Studying the Photodegradation of Congo Red Dye from Aqueous Solutions Using Bimetallic Au–Pd/TiO₂ Photocatalyst

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Abstract:

In this study, the photodegradation of Congo red dye (CR) in aqueous solution was investigated using Au-Pd/TiO₂ as photocatalyst. The concentration of dye, dosage of photocatalyst, amount of H_2O_2, pH of the medium and temperature were examined to find the optimum values of these parameters. It has been found that 28 ppm was the best dye concentration. The optimum amount of photocatalyst was 0.09 g/75 mL of dye solution when the degradation percent was ~ 96 % after irradiation time of 12 hours, while the best amount of hydrogen peroxide was 7μl/75 mL of dye solution at degradation percent ~97 % after irradiation time of 10 hours, whereas pH 5 was the best value to carry out the reaction at the highest degradation percent. In addition, temperature tested at range of (25-55) C°, and it has been figured out which photodegradation percent of dye increase with raising temperature (degradation percent was ~ 98% after irradiation time of 4 hours at 55 C°), and the activation energy of the reaction was calculated (34.8016 kJ/mole) from Arrhenius law. The thermodynamic functions $\Delta H^{\#}$, $\Delta G^{\#}$, and $\Delta S^{\#}$ were obtained, where $\Delta H^{\#}$ and $\Delta G^{\#}$ are positive value which means that the reaction is endothermic and non-spontaneous respectively, while $\Delta S^{\#}$ has a negative value, thus indicates that the reactants are more disordered than the excited intermediate formed. The kinetic of the reaction was studied, and it has been found that the photocatalytic reaction follows pseudo first order reaction.

Keywords: Congo red, Kinetic, Photodegradation, Thermodynamic, Titanium dioxide

Introduction:

Many studies have been extensively investigated the heterogeneous photocatalysis oxidations, which performed with light irradiated semiconductors dispersions due to their highly efficiency as an efficient rout for degradation of toxic organic and inorganic compounds to carbon dioxide and water (1). Among the semiconductors, titanium dioxide TiO₂ is considered as an important photocatalyst, because of intense catalytic activity, when is illuminated with photons, whose energy equal to band-gap energy thus creation of electron-hole pairs on the surface of TiO₂ (2). Excited-state electrons and holes can recombine and dissipate the input energy as heat, or react with adsorbed compounds on the surface of the TiO₂. After the reaction of the electron-hole pairs with mentioned compounds, OH radicals, O_2^{-}, H_2O_2 can be produced, which play important roles in the photocatalytic reaction (3). TiO₂ exhibits wide band gab of around 3.2 eV, which limits its absorption in the visible area, therefore, many researchers have used doping method to enhance the photocatalytic performance. Thus, the optical absorption range are extended from ultraviolet to visible light, that attributed to generate the new energy level in the band gab of TiO₂ due to the distribution of nanoparticles of metal in the TiO₂ (4-8). It has been found that the treatment of dye effluents is not easy because of their various synthetic origins and aromatic structure. Congo red Fig. 1 is one of the most common synthetic dyes used in the textile manufacturing, it belongs to azo dyes, which are known to be non-biodegradable, because the existence of one or more azo groups (-N=N-) in its structure (9). The release of these azo compounds into water is undesirable, and it can be toxic to the living organisms. Degradation of naphthalene and benzene rings in Congo red cannot be applied with ordinary methods. Because of its aromatic structure, Congo red possesses high physiochemical, thermal

and optical stability (10, 11). The absorption spectrum of the Congo red Fig. 2 shows two peaks, (334 nm and 497nm) .The absorption band at 344 nm is associated with the π–π^* transition of the aromatic ring and the band at 497 nm can be corresponding to the n–π^* transition of the lone pair present in the N atom of the azo groups (–N=N–) (12). Different studies have investigated the

mineralization of Congo red dye using different methods; photocatalytic degradation (13, 14), biodegradation (15), adsorption (16). In this study, Au-Pd/ TiO_2 (17) was used as photocatalyst to degrade the Congo red dye with studying the effect of various parameters; concentration of dye, dosage of photocatalyst, amount of H_2O_2, pH of the medium and the effect of temperature.
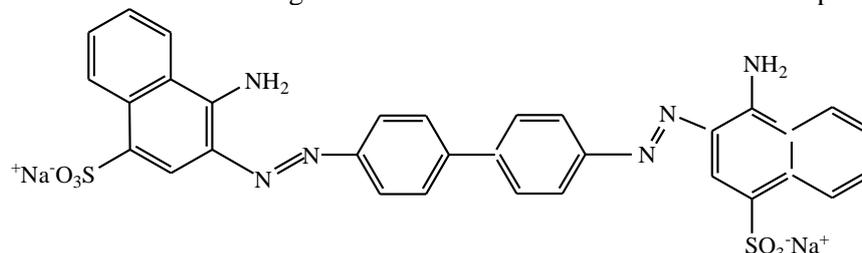
Figure 1. Molecular structure of Congo red dye (CR)
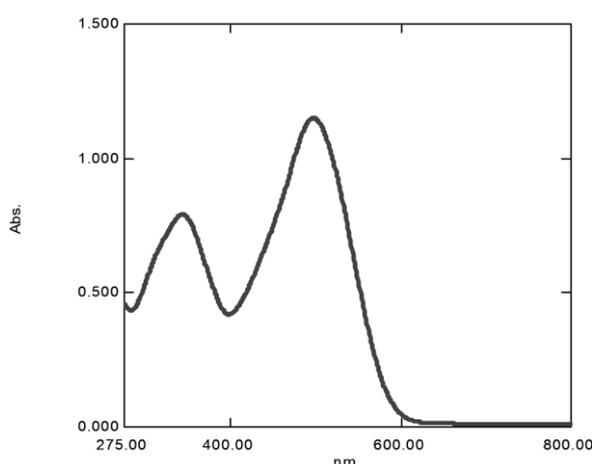
Figure 2. Absorption spectrum of Congo red dye

