

Available online at www.sciencedirect.com**ScienceDirect**

Procedia Technology 24 (2016) 611 – 618

Procedia
Technology

International Conference on Emerging Trends in Engineering, Science and Technology (ICETEST - 2015)

Synthesis and Evaluation of TiO₂/Chitosan based hydrogel for the Adsorptional Photocatalytic Degradation of Azo and Anthraquinone Dye under UV Light Irradiation

Dhanya A^a, Aparna K^{b*}^aResesach Scholar, Department of Chemical Engineering, NIT Calicut, Calicut-673601^bAssistant Professor, Department of Chemical Engineering, NIT Calicut, Calicut-673601

Abstract

The high rate of electron/hole pair recombination while using TiO₂ as a photocatalyst reduces the quantum yield of the process. Adding a co-adsorbent can increase the photocatalytic efficiency of TiO₂. In this study, a composite of TiO₂/Chitosan were synthesised in which chitosan also acts as an immobilization agent. The characterization of TiO₂ nanoparticles is done using Scanning Electron Micrograph and energy dispersive x-ray spectroscopy measurements. The experimental results show that TiO₂ nanoparticles encapsulated in Chitosan can remove the dyes from wastewater almost entirely. The parameters that affect the degradation process are initial concentration of the dye solution, contact time, catalyst concentration, effect of ions and pH. While using TiO₂ in slurry form requires separation of the photocatalyst from the treated solution, while in the immobilization technique, the requirement of separation can be avoided.

© 2016 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Peer-review under responsibility of the organizing committee of ICETEST – 2015

Keywords: TiO₂ nanoparticles; Chitosan; Azo dye; Anthraquinone dye; Photocatalytic degradation

* Corresponding author. Tel.: +91 9495669099

E-mail address: aparnak@nitc.ac.in

1. Introduction

Nowadays, research in wastewater treatment and purification is considered to be a hot area of research due to fresh water shortage and is a serious worldwide concern. Textile industries are the primary source that release synthetic dyes to the environment. The global consumption of dyes and pigments accounts to 7×10^5 tons/year, in which about two-thirds is being consumed by textile industry alone [1,2]. The textile dyes are having complex aromatic structures, which are tough to degrade into non-toxic materials. The conventional methods used for decolouration of textile effluents include precipitation, adsorption, flocculation, reverse osmosis, ultrafiltration, etc. [3]. Photocatalytic degradation has found to be of great importance nowadays, as the complex structure of the dye degrades into simpler and less toxic compounds. TiO_2 is the preferable semiconductor photocatalyst due to its excellent properties [4]. Due to the high oxidizing power and photostability of TiO_2 , it can be used as an exemplary semiconductor in photocatalysis [5]. TiO_2 , upon irradiation with UV light source, generates electrons and holes, which helps in the free radical formation that can oxidize the pollutant compounds efficiently. Mostly, TiO_2 is used in a slurry form in photocatalysis, and when using TiO_2 nanoparticles, the photocatalysis is more efficient, as nanoparticles have larger surface area compared to their bulk counterparts. But in the slurry form, the ultimate recovery of the photocatalyst is a costly process. Immobilization of TiO_2 on different supports started from the 1980s [6,7]. Chitosan is found to have extensive applications in biomedicine and agriculture and manufactured from a natural polymer chitin [8]. Therefore, Chitosan can be used as a support for immobilization of TiO_2 both environmentally and economically. The objective here is the removal of the organic pollutants from synthetic dye solution with the development of a photocatalytic reactor that uses immobilized TiO_2 nanoparticles. In the present work, the model dyes used were methyl orange and alizarin red s.

