control experiments, using UV irradiation in the absence of catalyst, showed no loss of colour after 60 minutes exposure, confirming the critical role played by the TiO₂ catalyst in dye degradation. The apparatus was found to be not much effective in case of liquor dyeing. Further studies were not carried out in the case of such dyes.

Effect of irradiation time on COD

The efficiency of photocatalytic treatment to mineralize three types of dyes was investigated. The percentage of COD removal efficiency has been plotted as a function of irradiation time (**Figure 6**). It is interesting to remark that the COD decreases slower than the discoloration of the solution. At 180 minutes the colour degradation efficiency observed was 100, 80 and 68 % respectively for azo dye, anthraquinone dye and reactive dye. But COD removal efficiency at 180 minutes was found to be 76, 100 and 73% respectively. This result can be explained due to the fact the dyes are not directly mineralized, but transformed in intermediate photoproducts. After total discoloration of the dye solutions, there still remain traces of COD (20 to 30%). This means that the discoloration can enhance the aesthetic quality of water, rather than the total purification and detoxification.

FTIR Analysis

The FTIR spectra of control Methyl orange (**Figure 7a**), displays peak at 2,924.06 cm⁻¹ for asymmetric CH₃ stretching vibrations; peaks at 1,519.78 and 1,421.71 cm⁻¹ for the

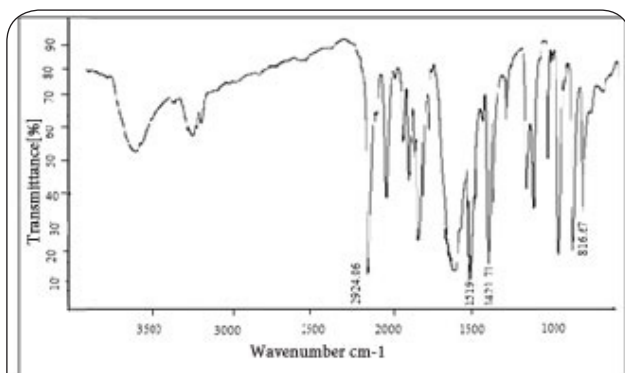


Figure 7a. FTIR Spectra of Initial solution of Methyl Orange.

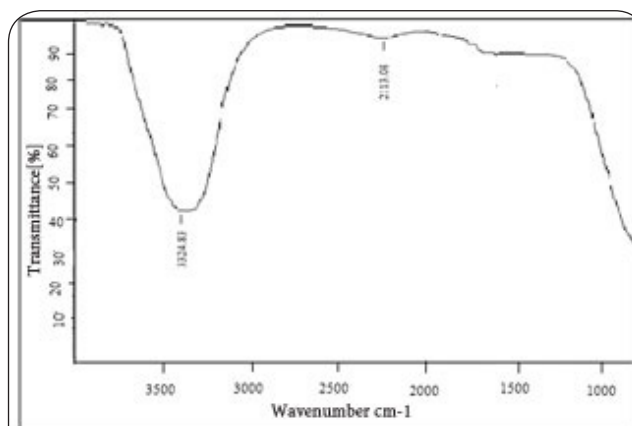


Figure 8b. FTIR Spectra of Alizarin Red S after treatment.

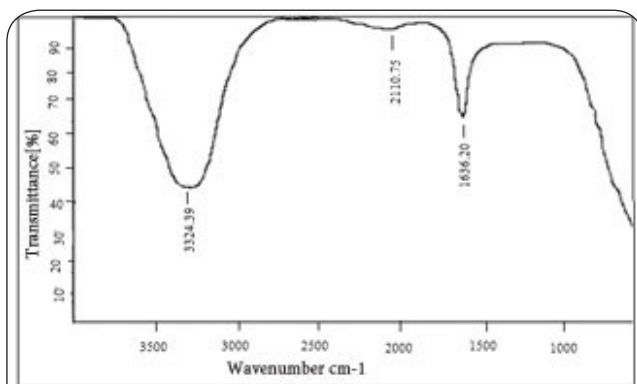


Figure 7b. FTIR Spectra of Methyl Orange solution after 180 min treatment.

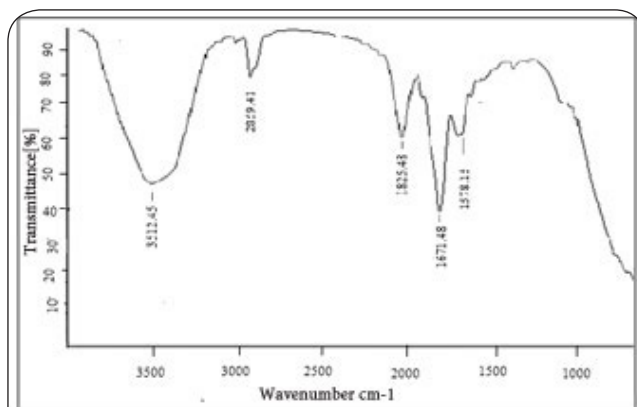


Figure 8a. FTIR Spectra of Initial solution of Alizarin Red S.

