

Photocatalytic Degradation of Azo Dyes Catalyzed by Ag Doped TiO₂ Photocatalyst

V. Mirkhani*, S. Tangestaninejad, M. Moghadam, M.H. Habibi and A. Rostami-Vartooni
Department of Chemistry, Catalysis Division, University of Isfahan, Isfahan, 81746-73441, Iran

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In this paper, photocatalytic degradation of commercial textile azo dyes catalyzed by titanium dioxide and modified titanium dioxide with Ag metal (1% w/w) in aqueous solution under irradiation with a 400 W high-pressure mercury lamp is reported. The effect of various parameters such as irradiation time of UV light, amount of photocatalyst, flow rate of oxygen, pH and temperature for the Ag-TiO₂ photocatalyst were investigated. Kinetic investigations of photodegradation indicated that reactions obey improved Langmuir-Hinshelwood model and pseudo-first-order law. The rate constant studies of photocatalytic degradation reactions for Ag-TiO₂ and TiO₂ photocatalysts indicated that in all cases the rate constant of the reaction for Ag-TiO₂ was higher than that of TiO₂.

Keywords: Azo dyes, Titanium dioxide, Photodegradation, Photocatalyst, Ag-TiO₂

INTRODUCTION

Different types of dyes are used in many industries such as textile, paint, ink, plastics and cosmetics. About a half of global production of synthetic textile dyes (700000 tons per year) are classified into azo compounds that have the chromophore of -N=N- unit in their molecular structure and over 15% of the textile dyes are lost in wastewater stream during dyeing operation. It is well known that soluble azo dyes when incorporated into the body are split into corresponding aromatic amines by liver enzymes and intestinal flora, which can cause cancer in human. The textile industry produces large quantity of highly colored effluents, which are generally toxic and resistant to destruction by biological treatment methods. Therefore, it is necessary to find an effective method to remove color from textile effluents [1].

Various chemical and physical processes such as coagulation, electrocoagulation [2] and adsorption on activated

carbon are not destructive but only transfer dye from one phase to another; hence, there is a need for developing treatment technologies for eliminating contaminants from wastewater. Photocatalytic degradation by semiconductors is a new, effective and rapid technique for the removal of pollutants from water [3,4]. The TiO₂ photocatalyst has attracted much interest in recent years for its highly active photocatalytic functions, like the ability to decompose of chemical compounds, as well as super hydrophilic and anti-bacteria properties [5-8]. This photocatalyst and most of other semiconductors have poor activity when used alone, but the presence of a metal on the semiconductor markedly increases their efficiency [9-11]. The role of loaded metal is trapping and subsequent transfer of photoexcited electron onto photocatalyst surface and decreasing the recombination of hole-electron pairs [12]. The loaded metals on TiO₂ should be chemically stable during the photocatalytic oxidation reaction or storage in atmospheric condition. Heterogeneous photocatalysis is a process in which the illumination of a semiconductor produces photo-excited electrons (e⁻) and

*Corresponding author. E-mail: mirkhani@sci.ui.ac.ir

positive charged holes (h^+). Under illumination, organic molecules react with photogenerated hole or, more probably, with photoinduced hydroxyl radicals, to give a number of hydroxylated reaction intermediates [13,14].

In this study, pure and surface modified TiO_2 with Ag, (Ag- TiO_2) particles were used for the photocatalytic degradation of azo dyes such as Congo Red (CR), C.I. Direct Red 80 (DR), C.I. Reactive Red 17 (RR), Methyl Orange (MO), C.I. Direct Yellow 50 (DY), Solophenyl Red 3BL (SR), Coperoxon Navy Blue RL (CN) and Nylosan Black 2-BC.S Acid Black 42 (NB) in the presence of UV-light.

EXPERIMENTAL

Materials

The commercially available TiO_2 powder, which was in anatase crystalline form, has a surface area of about $50 \text{ m}^2 \text{ g}^{-1}$ and primary particle size of 30 nm was obtained from Merck. Azo dyes were purchased from Merck, Ciba-Geigy and Bitterfeld and were used without further purification. Their chemical structures and other characteristics are listed in Table 1. The dye solutions were prepared using double distilled water. Solvents and other materials such as NaOH, HCl, KCl,

HgI_2 , KI, K_2HPO_4 , KH_2PO_4 , $Na_2B_4O_7 \cdot 10H_2O$, $KHC_8H_4O_4$ and $Ba(OH)_2$ were purchased from Merck.

Apparatus

The UV-Vis spectra were measured on a Shimadzu 160 UV-Vis spectrophotometer. A 400 W high-pressure mercury lamp was used for UV irradiation. A centrifuge was used for separation of photocatalyst from solution.