2. Formulation And Method Of Solution /Experimental Facility And Technique

2.1 Synthesis of TiO_2 nanoparticles and Immobilization on biopolymer chitosan

TiCl_3 (MERCK 15%) is used to synthesize TiO_2 nanoparticles. The pH of TiCl_3 solution is adjusted within the range 2.5 and 5.0 by using sodium hydroxide solution. By heating the solution in an oven, a white suspension is obtained, which upon centrifugation, the nanoparticles settle down. The solution is washed with distilled water and the TiO_2 nanopowder is thus obtained by drying the white colored suspended solution. Chitosan is used as a support for the immobilization of TiO_2 nanoparticles. Chitosan also acts as an adsorbent for the dye solution. TiO_2 nanoparticles were immobilized by encapsulation method in chitosan beads, which is semi-permeable. Chitosan manufactured by Sigma-Aldrich is used for this study. Solution containing chitosan in acetic acid is taken and to it TiO_2 nanoparticles (2.0 wt. %) and glutaraldehyde are added and stirred for 30 min. The solution is added dropwise to NaOH solution. The size of the spherical gel beads formed were off 1.5 - 2 mm. These beads were then washed with distilled water. TiO_2 immobilized Chitosan beads were further taken for the textile dye degradation studies.

2.2 Characterization of TiO_2 nanoparticles

The characterization of the nano photocatalyst TiO_2 is done by using UV – spectrophotometer and SEM/EDS.

2.3 Photocatalytic studies

The photocatalytic studies were carried out by using a set of degradation experiments concerning the degradation of azo and anthraquinone dye under irradiation with UV light. The UV source used is a mercury lamp with a predominant wavelength 292.3 nm. The spherical beads of TiO_2 nanoparticles immobilized in chitosan are the required catalyst. The photocatalytic activities were conducted on the synthetically prepared effluents. Methyl orange and alizarin red s is being used as model dye compounds for azo and anthraquinone dye respectively. The dye solution were treated in the photoreactor set up and at different intervals of time, the treated solutions were taken out from the reactor and were analyzed using UV-Vis spectrophotometer.

2.4 Photocatalytic Studies of Synthetically Prepared Dye Solutions

By measuring the following characteristics of the initial and treated dye solution, the photocatalytic activity of the photocatalyst can be determined.

(i) Absorbance: The absorbance is being measured at each interval of time. The absorbance measurement is done by using Evolution 201 UV-Visible Spectrophotometer. The decolouration efficiency is measured from the absorbance values before and after treatment in the photoreactor, where the absorbance values can be known from the UV Spectra at λ_{max} (maximum wavelength) of the respective dye. The expression is as in Equation (1)

$$\text{Decolouration} = \frac{(\text{Absorbance})_0 - (\text{Absorbance})_t}{(\text{Absorbance})_0} \quad (1)$$

Where, $(\text{Absorbance})_0$ is the initial value of absorbance of the dye solution and $(\text{Absorbance})_t$ is the value of absorbance after treatment with the photocatalyst at time t .

(ii) COD (Chemical Oxygen Demand): By measuring the COD of the dye solution initially and after each interval of treatment time, the degradation efficiency of the photocatalyst can be determined.

(iii) FTIR (Fourier Transform Infrared Spectroscopy) analysis: IR spectroscopy is used to confirm the degradation of the dye solution. The FTIR spectrum is a graph showing absorbance or transmittance versus frequency or wavelength. Bruker Alpha Spectrophotometer were used for the measurements.

2.5 Effect of pH and ions

Real effluent from textile industries contains organic and inorganic compounds that will positively or negatively affect the treatment process. Therefore, the study of pH and study of ions can be considered as an important factor in the degradation of the dye solution. By adding HNO_3 and NaOH , the pH values were adjusted in different ranges and then studied. Similarly, the effect of ions like chloride, sulfate and nitrate were investigated by adding 100 ppm of NaCl , K_2SO_4 and KNO_3 respectively to the dye solutions and then treating the dye solution using the photocatalyst.

3. Discussion On Results

3.1 Characterization of the Photocatalyst

3.1.1 UV analysis

Figure 1 shows the obtained absorption spectra of the prepared TiO_2 nanoparticles. TiO_2 nanoparticles exhibit an absorption band in the range 280 – 400 nm in the visible light region. By analyzing the spectra of the prepared TiO_2 nanoparticles, the absorption band showed a broad peak in the range 300 - 400 nm.

