Advanced Oxidation Process treatment for azo dyes pollutants using ultra-violet irradiation

Ahmed K. Abass and Suzan Dheyaa Raoof

Department of Chemistry, College of Science, University of Al-Qadisiya, Al-Qadisiya, Iraq.
Ahmed.Kadhim@qu.edu.iq

Abstract
The research included studying the photocatalytic efficiency of zinc oxide onto photo reaction of Alizarin yellow (A.Y) in the presence of ultraviolet radiation. Several parameters affect the photolysis rate of dye were studied such as: effect of acidic function, different oxidants and supporting of zinc oxide surface. The solution of dye was irradiated using medium pressure mercury lamp 400 W. The results showed that the maximum percentage of dye photolysis was at a natural acidic function using hydrogen peroxide as oxidant and activated charcoal as support. The kinetics of reaction were also studied and the results proved that the reaction from pseudo first order.

Keywords: zinc oxide, advanced oxidation process, water pollution, azo dyes and supports.

Introduction
Pollutants can be defined as materials that change the characteristics of the environment negatively and exposure life of living with the risk [1]. One of the important properties of pollutants is it's the interaction with the other or with other materials which have a more severe impact than would be expected from the effect of each pollutant separately [2]. Therefore, pollution can be defined as any change in the natural conditions of the air, water and soil, which affect human, animal and plant. The environmental pollution can be classified into three types: air pollution, water pollution, soil pollution and radioactive contamination and other [1] - [3].

Water pollution is defined as the presence of any foreign substance, whether it was organic or radiological or biomaterial in the water, which is trying to reduce its quality and quality [4]. Water pollution is the physical or chemical or biological changes occur
in the water and lead to change its quality so that it becomes harmful substance [5]. One of the water pollutants is pesticides, industrial dyes, heavy metals and toxic ions that represent a risk to human wellness. The pollution by dyes represents a major source of pollution of the environment that lead to be the case of undesirable not only because of their colors, but because a lot of secretions and outputs toxic incoherent that are carcinogenic [6], [7]. Among these dyes are azo dyes containing chromophoric azo group with double bond (-N = N-) that causes high stability of these dyes which make up more than half of the dyes used in the present time [8]. Alizarin yellow is the type of azo dyes also called Alizarian Yellow Sodium Salt or 5- (m-nitrophenylazo) Salicylic Acid Sodium Salt prepared by Rudolf Nietzki in 1887, producing from dialysis m-nitroaniline and associate with salicylic acid [9]

In that respect are three methods employed to treat water pollution are [10]: physical, biological and chemical methods. The advanced oxidation process (AOP) is of the chemical methods and which is referring to a set of processing techniques designed to remove organic and inorganic materials in water and wastewater by oxidation [11]. These methods include the generation of highly effective radicals (especially hydroxyl radicals HO•), and are classified into heterogeneous methods which are include non-photo methods (O3, O3 / H2O2, H2O2 / Fe²⁺ (Fenton system), O3 / catalyst (CAT), H2O2 / Ultrasound (US), O3 / US) and photo methods (O3 / UV, H2O2 / UV, O3 / H2O2 / UV, H2O2 / Fe²⁺ / UV (Photo-Fenton), UV / TiO2, H2O2 / TiO2 / UV, O2 / TiO2 / UV, UV / US), and heterogeneous methods in the presence of semiconductors materials: ZnO / UV, SnO2 / UV, TiO2 / UV, TiO2 / H2O2 / UV) [10] - [12]

Figure (1): Structural formula of Alizarin yellow dye

Materials and methods
Materials used: Alizarin yellow, activated charcoal and potassium chromate have been obtained from Merck Company. Zinc chloride obtained from SDFCL Company, sodium hydroxide, hydrogen peroxide and pure ethanol have been getting them from Scharlau Chemie SA. Hydrochloric acid, Bentonite and Sodium persulfut obtained from BDH Company.

Instruments used: the structure of zinc oxide was examined using X-ray Diffraction Shimadzu (LabX XRD-6000), Infrared Spectra were recorded using Shimadzu (FTIR 8000 Series), the electronic spectra was scanned using Ultraviolet Spectrophotometer (UV-1650) Shimadzu, pH measurements were done using 211-Instrument Hanna.

