

Role of β -Cyclodextrin in Enhanced Photocatalytic Decolorization of Metanil Yellow Dye with TiO_2

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Received: 22 May 2018;

Accepted: 13 June 2018;

Published online: 31 August 2018;

AJC-19061

Photocatalytic decolorization of metanil yellow dye (azo dye) in aqueous solution was performed using pure TiO_2 and TiO_2 - β -cyclodextrin catalysts. The photocatalytic decolorization of metanil yellow was carried out under UV light irradiation for 60 min. TiO_2 - β -cyclodextrin system showed higher decolorization efficiency than pure TiO_2 . The effect of significant operational parameters such as initial concentration of dye, catalysts loading, initial pH of dye solution and irradiation time were investigated. The photocatalytic decolorization by TiO_2 and TiO_2 - β -cyclodextrin systems followed Langmuir-Hinshelwood mechanism. The mechanism of enhanced photodecolorization of metanil yellow in presence of β -cyclodextrin is proposed.

Keywords: Metanil yellow dye, β -Cyclodextrin, Photodecolorization.

INTRODUCTION

Titanium dioxide is used as an effective candidate for the heterogeneous photocatalytic processes because it is highly photoactive, inexpensive, non-toxic, photostable, commercially available and chemically inert [1]. Various industries such as paper, textile, ink, varnishes and paints discharge their large amount of unreacted dyes and dye intermediates into the aquatic systems. These contaminants result in high BOD, COD, toxicity, bad smell and colouration [2]. The presence of colour and its causative compounds in water make them undesirable for domestic or industrial usages as colour is visible and can be an indication of pollution [3]. Hence, the decolorization and mineralization of wastewater have received an increased attention.

Several methods have been developed for treatment of wastewater. The dye effluents can be treated by various traditional methods such as biological methods, flocculation, reverse osmosis, adsorption on activated carbon and ion-exchange method [4-6]. These methods transfer the pollutants from one phase to other phase causing secondary pollution. Heterogeneous photocatalysis is one of the promising advanced oxidation techniques applied for the degradation and mineralization of pollutants such as organic compounds, dyes and fertilizers [7]. Hence, in recent years, researches on semiconductor based heterogeneous photocatalysis for the remediation of pollutants have grown remarkably.

The energy gap of TiO_2 is about 3.0-3.4 eV. Therefore, to trigger the photocatalytic activity of TiO_2 , light having energy in the UV region is required. Another drawback of TiO_2 is its high rate of recombination of photogenerated electrons and holes. Efforts have been taken to prevent the recombination and to enhance the photocatalytic activity by surface modification and doping. Doping of metals or non-metals into metal oxide could promote the visible light activity; but it can also cause thermal instability, crystal instability and increases the trapping of charge carriers which may reduce the photocatalytic efficiency [8]. Therefore, design and synthesis of novel photocatalysts are becoming a quest in the photocatalytic field.

β -Cyclodextrins (β -CDs) are doughnut shaped oligosaccharides composed of seven glucopyranose monomer units with hydrophobic inner cavity and hydrophilic outer ring. Through non-covalent interactions, the β -CD can form host-guest inclusion complexes with organic compounds in both solid and liquid phases. The encapsulation of guest molecules into the cavity of β -CD modifies their physicochemical properties [9]. β -Cyclodextrin improves the photocatalytic decomposition of the guests entrapped into its hydrophobic cavity through charge transfer from the photoexcited semiconductor surface to electron acceptors (guests) [10,11]. This research work was aimed to explore and utilize β -CD's property of trapping the guests and holes to enhance the photodegradation of dyes.

Metanil yellow is an acidic monoazo dye and known to cause irreparable damage to the liver and heart [12]. Hence, Metanil yellow dye was chosen as the model dye pollutant. The effects of initial concentration of dye, initial pH of metanil yellow dye solution, the amount of TiO_2 and illumination time on the removal of metanil yellow dye were investigated.