Materials and Methods

Materials

Congo red (CR), ($C_{32}H_{22}N_6Na_2O_6S_2$) sodium salt of benzidinediazo-bis-1- naphthylamine-4-sulfonic acid was supplied from Reidel- De Haen (Germany), Au-Pd/TiO_2 from Dr. Sanaa Tareq (17), Hydrogen peroxide (H_2O_2) was from Carlo Erba company at purity 30%. Hydrochloric acid was provided from BDH and sodium hydroxide was supplied from Riedel-De Haen AG Seelze-Hannover.

Irradiation System

In this work, the irradiation system

Figure consists of Pyrex photoreaction cell 75 mL capacity with a quartz window fitted with a focusing lens to ensure parallel beam of light. The mercury lamp 125 watt is placed 10 cm apart from the photoreaction cell. The cell is supplied with two openings of 0.5 cm in diameter and one of these is used for sampling processes. The magnetic stirrer (wise) from Daihan scientific is used to keep the catalyst aqueous suspension in homogeneous form during the photolysis experiments, and the circulating thermostat (Recirculationg chiller) from

Daihan scientific is used to control the reaction temperature. Absorption values were recorded with SmartSpec^{TM} plus spectrophotometer (BIO-RAD). All of samples were centrifuged using (centrifuge model 800 electric centrifuge), and photocatalysts were weighed using analytic sensitive balance (Sartorius) from Germany.
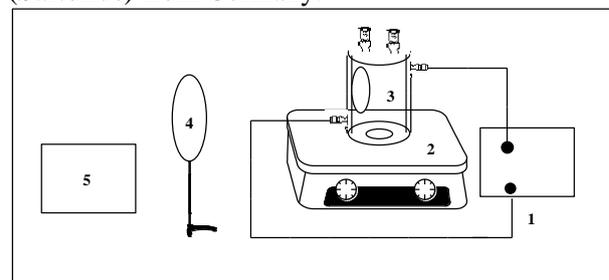
Figure 3. Irradiation System; 1- Circulator, 2-Magnetic stirrer, 3- Photoreaction cell, 4-Lens, and 5- UV- source

Standard Calibration Curve of Congo Red Dye

Figure 4 shows the standard calibration curve of Congo red of 497 nm, which was used to convert absorbance values of dye (before and after irradiation) to concentration according to beer-lambert law.

$y = 0.0534x + 0.0623$
$R^2 = 0.9983$
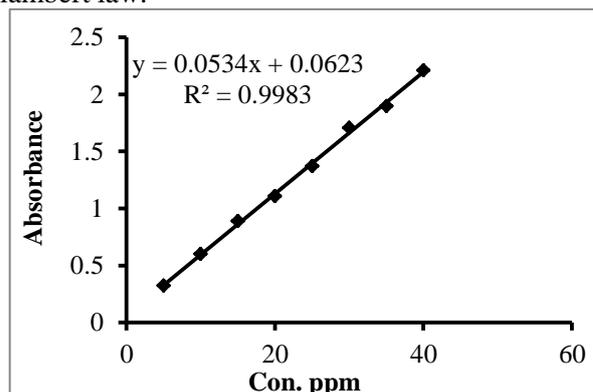
Figure 4. Calibration curve of Congo red of 497 nm

Procedure of the Degradation of Congo Red Dye

All of the experiments have been carried out in the photoreaction cell using (irradiation system) Fig. 3. Firstly, several concentrations of photocatalyst [Au- Pd/ TiO$_2$], (0.03-0.09g) were added. Circulating thermostat has been used to control the reaction temperature, while magnetic stirrer has been used to mix the mixture. The solutions were irradiated with medium mercury lamp (125 watt). A sample of 5mL of the mixture from each experiment is taken at various time intervals (1 hour), and then the photocatalyst is removed from the samples by using centrifuge. After that, observing the photolysis process has been controlled by following up the absorbance of the Congo red dye (CR) at λ_{max} 497 nm using UV-visible spectrophotometer. A series of experiments is repeated using different pH values (5-11), and the pH of the solution has been adjusted using hydrochloric acid (0.1M) and sodium hydroxide (0.1M). In addition, some experiments are carried out at various temperatures (25, 35, 45, and 55) °C to determine the best media and temperature for degradation of dye at optimum values of catalysts. The photodegradation percentage of Congo red dye is calculated using the following equation (18):

$$\% D = \frac{C_0 - C_t}{C_0} \times 100 \qquad (1)$$

where, %D: The percentage degradation, C$_0$: The initial concentration (ppm) at zero time. C$_t$: The final concentration (mg/L) at any time.

