Photocatalytic decolorization of Methyl Red dye under solar light
إزالة صبغة المثيل الحمراء تحت ضوء الشمس

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Abstract

Environmental problems associated with hazardous wastes and toxic water pollutants have attracted much attention. Among them, organic dyes are one of the major groups of pollutants inwastewaters produced from textile and other industrial processes. Among various physical, chemical and biological techniques for treatment of wastewaters, heterogeneous photocatalysis has been considered as a cost-effective alternative for water remediation. The superiority of photocatalytic technique in wastewater treatment is due to its advantages over the traditional techniques, such as quick oxidation, no formation of polycyclic products, oxidation of pollutants in the (ppb) range.

Photocatalysis is a process by which a semiconductor material absorbs light of energy more than or equal to its band-gap, thereby generating electrons and holes which can further generate free radicals in the system to oxidize the substrate. The resulting free radicals are very efficient oxidizers of organic matter. TiO_2 is the most promising photocatalyst due to its facile and cheap application in removing inorganic and organic pollutants from waste waters.

In the present study the photocatalytic decolorizaion of Methyl Red (MR) dye has been investigated by employing heterogeneous photocatalysis under solar light. The photocatalytic activity in presence of TiO_2 as a semiconductor has been investigated. Thereafter different operational parameters like catalyst loading, pH, initial dye concentration and recycling of catalyst on the photocatalytic decolorizaion which affect the decolorization process have been optimized.

The results shows the solar photocatalytic completely degradation of MR dye was noticed in acidic region with a catalyst dose of 2.0 g L^{-1} and pH = 3 within 225 minutes The experiments also shows the degradation of MR decrease with increase of dye concentration at optimum conditions and performed to evaluate the reusability of the TiO_2 for decolorization of Methyl Red.

الخلاصــــــــة

أن مخلفات المياه الصناعية الملوثة بالمواد الخطرة والسامة والتي ترافقها مشاكل للبيئة أثارت اهتمام الباحثين ومن بين هذه الملوثات هي الصبغات العضوية والتي تعتبر من المجاميع الرئيسية الملوثة للمياه وغالبا ما تنتج هذه الإصباغ من معامل الأنسجة وبكميات كبيرة جدا.

أن الطريقة الضوئية المحفزة الغير المتجانسة تفوقت وبشكل كبير على الطرق التقليدية الأخرى المستخدمة في معالجة مخلفات المياه الناتجة من المصانع بشكل عام ومصانع الأنسجة بشكل خاص وذلك لأنها تمتاز بكونها (ذات أكسدة سريعة ، لا تحتوي على نواتج عرضية ، وأكسدة الملوثات عالية جدا تصل إلى أجزاء المليون).

ان ميكانيكية التفاعل تتم من خلال امتصاص الضوء من قبل العامل المساعد (شبه الموصل) وهذا الضوء يحتوي على طاقة اكبر او مساوية الى طاقة الفجوة بين الأواصر في شبه الموصل وبذلك يتهيج الإليكترون ويقفز من مستوى طاقة اوطأ الى المستوى الأعلى فيتولد إليكترون بشحنة سالبة وفجوة بشحنة موجبة وبالتالي تتكون لنا جذور حرة (الاليكترونات والفجوات) في النظام حيث تقوم هذه الجذور بأكسدة الملوثات (أن الجذور الحرة الناتجة تكون ذات كفاءة عالية لعمليات الأكسدة للمواد العضوية).

يعتبر ثنائي اوكسيد التتانيوم من أشباه الموصلات الجيدة التي تستخدم كعامل مساعد في هذه العملية وذلك لتوفره

ولرخص تطبيقاته في إزالة الملوثات العضوية والغير عضوية من مخلفات المياه.

