Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.932706

55 (2015) 2229–2236
August

Taylor & Francis
Taylor & Francis Group

Evaluation on the molecular structure of azo dye in photocatalytic mineralization under solar light irradiation

Wan Fadhilah Khalik[a], Soon-An Ong[a,*], Li-Ngee Ho[b], Yee-Shian Wong[a], Nik Athirah Yusoff[a], Fahmi Ridwan[a]

[a]*School of Environmental Engineering, University Malaysia Perlis, Arau 02600, Perlis, Malaysia, Tel. +6011 14920901; Fax: +604 9798636; email: wanfadhilah@ymail.com (W.F. Khalik), Tel. +604 9798986; emails: ongsoonan@yahoo.com, saong@unimap.edu.my (S.-A. Ong), Tel. +604 9798971; email: yswong@unimap.edu.my (Y.-S. Wong), Tel. +6013 4725670; email: athirah_yusoff@ymail.com (N.A. Yusoff), Tel. +604 9798981; email: drfahmi@unimap.edu.my (F. Ridwan)*
[b]*School of Material Engineering, University Malaysia Perlis, Arau 02600, Perlis, Malaysia, Tel. +604 9768196; email: holingee@yahoo.com*

Received 4 October 2013; Accepted 28 May 2014

ABSTRACT

The aim of this study was to investigate the effects of number of sulphonic groups on solar photocatalytic degradation of Acid Orange 7 (AO7), Orange G (OG), New Coccine (NC), Reactive Black 5 (RB5) and Reactive Green 19 (RG19) in aqueous solution. The data obtained for photocatalytic degradation of AO7, OG, NC, RB5 and RG19 were well fitted with the Langmuir–Hinshelwood kinetic model. The pseudo-first-order rate constant of RG19 with six sulphonic groups was the highest among the dyes in this study. Results showed that photocatalytic degradation rate of the azo dyes increased following the increase of the number of sulphonic groups of the dyes in the sequence of: AO7 < OG < NC < RB5 < RG19.

Keywords: Azo dye; Mineralization; Photocatalytic; Solar light irradiation; Sulphonic group

1. Introduction

Textile, pulp and paper mills, printing and leather industries are the primary sources in the discharge of partially treated dyes contained in the wastewater. The dye effluents that are released have one or more azo bonds such as Reactive Green 19 (RG19), Orange G (OG) and New Coccine (NC) [1]. These dyes will become toxic and hazardous to human and aquatic life when they are released into the environment in high concentration. There are many treatment techniques that can be employed for dye removal such as adsorption [2], coagulation and flocculation [3], biological processes [4] and membrane filtration [5]. However, most of the treatment techniques could only transfer the azo dyes from one phase to another, and they also generate plenty of chemical and biological sludge, which requires additional operating cost for further disposal [6].

The treatment technique of solar photocatalysis with a combination of solar energy and photocatalyst from semiconductor attracts the attention of researchers due to its higher treatment efficiency. It could be considered as a green technology compared with other methods [7]. The selection of semiconductor as photocatalyst for mineralization of azo dyes is important

---

*Corresponding author.

because the band gap energy of the semiconductor would affect the efficiency in colour removal. Although ZnO and TiO_2 have the same band gap energy, it was reported that ZnO was more effective in dye removal compared with TiO_2 under solar irradiation [7]. There are many reports on the photocatalytic degradation of azo dyes such as synthesis of nanophotocatalysts with different methods [8,9], doping to increase the reactivity of photocatalyst [10], effects of various operating parameters [11,12] and determination of the intermediate products [13]. However, study on the effects of the number of sulphonic groups in azo dyes on the photocatalytic degradation rate has still not well documented. The main objective of this study was to investigate the effects of sulphonic groups of the dyes on the solar photocatalytic degradation rate. A total of five azo dyes: Acid Orange 7 (AO7), OG, NC, Reactive Black 5 (RB5) and RG19 with different number of sulphonic groups were selected in this study.

2. Materials and methods

2.1. Chemical

Five azo dyes: AO7, OG, NC, RB5 and RG19 were supplied by Acros Organic and Sigma Aldrich. The chemical structure and molecular weight of all dyes are shown in Table 1. Zinc oxide (ZnO) was supplied by HmBG with molecular weight of 81.37 g/mol. All chemicals were analytical graded and used without further purification. The water used in sample preparation and dilution was ultrapure water.

