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Preparation And Characterization Of TiO_2/Ag_2O Nano Particles In Degradation Photocatalyst Environmental Pollutants Direct Red 23 In Photo Reactor CFBR

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Abstract*—In this study, photocatalytic degradation of azo dye Direct Red 23(DR23) in aqueous solution using TiO_2/Ag_2O nano particles was employed to the degradation rate of dye enhances. Using of sol-gel method for synthesis nano particles TiO_2/Ag_2O. Nano particles have been characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), BET surface area analysis and Fourier transform infrared spectroscopy (FT-IR). A circulating fludized bed photo reactor (CFBR) with capacity 3 L, and equipped with a lamp UV-C (15 W) was used. The effect of operational parameters such as: pH, catalyst amount, dye concentration and H_2O_2 concentration were studied. The results showed that pH= 6, catalyst amount = 25 (mg/lit), dye concentration= 30 ppm and H_2O_2 concentration = 30 ppm was optimum conditions for this reaction. A first order reaction with k= 0.0678 min^{-1} was observed for the photocatalytic degradation reaction. The COD measurement results indicated that all organic substances were completely mineralized.

***Keywords*— Nano particles, Reactor, Photocatalytic degradation, Pollutants**

I. INTRODUCTION

Different types of dyes have been extensively used in industry for applications such as textiles, leathers, papers, foodstuffs, additives, gasoline, cosmetics, xerography, laser materials, and so on [1]. The release of wastewater containing these dyes is a dramatic source of aesthetic pollution, eutrophication and perturbations to the environment and aquatic life. Due to the complex molecule structure of azo dyes, conventional methods for waste treatment [2-4] are having several drawbacks and not effective for complete degradation of azo dye. Most of these technologies including chemical or biological ways [5] can only break little part of the azo bonds and remove some degree of color, while the azo linkages are just reduced to aromatic amines that are colorless but can also be toxic and potentially carcinogenic. Therefore, it is urgent to develop novel technology of water purification leading to complete destruction of the dangerous azo dyes. Recently, advanced oxidation processes (AOP_s) have been widely investigated of which heterogeneous photocatalysis has become the most popular. Most studies related to photocatalytic degradation of organic pollutants have been carried out using suspensions of powder TiO_2/Ag_2O in the treated solution [6-7].

TiO_2 is a cheap, readily available material, highly stable chemically and the photogenerated holes are highly oxidizing. In addition, TiO_2 is capable of oxidation of a wide range of organic compounds into harmless compounds such as CO_2 and H_2O [8]. The scientific contribution and aim of this paper are: 1) the process offers great potential as an industrial technology to detoxify wastewaters; 2) wastewater treatment sectors and textile industry will benefit from the results. In this paper, the prepared TiO_2/Ag_2O photocatalyst were characterized by SEM, XRD, BET and FT-IR analysis. The reaction kinetic of dye was studied. The effects of operational parameter such as pH, catalyst amount, dye concentration and H_2O_2 concentration on the process were studied and optimized. The present investigation discusses the use of nano particles TiO_2/Ag_2O the dye removal efficiency of azo dye Direct Red 23 solutions by UV/H_2O_2 process.

II. EXPERIMENTAL

A. Materials

The azo dye, Direct Red 23(DR23) was obtained from Alvan Sabet Company (Iran) and was used without further purification. The structure and characteristics of Direct Red 23 is shown in Table 1. The pH values were adjusted at desired level using dilute NaOH

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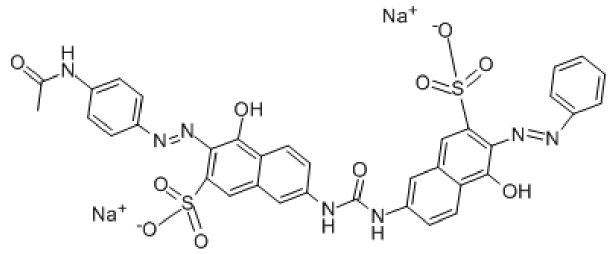
and H_2SO_4. Other materials such as $AgNO_3$, H_2O_2, titanium tetraisopropoxide and isopropyl alcohol were all Merck products. Double distilled water was used for preparation of requisite solutions.

Table I
The structure and characteristics of dye Direct Red 23

Dye	Structure	λ_{max} (nm)	MW (g/mol)
Direct Red 23 (DR23)		500	813.72

B. Apparatus

Fig. 1 shows the schematic diagram of Circulating Fludized Bed Reactor (C.F.B.R) which was used for photocatalytic decomposition of Direct Red 23. In this equipment, the total volume of photoreactor was 3 liters with three mercury lamp Philips 15W (UV-C) was used in photoreactor. UV/VIS Spectrophotometer, Jenway (6505) was employed for measuring absorbance using glass cells of path length 1 Cm. XRD analysis of the samples was done using a X-ray diffractometer Philips-XPert MPD, tube: Co kα , wavelength: λ=1.78897Å , Voltage: 40 kV, Current: 30 mA. The morphologies and specific surface areas of the photocatalyst were taken using a Philips XL30 scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FT-IR) PerkinElmer, COD analyzer Aqualytic and a Micrometric-100E Brunauer Emmett Teller (BET).