Zinc oxide was prepared by precipitation method. 32000 mg/L of an aqueous solution of sodium hydroxide was added drop by drop to 54400 mg/L aqueous solution of zinc chloride for 20 minutes with stirring for two hours and keep overnight, then filtered and washed several times with warm water to remove free ions then the precipitate dried and burned for two hours at 773 K.

The calibration curve of the dye was prepared by set of solutions with known concentrations ranging from (5-50) mg/L then the absorbance of each concentration was measured at $\lambda_{\text{max}} = 353$ nm. In all experiments the concentration of dye was 40 mg/L, weight of zinc oxide was 0.3 gm, the temperature was 30 C and at natural pH. The reaction of the dye in the dark was examined at different conditions first dye with oxygen only second dye with zinc oxide only and third dye with oxygen and zinc oxide. Also the effect of pH was studied at different values ranging from (3-11) and pH of the solution was adjusted by adding drops of 0.1 M of Hcl or by adding drops of 0.1 M of NaOH. The effect of oxidant type was studied using different oxidants as potassium chromate, potassium persulfate and hydrogen peroxide.the effect of support with zinc oxide was studied using different sporting material as bintonite, silicon dioxide and aluminium oxide.in all photo reactions the ultra violet source used was medium pressure mercury lamp 400 watt, the irradiation exposure time was two hours and drawing 3 mL of solution each 15 min.

The conversion % was calculated as following equation:

$$\text{Conversion} \% = \frac{(C_0-C)}{C} \times 100 \ldots \ldots (1)$$
Where \( C_0 \) = initial concentration of the dye and \( C \) = concentration of the dye at any time.

**Results and discussion:**

1. **Study of X-ray diffraction spectrum**

   X-ray diffraction technique was applied to study the crystallinity of the prepared catalyst calcined at 773 K and through one hour. It was noted that the values of the peaks correspond to the hexagonal (wurtzite) of zinc oxide [13], as exhibited in Figure 2. The crystal size of zinc oxide was measured using Debye Scherrer equation [14]:

   \[
   D = \frac{K \lambda}{\beta \cos \theta}
   \]

   Since the \( D \) = crystal size of catalyst, \( K \) = Debye coefficient equal to (0.9), \( \lambda \) = wavelength (0.15405 Å), \( \beta \) = represents a FWHM of the highest peak of catalyst, \( \theta \) = angle of diffraction.

   ![XRD of ZnO prepared at 773 K calcination temperature.](image)

2. **Study the infrared spectrum**
The infrared spectrum of ZnO was recorded within the range (400-4000) cm\(^{-1}\) using KBr disk. A broad band of IR spectrum was noticed at 3400 cm\(^{-1}\) belongs to stretching vibration of the hydroxyl group. The absorption peak at 1625 cm\(^{-1}\) represents bending vibration of the hydroxyl group and the appearance of absorption bands between 501-401cm\(^{-1}\) represents stretching vibration of Zn-O [15], [16], as shown in Figure 3.

![Figure (3): IR spectrum of ZnO calcined at 773 K.](image)

3. Study the electronic spectrum

The electronic spectrum of ZnO was determined. The appearance of absorption band at 390 nm [17] belong to band gap of ZnO due to transition of electrons from valance band to conduction band (O 2p → Zn 3d) [15].
4. Determine the calibration curve

Figure (5) represents the electronic spectrum of the dye, which showed the maximum absorption at the wavelength of 353 nm belonging to the transitions $\eta \rightarrow \pi^*$ for azo group (-N = N-) [18], [19] which it a monitor for follow-up photo reaction of dye.

Figure (5): Electronic spectrum of A.Y dye using water as a solvent.
The calibration curve of dye was determined by set of concentrations ranging (5-50) mg/L and the absorbance at 352 nm of each concentration was measured. Then the concentration at (x) axis was plotted against observance at (y) axis the result appears straight line obey Beer-Lambert law as illustrated in equation (2) [20]

\[ A = \varepsilon bc \] .......... ... (3)

Where \( A \) = absorbance, \( \varepsilon \) = molar absorbance, \( c \) = concentration.