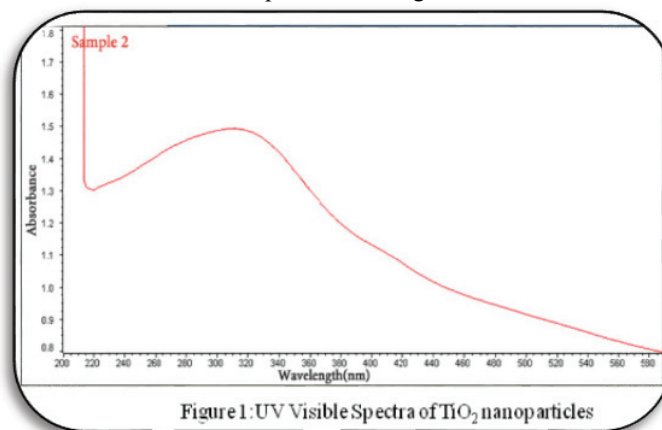


Figure 1: UV Visible Spectra of TiO_2 nanoparticles

3.1.2 SEM and EDAX

SEM (Scanning electron microscope) analysis was done to estimate the size of the TiO₂ nanoparticles and to see the distribution pattern of the TiO₂ nanoparticles in the chitosan polymer. The SEM image (Figure 2) indicates that the nanoparticles are well distributed. The particle size was estimated from the SEM image to be about 40 nm. EDAX (energy dispersive X-ray) spectroscopy measurements were done to analyze the photocatalyst quantitatively, and it showed that TiO₂ were present in the beads, and is as in figure 3.

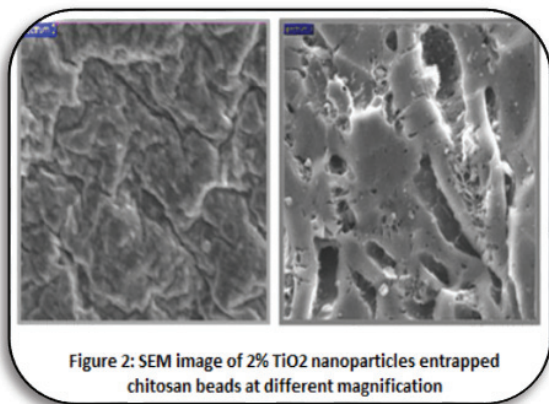


Figure 2: SEM image of 2% TiO₂ nanoparticles entrapped chitosan beads at different magnification

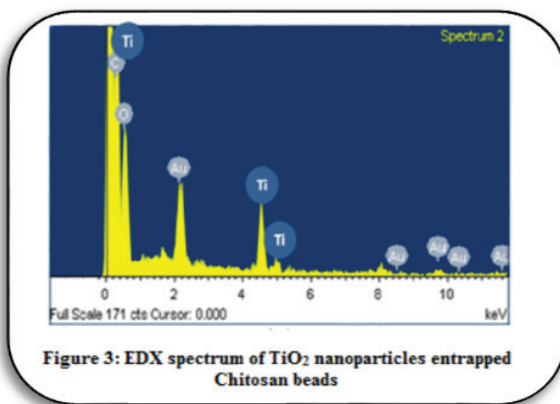


Figure 3: EDX spectrum of TiO₂ nanoparticles entrapped Chitosan beads

3.2 Photocatalytic Studies

There are many factors on which the photocatalytic degradation rate depends on, which include the intensity of light radiation, pH, catalyst type, the presence of ions, catalyst concentration, temperature, etc.

3.2.1 Effect of Contact Time

3.2.1.1 Absorbance Measurements

The maximum UV-Vis absorption of Methyl Orange is found to be at a wavelength of 462 nm. The absorbance of the dye solutions decreased with increase in treatment time, and 100% color removal was reached within 6 hours of irradiation for alizarin red s and 3 hours for methyl orange. This UV absorption peak indicates that the chromophore in the dye solution was broken down. The decolouration efficiency obtained at each interval of time is as shown in figure 4.