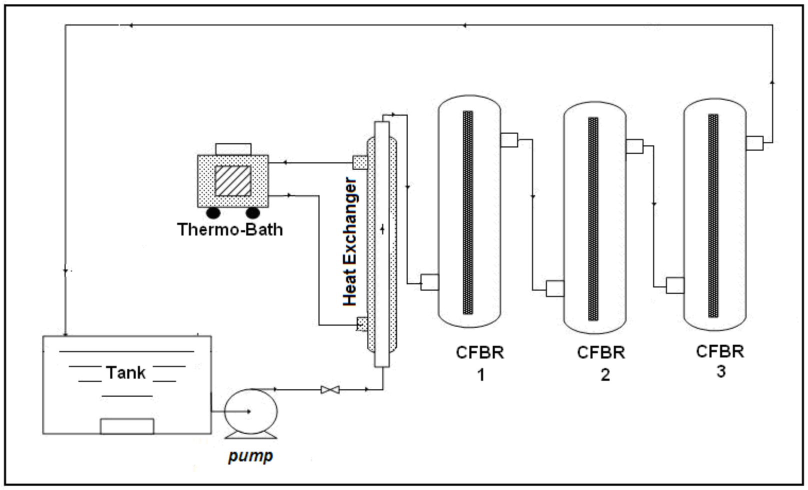


Fig.1 Schematic diagram of C.F.B.R.

C. Procedures

For the photodegradation of DR23, a solution containing known concentration of dye and photocatalyst were prepared. The suspension pH values were adjusted at the desired level using dilute NaOH 0.1N and H_2SO_4 0.1N (the pH values were measured with Horiba M12 pH meter) and then were allowed to equilibrate for 30 min in darkness. Then the prepared suspension was transferred to a 3.5 liter Pyrex tank. The photodegradation reaction took place under the radiation of Mercury lamp in 3 photoreactors is shown in the, schematic diagram Fig. 1. The concentration of the samples was determined (at 5 min intervals and centrifuged to discard any sediment) using a spectrophotometer (UV-vis spectrophotometer, Jenway (6505) at λmax = 500 nm. The

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degree of photodegradation (X) as a function of time is given by:

$$X = \frac{C_{\circ} - C}{C_{\circ}} \quad (1)$$

Where C_0 and C are the concentration of dye at $t = 0$ and t, respectively.

D. Preparation Of TiO_2/Ag_2O Nano Particles

In order to preparation TiO_2/Ag_2O nano particles the sol-gel method [9] was used in two stages. In the first stage, titanium dioxide nano particles were prepared from titanium tetraisopropoxide (TTIP) in organic solvent isopropyl alcohol (IsoprOH). First, TTIP, IsoprOH and distilled water were mixed with molar ratio of 1:1:50. Distilled water was added drop wise into the titanium solution during 2 h under magnetic stirring. Then the obtained sol dried in an oven at 100°C for 8 h. Calcination was carried out in an electric furnace at 450°C during 4 h. In the second stage, to stabilize the Ag_2O particles on the synthesized titanium dioxide obtained in the first stage, 2 g titanium dioxide particles were added to the 50 ml solution 6 M $AgNO_3$ and the obtained solution was stirred by magnetic stirrer. Then ethanol was added drop by drop to the solution and it was exposed to room air for 12 h. The obtained mixture finally washed with ethanol and deionized water, respectively, and dried in an oven at 110°C for 2 h. Then TiO_2/Ag_2O calcined an electric furnace at 500°C during 4 h. The precipitation was sieved using 100 mesh standard sieve.

III. RESULTS AND DISCUSSION

A. The Characterization Of TiO_2/Ag_2O Nano Particles

Fig. 2 shows the SEM images of (A) TiO_2 nano particles, (B) TiO_2/Ag_2O nano particles. It seems that the Ag_2O particles take place on the surface of TiO_2 particles. Regarding the specified scale in the Fig. 2, the size of particles is nanometer. Specific surface areas are commonly reported as BET surface areas obtained by applying the theory of BET to nitrogen adsorption/desorption isotherms measured at 77 K. The BET surface areas of TiO_2 particles, TiO_2/Ag_2O nano particles calculated by BET equation were 55, 35 m^2g^{-1}, respectively. The EDX spectrum image, TiO_2/Ag_2O nano particles is presented in Fig. 3. As it can be seen, elemental of each peak has been identified.

The XRD patterns of samples are illustrated in the Fig. 4. XRD patterns of the as-prepared samples (2θ ranges from 10° to 90°). Clearly the XRD patterns of TiO_2/Ag_2O consist of the TiO_2 which can be calcined at 500 ^{O}C for 4 h. The comparison of XRD patterns of TiO_2/Ag_2O nano particles being calcined at 700 ^{O}C indicated that the crystalline phase and TiO_2 nano particles was stable during the heat treatment process. The crystallite size of TiO_2/Ag_2O nano particles was calculated using the Debye-Scherer formula [10-11]:

$$D = 0.9\,\lambda / \beta \cos\theta \qquad (2)$$

Where D is the average crystallite size, λ is the wavelength of Co kα , β is the full width at half maximum (FWHM) of the diffraction peaks, and θ is the Bragg's angle. The average crystallite size of TiO_2/Ag_2O nano particles was estimated about 75 nm.

Fig. 5 shows the FT-IR spectra of (A) TiO_2 nano particles, (B) TiO_2/Ag_2O nano particles in the wave number range from 400 of 4000 cm^{-1}. The stretching vibration of the OH group appears in the range of 3200–3500 cm^{-1}. The absorption peak in the range of 2800 cm^{-1} related to stretching vibration bonding in C-H was observed in TiO_2/Ag_2O spectrum. The absorption peaks in the 688 and 517 were related to the bonding in stretching vibration of Ti-O and Ag-O in the spectrum TiO_2/Ag_2O respectively[12].