Results and Discussion
Effect of Dye Concentration

Various concentrations of Congo red dye were irradiated under light of mercury lamp (125 watt) at irradiation time of an hour to examine the best concentration of dye. From Fig. 5, it is evident that the best degradation percent was at 28 ppm, which means the penetration of light was the best at this concentration (12), for this reason, 28 ppm

became the optimum value to use through this study.
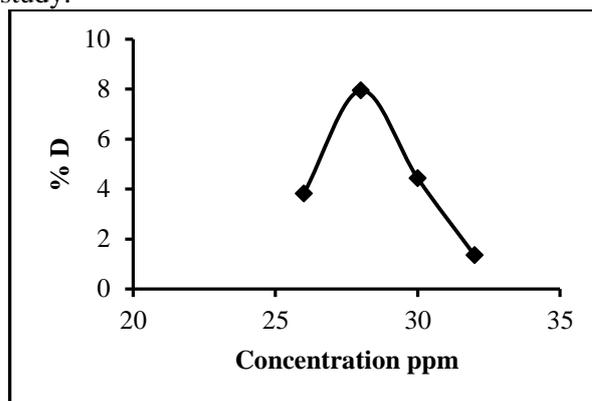
Figure 5. The relation between % D of Congo red dye solution and various concentrations.

Effect of Catalyst Dosage

Photocatalytic process of Congo red dye (CR) with different dosage of Au-Pd/ TiO$_2$ catalyst was investigated. A series of experiments were carried out to assess the optimum catalyst loading by varying the amount of catalyst (Au-Pd /TiO$_2$) from 0.03-0.1g in aqueous solution of CR (28 ppm) at 25 C°. The percentage of degradation of dye (%D) has shown appreciable results, where Fig. 6 shows the highest degradation percentage of CR dye (~ 96%), which was at 0.09 g after 12 hours of irradiation time. The photodegradation percentage of the CR was found to speed up with increase in the catalyst loading, where on the surface of the photocatalyst (Au-Pd /TiO$_2$), the formed pair of positive hole (h$^+$) at valance band (VB) and electron (e$^-$) at conductive band (CB) will react with adsorbed water molecules, dissolved oxygen, and hydroxyl groups of the surface, producing free radicals of hydroxyl and superoxide radicals. These photogenerated radicals will attack the dye molecules, which are adsorbed on the photocatalyst surface forming intermediate compounds, which break into CO$_2$, H$_2$O, and ions of NO$_3^-$ and NH$_4^+$ as expressed in the following equations

$$Au - Pd/TiO_2 + h\nu \rightarrow Au - Pd/TiO_2 \left(h^+_{(VB)} + e^-_{(CB)} \right) \quad (2)$$

$$Au - Pd/TiO_2 \left(h^+_{VB} \right) + H_2O \rightarrow H^+ + OH^\bullet \qquad (3)$$

$$Au - Pd/TiO_2 \left(e^-_{(CB)} \right) + O_2 \rightarrow Au - Pd/TiO_2 + O_2^{\bullet -} \qquad (4)$$

$$CR \text{ molecules} + OH^\bullet + O_2^{\bullet -} \rightarrow \text{intermediate compounds}$$

$$\rightarrow CO_2 + H_2O + NO_3^- + NH_4^+ \quad (5)$$
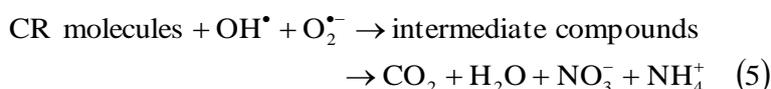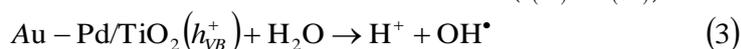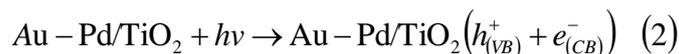
It has been observed that the increase of the photocatalyst dosage more than the optimum value causes a decrease in the photodegradation percentage of CR dye, due to the reduce of the light penetration through the solution (11), and to the

decrease in the number of active site on the surface of the catalyst resulted from the aggregation of Au-Pd/TiO$_2$ at high concentration. Our results are in good agreement with the literatures (11, 19).