5. Dark reactions

The reaction of the dye in the dark was studied in three cases: first case in the presence of oxygen only second case in the presence ZnO only and third case in the presence of oxygen and ZnO.

It has been observed that the highest percentage of dye conversion was using oxygen and zinc oxide equal to 10.296 % as in figure (7) and the highest value of the first order constant was \( 0.08 \times 10^{-2} \text{ min}^{-1} \).
6. Effect of pH

The study showed the effect of different values of the acidic function (pH = 3, 5, 7, 9, 11) onto A.Y dye using a concentration of 40 ppm and the presence of oxygen and zinc oxide and weight of catalyst 0.3 g. The solution was exposed to ultraviolet radiation for a period 120 min. It can be seen that the conversion % of dye increases with increasing pH values where gave the highest percentage of dye conversion was at the natural pH of the dye (pH = 8). The amphoteric manner of zinc oxide is very significant to hold the rate of reaction that takes space on the airfoil of the particles where the force on the airfoil of the catalyst charge. The zpc of ZnO is 9.0 ± 0.3 this mean that the of surface zinc oxide is positive at pH less than 9 and be negatively charged at pH higher due to the adsorption of ions HO\(^-\). The presence of large amounts of HO\(^-\) on the surface of zinc oxide particles will form hydroxyl radicals, which the photo stimulation increases with increasing pH due to the dissolution of zinc oxide at low pH [21], [22]. Figure (8) referred that the maximum percentage of photolysis was 92.541% at pH = 8, having rate constant 1.9 \times 10^{-2} \text{ min}^{-1}.
The reason can be explained as a result of electrostatic interactions between the positively charged of the catalyst and anions of dye leading to strong adsorption of the dye on the zinc oxide. In alkaline media, the adsorption of the dye molecules is reduced and the potential causes of this behavior is to be a lot of hydroxyl radicals [21].

7. Effect of oxidants

The effect of different oxidants (potassium dichromate, persulfate potassium and hydrogen peroxide) was studied onto photoreaction of the dye with concentration equal to 40 mg/L for the oxidizer. The solution of dye was exposed to ultraviolet radiation for a period of 120 min the presence of 0.3 gm zinc oxide, it was noted that the highest percentage of conversion of the dye was by using of hydrogen peroxide which was 93.172% and the rate constant was 2.0x10^{-2} min^{-1} as in figure (9).

Figure (8): Conversion % of the dye at different pHs
Where the addition of hydrogen peroxide inhibits the recombination of electron-hole by the electron received from photolysis and coming from the conduction band of semiconductor which forms hydroxyl radicals, this electron is regarded as a strong oxidizer [23].

8. Effect of support onto surface of catalyst

The effect of the nature of the support onto the photo activity of catalyst was studied using different supports (alumina, silica, bentonite, activated charcoal). It has been found that the highest percentage of conversion shown (figure 10) was 99.779% when using activated charcoal and the rate constant was $1.3 \times 10^{-2}$ min$^{-1}$. 

Figure (9): conversion % of the dye at different oxidizers
This can be excused as the activated charcoal is a good adsorbent material because the high specific surface area. The basic unit of activated charcoal is carbon with the possibility of the existence of charge sites positively charged and the other a negative addition to high porosity [24]. While alumina gave a less percentage of conversion due to existence of positive charges therefor weak functional groups [25].