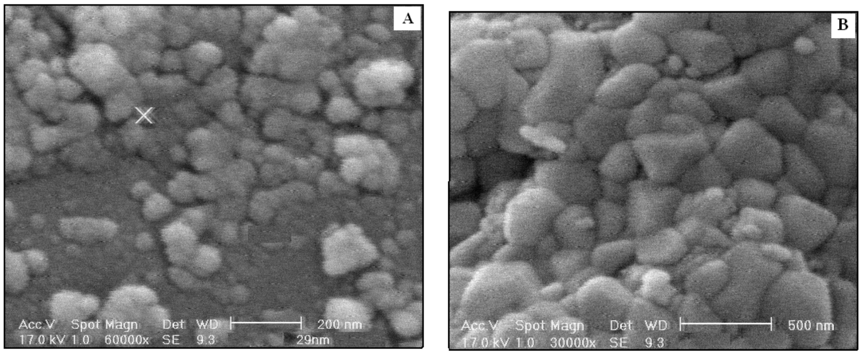

Fig. 2 SEM images of (A) TiO_2 nano particles, (B) TiO_2/Ag_2O nano particles.

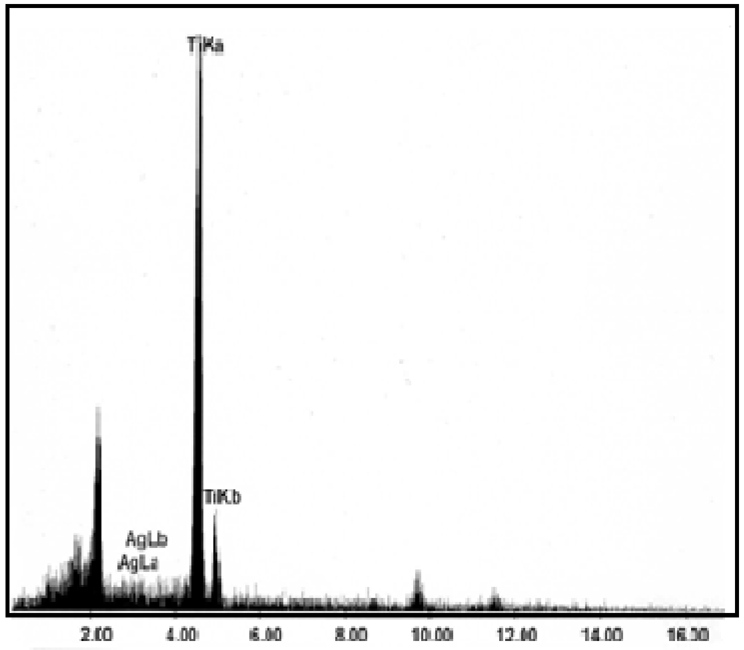

Fig. 3 EDX spectrum image of TiO_2/Ag_2O nano particles.

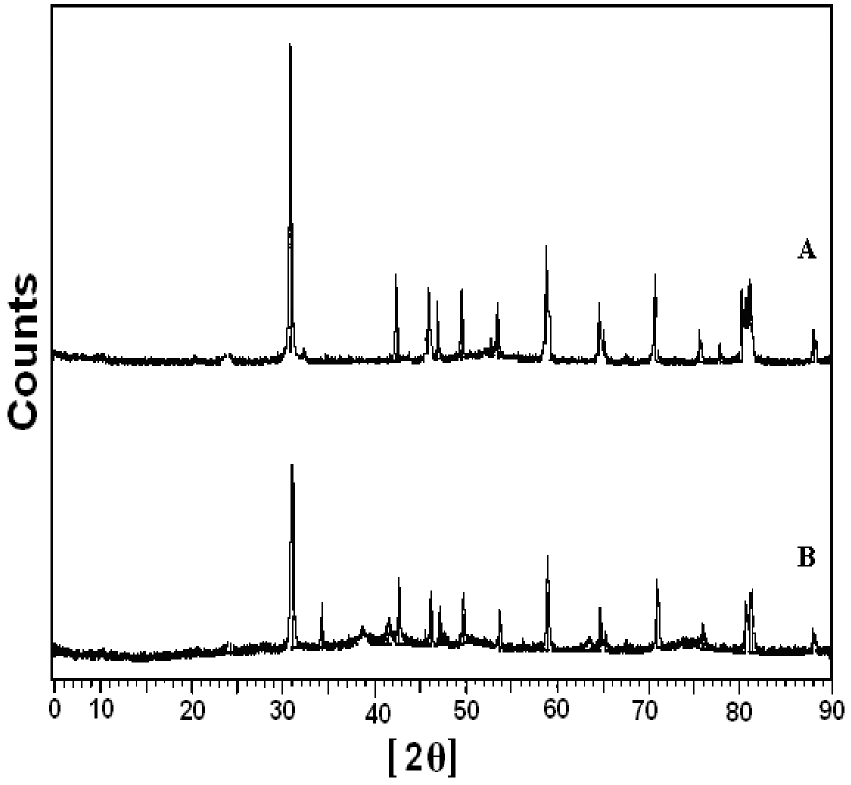

Fig. 4 XRD pattern of (A) TiO_2 nano particles, (B) TiO_2/Ag_2O nano particles.