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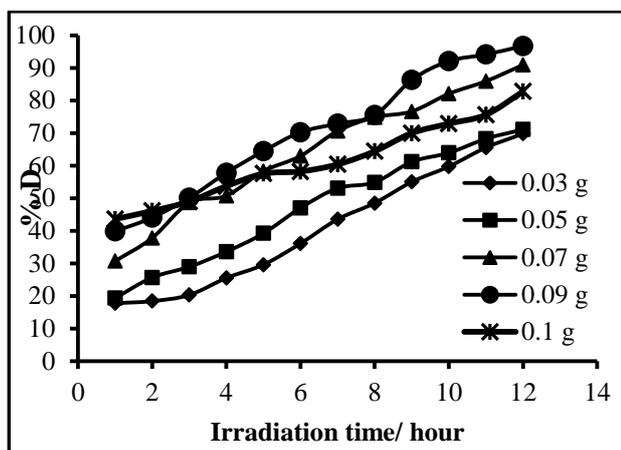
Figure 6. The relation between % D of Congo red dye solution and irradiation time at various amount of Au-Pd/TiO$_2$

Effect of H$_2$O$_2$

The effect of adding H$_2$O$_2$ on the photodegradation of Congo red dye (CR) was studied in the range of 3-9 μl/75 mL of the aqueous solution of CR at concentration of 28 ppm and using optimum value of photocatalyst (Au-Pd/TiO$_2$, 0.09 g/75 mL of solution) at 25 C°. The results revealed that the optimum addition was 7 μL/75 mL of dye solution; where the photodegradation percent was ($\sim$ 97 %) after 10 hours of irradiation time. Figure 7 shows the experimental results of adding H$_2$O$_2$ to the photocatalytic reaction. It has been observed that degradation percentage of dye increased with increase the amount of H$_2$O$_2$, which can be explained that the amount of oxygen is an important factor in the photocatalytic reaction. The oxygen is required as an electron scavenger to keep the reaction, so the oxygen flow into the photocatalytic reaction should be well regulated, as poor flow of oxygen can cause in the decrease of the efficiency of the photocatalytic reaction. For these reasons, H$_2$O$_2$ add to the photocatalytic reaction to generate more hydroxyl radicals, the effect can be expressed as in the following equations (20, 21):

$$H_2O_2 + O_2^{\bullet -} \rightarrow OH^{\bullet} + OH^{-} + O_2 \qquad (6)$$

$$H_2O_2 + h\nu \rightarrow 2OH^{\bullet} \qquad (7)$$

$$H_2O_2 + e_{CB}^{-} \rightarrow OH^{\bullet} + OH^{-} \qquad (8)$$
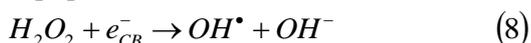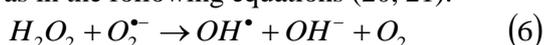
The photodegradation of CR dye decreased at higher amount of H$_2$O$_2$ beyond the optimum value, which can be attributed to hydroxyl radicals OH$^{\bullet}$ and valence band holes could be consumed by H$_2$O$_2$, and radical-radical recombination as a competitive reaction can be taken in account, as described in the following equations:

$$OH^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \qquad (9)$$

$$OH^{\bullet} + HO_2^{\bullet} \rightarrow O_2 + H_2O \qquad (10)$$

$$Au-Pd/TiO_2\left(h_{(VB)}^{+}\right) + H_2O_2 \rightarrow Au-Pd/TiO_2 + O_2 + 2H^{+} \qquad (11)$$

$$OH^{\bullet} + OH^{\bullet} \rightarrow H_2O_2 \qquad (12)$$
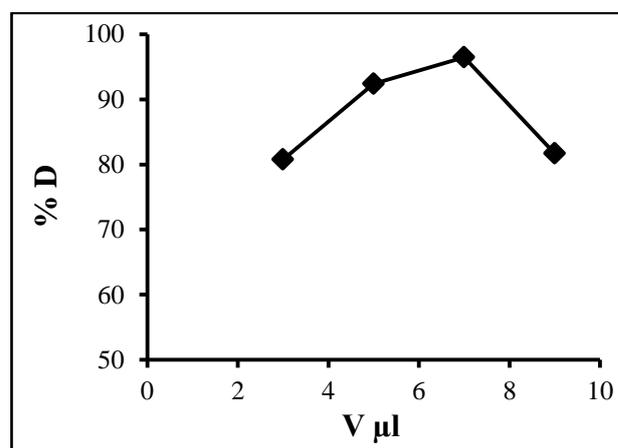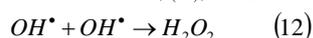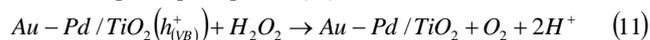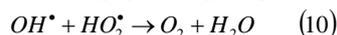
Figure 7. The relation between % D of Congo red dye solution and the volume of H$_2$O$_2$

