Journal of Engineering and Applied Sciences 13 (23): 10013-10018, 2018
ISSN: 1816-949X

Comparison Activity of ZnO and ZnO Nanoparticle as Photodegradation Catalysts

Amer Muosa Juda Douaa Raheem Hady and Ayad F. Alkaim
[1]Department of Chemistry, Faculty of Science, University of Kufa, Kufa, Iraq
[2]Department of Chemistry, College of Science for Women, University of Babylon, Hillah, Iraq

Abstract: This study involves the photocatalytic degradation of Carmine dye, employing heterogeneous photocatalytic process. Photocatalytic activity of different catalysts such as Zinc Oxide (ZnO) and nano ZnO has been investigated. An attempt has been made to study the effect of process parameters through amount of catalysts, concentration of dye, pH of dye solution and temperature on photocatalytic degradation of dye solutions. The optimum catalyst dose was found to be (0.75 g and 1) g\L for nano ZnO, ZnO, respectively. In the case of for nano ZnO, ZnO, maximum rate of photoreaction of dye solutions was observed in acidic medium at pH 4 for ZnO whereas the degradation of dye reached maximum at pH 2 when using nano ZnO catalyst. The performance of photocatalytic system employing nano ZnO/UV light was observed to be better than ZnO/UV system. Photocatalytic degradation was found to increase with increasing temperature. Arrhenius plot shows that the activation energy is equal to 8.07 kJ/mol^{-1} with ZnO and 1.2389 kJ/mol^{-1} with nano ZnO catalyst. The results display that the action of dissimilar kinds of catalyst used in this research is of the sequence

Key words: Nano ZnO>ZnO, carmine dye, photocatalytic activity, parameters, pH, observed, activation energy

INTRODUCTION

Photocatalysis uses a semiconductor metal oxide and irradiation for the squalor of recalcitrant contaminants in wastewater. The procedure involves the illumination of the metal oxide in aqueous postponement with irradiation consuming photon energy (hυ) equivalent to or better than its band hole energy. This generate valence band fleabags and transmission band electrons which can react with water and the hydroxyl ion to produce ˙OH (Fatta-Kassinos *et al*., 2010).

Adsorption is a physicochemical separation process involving inter-phase transfer between an adsorbent and a solution. The pollutant (adsorbate) to be removed is adsorbed onto the surface of the adsorbent. Adsorption has been recognized as an effective way for the elimination of organic contaminants from wastewater. Besides its effectiveness, adsorption is usually a reversible process, offering possibility for the regeneration of the adsorbent via desorption (Fu and Wang, 2011). Adsorption mechanism may be dominated by physical forces (physisorption) or chemical interactions (chemisorption) between the adsorbent and the adsorbate. In either case, the adsorption will be influenced by the characteristics of the adsorbent (such as specific surface area, porosity, surface charge, etc.,) the chemical structure of the adsorbate and the environmental condition (such temperature, pH, solubility, ionic strength, etc.,) (Kyriakopoulos and Doulia, 2006).

The adsorbed colors particles on the surface of the semiconductor can absorb a radiation in the visible variety besides the radiation with a small wavelength and with energy which is less than the E_g of the radiated semiconductor. The dye molecules will suffer decolorization through a free radical mechanism which is summarized by the following equations (Hussein, 2011).

$$Dye+h\nu \rightarrow 1Dye^* \text{ or } 3Dye^*$$
$$1Dye^* \text{ or } 3Dye^*+semiconductor \rightarrow Dye^{*+}+e^-$$
$$e^-+O_2 \rightarrow O_2^{*-}+semiconductor$$
$$Dye^{*+}+O_2^{*-} \rightarrow DyeO_2 \rightarrow degradation\ products$$
$$Dye^{*+}+OH^* \rightarrow degradation\ products$$
$$Dye+2OH^* \rightarrow H_2O+oxidation\ products$$
$$Dye^{*+}+OH^- \rightarrow Dye+OH^*$$
$$Dye^{*+}+H_2O \rightarrow Dye+OH^*+H^+$$

Zinc Oxide (ZnO) is a multifunctional substantial by way of a great refractive directory a widespread band hole (3.37 eV) and little toxicity. It has been used in various requests plus photovoltaic systems, light producing diodes, optoelectronics, photocatalysis, pharmaceuticals, cosmetics, textile and antimicrobial resources. Near are some means for the synthesis of zinc oxide which comprises sol-gel, micro-emulsification, solvothermal, hydrothermal, template hydrothermal, reflux, pyrolysis devices.