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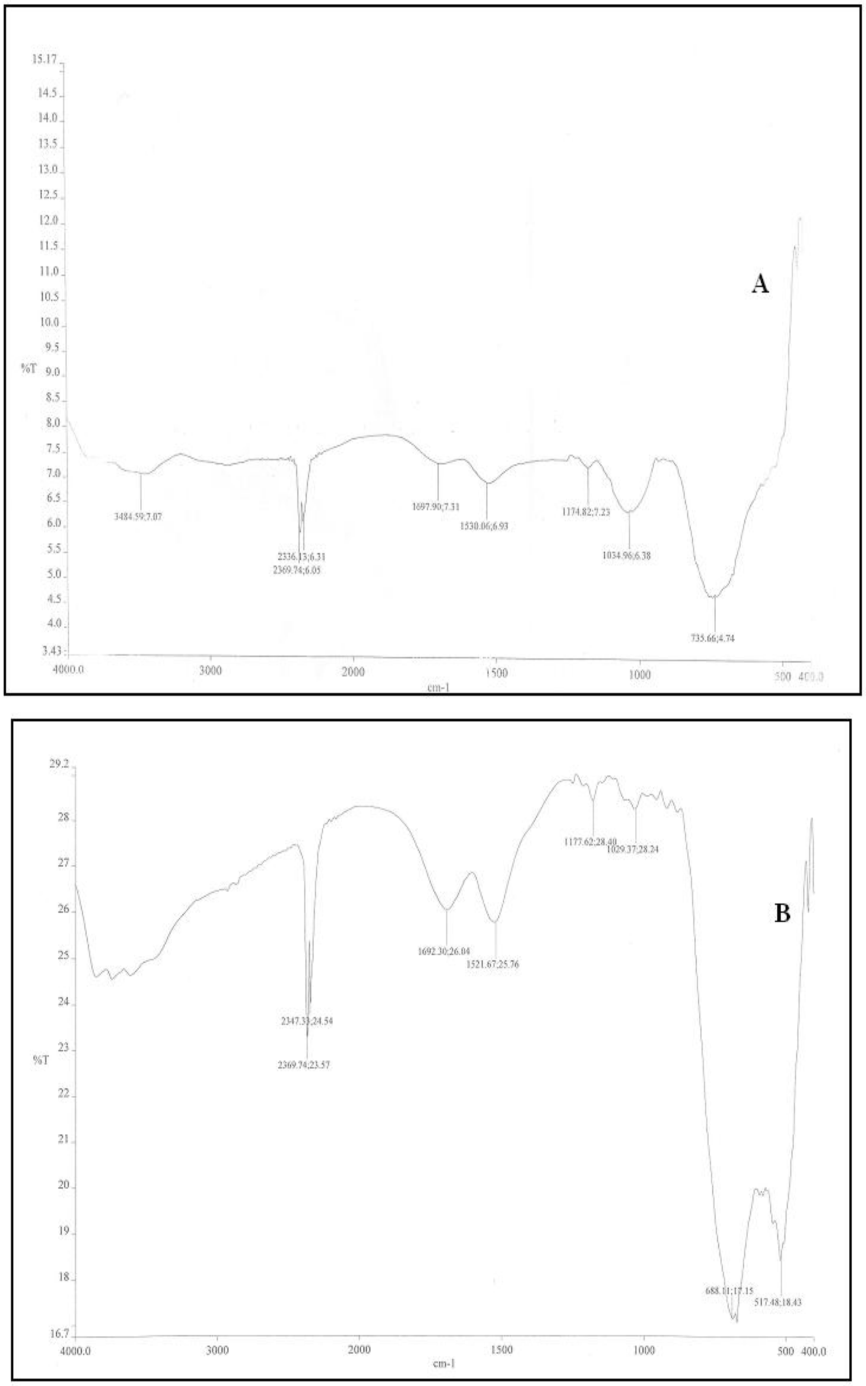

Fig. 5 FT-IR spectra of (A) TiO_2 nano particles, (B) TiO_2/Ag_2O nano particles.

B. UV- Vis Spectra

Fig. 6 shows typical time dependent UV-vis spectrum of DR23, respectively during photoirradiation with TiO_2/Ag_2O nano particles. The spectrum of DR23 in the visible region exhibits a main band with a maximum at 500 nm. Based on these results, it was shown that the ultraviolet radiation are broken the structure of dye molecules and reduced absorption intensity. Complete discoloration of dye was observed after 60 min under optimum conditions.

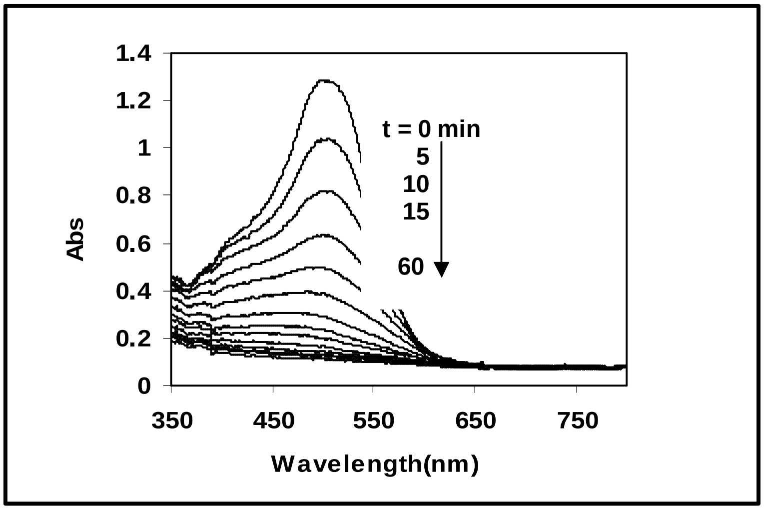

Fig. 6 UV- vis spectra of DR23 dye on photo degradation (dye concentration = 30 ppm, catalyst amount = 25 mg/l, H_2O_2 concentration= 30 ppm, pH= 6, T=298 K, irradiation time= 60 min).

