ISSN 2321-807X

Immobilization of ZnO Suspension on Glass Substrate to Remove Filtration During the Removal of Remazol Red R from Aqueous Solution

Md. Nazmul Kayes,[1,2] Md Jalil Miah,[1,2] Md. Obaidullah,[1,2] M. Akter Hossain,[1,3] Md. Mufazzal Hossain[1]

[1]Department of Chemistry, University of Dhaka, Dhaka-1000, Bangladesh.
mufazzal@du.ac.bd

[2]Department of Innovation Systems Engineering, Utsunomiya University, 7-1-2 Yoto, Tochigi, Japan, 321-8585.
mnkayes46@gmail.com *

[3]Department of Mathematics and Natural Sciences, Brac University, Dhaka-1212, Bangladesh.
akter.hossain@bracu.ac.bd

ABSTRACT

Photodegradation of textile dyes in the presence of an aqueous suspension of semiconductor oxides has been of growing interest. Although this method of destruction of dyes is efficient, the main obstacle of applying this technique in the industry is the time and cost involving separation of oxides from an aqueous suspension. In this research, an attempted was made to develop ZnO films on a glass substrate by simple immobilization method for the adsorption and photodegradation of a typical dye, Remazol Red R (RRR) from aqueous solution. Adsorption and photodegradation of RRR were performed in the presence of glass supported ZnO film. Photodegradation of the dye was carried out by varying different parameters such as the catalyst dosage, initial concentrations of RRR, and light sources. The percentage of adsorption as well as photodegradation increased with the amount of ZnO, reaches a maximum and then decreased. Maximum degradation has been found under solar light irradiation as compared to UV-light irradiation. Removal efficiency was also found to be influenced by the pre-sonication of ZnO suspension.

Keywords

ZnO film, RRR, Adsorption, Photodegradation, Sonication.

Academic Discipline And Sub-Disciplines

Chemistry

SUBJECT CLASSIFICATION

Photochemistry

TYPE (METHOD/APPROACH)

Immobilization

Council for Innovative Research

Peer Review Research Publishing System

Journal: Journal of Advances in Chemistry

Vol.12, No.6

editorjaconline@gmail.com, www.cirjac.com

INTRODUCTION

Dyes have become a part and parcel of human life from the commencement of modern civilization. Dye producers and users are very much concern about the stability and fastness, especially the quality of the product. As a result, it becomes harder to degrade the dyes after use [1]. Direct dyes are water soluble for containing ionic groups such as sulfonic or amino groups. These dyes are not biodegradable and cause allergy, skin irritation, cancer and mutagenic diseases to living organisms [2]. The release of dyestuffs not only produce toxic amines by reductive cleavage of azo linkages which may cause severe effects on human beings through damaging their vital organs such as the brain, liver, kidneys, central nervous and reproductive systems [3,4] in an aquatic environment but damage the ecosystem also. Therefore, their removal becomes a prime environmental anxiety in industrialized countries and is subjected to many types of scientific research. The effluent of dyes produced from different industries causes a severe destruction of the environment. Drainage of dyestuff from industry to canals, rivers, and seas destroy the ecosystem of water as well as the whole environment. The abundance of non-biodegradable compounds in the wastewater is a new challenge for the future world. Some methods like biosorption [5], conventional activated sludge treatment process [6], electrochemical technologies [7,8], and reverse osmosis [9], had been applied for the treatment of industrial wastewater. Photocatalysis using a semiconductor as a photocatalyst is an alternative to conventional methods [10-12]. Complete mineralization of the dyestuff takes place by this method without the formation of sludge at atmospheric pressure and near ambient temperature [13]. When light is illuminated on semiconductor (i.e. ZnO, TiO_2, CdO, CdS, etc.) with photon energy greater or equal to the band gap energy of the semiconductor, valence band electrons are excited to the conduction band creating a hole behind. ZnO has broad band gap energy of 3.37 eV at room temperature and exciton energy 60 meV [14]. It has no adverse effect on the environment and also readily available at low cost. Superoxide anion radicals ($\bullet O_2^-$) and hydroxyl radicals (•OH) are being generated in the aqueous medium of ZnO, and these species are responsible for accelerating the oxidation of pollutants [15,16]. ZnO absorbs a significant fraction of the solar spectrum and more light quanta than TiO_2 [17]. Some researchers highlighted the better degradation efficiency of ZnO than TiO_2 [18,19]. Incorporation of other metals to semiconductor also enhanced the photocatalytic degradation [20,21]. The use of an aqueous suspension of photocatalyst for the treatment of industrial wastewater is common one [22]. The major obstacle of this procedure is the filtration, which is time-consuming and cost-intensive too. To overcome these disadvantages, coating of active materials on the solid support can be used as a photocatalyst or adsorbent instead of suspension, where filtration of the suspension would not be required. Preparation of films on a solid substrate is very common and efficient in different industries and laboratories, which depends on the available technology. Spin coating of a solution [23] and direct deposition during chemical reactions [24] on solid substrates had already been reported. Expensive plant requirements or operational costs discourage the industrialists to depollute or detoxify wastewater. In this respect, films of ZnO was prepared by simple immobilization method on the glass substrate without high-cost instrumental set up for the purpose of removing filtration. The experimental results demonstrated the coating of ZnO on the solid support effectively worked as a photocatalysis as well as an adsorbent for removing dyes from the aqueous solution under both in UV and sunlight irradiation.