Corresponding Author: Amer Muosa Juda Douaa Raheem Hady, Department of Chemistry, Faculty of Science, University of Kufa, Kufa, Iraq

Zinc Oxide (ZnO) nanomaterial has been accepted as a talented material for dissimilar applications such as water and air disinfection, antiseptic agent, anticancer manager, etc., (Zhang *et al*., 2014). Also, the applications, ZnO nanomaterials are vcommonly used for electronic, optical, magnetic, photocatalytic requests etc., (Zhang *et al*., 2014; Srivastava *et al*., 2013). However, prison cell permeabilization because of lesser bulk and great exact surface area is the material of concern when the particle is life careful for organic applications (Wang *et al*., 2014; Tian *et al*., 2015).

Carmine likewise named cochineal, cochineal extract, pink river or carmine lake, natural red 4, C.I. 75470 or E120 is a pigment of a bright-red color gotten from the aluminium salt of carminic acid, it is likewise a overall period for a chiefly deep-red color. The color is manufactured from several scale insects such as the cochineal scale and convinced Porphyrophora class (Armenian cochineal and Polish cochineal). Carmine is rummage-sale in the production of artificial florae, coats, crimson ink, blusher and other cosmetics besides some treatments. It is routinely added to food products such as yogurt, candy and certain brands of juice, the most notable ones being those of the ruby-red variety Fig. 1.

MATERIALS AND METHODS

Experimental: These tests were finished to control the conditions best for photocatalytic degradation of carmine solution. They were carried out to assess the influence of catalyst and the UV light on photocatalytic degradation reaction.

Dark reaction: In this part, a sequence of experimental has been done as blank experimental. In each one 200 mL of carmine solution in concentration 40 ppm by using ZnO and 100 ppm by using nano ZnO at temperature 293 K was moved to 60 min in the company of the catalyst and the nonappearance of the irradiation (Attia *et al*., 2008).

Photoreaction of carmine solution: In this part, a sequence of experiments were performed. In each one 200 mL of carmine solution in concentration 40 ppm was irradiation with ultraviolet without using catalyst and continuous moving for 120 min at 293 K **(**Hussein and Alkhateeb, 2007).

Photodegradation studies of carmine solution by using ZnO and nano ZnO as semiconductor and UV light:

- Effect of catalysts (ZnO and nano ZnO amount on photoreaction)
- Effect of pH on photoreaction of carmine solution

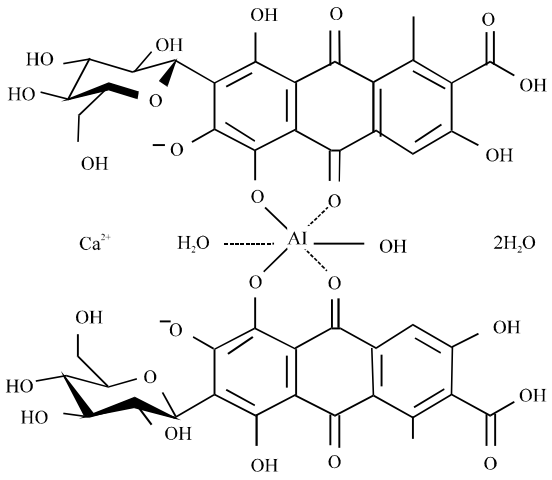

Fig. 1: Carmine dye structure

- Effect of initial dye concentration on photoreaction
- Effect of temperature on photoreaction of carmine solution

RESULTS AND DISCUSSION

Dark reaction: Two reactions were carried out in the absence of UV light. The first reaction was carried out using 40 ppm of carmine dye with the addition of 1.0 g of ZnO while the second reaction was carried using the same solution but with addition of 1.0 g of nano ZnO. The results which are expressed in Fig. 2. Those results show that there is no degradation in the absence of the ultraviolet radiation. The addition catalyst to the dye solution in the dark showed a very little change in the dyes concentration. Initially the dyes concentrations decrease with incubation time then becomes constant after a limit time because of the monolayer formation on the catalyst surface. After forming monolayer there were no available free active sites for further adsorption, so, no further decrease in dyes concentrations is observed. Thus, results observed from adsorption experiment confirmed that decrease in concentration of carmine solutions were due to adsorption of dyes on catalysts surface no degradation of dyes solutions was confirmed. The results indicate that the equilibrium is occur after 25 min.