C. Effect Of pH

pH is one of the main factors influencing the rate of degradation of some organic compounds in the photocatalytic process [13]. It is also an important operational variable in actual wastewater treatment. Fig. 7 shown the photodegradation of DR23 at different pH from 2-12, which clearly shown that the best results were obtained in acidic solution, (pH =6, X =94.76%). The charge of TiO_2/Ag_2O, its surface is presumably positively charged in acidic solution and negatively charged in alkaline solution. For the above reasons, dyes that have a sulfuric group in its structure, which is negatively charged, the acidic solution favors adsorption of dye onto the photocatalyst surface, thus the photodegradation efficiency increases. There is also the photocatalytic degradation of DR23 in acidic solutions, which is probably due to the formation of $OH^{\bullet}$ as it can be inferred from the reactions (3)–(6) [14].

$$e^-_{CB} + O_{2(ads)} \rightarrow {}^{\bullet}O^-_{2(ads)} \quad (3)$$

$$^{\bullet}O^-_{2(ads)} + H^+ \rightarrow HO^{\bullet}_2 \quad (4)$$

$$2HO^{\bullet}_2 \rightarrow O_2 + H_2O_2 \quad (5)$$

$$H_2O_2 + {}^{\bullet}O^-_{2(ads)} \rightarrow {}^{\bullet}OH + OH^- + O_2 \quad (6)$$

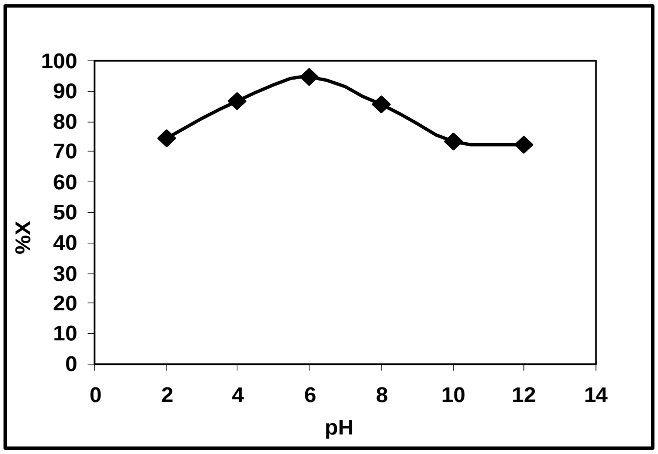

Fig. 7 Effect of pH on photo degradation of DR23 dye (dye concentration = 30 ppm, catalyst amount = 25 mg/l, H_2O_2 concentration= 30 ppm, T=298 K, irradiation time= 60 min).

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D. Effect Of Initial DR23 Concentration

The effect of initial concentration of DR23 on photo degradation efficiency is shown in Fig. 8. The photo degradation conversion of DR23 decreases with an increase in the initial concentration of DR23. The presumed reason is that when the initial concentration of dye is increased, more and more dye molecules are adsorbed on the surface of TiO_2/Ag_2O. The large amount of adsorbed dye is thought to have an inhibitive effect on the reaction of dye molecules with photogenerated sites or hydroxyl radicals, which is due the lack of any direct contact between them. Once the concentration of dye is increased, it also causes the dye molecules to adsorb light and the photons never reach the photocatalyst surface, thus the photodegradation efficiency decreases [15].

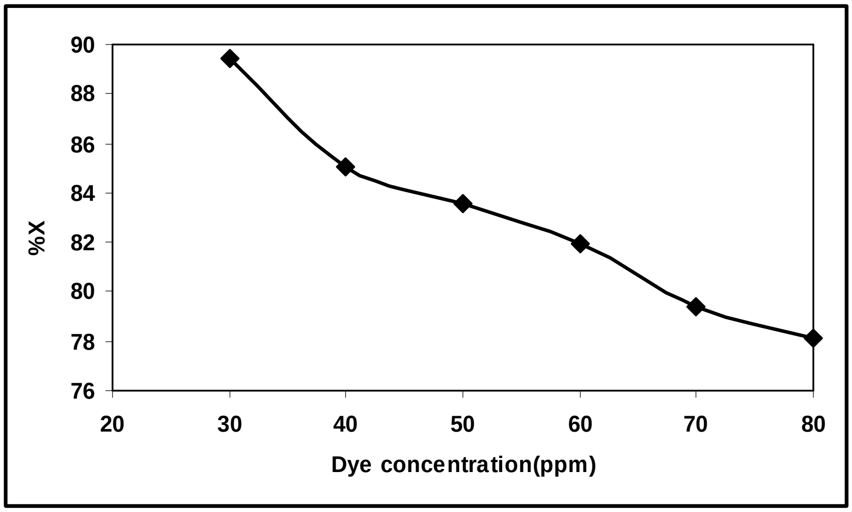

Fig. 8 Effect of initial DR23 concentration on photo degradation (catalyst amount = 25 mg/l, H_2O_2 concentration= 30 ppm, pH= 6, T=298 K, irradiation time= 60 min).

E. Effect Of Catalyst Amount

At this stage, the effect of different amounts of catalyst between 10 to 35 mg/l was tested. The results in Fig. 9 shows that increasing the catalyst amount to 25 mg/l reaction rate increased and with increasing amount of catalyst amount, reaction rate decreased. Because of reduced activity of photocatalytic in amount than 25 mg/l, which increases the photocatalytic phenomenon spread of light due to light rays with the catalyst dispersed in the solution occurred, and lost the number of photons of light energy and thus is reduced the amount photocatalytic reactions[16].

