Chapter VI

Heterogeneous Photocatalyst in Degradation of Textile Dyes
6.1 Introduction

Textiles are one among the basic needs of human being. They have been endeavouring to add colour to the world around us. Textile industry is one of the most important and rapidly developing industrial sectors. It is a significant contributor to many national economies, encompassing both small and large-scale operations worldwide. The textile industries therefore have great economic significance by virtue of its contribution to overall industrial output and employment generation. This sector has wide spectrum of industries ranging from small scale units that use traditional manufacturing process, to large integrated mills using modern machineries and equipment. The textile industry has been condemned as being one of the world’s worst offenders in terms of pollution because it requires a great amount of two components: Chemicals: Around 2,000 different chemicals are used in the textile industry, from dyes to transfer agents. Water: a finite resource that is quickly becoming scarce, and is used at every step of the process both to convey the chemicals used during that step and to wash them out before beginning the next step.

Textile industry is one of the leading consumers of water. It consumes about 3.2% of total consumption of water for various processes such as sizing, scouring, bleaching, dyeing, printing and other finishing processes. The traditional textile finishing industry consumes about 100 liters of water to process about 1 kg of textile material. The used water containing various constituents such as dyes, chemicals is directly released into the sources of water which gets contaminated and thus resulting into water pollution. New dyes are regularly developed for meeting the demands of new technology, new kinds of fabrics, detergents, advances in dyeing machineries, along with overcoming the serious environmental concerns posed by some existing dyes.

6.1.1 Classification of Textile Dyes

For thousands of years dyeing has been used by humans to decorate clothing, or fabrics for
other uses. The primary source of dye has been nature, with the dyes being extracted from animals or plants. In the last 150 years, man has produced artificial dyes to achieve a broader range of colors, and to render the dyes more stable to resist washing and general use. Different classes of dyes are used for different types of fiber and at different stages of the textile production process from loose fibers through yarn and cloth to make up garments. Approximately, 10,000 different dyes and pigments are used industrially, and over $7 \times 10^5$ tons of synthetic dyes are produced annually worldwide.

Dyes contain chromophores (delocalized electron systems with conjugated double bonds) and auxochromes (electron-withdrawing or electron-donating substituents that intensify the colour of the chromophore by altering the overall energy of the electron system). Usual chromophores are -C=C-, -C=N-, -C=O, -N=N-, -NO$_2$ and quinoid rings, usual auxochromes are -NH$_3$, -COOH, -SO$_3$H and –OH. The dye is generally applied in an aqueous solution, and requires a mordant to improve the fastness of the dye on the fiber. Based on chemical structure of chromophores, 20-30 different groups of dyes can be discerned. Textile dyestuffs can be grouped into 9 categories or classes:

Acid Dyes, Basic Dyes, Direct Dyes, Mordant Dyes, Vat Dyes, Reactive Dyes, Disperse Dyes, Azoic Dyes, Sulphur Dyes

6.1.2 Environmental Concerns and Pollution Problems

Day to day the textile dye segment is characterized by new dyes. New dyes are continuously being developed to meet the demands of new technology, new fabrics, advances in dyeing equipment, and to overcome the serious environmental concerns associated with some existing dyes. With the increased use of a wide variety of dyes, pollution by dye's wastewater is becoming increasingly alarming. Around 10-15% of all the dyes used in the industry are lost within waste water during synthesis and processing (Robinson 2001). Dye contaminated effluent, is one which
contains residual dye. Due to its complex chemical structure, dye is one of the most difficult constituents in textile waste water to treat (Mahmoud 2009). This waste represents a great hazard to human and environmental health due to the toxicity of these dyes. Azo dyes are the most toxic of the dye types. Due to their toxicity and recalcitrance, these dyes are hazardous to the environment and even when they are present in very low concentrations, can present serious carcinogenic effects (Brown and DeVito 1993).

Untreated effluents from textile industries are usually highly coloured and contain a considerable amount of contaminants and pollutants. Wastewater from textile industries pose a threat to the environment as large amount of chemically different dyes are used for various industrial applications such as textile dyeing and a significant proportion of these dyes enter the environment via wastewater. The presence of even very low concentrations of dyes in effluent is highly visible and degradation products of these textile dyes are often carcinogenic (Kim et al. 2003). Due to its complex chemical structure, dye is one of the most difficult constituents in textile wastewater to treat. Many dyes are visible in water at concentrations as low as 1mg/L. Textile-processing wastewaters, typically with dye content in the range 10-200mg/L (O'Neill et al. 1999) 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. While much research has been performed to develop effective treatment technologies for waste waters containing azo dyes, no single solution has been satisfactory for remediating the broad diversity of textile wastes. The majority of dyes pose a potential health hazard to all forms of life. These dyes may cause allergic responses, skin dermatoses, eczema, and may affect the liver, the lungs, the vasco-circulatory system, the immune system and the reproductive system of experimental animals as well as humans. The chemicals in the effluents are not only
poisonous to humans but also found toxic to aquatic life and they may result in food contamination. The presence of potentially toxic compounds in waste waters from textile dyeing industries has led to environmental research to identify methods that can effectively treat these waste waters.

6.1.3 Problems Related to Textile Industry

Effluents from the textile industry usually contain high concentrations of organic compounds and are characterized by strong colour as well as high COD values. Textile dyes have found to be toxic, genotoxic and mutagenic in various test systems.

6.1.3.1 Colour

Presence of colour in the waste water is one of the main problems in textile industry. Colours are easily visible to human eyes even at very low concentration. Hence, colour from textile wastes carries significant aesthetic importance. Most of the dyes are stable and has no effect of light or oxidizing agents. They are also not easily degradable by the conventional treatment methods. Removal of dyes from the effluent is a major problem in most of textile industries.

