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Research Article

Solar Light Induced and TiO_2 Assisted Heterogeneous Degradation of Textile Dye Janus Green

Sangita Sharma* and Kulsum Shaikh

Department of chemistry, Hemchandracharya North Gujrat University Patan-384265, Gujarat, INDIA

Abstract

The photocatalytic degradation of textile dye Janus Green has been investigated in presence of H_2O_2. The influence of various reaction parameters such as concentration of dye, amount of photocatalyst, change of pH, Hydrogen peroxide, light intensity, etc. It was found that the dye degradation followed pseudo first order kinetics. Process of degradation was followed spectrophotometrically at maximum wavelength 615 nm. Rate of photodegradation of Janus Green dye and optimal conditions are explained. Participation of *OH* radical is confirmed by the use of scavengers. A tentative mechanism of photodegradation of Janus Green is reported.

Keywords: Titanium dioxide, Hydrogen peroxide, Janus Green

***Correspondence**
Author: Sangita Sharma
Email: sangitamem2000@gmail.com

Introduction

The methods used for the removal of organic dyes and pigments from wastewaters are classified into three main categories: physical, chemical and biological methods, such as coagulation, adsorption, membrane process and advanced oxidation process (AOP) [1-7]. Titanium dioxide (TiO_2) has emerged as an excellent photocatalyst material for removal of environmental contaminants [8]. Synthetic dyes have been used in the textile, leather, paper, printing inks, plastics, cosmetics, paints, pharmaceutical, and food industries. It is estimated that 15% of these dyes is lost in the synthesis, processing of colorants, dyeing, printing and finishing [9-11]. Many processes have been proposed over the years and are currently employed to destroy toxic chemicals discharged along with textile wastewater. Photocatalytic detoxification (AOPs) has been focussed as an alternative method to clean up polluted water. This technique adopts the possibility of combining the heterogeneous catalysis with solar light to achieve mineralisation of toxic pollutants present in textile wastewater [12]. Photocatalytic degradation of Direct Blue 1 dye in the presence of an aqueous heterogeneous suspension of ZnO irradiated with visible light has been investigated [13]. TiO_2 has been reported as a good semiconductor for removal of many organic compounds, may be due to high oxidation efficiency, complete decomposition process, cheap and nontoxic material [14-15]. A photocatalysts could be heterogeneous if it is present in a different phase than the reaction mixture. The advantages of heterogeneous catalysts are cheap, non-toxic can be easily separated from the reaction mixture, and can be reused [16-17]. Many commercially available dyes are known and approximately one million tons of these dyes are produced annually worldwide. Also, the synthetic dyes represent a relatively large group of organic chemicals that are met in practically all spheres of our daily life. The cationic dye such as Janus Green is an important group of organic compounds which have a variety of scientific and industrial applications [18-19]. Here solar induced and TiO_2 assisted Heterogeneous degradation of studied.

Experimental

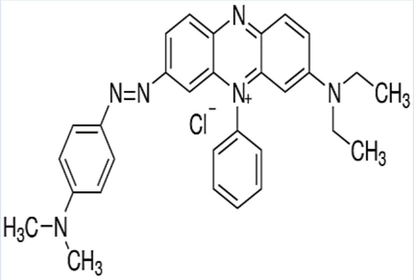
Chemical Used

Janus Green was obtained from ACS chemicals India Ltd. and its characterised are given in **Table 1**. Hydrogen peroxide with 30% volume was brought from FINAR India Ltd. and was used as received. A commercial product of Titanium dioxide was supplied by CHITI CHEM Vadodara, India Ltd. and it is used as a photocatalyst. All chemicals were of analytical grade and used without further purification.

Instrumentation

The concentration of the dye solution was monitored using absorbance recorded on UV-visible double beam spectrophotometer (Thermo scientific-evolution 201) and pH was checked with pH meter (Systronics model n EQ - 361). The stock solution of dye was prepared in double distilled and deionized water with conductance 1.5×10^{-6} and pH 6.8. This deionized and doubly distilled water was used throughout this study. Absorbance was measured at different time intervals by UV-visible spectrophotometer and decrease in colour of the dye was monitored spectrophotometrically at wavelength of 615nm. Digital Lux meter (TES - 1332A) supplied by Mumbai, Maharashtra India, Model- TES 1332A with analog output jack for recording data is used. The intensity of the solar light was measured using Lux meter which has range of 20/200/2000/20000 Lux.