في هذا البحث تم توظيف الطريقة الضوئية المحفزة الغير متجانسة تحت أشعة الشمس في ازلة صبغة المثيل الحمراء هذه العملية تمت باستخدام ثنائي اوكسيد التتنانيوم كعامل مساعد.تمت دراسة العوامل المؤثرة على عملية المعالجة واختيار الأمثل منها مثل كمية العامل المساعد ودالة الحامضية pH و تركيز الملوثات بالإضافة الى دراسة إمكانية أعادة استخدام العامل المساعد ومدى فعاليته لأربع دورات. وقد اوضحت النتائج ان صبغة المثيل الحمراء قد تمت ازالتها بصورة تامة في عملية الاكسدة الضوئية بالعامل المساعد خلال 225 دقيقة عند الظروف المثالية وبالوسط الحامضي للمحلول الملون.
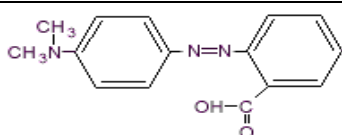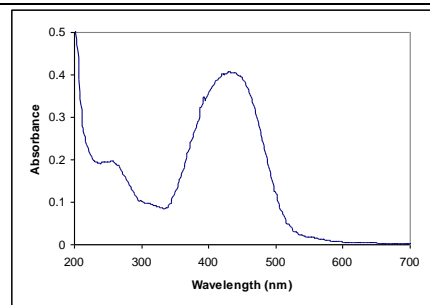
1. Introduction

Treatment of the effluent from the dyeing and finishing processes in the textile industry is one of the most significant environmental problems. Since most synthetic dyes have complex aromatic molecular structures which make them inert and biodegradable, and difficult when discharged into the environment. Colored wastes are harmful to aquatic life in rivers, lakes and sea when they are discharged [1,2]. Colored water hinders light penetration and may in consequence disturb biological processes in water-bodies. Moreover, dyes itself are highly toxic to some organisms and hence disturb the ecosystem [3,4]. Dyes can cause allergic dermatitis, skin irritation, cancer, mutation, etc. In addition, biodecolorization of some of them produce aromatic amines, which are highly carcinogenic [5,6].

In recent years, heterogeneous photocatalysis was proved to be an effective advanced oxidation technique for the complete decolorization of hazardous and refractory organic compounds, due to the high oxidation potential of active hydroxyl free radical ($OH^{\bullet}$) which is generated from irradiated semiconductor catalyst [7–8]. Among the various semiconductor catalysts employed, TiO_2 has been extensively studied because it's one of the most commonly used oxide semiconductor materials due to its wide band gap (3.2 eV), low cost, nontoxic nature, strong oxidizing power, high resistance to chemical or photo-induced corrosion, and maximum light scattering with virtually no absorption. It has been widely used in photocatalysis, photovoltaic, solar energy conversion, sensors, textiles, paints, cosmetics, etc. [9]. The commercially available TiO_2 (Degussa P-25, Anatase 70% and Rutile 30%) with particle size of 20 nm and surface area of 50 m^2/g [10].

Methyl Red is also known as 2-((4-(dimethylamino)phenyl)azo)-benzoic acid, hydrochloride; Methyl Red hydrochloride. The properties, structure and absorption spectra of Methyl Red dye are given in Table 1. It is an important dye used in biological and chemical assays. It is used as a dye for coloring textiles (cotton, wool, silks, and acrylics), china clay products, leather, printing inks, and as a filter dye in photography [11].

In the present work, the effects of various experimental parameters, such as amount of photocatalyst, pH, initial dye concentration and recycling of catalyst on the photocatalytic decolorizaion of Methyl Red dye were examined using a solar light with semiconductors TiO_2 as a catalyst UV-Vis spectroscopy was employed to rationalize the result of photocatalytic decolorizaion. Thus the purpose of this work was to study the decolorizaion of Methyl Red with a particular emphasis on experimental parameters.

Table 1 Properties and absorption spectra of Methyl Red (MR) dye[12]

Name	Methyl Red
Other name	Methyl Red hydrochloride
C.I. name	Acid Red 2
Natural	Acid dye
Molecular formula	$C_{15}H_{15}N_3O_2$
Maximum wavelength (λ_{max})	440 nm
Molecular weight	269.3 g mol^{-1}
Molecular structure	
UV-visible spectra	

2. Experimental

2.1 Chemicals

All chemicals were of the highest purity available and were used as received without further purification. Methyl Red dye and titanium dioxide were obtained from Loba Chemie (India). Double distilled water was used for preparation of various solutions. The pH of the solution was adjusted by adding 0.01N NaOH or 0.01N HCl.