6.1.3.2 Dissolved Solids

Dissolved solids contained in the industry effluents are also a critical parameter. Use of common salt and glauber salt etc. in processes directly increase total dissolved solids (TDS) level in the effluent. TDS are difficult to be treated with conventional treatment systems. Disposal of high TDS bearing effluents can lead to increase in TDS of ground water and surface water. Dissolved solids in effluent may also be harmful to vegetation and restrict its use for agricultural purpose.

6.1.3.4 Toxic Metals

Waste water of textiles is not free from metal contents. There are mainly two sources of metals. Firstly, the metals may come as impurity with the chemicals used during processing such as caustic soda, sodium carbonate and salts. For instance, caustic soda may contain mercury if
produced using mercury cell processes. Secondly, the source of metal could be dye stuffs like metallised mordant dyes. The metal complex dyes are mostly based on chromium.

### 6.1.3.5 Residual Chlorine

The use of chlorine compounds in textile processing, residual chlorine is found in the waste stream. The waste water (if disposed without treatment) depletes dissolved oxygen in the receiving water body and as such aquatic life gets affected. Residual chlorine may also react with other compounds in the waste water stream to form toxic substances.

### 6.1.3.6 Others

Textile effluents are often contaminated with non-biodegradable organics termed as refractory materials. Detergents are typical example of such materials. The presence of these chemicals results in high chemical oxygen demand (COD) value of the effluent. Organic pollutants, which originate from organic compounds of dye stuffs, acids, sizing materials, enzymes, tallow etc. are also found in textile effluent. Such impurities are reflected in the analysis of bio-chemical oxygen demand (BOD) and COD. These pollutants are controlled by use of biological treatment processes. In many textile units, particularly engaged in synthetic processing, low BOD/COD ratio of effluent is observed which makes even biological treatment not a ready proposition. The waste water of cotton based textile units is usually alkaline, whereas synthetic and woolen fabric processing generates acidic effluent.

### 6.1.4 Conventional Effluent Treatment Methods

Continual dye improvement to develop shades that withstand harsh environmental conditions and to satisfy the ever-growing market has exacerbated the pollution problem by dye effluents. Colour is the first contaminant to be recognized in wastewater and has to be removed before discharging into water bodies or on land. The removal of color from wastewater is often more
important than the removal of the soluble colourless organic substances. Many methods have been reported for removing textile dyes from wastewater, among which are membrane filtration, coagulation/flocculation, precipitation, flotation, adsorption, ion exchange, ion pair extraction, ultrasonic, mineralization, electrolysis, advanced oxidation (chlorination, bleaching, ozonation, Fenton oxidation and photocatalytic oxidation) and chemical reduction. However, these approaches often involve complicated procedures (Cheima Fersi and Mahmoud Dhahbi 2008).

6.1.4.1 Adsorption

The adsorption process is used to remove colour and other soluble organic pollutants from effluent. The process also removes toxic chemicals such as pesticides, phenols, cyanides and organic dyes. Dissolved organics are adsorbed on surface, as waste water containing these is made to pass through adsorbent.

6.1.4.2 Ion Exchange

Ion exchange process is normally used for the removal of inorganic salts and some specific organic anionic components such as phenol. All salts are composed of a positive ion of a base and a negative ion of an acid. Ion exchange materials are capable of exchanging soluble ions and cations with electrolyte solutions. The process cannot be used for removal of non-ionic compounds.

6.1.4.3 Membrane Filtration

I) Reverse Osmosis

The process of reverse osmosis is based on the ability of certain specific polymeric membranes, usually cellulose acetate or nylon to pass pure water at fairly high rates and to reject salts. To achieve this, water or waste water stream is passed at high pressures through the membrane.

ii) Ultrafiltration

This process is similar to reverse osmosis. The difference between reverse osmosis and
ultrafiltration is primarily the retention properties of the membranes. Reverse osmosis membranes retain all solutes including salts, while ultrafiltration membranes retain only macro molecules and suspended solids.

iii) Nanofiltration

Nanofiltration can be positioned between reverse osmosis and ultrafiltration. Nanofiltration is essentially a lower pressure version membrane where the purity of permeate water less important. This process is used where the high salt rejection of reverse osmosis is not necessary. The nanofiltration is capable of removing hardness elements such as calcium or magnesium together with bacteria, viruses, and colour.

6.1.4.4 Electrochemical Process

The Electrochemical processes have found use in destruction of toxic and non-biodegradable organic matter by direct or indirect oxidation/reduction. A typical electrochemical treatment process consists of electrolytic cell, which uses electrical energy to affect a chemical change. The chemical processes occurring in such cells are oxidation and reduction, taking place at the electrode/electrolyte interface.

6.1.4.5 Ozonation

Ozone is one of the strongest oxidizers commercially available and popular for disinfection of potable water. Among the industrial applications, oxidation of organics and inorganics, deodorisation, and decolourisation are the main usages.

6.1.4.6 Advanced Oxidation Processes (AOPS)

The aim of AOP is the generation of free hydroxyl radical (OH\(^\cdot\)), a highly reactive, non-selective oxidizing agent, which can destroy even the recalcitrant pollutants. The generation of hydroxyl is highly accelerated by combining ozone (O\(_3\)), hydrogen peroxide (H\(_2\)O\(_2\)), titanium
dioxide (TiO$_2$), heterogeneous photo-catalysis, UV radiation or high electron beam radiation.

6.1.4.7 Coagulation / Flocculation

Coagulation/flocculation is one of the most effective chemical treatment methods for dye removal from industrial wastewaters. Both suspended and colloidal particles don’t settle under gravity so they can’t be removed by physical processes. Coagulation process neutralizes the charge present on the particles surfaces with the help of coagulants whereas flocculation makes them to come close to each other to make flocs by slow agitation. Settling follows coagulation and flocculation to remove resultant flocs from the wastewater.