Table 1 Characteristics & chemical structure of eosin yellow

Name	**Janus Green**
λ (nm)	615
Molecular weight (g/mol)	511.07
Melting point	160 °C
Solubility	Water
Molecular formula	$C_{30}H_{31}ClN_6$
C.I.No.	11050
Chemical Structure	

Procedure

- First beaker containing Janus Green solution was kept in dark.
- 100 mg TiO_2 was added to the second beaker containing Janus green solution and was kept in dark.
- 100 mg TiO_2 and 1500 mgL^{-1} H_2O_2 was added to third beaker containing Janus green solution and was kept in dark.
- Fourth beaker containing Janus Green solution was exposed to solar light.
- 100 mg TiO_2 was added to the fifth beaker containing Janus green solution and was exposed to solar light.
- 100 mg TiO_2 and 1500 mgL^{-1} H_2O_2 was added to sixth beaker containing Janus green solution and was exposed to solar light.

These beakers were kept for 120 min and then the absorbance of each solution was measured with the help of a spectrophotometer. It was observed that the absorbance of solutions of first five beakers remained virtually constant, while the solution of sixth beaker showed reasonable decrease in absorbance as compared to initial value. This observation suggests that this reaction requires both the presence of light as well as semiconductor TiO_2.

Typical Run

Considering various constraints a typical run is decided and absorbance is measured of 615 nm. The plot of 2+log O.D versus exposure time was found to be a straight line, as shown in **Figure 1**. This indicates that the solar degradation of dye in presence of titanium dioxide follows pseudo first order kinetics and the rate constant for this reaction was determined using the expression: k = 2.303 x slope.

Anaylysis

The discoloration yield is calculated as:

$$Y = 100\left(\frac{1 - A_{615}(t)}{A_{615}(0)}\right)$$

Where, Y= discoloration yield, $A_{615}(t)$ = absorbance of (t) time, $A_{615}(0)$ = absorbance of (0) time.

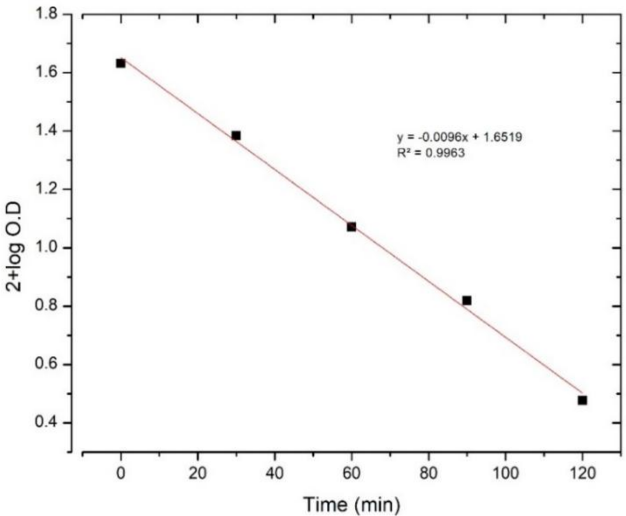


Figure 1 Typical run of Janus green at wave length of 615 nm [1000 mgL^{-1} concentration of dye, 1500 mgL^{-1} of $H_2 O_2$,10.0 pH,100 mg of TiO_2, Light intensity 450×10^{2}Lux]

Results and Discussion

Janus Green is a basic azo and cationic and it is IUPAC name is 8-(4-Dimethylaminophenyl) diazenyl-*N*, *N*-diethyl-10-phenylphenazin-10-ium-2-amine chloride. This dye is also known as Diazin Green S and Union Green B. At room temperature it appears as solid, odourless, dark blue crystalline powder which yields a dark blue solution, when dissolved in water. It acts as an indicator and changes colour according to the amount of oxygen present. If oxygen is present, the indicator is oxidised to blue colour and if oxygen is absent the indicator is reduced to pink colour.