Photolysis of carmine dye: The photolysis reaction for 40 ppm of carmine solution at 293 K was carried out in the absence of the catalysts. The results which are plotted in Fig. 3 show that there is no reaction takes place in the absence of the catalyst.

The results indicate that after 90 min of UV treatment the photodegradation efficiency is equal to 18.5% for

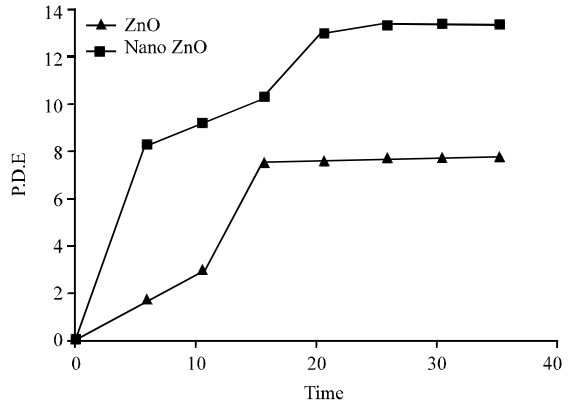

Fig. 2: Photodegradation efficiency of dye solution in dark condition

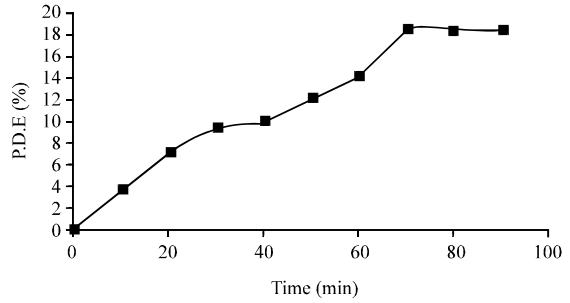

Fig. 3: The photodegradation efficiency of carmine dyes in absence the catalyst

carmine dye. These results show of dyes are slightly affected by the ultraviolet radiation in absense catalyst.

Parameters effect on photocatalytic degradation of carmine dyes

Effect of mass of catalyst on the rate of photocatalytic degradation of carmine dyes: The effect of mass of catalysts on the photocatalytic degradation of carmine solutions is investigated underseries of experiments were conducted using different masses of ZnO and nano ZnO, a predetermined experimental conditions with dye concentration of 40 ppm, light intensity equal to 250 W at pH = 6.00, the temperature is equal to 298°k. The result observed from these results that the rate of photocatalytic degradation increased with increase of the catalysts concentration up to a maximum value and remained constant after that the rate of photocatalytic degradation decrease with the increase of catalyst concentration. The best weight of Z 1.0 and 0.75 g for ZnO and nano ZnO, respectivly which gives the maximum photodegradation efficiency which is equal to 81.5 and 70.5% Fig. 4. This behavior can be illustrated on the basis that the increase

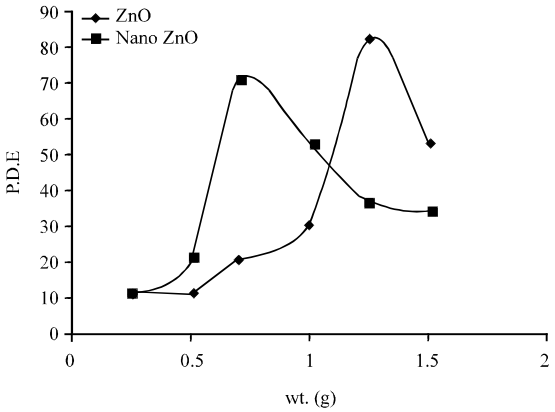

Fig. 4: Effect of weight of nano ZnO and ZnO catalysts on photo degradation efficiency of carmine dyes

of the amount of catalyst lead to increase the amount of active sites on catalyst surface as result the number of dye molecules adsorbed on the surface of catalyst increase which lead to increase in the number of particles in the area of illumination, also, the increase in the amount of catalyst lead to increase in the number of photons absorbed (Kim and Lee, 2010).