6.1.4.8 Photocatalytic Degradation

This is an advanced method to decolorize a wide range of dyes depending upon their molecular structure. In this process, photoactive catalyst illuminates with UV light, generates highly reactive radical, which can decompose organic compounds.

6.1.5 Drawbacks of Conventional Treatment Methods

These methods do not generally degrade the pollutant; they cause an accumulation of the dye as sludge creating a disposal problem (Poonam Dayaram and Debjani Dasgupta 2008). The use of one individual process may often not be sufficient to achieve complete decolorization. Dye removal strategies consist therefore mostly of a combination of different techniques. However, these processes just transfer these contaminants to a different matrix, rather than completely eliminating these chemicals. Therefore, attention has to be focused on techniques that can lead to the complete destruction of the dye molecules. Thus, there is a need for developing treatment methods that are more effective in eliminating dyes from waste stream at its source. This led to the study of other effective methods. Recent studies have demonstrated that photocatalysis can be used to destroy dye compounds using semiconductor photocatalysts under light irradiation (Neppolian et al.
Removal of dyes from the effluent is a major problem in most of textile industries. For this reason, photocatalysis using titanium dioxide as a photocatalyst has been extensively studied as an alternative

6.1.6 Role of Photocatalyst

Titanium dioxide (TiO$_2$) has emerged as an excellent photocatalyst material for environmental purification. Photocatalytic activity (PCA) is the ability of a material to create an electron hole pair as a result of exposure to ultraviolet radiation. The resulting free-radicals are very efficient oxidizers of organic matter. Photocatalytic activity in TiO$_2$ has been extensively studied because of its potential use in sterilization, sanitation, and remediation applications. The ability to control PCA is important in many other applications utilizing TiO$_2$ including paint pigments and cosmetics that require low PCA.

Interest in this photocatalytic process stems mainly from its low cost, combined with the nontoxicity, insolubility, stability, high photoactivity of the catalyst (TiO$_2$). A further important advantage is the fact that the process can be powered by natural sunlight, thus reducing significantly the electrical power requirements and operating costs. 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

6.1.7 Titanium Dioxide Nanoparticles

TiO$_2$ nanoparticles have broad and potential application field in light catalysis, air purification, ultraviolet absorbent, efficient light-sensitive catalyst, suntan cream, solar cells, wastewater treatment, fine ceramics and air-sensitive sensing elements because 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.

When used with light, nano-TiO$_2$ can photocatalytically oxidize organic compounds. TiO$_2$ has been used widely for the preparation of different types of nanomaterials, including nanoparticles, nanorods, nanowires, nanotubes, and mesoporous and nanoporous TiO$_2$ containing materials. Regardless of scale, TiO$_2$ maintains its photocatalytic abilities.

When being integrated with photocatalytic degradation using TiO$_2$ nanophotocatalyst, the applications of polymeric nanoparticles for water treatment may provide a sustainable treatment approach with potentially low energy consumption and CO$_2$ emission, thus contributing to a green environment (Rassaei et al. 2008).

Anatase nanoparticles are effective in catalysis and photocatalysis applications. It is also considered as the best candidate for photovoltaic and electrochromic devices. The particles size has also an important impact on the surface properties When aqueous TiO$_2$ suspension is irradiated with light energy greater than the band gap energy of the pigment ($h\nu > E_g = 3.2 \text{ eV}; < 390 \text{ nm}$), conduction band electrons ($e^-$) and valence band holes ($h^+$) are formed. The photogenerated electrons react with adsorbed molecular O$_2$, reducing it to superoxide radical anion O$_2^-$, and the photogenerated holes can oxidize either the organic molecules directly, or can oxidise OH$^-$ ions and water molecules adsorbed on the TiO$_2$ surface to OH radicals. These will act as strong oxidizing agents that can easily attack any organic molecules adsorbed on, or located close to, the surface of the catalyst, thus leading to their complete degradation into small inorganic species (eq. 1-5)
Mechanism of the TiO\textsubscript{2} - catalysed UV oxidative degradation of organic species.

Among the many processes proposed and being developed for the destruction of organic contaminants, photocatalytic process involving TiO\textsubscript{2} particles under UV illumination has shown to be potentially advantageous and is useful in the treatment of wastewater pollutants (Gogate and Pandit 2004). The TiO\textsubscript{2} catalyst could transform organic pollutants into biodegradable compounds of low molecular weight.

The advantage of photocatalysis in water purification is the complete mineralization of organics caused by the photogeneration of OH radicals originating from water via the OH groups of the TiO\textsubscript{2} surface. TiO\textsubscript{2} is a commonly used photo-catalyst because of its stability in UV light and water. TiO\textsubscript{2} can function as both an oxidative and reductive catalyst. TiO\textsubscript{2} is considered very close to an ideal semiconductor for photocatalysis because of its high stability, low cost and safety towards both human and the environment.

UV irradiation is yet another high energy source for degradation of organics present in the effluents. Photocatalyst coupled with UV lights can oxidize organic pollutants into nontoxic materials, such as CO\textsubscript{2} and water and can disinfect certain bacteria. This technology is very effective at removing further hazardous organic compounds and at killing a variety of bacteria and some viruses in the secondary wastewater treatment. The combination of UV irradiation with photocatalysts such as TiO\textsubscript{2} is one of such methods which have attracted considerable attention in
recent years, due to its effectiveness in mineralization (i.e. conversion to inorganic species) of organic compounds.

6.2 Materials and method

6.2.1 Synthesis of TiO$_2$ Nanoparticles

Chemical precipitation method was adopted to synthesize TiO$_2$ nanoparticles. TiCl$_3$ (MERCK 15%) solution in HCl (10–15%) was introduced under vigorous stirring in deionized water ([Ti$^{3+}$] = 0.15 mol/L). 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°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°C for 12 hour and calcined in a muffle furnace at 450°C for 3 hour.

6.2.2 Preparation of Photocatalyst

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°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. These beads were used for further photo catalytic studies.