EXPERIMENTAL

All the chemicals, β -CD, TiO_2 and metanil yellow dye were utilized as procured from Merck, India. The stock solution of 1000 ppm of metanil yellow dye was prepared by dissolving 1 g of dye powder in 1 L of water and working solutions of required concentrations were prepared by dilution.

Photocatalytic experiment: The batch type of photocatalytic reactions were carried out in Heber Multi Lamp photoreactor (Model: HMP 88). The reaction solutions containing metanil yellow dye and TiO_2 with and without β -CD were stirred for 0.5 h in dark to ensure the adsorption-desorption equilibrium. The reaction solutions were withdrawn from the reactor at different time intervals and centrifuged. The absorbance of supernatant solutions was measured using UV-visible spectrophotometer. The concentration of metanil yellow dye in the analytes was calculated and the percentage of removal of dye was estimated using the following equation:

$$\text{Removal of dye (\%)} = \frac{C_i - C_t}{C_i} \times 100$$

where, C_i is the initial concentration of metanil yellow dye and C_t is the concentration of metanil yellow dye at time 't'.

RESULTS AND DISCUSSION

Effect of initial concentration of metanil yellow dye:

The effect of initial concentration of metanil yellow dye on the photodecolorization was studied with different concentrations of it ranging from 20 to 40 ppm for pure TiO_2 and TiO_2 - β -cyclodextrin systems at its natural pH 6.7. The overall illumination time was fixed at 60 min. The dose of TiO_2 was fixed as 0.5 g L^{-1} . For TiO_2 - β -cyclodextrin systems, the molar ratio of metanil yellow dye: β -CD was kept as 1:1. It was observed that the percentage of decolorization was decreased with increase in concentration of metanil yellow dye for both pure TiO_2 and TiO_2 - β -cyclodextrin photocatalytic systems and is shown in Fig. 1. As the concentration of dye increases, more number of metanil yellow dye molecules gets adsorbed on the surface of photocatalyst and therefore the light photons could not react with the catalyst surface. Also at higher concentration, the light photons travel up to a smaller distance only due to scattering of photons by dye molecules [13]. For the further studies, the optimum concentration of metanil yellow dye was taken as 40 ppm.

Effect of catalyst dose: Experiments were carried out to investigate the effect of TiO_2 loading for the maximum removal of colour from the aqueous solution of metanil yellow dye. TiO_2 dosage varied from 0.1 to 0.6 g L^{-1} . Fig. 2 revealed that the percentage of decolorization increases with increase in dose of the catalysts up to 0.5 g L^{-1} and then decreases. With increase in the amount of photocatalyst, the number of active sites available on the surface of photocatalysts for the adsorption

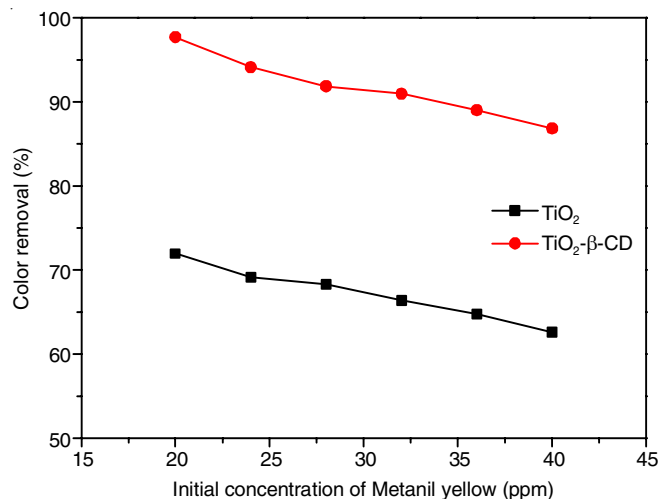


Fig. 1. Percentage of color removal of metanil yellow dye with various initial concentrations by pure TiO_2 and TiO_2 - β -CD