2.2 Preparation of Dye Solutions

Dye solutions were prepared by dissolving required amounts (25 mg) of Methyl Red (MR) dye in one liter distilled water by continuous stirring (with 15 minutes mixing time)

2.3 Photocatalytic Decolorizaion

For solar experiments, dye solution of 500 ml (25 ppm) is taken in an open glass reactor with a known amount of the catalyst (0.5–2.5) g/L. The slurry solution is continuously stirred in a shaking unit at 180 rpm and is illuminated under bright sunlight for five hours. Distilled water is added at regular intervals to avoid concentration changes due to evaporation with the help of markings present on the reactor. In all solar experiments the intensity was measured by Radiometer (Model UVA-365, Lutron Electronic, Taiwan) 33–38 W m^{-2} and temperature 35 ^{o}C .

An aliquot of 5 ml of dye solution was taken from the glass reactor at regular intervals of time with the help of a syringe. The catalyst was filtered from the sample by using a Millipore filter (0.45 μm). These samples were analyzed using a UV-Vis spectrophotometer analysis (UV-1800 Shimadzu, Japan).

The various experiments were conducted for optimizing the parameters like catalyst loading, pH and initial concentration of dye.

2.4 Analysis Procedure

The decolorizaion rate of Methyl Red (MR) was calculated from the following equation:

$$\% \text{ Decolorization} = (A_o - A_t) / A \qquad \ldots\ldots\ldots\ldots (1)$$

Where A_o and A_t corresponded to the initial absorbency and the absorbency at certain time intervals, respectively. The decolorizaion rate was used to evaluate the photocatalytic activities of different TiO_2 catalyst.

3. Results and Discussion

3.1 UV–vis spectral change

The temporal absorption spectral changes taking place during the photocatalytic decolorization of Methyl Red by TiO_2 particles under sunlight illumination are investigated. Figure 1 shows a major absorption band at 440 nm. From the observed absorbance, absorptivity at 440 nm was estimated to be 0.406. The well-defined absorption bands disappeared after irradiation for 150 minutes indicating that Methyl Red had degraded in the presence of TiO_2 particles with sunlight illumination [13].
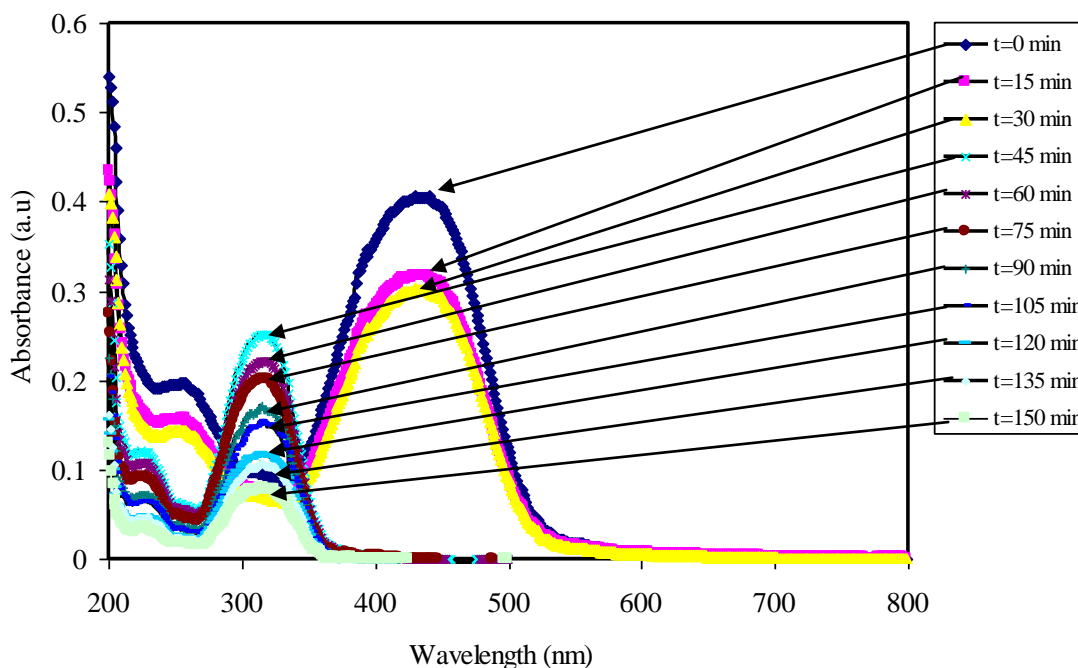