2.2. Photocatalytic procedures

The stock solutions of the five azo dyes: AO7, OG, NC, RB5 and RG19 were prepared in concentrations of 1.0 g/L at pH 9. The experimental set-up is shown in Fig. 1. The photocatalytic degradation of dyes was conducted in 1,000 mL beakers, well mixed with magnetic stirrer and exposed to solar light irradiation. In each experiment, an appropriate amount of azo dyes from stock solution was diluted to 500 mL with ultrapure water. The concentration of azo dyes tested in this study was 100 mg/L. The amount of ZnO added as photocatalyst into the azo dye solutions was 0.1 g. The solar photocatalytic process was conducted for 5 h and about 15 mL of water sample was collected from the beakers with a syringe at interval time of 0, 0.5, 1, 1.5, 2, 3, 4 and 5 h. The collected water samples were filtered to remove the ZnO particles. The clear water samples would be analysed to determine the concentration of AO7, OG, NC, RB5 and RG19 by UV–Vis spectrophotometer (Hitachi U-2800, Japan). The maximum absorbance wavelength (λ_{max}) of AO7, OG, NC, RB5 and RG19 was set at 486, 512, 536, 597 and 627 nm, respectively. The mineralization of azo dyes was monitored through changes in UV–vis spectrum and chemical oxygen demand (COD). The COD value was determined by HACH DR2800 spectrophotometer.

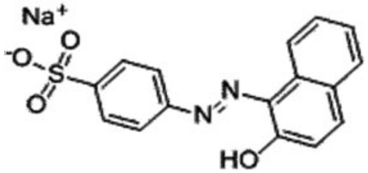
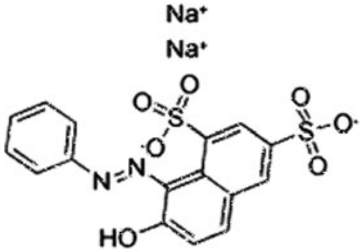
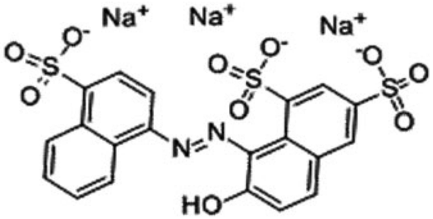
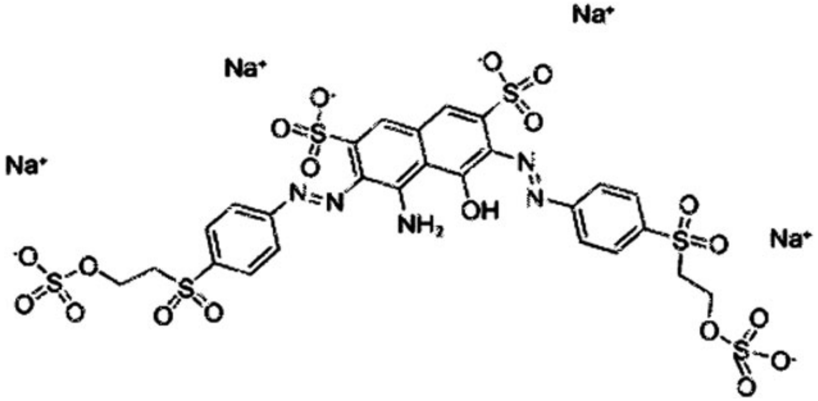
3. Results and discussion

3.1. Photocatalytic degradation of dyes

Most of the photocatalytic research was carried out under UV light irradiation in laboratory [14–16]. However, in this study, natural sunlight was the main source of irradiation. Sunlight contains 4% of UV light and 43% of visible light [17], the photocatalytic degradation of dyes in this study was mainly due to visible light irradiation. Five azo dyes (AO7, OG, NC, RB5 and RG19) with initial concentration of 100 mg/L were placed under direct solar light irradiation and in a dark place, respectively, with 0.1 g ZnO for 5 h. As shown in Fig. 2(a), the concentration of AO7, OG, NC, RB5 and RG19 was reduced to 79.5, 65.6, 10.9, 0 and 0 mg/L, respectively, after 5 h irradiated with solar light. The colour removal could achieve 100% for RB5 and RG19 within 3 h of solar light irradiation whereas only 13, 25 and 69% in the case of AO7, OG and NC, respectively. This showed that the combination between ZnO and solar energy could degrade the azo dyes and the solar energy was sufficient to activate the catalyst [18]. The main oxidizing species involved in the photocatalytic oxidation by ZnO were positive holes (h^+) and hydroxyl radical (OH•) [18,19]. Richard et al. [20] reported that the main process at low substrate concentration was mainly due to the oxidation by OH• whereas the oxidation by positive holes (h^+) was at high substrate concentration.