Effect of dye concentration

Initial concentration of dye plays a major role and has a significant influence on the degradation rate. Different initial concentrations of Janus green with rang from 500 mg to 2500 mgL^{-1} were used. **Figure 2** shows the effect of initial concentration of dye and the complete discoloration of the dye was achieved in 120 minutes for 1000 mgL^{-1} dye concentration. From the above data, it is evident that the rate of photocatalytic degradation increases with increasing concentration of the dyes 500-1000 mgL^{-1}. The rate of photocatalytic degradation was found to decrease with further increase in the concentration of dye. Figure2 showed that maximum discoloration of 1000 mgL^{-1} Janus Green was almost complete at 120 min and colour removal rate was up to 93.01%. However, when dye concentration was 500, 1500, 2000, 2500 mgL^{-1} only 74.53%, 80.70%, 88.82%, 87.76% was obtained respectively. After a particular concentration of dye light cannot enter the highly coloured dye solution i.e. at concentrations like 1500, 2000, 2500 mgL^{-1}.

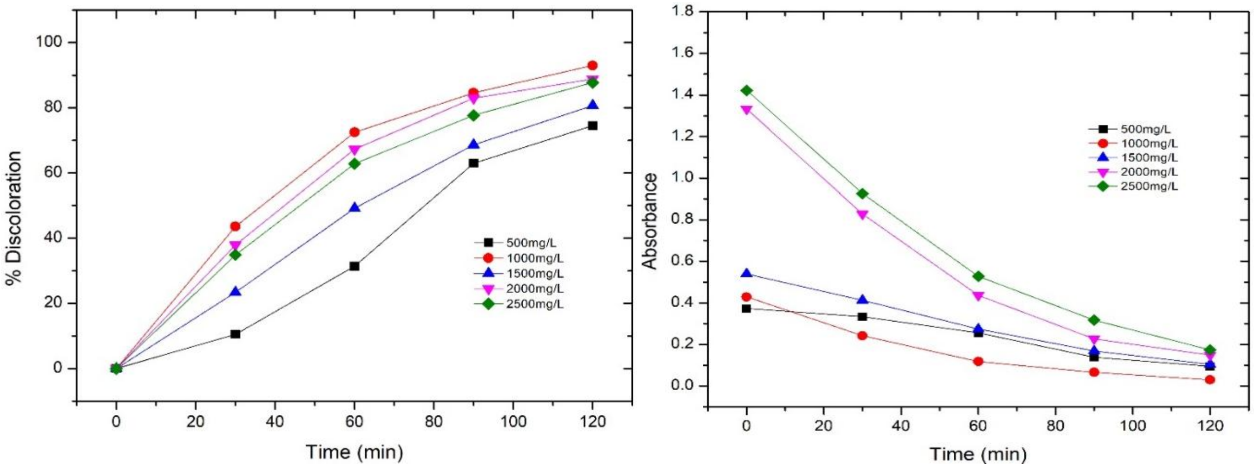


Figure 2 Effect of concentration on degradation of Janus Green. [500-2500 mgL^{-1}concentration of dye, 1500mgL^{-1} of $H_2 O_2$,10.0 pH,100 mg of TiO_2, Light intensity 450×10^2 Lux]

Effect of pH

Figure 3 showed that maximum discoloration of dye is observed at 10.0 pH at 120 min and colour removal rate was up to 93.01%. However, at 2.5 pH, 5.0 pH, 7.5 pH, 12.5 pH only 86.16%, 82.89%, 88.36%, 84.73% was obtained respectively. Hence pH 10.0 was found to be optimum pH for this study and maximum solar degradation of Janus Green was found at pH 10.0. It has been observed that with an increase in pH beyond 10.0 pH resulted into a decrease in the rate of photocatalytic degradation. These observations can be explained on the basis that as the pH of the solution increases, more OH^-ions are available. OH^- ions will generate moreOH radicals by combining with the hole of the semiconductor. These OH are considered to be responsible for this photocatalytic degradation. But the rate of photocatalytic degradation of dye is expected to decreases. There are chances of recombination of OH radicals at higher pH.