C=C-H in plane C-H bend; peaks at 1,040.00, 1,007.29, and 846.66 cm^{-1} for ring vibrations; and a peak at 816.67 cm^{-1} for the 1, 4 disubstituted (Para) benzene ring. All these peaks confirm the aromatic nature of the dye. But in **Figure 7b** the peaks at 1600-1400 cm^{-1} which indicates aromatic C=C bond and Phenyl ring Substitution band due to C-H at 870-675 cm^{-1} was entirely absent. The FTIR spectrum of the degradation products formed by photocatalytic degradation had displayed entirely new peaks compared to the initial control dye, which confirms the degradation

of Methyl orange. The new peaks at 3324 cm^{-1} and 1636 cm^{-1} corresponds to N-H (m) stretch and asymmetrical stretch of Nitro compounds. This indicates that TiO_2 nanoparticle immobilized in Calcium- Alginate used in the experiment had resulted in the photodegradation of the dye. The FTIR spectra of Alizarin (**Figure 8a**), displays peak at 1671.48 cm^{-1} 1578.15 cm^{-1} for aromatic C=C bond; peak at 3512.45 cm^{-1} for the OH stretch; peak at 1825.48 cm^{-1} for multiple bonded CO group and 2859.41 cm^{-1} for the C-H stretch. All these peaks confirm the aromatic nature of the dye. But in **Figure 5. 16** the peaks at 1600 cm^{-1} - 1400 cm^{-1} which indicates aromatic C=C bond and C=O at 1850 cm^{-1} - 1650 cm^{-1} was entirely absent. The FTIR spectrum (**Figure 8b**) of the degradation products formed by photocatalytic degradation had displayed entirely new peaks compared to the initial control dye, which confirms the degradation of Alizarin Red S. The new peaks at 3324.83 cm^{-1} and 2113.08 cm^{-1} correspond to C-H stretch. This indicates that TiO_2 nanoparticle immobilized in Calcium Alginate used in the experiment had resulted in the photodegradation of the dye.

The FTIR spectrum of the degradation products formed by photocatalytic degradation (**Figure 9a**) had displayed entirely new peaks compared to the raw effluent (**Figure 9b**), which confirms the degradation of the dyes in the textile effluent. This indicates that TiO_2 nanoparticle immobilized in Calcium Alginate prepared in the experiment had high photocatalytic activity.

Effect of pH

pH of the real effluent may vary according to the type of dyes used and the organic and inorganic compounds added to it. Therefore study of pH is an important parameter in the degradation of dyes. The absorbance of Methyl Orange at 462 nm and Alizarin at 445 nm for different pH is as shown in **Figure 10**. The absorbance values showed that the photodecolouration efficiency of methyl orange decreased in the order of $\text{pH } 3 > \text{pH } 5 > \text{pH } 7 > \text{pH } 9 > \text{pH } 11$. Such a result can be better understood by taking

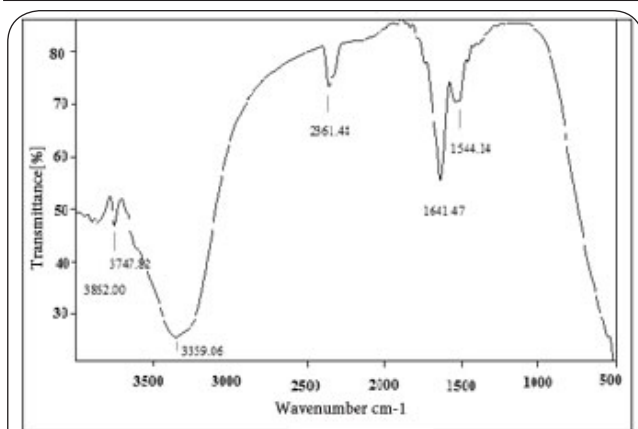


Figure 9a. FTIR Spectra of Initial solution of textile effluent.