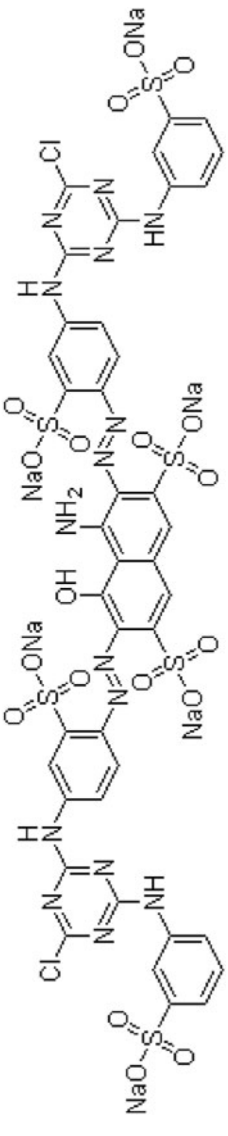
The azo dye removal also occurred in the absence of solar light through the adsorption process on the ZnO surface as shown in Fig. 2(b). AO7, OG, NC, RB5 and RG9 with the number of sulphonic groups of one, two, three, five and six, respectively, showed removal efficiency of 1, 5, 10, 12 and 13% within 5 h of contact time. This indicates that the number of sulphonic group could contribute to the adsorption capacity of the azo dye onto the surface of ZnO. Although, in the study of the effect of molecular structure conducted by Tanaka et al. [19] showed that the photodegradation rates of diazo dyes (Acid Black 1 and Congo Red) were lower compared with the monoazo dyes (OG and AO7) in this study, the results showed that sulphonic groups play an important role in the degradation of azo dyes. As shown in Fig. 2(a), the

Table 1
Molecular structure and molecular weight of azo dyes

Type of dyes	Molecular structure	Molecular weight (g/mol)
Acid Orange 7 (AO7)		350.32
Orange G (OG)		425.27
New Coccine (NC)		604.47
Reactive Black 5 (RB5)		991.82

(*Continued*)

Table 1. (*Continued*).

Type of dyes	Molecular structure	Molecular weight (g/mol)
Reactive Green 19 (RG19)		1,418.92

degradation rate of diazo dyes (RB5 and RG19) was higher compared with monoazo dyes (AO7, OG and NC). Furthermore, it could be observed that the removal efficiency increased in the sequence of AO7 < OG < NC < RB5 < RG19, while the number of sulphonic groups also increased following the same sequence: AO7 < OG < NC < RB5 < RG19. Hence, this attested that the enhanced degradation rate of azo dyes in this study was affected by the increasing number of sulphonic groups in the dyes. The interaction between ZnO and dye can cause adsorption of the dye molecule onto the surface of ZnO. The higher number of sulphonic groups in dye molecule will lead to the higher photocatalytic degradation rate. The results obtained in this study were compatible with the study of Wang [21] who investigated the photocatalytic degradation of eight commercial dyes with different structure and substitute groups. He reported that Reactive Brilliant Red (K-2G) with four sulphonic groups exhibited higher photodegradation rate that Reactive Brilliant Red (K-2BP) with three sulphonic groups.

Langmuir–Hinshelwood kinetic model was used to describe the photo-oxidation kinetics of the dyes due to the involvement of adsorption process in the heterogeneous photocatalytic oxidation process [22–24]. The Langmuir–Hinshelwood model is shown as below:

$$Rate = -\left(\frac{dC}{dt}\right) = \frac{kKC}{1 + KC} \tag{1}$$

where C is the concentration of azo dye (mg/L), t is the irradiation time, k is the reaction rate constant (mg/L h) and K is the adsorption coefficient of dye onto the photocatalyst particle (L/mg). For low concentrations of dyes ($KC \ll 1$), KC in the denominator can be neglected and integrated with respect to time t.

$$\ln\,(C_0/C) = kKt = k_{\text{app}} \cdot t \tag{2}$$

When a plot of ln (C_0/C) vs. time results in a straight line, its slope is the pseudo-first-order decolourization constant (k_{app}). k_{app} is the apparent rate constant calculated from the curves (per h). C_0 is the initial concentration of azo dye (mg/L).