Effect of initial p[H on photocatalytic degradation of carmine dyes: pH of aqueous solution is an important variable in the evaluation of the rate of photocatalytic degradation reactions. pH change affects the adsorption quantity of organic pollutants and the ways of adsorption on the surface of photocatalyst (coordination) (Obies, 2011). As result, the photocatalytic degradation efficiency will greatly be effected by pH changes, under the determined experimental conditions with initial dye concentration 40 ppm of carmine, ZnO catalyst dosage (1.0) g, nano ZnO weight 0.75 g light intensity equal to 250 W at temperature 298°k. The effect of change in pH solution on degradation percentage was studied, the results are plotted in Fig. 5.

These results indicate the rate of photocatalytic degradation increases at acidic solution after that the rate of photocatalytic degradation decrease with increase of pH solution. It is observed from these results that the degradation percentage of carmine dyes increases with the increase in pH solution, exhibiting maximum degradation efficiency equal to 82% at pH = 4 by using ZnO and at pH = 2.0 by using nano ZnO for carmine dyes.

Effect of initial dye concentration on photocatalytic degradation of carmine dyes: The effect of initial dye concentration on the rate of photocatalytic degradation is studied by keeping all other experimental conditions and changing the nitial dye concentration,

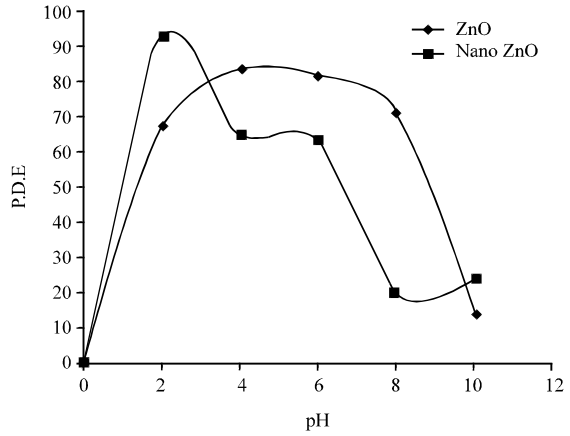

Fig. 5: Effect of pH on photocatalytic degradation efficiency of carmine in presence 1.0 ZnO and 0.75g nano ZnO

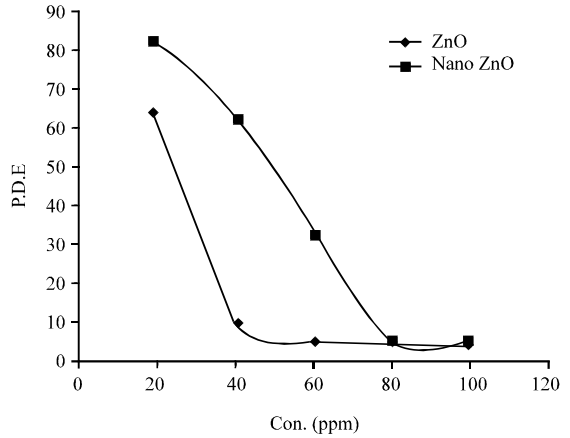

Fig. 6: Effect of dye concentration on photocatalytic degradation efficiency of carmine in presence 1.0 ZnO and 0.75g nano ZnO

ZnO concentration equal to 1.0 g, ZnO mass 0.75 g, the pH was 4.00 for carmine dyes, 250 W of light intensity and at temperature equal to 298 K the results are show that the rate of photocatalytic degradation increased with the decreasing of initial dye concentration Fig. 6.

This behavior may be due to following reason, as initial dye concentration increases, the path length of the photon entering the solution decrease, so, the number of photons reaching to catalyst surface decrease and hence, rate of formation hydroxyl radicals and super oxide ions (O_2^-). Is decreased thereby decreasing rate of degradation because less number of catalyst molecules undergoes excitation (Daneshvar *et al*., 2004).