Effect of pH

The pH plays a main role in generation of hydroxyl radicals of photodegradation reactions. The degradation of CR dye (28 ppm) was monitored varying pH ranging from 5 to 11 using optimum value of catalyst Au-Pd/TiO$_2$ (0.09 g/75 mL of dye solution) and 7μL/75mL of H$_2$O$_2$ at 25C°. Figure 8 illustrates the effect of pH of the solution on the photodegradation of CR dye; it can be observed that the best value of pH was 5, when the photodegradation percentages were recorded higher values at this pH, the percentage was 98.6% after irritation time of 8 hours. it can explain that on the basis of zero point charge (pH$_{zpc}$) of the photocatalyst that; at lower pH, the surface of the photocatalyst is positively charged below the zero point charge (zpc), as the zero point charge of the TiO$_2$ is at 5.9 (22). Moreover, the decomposition of some dyes occurs on the surface of the photocatalyst, so the adsorption is the essential step in a photocatalytic degradation process. The electrostatic interaction between positive charged surface of Au-Pd/TiO$_2$ and anionic Congo red dye leads to the strong adsorption and increasing the generation of hydroxyl radicals, which are the main oxidizing species responsible for the photocatalytic degradation (23-25)
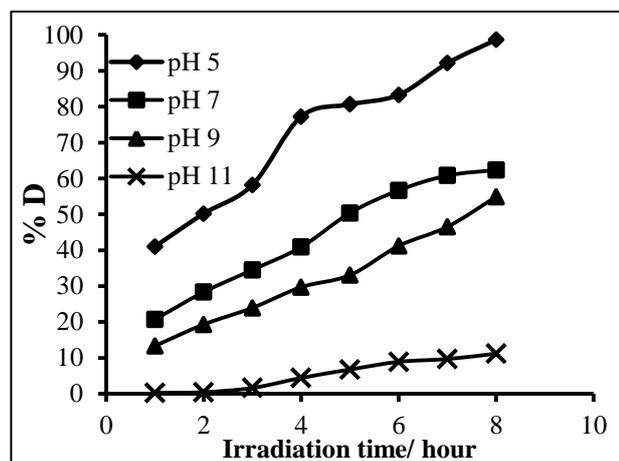
Figure 8. The relation between % D of Congo red dye solution and irradiation time at different pH

Effect of Temperature

The effect of temperature has been investigated in the range of (25-55C°) in the aqueous solution of CR dye at the concentration 28 ppm and using optimum values of catalyst Au-Pd/TiO$_2$ (0.09 g/75 mL of dye solution) and (7μL/75mL of dye solution) of H$_2$O$_2$. From Fig. 9, It can be noticed that the photodegradation of the dye increased with increasing temperature, as the photodegradation percentage at 55C° was (~ 98%) after irradiation time of 4 hours, when the colour of the dye disappeared completely. It has been reported that when the temperature of the photoreaction raised above of 80C°, it will enhanced the recombination of (electron-hole) and desorption reaction of the adsorbed compounds on the surface of photocatalyst leading to decrease the photocatalytic activity (26).
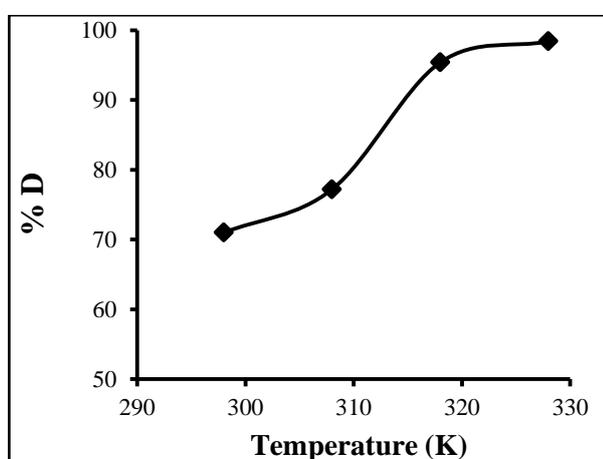
Figure 9. The relation between % D of Congo red dye solution and temperature

The activation energy E$_a$ was calculated from the Arrhenius equation (27):

$$\ln k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A \qquad (13)$$

where k is the rate constant of the photoreaction, E$_a$ is the activation energy of the reaction, R is the gas constant, T is the absolute temperature in kelvin, and A is the frequency factor. Figure 10 shows the plot of ln k against 1/T where the slope of linear relationship is equal to –E$_a$/R. The entropy of activation $\Delta S^{\#}$, the enthalpy of activation $\Delta H^{\#}$ and the free energy of activation $\Delta G^{\#}$ were calculated (Table 1) from the following equations (28)

$$\ln A = \ln (kT/h) + \frac{\Delta S^{\#}}{R} \qquad (14)$$

$$\Delta H^{\#} = E_a - RT \qquad (15)$$

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#} \qquad (16)$$

From Table 1, It can be observed that the resulted activation energy of the photoreaction is very low (E$_a$ = 34.8016 kJ mol^{-1}), which can be called the apparent activation as the true activation energy is nil. Because of that the photocatalytic reaction do not require the heating but it is accomplished by light leading to production of the excited (electron – hole) pair which consider the essential species for complete the reaction (29). The positive values of $\Delta H^{\#}$ and $\Delta G^{\#}$ refer to endothermic reaction and the reaction is non-spontaneous, respectively. Negative entropy was obtained which indicates that the reactants are more disordered than the formed intermediate (excited complex) (30).
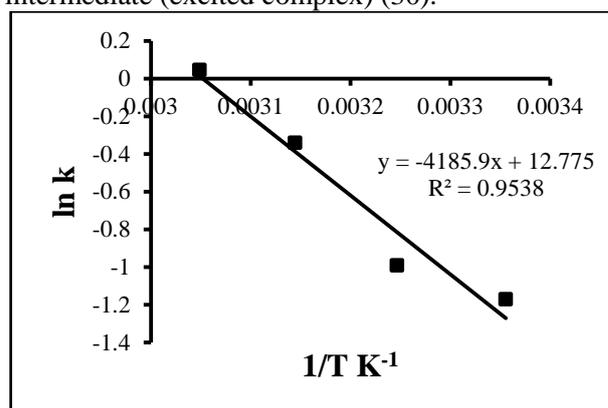
Figure 10. Plot ln k against 1/T using Au-Pd/TiO$_2$ as catalyst with Congo red dye