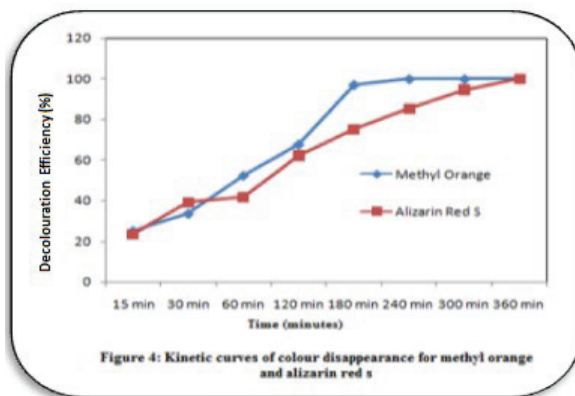
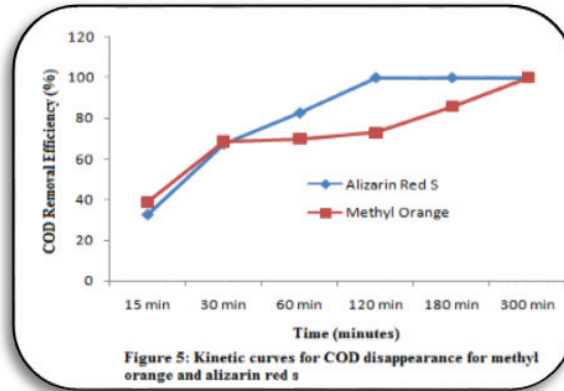


Figure 4: Kinetic curves of colour disappearance for methyl orange and alizarin red s

3.2.1.2 COD Analysis

The COD removal efficiency of the dye solutions is plotted with respect to time as in Figure 5. It can be seen that the COD values of the dye solution decrease slower than its decolouration rate. At 180 minutes the decolouration

efficiency is found to be 100 %, but COD removal efficiency is only 80% for methyl orange, which shows that dyes are transformed into intermediate products.



3.2.1.3 FTIR Analysis

The initial solution of Methyl orange gave an FTIR spectra as in Figure 6(a). The transmittance peaks were observed at 3688 cm^{-1} , 3211 cm^{-1} , 2924.06 cm^{-1} , 1421.71 cm^{-1} , 1040 cm^{-1} , 1007 cm^{-1} , 816 cm^{-1} and 1519.78 cm^{-1} that indicate the presence of free NH group, O – H vibration, alkyl C–H stretch, stretching vibrations of S = O, stretching vibration for C–N, C–O stretch, benzene disubstituted compounds and –N=N– stretching of azo compounds respectively. All these peaks confirm that methyl orange is aromatic in nature.