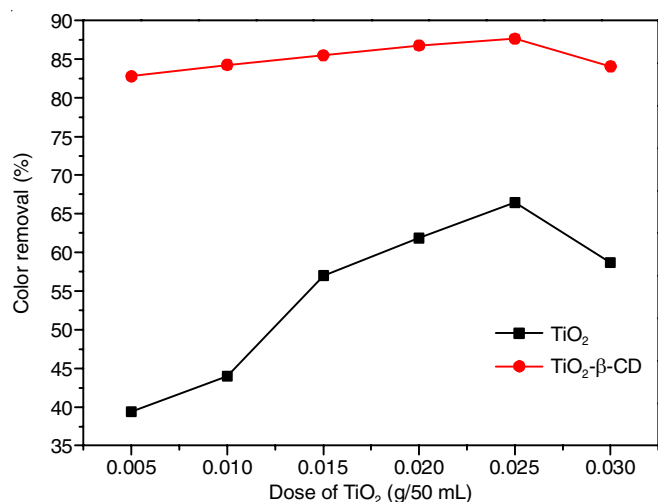


Fig. 2. Percentage of color removal of metanil yellow dye by different loadings of pure TiO_2 and TiO_2 - β -CD

of metanil yellow dye molecules increases and this led to the higher percentage of decolorization [14]. Further increase in the amount of photocatalysts cause agglomeration of the catalyst particles and so a part of catalyst surface was unavailable for photon absorption. This leads to reduced generation of $\text{OH}^\bullet$ radicals and superoxide radicals which are respectively the principal oxidizing and reducing species in photocatalysis [15]. Also, increased concentration of TiO_2 leads to opaqueness and scatter the light photons. Thus, the interaction of light photons with the over dosage of photocatalysts was limited and led to decreased percentage of removal dye [16].

Effect of pH: The industrial effluents discharged into the water stream are either acidic or basic. Therefore, the study of pH effect is inevitable. The zero point charge (Pzc) value of TiO_2 is about 6.4. At $\text{pH} < \text{Pzc}$, the surface of TiO_2 is positively charged and at $\text{pH} > \text{Pzc}$, the surface is negatively charged as per the following reactions:



Metanil yellow dye, an anionic azo dye with sulphonate group. Therefore, at different pH less than Pzc of TiO_2 , more

metanil yellow dye molecules are attracted towards TiO_2 due to the electrostatic force of attraction existing among the positively charged TiO_2 and dye anion. The maximum percentage of removal of metanil yellow dye was observed at acidic pHs in both the systems (Fig. 3). The coulombic repulsion of dye anion by increased density of TiO^- at higher pHs was resulted in the decrease in percentage of removal [17].

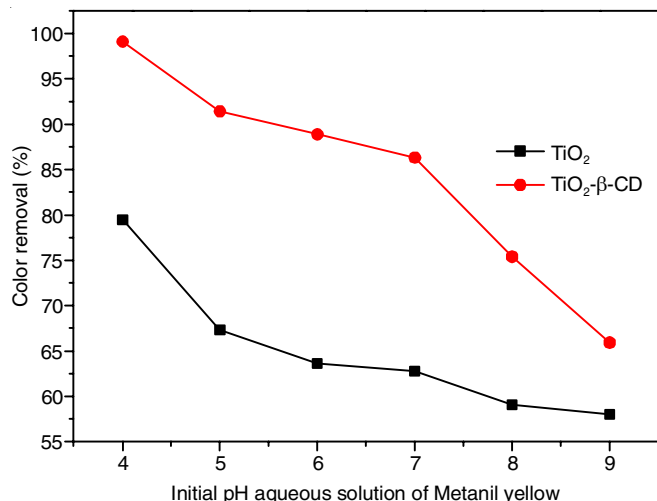


Fig. 3. Percentage of color removal of metanil yellow dye under different pHs by pure TiO_2 and TiO_2 - β -CD