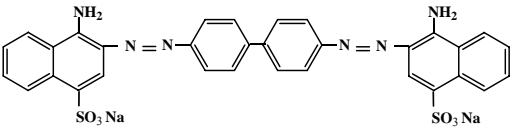
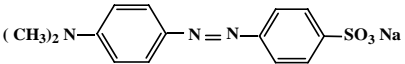
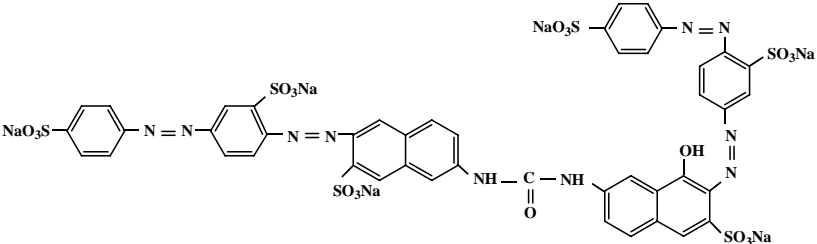
Preparation of Ag- TiO_2 (1% w/w)

To a solution of 0.1 M $AgNO_3$ (9.2 ml) was added TiO_2 (10 g). To this slurry a 1.0% (w/v) solution of Na_2CO_3 (10 ml) was added and the suspension dried at room temperature and heated at $400^\circ C$ for 6 h [15].

Degradation Procedure

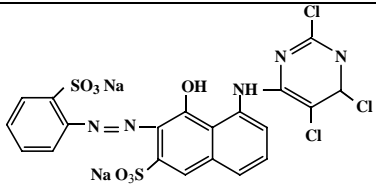
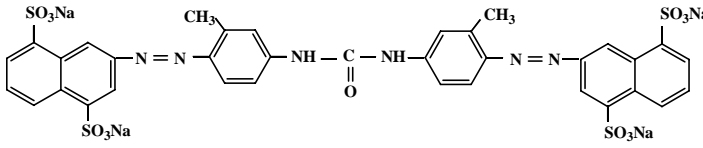
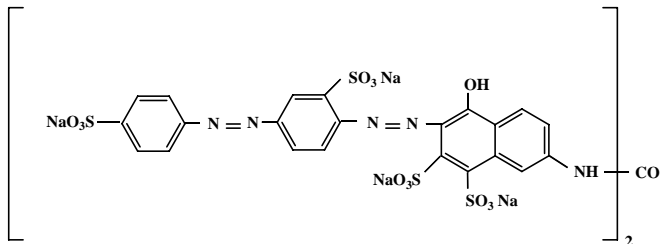
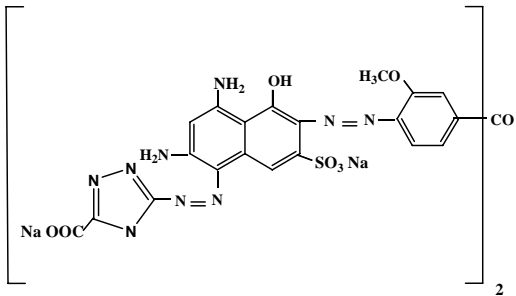
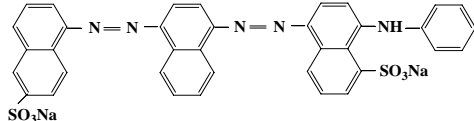
For the photodegradation of azo dyes, a suspension of dye (15 ml, 30 ppm) and photocatalyst (25 mg) was prepared in a Pyrex photoreactor. Water circulating jacket was used for cooling the Pyrex photoreactor, elimination of IR-radiation and short-wavelength UV-radiation. The photoreactor was illuminated with a 400 W high-pressure mercury lamp. The reaction mixture was magnetically stirred during photolysis.

Table 1. Characteristics of Azo Dyes

Azo dyes	Structure	λ_{max} (nm)	MW (g mol^{-1})
Congo red (CR)		497	696.67
Methyl orange (MO)		462	327.74
C.I. Direct red 80 (DR)		528	1356.13

Photocatalytic Degradation of Azo Dyes

Table 1. Continued

C.I. Reactive red 17 (RR)		534	602.48
C.I. Direct yellow 50 (DY)		396	956.14
Solophenyl red 3BL (SR)		530	1373.3
Coperoxon navy blue RL (CN)		570	1110
Nylosan black 2-BC.S Acid black 42 (NB)		568	731.26

Aliquots of the reaction mixture were withdrawn, filtered and determined by UV-Vis spectrophotometer at λ_{\max} . The formation of CO_2 was detected as $\text{BaCO}_3(\text{s})$ separated in aqueous solution saturated with $\text{Ba}(\text{OH})_2$ in which the gases exiting from the reactor were bubbled. Ammonia concentration was determined spectrophotometrically at $\lambda = 410 \text{ nm}$ with Nessler's reagent, and concentration of SO_4^{2-} ion was determined by standard procedure [16]. Mineralization into CO_2 was also determined by measuring the total organic

carbon (TOC) for dyes before and after irradiation of light.

