Photodegradation of Dye Pollutant on Ag/ZnO Nanocatalyst under UV-irradiation

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ABSTRACT

Ag/ZnO heterostructure nanocatalyst was successfully prepared. The degradation of reactive blue 49, commonly used as a textile dye, can be photocatalysed by Ag/ZnO. Photodegradation efficiency was small when the photolysis was carried out in the absence of Ag/ZnO. Dye solution underwent a decolourization and the reaction was monitored spectrophotometrically by measuring the absorbance of dyes at special wavelength. The experimental variables included amount of photocatalyst, concentration of H_2O_2 and initial concentration of dyes. More than 90% of 100 mgl^{-1} Reactive Blue 49 decolourization in 30-minute reaction time.

Key words: Dye Pollutant, Photodegradation, Nanocatalyst, UV-irradiation.

INTRODUCTION

Textile industries produce large volume of colored dye effluents which are toxic and non-biodegradable. Reactive dyes are commercially, a very important class of textile dyes, whose losses through processing are particularly significant and difficult to treat. It is estimated that about 20-50 percent of the reactive dyes is lost during the dyeing[1]. For the treatment of dye-containing wastewater, various biological, physical and chemical methods such as microbial biodegradation, membrane filtration, oxidation, ozonation, adsorption, and ultra filtration have been used[2-5]. However, many of these technologies are cost prohibitive, especially when applied for treating large waste streams and some of them merely transfer dyes from the liquid- to the solid-phase, requiring further treatment and causing secondary pollution[6]. Thus, there is a need for developing treatment methods that are more effective in elimination dyes from wastewater. Advanced oxidation process (AOPs) is alternative method for the complete degradation many organic pollutants[7-10]. When a photocatalyst absorbs radiation whose energy $h\nu > Eg$ (Eg is thesemiconductor band gap energy), an e from its filled valance band (VB) is promoted to its conduction band (CB) and valance band holes h$^+$ are formed (Fig. 1). Electron would reduce any available species, including O_2, water and hydroxide ion to form hydroxyl radicals. The OH$^-$ radicals are very strong oxidizing agents and can easily attack the organic molecules, Thus leading finally to their complete mineralization.

Among the various semiconductors employed as photocatalyst, TiO_2 and ZnO are the most preferable material due to their non-toxic, insoluble, stability and high photoactivity properties. Recently semiconductor-based heterostructures have been attracted, due to their potential applications in various fields. Metal/semiconductor is one of the most popular heterostructures and has been extensively studied because of its excellent catalytic activity. Ag/ZnO is one of the heterostructure photocatalyst with high catalytic activity that has attracted much research attention[11]. In this communication, we wish to report synthesis and application of Ag/ZnO nanoparticles as an efficient photocatalyst on degradation of reactive blue 49 (RB49).

MATERIAL AND METHODS

Reactive dye Blue 49 was commercial products and used without further purification. It's chemical structure is shown in scheme 1. Ag/ZnO was prepared according to litterateurs procedures[12]. A general photocatalytic procedure was carried out as follows: 0.02 g of catalyst Ag/ZnO was suspended in an aqueous RB49 (100 mg/L, pH = 6.8) and appropriate H_2O_2 solution. The suspension (20 ml) was stirred in the dark for 30 min to obtain establish adsorption–desorption equilibrium between the dye and the surface of the catalyst. The degradation experiment was carried out using Philips HPK 400 W lamp. The temperature was kept at 30$\pm$2 °C. At the specific time, the colloid solutions of Ag/ZnO

particles were separated by centrifuged and filtered. Decreasing in the concentration of dye was monitored with a Shimadzu Model 160-A UV-VIS spectrophotometer with a 1-cm quarts cell at λ = 595 nm. All photocalytic experiments were carried out at 6.8 pH. For The degree of photodegradation (X) as a function of time is given by:

$$X = \frac{C_0 - C}{C_0}$$

where C_0 is the initial concentration of RB49, and C the concentration of RB49 at time *t*.

RESULTS AND DISCUSSION

Fig. 2 shows the XRD patterns of the ZnO/Ag composites. In Fig. 2, three additional peaks at 36.18°, 48.36° and 68.58° compared to pure hexagonal-wurtzite ZnO (JCPDS Card Pattern: 3-888), can be assigned to the face-centered cubic (fcc) structure of Ag crystallite (JCPDS Card Pattern: 1-1167), revealing that fcc structured Ag is produced in the reaction.