Effect of illumination time and kinetic analysis: The effects of the illumination time on photocatalytic efficiency of pure TiO_2 and TiO_2 - β -CD systems for maximum percentage of colour removal are shown in Fig. 4. The temporal changes in the UV-visible absorbance of Metanil yellow dye upon photocatalysis by pure TiO_2 and TiO_2 - β -cyclodextrin systems are shown in Fig. 5 and 6, respectively. It was seen that there is no significant change in the absorption pattern of UV-visible spectra during illumination except that intensity of peak at 434 nm decreases gradually. The gradual decrease in the absorbance value revealed the degradation of metanil yellow dye with increase in illumination time and no new peaks were found in the absorption spectra. Moreover, absorbance peak at $\lambda_{\text{max}} = 275 \text{ nm}$ was decreased gradually and finally disappeared in both the cases. This trend confirmed that the dye is completely degraded and no intermediate compound is formed during the photocatalytic decolorization reaction [18]. The plots of $\log C_0/C_t$ vs. time (Fig. 7) is a straight line indicated that photodecolorization followed Langmuir-Hinshelwood's pseudo-first order kinetics [19]. The rate constants were determined from the slopes of linear regressions. The linear regression coefficients R^2 and rate constants are listed in Table-1. It is observed that the rate of decolorization by TiO_2 - β -cyclodextrin system was faster than pure TiO_2 .

TABLE-1
COMPARISON OF PERCENTAGES OF DECOLORIZATION, R^2
AND RATE CONSTANTS FOR PURE TiO_2 AND TiO_2 - β -CD

Photocatalytic system	Optimum weight of the photocatalyst	Decolorization (%)	R^2	Rate constant (min^{-1})
Pure TiO_2	0.5 g L^{-1}	67.44	0.9359	0.0067
TiO_2 - β -CD	0.5 g L^{-1}	94.52	0.9909	0.0221

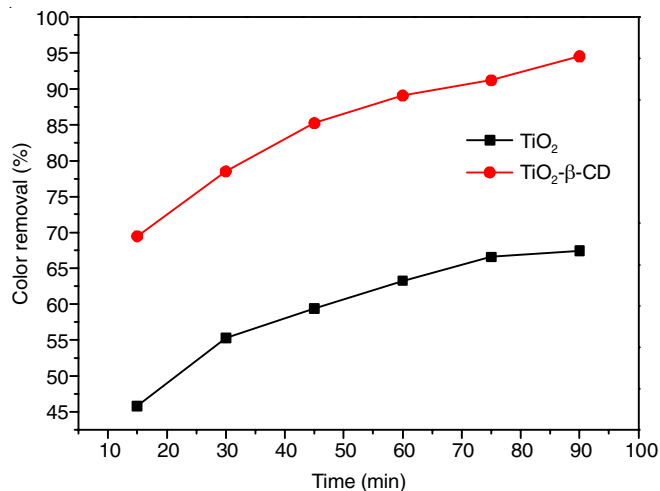


Fig. 4. Percentage of color removal of metanil yellow dye with contact time

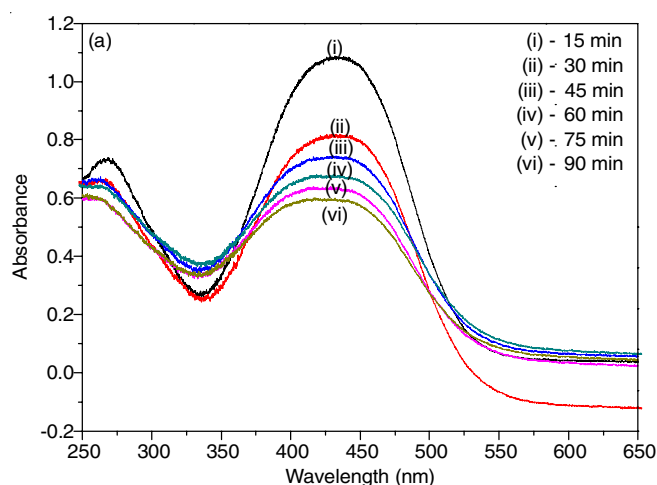


Fig. 5. Absorbance spectra of metanil yellow dye under different illumination time for pure TiO_2