Table 1. Values of kinetics and thermodynamic parameters for the photocatalytic degradation of Congo red dye by using Au-Pd/TiO$_2$ catalyst

T K	k h^{-1}	E$_a$ kJ. mol^{-1}	ΔH^{*} kJ. mol^{-1}	ΔS^{*} kJ. mol^{-1}	ΔG^{*} kJ. mol^{-1}
298	0.3097		32.3240		74.0380
308	0.3705	34.8016	32.2408	-	75.3547
318	0.7102		32.1577	0.1399	76.6714
328	1.0450		32.0746		77.9880

Kinetics

A monomolecular Langmuir-Hinshelwood (L-H) modal is usually considered to quantify the heterogeneous photodegradation activity, where an adsorbed substrate is consumed at an initial rate given as shown in equation17 (31):

$$-\frac{dC}{dt} = \frac{kKC}{1+KC} \qquad (17)$$

where k is the specific rate constant, that change during photocatalytic reaction and K is the thermodynamic adsorption constant. In photocatalytic reaction, the photocatalyst concentration remains unchanged, so the rate of the reaction depends on the concentration of dye and the term pseudo can be used to prefix the rate of reaction. When the dye concentration is very high, so the surface of photocatalyst is saturated; a pseudo zero order reaction is assumed where, the rate constant of the reaction is independent on the concentration of the dye, as shown in the following equation (32)

$$-\frac{dC}{dt} = k \qquad (18)$$

While at low concentration of the dye; the photodegradation rate is dependent on the change in the dye concentration, which means the driving force of degradation is proportional to the dye concentration, in this case, equation 18 can be expressed in the following equation (33);

$$-\frac{dC}{dt} = k_1 C \qquad (19)$$

Figure 11illustrates the plot of ln C against irradiation time of first order of reaction after integrated the equation of Congo red dye (CR) at optimum values of dosage of photocatalyst, amount of H_2O_2, pH of the reaction and optimum temperature of the reaction, while Table 2 shows values of rate constant of reaction and regression coefficients (R^2) for first, zero, and second orders of reaction. It can be compared the values of rate constant and regression coefficients to conclude that the reaction can be described by the pseudo first-order kinetic, as the plot of ln C against irradiation time gives a straight line with relatively high regression coefficients (R^2).
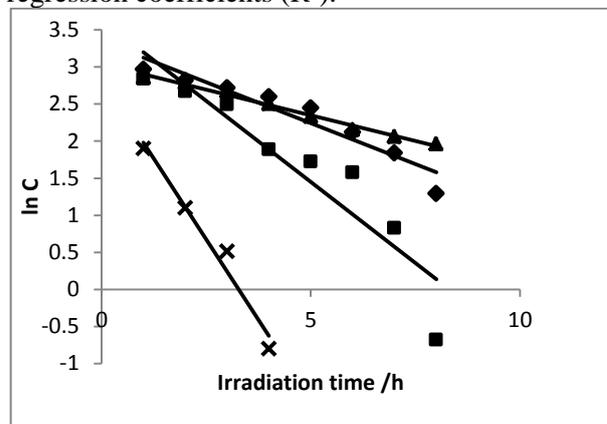
Figure 11. Plot ln C against irradiation time of Congo dye at optimum value of Au-Pd/TiO₂, amount of H₂O₂, pH and temperature as following (▲0.09g of Au-Pd/TiO₂), (♦ 7μL of H₂O₂), (■ pH 5) and (× 55C°)

Table 2. Values of R^2 and rate constant for photodegradation of Cong red dye from plotting of relationships of first, second and zero orders at optimum values.

Optimum values	First order reaction (plot ln C against t)		Second order reaction (plot 1/C against t)		Zero order reaction (plot (C₀-C) against t)	
	R^2	k h^{-1}	R^2	k M^{-1}h^{-1}	R^2	k M h^{-1}
0.09g of Au-Pd/TiO₂	0.9889	0.1384	0.9774	0.0127	0.5530	3.3655
7μL of H₂O₂	0.9169	0.2211	0.7565	0.0265	0.6733	3.3258
pH 5	0.8612	0.4380	0.4931	0.1866	0.2460	4.2100
55C°	0.9722	0.8694	0.7784	0.6494	-12.9700	9.1442

Conclusion:

To conclude, using of bimetallic Au-Pd/ TiO₂ as a photocatalyst to break down the Congo red dye was efficient. The photodegradation was enhanced with testing different parameters such as; concentration of dye, dosage of the photocatalyst, amount of H_2O_2, pH of the solution and the temperature. It has been shown that the photodegradation percentages and rate of reaction increased respectively at the optimum values of these parameters. From calculated thermodynamic functions, it can be suggested that the reaction is endothermic and it is unspontaneous. By comparing the rate constant and regression coefficients, it can be indicated that the reaction follows pseudo first order.

Authors' declaration:

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are mine ours. Besides, the Figures and images, which are not mine ours, have been given the permission for re-publication attached with the manuscript.