Since, catalyst surface area is fixed, so, as initial concentration of dye increases rate of photocatalytic degradation decreases because there are only fewer active

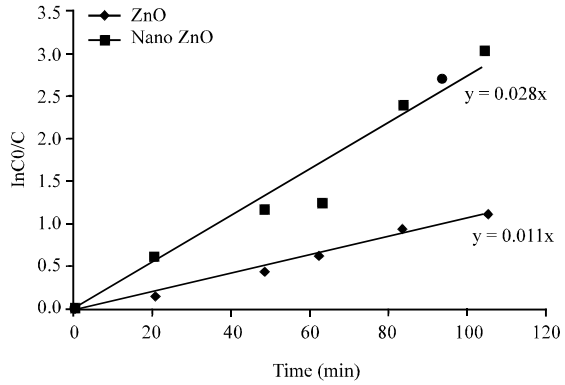

Fig. 7: Kinetics analysis for carmine dye (dye initial concentration 40 ppm), (1g ZnO) and 0.75 g nano ZnO

sites in the system causing little adsorption of dye molecules at active site of catalyst and remaining dye molecules persist in dye solution until earlier attached molecules are degraded.

Kinetic study: Figure 7 show the kinetics of disappearance of carmine dye for an initial concentration of 40 ppm under optimized conditions. The results show that the photocatalytic degradation of dye in aqueous ZnO and nano ZnO can be described by the first-order kinetic according to, the Langmuir-Hinshelwood Model (Egzar *et al*., 2013). ln (C0/C) = kt where C0 is the initial concentration and C is the concentration at any time, t. The semi-logarithmic plots of the concentration data gave a straight line. The rate constants were calculated to be (0.0111) min^{-1} and (0.0285) min^{-1} for ZnO and nano ZnO, respectively.

Effect of temperature on photocatalytic degradation of carmine dyes: The effect of temperature on photocatalytic degradation of carmine was studied in the range of temperature 288-313°k by using initial dye concentration of 40 ppm, ZnO catalyst dosage 1.0 g, nano ZnO catalyst dosage 0.75 g and pH equal to 6.00 for carmine dyes the light intensity was 250 W. These results indicate that the degradation efficiency not significantly affected with the increase of temperature Fig. 8 and 9. According to, Arrhenius law the rate of most reactions varies with temperature in such a way. The activation energy for photodegradation and decolorization of carmine solutions by using zinc oxide and nano zinc oxide catalysts in the temperature range 288-308°K was equal to 8.072 and 1.2389 kJ/mol^{-1}, respectivly.

The thermodynamic parameters of the degradation of sunset yellow and Amaranth have been reported. The

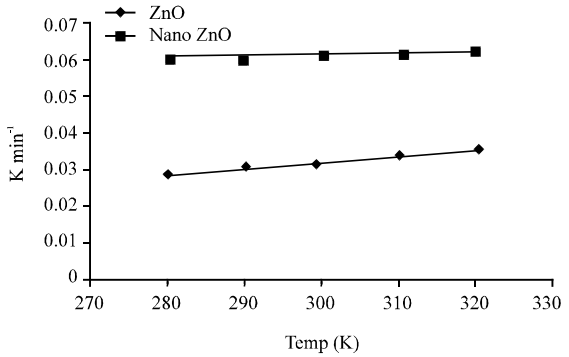

Fig. 8: The relation between rate constant and temperture

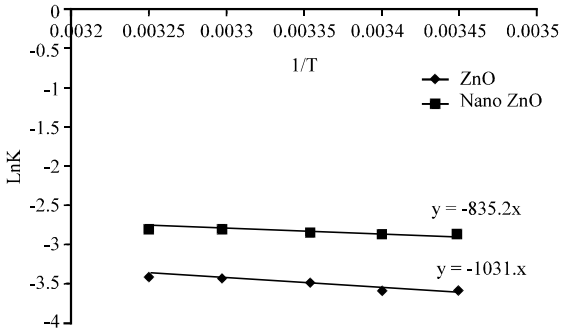

Fig. 9: Arrhenius plot by using nano ZnO and ZnO as catalyst with Carmine dye

Table 1: Values of kinetics and thermodynamic parameters for the photocatalytic degradation of Carmine solution in present ZnO

T(k°)	Ea (kJ/mol^{-1})	$\Delta H^{\#}$(kJ/mol^{-1})	$\Delta S^{\#}$(kJ/mol^{-1})	$\Delta G^{\#}$(kJ/mol^{-1})
288		5.6796		75.3756
293	8.072	5.6350	-0.242	76.5410
298		5.5940		77.7100
303		5.5520		78.8780
308		5.5110		80.0470

positive $\Delta H^{\#}$ refers to endothermic reaction, the positive $\Delta G^{\#}$ obtained indicate that the reaction is non-spontaneous. Positive $\Delta G^{\#}$ this could be because the activated state is a well solvated structure formed between the dye molecules and the reaction intermediates that is hydroxyl radicalswhich is also, supported by negative entropy of activation. In the present case, the value of $\Delta S^{\#}$ is negative as in Table 1, so that, the complex formed is more ordered than the reactants.