Table 2 depicts the k_{app} and correlation constant (R^2) value for five azo dyes under solar photocatalytic process. The data obtained from photocatalytic degradation of AO7, OG, NC, RB5 and RG19 followed the Langmuir–Hinshelwood model. As shown in Table 2, the pseudo-first-order rate constant of five dyes increased which showed that the degradation rate of dye increased with the increasing number of sulphonic groups in the azo dye molecule. As

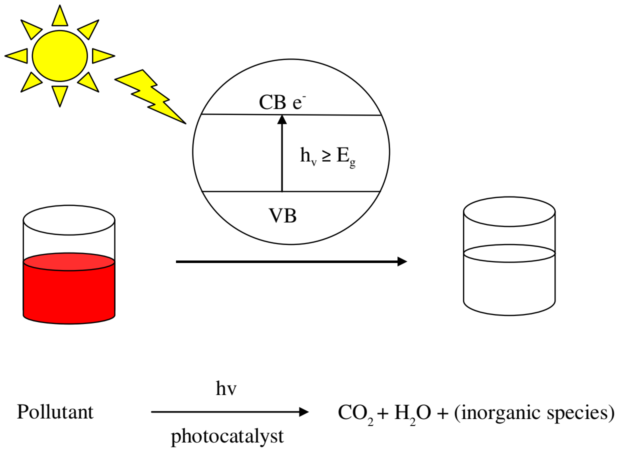


Fig. 1. Schematic diagram for experimental set up.

suggested by Konstantinou and Albanis [25], the expression for the rate of photomineralization of organic substrates such dyes with irradiated TiO_2 follows the Langmuir–Hinshelwood law for four possible situations: reaction (a) occurs with both of species being in solution, (b) occurs between a radical in solution and an adsorbed substrate molecule, (c) takes place between two adsorbed substances and (d) takes place between a radical which linked to the surface and a substrate molecule in solution. The photocatalytic degradation rate of azo dye may also be affected by other factors such as molecular structure and weight [26], number of azo bonds [19] and adsorption capacity onto the catalyst [19]. However, the result of this study showed that the number of sulphonic groups in a dye molecule played an important role in determining sequence of photocatalytic degradation rate. Besides the first-order process and azo bond breakage, the intensity of solar light also needs to be taken into consideration. This was reported by Tsuchiya et al. [27] who stated that the concentration of the active oxygen species, which was proportional to the UV intensity, would affect the decomposition rates of azo dye. The degradation of azo dye followed a multi-step reaction where intermediate products were produced when azo bond was attacked by hydroxyl radicals, which delocalized the electron in the double bonds to connect the left and right parts of the π-electron [27].

Table 2
Kinetic photocatalytic degradation of AO7, OG, NC, RB5 and RG19 at concentration 100 mg/L

Dyes	k_{app} (h^{-1})	R^2
AO7	0.046	0.926
OG	0.087	0.955
NC	0.383	0.975
RB5	0.783	0.984
RG19	1.177	0.993

Notes: (R^2 is correlation constant)

3.2. Wavelength scan

Fig. 3 illustrates the changes of UV–vis spectra for AO7, OG, NC, RB5 and RG19, respectively, in an aqueous solution with 100 mg/L concentration. There are peaks for all dyes AO7 (483, 308 and 228 nm), OG (477, 329 and 247 nm), NC (505, 331 and 215 nm), RB5 (600, 392, 306 and 254 nm) and RG19 (628, 419, 258 and 216 nm), respectively. The maximum wavelength, λ_{max} of RG19 declined till the baseline of the spectra within 5 h of solar light irradiation compared with the AO7. This showed that the degradation rate of RG19 rapidly decreased compared with AO7. This might suggest that the number of sulphonic groups plays a significant role in the degradation rate of the dyes than the number of azo bonds in the dye molecule. As shown in Fig. 3(d) and (e), the peaks at UV region were decreased till the baseline within 5 h of solar light irradiation, which indicated the destruction of

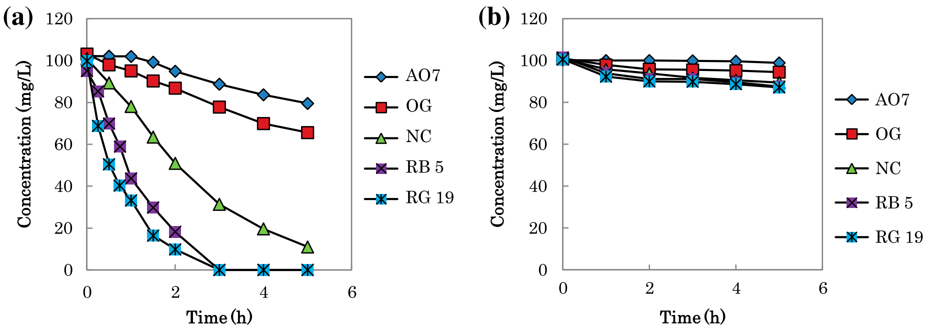


Fig. 2. Photocatalytic degradation of azo dyes (a) with and (b) without solar light irradiation.