EXPERIMENTAL

RRR (supplied by Dystar, Germany) and ZnO (purchased from Merck, Germany) were used without further purification. About 4 g of ZnO was taken in a beaker with 50 mL deionized water. Then the aqueous suspension was sonicated for 2 hours and taken on a previously weighed glass plate (Area: 25.4 × 76.2 mm^2 & 1-1.2 mm thick, China) with a dropper. The suspension taken on the bare substrate was tried to distribute uniformly with the help of a spatula and kept overnight to dry. The film was heated for 3 hours at 110°C temperature in an oven to remove water. The amount of ZnO required for the preparation of film was calculated from the weight of the bare substrate and the weight of ZnO film after heating. About 200 mL of 1×10^{-4} M RRR solution was taken in a 500 mL beaker and placed into photolysis chamber. A film of ZnO was immersed into the solution with the help of Aluminium wire. A magnetic stirrer was used for the continuous rotation of the solution at a speed of 500 rpm. Adsorption study was carried out in the absence of light until equilibrium time for adsorption was determined. The UV heating light was then switched on and the degradation time was monitored using a stopwatch. A particular portion of the irradiated solution was taken out after a definite time interval and the absorbance of the solution were measured using Shimadzu 1800 UV-Visible spectrophotometer.

RESULTS AND DISCUSSION

Effect of Catalyst Dosage

The removal efficiency was monitored by UV-visible analysis. Maximum peaks of RRR were found at 523, 383 and 285 nm. Almost same type of spectra was found for a reactive red dye [25]. Beer-Lambert law ($A=\varepsilon cl$) was used to determine the value of molar extinction coefficient (ε), which were 1.333×10^4, 3.646×10^3 and 1.296×10^4 $Lmol^{-1}cm^{-1}$ for the corresponding wavelengths, respectively. A decrease in the absorbance of RRR solution indicates the degradation of the dye. An overlay spectra of RRR at different time intervals in the presence of ZnO films under UV irradiation is shown in supporting information (Fig. S1). As the amount of ZnO increases adsorption also increases up to a maximum of about 0.15 g and then decreases for both adsorption (blue line) and photodegradation (red line) (Fig. 1). The degradation efficiency might be attributed to the high surface areas including an internal surface and an appropriate thickness of the film that assists more efficient separation of electron-hole pairs [26-28]. It is expected that, after the immobilization of a certain amount of ZnO, the surface area would remain constant. Accordingly, the percentage removal would show a steady value after that amount of ZnO but in actual case was found to decrease, which might be due to retarded separation of the electron-hole pair with higher coating thickness. These results are consistency with literature results,

where TiO_2 nanoparticles were deposited on a glass substrate and used as a photocatalyst for removing methylene blue from aqueous solution [26].