RESULTS AND DISCUSSION

Degradation Monitoring by UV-Vis Spectra Changes

The changes in the absorption spectra of some studied azo dyes during the photocatalytic process at different irradiation times are shown in Fig. 1. Decreasing the absorption bands of dyes at λ_{\max} briefly indicates the degradation of azo dyes,

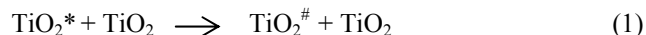
qualitatively.

Effect of Photocatalyst Amount and Irradiation Time

Aqueous samples of textile dyes were first irradiated with UV light in the absence of photocatalyst, and then another sample was stirred with photocatalyst in the absence of UV light. In both cases, the degradation was negligible.

Figure 2 shows that 98-100% of target compounds were degraded in the presence of Ag-TiO₂ photocatalyst (30 mg) at the irradiation time of 30-150 min. The effect of the amount of Ag-TiO₂ photocatalyst on the photodegradation is illustrated in Fig. 3. The results indicate that degradation increases by increasing the photocatalyst amount, and reaches to a constant value and then decreases. The availability of active sites increases with the catalyst amount, but the light penetration and consequently the photoactivated volume of the suspension shrinks [17]. When all dye molecules are absorbed on

photocatalyst, the addition of higher quantities of Ag-TiO₂ have no effect on the degradation efficiency. The decrease of the degradation at higher photocatalyst amount may be due to deactivation of activated molecules by collision with ground state molecules. Shielding by TiO₂ may also take place (Eq. 1).



where TiO₂* is the TiO₂ with active species adsorbed on its surface and TiO₂# is deactivated form of TiO₂ [18].

Effect of Oxygen

Photocatalytic degradation of dyes in the presence of argon gas and different flow rate of oxygen was investigated. The results indicated that the presence of O₂ is necessary but the oxygen flow rate has no significant effect on the degradation process (Fig. 4). Degradation of azo dyes for argon bubbled