Initially the complex formed is unstable and degradation of the reactants into products is not very slow but takes place rapidly under present experimental conditions (Al-Ekabi and Mayo, 1985; Gajbhiye, 2012).

The obtained activation energy is very small which indicates that the photocatalytic reaction is temperature independe. This behavior could be explained on the basis of photonic activation as well known the irradiation is the primary source of electron-hole pair generation which responsible for initiation photoreaction, so, photocatalytic systems do not require heating and operate at near ambient temperature (Zainal *et al*., 2005).

Table 2: Values of kinetics and thermodynamic parameters for the photocatalytic degradation of Carmine solution in present Nano ZnO

T(k°)	Ea(kJ/mol^{-1})	$\Delta H^{\#}$(kJ/mol^{-1})	$\Delta S^{\#}$(kJ/mol^{-1})	$\Delta G^{\#}$(kJ/mol^{-1})
288		-1.1575		7.7417
293	1.2389	-1.1971	-0.0309	7.8562
298		-1.2386		7.9702
303		-1.2802		8.0827
308		-1.3218		8.1962

The true activation energy for photocatalytic systems Ea is nil whereas the apparent activation energy Ea is often very low (a few kJ/mol) in the medium temperature range (15-35°C) (Galvez and Malato, 2003). The activation energy of photocatalysis reaction is reported as 5-20 kJ/mol in the literature (Movahedi *et al*., 2009).

However, at very low temperatures (-40-0°C) adsorption of final products formed is favors, desorption of which tends to be the rate-limiting step. Because it is slower than the degradation on the surface and the adsorption of the reactants on the surface of catalyst at "high" temperatures (>70-80°C) for various types of photocatalytic reactions, the limited stag is the adsorption of the dye on the surface of catalyst (Chen and Ray, 1998).

The activation energy for photodegradation and decolorization of dye solutions by nano zinc oxide catalyst is very small which indicates that the photocatalytic reaction is temperature independ. This behavior could be explained on the basis of photonic activation as well known the irradiation is the primary source of electron-hole pair generation which responsible for initiation photoreaction, so, photocatalytic systems do not require heating and operate at near ambient temperature (Zainal *et al*., 2005).

The true activation energy for photocatalytic systems Ea is nil whereas the apparent activation energy Ea is often very low (a few kJ/mol) in the medium temperature range (15-35°C) (Galvez and Malato, 2003). The activation energy of photocatalysis reaction is reported as 5-20 kJ/mol in the literature (Gajbhiye, 2012).

The negative $\Delta H^{\#}$ refers to exothermic reaction, the positive $\Delta G^{\#}$ obtained indicate that the reaction is non-spontaneous. Positive $\Delta G^{\#}$ this could be because the activated state is a well solvated structure formed between. The dye molecules and the reaction intermediates that is hydroxyl radicals which is also, supported by negative entropy of activation. In the present case the value of $\Delta S^{\#}$ is negative as in Table 2, so that, the complex formed is more ordered than the reactants.

Initially the complex formed is unstable and degradation of the reactants into products is not very slow but takes place rapidly under present experimental conditions (Al-Ekabi and Mayo, 1985; Gajbhiye, 2012).

CONCLUSION

Experimental results indicated that the degradation of dye is facilitated in the presence of catalysts. Comparison of photocatalytic activity of different catalysts has clearly indicated that the nano ZnO is better photocatalyst for degradation of carmine dye solution The initial rate of photodegradation increased with increase in catalyst dose up to an optimum loading. Further increase in catalyst dose showed no effect. As the initial concentration of dyes was increased, the rate of degradation decreased in each both catalysts, experimental results indicated that the decolorization of dyes is facilitated in the presence of catalyst and were favorable in acidic region and the rate of decolorization and degradation of carmine dye solution increases with the increase of the temperature. The photocatalytic degradation followed pseudo-first order kinetics.