Effect of $H_2\,O_2$ addition

Figure 4 showed that maximum discoloration of dye was almost complete with 1500 mgL^{-1} of $H_2\,O_2$at 120 min where as at750 mgL^{-1}, 2250 mgL^{-1}, 3000 mgL^{-1}, 3750 mgL^{-1} of $H_2\,O_2$ only 81.08%, 81.21%, 80.63%, 81.98 % was obtained respectively. Again recombination of OH radical may be the reason for decreases in decoloration.

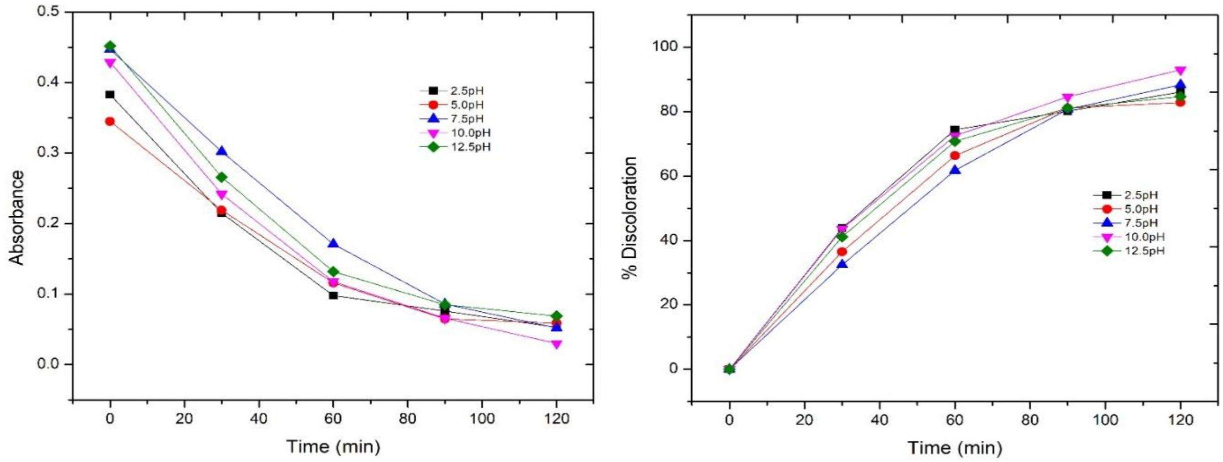


Figure 3 Effect of pH on degradation of Janus Green [1000 mgL^{-1} concentration of dye, 1500mgL^{-1} of $H_2\,O_2$, 2-10.0 pH,100mg of TiO$_2$, Light intensity 450×10^2 Lux]