The changes in absorption spectra of dye during UV/Ag/ZnO process at different time irradiation intervals were shown in Fig. 3. The decrease of the absorption band of RB49 at λ = 595 nm indicates a rapid degradation of dye. Complete discoloration of dye was observed after 60 minutes in the optimized conditions.
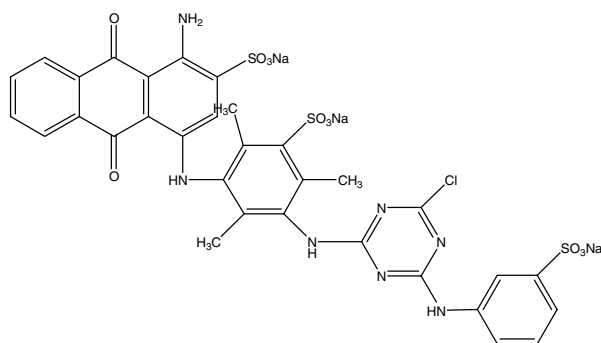
Scheme 1: Chemical structure of Reactive Blue 49

Effect of UV irradiation and Ag/ZnO nanoparticles

At first, experiments concerning the decomposition of dye (100 mgL^{-1}) were performed in the presence of Ag/ZnO semiconductor, illumination and H_2O_2, a blank experiment in the absence of semiconductor and another blank experiment in the absence of hí. Results of these experiments (Fig. 4) show that degradation of dye in the presence of the photocatalyst, irradiation and H_2O_2 could lead to the disappearance approximately 94% of dye after 30 min. This was contrasted with 11% degradation for the same experiment performed in the absence of Ag/ZnO and 32% in the absence of H_2O_2. A blank experiment in the absence of illumination demonstrated approximately 13% during of stirring of dyes and photocatalyst in dark and it is due to adsorption–desorption equilibrium between the dye and the surface of the catalyst.

Effect of catalyst concentration

The effect of the amount of Ag/ZnO on the photodegradation efficiency was shown in Fig. 5. Experiments performed with different concentrations of synthesized Ag/ZnO showed that the photodegradation efficiency increases with an increase in photocatalyst concentration up to 160 ppm, and is then decreased. This observation can be explained in terms of availability of active sites
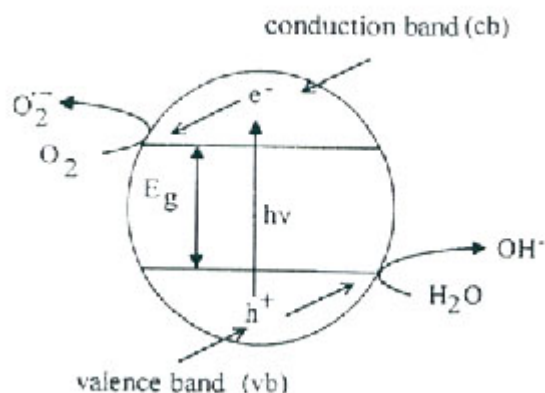

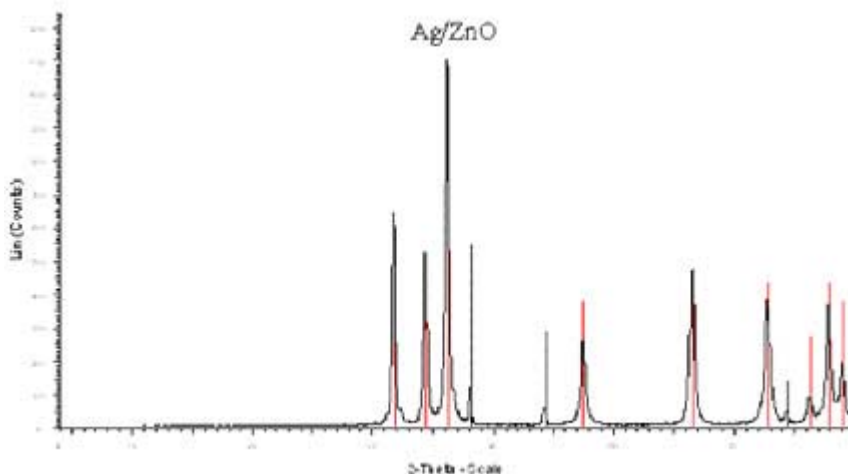**Fig. 1: The photocatalyst interface under UV- illumination**