6.2.3 Characterization of Nanoparticles

The characterization of nanoparticles was done using UV- visible spectrophotometer and SEM/EDS.
6.2.3.1 UV-Visible Spectrophotometer

The characterization of nanoparticles was done using UV-visible spectrophotometer Evolution 201 UV-Visible Spectrophotometer (Thermo Scientific, USA) was used for the characterisation 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.

6.2.3.2 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 2.00µm with an accelerating voltage of 15.0kV.

6.2.4 The 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 photo catalytic
reactor was fixed as vertical hung. The experimental set up of the photocatalytic reactor is as shown in Fig 6.1. The photocatalytic reactor is vertically hunged 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.

Fig. 6.1 Experimental set up

6.2.5 Preparation of Synthetic Dye Solutions

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.

6.2.5.1 Methyl Orange

Standard solution of 1M Methyl Orange was prepared by weighing out exactly 81.8 gm in a 250 ml Standard flask. Then by serial dilution 0.001M of Methyl Orange solution was prepared. Characteristics of Methyl Orange dye is illustrated in Table 6.1.
Table 6.1: Characteristics of Methyl Orange

<table>
<thead>
<tr>
<th>Chemical structure</th>
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<tbody>
<tr>
<td>Type of dye</td>
<td>Azo</td>
</tr>
<tr>
<td>Molecular formula</td>
<td>C₁₄H₁₄N₃NaO₃S</td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
<td>327.33 g/mol</td>
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<tr>
<td>Maximum absorption wavelength</td>
<td>464 nm</td>
</tr>
</tbody>
</table>

6.2.5.2 Methyl Red

Standard solution of 1M Methyl Red was prepared by weighing out exactly 67.3 gm in a 250 ml Standard flask. Then by serial dilution 0.001M of Methyl Red solution was prepared. Characteristics of Methyl Red dye is illustrated in Table 6.2.

Table 6.2: Characteristics of Methyl Red

<table>
<thead>
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<th>Chemical structure</th>
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</tr>
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<tbody>
<tr>
<td>Type of dye</td>
<td>Azo</td>
</tr>
<tr>
<td>Molecular formula</td>
<td>C₁₅H₁₅N₃O₂</td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
<td>269.3</td>
</tr>
<tr>
<td>Maximum absorption wavelength</td>
<td>498 nm</td>
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6.2.5.3 Alizarin Red S

Standard solution of 1M Alizarin Red S was prepared by weighing out exactly 85.6 gm in a 250 ml Standard flask. Then by serial dilution 0.001M of Alizarin Red S solution was prepared. Characteristics of Alizarin Red S dye is illustrated in Table 6.3.

**Table 6.3: Characteristics of Alizarin Red S**

<table>
<thead>
<tr>
<th>Chemical structure</th>
<th><img src="image" alt="Chemical structure of Alizarin Red S" /></th>
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<tr>
<td>Type of dye</td>
<td>Anthraquinone</td>
</tr>
<tr>
<td>Molecular formula</td>
<td>C_{14}H_{8}O_{4}</td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
<td>240.21</td>
</tr>
<tr>
<td>Maximum absorption wavelength</td>
<td>425 nm</td>
</tr>
</tbody>
</table>

6.2.5.4 Effluent

Real time effluents from the field were collected from two local dyeing industries. 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.

6.2.6 Photo catalytic Studies

The photo catalytic 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. The 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.

The degradation of the dyes were monitored for various parameters like

- pH
- Time
- Effect of ions

6.2.7 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.

6.2.7.1 Absorbance Measurement - UV Spectrophotometer

The absorbance of the prepared dye solutions and the effluent collected before and after degradation were measured 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 $\lambda$ 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 disappearance was calculated using the following:

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

\[(\text{Absorbance})_0 \text{ is the absorbance before irradiation and} \]
\[(\text{Absorbance})_t \text{ is the absorbance at time } t.\]

6.2.7.2 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 degradation of the different dye solutions were calculated by:

\[
\text{Photodegradation efficiency} = \frac{(\text{COD})_0 - (\text{COD})_t}{(\text{COD})_0} \times 100
\]

Where

\(\text{COD}_0\) is the absorbance of the initial dye solution
\(\text{COD}\) is the absorbance of the treated solution

6.2.7.3 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. The frequencies at which there are absorptions of IR radiation ("peaks" or "signals") can be correlated directly to bonds within the compound. 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.

6.2.8 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.

6.2.9 Physico – chemical characteristics of real effluent

6.2.9.1 pH

The pH of a solution refers to its hydrogen ion activity and is expressed as the logarithm of the reciprocal of the hydrogen ion activity in moles per liter at a given temperature. pH values from 0 to 7 are diminishingly acidic, 7 to 14 increasingly alkaline and 7 is neutral. pH of the sample was analyzed using portable pH meter.

The pH of a solution is the negative common logarithm of hydrogen ion activity

\[
pH = -\log_{10}(H^+) \]

pH of the samples were measured using Systronics digital pH meter.

6.2.9.2 Electrical Conductivity

Electrical conductivity is a measure of water capacity to convey electric current. Electrical conductivity of water is directly proportional to its dissolved mineral matter content. It is the overall concentration of ions presents in water that influences conductivity the most. Conductivity becomes an indicator of dissolved ions present in any water sample. EC was measured using ELICO conductivity meter. The conductance is directly measured from the conductivity meter. The cell constant is taken as unity.

6.2.9.3 Total Dissolved Solids

In natural waters, the dissolved solids consist mainly of bicarbonates, carbonates, sulphates, chlorides, nitrates and possibly phosphates of calcium, magnesium, sodium and potassium with traces
of iron, manganese and other substances. The amount of dissolved solids present in water is a consideration for its suitability for domestic use. In general, water with total solids content less than 500 mg/L is most desirable.