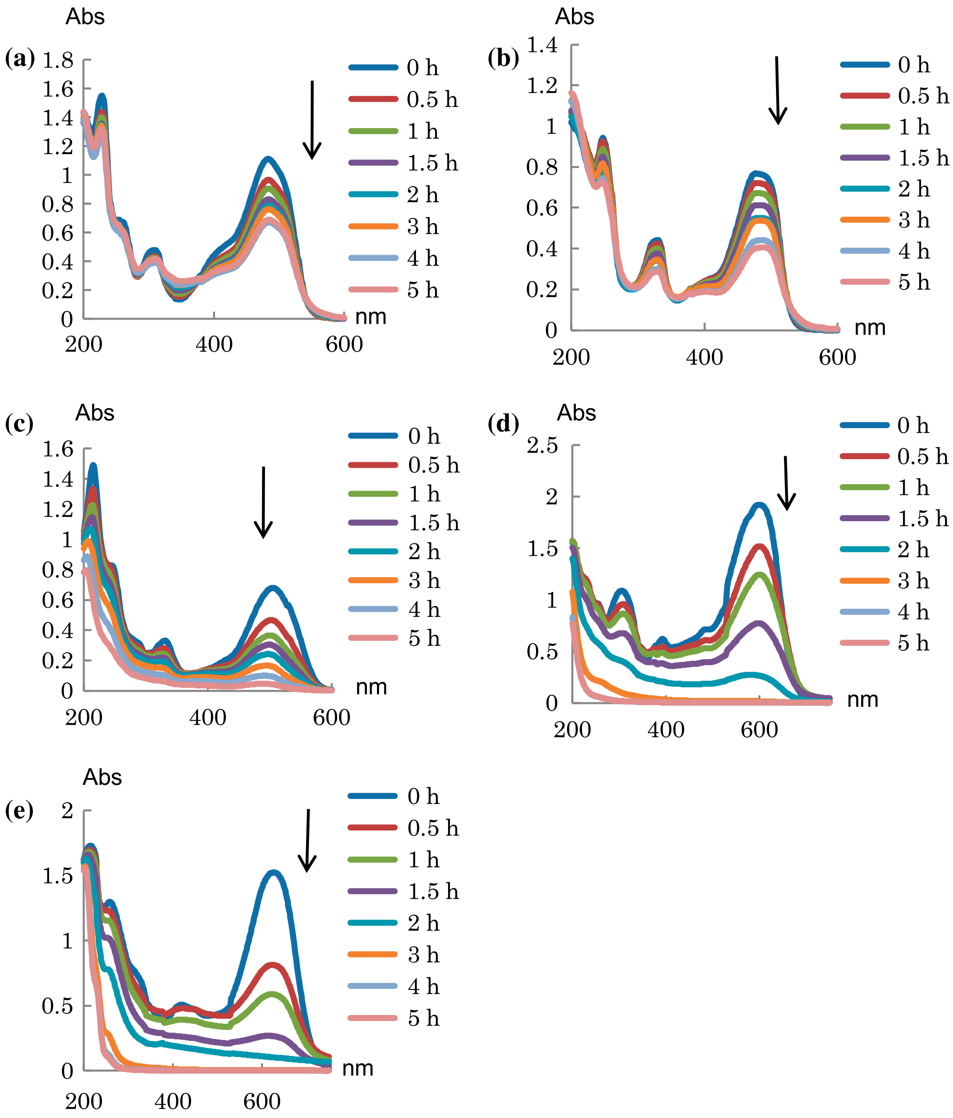


Fig. 3. UV–vis spectrum analysis of photocatalytic degradation of (a) AO7, (b) OG, (c) NC, (d) RB5 and (e) RG19.