Figure 1: UV–vis spectral changes with time

3.2 Effect of Catalyst Dose

Catalyst (TiO_2) concentration was varied from 0.5 g L^{-1} to 2.5 g L^{-1} during photocatalytic reactions under sunlight. It was observed that the rate increases with increase in catalyst concentration and becomes constant above a certain level as shown Figure 2 and it is seen that the optimum amount of TiO_2 is found to be 2.0 g L^{-1}. This concentration of TiO_2 has been taken for the subsequent experiments for studying the effect of pH of the solution and different initial concentrations. The excess of catalyst concentration might increase the turbidity of the solutions leading to a shielding effect on the penetration of sunlight. Hence the photoactivated volume of the suspension decreases. The decreased percentage decolorization at higher catalyst loading may also be due to the deactivation of activated molecules by collision with ground state molecules. Thus optimum catalyst concentration has been found in order to avoid the excess of catalyst and ensure total absorption of efficient photons (as found by Ahmed H. Ali, 2011) [14].
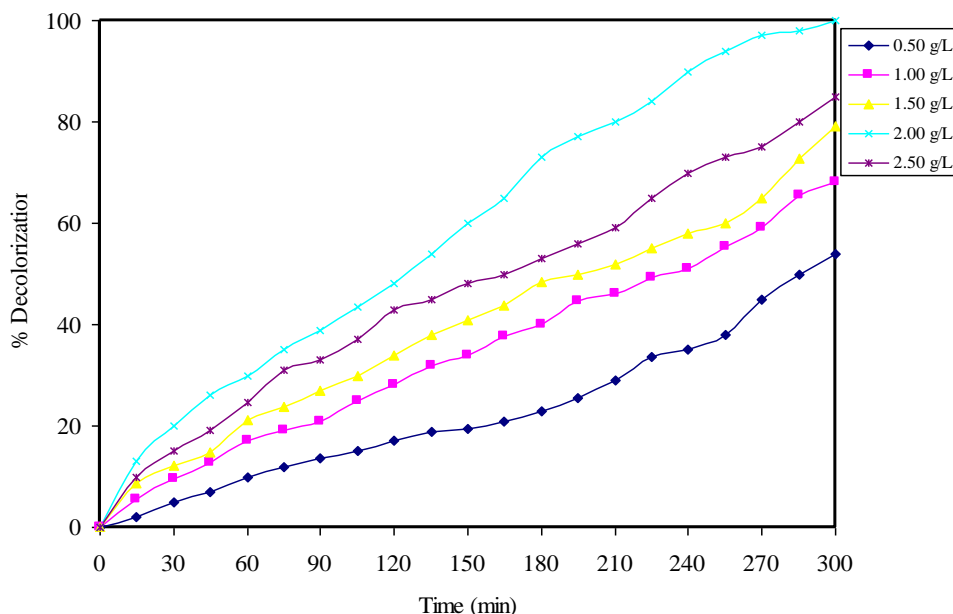
Figure 2 Effect of catalyst dose for the decolorization of Methyl Red dye natural pH=6.73

3.3 Effect of pH

The solution pH is not only an important parameter for sunlight decolorization process, but also a chief operational parameter in actual wastewater treatment. To study the effect of pH on the decolorization efficiency, experiments were carried out at various pH values, ranging from 3–11 for constant dye concentration (25 mg/L) and catalyst loading (2 g/L). Figure 3 presents the Methyl Red decolorization as a function of pH. The highest decolorization activity was attained under pH=3, where the Methyl Red removal percentage reached near 95 % in 195 min. This result was in line with that observed previously, which indicated the optimal pH 3 [15–16].