6.2.9.4 Chemical Oxygen Demand (COD)

Chemical oxygen demand (COD) is a measure of the oxygen equivalent to that portion of organic matter present in the waste water sample that is susceptible to oxidation by potassium dichromate. This is an important and quickly measured parameter for stream, sewage and industrial waste samples to determine their pollution strength. When the waste water sample is refluxed with a known excess of potassium dichromate in a 50% H₂SO₄ solution in presence of AgSO₄ (as catalyst) and H₂SO₄ (to eliminate interference due to chloride), the organic matter of the sample is oxidized to water, CO₂ and ammonia. The excess of dichromate remaining unreacted in the solution is titrated with a standard solution of ferrous ammonium sulphate.

**Procedure:** To 25ml of the sample taken in a refluxing flask 12.5 ml of 0.25N (0.0417M) potassium dichromate solution and 37.5ml of 0.25 N sulphuric acid was added and refluxed for two hours. After this process the refluxing flask with the contents were cooled and to it 5 drops of ferroin indicator were added and titrated with ferrous ammonium sulphate. The colour change from bluish green to reddish brown was noted. By performing the same steps distilled water was also refluxed and titrated, and this was considered as the blank.

\[
COD = \frac{(A - B) \times M \times 8000}{\text{volume of sample}}
\]

where

\[
A = \text{FAS used for blank, ml}
\]

\[
B = \text{FAS used for sample, ml}
\]

\[
M = \text{Molarity of FAS}
\]
6.2.9.5 Chloride:

Chlorine in the form of chloride ion is one of the major inorganic anions in the water and waste water. Chloride ion concentration is measured by Mohr method which uses chromate ions as an indicator in the titration of chloride ions with a silver nitrate standard solution. After all the chloride has been precipitated as white silver chloride, the first excess of titrant results in the formation of a silver chromate precipitate, which signals the end point.

**Procedure:** To 25 ml of the sample, potassium chromate indicator was added and titrated with Silver nitrate solution.

6.2.9.6 Sulphate

Sulphates are discharged in to the aquatic environment in the wastes from many different industries. Atmospheric SO$_2$, formed by the combustion of fossil fuels and emitted by the metallurgical roasting processes, may also be contribute to the sulphate content of surface water. Sulphur trioxide (SO$_3$) produced by the photolytic or catalytic oxidation of sulphur dioxide combines with water vapour to form sulfuric acid, which is precipitated as “acid rain” or snow. Sulphates salts are mostly soluble in water and import hardness. Waters with about 500mg/L sulphates have a bitter taste and those with 1000mg/L or more may cause disorders.

**Procedure:** Take 25 ml sample in a 100ml conical flask. Add 1.25 ml conditioning reagent and mix. Add a pinch of BaCl$_2$ crystals and shake well for 1 minute. Immediately after the stirring period has ended, pour some of the solution to the absorption cell of the photometer and measure the turbidity at 30 sec intervals for 4 minutes because max turbidity occurs in 2 minutes and readings remain constant for 3-10 minutes. Use 0-40ppm standard sulphate solutions for calibrating the instrument.

6.2.10 Regeneration 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 regenerated 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 regeneration capacity.

6.3 RESULTS AND DISCUSSION

6.3.1 Preparation of Photocatalyst

Chemical precipitation method was adopted to synthesize TiO$_2$ 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 TiO$_2$ could be formed (Cheng et al. 1995).

6.3.2 Characterisation

The formation of nanoscale TiO$_2$ at pH 5 was confirmed by UV and EDAX examination of the product.

6.3 2.1 UV-visible Spectrum

![UV-Visible Spectra](image)

Fig 6.2: UV-Visible spectra of the solution with TiO$_2$ nano particles
The room temperature absorption spectrum of the TiO$_2$ nanoparticles is shown in Fig. 5.1. TiO$_2$ exhibited larger absorption in the visible light region with an onset absorption band at 280–400 nm. The absorption spectrum of TiO$_2$ 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 Ti$^{4+}$ cations) (Sakthivel et al. 2004). The obtained result showed a strong, but broad peak located at a range 290–400 nm (Fig: 6.2).

6.3.2.2 Scanning Electron Micrograph (SEM)

SEM study was carried out to confirm the size of the particles, and its distribution pattern in polymeric matrix. A representative SEM image in Fig. 6.3 shows that most of the particles are well distributed. The particle size of the samples estimated from the SEM micrographs was below 50 nm.

![SEM image of 2% TiO$_2$ nanoparticles entrapped Alginate beads at different magnification](image)

6.3.2.3 EDX Spectrum

The quantitative compositional analysis of the TiO$_2$ nanoparticle entrapped beads was analyzed using energy dispersive x-ray (EDAX) spectroscopy measurements. The spectra confirm
The presence of TiO$_2$ in the structure, as shown in Fig 6.4. 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% O$_2$, 14.82% Ca, 10.18% Na and 48.83% Cl$_2$. EDX analysis showed no significant levels of impurities which could have originated from the process.

![Fig. 6.4: EDX spectrum of TiO$_2$ nano particles entrapped Calcium Alginate beads](image)

6.3.3 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 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.

6.3.3.1 Azo dyes

Azo dyes represent the largest class of organic colorants listed in the Color Index (60-70% of
the total) and their relative share among reactive, acid and direct dyes is even higher, it can be expected that they make up the vast majority of the dyes discharged by textile-processing industries. So methyl orange was taken as a model dye to study the photodegradation of azo dyes.