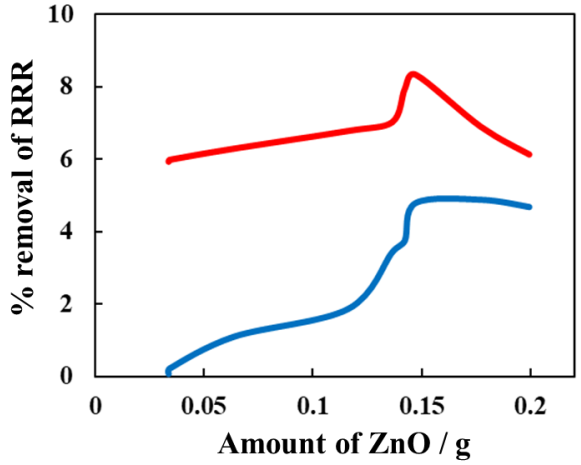

Fig. 1: Removal efficiency of RRR by adsorption (blue) and photodegradation (red) with the amount of ZnO.

Effect of Initial Dye Concentration

Adsorption experiments were carried out with varying the concentration of RRR solution from (0.5 - 2.5) × 10^{-4} M to find the intrinsic kinetic parameters. The amount of ZnO, immobilized on glass substrate were 0.15 (± 5%) g. Under these conditions, the equilibrium time for the adsorption of RRR was found to be 40 minutes. The amount of adsorbate adsorbed (q_e) per unit mass of adsorbent for 1 × 10^{-4} M RRR solution was found 5.26 mg/g. The pseudo-first and second order kinetic equations [29, 30] were compared to determine the order of adsorption.

$$\log (q_e - q_t) = \log q_e - k_1 t \text{.....(1)},$$

$$t/q_t = 1/(k_2 q_e^2) + t/q_e \text{.....(2)}.$$

Sigma plot software was used to determine the value of all parameters, which are given in Table 1. All the correlation coefficient (R^2) values for the pseudo-first order kinetic model are closer to one than the pseudo-second order model suggests that the adsorption of RRR on ZnO follows the pseudo-first order kinetics.

Table 1: Data for kinetic parameters of pseudo-first order and pseudo-second order models for RRR.

C_o	Pseudo-first order model		Pseudo-second order model	
(M)	k_1 (min^{-1})	R_1^2	k_2 (mg/g.min)	R_2^2
4.90×10^{-4}	0.0161	0.9455	0.0775	0.4208
10.03×10^{-4}	0.0327	0.9235	0.1010	0.9107
15.06×10^{-4}	0.0152	0.9691	0.0530	0.5023
19.96×10^{-4}	0.0380	0.8597	0.0530	0.8478
24.93×10^{-4}	0.0199	0.9956	0.0411	0.9309

To explain adsorption isotherm, two widely used mathematical equations such as Freundlich and Langmuir's equation were used.