The point of zero charge (pzc) of the TiO_2 (Degussa P25) is at pH 6.8. Thus, the TiO_2 surface is positively charged in acidic media (pH < 6.8), whereas it is negatively charged under alkaline conditions (pH > 6.8), and Methyl Red dye anions lead to strong adsorption and thus enhancing the decolorization rate. In the alkaline pH there was poor adsorption because the catalyst and dye both are negatively charged in the alkaline media. Therefore decrease in pH causes increase in decolorization rate. Similar findings have been reported by other workers for the photocatalytic decolorization of Ethyl Violet and Basic Blue dyes using ZnO [17]
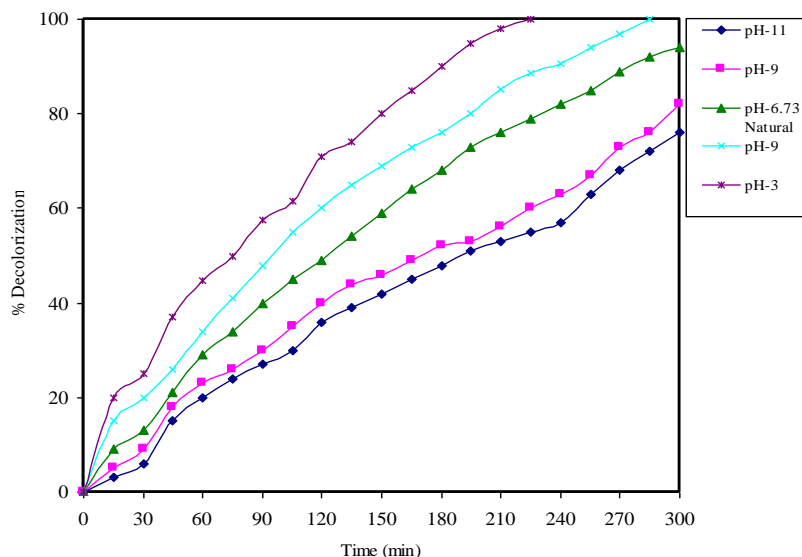
Figure 3 Effect of pH for the decolorization of Methyl Red dye.
(25 mg/L dye solution, TiO$_2$–2 g/L)

3.4 Effect of Concentration of Dye

After optimizing the pH conditions and catalyst dose (pH = 3 and catalyst dose = 2 g/L). The photocatalytic decolorization of Methyl Red dye was carried out at different initial concentrations (C_0 = 5–100 mg/L)in the TiO$_2$/sunlight system are compared in Figure 4. As the concentration of the dye was increased, the percentage of photodecolorization decreased indicating either to increase the catalyst dose or time span for the complete removal.

The fraction of unreacted Methyl Red dye (C/C_0) decreases with increasing C_0 under the conditions studied; however, the total amount of dye degraded actually decreases. The limited number of surface sites of the TiO$_2$ catalyst may control dye photodegradation. In case of dye solutions of 5 mg/L, 10 mg/L and 25 mg/L, 100 % decolorization occurred within 180 minutes, 210 minutes and 225 minutes, respectively and in case of 50 and 100 mg/L, complete decolorization in 255 and 300 minutes. This is due to the increase of incidental photonic flux irradiating the catalyst in the dilute lignin solution. Thus the rate of hydroxyl radical production increases which would allow the decolorizaion to be faster [18-20].
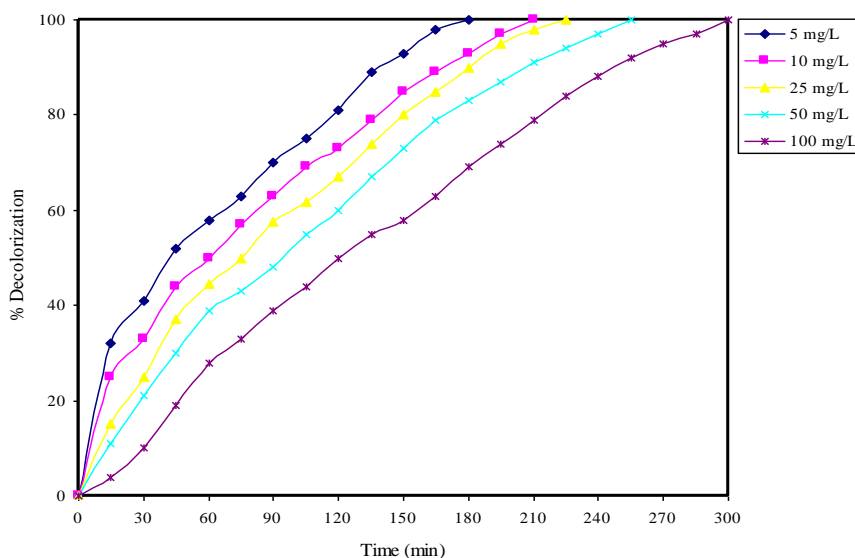