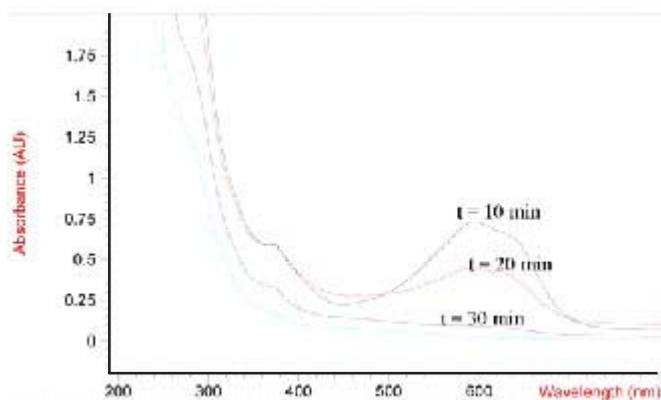**Fig. 2: XRD patterns of the synthesized Ag/ZnO nanoparticles**

Fig. 3: UV-Vis spectral changes of RB49, recorded during the dye degradation at different irradiation times, (dye: 100mgL^{-1}, Ag/ZnO: 1 g/L, H$_2$O$_2$:10 mmolL^{-1})
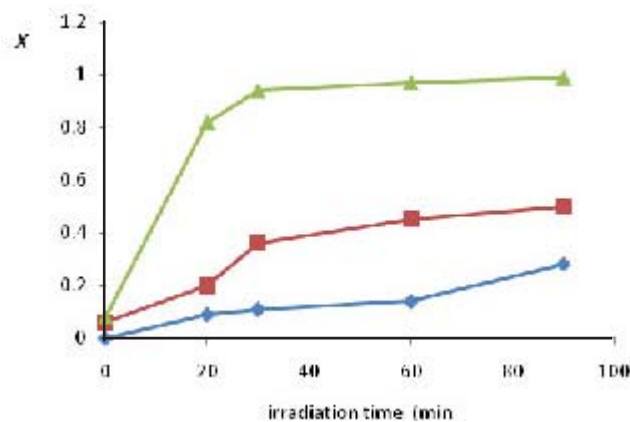

Fig. 4: Plot of the degree of photodegradation (*X*) *vs* irradiation time. a: dye (100mgL^{-1}), H$_2$O$_2$ (10 mmolL^{-1}) and UV irradiation. b: dye (100mgL^{-1}), Ag/ZnO 1 g/L and UV irradiation. c: (100mgL^{-1}), Ag/ZnO 1g/L, H$_2$O$_2$ (10 mmolL^{-1}) and UV irradiation
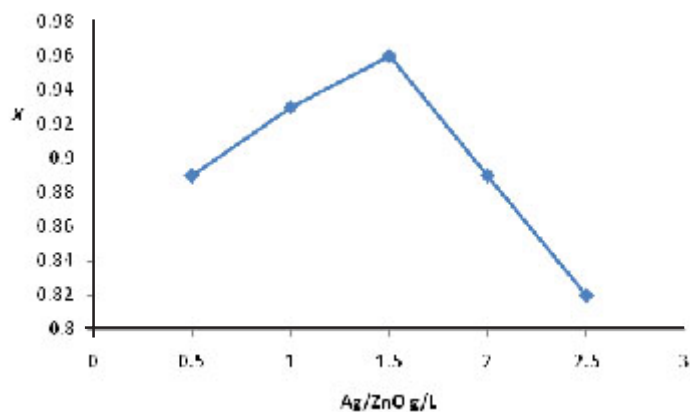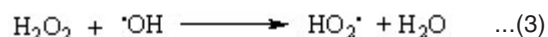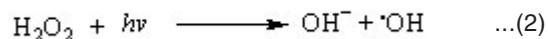

Fig. 5: Photodegradation of RB49 *vs* different Ag/ZnO concentration (dye (100mgL^{-1}), H$_2$O$_2$ (10 mmolL^{-1}) and irradiation time (30 min)

on the catalyst surface and the penetration of UV light into the suspension[13].