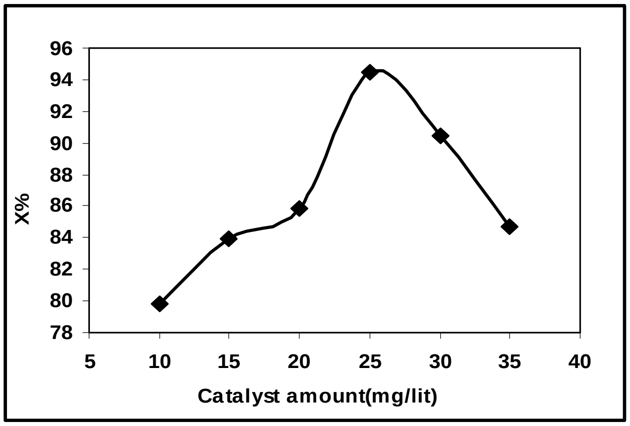

Fig. 9 Effect of catalyst amount on photo degradation of DR23 dye (dye concentration = 30 ppm, H_2O_2 concentration= 30 ppm, pH= 6, T=298 K, irradiation time= 60 min).

F. Effect Of H_2O_2 Concentration

As it can be seen in Fig. 10, the decolorization rate increased when H_2O_2 concentration changed from 5- 30 ppm. In H_2O_2 solution, the formation rate of hydroxyl radical was increased in two ways. First, symmetrical breaking of hydrogen peroxide molecule by

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illumination would also produce hydroxyl radicals. Second, the reduction of H_2O_2 in the conduction band would produce hydroxyl radicals [17-18]. So the optimal amount of H_2O_2 concentration was 30 ppm.

$$H_2O_2 + h\upsilon \longrightarrow 2OH^{\bullet} \qquad (7)$$

$$H_2O_2 + photocatalyst(e_{CB}^{-}) \longrightarrow photocatalyst + OH^{\bullet} + OH^{-} \qquad (8)$$

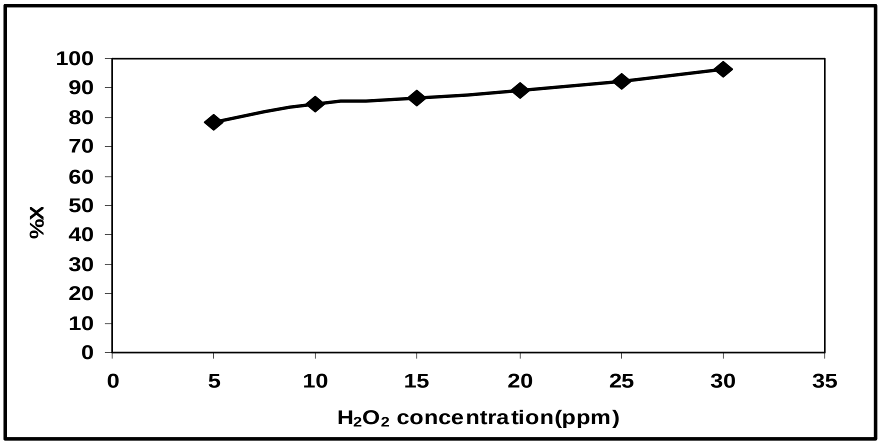

Fig. 10 Effect of H_2O_2 concentration on photo degradation of DR23 dye (dye concentration = 30 ppm, catalyst amount = 25 mg/l, pH= 6, T=298 K, irradiation time= 60 min).

G. Kinetics Of Photocatalytic Degradation Of DR23 Dye

Photocatalytic decomposition reaction kinetics of DR23 completely corresponds to the kinetic of pseudo-first-order model reaction [19]. In the kinetic equation of pseudo-first-order, the relationship between concentration(C) and time (t) is as follows:

$$\frac{-dC}{dt} = k_{app}C \qquad (9)$$

The integral equation is as follows:

$$\ln(\frac{C_0}{C}) = k_{app}t \qquad (10)$$

in which k_{app} is the apparent pseudo-first-order rate constant (that is affected by dye concentration), and t, is the reaction time.
A plot of ln (C_0/C) versus t, in optimal condition for photocatalytic degradation of DR23 is shown in Fig. 11. The linear plot suggests that the photodegradation reaction approximately follows the pseudo-first-order kinetics with rate coefficient k= 0.0678min^{-1}.

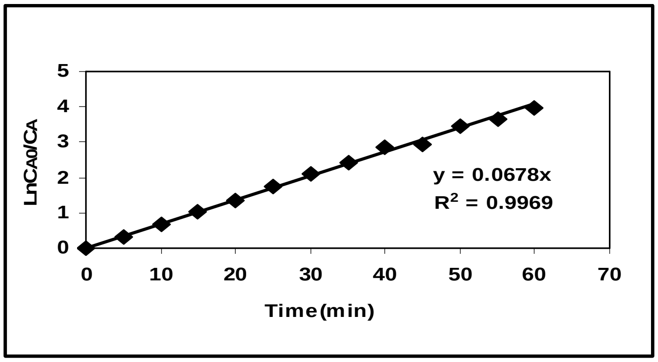

Fig.11 Kinetics of photocatalytic degradation of DR23 dye (dye concentration = 30 ppm, catalyst amount = 25 mg/l, H_2O_2 concentration= 30 ppm, pH= 6, T=298 K, irradiation time= 60 min).