$$\log q_e = \log K_F + (1/n) \log C_e \text{.....(3)},$$

$$1/q_e = (1/K_L C_e) + (a_L/K_L) \text{.....(4)}.$$

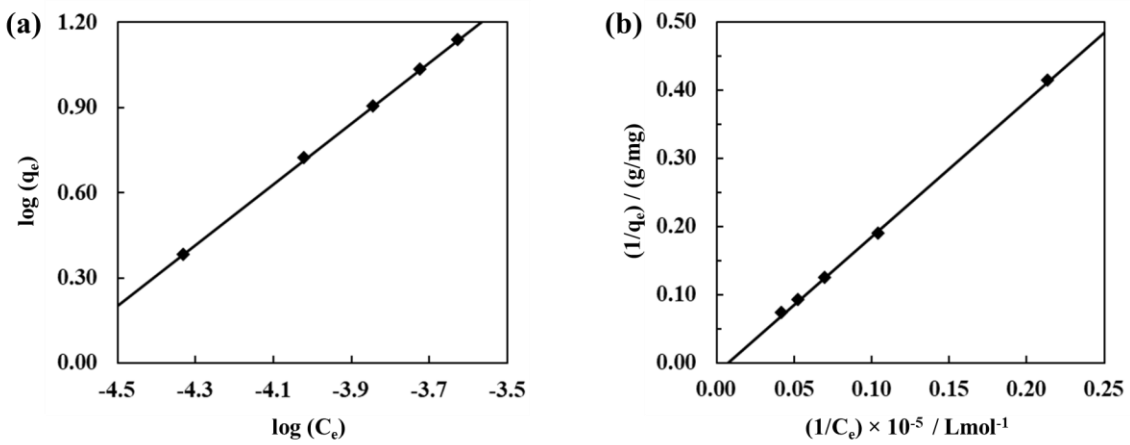

Fig. 2: Adsorption isotherm of RRR on ZnO (a) Freundlich and (b) Langmuir at 30 °C with (0.15 g ± 5%) ZnO / 200 mL.

The plot of (log q_e vs log C_e) and ($1/q_e$ vs $1/C_e$) is shown in Fig. 2 (a) and (b) respectively. Freundlich and Langmuir's parameters are enlisted in Table 2. The value of 1/n (>1) indicated a cooperative adsorption [30]. But the regression value suggested that the Freundlich equation could explain the adsorption isotherm more precisely.

Table 2: Characteristic parameters for the adsorption isotherm of reactive dye RRR on ZnO.

Temperature	Freundlich isotherm			Langmuir isotherm		
(^oC)	K_F (mg/g)(L/mol)$^{1/n}$	n	R^2	q_m (mg/g)	K_L (L/mol)	R^2
30	11.787	0.935	0.9999	71.47	0.5003	0.9995

The effect of initial dye concentration on photodegradation of RRR on the ZnO-coated glass substrate under UV-light irradiation is given in Fig.3. The concentration of RRR solution was varied from (0.5 - 2.5) × 10^{-4} M and the amount of ZnO immobilized on glass substrate was 0.15 (± 5%) g. The photodegradation efficiency was found to be inversely affected by the dye concentration. With the increase of dye concentration, the equilibrium adsorption of dye increases on the catalyst surface active sites; hence competitive adsorption of OH^- on the same sites decreases, meaning a lower formation rate of •OH radical, which is the principal oxidant necessary for high degradation efficiency [31]. On the other hand, considering the Beer-Lambert law, as the initial dye concentration increases, the path length of photons entering the solution decreases, resulting in lower photon absorption on catalyst particles and consequently a lower photodegradation rate.

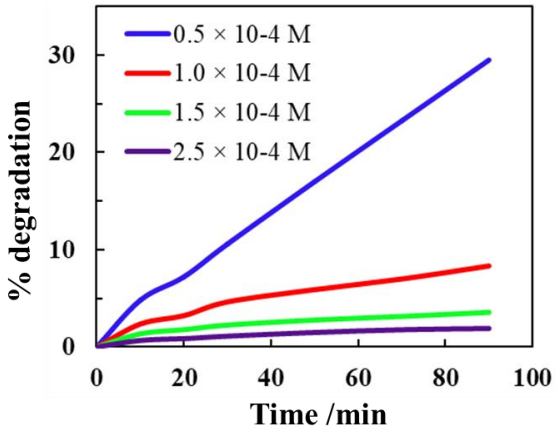

Fig. 3: Effect of initial concentration on photodegradation of RRR.