Figure 4 Effect of initial concentration of dye for the decolorization of Methyl Red dye
optimum condition (TiO$_2$–2 g/L, pH–3)

3.5 Recycling of TiO_2

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 as shown in Figure 5. After the optimized conditions for the decolorizaion of the effluent were determined, the catalyst was recovered by filtration and activated at 100 ^{0}C and again used to study its recyclibility. As shown in Figure 5, TiO_2 can be recycled effectively which makes the process cost effective. The process was repeated until reasonable dye decolorization upto 78 % was achieved after the fourth cycle [13,14].
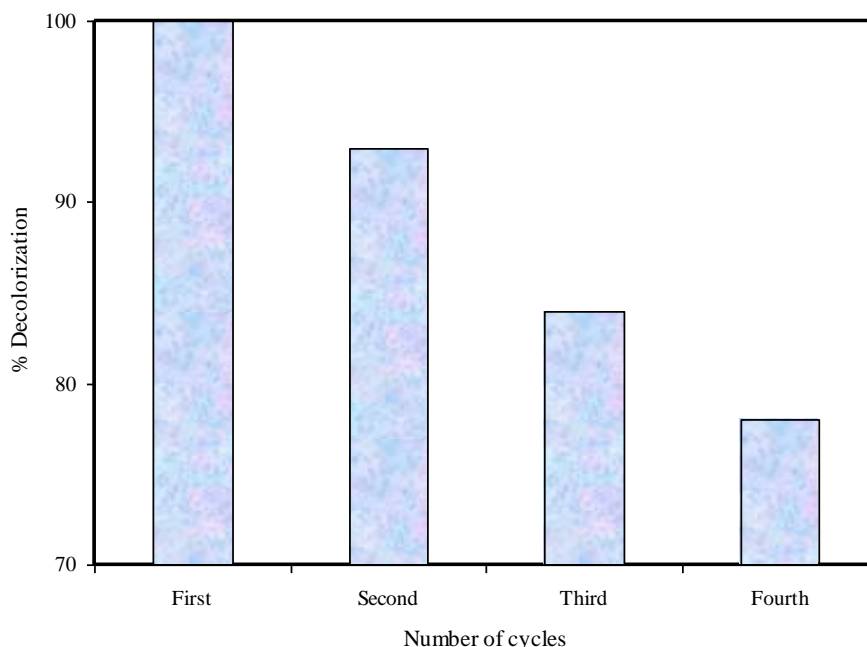

Figure 5 Reusability of TiO_2 at optimum conditions
(catalyst dose-2 g/L, pH-3)

4. Conclusion

The optimization of the photocatalytic decolorization conditions of Methyl Red in water using titanium dioxide was investigated under sunlight illumination. The final degradation products were carbon dioxide, nitrate and ammonium ions. All carbon and nitrogen atoms were transformed into inorganic compounds. Since the artificial lamp device is particularly expensive in the nonexclusive areas, the solar photocatalytic degradation technology developed may be available in those areas. Maximum decolorization of the dye was noticed in acidic region with a catalyst dose of 2.0 g L^{-1} and pH = 3. The experiments were performed to evaluate the reusability of the TiO_2 for decolorization of Methyl Red.

5. References

[1] Shenai V.A. (1996). Azo dyes on textiles vs. German ban: an objective assessment. Part III. Another study, Colourage XLIII (8) 41.
[2] Greene J.C. and Baughman G.L. (1996). Effects of 46 dyes on population growth of fresh green algae Selenastrum capricornutum, Text. Chem. Color. 28 (4) 23.
[3] Saha C. (1996). Eco-textile: a novel concept of cleaner product, Text Dyer Printer XXIX (21) 13.