6.3.3.1(a) Absorbance Measurements

Fig 6.5 displays the absorption spectra of Methyl Orange degradation with time. The maximum UV-Vis absorption of Methyl Orange is found to be at a wavelength of 462 nm. The absorption peak of the spectra rapidly decreased with increased time and almost disappeared for 180 min light irradiation. It indicates that the chromophores responsible for characteristic colour of the Methyl Orange were broken down. The values of maximum absorption and the calculated decolouration efficiency is shown in Table 6.4. Fig 6.6 displays the absorption spectra of Methyl Red with treatment time. The maximum UV-vis absorption of Methyl Red is found to be at a wavelength of 495 nm. The absorbance value was not much affected by the photocatalytic activity. The efficiency reached only 26.5% within 3 hours. So the photocatalytic treatment was dropped for methyl red and further studies were not carried out. The apparatus was found to be not much effective in case of Methyl Red. Liquor dying was mostly used in the case of Methyl Red. This may be the reason of low efficiency.
Fig. 6.5: Absorption Spectra of Methyl Orange Degradation

Fig. 6.6: Effect of contact time on decolouration efficiency of Methyl Red

Fig 6.7 shows the trend of gradual decomposition of the azo dyes which was monitored by measuring the absorbance at regular intervals. It was noticed that among these 2 dyes, Methyl
orange, suffers degradation with the higher rate than the others. The efficiency reached only around 25.5% after 3 hours in the case of methyl red. 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 TiO$_2$ catalyst in dye degradation. The apparatus was found to be not much effective in case of liquor dying. Further studies were not carried out in the case of such dyes.

Table 6.4: Absorbance and decolouration efficiency of Methyl Orange and methyl Red

<table>
<thead>
<tr>
<th>Time</th>
<th>Absorbance</th>
<th>Decolouration Efficiency(%)</th>
<th>Methyl Orange</th>
<th>Methyl Red</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>2.66</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>15 min</td>
<td>2.49</td>
<td>6.39</td>
<td>9.22</td>
<td></td>
</tr>
<tr>
<td>30 min</td>
<td>2.31</td>
<td>13.16</td>
<td>17.25</td>
<td></td>
</tr>
<tr>
<td>60 min</td>
<td>1.53</td>
<td>42.48</td>
<td>17.37</td>
<td></td>
</tr>
<tr>
<td>120 min</td>
<td>1.12</td>
<td>57.89</td>
<td>20.19</td>
<td></td>
</tr>
<tr>
<td>180 min</td>
<td>-</td>
<td>100</td>
<td>26.50</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 6.7: Effect of Treatment Time on Decolouration Efficiency of Methyl Orange
6.3.3.1 (b) COD Removal efficiency

COD values of the initial Methyl Orange solution and the final solution after treatment is presented in Table 6.5. The performance of 75.65% for COD removal was reached within 3 hours of photocatalytic treatment. Fig. 5.6 shows the photodegradation efficiency with treatment time.

Table 6.5: COD values of Methyl Orange Solution Before and After Treatment

<table>
<thead>
<tr>
<th>Time</th>
<th>COD</th>
<th>Degradation Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>1544</td>
<td>-</td>
</tr>
<tr>
<td>15 min</td>
<td>1200</td>
<td>22.28</td>
</tr>
<tr>
<td>30 min</td>
<td>760</td>
<td>50.78</td>
</tr>
<tr>
<td>60 min</td>
<td>520</td>
<td>66.32</td>
</tr>
<tr>
<td>120 min</td>
<td>432</td>
<td>72.02</td>
</tr>
<tr>
<td>180 min</td>
<td>376</td>
<td>75.65</td>
</tr>
</tbody>
</table>

Fig. 6.8: Kinetics of COD removal of Methyl Orange
6.3.3.1(c) FTIR Analysis

Fig. 6.9(a): FTIR Spectra of Initial Solution of Methyl Orange

Fig. 6.9(b): FTIR Spectra of Methyl Orange after 180 min Treatment
The FTIR spectra of control Methyl orange Fig. 6.9(a), displays peak at 2,924.06 cm\(^{-1}\) for asymmetric CH\(_3\) stretching vibrations; peaks at 1,519.78 and 1,421.71 cm\(^{-1}\) for the 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 Fig. 6.9(b) 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.

6.3.3.2 Anthraquinone dyes

Anthraquinone dyes are the second largest class (~15%), followed by triarylmethanes (~3%) and phthalocyanines (~2%) of the entries in the Color Index. Alizarin belongs to Anthraquinone dyes. The efficiency of photoreactor in treatment of Anthraquinone dye was studied by using Alizarin Red S.

6.3.3.2.(a) Absorbance Measurements

Fig 6.10 displays the absorption spectra of Alizarin degradation with time. The maximum UV-vis absorption of Alizarin is found to be at a wavelength of 445nm. The \(\lambda_{\text{max}}\) was found to be constant during photodegradation process. Only the intensity of absorption decreased which is an indication of the degradation of the dyes. So it was possible to measure the absorbance at 445nm each time. The absorption peak of the spectra rapidly decreased with increased time and almost disappeared for 300 min light irradiation. It indicates that the chromophores responsible for
characteristic colour of the Alizarin were broken down. The maximum absorption value and calculated degradation efficiency is as shown in Table 6.6.

![Absorption spectra of Alizarin Degradation](image)

**Fig 6.10: Absorption spectra of Alizarin Degradation**

**Table 6.6: Absorbance and Decolourisation efficiency of Alizarin Red S**

<table>
<thead>
<tr>
<th>Time</th>
<th>Absorbance</th>
<th>Decolourisation Efficiency(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>2.985</td>
<td>-</td>
</tr>
<tr>
<td>15 min</td>
<td>2.233</td>
<td>25.19</td>
</tr>
<tr>
<td>30 min</td>
<td>1.917</td>
<td>35.78</td>
</tr>
<tr>
<td>60 min</td>
<td>1.138</td>
<td>61.88</td>
</tr>
<tr>
<td>180 min</td>
<td>0.597</td>
<td>80.00</td>
</tr>
<tr>
<td>300 min</td>
<td>-</td>
<td>100</td>
</tr>
</tbody>
</table>
Fig. 6.11: Effect of Treatment Time on Decolouration Efficiency of Alizarin Red S

Fig 6.11 represents the decolouration efficiency of Alizarin Red S with treatment time and it shows that the performance of 100% for colour removal was reached within 5 hours.