ISSN 2321-807X

Effect of Light Source

The Efficiency of photodegradation on light irradiation is shown in Fig. 4. Three different light sources (UV, Solar, and Visible light) were applied for photodegradation experiments. The measured intensity of UV and the solar light was 0.14 $mWcm^{-2}$ and 700-750 Wm^{-2} respectively. After 90 min of light irradiation, the photocatalytic activity under sunlight was found to 24.05 % and 31.41 % higher than the artificial UV light and visible light, respectively. ZnO is a semiconductor having band gap energy of 3.37 eV corresponds to 368 nm of the radiation. Thus, any light having a wavelength equal or less than 368 nm would be capable of producing electron-hole pairs and enabled photodegradation of dye. This mechanism of photodegradation involving semiconductor oxide as a photocatalyst under UV light is now well established [31,32].

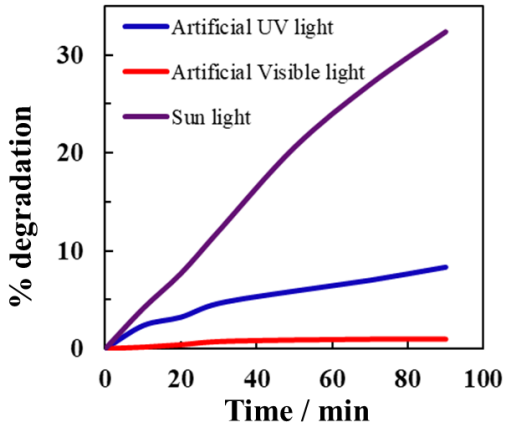

Fig. 4: Percentage of photodegradation under the illumination of different light sources.

In a photosensitization reaction, the dye molecules become excited by absorbing the photon. These excited molecules then transfer electrons to the conduction band of ZnO and proceed the photodegradation process. Photosensitization reaction occurred in the case of artificial visible light and solar light, the mechanism of which is already reported by Gary A. Epling [31]. However, a higher rate of degradation by the sunlight than the artificial visible light should be related to the intensity of light.

Effect of Sonication

Pre-sonication of ZnO suspension was carried out by using a Sonicator (Eyela, Tokyo Rikakikai Co.Ltd). Adsorption as well as photodegradation both was increased with sonication time of ZnO suspension (Fig. 5). The amount of adsorption was about 4.64 % for the film of ZnO prepared without sonication. A slight increase up to 4.99% had been found with 5 hours sonication of ZnO suspension. Under the same conditions, the photodegradation after 90 min UV irradiation were 8.15 % and 10.33 %, respectively.

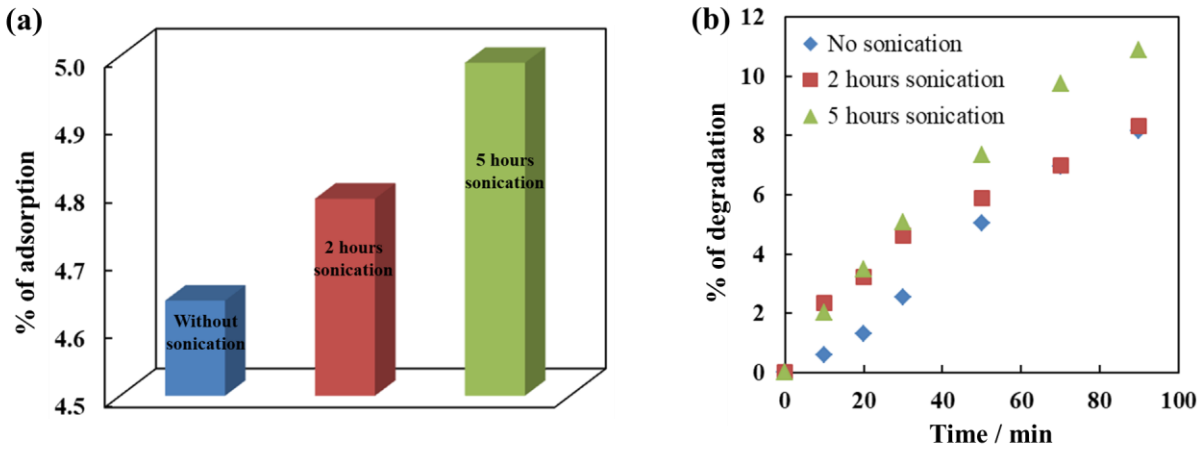

Fig. 5: Effect of sonication of ZnO suspension on (a) adsorption and (b) photodegradation of RRR.