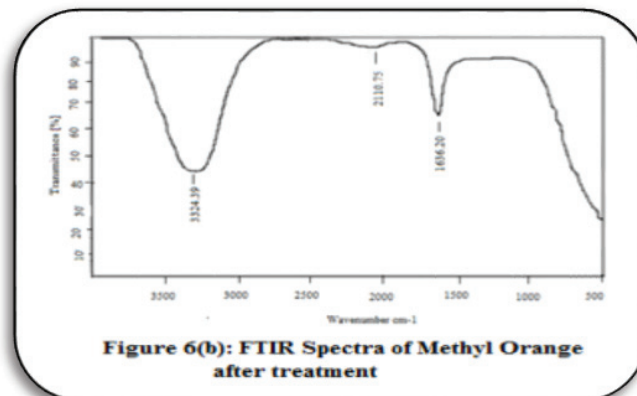
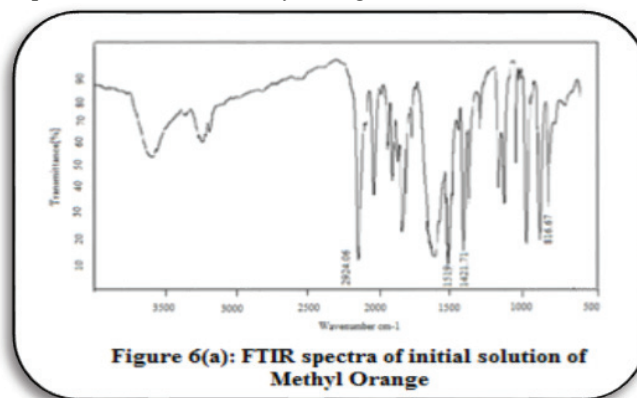
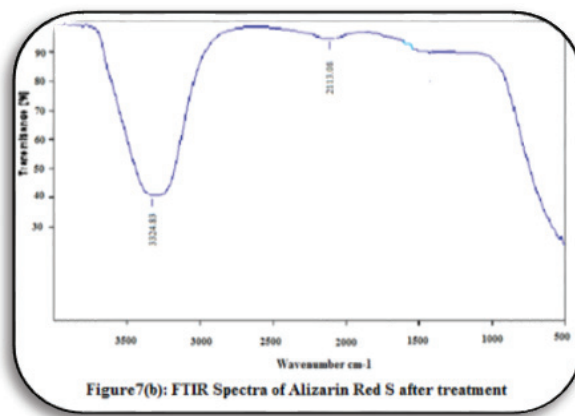
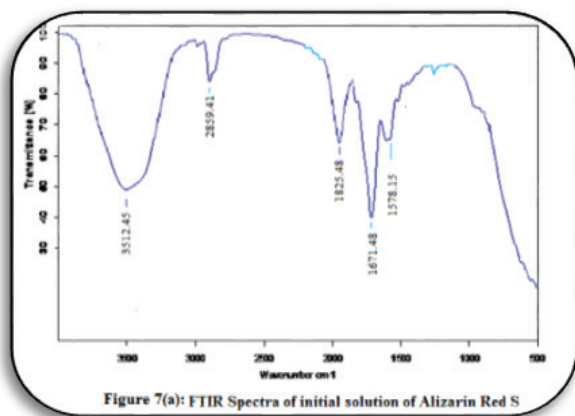


Figure 6(b), which is the FTIR spectra of the treated methyl orange solution, 790-840 cm^{-1} peak is absent, which indicated para disubstituted aromatic compound and the peaks which indicate the presence of -N = N- and -S = O- compounds are also not present. FTIR spectrum of the treated dye solution have displayed different peaks compared to the initial solution of methyl orange dye, which confirms that Methyl orange has been degraded.

Figure 7(a) shows the FTIR spectra of Alizarin red S dye solution. It is seen that the dye solution displays the peak at 1671.48 cm^{-1} , 1578.15 cm^{-1} , which shows aromatic C=C bond; 3512.45 cm^{-1} , 1825.48 cm^{-1} , and 2859.41 cm^{-1} presents the OH stretch, CO group, and C-H stretch respectively. But in Figure 7 (b) which is the FTIR spectra of Alizarin red S after treatment with the photocatalyst, new peaks are found, which is at 3324.83 cm^{-1} and 2113.08 cm^{-1} , indicating the C-H stretch. The other peaks in FTIR spectrum obtained in the initial Alizarin red s solution are absent in the treated solution, which confirms that the photocatalyst has completely degraded alizarin red s dye solution.



2.2 Effect of pH

Effect of pH is taken into consideration as it is a major factor in the degradation of dye solutions as real textile effluent pH may vary with the chemical compounds added to the dye during processing and the type of each dye used. The decolouration efficiency is calculated by taking the absorbance values at 462 nm for methyl orange and 445 nm for alizarin red s and is as shown in Figure 8. In the actual case, the decolouration rate is expected to increase with pH as by trapping photoinduced holes the hydroxyl radical concentration on the surface of TiO₂ increases in alkaline medium [10]. But here, in this study, the absorbance values of methyl orange at the maximum wavelength of the dye for different pH showed that the decolouration efficiency increased as for pH 11 < pH 9 < pH 7 < pH 5 < pH 3. The efficiency of decolouration is higher in the low pH region and lower in the region of high pH. In one previous study in literature, in the degradation of 3-chlorophenol, such results were obtained in which it was explained that HO₂ radicals are formed at low pH, which will decrease the hydroxyl ions concentration [11]. And also, at low pH, the oxidation rate will increase if oxidation attack of the hole is the rate determining step [12]. In the case of Alizarin dye, the photodecolouration efficiency is seen to increase from pH 3 to 7 and then decrease from pH 7 to 11. The efficiency is higher towards the neutral region and lowers towards both alkaline and acidic region.