6.3.3.2.(b) COD Removal Efficiency

COD values of the initial Alizarin solution and the final solution after treatment are presented in table 6.7. An efficiency of 85.3% for COD removal was reached within 5 hours of photocatalytic treatment as indicated in Fig 6.12

Table 6.7: COD values of Alizarin solution before and after treatment

<table>
<thead>
<tr>
<th>Time</th>
<th>COD</th>
<th>Degradation Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>1200</td>
<td>-</td>
</tr>
<tr>
<td>30 min</td>
<td>800</td>
<td>33.33</td>
</tr>
<tr>
<td>60 min</td>
<td>536</td>
<td>55.33</td>
</tr>
<tr>
<td>180 min</td>
<td>360</td>
<td>70.00</td>
</tr>
<tr>
<td>300 min</td>
<td>176</td>
<td>85.33</td>
</tr>
</tbody>
</table>
Fig. 6.12: Kinetics of COD removal of Alizarin Red S

6.3.3.2.(c) FTIR Spectra

The FTIR spectra of Alizarin Fig. 6.13(a), 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 Fig. 6.13(a), 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 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.
Fig. 6.13(a): FTIR Spectra of initial solution of Alizarin Red

Fig. 6.13 (b): FTIR Spectra of final solution of Alizarin Red S after 360 min treatment
6.3.3.3. Reactive Dyes

Reactive dyes are known to form a covalent bond with the fibre in the dyeing process. However, unfixed dye reacts with water to form hydrolyzed or oxo-dye intermediate that has lost its bonding capacity and thus cannot be re-used. Therefore dye recovery is not an option with reactive dyes and the treatment process must lead to final destruction or disposal of these contaminants. In order to study the photo degradation of reactive dye real effluent consisting of a mixture of three reactive dye was used

6.3.3.3. (a) Characteristics of Textile Effluent before and after treatment

The characteristics of the textile effluent before and after photocatalytic treatment with TiO\(_2\) nanoparticles are as shown in Table 6.8.

Table 6.8: Characteristics of textile effluent before and after treatment

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Before Treatment</th>
<th>After Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>10.07</td>
<td>6.34</td>
</tr>
<tr>
<td>TDS, mg/L</td>
<td>5100</td>
<td>2530</td>
</tr>
<tr>
<td>EC, µs/cm</td>
<td>7150</td>
<td>3560</td>
</tr>
<tr>
<td>Chloride, mg/L</td>
<td>14837</td>
<td>300.75</td>
</tr>
<tr>
<td>Sulphate, mg/L</td>
<td>1025</td>
<td>325.0</td>
</tr>
<tr>
<td>COD, mg/L</td>
<td>2720</td>
<td>448</td>
</tr>
</tbody>
</table>

6.3.3.3. (b) Absorption Spectrum

Fig. 6.14 displays the absorption spectra of the textile effluent degradation which is a mixture of reactive dyes with time. The maximum UV-vis absorption of the reactive dyes is found to be at a wavelength of 422 nm. The absorption peak of the spectra rapidly decreased with increased time and
almost disappeared for 360 min light irradiation. It indicates that the chromophores responsible for characteristic colour of the reactive dyes were broken down. The maximum absorption value and calculated decolouration efficiency is as shown in Table 6.9

![Absorption Spectra of Textile Effluent](image)

**Fig. 6.14: Absorption Spectra of Textile Effluent**

**Table 6.9: Absorbance and decolouration efficiency of the textile effluent**

<table>
<thead>
<tr>
<th>Time</th>
<th>Absorbance</th>
<th>Photodecolouration Efficiency(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.797</td>
<td>-</td>
</tr>
<tr>
<td>15 min</td>
<td>0.658</td>
<td>17.44</td>
</tr>
<tr>
<td>30 min</td>
<td>0.543</td>
<td>31.87</td>
</tr>
<tr>
<td>60 min</td>
<td>0.460</td>
<td>42.28</td>
</tr>
<tr>
<td>120 min</td>
<td>0.331</td>
<td>58.47</td>
</tr>
<tr>
<td>180 min</td>
<td>0.253</td>
<td>68.26</td>
</tr>
<tr>
<td>240</td>
<td>0.165</td>
<td>79.29</td>
</tr>
<tr>
<td>300</td>
<td>0.049</td>
<td>93.85</td>
</tr>
<tr>
<td>360 min</td>
<td>-</td>
<td>100</td>
</tr>
</tbody>
</table>
From **Fig 6.15** representing the decolourisation efficiency of the reactive dye with time, it can be concluded that the performance of 100% for colour removal was reached within 6 hours of contact time.

**6.3.3.3.(c) COD Removal Efficiency**

COD values of the initial textile effluent solution and the final solution after treatment are presented in Table6.10. The performance of 83.53% for COD removal was reached within 5 hours of photocatalytic treatment (**Fig.6.16**).
Table 6.10: COD Values of the Textile Effluent Solution Before and After Treatment

<table>
<thead>
<tr>
<th>Time</th>
<th>COD</th>
<th>Degradation Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Solution</td>
<td>2720</td>
<td>-</td>
</tr>
<tr>
<td>30 min</td>
<td>2368</td>
<td>12.94</td>
</tr>
<tr>
<td>60 min</td>
<td>1928</td>
<td>29.12</td>
</tr>
<tr>
<td>120 min</td>
<td>1544</td>
<td>43.24</td>
</tr>
<tr>
<td>180 min</td>
<td>984</td>
<td>63.82</td>
</tr>
<tr>
<td>240 min</td>
<td>712</td>
<td>73.82</td>
</tr>
<tr>
<td>300 min</td>
<td>526</td>
<td>80.66</td>
</tr>
<tr>
<td>360 min</td>
<td>448</td>
<td>83.53</td>
</tr>
</tbody>
</table>

Fig. 6.16: Kinetics of COD removal at Various Time Intervals
6.3.3.3.(d) FTIR Spectra

Fig. 6.17(a): FTIR Spectra of initial solution of the textile effluent

Fig. 6.17(b): FTIR Spectra of final solution of the textile effluent after 360 min treatment
The FTIR spectrum of the degradation products formed by photocatalytic degradation (Fig. 6.17(b)) had displayed entirely new peaks compared to the raw effluent (Fig. 6.17.a), 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.