Effect of hydrogen peroxide

The rates and efficiencies of photoassisted degradation of organic substrates are significantly improved in the presence of peroxides[14,15]. The photocatalytic degradation of RB49 has been studied at different hydrogen peroxide concentrations. Results show that the degradation rate of **RB49** increased with increasing H_2O_2 concentration up to 12 mmol/L, but above it, the degradation rate decreased. H_2O_2 can be converted to hydroxyl radical (Eq. 1). But at high amounts of H_2O_2, it can act as scavenger of $^{\cdot}OH$ according to Eq. 2 [16].

$$H_2O_2 + e^- \longrightarrow OH^- + {}^{\cdot}OH \quad ...(1)$$

$$H_2O_2 + h\nu \longrightarrow OH^- + {}^{\cdot}OH \quad ...(2)$$

$$H_2O_2 + {}^{\cdot}OH \longrightarrow HO_2^{\cdot} + H_2O \quad ...(3)$$

Degradation of dye at various dye concentration

Fig. 6 shows the photolysis of various initial concentrations of RB49 in the presence of Ag/ZnO (1 gL^{-1}) and appropriate of H_2O_2. A little adsorption was observed during of stirring of dye after 30 minutes in dark.
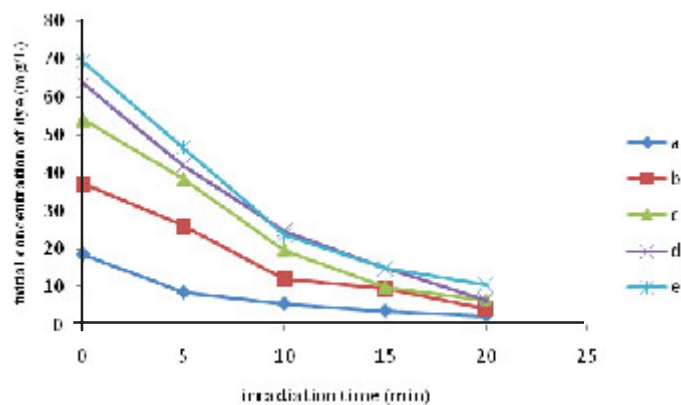

Fig. 6: Photolysis of various initial concentrations of RB49 in the presence of Ag/ZnO (1 gL^{-1}) and H$_2$O$_2$ (12 mmol/L)
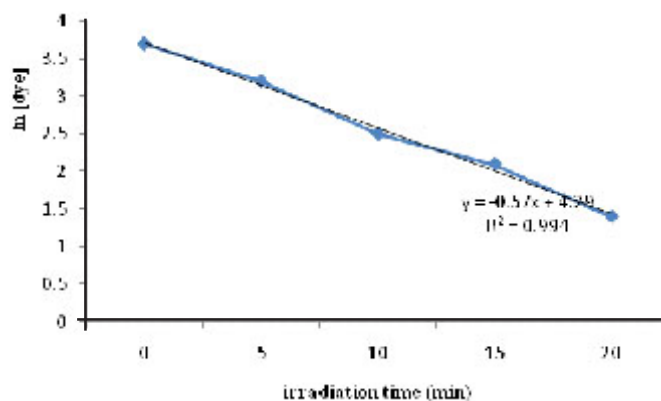

Fig. 7: Plot of ln[dye] versus irradiation time for RB49

Study of Kinetic modeling

According to many researchers the kinetics of the photocatalytic degradation rate of most organic compounds is described by a pseudo-first kinetic order[13,14].

As was shown in Fig. 6, the plot of ln[dye] versus irradiation time for RB49 is linear and can be assigned that the photodegradation reaction approximately follows the first order kinetics and rate constant (K) is 0.57 min^{-1}.

CONCLUSION

In this work the photocatalytic oxidative degradations of a reactive dye (RB49) has been studied. It was observed that, heterogonous photocatalyst (Ag/ZnO) can degrade dye. Approximately 90-95% dyes have been eliminated after 30 minutes in presences of Ag/ZnO as catalyst, H_2O_2 and optimize conditions

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