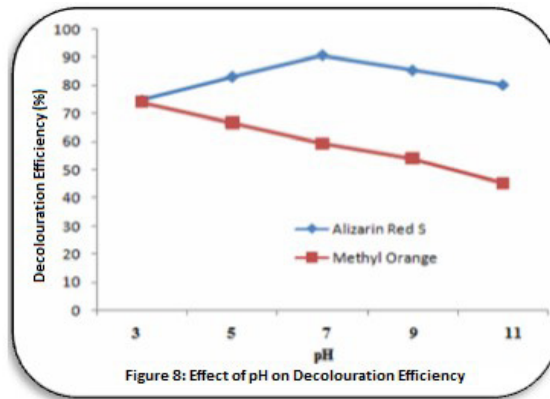


Figure 8: Effect of pH on Decolouration Efficiency

3.2.3 Effect of Ions

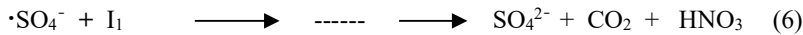
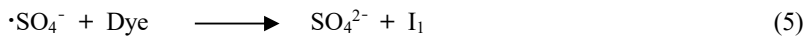
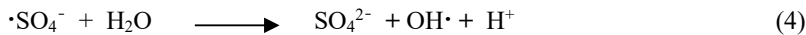
From the study, it is known that chloride, sulphate and nitrate anions increases the effectiveness of the photocatalytic degradation is shown in Table 1. By the addition of chloride ions to the dye solution and then treating the solution with the photocatalyst, the photo produced $\text{OH}\cdot$ and $\text{Cl}\cdot$ react as per equation (2) [13]



The $\text{Cl}\cdot$ radicals act as agents for oxidising the pollutants. On the addition of sulphate (SO_4^{2-}) ions, SO_4^{2-} ions are adsorbed on TiO_2 surface and then SO_4^{2-} ions react with photo – induced holes (h^+) as per reaction (3) [14]



As sulphate radical anion ($\cdot\text{SO}_4^-$) is a very strong oxidant [15], it can accelerate the degradation process. The participation of $\cdot\text{SO}_4^-$ in the decolouration process can be represented by the following reactions (4), (5), (6) [16].



Here I_1 represents the first reaction intermediates. Equation(4) enhances the photocatalytic reaction rate. When nitrate (NO_3^-) ions are added to the dye solution, NO_3^- ions are adsorbed weakly on TiO_2 surface[17].

Ions	Degradation Efficiency (%)							
	½ hour		1 hour		1½ hours		2 hours	
	Methyl Orange	Alizarin Red S	Methyl Orange	Alizarin Red S	Methyl Orange	Alizarin Red S	Methyl Orange	Alizarin Red S
Chloride	30.62	43.62	50.14	66.43	55.56	75.53	65.83	89.21
Sulphate	26.57	45.57	52.50	83.84	57.64	90.88	73.80	98.89
Nitrate	31.76	38.76	56.79	74.14	62.59	81.12	76.43	93.43
Control	19.72	32.50	45.48	61.88	51.25	69.79	59.87	82.65

4. Recycling of Photocatalyst

Catalyst's lifetime is a critical factor in determining the efficiency of the photocatalytic degradation process, as significant cost reduction can be acquired if the photocatalyst can be used for a longer period. Therefore, here the catalyst was recycled three times. The catalyst was recovered by washing with dilute HCl and water, and the recyclability was studied. It is found that the efficiency decreased to 65%.