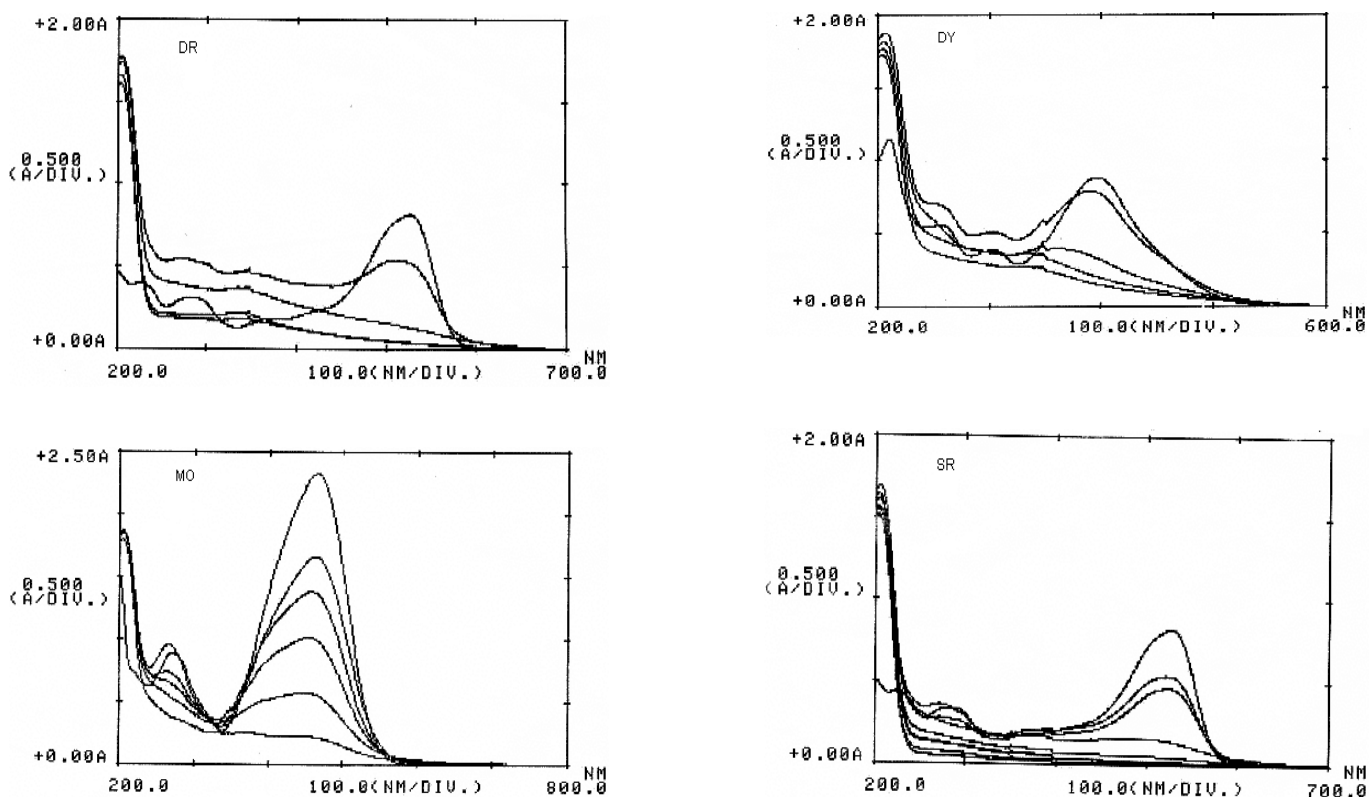


Fig. 1. The UV-Vis spectra for degradation of some azo dyes during the irradiation time. Reaction conditions: concentration of azo dyes, 30 ppm; Ag-TiO₂, 30 mg; temperature, 25 °C; irradiation time: DR (30 min), MO (100 min), DY (30 min) and SR (35 min).

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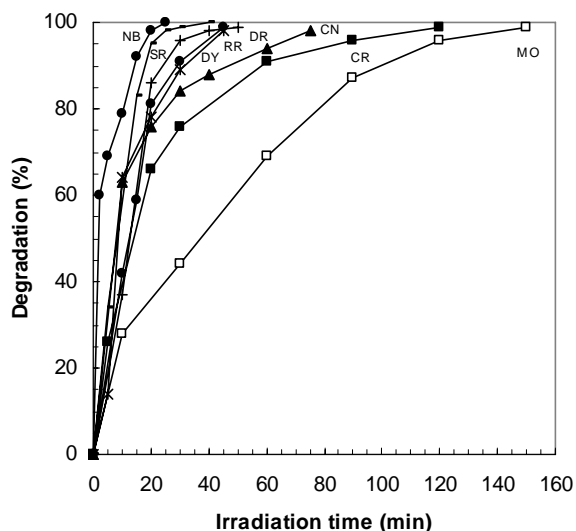


Fig. 2. Effect of irradiation time on photodegradation of azo dyes. Conditions: concentration of azo dyes, 30 ppm; Ag-TiO₂, 30 mg.

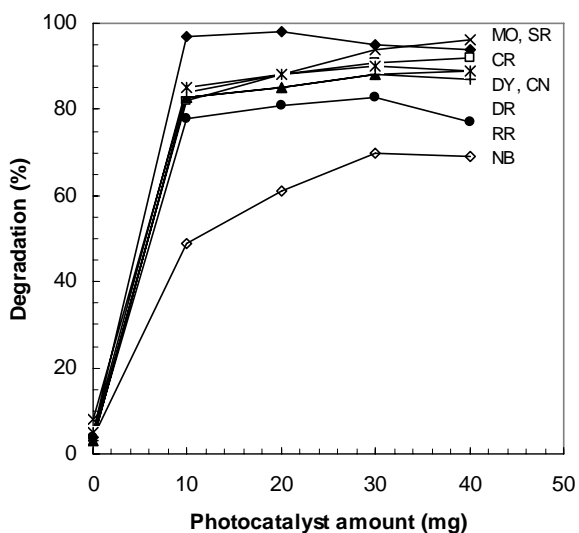


Fig. 3. Effect of amount of Ag-TiO₂ on degradation of azo dyes. Conditions: concentration of azo dyes, 30 ppm; irradiation time, MO (100 min), SR (20 min), CR (60 min), DY (30 min), CN (30 min), DR (20 min), RR (20 min) and NB (5 min).

suspensions were 28, 42, 29, 51, 35, 39, 53 and 71% for SR, CR, CN, MO, DY, RR, DR and NB dyes, respectively.