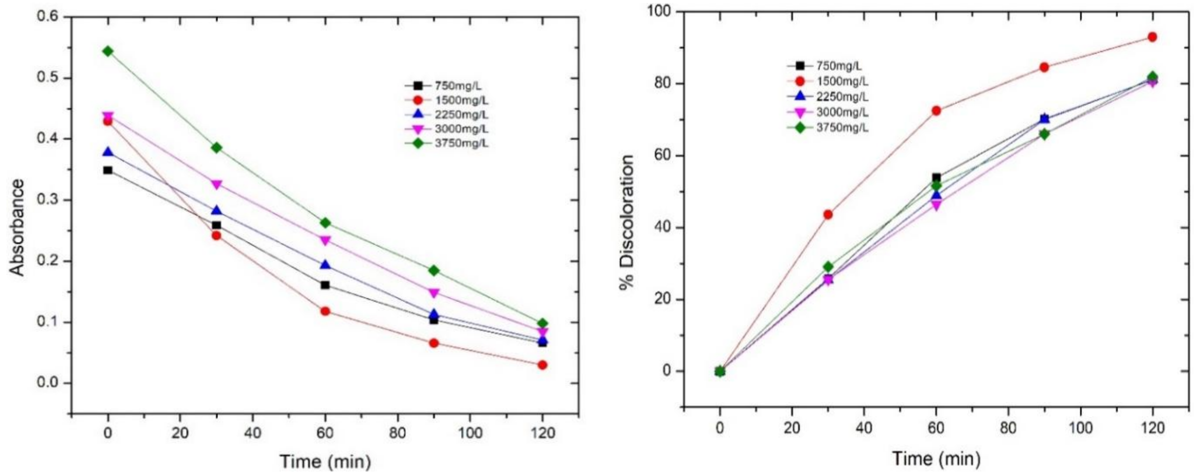


Figure 4 Effect of Hydrogen peroxide on degradation of Janus Green. [1000 mgL^{-1}concentration of dye,750-3750 mgL^{-1} of$H_2\,O_2$,10.0 pH, 100mg of TiO$_2$, Light intensity 450×10^2 Lux]

Effect of amount of semiconductor

The amount of semiconductor also affects the process of dyes degradation and therefore, different amounts of semiconductor were used from 25mg to 125mg. **Figure 5** shows the effect of amount of the TiO$_2$ on photocatalytic degradation of Janus green. In the presence of TiO_2 with Janus green under the dark condition no degradation is observed at 120 min. The result was negligible when solar was used alone. However, in the presence of TiO_2 and H_2O_2in presence of solar light, Janus green was 93.01% degraded within 120 minutes. Figure 5 showed that maximum discoloration of dye was almost complete with 100 mg TiO_2 semiconductor at 120 min. When the amount of semiconductor was 25mg, 50mg, 75mg, 125mg only 86.59%, 89.61%, 88.64%, 86.41% was obtained respectively. Again an optimum of photocatalyst is required for reaction to take place, more amount of photocatalyst makes milky solution and light cannot pass in it.

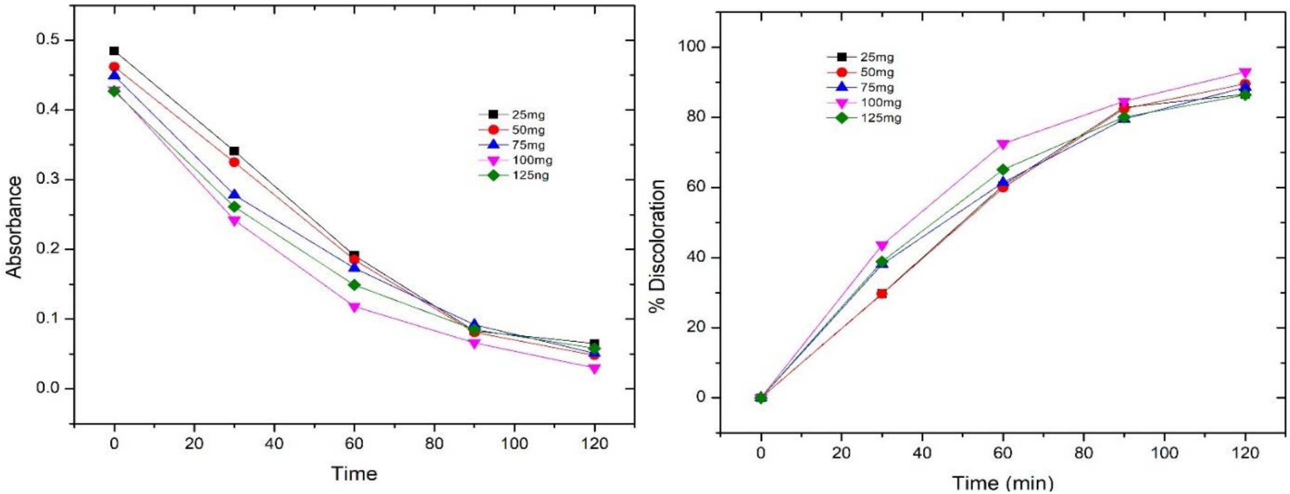


Figure 5 Effect of TiO_2 on degradation of Janus Green. [1000 $mgL^{-1}$of dye,1500mgL^{-1} of H_2O_2,10.0 pH, 25-125mg of TiO_2, Light intensity 450×10^2 Lux]

Effect of light intensity

These data in **Figure 6** indicate that dye degradation is accelerated as the intensity of light was increased, because any increase in light intensity will increase the number of photons striking per unit area of the semiconductor. An almost linear behaviour between light intensity and the rate of reaction was observed. These results confirmed that presence of the solar light was more effective factor especially on sunny day as reported.