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H. The COD Measurements

The chemical oxygen demand (COD) test is commonly used to indirectly measure the amount of organic compounds in colored wastewater. In this research, COD test was used to confirm that the organic pollutants are decomposed and are converted to CO_2 and H_2O. The results of these experiments are shown in Fig. 12. These results can be confirmed by the decomposition of organic matter that was present in the colored wastewater sample.

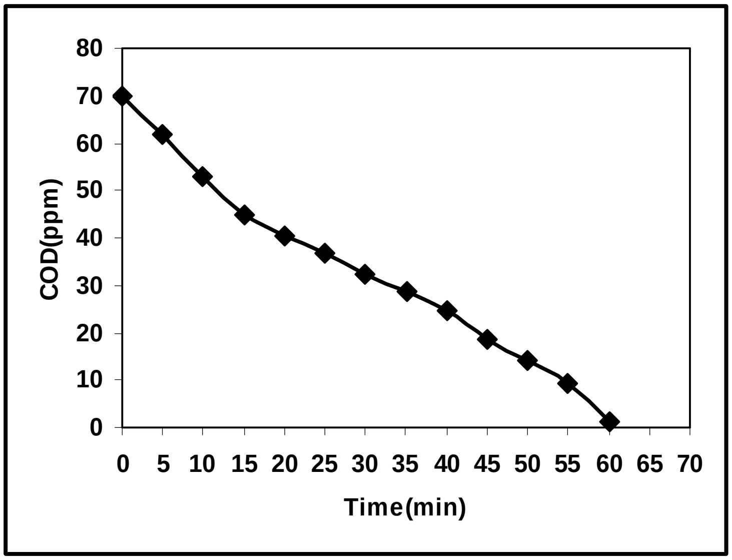

Fig.12 COD measurements of DR23 dye (dye concentration = 30 ppm, catalyst amount = 25 mg/l, H_2O_2 concentration= 30 ppm, pH= 6, T=298 K, irradiation time= 60 min).

IV. CONCLUSIONS

In this study, photocatalytic decolorization of the azo dye Direct Red 23 was investigated by the use of TiO_2/Ag_2O nanocatalyst. Physical and chemical characterization of supported nanocatalyst via sol-gel method was determined by SEM, XRD, BET and FT-IR techniques. According to the literature, the results demonstrated that the produced TiO_2/Ag_2O have sufficient properties as a photocatalyst for degradation of dye. A photo reactor CFBR was used for degradation reaction. Various factors affecting in the degradation process such as: pH, catalyst amount, dye concentration and H_2O_2 concentration were analyzed and optimized. Kinetics of photocatalytic decomposition reaction was determined. Pseudo-first-order model reaction corresponds to the experiment data of photocatalytic degradation of dye.

V. ACKNOWLEDGMENT

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REFERENCES

[1] H. Zollinger, Color Chemistry. Synthesis, Properties and Applications of Organic Dyes and Pigments, 2nd Rrevised Edition,VCH, 1991.
[2] C.M. Zhu, L.Y. Wang, L.R. Kong, Photocatalytic degradation of azo dyes by supported TiO_2 +UV in aqueous solution, Chemosphere, vol. 41, pp. 303–309, 2000.
[3] T. Sauer, G.C. Neto, H.J. Jose, Kinetics of photocatalytic degradation of reactive dyes in a TiO_2 slurry reactor, J. Photochem. Photobiol. A: Chem., vol. 149, pp. 147–154, 2002.
[4] S. Mozia, et al., Effect of process parameters on photodegradation of Acid Yellow 36 in a hybrid photocatalysis– membrane distillation system, Chem. Eng. J. , vol. 32, pp. 134-138, 2009.
[5] N. Guettai, H. Ait Amar, Photocatalytic oxidation of methyl orange in presence of titanium dioxide in aqueous suspension. Part II. Kinetics study, Desalination, vol. 185, pp. 439-448, 2005.
[6] C. Liu, C. Cao, X. Luo, S. Luo, Ag-bridged Ag_2O nanowire network/TiO_2 nanotube array p–n heterojunction as a highly efficient and stable visible light Photocatalyst, j. Hazard. Mater., vol. 285, pp. 319–324, 2015.
[7] N. Sobana, K. Selvam, M. Swaminathan, Optimization of photocatalytic degradation conditions of Direct Red 23 using nano-Ag doped TiO_2, Separation and