Molecular oxygen, adsorbed on the surface of the Ag-TiO₂

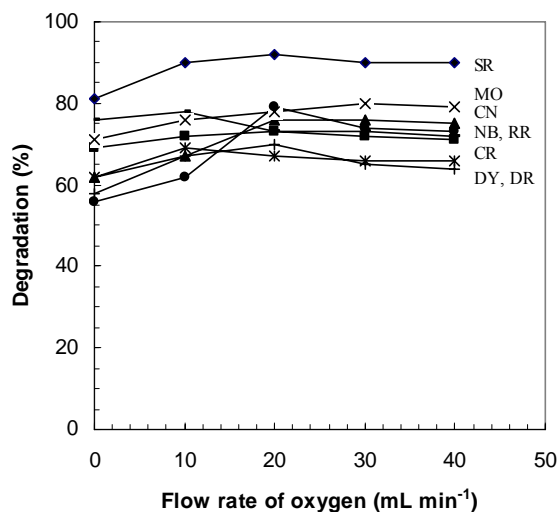
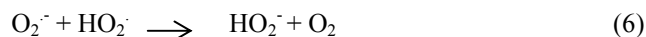
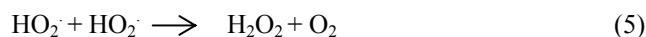
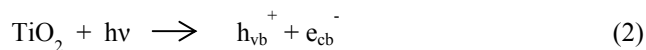
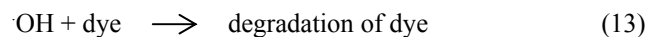
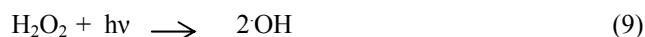


Fig. 4. Influence of oxygen flow rate on photodegradation of azo dyes. Conditions: concentration of azo dyes, 30 ppm; irradiation time and photocatalyst amount, SR (15 min; 10 mg), MO (60 min; 30 mg), CN (20 min; 10 mg), NB (10 min; 20 mg), RR (15 min; 20 mg), CR (25 min; 30 mg), DY (10 min; 30 mg), DR (15 min; 20 mg).

photocatalyst, prevents the hole-electron pair recombination process [19,20]. Recombination of hole-electron pairs decreases the rate of photocatalytic degradation. It was observed that superoxide may be the source of hydroxyl radicals.

The following reactions describe the formation of hydroxyl radicals and organic peroxides, which are significant species for the oxidation of organic molecules [21,22].





Effect of pH and Temperature

The pH of electrolyte can vary the surface charge of the photocatalyst and also shifts the potential of some redox reaction. Thus, it affects the adsorption of organic solutes, and consequently its reactivity and some reaction rate. The amphoteric behavior of most semiconductor oxides influences the surface charge of the photocatalyst [23]. Due to the amphoteric behavior of most metal hydroxides, the following two equilibria are considered [24]:



Photocatalyst surface is positively charged in acidic media, whereas it is negatively charged under alkaline condition. The effect of pH on the photodegradation efficiency, which include optimum amount of Ag-TiO₂ photocatalyst and fixed concentration of dyes (30 ppm) were examined in a range of 3-11.

The results showed that removal efficiency of dyes was carried out effectively at pH = 8-9 and also in acidic solutions (Fig. 5). Thus, for the azo dyes with sulfonic group in their structures, at low pH range, electrostatic interactions between the positive catalyst surface and dye anions lead to strong adsorption of the latter on the metal oxide support [23,25 and 26]. It seems that at the lowest pH, surface adsorption is more effective than photocatalytic degradation for removal of dyes. However, surface adsorption merely transfers dye from solution to solid and mineralization does not occur. For example, in the photodegradation of NB dye, the change of photocatalyst and solution colors after adding alkaline agent confirmed this behavior. There was also the photodegradation of azo dyes in acidic solutions, which is probably due to the formation of hydroxyl radicals as it could be inferred from