There might be two possibilities for the enhanced removal efficiency with sonication; one would be the decrease in the particle size of the ZnO, which would increase the surface area of the ZnO and other would be the increase dispersion ability of these particles. SEM images of the ZnO suspensions were observed by Hitachi S-4500 to clarify the exact reason for the enhancement of removal efficiency (shown in Fig. 6). The SEM images clearly predicted that there was almost no change in the size and the shape of the ZnO particles. Therefore, it could be concluded that the better dispersion of the ZnO particles made a rather smooth surface for the glass supported film and increased its effectiveness.

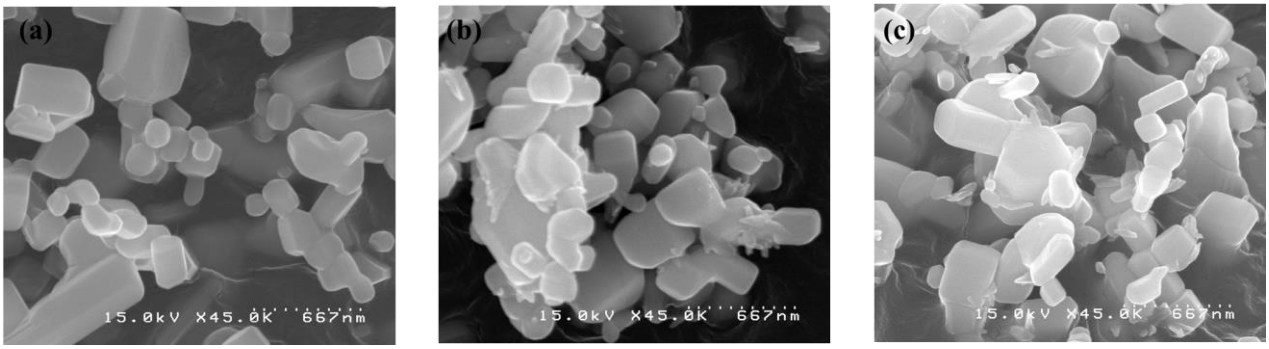

Fig. 6: SEM images of ZnO particles (a) without sonication, (b) after 2 hours and (c) 5 hours sonication.

CONCLUSION

In the present research, we have shown a simple and facile route for immobilization of ZnO on a glass substrate, which enables to eliminate the problem of filtration during the traditional dye removal process. Since filtration is not required in this process and photodegradation follows adsorption, the removal efficiency will be significant rather than individual adsorption and photodegradation process. We used the ZnO-coated glass substrate for the adsorption of textile dye RRR untill the equilibrium was achieved. The same substrate was then used for photodegradation. Sunlight has been found to be more effective than the artificial UV & visible light due to the different mechanism of photodegradation and intensity of light. Adsorption on semiconducting materials containing film enhances the photodegradation under solar light rather than UV light is a new finding of this study which increases the feasibility of the process. We expect the successive adsorption and photodegradation process will be cost effective for long term application to depollute and detoxify industrial wastewater.

REFERENCES

[1] Choy, K.K.H., McKay, G. and Porter, J.F., (1999). Sorption of Acid Dyes from Effluents Using Activated Carbon. Resources, Conservation and Recycling, 27, 57-71.

[2] Anouzla, A., Abrouki, Y., Souabi, S., Safi, M. and Rhbal, H., (2009). Colour and COD Removal of Disperse Dye Solution by a Novel Coagulant: Application of Statistical Design for the Optimization and Regression Analysis. Journal of Hazardous Materials, 166, 1302–1306.