benzene ring of the dyes. The photocatalytic degradation of azo dye involved the breakdown of azo bond at the initial stage followed by the mineralization of the intermediate compounds such as aromatic amine and phenolic as reported by previous studies [19]. As reported by Khezrianjoo and Revanasiddappa [28], the decrease of adsorbance peaks relating to the –N=N– double bond of the azo dye revealed decolourization of dyes in the presence of ZnO in suspension. The decrease of all adsorption peaks in AO7, OG, NC, RB5 and RG19 also may indicate the mineralization of dyes under photocatalytic process. The colour of azo dyes is determined by azo bond linkage and their associated auxochromes and chromophores. The interaction between solar light and ZnO results in cleavage of dye molecule followed by the formation of molecules containing benzene- and naphthalene-type rings [29]. This study also proved by Guettaï and Amar [30] in their studies regarding the photocatalytic degradation of methyl orange (MeO) in the presence of titanium dioxide in aqueous suspension. They found that the adsorption maxima for both MeO and intermediates products disappeared after 5 h irradiation which indicated that photocatalytic degradation destroyed both conjugate systems (including –N=N–) and intermediate products. Ong et al. [31] had found that sulphate ions were released after 1 h of photocatalytic degradation of AO7 under solar light irradiation. This indicated that the solar photocatalysis could mineralize azo dyes.

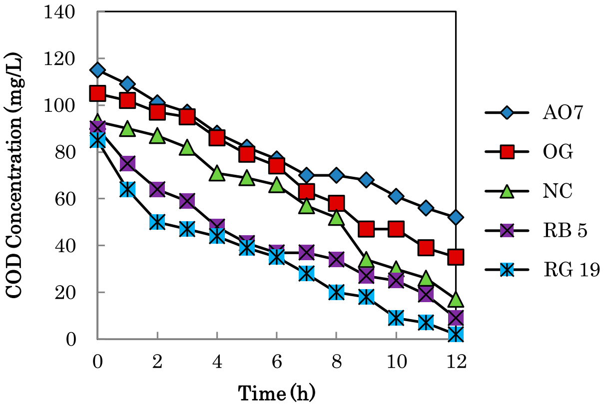


Fig. 4. COD monitoring for five dyes examined via solar photocatalytic process.

3.3. Mineralization curve

The mineralization curve can be determined by COD. The COD test is widely used as an effective method to measure the organic strength of wastewater as reported by Gupta et al. [32] and they observed drastic drop of COD values on the photocatalytic degradation of tartrazine, which indicated good potential of this technique to be employed. As shown in Fig. 4, the COD values for AO7, OG, NC, RB5 and RG19 decreased to 52, 35, 17, 9 and 2 mg/L, respectively, after 12 h of solar light irradiation. The time interval for COD analysis was longer compared with photocatalytic activity in order to ensure the complete mineralization of the azo dyes. As the COD value decreased with the solar light irradiation time, the results showed that the intermediate formed from the reduction of the azo bond was then further mineralized by the photocatalytic reactions. This was also studied by Stylidi et al. [13] who used TiO_2 as a catalyst in order to investigate the pathways of solar light-induced photocatalytic degradation towards azo dye. The complete decolourization of AO7, OG, NC, RB5 and RG19 occurred within 5 h, whereas complete mineralization required more than 12 h. This might be due to the formation of intermediate product and competitiveness between intermediates and parent dye molecules in the photocatalytic degradation process [33]. Soutsas et al. [34] reported that as the initial dye concentration increased, the degradation efficiency (%) will be affected due to the increase of intermediate product formed from the reaction. From the results, the degradation efficiency of AO7, OG, NC, RB5 and RG19 was 54.8, 66.7, 81.7, 90 and 97.6%, respectively. The final products resulted from complete mineralization of each dye were inorganic ions such as carbon dioxide (CO_2), water (H_2O), nitrates ion (NO_3^-), natrium ion (Na^+), sulphate ion (SO_4^{2-}) and hydrogen ion (H^+) [35–37].

4. Conclusion

Solar photocatalytic degradation of azo dyes: AO7, OG, NC, RB5 and RG19 was investigated, respectively, in aqueous solution with ZnO as a photocatalyst. It was observed that RG19, with the highest number of sulphonic groups, was decolourized within 3 h under solar light irradiation. The solar photocatalytic degradation of AO7, OG, NC, RB5 and RG19 followed the Langmuir–Hinshelwood kinetic model. The pseudo-first-order rate constants of AO7, OG, NC, RB5 and RG19 were 0.046, 0.087, 0.383, 0.783 and 1.177, respectively, which showed the increase of degradation rate following the increase number of sulphonic groups in the azo dye molecules. Results from the UV–vis analysis and COD measurement confirmed the mineralization of the azo dye molecule under solar photocatalytic process.