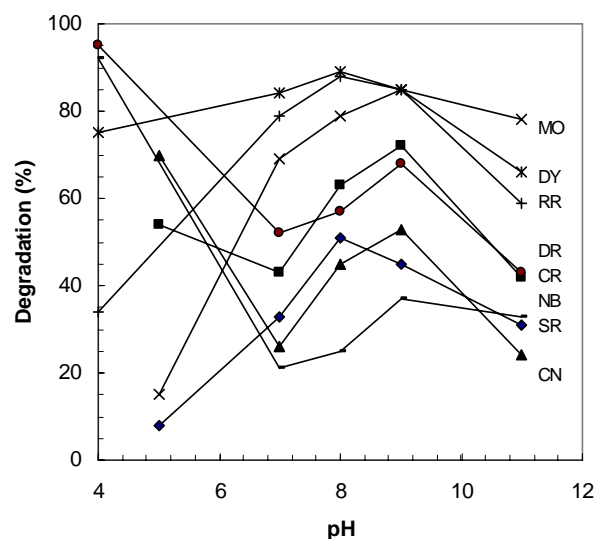


Fig. 5. Effect of pH on photodegradation of azo dyes. Conditions: irradiation time and photocatalyst amount, MO (75 min; 30 mg), DY (20 min; 30 mg), RR (20 min; 20 mg), DR (15 min; 20 mg), CR (40 min; 30 mg), NB (8 min; 20 mg), SR (15 min; 10 mg) and CN (25 min; 10 mg).

Eqs. (3)-(10) [27].

In the alkaline solution, dyes may not be adsorbed onto negative surface of photocatalyst effectively; thus the photodegradation efficiency decreases. Probably, in the pH range 5-10, formation of more hydroxyl radical due to the presence of large quantities of OH⁻ ions (Eq. (14)) would enhance the photodegradation of azo dyes [28].



The observed rates are not affected much by temperatures in the range of 25-60 °C, and photocatalytic process could be carried out effectively at laboratory temperature.

Kinetic Analysis

Many studies [29-31] have applied the Langmuir-Hinshelwood (L-H) expression [Eq. (15)] for the analysis of heterogeneous photocatalytic reactions

$$\text{rate} = \frac{-dC}{dt} = \frac{k_{\text{L-H}} K_{\text{ads}} C}{1 + K_{\text{ads}} C} \quad (15)$$

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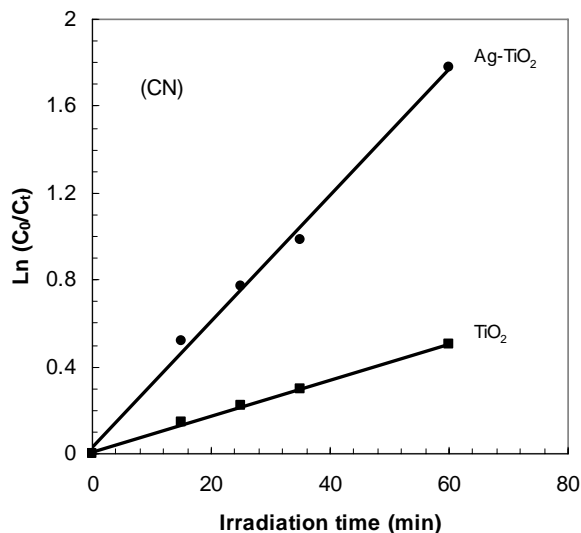
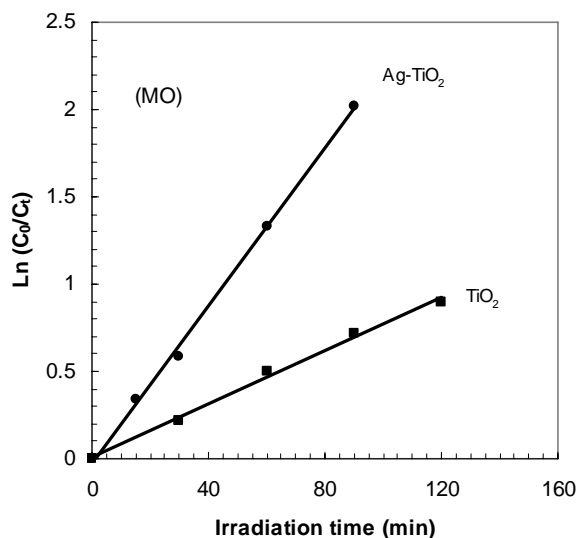
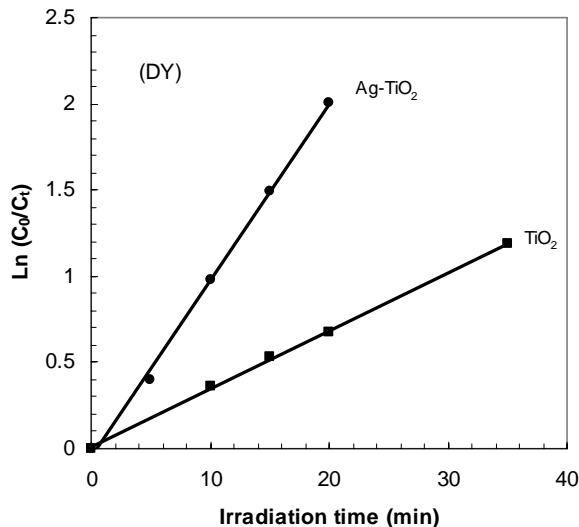
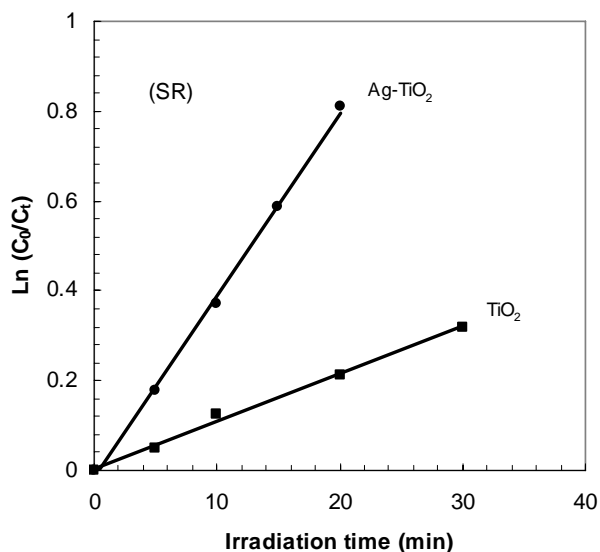
where k_{L-H} is the reaction rate constant in $\text{mol dm}^{-3} \text{min}^{-1}$; K_{ads} the adsorption coefficient of the reactant on TiO_2 in $(\text{mol dm}^{-3})^{-1}$; and C is the concentration of the solute in mol dm^{-3} . Integration of Eq. (15) yields the following equation:

$$\ln\left(\frac{C_0}{C}\right) + K(C_0 - C) = k_{L-H} K_{\text{ads}} t \quad (16)$$

when the initial concentration C_0 is small, Eq. (16) changes to Eq. (17), which expresses a pseudo-first-order reaction kinetic regime.

$$\ln\left(\frac{C_0}{C}\right) = k_{L-H} K_{\text{ads}} t = kt \quad (17)$$

where k is the pseudo-first-order reaction rate constant, $k = k_{L-H} \times K_{\text{ads}}$ in min^{-1} . The plots $\ln(C_0/C_t)$ vs. irradiation time (Fig. 6) for dyes (where C_0 is the initial concentration of pollutant and C_t is the concentration of pollutant in the reaction time) were linear, and this suggests that photodegradation reactions follow pseudo-first-order reaction kinetics. Rate constant of the reactions and ratio of these values are listed in Table 2. Discrepancy between the pseudo-



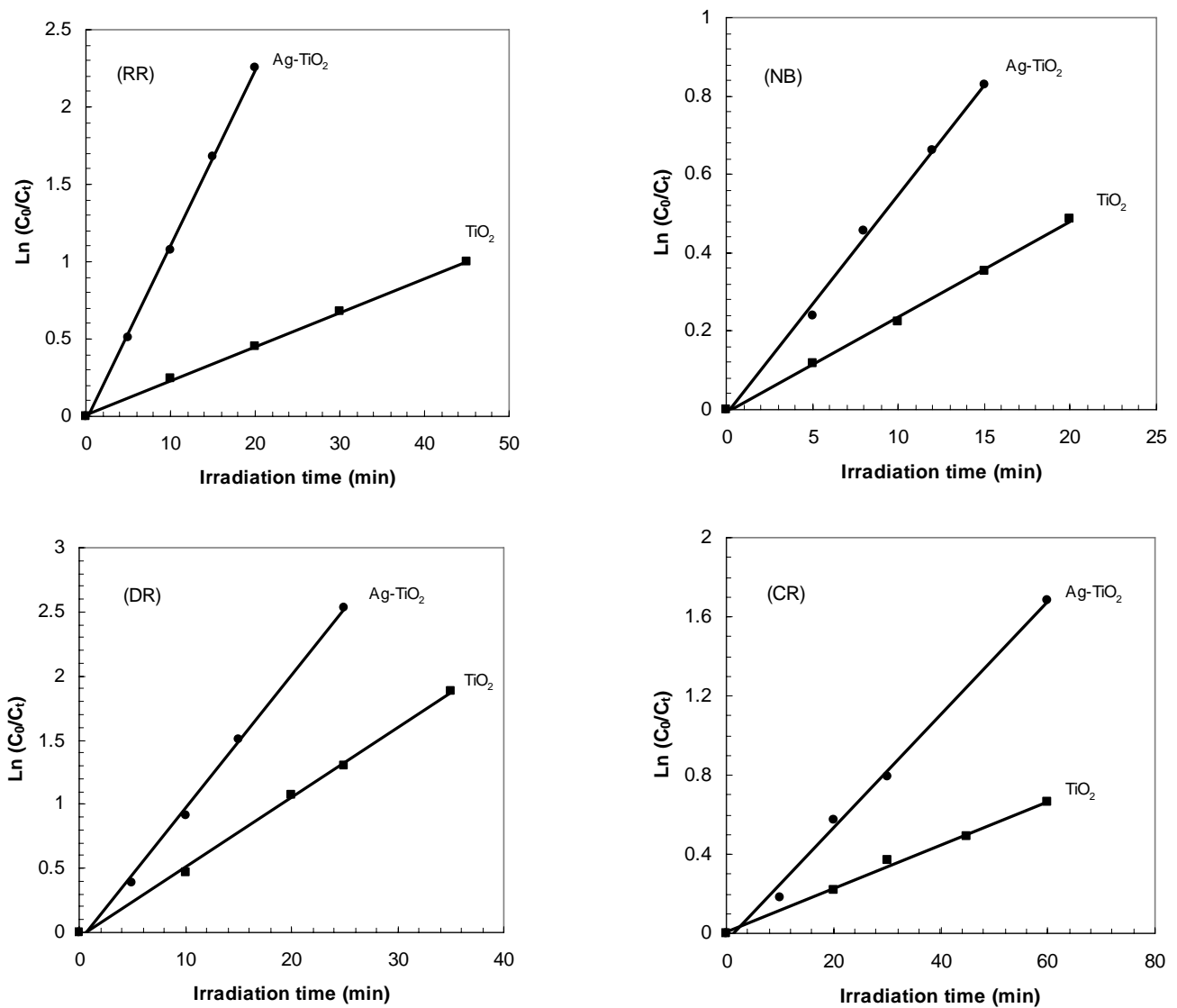


Fig. 6. Plots of $\ln(C_0/C_t)$ vs. irradiation time for different azo dyes. Conditions: pH and amount of photocatalyst, NB (pH = 9; 20 mg), SR (pH = 8; 10 mg), CR (pH = 9; 30 mg), CN (pH = 9; 10 mg), MO (pH = 9; 30 mg), DY (pH = 8; 30 mg), RR (pH = 8; 20 mg), DR (pH = 9; 20 mg).

first-order reaction rate constants may be either due to different photocatalytic degradation mechanisms or a competition for degradation between the reactant and the intermediate products.

CONCLUSIONS

Eight different azo dyes were not only successfully