[3] Aksu, Z. and Çağatay, Ş. Ş., (2006). Investigation of Biosorption of Gemazol Turquise Blue-G Reactive Dye by Dried Rhizopus Arrhizus in Batch and Continuous Systems. Separation and Purification Technology, 48 (1), 24-35.

[4] Mahony, O', T., Guibal, E. and Tobin, J. M., (2002). Reactive Dye Biosorption by Rhizopus Arrhizus Biomass. Enzyme and Microbial Technology, 31 (4), 456-463.

[5] Safa, Y. and Bhatti, H. N., (2011). Biosorption of Direct Red-31 and Direct Orange-26 Dyes by Rice Husk: Application of Factorial Design Analysis. Chemical Engineering Research and Design, 89, 2566–2574.

[6] Fuhs, G. W., and Chen, M., (1975). Microbiological Basis of Phosphate Removal in the Activated Sludge Process for the Treatment of Wastewater. Microbial Ecology, 2, 119-138.

[7] Rajkumar, D., Song, B. J. and Kim, J. G., (2007). Electrochemical Degradation of Reactive Blue 19 in Chloride Medium for the Treatment of Textile Dyeing Wastewater with Identification of Intermediate Compounds. Dyes and Pigments, 72 (1), 1–7.

[8] Pelegrini, R., Peralta-Zamora, P., de Andrade, A. R., Reyes, J. and Durán, N., (1999). Electrochemically Assisted Photocatalytic Degradation of Reactive Dyes. Applied Catalysis B: Environmental, 22 (2), 83–90.

[9] Bódalo-Santoyo, A., Gómez-Carrasco, J.L., Gómez-Gómez, E., Máximo-Martín, F. and Hidalgo-Montesinos, A.M., (2003). Application of Reverse Osmosis to Reduce Pollutants Present in Industrial Wastewater. Desalination, 155 (2), 101-108.

[10] Lee, J. M., Kim, M. S., Hwang, B., Bae, W. and Kim, B. W., (2003). Photodegradation of Acid Red 114 Dissolved Using a Photo-Fenton Process with TiO_2. Dyes and Pigments, 56, 59–67.

[11] Neamtu, M., Siminiceanu, I., Yediler, A. and Kettrup, A., (2002). Kinetics of Decolorization and Mineralization of Reactive Azo Dyes in Aqueous Solution by the UV/H_2O_2 Oxidation. Dyes and Pigments, 53 (2), 93–99.

[12] Saquib, M. and Muneer, M., (2002). Semiconductor Mediated Photocatalysed Degradation of an Anthraquinone Dye, Remazol Brilliant Blue R Under Sunlight and Artificial light source. Dyes and Pigments, 53 (3), 237–249.

[13] Robertson, P.K.J., (1996). Semiconductor Photocatalysis: An Environmentally Acceptable Alternative Production Technique and Effluent Treatment Process. J. Cleaner Production, 4 (3-4), 203-212.

[14] Shan, F.K. and Yu, Y.S., (2004). Band Gap Energy of Pure and Al-doped ZnO Thin Films. Journal of the European Ceramic Society, 24 (6), 1869–1872.

[15] Mills, A. and Le Hunte, S. (1997). An Overview of Semiconductor Photocatalysis. Journal of Photochemistry and Photobiology A: Chemistry, 108, 1-35.

[16] Vidal, A., Dinya, Z., Mogyorodi Jr., F. and Mogyorodi, F., (1999). Photocatalytic of Thiocarbamate Herbicide Active Ingredients in Water. Applied Catalyst B: Environmental, 21 (4), 259–267.

[17] Sakthivel, S., Neppolian, B., Shankar, M. V., Arabindoo, B., Palanichamy, M. and Murugesan, V., (2003). Solar Photocatalytic Degradation of Azo Dye: Comparison of Photocatalytic Efficiency of ZnO and TiO_2. Solar Energy Materials and Solar Cells, 77 (1), 65–82.

[18] Lizama, C., Freer, J., Baeza, J. and Mansilla, H. D., (2002). Optimized Photodegradation of Reactive Blue 19 on TiO_2 and ZnO Suspensions. Catalysis Today, 76 (2–4), 235–246.