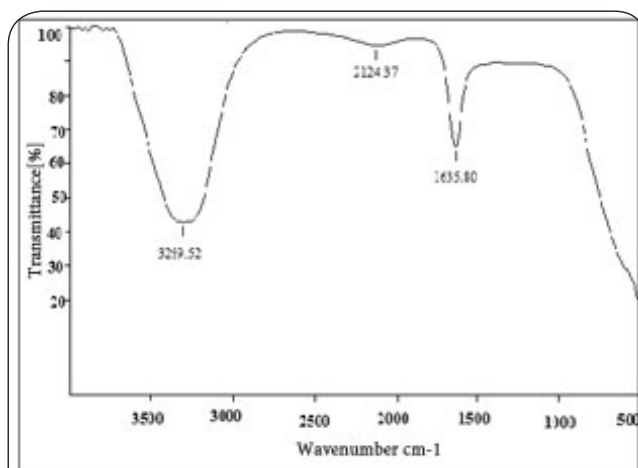


Figure 9b. FTIR Spectra of Initial solution of textile effluent after treatment.

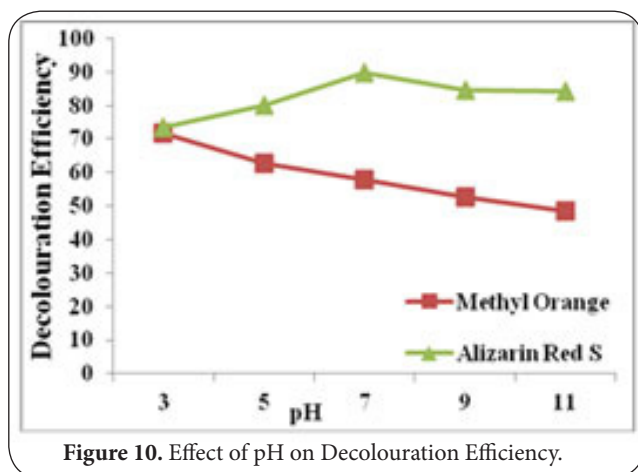
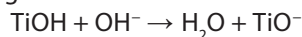


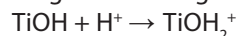
Figure 10. Effect of pH on Decolouration Efficiency.

account that both the surface state of the photocatalyst and the ionisation state of Methyl Orange depend on the pH of the solutions. The pH of zero charge (pH pzc) of TiO_2 is known to be close to pH = 6.8 which means that for pH higher than 6.8, the surface becomes negatively charged

according to the electrochemical equilibrium [23]



and at pH lower than pH pzc, the surface of Titania is positively charged according to



From the **Figure 10**, it can be seen that the rate of degradation of methyl Orange decreases for a pH higher than three, in correlation with the decrease of the amount of TiOH_2^+ . The adsorption at basic pH is not favoured because repulsive electrostatic force due to predominant TiO^- in this range of pH. The photodecolouration efficiency of alizarin increases from pH 3 to pH 7 and then decreases from pH 7 to pH 11. The reason for increase in efficiency up to pH 7 is due to strong adsorption of the dye on to the TiO_2 particles as a result of the electrostatic attraction of the positively charged TiO_2 with the ionized dye. A decrease in the reaction rate has been observed, with a minimum at pH 11, reflects the difficulty of anionic dye in approaching the negatively charged TiO_2 surface when increasing the solution pH.

Effect of ions

In the real effluents, the dyes are present with many organic and inorganic species that can affect the photocatalytic degradation. In this study, the effects of various ions were investigated. The effect of ions like chloride, sulphate nitrate and phosphate on the decolouration efficiency was studied and is tabulated in **Table 1**. The values in the table shows that the presence of Cl^- , SO_4^{2-} and NO_3^- anions leads to an increase of the effectiveness of the photo catalytic degradation and the presence of HPO_4^{2-} anion decreases the photocatalytic efficiency. This is because in the case of chloride ions the formation of Cl^\cdot radical by the reaction of photo produced OH^\cdot with Cl^- oxidizes pollutants results in increase in efficiency of degradation. [24] Similarly the SO_4^{2-} ions adsorbed in the surface of TiO_2 react with photo-induced holes (h^+) to form sulphate radical anion ($\cdot\text{SO}_4^-$) which is a strong oxidant [25]. The NO_3^- ions, weakly adsorbed on the surface of TiO_2 may cause acidification of the solution with the nitric acid and therefore increase the photocatalytic degradation by decreasing pH. The same interpretation is proposed for HPO_4^{2-} ions which increase the pH of the solution and consequently decrease the photo catalytic degradation.

Recycling of Photocatalyst

Photocatalyst can be recycled effectively which makes the process cost effective. For this reason, the catalyst was recycled four times as shown in **Figure 11**. After the optimized conditions for the degradation of Methyl Orange were determined, the catalyst was recovered by giving acid wash and again used to study its recyclability. The obtained results showed that the efficiency decreases from 88 to 54%. This is likely due to the fouling of the

Table 1. Effects of ions on the Photo degradation efficiency.