decolorized, but also totally degraded and mineralized in the presence of Ag-TiO₂ as a photocatalyst. Degradation of azo dyes was negligible in the absence of photocatalyst and the UV light. Increasing amount of photocatalyst to more than an optimized limit (10-30 mg for different dyes), decreases the degradation rate. Results obtained from photocatalytic degradation experiments of azo dyes with varying pH from 3-11, showed that the degradation process is more effective at

Photocatalytic Degradation of Azo Dyes

Table 2. Rate Constants for different Photoreactions in the Presence of TiO₂ and Ag-TiO₂

Azo dye	k _{TiO₂} (min ⁻¹)	k _{Ag-TiO₂} (min ⁻¹)	k _{Ag-TiO₂} /k _{TiO₂}
Congo red	0.011	0.0285	2.5
Methyl orange	7.64 × 10 ⁻³	0.0225	3.0
C.I. Direct red 80	0.0541	0.1034	2.0
Solophenyl red 3BL	0.0110	0.0410	4.0
C.I. Direct yellow 50	0.0336	0.1022	3.0
C.I. Reactive red 17	0.0220	0.1134	5.0
Coperoxon navy blue	8.28 × 10 ⁻³	0.0290	3.5
Nylosan black 2-BC.S	0.0242	0.0561	2.5

pH = 8-9 and also in acidic medium. Usually, temperature in the range 25-60 °C does not affect the photodegradation efficiency. Decreasing TOC amount with irradiation time (45 min) from 11.97 ppm to 2.39 ppm and 10.04 ppm to 1.2 ppm in photocatalytic degradation of CN and DR respectively, and identification of carbon dioxide confirmed the total mineralization in these reactions. Degradation kinetic of azo dyes can be described by Langmuir-Hinshelwood equation. The rate constant of photodegradation reactions in the presence of Ag-TiO₂ particles was higher than TiO₂ particles. Thus, the photocatalytic degradation of azo dyes by Ag-TiO₂ photocatalyst could be used as a practical and useful technique for the removal of environmental pollutants that contribute to industrial waste-water treatment plants.

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