REFERANCES

Al-Ekabi, H. and P.D. Mayo, 1985. Surface photochemistry: Cadmium sulfide photoinduced cis-trans isomerization of olefins. J. Phys. Chem., 89: 5815-5821.

Attia, A.J., S.H. Kadhim and F.H. Hussein, 2008. Photocatalytic degradation of textile dyeing wastewater using titanium dioxide and zinc oxide. J. Chem., 5: 219-223.

Chen, D. and A.K. Ray, 1998. Photodegradation kinetics of 4-nitrophenol in TiO2 suspension. Wat. Res., 32: 3223-3234.

Daneshvar, N., D. Salari and A.R. Khataee, 2004. Photocatalytic degradation of azo dye acid red 14 in water on ZnO as an alternative catalyst to TiO_2. J. Photochem. Photobiol. A. Chem., 162: 317-322.

Egzar, H.K., M.S. Mashkour and M. Juda, 2013. Study the Photodegradation of aniline blue dye in aqueous phase by using different photocatalysts. Intl. J. Eng. Technol., 13: 26-33.

Fatta-Kassinos, D., K. Bester and K. Kummerer, 2010. Xenobiotics in the Urban Water Cycle: Mass Flows, Environmental Processes, Mitigation and Treatment Strategies. Vol. 16, Springer, Berlin, Germany, ISBN:978-90-481-3508-0, Pages: 507.

Fu, F. and Q. Wang, 2011. Removal of heavy metal ions from wastewaters: A review. J. Environ. Manage., 92: 407-418.

Gajbhiye, S.B., 2012. Photocatalytic degradation study of methylene blue solutions and its application to dye industry effluent. Intl. J. Mod. Eng. Res., 2: 1204-1208.

Galvez, J.B. and R. Malato, 2003. Solar Detoxification. United Nations Educational, Scientific and Cultural Organization, Paris, France, ISBN:9789231039164, Pages: 187.

Hussein, F.H. and A.N. Alkhateeb, 2007. Photo-oxidation of benzyl alcohol under natural weathering conditions. Desalin., 209: 350-355.

Hussein, F.H., 2011. Photochemical Treatments of Textile Industries Wastewater. In: Advances in Treating Textile Effluent, Hauser, P.J. (Ed.). In Tech Open, London, England, UK., ISBN:978-953-307-704-8, pp: 118-144.

Kim, T.W. and M.J. Lee, 2010. Effect of pH and temperature for photocatalytic degradation of organic compound on carbon-coated TiO_2. J. Adv. Eng. Technol., 3: 193-198.

Kyriakopoulos, G. and D. Doulia, 2006. Adsorption of Pesticides on Carbonaceous and Polymeric Materials from Aqueous Solutions: A Review. Sep. Purif. Rev., 35: 97-191.

Movahedi, M., A.R. Mahjoub and S. Janitabar-Darzi, 2009. Photodegradation of congo red in aqueous solution on ZnO as an alternative catalyst to TiO_2. J. Iran. Chem. Soc., 6: 570-577.

Obies, M., 2011. Photocatalytic decolorization of Bismarck brown R. MSc Thesis, Chemistry Department, College of Science, Babylon University, Hillah, Iraq.

Srivastava, V., D. Gusain and Y.C. Sharma, 2013. Synthesis, characterization and application of zinc oxide nanoparticles (n-ZnO). Ceram. Intl., 39: 9803-9808.

Tian, L., B. Lin, L. Wu, K. Li and H. Liu *et al*., 2015. Neurotoxicity induced by zinc oxide nanoparticles: Age-related differences and interaction. Sci. Rep., 5: 1-12.

Wang, J., X. Deng, F. Zhang, D. Chen and W. Ding, 2014. ZnO nanoparticle-induced oxidative stress triggers apoptosis by activating JNK signaling pathway in cultured primary astrocytes. Nanoscale Res. Lett., 9: 1-12.

Zainal, Z., C.Y. Lee, M.Z. Hussein, A. Kassim and N.A. Yusof, 2005. Electrochemical-assisted photodegradation of dye on TiO_2 thin films: Investigation on the effect of operational parameters. J. Hazard. Mater., 118: 197-203.

Zhang, X., J. Qin, Y. Xue, P. Yu and B. Zhang *et al*., 2014. Effect of aspect ratio and surface defects on the photocatalytic activity of ZnO nanorods. Sci. Rep., 4: 4-11.