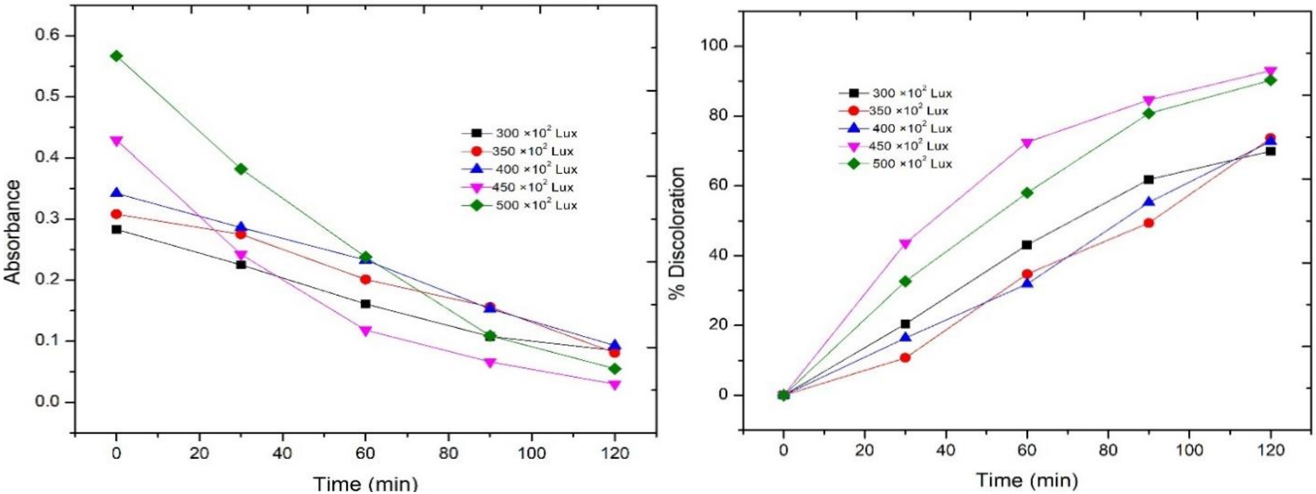


Figure 6 Effect of Light intensity on degradation of Janus Green. [1000 mgL^{-1} of dye,1500mgL^{-1} ofH_2O_2,10.0 pH,100mg of TiO_2,Light intensity 300-500×10^2 Lux]

Addition of scavenger

Scavengers like, methanol, isopropanol were added to experimental set up in range of 1.0 ml– 3.0 ml. It was observed that negligible degradation was observed in presence of methanol and isopropanol because OH radical were removed with the scavenger.

Mechanism

On the basis of above experimental observation, a tentative mechanism has been proposed for the degradation of dye by titanium dioxide semiconductor.

$$1_{Dye_0} \rightarrow 1_{Dye_1} \text{ (Singlet excited state)}$$

$$1_{Dye_1} \rightarrow 3_{Dye_1} \text{ (Triplet excited state)}$$

$$\mathrm{SC} \rightarrow e^{+}h^{+} \text{ or } SC^{+}$$

$$h^{+} + OH^{-}\ (from\ base) \rightarrow {}^{\cdot}OH$$

$$3_{Dye_1} + {}^{\cdot}OH \rightarrow \text{Products}$$

Dye absorbs the light and gets excited to its first singlet state. This gets converted to triplet state through intersystem crossing. On the other hand, the semiconductor gets excited by absorbing light and an electron is excited from its valence band to conduction band leaving behind a hole. This hole abstracts an electron from OH ions generatingOH free radical. The dye is bleached by this OH radical. The participation of OH radical was confirmed by using scavenger which almost stops the degradation reaction.

Conclusion

The photocatalytic degradation of Janus green was examined using Titanium dioxide semiconductor and Hydrogen peroxide under direct solar light. Some parameters such as pH of solution, loading of catalyst and concentration of $H_2 O_2$ are influencing % discoloration of photocatalysis process. Maximum solar degradation was observed at 1000 mgL^{-1}concentration of dye solution, 1500 mgL^{-1}of $H_2 O_2$, 100mg of TiO_2, 10.0 pH, under 450 Lux after 120 minutes.