Dyes	Degradation Efficiency							
	30 min		60 min		90 min		120 min	
	Methyl Orange	Alizarin Red S	Methyl Orange	Alizarin Red S	Methyl Orange	Alizarin Red S	Methyl Orange	Alizarin Red S
Chloride	24.06	42.35	53.01	69.15	58.65	74.51	72.93	88.17
Sulphate	20.30	59.46	48.50	85.83	55.64	89.88	71.80	97.19
Nitrate	25.56	48.38	53.76	75.14	60.53	79.10	74.43	91.56
Phosphate	10.56	30.33	36.47	48.29	36.59	56.45	59.99	71.52
Control	13.16	35.78	42.48	61.88	49.25	68.78	57.89	80.00

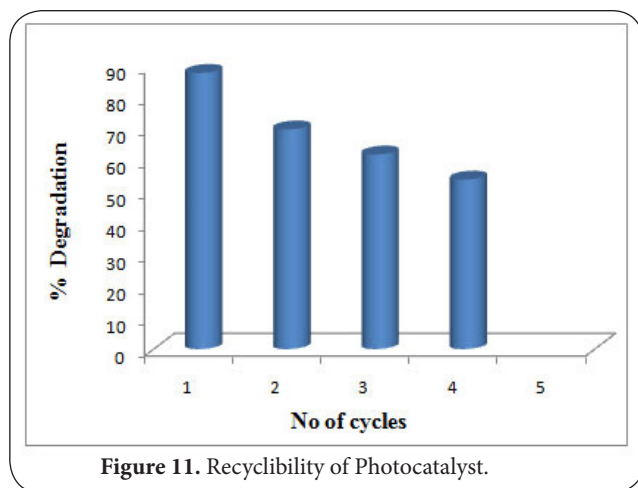


Figure 11. Recyclability of Photocatalyst.

catalyst and loss due to repeated acid wash.

Conclusion

The results of this study have shown that the degradation of different textile dyes was successfully carried out in laboratory scale photo reactor containing coated TiO₂ as photo catalyst. The experimental results showed that the rate of degradation depends on the chemical structure of different dyes as well as surface adsorption of dyes by TiO₂ which is directly proportional to the surface area and dispersion of the catalyst, the adsorption of light by the dye. The COD decreases slower than the discoloration of the solution. The use of TiO₂ coated on alginate could be a promising method as it can avoid the tedious final filtration of Titania in slurries and permit the photocatalyst recycling. Calcium alginate can be used as a green support for immobilizing TiO₂ nanoparticles and can be used for developing a new environment friendly immobilization system for large scale water treatment. Also the commercial potential of this technique as an economic means of treating dye house effluent is very high.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

First author contributed in conception, research design, data interpretation and manuscript draft. Second and third authors contributed to fulfill the experiments and

analyses, data interpretation and drafting the manuscript.

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References

- Robinson T, McMullan G, Marchant R and Nigam P: **Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative.** *Bioresour Technol* 2001, **77**:247-55. | [Article](#) | [PubMed](#)
- Mahmoud E K: **Chemically enhanced primary treatment of textile industrial effluents.** *Polish Journal of Environmental studies* 2009, **18**: 651-655.
- Kim S, Park C, Kim TH, Lee J and Kim SW: **COD reduction and decolorization of textile effluent using a combined process.** *J Biosci Bioeng* 2003, **95**:102-5. | [Article](#) | [PubMed](#)
- O'Neill C, Hawkes F R, Hawkes D L, Lourenco N D, Pinheiro H M and Wouter Delée: **Colour in textile effluents-sources, measurement, discharge consents and simulation: a review.** *J. Chem. Technol. Biotechnol* 1999, **74**:10009-10018. | [Article](#)
- Harikumar P S and Bindhya Mol K: **A synoptic study on the preparation of a liquid waste management plan for Kerala state, India.** *Environment and Natural Resources Research* 2012, **2**:74-83. | [Article](#)
- Gong R, Li M, Yang C, Sun Y and Chen J: **Removal of cationic dyes from aqueous solution by adsorption on peanut hull.** *J Hazard Mater* 2005, **121**:247-50. | [Article](#) | [PubMed](#)
- Dave R S and Patel A R: **Photochemical and photocatalytic of cypermethrin under UV radiation.** *Der pharma chemical* 2010, **2**:152-158. | [PDF](#)
- Iqbal MJ and Ashiq MN: **Adsorption of dyes from aqueous solutions on activated charcoal.** *J Hazard Mater* 2007, **139**:57-66. | [Article](#) | [PubMed](#)
- Kanan N and Sundaram M M: **Kinetics and mechanism of removal of methylene blue by adsorption on various carbons a comparative study.** *Dyes and pigment* 2001, **51**: 25-40. | [Article](#)
- Arami M, Limaee NY, Mahmoodi NM and Tabrizi NS: **Removal of dyes from colored textile wastewater by orange peel adsorbent: equilibrium and kinetic studies.** *J Colloid Interface Sci* 2005, **288**:371-6. | [Article](#) | [PubMed](#)
- Saad S A, Daud S, Kasim F H and Saleh M N: **Methylene blue removal from simulated wastewater by adsorption using treated oil palm empty fruit bunch.** 2007 : 293-296. | [PDF](#)
- Al-Momani F, Touraud E, Degorce-Dumas J, Roussy J and Thomas O: **Biodegradability enhancement of textile dyes and textile wastewater by UV photolysis.** *Journal of photochemistry and Photobiology A: Chemistry* 2002, **153**: 191-197. | [PDF](#)
- Behnajady MA and Modirshahla N: **Kinetic modeling on photooxidative degradation of C.I. Acid Orange 7 in a tubular continuous-flow photoreactor.** *Chemosphere* 2006, **62**:1543-8. | [Article](#) | [PubMed](#)