References

[1] C.-H. Wu, Comparison of azo dye degradation efficiency using UV/single semiconductor and UV/coupled semiconductor systems, Chemosphere 57 (2004) 601–608.

[2] Gh. Ghanizadeh, G. Asgari, Adsorption kinetics and isotherm of methylene blue and its removal from aqueous solution using bone charcoal, React. Kinet. Mech. Catal. 102 (2011) 127–242.

[3] A.K. Verma, R.R. Dash, P. Bhunia, A review on chemical coagulation/flocculation technologies for removal of colour from textile wastewaters, J. Environ. Manage. 93 (2012) 154–168.

[4] S. Andleeb, N. Atiq, M.I. Ali, R. Razi-Ul-Hussnain, M. Shafique, B. Ahamad, P.B. Ghumro, S. Ahmad, Biological treatment of textile effluent in stirred tank bioreactor, Int. J. Agric. Biol. 12 (2010) 256–260.

[5] X. Ren, T. Wang, C. Zhou, S. Du, Z. Luan, J. Wang, D. Hou, Treatment of dye aqueous solution using a novel aromatic polyamide asymmetric nanofiltration membrane, Fresenius Environ. Bull. 19 (2010) 1441–1446.

[6] H. Chenini, K. Djebbar, S.M. Zendaoui, T. Sehili, B. Zouchoune, Removal of and azo dye (Orange G) by various methods in homogeneous phase comparative study, Jordan J. Chem. 6 (2011) 307–319.

[7] S.B. Gajbhiye, Photocatalytic degradation study of methylene blue solutions and its application to dye industry effluent, Int. J. Mod. Eng. Res. 2 (2012) 1204–1208.

[8] A. Kajbafvala, H. Ghorbani, A. Paravar, J.P. Samberg, E. Kajbafvala, S.K. Sadrnezhaad, Effects of morphology on photocatalytic performance of zinc oxide nanostructures synthesized by rapid microwave irradiation methods, Superlattices Microstruct. 51 (2012) 512–522.

[9] J.Z. Kong, A.D. Li, H.F. Zhai, H. Li, Q.Y. Yan, J. Ma, D. Wu, Preparation, characterization and photocatalytic properties of $ZnTiO_3$ powders, J. Hazard. Mater. 171 (2009) 918–923.

[10] C.M. Teh, A.R. Mohamed, Roles of titanium dioxide and ion-doped titanium dioxide on photocatalytic

degradation of organic pollutants (phenolic compounds and dyes) in aqueous solutions: A review, J. Alloys Compd. 509 (2011) 1648–1660.

[11] J.H. Sun, S.P. Sun, G.L. Wang, L.P. Qiao, Degradation of azo dye Amido Black 10B in aqueous solution by Fenton oxidation process, Dyes Pigm. 74 (2007) 647–652.

[12] Y. Jiang, Y. Sun, H. Liu, F. Zhu, H. Yin, Solar photocatalytic decolorization of C.I. Basic blue 41 in an aqueous suspension of TiO_2–ZnO, Dyes Pigm. 78 (2008) 77–83.

[13] M. Stylidi, D.I. Kondarides, X.E. Verykios, Pathways of solar light-induced photocatalytic degradation of azo dyes in aqueous TiO_2 suspensions, Appl. Catal., B 40 (2003) 271–286.

[14] R. Nagaraja, N. Kottam, C.R. Girija, B.M. Nagabhushana, Photocatalytic degradation of Rhodamine B dye under UV/solar light using ZnO nanopowder synthesized by solution combustion route, Powder Technol. 215–216 (2012) 91–97.

[15] P. Bansal, D. Sud, Photodegradation of commercial dye, Procion Blue HERD from real textile wastewater using nanocatalysts, Desalination 267 (2011) 244–249.

[16] M.A. Behnajady, N. Modirshahla, R. Hamzavi, Kinetic study on photocatalytic degradation of C.I. Acid Yellow 23 by ZnO photocatalyst, J. Hazard. Mater. 133 (2006) 226–432.

[17] R. Velmurugan, M. Swaminathan, An efficient nanostructured ZnO for dye sensitized degradation of reactive red 120 dye under solar light, Sol. Energy. Mater. Sol. Cells 95 (2011) 942–950.

[18] C. Richard, P. Boule, Reactive species involved in photocatalytic transformations on zinc oxide, Sol. Energy Mater. Sol. Cells 38 (1995) 431–440.