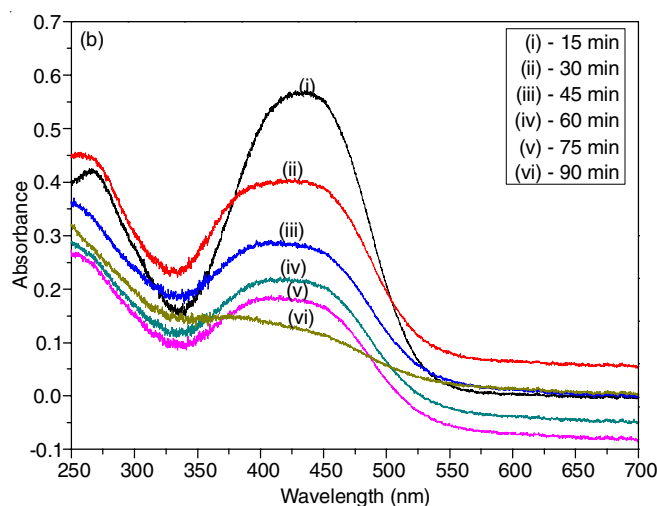


Fig. 6. Absorbance spectra of metanil yellow dye under different illumination time for TiO_2 - β -CD

Fig. 8 shows the photostability and adsorptive property of metanil yellow dye with and without β -cyclodextrin. It was observed that metanil yellow dye undergo photolysis to a very small extent of 1 % and the amount of metanil yellow dye adsorbed onto TiO_2 was increased 1.8 times in presence of β -cyclodextrin.

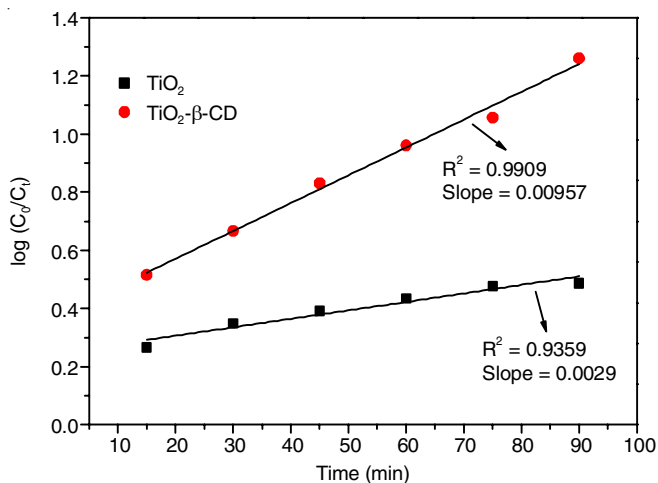


Fig. 7. Langmuir-Hinshelwood kinetics for decolorization of metanil yellow dye by pure TiO_2 and TiO_2 - β -CD

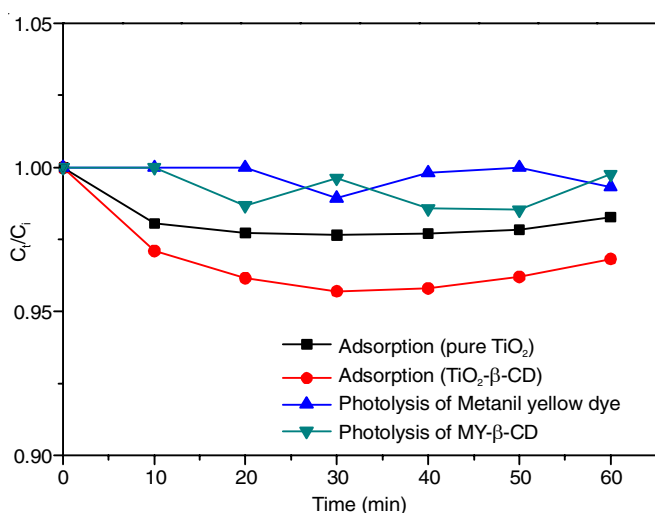
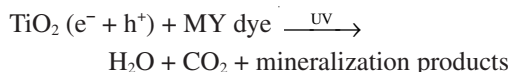


Fig. 8. Extent of color removal of metanil yellow dye under different experimental conditions

Mechanism of enhanced photodecolorization of metanil yellow dye: On the basis of above results, the mechanism of enhancement of photocatalytic efficiency of TiO_2 for the decolorization of metanil yellow dye in presence of β -cyclodextrin is explained schematically (Fig. 9). The more generalized one step mechanism for heterogeneous photocatalytic decolorization of metanil yellow dye by bare TiO_2 could be written as:



The following reactions explain the stepwise mechanism of enhanced photodecolorization of metanil yellow dye by TiO_2 - β -cyclodextrin system [20,21].