14. Khataee AR, Pons MN and Zahraa O: **Photocatalytic degradation of three azo dyes using immobilized TiO₂ nanoparticles on glass plates activated by UV light irradiation: influence of dye molecular structure.** *J Hazard Mater* 2009, **168**:451-7. | [Article](#) | [PubMed](#)
15. Gupta Shipra Mital AND Tripathi Manoj: **A review of TiO₂ nanoparticles.** *Chinese Science Bulletin* 2011, **56**: 1639-1657. | [Article](#)
16. Harikumar P S and Litty Joseph: **Kinetic and thermodynamics studies of as (III) adsorption onto iron nanoparticles entrapped ca-alginate beads.** *International Journal of Plant, Animal and Environmental Sciences* 2012, **2**:159-156.
17. Santos D T, Sarrouh B F, Rivaldia J D, Converti A and Silva S S: **Use of sugarcane bagasse as biomaterial for cell immobilization for xylitol production.** *J. Food Eng* 2008 **86**:542-548. | [Article](#)
18. Juliana A H, Paridah M T, Rahim S, Nor Azowa I and Anwar U M K: **Production of particleboard from kenaf (*Hibiscus cannabinus*L.) as function of particle geometry.** *Matter. Design* 2012, **34**: 406-411.
19. Harikumar P S, Litty Joseph and Manjusha C M: **Bio synthesis of silver nanoparticles and its application in microbial treatment of drinking water.** *Nano Science and Nano Technology* 2011, **5**:23-27.
20. Margaret E Lyn and DanYang Ying: **Drying model for calcium alginate beads.** *Ind. Eng. Chem.* 2010, **49**: 1986-1990. | [Article](#)
21. Cheng H, Ma J, Zhao Z and Qi L (1995) **Hydrothermal preparation of uniform nanosize rutile and anatase particles.** *Chem. Mater* 1995, **7**:663-671. | [Article](#)
22. Sakthivel S, Shankar MV, Palanichamy M, Arabindoo B, Bahnemann DW and Murugesan V: **Enhancement of photocatalytic activity by metal deposition: characterisation and photonic efficiency of Pt, Au and Pd deposited on TiO₂ catalyst.** *Water Res* 2004, **38**:3001-8. | [Article](#) | [PubMed](#)
23. Bouzaida I, Ferronato, Chovelon J M, Rammah M E and Hermann J M: **Photocatalytic degradation of the anthraquinonic dye, Acid Blue (AB25): a kinetic approach.** *J. Photochem. Photobiol. A: Chem.* 2004, **168**:23-30. | [Article](#)
24. Arslan I, Balcioglu I A and Bahnemann DW: **Heterogeneous photocatalytic treatment of simulated dyehouse effluents using novel TiO₂-photocatalysts.** *Applied Catalysis B-Environmental* 2000 **26**:193-206. | [Article](#)
25. Barka N, Qourzal S, Assabbane A, Nounah A and Ait-Ichou Y: **Factors influencing the photocatalytic degradation of Rhodamine B by TiO₂-coated non-woven paper.** *J. Photochem. Photobiol.A: Chem* 2008, **195**:346-351. | [Article](#)

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