[19] K. Tanaka, K. Padermpole, T. Hisanaga, Photocatalytic degradation of commercial azo dyes, Water Res. 34 (2000) 327–333.

[20] C. Richard, F. Bosquet, J.F. Pilichowski, Photocatalytic transformation of aromatic compounds in aqueous zinc oxide suspensions: Effect of substrate concentration on the distribution of products, J. Photochem. Photobiol., A 108 (1997) 45–49.

[21] Y. Wang, Solar photocatalytic degradation of eight commercial dyes in TiO_2 suspension, Water Res. 34 (2000) 990–994.

[22] E. Bizani, K. Fytianos, I. Poulios, V. Tsiridis, Photocatalytic decolorization and degradation of dye solutions and wastewaters in the presence of titanium dioxide, J. Hazard. Mater. 136 (2006) 85–94.

[23] A. Houas, H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard, J.M. Hermann, Photocatalytic degradation pathway of methylene blue in water, Appl. Catal., B 31 (2001) 145–157.

[24] C. Hachem, F. Bocquillon, O. Zahraa, M. Bouchy, Decolourization of textile industry wastewater by the photocatalytic degradation process, Dyes Pigm. 49 (2001) 117–125.

[25] I.K. Konstantinou, T.A. Albanis, TiO_2-assisted photocatalytic degradation of azo dyes in aqueous solution: Kinetic and mechanistic investigations, Appl. Catal., B 49 (2004) 1–14.

[26] A.R. Khataee, M.N. Pons, O. Zahraa, Photocatalytic degradation of three azo dyes using immobilized TiO_2 nanoparticles on glass plates activated by UV light irradiation: Influence of dye molecular structure, J. Hazard. Mater. 168 (2009) 133–137.

[27] N. Tsuchiya, K. Kuwabara, A. Hidaka, K. Oda, K. Katayama, Reaction kinetics of dye decomposition processes monitored inside a photocatalytic microreactor, Phys. Chem. Chem. Phys. 14 (2012) 4734–4741.

[28] S. Khezrianjoo, H.D. Revanasiddappa, Photocatalytic degradation of Acid Yellow 36 using Zinc Oxide photocatalyst in aqueous media, J. Catal. 2013 (2013) 1–6.

[29] M.A. Rauf, S.S. Ashraf, Fundamental principles and application of heterogeneous photocatalytic degradation of dyes in solution, Chem. Eng. J. 151 (2009) 10–18.

[30] N. Guettaï, H.A. Ait Amar, Photocatalytic oxidation of methyl orange in presence of titanium dioxide in aqueous suspension. Part I: Parametric study, Desalination 185 (2005) 427–437.

[31] S.-A. Ong, L.-N. Ho, Y.-S. Wong, O.-M. Min, L.-S. Lai, S.-K. Khiew, V. Murali, Photocatalytic mineralization of azo dye Acid Orange 7 under solar light irradiation, Desal. Wat. Treat. 48 (2012) 245–251.

[32] V.K. Gupta, R. Jain, A. Nayak, S. Agarwal, Removal of the hazardous dye—Tartrazine by photodegradation on titanium dioxide surface, Mat. Sci. Eng. C 31 (2011) 1062–1067.

[33] J. Nishio, M. Tokumura, H.T. Znad, Y. Kawase, Photocatalytic decolorization of azo-dye with zinc oxide powder in an external UV light irradiation slurry photoreactor, J. Hazard. Mater. 138 (2006) 106–115.

[34] K. Soutsas, V. Karayannis, I. Poulios, A. Riga, K. Ntampegliotis, X. Spiliotis, G. Papapolymerou, Decolorization and degradation of reactive azo dyes via heterogeneous photocatalytic processes, Desalination 250 (2010) 345–350.

[35] S.A. Ong, O.M. Min, L.N. Ho, Y.S. Wong, Comparative study on photocatalytic degradation of mono azo dye acid orange 7 and methyl orange under solar light irradiation, Water Air Soil Pollut. 223 (2012) 5483–5493.

[36] S.K. Pardeshi, A.B. Patil, Effect of morphology and crystallite size on solar photocatalytic activity of zinc oxide synthesized by solution free mechanochemical method, J. Mol. Catal. A, Chem. 308 (2009) 32–40.

[37] X. Vargas, E. Tauchert, J.M. Marin, G. Restrepo, R. Dillert, D. Bahnemann, Fe-doped titanium dioxide synthesized: Photocatalytic activity and mineralization study for azo dye, J. Photochem. Photobiol., A 243 (2012) 17–22.