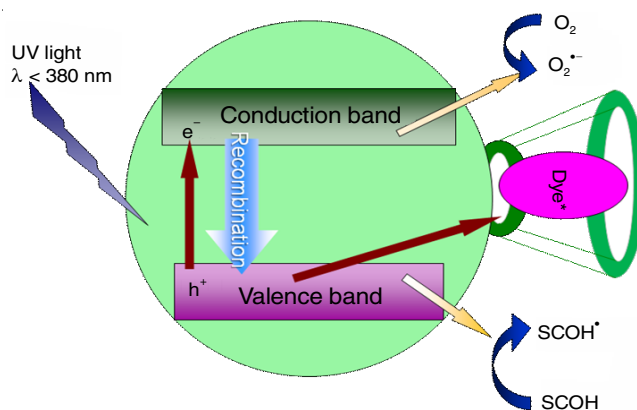
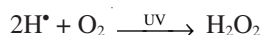
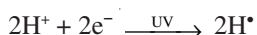
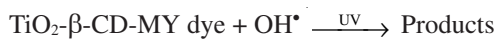
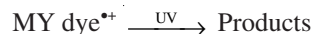
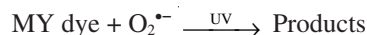
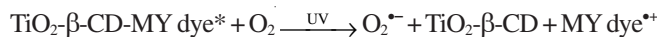
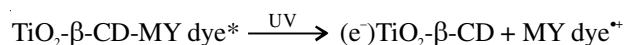
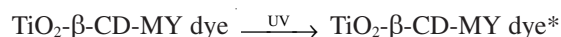
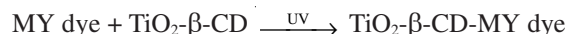
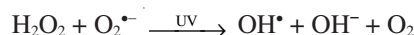


Fig. 9. Schematic diagram illustrating the mechanism of photocatalysis by TiO_2 - β -CD (SC-Semiconductor- TiO_2)



Conclusion

It is concluded from the results of the present study that TiO_2 - β -cyclodextrin system exhibited higher photocatalytic decolorization efficiency than pure TiO_2 under UV light illumination. The effects of various operational parameters were studied for both TiO_2 and TiO_2 - β -cyclodextrin systems. It was found that the presence of β -cyclodextrin in the suspension containing TiO_2 and metanil yellow dye has enhanced the photodecolorization efficiency of TiO_2 . Thus, β -cyclodextrin could be successfully utilized in the photocatalysis process for the enhancement of photocatalytic efficiency of semiconductor oxides.

ACKNOWLEDGEMENTS

The author gratefully acknowledges to The Principal and Management of The Standard Fireworks Rajaratnam College for Women, Sivakasi and UGC, New Delhi, India for the financial assistance provided through F. MRP-4208/12 (MRP/UGC-SERO).

REFERENCES

- Y.Y. Gurkan, E. Kasapbasi and Z. Cinar, *Chem. Eng. J.*, **214**, 34 (2013); <https://doi.org/10.1016/j.cej.2012.10.025>.
- S. Senthilvelan, V.L. Chandraboss, B. Karthikeyan, L. Natanapatham and M. Murugavelu, *Mater. Sci. Semicond. Process.*, **16**, 185 (2013); <https://doi.org/10.1016/j.mssp.2012.04.018>.
- M.A. Saepurahman, M.A. Abdullah and F.K. Chong, *J. Hazard. Mater.*, **176**, 451 (2010); <https://doi.org/10.1016/j.jhazmat.2009.11.050>.