- Ethical Clearance: The project was approved by the local ethical committee in University of Baghdad.

References:

1. Li Y, Wang W, Wang F, Di L, Yang S, Zhu S, et al. Enhanced Photocatalytic Degradation of Organic Dyes via Defect-Rich TiO$_2$ Prepared by Dielectric Barrier Discharge Plasma. Nanomaterials.2019; 9: 720.

2. Mahendra IP, Huda A, Ngoc HM , Nghia PT, Tamrin T, Wirjosentono B. Investigation of TiO$_2$ doped with nitrogen and vanadium using hydrothermal/Sol-Gel method and its application for dyes photodegradation. Arab J Basic Applied Sci. 2019; 26(1): 242–253.

3. Cambrussi AN, Morais AS, Neris AM, Osajima JA, Silva Filho EC, Ribeiro AB. Photodegradation study of TiO$_2$ and ZnO in suspension using miniaturized tests. Revista Matéria. 2019; 24(4).

4. Filippatos PP, Kelaidis N, Vasilopoulou M, Davazoglou D, Lathiotakis NN , Chroneos A. Defect processes in F and Cl doped anatase TiO$_2$. Sci Rep. 2019; 9: 19970.

5. Yalçın Y, Kılıç M Z. The Role of Non-Metal Doping in TiO$_2$ Photocatalysis. J Adv Oxid. Technol. 2019; 13 (3): 281-296.

6. Archana S, Munisamy M. Photoluminescence Properties of Polyphenylenediamine Doped with TiO$_2$ Nanoparticles. Asian J Chem. 2019; 31 (2): 343-347.

7. Yadav S, Jaiswar G. Review on Undoped/Doped TiO$_2$ Nanomaterial; Synthesis and Photocatalytic and Antimicrobial Activity. J Chin Chem Soc.2017; 64 (1) 103-116.

8. Kumaravel V, Mathew S, Bartlett J, Pillai SC. Photocatalytic hydrogen production using metal doped TiO$_2$: A review of recent advances. Applied Catal B: Env. 2019; 244: 1021-1064.

9. Taher T, Rohendi D, Mohadi R, Lesbani A. Congo red dye removal from aqueous solution by acid-activated bentonite from sarolangun: kinetic, equilibrium, and thermodynamic studies. Arab J basic appl sci.2019; 26 (1):125–136.

10. Bokare AD, Chikate RC, Rode CV, Paknikar KM. Iron-nickel bimetallic nanoparticles for reductive degradation of azo dye Orange G in aqueous solution. Appl Catal B: Env. 2008; 79 (3): 270-278.

11. Santhosh AM, Yogendra K, Mahadevan KM, Madhusudhana N. Photodegradation of Congo red azo dye, a Carcinogenic Textile dye by using synthesized Nickel Calciate Nanoparticles. In J Adv Res Sci Eng. 2017; 6 (7): 51-64.

12. Wang L, Li J, Wang Z, Zhao L, Jiang Q. Low-temperature hydrothermal synthesis of α-Fe/Fe$_3$O$_4$ nanocomposite for fast Congo red removal. Dalton Trans. 2013; 42(7): 2572.

13. Adam RE, Pozina G, Willander M, Nur O. Synthesis of ZnO nanoparticles by co-precipitation method for solar driven photodegradation of Congo red dye at different pH. PHOTONIC NANOSTRUCT. 2018; 32: 11-18.

14. Namdrian AH, Tabrizi AG, Arsalani N, Khataee A, Mohammadi A. Synthesis of PANi nanoarrays anchored on 2D BiOCl nanoplates for photodegradation of Congo Red in visible light region. J Ind Eng Chem.2020; 81: 228-236.

15. Patel U, Shah C, George LB, Solanki H. Biodegradation of Congo red dye by bacterial strain. Univ Rev. 2019; VIII, (III): 696-705

16. Lafi R, Montasser I, Hafiane A. Adsorption of Congo red dye from aqueous solutions by prepared activated carbon with oxygen-containing functional groups and its regeneration. Ads Sci & Techn. 2019; 37(1-2):160-181.

17. Sarhan ST, Mohd IS, Taufiq-Yap YH, Abdual Halim A, Umer R. The impact of hydrogen peroxide as an oxidant for solvent –free liquid phase oxidation of benzyl alcohol using Au-Pd supported carbon and titanium catalysts. BCREC. 2018; 13 (2): 373-385.

18. Kumar BN, Anjaneyulu Y, Himabindu V. Comparative studies of degradation of dye intermediate (H-acid) using TiO$_2$/UV/H$_2$O$_2$ and photo - Fenton process. J Chem. Pharm. Res.2011; 3(2):718-731.

19. Alshabanat MN, AL-Anazy MM. An Experimental Study of Photocatalytic Degradation of Congo Red Using Polymer Nanocomposite Films. J Chem. 2018; https://doi.org/10.1155/2018/9651850

20. Coleman HM, Vimonses V, Leslie G, Amal R. Degradation of 1,4-dioxane in water using TiO$_2$ based photocatalytic and H$_2$O$_2$/UV processes. J Hazard Mater. 2007; 146, (3): 496-501.