Purification Technology, vol. 62, pp. 648–653, 2008.
[8] D. Chatterjee, S. Dasgupta, Visible light induced photocatalytic degradation of organic pollutants, J. Photochem. Photobiol., vol. 6, pp. 186–205, 2005.
[9] H. Hua, Y. Xi, Z. Zhao, X. Xie, C. Hu, H. Liu, Gram-scale wet chemical synthesis of Ag_2O/TiO_2 aggregated sphere heterostructure with high photocatalytic activity, Materials Letters, vol. 91, pp. 81–83, 2013.
[10] C. Liu, C. Cao, X. Luo, S. Luo, Ag-bridged Ag_2O nanowire network/TiO_2 nanotube array p–n heterojunction as a highly efficient and stable visible light photocatalyst, J. Hazard. Mater., vol. 285, pp. 319–324, 2015.
[11] C. Li, J.H. Hsieh, J.C. Cheng, C.C. Huang, Optical and photoelectrochemical studies on Ag_2O/TiO_2 double-layer thin films, Thin Solid Films, vol. 570, pp. 436–444, 2014.
[12] J. Coates, Interpretation of Infrared Spectra, A Practical Approach. Encyclopedia of Analytical Chemistry, John Wiley & Sons Ltd, Chichester, 2000.
[13] C. Wu, X. Liu, D. Wei, J. Fan, L. Wang, Photosonochemical degradation of Phenol in water, Water Res., vol. 35, pp. 3927–3933, 2001.
[14] J. Saien, M. Asgari, A.R. Soleymani, N. Taghavinia, Photocatalytic decomposition of direct red 16 and kinetics analysis in a conic body packed bed reactor with nanostructure titania coated Raschig rings, Chemical Engineering Journal, vol. 151, pp. 295-301, 2009
[15] Z. Zhang, Y. Xu, X. Ma, F. Li, D. Liu, Z. Chen, F. Zhang, D. D. Dionysiou, Microwave degradation of methyl orange dye in aqueous solution in the presence of nano-TiO_2-supported activated carbon (supported- TiO_2/AC/MW), j. Hazard. Mater., vol. 209, pp. 271-277, 2012.
[16] A. Fujishima, T.N. Rao, D.A. Tryk, Titanium dioxide photocatalysis, J. Photochem. Photobiol. C: Photochem. Rev., vol. 1, pp. 1-21, 2000.
[17] C.M. So, M.Y. Cheng, J.C. Yu, P.K. Wong, Degradation of azo dye Procion Red MX-5B by photocatalytic oxidation, Chemosphere, vol. 46, pp. 905-912, 2002.
[18] J.M. Lee, M.S. Kim, B. Hwang, W. Bae, B.W. Kim, Photodegradation of acid red 114 dissolved using a photo- Fenton process with TiO_2, Dyes Pigments, vol. 56, pp. 59-67, 2003.
[19] M. Saquib, M. Muneer, TiO_2-mediated photocatalytic degradation of a triphenylmethane dye (gentian violet), in aqueous suspensions, Dyes Pigments, vol. 56, pp. 37 -49, 2003.

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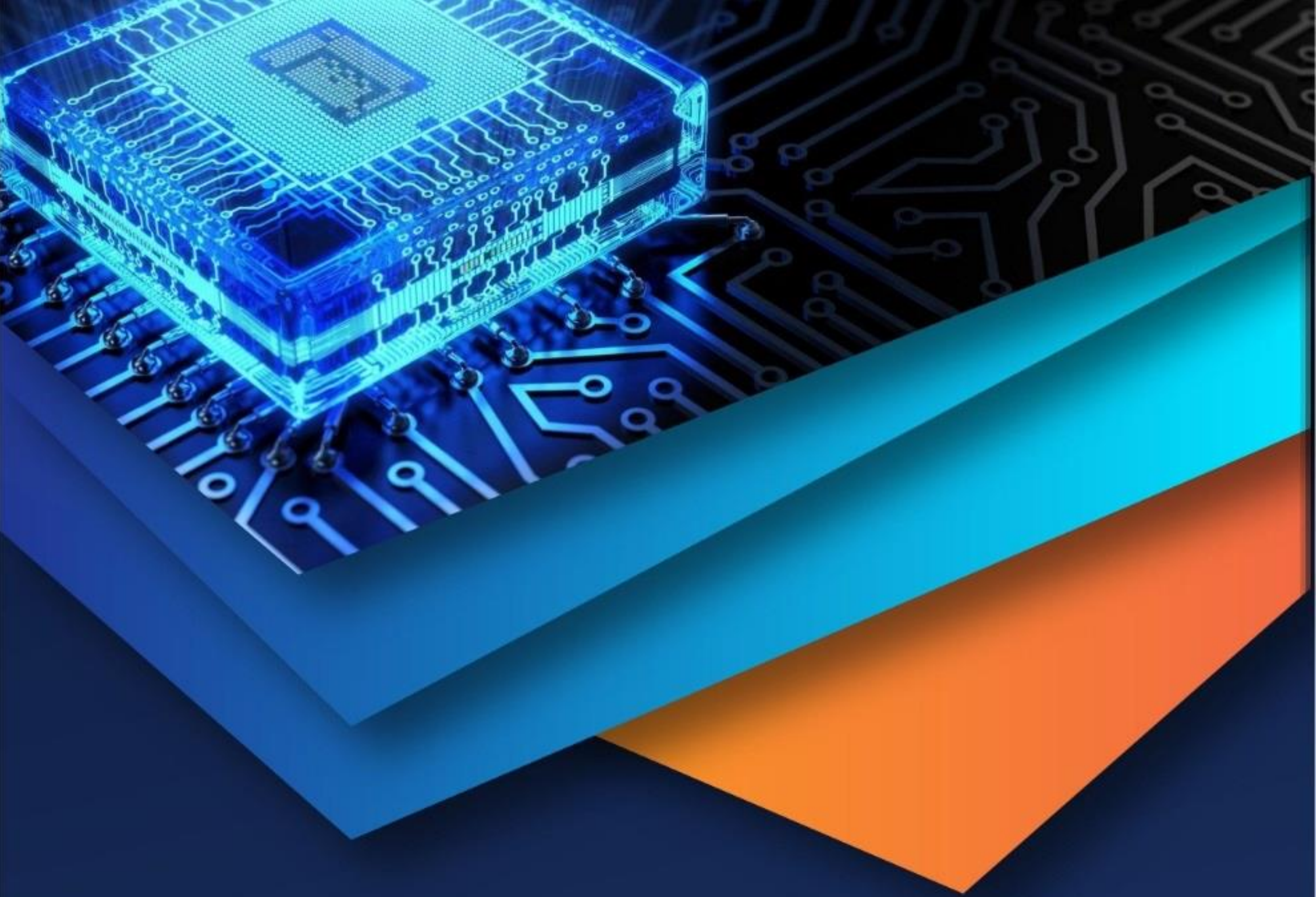

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