4. C. Sahoo, A. Gupta and A. Pal, *Dyes Pigments*, **66**, 189 (2005); <https://doi.org/10.1016/j.dyepig.2004.09.003>.
5. U.G. Akpan and B.H. Hameed, *J. Hazard. Mater.*, **170**, 520 (2009); <https://doi.org/10.1016/j.jhazmat.2009.05.039>.
6. Z. Mesgari, M. Gharagozlou, A. Khosravi and K. Gharanjig, *Appl. Catal. A Gen.*, **411-412**, 139 (2012); <https://doi.org/10.1016/j.apcata.2011.10.031>.
7. S. Valencia, X. Vargas, L. Rios, G. Restrepo and J.M. Marín, *J. Photochem. Photobiol. Chem.*, **251**, 175 (2013); <https://doi.org/10.1016/j.jphotochem.2012.10.025>.
8. M.Y. Xing, W.Z. Fang, M. Nasir, Y. Ma, J. Zhang and M. Anpo, *J. Catal.*, **297**, 236 (2013); <https://doi.org/10.1016/j.jcat.2012.10.014>.
9. P. Mura, *J. Pharm. Biomed. Anal.*, **101**, 238 (2014); <https://doi.org/10.1016/j.jpba.2014.02.022>.
10. M. Chen, G. Diao and E. Zhang, *Chemosphere*, **63**, 522 (2006); <https://doi.org/10.1016/j.chemosphere.2005.08.033>.
11. G. Wang, F. Wu, X. Zhang, M. Luo and N. Deng, *Fresenius Environ. Bull.*, **15**, 61 (2006).
12. P.P. Nath, K. Sarkar, P. Tarafder and G. Paul, *Int. J. Pharma Bio Sci.*, **4**, 685 (2013).
13. S. Naskar, S.A. Pillay and M. Chanda, *J. Photochem. Photobiol. Chem.*, **113**, 257 (1998); [https://doi.org/10.1016/S1010-6030\(97\)00258-X](https://doi.org/10.1016/S1010-6030(97)00258-X).
14. C.F. Cano-Guzmán, J.P. Pérez-Orozco, I. Hernández-Pérez, L. González-Reyes, V. Garibay-Febles and R. Suárez-Parra, *J. Textile Sci. Eng.*, **4**, 155 (2014); <https://doi.org/10.4172/2165-8064.1000155>.
15. N.U. Sangari, B. Jothi, S.C. Devi and S. Rajamani, *J. Water Process Eng.*, **12**, 1 (2008); <https://doi.org/10.1016/j.jwpe.2016.05.011>.
16. S. Chakrabarti and B.K. Dutta, *J. Hazard. Mater.*, **112**, 269 (2004); <https://doi.org/10.1016/j.jhazmat.2004.05.013>.
17. N.M. Mahmoodi, M. Arami, N.Y. Limaee, K. Gharanjig and F.D. Ardejani, *Colloids Surf. A Physicochem. Eng. Asp.*, **290**, 125 (2006); <https://doi.org/10.1016/j.colsurfa.2006.05.012>.
18. J. Bandara, K. Tennakone and P.P.B. Jayatilaka, *Chemosphere*, **49**, 439 (2002); [https://doi.org/10.1016/S0045-6535\(02\)00306-5](https://doi.org/10.1016/S0045-6535(02)00306-5).
19. J.H. Zeng, B.B. Jin and Y.F. Wang, *Chem. Phys. Lett.*, **472**, 90 (2009); <https://doi.org/10.1016/j.cplett.2009.02.082>.
20. S. Pitchaimuthu, S. Rajalakshmi, N. Kannan and P. Velusamy, *Appl. Water Sci.*, **5**, 201 (2015); <https://doi.org/10.1007/s13201-014-0181-y>.
21. S. Rajalakshmi, S. Pitchaimuthu, N. Kannan and P. Velusamy, *Desal. Water Treat.*, **52**, 3432 (2014); <https://doi.org/10.1080/19443994.2013.809024>.