21. Akpan UG, Hameed BH, Parameters affecting the photocatalytic degradation of dyes using TiO$_2$-based photocatalysts: A review. J Hazard Mater. 2009; 170: 520-529.

22. Kosmulski M. the significance of the difference in the point of zero charge between rutile and anatase. J adv Colloid Interface Sci. 2002; 99 (3): 181-264.

23. Habib A, Muslim M, Shahadat MT, Islam MN, Ismail IMI, Islam TS, et al. Photocatalytic decolorization of crystal violet in aqueous nano-ZnO suspension under visible light irradiation. J nanostructure chem. 2013; 3-70.

24. Sakthivel S, Neppolian B, Shankar MV, Arabindoo B, Palanichamy M, Murugesan V. Solar photocatalytic degradation of azo dye: comparison of photocatalytic efficiency of ZnO and TiO2. Sol. Energy Mater. Sol. Cells. 2003; 77: 65-82.

25. Sadollahkhani A, Kazeminezhad I, Lu J, Nur O, Hultman L, Willander LM. Synthesis, structural characterization and photocatalytic application of ZnO@ZnS core shell nanoparticles. RSC Adv. 2014; 4: 36940–36950.

26. Chatterjee D, Dasgupta S. Visible light induced photocatalytic degradation of organic pollutants. Journal of Photochemistry and Photobiology C: Photochemistry Reviews. 2005; 6(2–3): 186-205.

27. Laidler KJ. Chemical kinetics. part 1. Second edition, MeCraw-Hill, Ine. USA. 1965: p 50.

28. Suhail FS, Mashkour MS, Saeb D. The study on photodegradation of crystal violet by polarographic

technique. Int J Sci Basic Appl Res.2015; 15 (3):12-19.

29. Gajbhiye SB. Photocatalytic degradation study of methylene blue solutions and its application to dye industry effluent. Int J Mod Eng Res. 2012; 2 (3): 1204-1208.

30. Rio LD, Aberg J, Renner R, Dahlsten OC, Vedral V. The thermodynamic meaning of negative entropy. Nature. 2011; 474:61-3.

31. Kumar KV, Porkodi K, Rocha F. Langmuir–Hinshelwood kinetics – A theoretical study. Catal Comm. 2008; 9: 82-84.

32. Khorshdil N, Abedinikhorrmi S, Molya ME, Mottiee F. Photodegradation of basic dyes using nanocomposite (silver zinc oxide- copper oxide) and kinetic studies. Orient J Chem. 2016; 32 (2): 1205-1214.

33. Chiu YH, Chang TM, Chen CY, Sone M, Hsu YJ. Mechanistic insights into photodegradation of organic dyes using heterostructure photocatalysts. Catal. 2019; 9: 430.

دراسة التحلل الضوئي لصبغة الكونغو الحمراء في محاليلها المائية باستخدام العامل المساعد ثنائي الفلز
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الخلاصة :

في هذه البحث ، تم دراسة التحلل الضوئي لصبغة الكونغو الحمراء في محاليلها المائية باستخدام العامل المساعد ثنائي الفلز (Au-Pd/TiO$_2$). تم تحديد الكميات والظروف المثلى لاجراء التفاعل ومنها : تركيز الصبغة، كمية العامل المساعد، حامضية الوسط ودرجة الحرارة. ووجد ان افضل تركيز للصبغة لاجراء التفاعل الضوئي كان عند 28 جزء بالمليون، في حين ان افضل كمية للعامل المساعد كانت عند 0.09 غم/ 75 مللليتر من المحلول والتي عندها تم تسجيل اعلى نسبة مئوية لتحلل الصبغة تقريباً 96% بعد وقت تشعيع لمدة 12 ساعة. اما كمية بيروكسيد الهيدروجين المثلى المستخدمة كعامل مؤكسد اضافي فكانت 7 مايكروليتر/ 75 مللليتر من المحلول حيث زادت النسبة المئوية للتحلل لتصبح تقريبا 97% بعد زمن تشعيع لمدة 10 ساعة. وقد اختبرت الدالة الحامضية للمحاليل لمدى (5-11) لنجد ان التفاعل يعطي نتائج تحلل عالية للصبغة في الوسط الحامضي عند الدالة الحامضية 5. وقد وجد ان التحلل الضوئي للصبغة يزداد مع زيادة درجة الحرارة عند اجراء التجارب في مدى حراري (25-55) درجة مئوية، حيث سجلت اعلى نسبة تفكك ضوئي للصبغة تقريبا 98% عند 55 درجة مئوية. تم تحديد طاقة التنشيط للتفاعل من تطبيق معادلة ارينيوس كما تم تحديد قيم التغير في الدوال الثرموداينميكية (الانثالبي والطاقة الحرة لكبس والانتروبي) من تطبيق معادلات الدوال الثرموداينميكية.تم دراسة حركية التفاعل من قيم معدلات ثابت التفاعل و زمن التشعيع وقد وجد ان رتبة التفاعل هي من المرتبة الاولى.

الكلمات المفتاحية: الدوال الثرموداينميكية، التفكك الضوئي، الحركية، صبغة الكونكو الحمراء، ثاني اوكسيد التيتانيوم