References:
1- DX, 1990. Environmental pollution, translation: a. Dr. Korkees Abdul-Adam, Ministry of Higher Education and Scientific Research, University of Basra, Dar Al-Hekma.
2- Warren, C.E.,1971. Biology and water pollution and its control.W.B Saund company, London , p: 434.
3- Siegel, F.R and Wiley, J., 1971. Applied geochemistry, pp. 352.
4- Muir, G.D., 1977. Hazards in the chemical laboratory, 2nd edition, the Chemical society, London.
5- Farouha, P.O., Qanbour, FE, 1989. Environmental pollution. Ministry of Higher Education and Scientific Research, University of Baghdad, p. 669.
6- Suteu, D., Zaharia, C., Muresan, A., Muresan, R. and Popescu, A., 2009. Environmental Engineering and Management Journal, 5, pp. 1097-1102.
7- Zaharia, C., Suteu, D., Muresan, A., Muresan, R. and Popescu, A., 2009. Environmental Engineering and Management Journal, 6, pp.1359-1369.
8- Hunger, K., 2003. Industrial Dyes: Chemistry-Properties-Applications, WILEY-VCH, Germany, p:14.
9- Bowes, A., Elliott, S.C., Harris, L.T., Methe, E., Razak, M. and Subagiyo, P.Y., 1991. Important Early Synthetic Dyes Chemistry Constitution Date Properties, Conservation
Analytical Laboratory Smithsonian Institution, p: 31.
10- Loures, C.A., Alcântara, M.A., IzárioFilho, H.J., Teixeira, A.C., Silva, F.T. and Paiva, T.C., 2013. International Review of Chemical Engineering, 5, pp.102-120.
11- Mota, A.L., Albuquerque, L. F. Beltrame, L. T.C., Chiavone-Filho, O., Machulek Jr., A. and Nascimento, C.A.O., 2008. Brazilian Journal of Petroleum and Gas, 2, pp. 122-142.
12- Munter, R., 2001. Proc. Estonian Acad. Sci. Chem, 50, pp. 59–80.
13- Rahimi, R., Shokrayian, J. and Rabbani, M., 2013. Synthesis of ZnO nanorods modified with TPP, TPSPS and Cu-TPPS for photodegradation of MB, 17th International Electronic Conference on Synthetic Organic Chemistry, pp. 1-14.
14- Chen, J., Wen, X., Shi, X. and Pan, R., 2012. Synthesis of Zinc Oxide/Activated Carbon Nano-Composites and Photodegradation of Rhodamine B, Environmental Engineering Science, 29, 6, pp. 392-398.
15- Rahimi, R. Shokrayian, J. and Rabbani, M., 2013. Photocatalytic removing of methylene blue by using of Cu-doped ZnO, Ag-doped ZnO and Cu,Ag-codoped ZnO nanostructures, 17th International Electronic Conference on Synthetic Organic Chemistry.
16- Lavand, A.B. and Malghe, Y.S., 2014. Synthesis, Characterization, and Visible Light Photocatalytic Activity of Nanosized Carbon Doped Zinc Oxide, International Journal of Photochemistry, 2015, pp.1-9.
17- Amer, H. A., 2012. ZnO nano-particle catalysts in contaminant degradation processes with solar light Naked and supported systems, Thesis M.Sc., An-Najah National University.
18- Pavia, D., Lampman, G., Kriz, G., 2001. Introduction to Spectroscopy, 3th edition, p: 390.
19- Sun, W., Chen, L., Tian, J., Wang, J. and He, S., 2013. Degradation of a monoazo dye Alizarin Yellow GG in aqueous solutions by gamma irradiation: Decolorization and biodegradability enhancement, Radiation Physics and Chemistry, 83, pp.86–89.
20- Hardesty, J.H. and Attili, B., 2010. Spectrophotometry and the Beer-Lambert Law: An Important Analytical Technique in Chemistry, pp.1-6.
21- Mashkour, M.S.,2012. Decolorization of Bromo phenol blue Dye Under UV-Radiation with ZnO as Catalyst, Iraqi National Journal of Chemistry, 46, pp. 189-198.
22- Ali, A. H., 2013. Photocatalytic Degradation and COD Removal for Indigo Carmine Dye Using aqueous Suspension of Zinc Oxide, Iraqi National Journal of Chemistry, 51, pp.288-300.
23- Para, B., Singh, P. and Jonnalagadda, S.B., 2009. Artificial light assisted photocatalytic degradation of lissamine fast yellow dye in ZnO suspension in a slurry batch reactor, Indian Journal of Chemistry, 48A, pp.1364-1369.
24- Hoehn, R.C., 1996. Class Notes CE 4104 Water and Waste water Design, VirginiaTech. 10, 37, 48, pp. 227-236.
25- Alwan, LH, Jabr, LL. Mahmoud, R., 2009. Study of the effect of the nature of the adsorbent substance on benzidine, Kirkuk University Journal - Scientific Studies, 4, 2.