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References

[1] A. Afkhami, R. Moosavi, Adsorptive removal of Congo red, a carcinogenic textiledye,from aqueous solutions by maghemite nanoparticles, J. Hazard. Mater., 2010,174, 398–403.

[2] I. Arslan, I.A. Balcioglu, Degradation of remazol black b dye and its simulated dye bath wastewater by advanced oxidation processes in heterogeneous and homogeneous media, Color Technol., 2001,117, 38–42.

[3] M.C. Gutierrez, M. Pepio, M. Crespi, Electrochemical oxidation of reactive dyes method validation and application, Color Technol., 2002, 118, 1–5.

[4] A. Stolz, Basic applied aspects in the microbial degradation of azo dyes: a review, Appl. Microbiol. Biotechnol., 2001,56 69–80.

[5] M. Derudi, G. Venturini, G. Lombardi, G. Nano and R. Rota, Biodegradation combined with ozone for the remediation of contaminated soils, European Journal of Soil Biology., 2007, 43(5), 297-303.

[6] M. J. Martin, A. Artola, M. D. Balaguer and M. Rigola, Activated carbons developed from surplus sewage sludge for the removal of dyes from dilute aqueous solutions, Chemical Engineering Journal., 2003, 94(3), 231-239.

[7] A. Ahmad and S. Puasa, Reactive dyes decolourization from an aqueous solution by combined coagulation/micellar-enhanced ultrafiltration process, Chemical Engineering Journal., 2007,132(1), 257- 265.

[8] A. Fujishima, T. N. Rao and D. A. Tryk, Titanium dioxide photocatalysis, Journal of Photochemistry and Photobiology C: Photochemistry Reviews., 2000, 1(1), 1-21.

[9] T. Aye, W.A. Anderson and M. Mehrvar, Photocatalytic treatment of Cibacron Brilliant Yellow 3G-P, Journal of Environmental Science and Health,Part A-Toxic/Hazardous Substances and Environmental Engineering., 2013,38, 1903-1914.

[10] D.M. Marmion, Foods, Drugs, Cosmetics and Medical Devices, third ed, Wiley, New York, Handbook of US Colorants, 1991, 302-308.
[11] Slokar, Y.M., A.M. Le Marechal, 1998. Methods of decoloration of textile wastewaters, Dyes and Pigments, 37(4): 335.
[12] B. Neppolian, H. C. Choi, S. Sakthivel, A. Banunathi, and V. Murugesan, Chemosphere., 2002, 46, 1173.
[13] C. Maynard, Handbook of Industrial Chemistry, Van Nostrand Publ, New York 1983.
[14] Mahvi, A.H., M. Ghanbarian, S. Nasseri, A. Khairi, Mineralization and discoloration of textile wastewater by TiO2 nanoparticles, Journal Desalination., 2009, 239(1), 309-316.
[15] Qamar, M., M. Muneer, A comparative photocatalytic activity of titanium dioxide and zinc oxide by investigating the degradation of vanillin. Desalination., 2009, 249(2), 535-540.
[16] A1be R, et al. Preparation of porous niobium oxides by soft-chemical process and their photocatalytic activity. Chemistry of Materials.,1997, 9(10),2179-2184.
[17] Mishra M, Chun D-M. α-Fe_2O_3 as a photocatalytic material: A review. Applied Catalysis., A: General2015, 498(0),126-141.
[18] A. Afkhami, M. Saber-Tehrani, H. Bagheri,Modified maghemite nanoparticles as an efficientadsorbentfor removing some cationic dyes fromaqueous solution, Desalination., 2010,263, 240-248.
[19] C. E. Bonancea, G. M. do Nascimento, M. L. deSouza, M. L. A. Temperini, P. Corio, Surfaceenhancedraman study of electrochemical andphotocatalytic degradation of the azo dye Janus Green b, Appl. Catal., B: Environ., 2008, 77, 339-345.

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