5. Conclusion

The photocatalytic degradation of methyl orange and alizarin red s dye solutions have been carried out in the laboratory scale photoreactor with TiO₂ immobilized in chitosan as the photocatalyst, and the results indicate better degradation of the textile dye solution with this photocatalyst. The experimental results show that the COD decrease is much slower than the degradation of the dye solutions. Both environmentally and economically, chitosan can be a good support for TiO₂ immobilization, and the photocatalyst can be recycled three times without a sufficient decrease in efficiency

References

- [1] P. Nigam, I.M. Banat, D. Singh, and R. Marchant, 1996. "Microbial Process for the Decolorization of Textile Effluent Containing Azo, Diazo and Reactive Dyes," *Process Biochemistry*, 31(5), June, pp. 435-442.
- [2] T. Robinson, G. McMullan, R. Marchant, and P. Nigam, 2001. "Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative," *Bioresource Technology*, 77(3), May, pp. 247-255.
- [3] Hamid Reza Ebrahimi Afarani., 2008. "Preparation of Metal Catalysts on Granule Glass for Degradation of Textile Dyes as Environmental Contaminants". *World Applied Sciences Journal*, 3 (5), pp. 738-741
- [4] Jean Marie Herrmann, 2010. "Photocatalysis fundamentals revisited to avoid several misconceptions". *Applied Catalysis B: Environmental*. 99(3-4), September, pp. 461 - 468.
- [5] Gupta Shipra Mital, Tripathi Manoj, 2011. "A review of TiO₂ nanoparticles". *Chinese Science Bulletin*, 56 (16), June, pp. 1639-1657.
- [6] K Hashimoto, H Irie, A Fujishima, 2005. "TiO₂ photocatalysis: a historical overview and future prospects". *Japanese Journal of Applied Physics*. 44 (12), December, pp. 8269 – 8285.
- [7] U I Gaya, A H Abdullah, 2008. "Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: a review of fundamentals, progress and problems". *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*. 9(1), March, pp. 1 – 12.
- [8] Dash M, Chiellini F, Ottenbrite R M and Chiellini E, 2011. "Chitosan – A versatile semi-synthetic polymer in biomedical applications". *Progress in Polymer Science*, 36 (8), August, pp. 981 – 1014.
- [9] <http://www.greenpeace.org/international/en/campaigns/detox/fashion/about/eleven-flagship-hazardous-chemicals>
- [10] J.C. D'Oliveira, G. Al-Sayyed, P. Pichat, 1990. "Photodegradation of 2- and 3-chlorophenols in TiO₂ aqueous suspensions". *Environ. Sci. Technol.* 24 , pp. 990 – 996.
- [11] A Mills, S Morris and R Davies, 1993. " Photomineralisation of 4 – Chlorophenol sensitised bt Titanium Dioxide: A study of the intermediates". *Journal of photochemistry and photobiology A: Chemistry*, 70 (2), pp.183 – 191.
- [12] U Stafford, K A Gray and P V Kamat, 1994. "Radiolytic and TiO₂ assisted photocatalytic degradation of 4-Chlorophenol: A comparative study.". *Journal of physical chemistry*, 98 (25), pp.6343 – 6351.
- [13] J.L. Lucas Vaz, A. Boussaoud, Y. Ait Ichou and M. Petit-Ramel, 1998. "Photomineralisation on titanium dioxide of uracil and 5-halogenouracils. Influence of pH and some anions on the photodegradation of uracil", *Analisis*, 26 (2) March, pp.83-87.
- [14] N. Barka, S. Qourzal, A. Assabbane, A. Nounah, Y. Ait-Ichou, 2008. "Factors influencing the photocatalytic degradation of Rhodamine B by TiO₂-coated non-woven paper", *Journal of Photochemistry and Photobiology A: Chemistry*, 195, pp.346–351.
- [15] C. Nsar, K. Vinodgopal, S. Kotchandani, A.K. Chattopadhyay, P. K. Kamat, 1997. "Photocatalytic reduction of azo dyes naphthol blue black and disperse blue 79", *Chem. Intermed.*, 23 (3) pp.219-231.
- [16] M. Kositzki, A. Antoniadis, I. Poulis, I. Kiridis, S. Malato, 2004. "Solar photocatalytic treatment of simulated dyestuff effluents", *Solar Energy*, 77, pp.591-600.
- [17] J.C. D'Oliveira, G. Al-Sayyed, P. Pichat, 1990. "Photodegradation of 2- and 3-Chlorophenol in TiO₂ Aqueous Suspensions", *Environ. Sci. Technol.*, 24 (7), pp. 990-994.