[19] Kormann, C., Bahnemann, D. W. and Hoffmann, M. R., (1988). Photocatalytic Production of Hydrogen Peroxides and Organic Peroxides in Aqueous Suspensions of Titanium Dioxide, Zinc Oxide, and Desert Sand. Environmental Science & Technology, 22 (7), 798-806.

[20] Chamjangali, M. A. and Boroumand, S., (2013). Synthesis of Flower-like Ag-ZnO Nanostructure and Its Application in the Photodegradation of Methyl Orange. Journal of the Brazilian Chemical Society, 24 (8), 1329-1338.

[21] Apollo, S., Moyo, S., Mabuoa, G. and Aoyi, O., (2014). Solar Photodegradation of Methyl Orange and Phenol Using Silica Supported ZnO Catalyst. International Journal of Innovation, Management and Technology, 5 (3), 203-206.

[22] Zhang, F., Zhao, J., Shen, T., Hidaka, H., Pelizzetti, E., and Serpone, N., (1998). TiO_2-Assisted Photodegradation of Dye Pollutants II. Adsorption and Degradation Kinetics of Eosin in TiO_2 Dispersions Under Visible Light Irradiation. Applied Catalysis B: Environmental, 15, 147-156.

[23] Hall, D. B., Underhill, P. and Torkelson, J. M., (1998). Spin Coating of Thin and Ultrathin Polymer Films. Polymer Engineering and Science, 38 (12), 2039-2045.

[24] Yao, I. C., Tseng, T. Y. and Lin, P., (2012). ZnO Nanorods Grown on Polymer Substrates as UV Photodetectors. Sensors and Actuators A: Physical, 178, 26–31.

[25] Shah, M. P., Patel, K. A., Nair, S. S., Darji, A. M. and Maharaul, S.,(2013). Microbial Degradation of Azo Dye by Pseudomonas spp. MPS-2 by an Application of Sequential Microaerophilic & Aerobic Process. American Journal of Microbiological Research, 1 (4), 105-112.

[26] Tan, L. K., Kumar, M. K., An, W. W. and Gao, H., (2010). Transparent, Well-Aligned TiO_2 Nanotube Arrays with Controllable Dimensions on Glass Substrates for Photocatalytic Applications. Applied Materials and Interfaces, 2 (2), 498–503.

[27] Kemell, M., Pore, V., Tupala, J., Ritala, M. and Leskela, M., (2007). Atomic Layer Deposition of Nanostructured TiO_2 Photocatalysts via Template Approach. Chemistry of Materials, 19 (7), 1816-1820.

[28] Zhuang, H. F., Lin, C. J., Lai, Y. K., Sun, L. and Li, J., (2007). Some Critical Structure Factors of Titanium Oxide Nanotube Array in Its Photocatalytic Activity. Environmental Science & Technology, 41, 4735-4740.

[29] Tseng R. L., Wu F. C. and Juang R. S., (2010). Characteristics and Applications of the Lagergren's First-order Equation for Adsorption Kinetics. Journal of the Taiwan Institute of Chemical Engineers, 41, 661–669.

[30] Fytianos K., Voudrias E. and Kokkalis E., (2000). Sorption-Desorption Behaviour of 2,4-Dichlorophenol by Marine Sediments. Chemosphere, 40 (1), 3-6.

[31] Epling G.A. and Lin C., (2002). Photoassisted Bleaching of Dyes Utilizing ZnO and Visible Light. Chemosphere, 46, 561-570.

[32] Nasr C., Vinodgopal K., Fisher L., Hotchandani S., Chattopadhyay A. K., and Kamat P. V., (1996). Environmental Photochemistry on Semiconductor Surfaces. Visible Light Induced Degradation of a Textile Diazo Dye, Naphthol Blue Black, on TiO_2 Nanoparticles. Journal of Physical Chemistry, 100 (20), 8436-8442.