6.3.4 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 Fig 6.18. The absorbance values showed that the photodecolouration efficiency of methyl orange decreased in the order of pH 3 > pH 5 > pH 7 > pH 9 > pH 11. Such a result can be better understood by taking 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 (Bouzaida et al. 2004)

$$\text{TiOH}^+ + \text{OH}^- \Leftrightarrow \text{H}_2\text{O} + \text{TiO}^-$$

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

$$\text{TiOH} + \text{H}^+ \Leftrightarrow \text{TiOH}_2^+$$

From the Fig 6.18, 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\textsubscript{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\textsubscript{2} surface when increasing the solution pH.

![Graph of pH vs. Decolouration Efficiency]

6.18 Effect of pH on Decolouration Efficiency

6.3.5 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 6.11. The values in the table shows that the presence of Cl\textsuperscript{−}, SO\textsubscript{4}\textsuperscript{2−} and NO\textsubscript{3}− anions leads to an increase of the effectiveness of the photo catalytic degradation and the presence of HPO\textsubscript{4}\textsuperscript{2−} anion decreases the photocatalytic efficiency. This is because in the case of chloride ions the formation of Cl\textsuperscript{−} radical by the reaction of photo produced OH\textsuperscript{−} with Cl\textsuperscript{−} oxidizes pollutants results in increase in efficiency of degradation (Arslan et al.2000). Similarly the SO\textsubscript{4}\textsuperscript{2−} ions adsorbed in the surface of TiO\textsubscript{2} react with photo-induced holes (h\textsuperscript{+}) to form sulphate radical anion (\textsuperscript{•}SO\textsubscript{4}) which is a strong oxidant (Barka et al.2008). The NO\textsubscript{3}− ions, weakly adsorbed on the surface of TiO\textsubscript{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 HPO₄²⁻ ions which increase the pH of the solution and consequently decrease the photo catalytic degradation.

Table 6.11 Effects of ions on the Photo degradation efficiency

<table>
<thead>
<tr>
<th>Dyes</th>
<th>Methyl Orange</th>
<th>Alizarin Red S</th>
<th>Methyl Orange</th>
<th>Alizarin Red S</th>
<th>Methyl Orange</th>
<th>Alizarin Red S</th>
<th>Methyl Orange</th>
<th>Alizarin Red S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride</td>
<td>24.06</td>
<td>42.35</td>
<td>53.01</td>
<td>69.15</td>
<td>58.65</td>
<td>74.51</td>
<td>72.93</td>
<td>88.17</td>
</tr>
<tr>
<td>Sulphate</td>
<td>20.30</td>
<td>59.46</td>
<td>48.50</td>
<td>85.83</td>
<td>55.64</td>
<td>89.88</td>
<td>71.80</td>
<td>97.19</td>
</tr>
<tr>
<td>Nitrate</td>
<td>25.56</td>
<td>48.38</td>
<td>53.76</td>
<td>75.14</td>
<td>60.53</td>
<td>79.10</td>
<td>74.43</td>
<td>91.56</td>
</tr>
<tr>
<td>Phosphate</td>
<td>10.56</td>
<td>30.33</td>
<td>36.47</td>
<td>48.29</td>
<td>36.59</td>
<td>56.45</td>
<td>59.99</td>
<td>71.52</td>
</tr>
<tr>
<td>Control</td>
<td>13.16</td>
<td>35.78</td>
<td>42.48</td>
<td>61.88</td>
<td>49.25</td>
<td>68.78</td>
<td>57.89</td>
<td>80.00</td>
</tr>
</tbody>
</table>

6.3.6 Regeneration of Photocatalyst

Photocatalyst can be regeneration effectively which makes the process cost effective. For this reason, the catalyst was regenerate four times as shown in Fig.6.19. After the optimized conditions for the degradation of effluent was determined, the catalyst was recovered by giving acid wash and again used to study its regeneration capacity. The process was repeated until reasonable COD reduction upto 54% was achieved. The obtained results showed that the efficiency decreases from 88 to 54%. This is likely due to the fouling of the catalyst and loss due to repeated acid wash.
6.4 Summary

Laboratory scale photocatalytic reactor was fabricated using immobilized TiO$_2$ nanoparticles, prepared by chemical precipitation. The photocatalytic degradation of azo dyes, anthraquinone dyes and textile effluent using this photocatalytic reactor was achieved. TiO$_2$ nanoparticles have a good capacity to decolourise and degrade textile industry effluent in an effective way. The observations of these investigations clearly demonstrate the importance of choosing the optimum degradation parameters to obtain a high degradation rate, which is essential for any practical application of photocatalytic oxidation process. Time dependent study showed that the photocatalytic activity of particles increases with increasing treatment time. Upto 100% decolouration was obtained by TiO$_2$ nanoparticles and this can be successfully used for breaking down many constituents of the textile effluent thus resulting in considerable reduction of COD. The photodegradation efficiency was affected by pH variations and presence of ions like chloride, nitrate and sulphate. The results of the study appear to be quite promising in the sense that they demonstrate the capacity of immobilized TiO$_2$ nanoparticles in photocatalytic degradation of dyes, but in the case of liquor dyes it is found to
be ineffective. It has been concluded that this process can be used as an efficient and environmental friendly technique for effluent treatment of industrial wastewater containing organic compounds and dyes from textile industry.