[4] Phillips D.A.S. (1996). Environmentally friendly, productive and reliable priorities for cotton dyes and dyeing processes, J. Soc. Dyers Color. 112 (6) 183.

[5] Boeniger M.F. (1980). Carcinogenity of Azo Dyes Derived from Benzidine, Department of Health and Human Services (NIOSH), Pub. No. 8-119, Cincinnati, OH.

[6] Kirk-Othmer (1994). Encyclopedia of Chemical Technology, Explosives and Propellants to Flame Retardants for Textiles, 4th ed., Wiley-Interscience Publishers, pp. 547–672, ISBN-13: 978-0471526780.

[7] Sobczyn A., Duczmal S.K., Dobosz A. (1999). Photocatalysis by illuminated titania: oxidation of hydroquinone and p-benzoquinone, Monatsh. Chem. 130 (6) 377–384.

[8] Li X., Zhao W., Zhao J. (2002). Visible light-sensitized semiconductor photocatalytic decolorizaion of 2,4-dichlorophenol, Sci. China Ser. B 45 (4) 421–425.

[9] Vulliet E., Emmelin C., Chovelon J.M., Guillard C., Herrmann J.M. (2003) Photocatalytic decolorizaion of the herbicide cinosulfuron in aqueous TiO_2 suspension, Environ. Chem. Lett. 156 (23) 62–67.

[10] Ibrahim U., Gayaa A., Abdullaha (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 (12) 1–12.

[11] Zhao J., Chen C., Ma W. (2005). Photocatalytic decolorizaion of organic pollutants under visible light irradiation, Top. Catal. 35 (3–4) 269–278.

[12] Hinda Lachheb, Eric Puzenat, Ammar Houas, Mohamed Ksibi, Elimame Elaloui, Chantal Guillard, Jean-Marie Herrmann (2002). Photocatalytic degradation of various types of dyes (Alizarin S, Crocein Orange G, Methyl Red, Congo Red, Methylene Blue) in water by UV-irradiated titania. Applied Catalysis B: Environmental, (39) 75–90.

[13] Kansal S.K., Kaur N., Singh S. (2009). Photocatalytic decolorizaion of two commercial reactive dyes in aqueous phase using nanophotocatalysts. Nanoscale Research Letters, 4 (53) 709–716.

[14] Ahmed Hassan Ali, Seema Kapoor, Sushil Kumar Kansal (2011). Studies on the photocatalytic decolorization of pararosaniline chloride dye and its simulated dyebath effluent. Desalination and Water Treatment, (25) 268–275.

[15] Kansal S.K., Ahmed Hassan Ali, Seema Kapoor (2010). Photocatalytic decolorization of biebrich scarlet dye in aqueous phase using different nanophotocatalysts. Desalination, (259) 147–155.

[16] Tang W.Z., Huang C.P. (1996) 2,4-Dichlorophenol oxidation kinetics by Fenton's reagent, Environ. Technol. (17)1371.

[17] Kwon B.G., Lee D.S., Kang N. (1999). Characteristics of p-chlorophenol oxidation by Fenton's reagent, Water Res. (33) 10–21 .

[18] Concalves M.S.T., Oliveira-Campos A.M.F., Pinto M.M.S., Plasencia P.M.S., Queiroz M.J.R.P. (1991). Photochemical treatment of solutions of azo dyes containing TiO_2, Chemosphere (39) 781.

[19] Guillard C., Disdier J., Monnet C., Dussaud J., Malato S., Blanco J., Maldonado M.I., Herrmann J.M. (2003). Solar efficiency of a new deposited titania photocatalyst: chlorophenol, pesticide and dye removal applications, Appl. Catal. B: Environ 46 (2) 319–332.

[20] Reutergarth L.B., Iangpashuk M. (1997). Photocatalytic decolorization of reactive azo dye: a comparison between TiO_2 and CdS photocatalysts, Chemosphere (35) 585–596.