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Application of a New Photocatalyst in the Preparation of Silver Nanoparticles and investigating Their Photocatalytic activity

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ABSTRACT

Synthesis of silver nanoparticles by photochemical reduction of silver nitrate was carried out in water as an environmentally safe solvent using Preyssler acid, $H_{14}[NaP_5W_{30}O_{110}]$, as the reaction promoter. Poly (*N*-vinyl-2-pyrrolidone) (PVP) and formaldehyde were used as stabilizer and reductant agent, respectively. Our results have shown that UV irradiation increased the rate of reaction and decreased the size of synthesized silver nanoparticles. Metal nanoparticles were characterized by ultraviolet-visible (UV-Vis) spectroscopy, x-ray diffraction (XRD) and transmission electron microscopy (TEM). The catalytic performance of silver nanoparticles for photodegradation of methyl orange (MeO) as an azo dye model, has been investigated in aqueous solution. UV-Vis studies showed that Ag nanoparticles catalyzed photodegradation of this azo dye and the reaction rate was increased by the amount of catalyst.

1. Introduction

Silver nanoparticles have been extensively investigated in the recent years due to their unique physical, electrical and chemical properties, due to their vast applications in chemical medicine, industry, electronics, etc. Several chemical and physical methods have been used to prepare these nanoparticles [1]. Among them, the chemical reduction of silver ions in the presence of a protecting agent is the most widespread way –[2].

In general, in the chemical reduction methods, common reductants used are elemental hydrogen, citrate, ascorbate, and borohydride [3-5]. In recent years, organic and inorganic bases are used as the reaction promoter –[3, 5, 2]. Based on the green chemistry principles, the green synthesis of silver nanoparticles involves selection of an ecofriendly solvent and environmentally benign reducing agent [1]. According to this basis, most of the applied reductants are opposing the green chemistry rules. Polyoxometalates (POMs) can be introduced as promising candidates for green materials. They are harmless to the environment with respect to corrosiveness, safety, quantity of waste, and separability. Other key green aspects of solid POMs are related to their synthesis in an aqueous process and achievements of successful practical applications. Moreover, the unique properties of POMs such as strong Bronsted acidity, high hydrolytic stability (pH = 0–12), high thermal stability, operating in pure water without any additive, and non-corrosiveness [6], motivate us to exploit them as suitable reagents for the preparation of silver nanoparticles in a chemical reduction method.

A literature survey shows that there are several reports for the synthesis of metal nanoparticles

using POMs [7-10]. Although the Keggin-type and mixed-valance POMs have been used in the synthesis of Ag NPs –[11], the role of Preyssler structure in this silver derivative has been largely overlooked. In recent years, we have studied a series of Preyssler catalyzed reactions [12-16] and their excellent catalytic and photocatalytic activities have been shown. Recently, we have focused on developing the applications of Preyssler in nanotechnology area [17-20].

We have found that in the most synthesis methods, Ag NPs have been synthesized in the presence of bases, such as sodium hydroxide, sodium carbonate, pyridine, and triethylamine, but the role of acids has been ignored. Therefore, in the line of green chemistry and its promotion, it is of great interest to know what occurs if these bases are replaced by Preyssler as a green and solid superacid.

In our previous work, for the first time we have synthesized Ag NPs using Preyssler acid as the reaction promoter in the ambient temperature [18]. In the preparation process, formaldehyde and PVP was used as reductant and protective agents, respectively. The objective of the present study was to investigate the effect of UV irradiation in the silver NPs synthesis reaction and also in the performance of these NPs for the photodecolorization of methyl orange (MeO).

2. Experimental

2.1. Chemicals and instruments

Silver nitrate (AgNO_3), Poly (N-vinyl-2-pyrrolidone) (PVP) and formaldehyde were purchased from Merck company and used as received. Preyssler acid ($\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$) was prepared according to our earlier works [21, 22].

To indicate preparation of Ag NPs and show methyl orange degradation, UV-Vis spectrophotometer (Agilent 8453, Hewlett–Packard, USA) was used. The synthesized Ag NPs were characterized mainly based on their particle size distribution (PSD), using a laser particle size analyzer (ZetaSizer Nano ZS, Malvern Instruments Ltd.). This instrument allows to measure particle size taking advantage of optoelectronic systems and particle size is measured by the non-invasive backscattering (NIBS) technique. Also, nanoparticles were characterized using Transmission Electron Microscopy (PHILIPS CM-120). Samples for TEM analysis were prepared by drop-coating films of the Ag solution on carbon-coated copper TEM grids, allowing the grid to stand for a few times following which the extra solution was removed using a blotting paper.

2.2. Preparation of Ag NPs

PVP was first dissolved in water and then silver nitrate (2.5×10^{-3} mole) and formaldehyde (5.6×10^{-2} mole) were added, respectively. The mixture was stirred for a few minutes and then preysler acid (10^{-5} mole) was added. The mixture solution was irradiated by UV light (125W high pressure mercury vapor lamp) under continuous stirring in temperature of 20 ± 1 °C.

Changing the color of the mixture to black, indicate the formation of silver nanoparticles. The nanoparticles were separated by high speed centrifugation and washed twice with acetone/water and then dried in a vacuum oven.

2.3. Typical Procedure for Photocatalytic Degradation

The photoreactor was designed in our laboratory. In a typical reaction, in a quartz glass reactor

equipped with a magnetic stirrer, 30 ml of azo dye solution ($30 \mu\text{M}$), 0.5 ml of hydrogen peroxide, and different amounts of Ag NPs were mixed. The mixture was purged with nitrogen for 15 min and stirred in a dark place for 30 min. Then, it was irradiated under the high pressure mercury lamp (125 W) as a UV light source. The temperature in the glass reactor was kept 20 ± 1 °C by circulating water. At a given irradiation time intervals, liquid samples were taken from the mixture, and absorbance of the azo dye solution were measured with a UV-Vis spectrophotometer.

The degree of azo dye decolorization was calculated according to the following equation:

$$C = (A_0 - A)/A_0 \times 100 \quad (1)$$

where C is decolorization degree (%), A_0 initial absorbance of MeO solution, and A absorbance of MeO solution after photocatalysis. The catalyst can be easily separated by filtration and can be recycled in the reaction.

3. Results and Discussions

3.1. Formation of Ag NPs and effect of UV irradiation

Figure 1 shows UV-Vis absorption spectra of solutions after 0, 30 and 150 min of initiation of Ag NPs photoreaction synthesis. Before irradiation, there is a peak at about 300 nm due to the presence of silver ions. After UV irradiation, it was observed that the color of the solution was changed. This phenomenon is obviously shown in the figure as a change in UV–vis spectrum. The absorption peak at 300 nm was decreased and a new peak was appeared at 426 nm. This peak was appeared by silver nanoparticles –[23]. Peak alteration is the indication of concentration reduction of silver ions

and generation of silver nanoparticles.

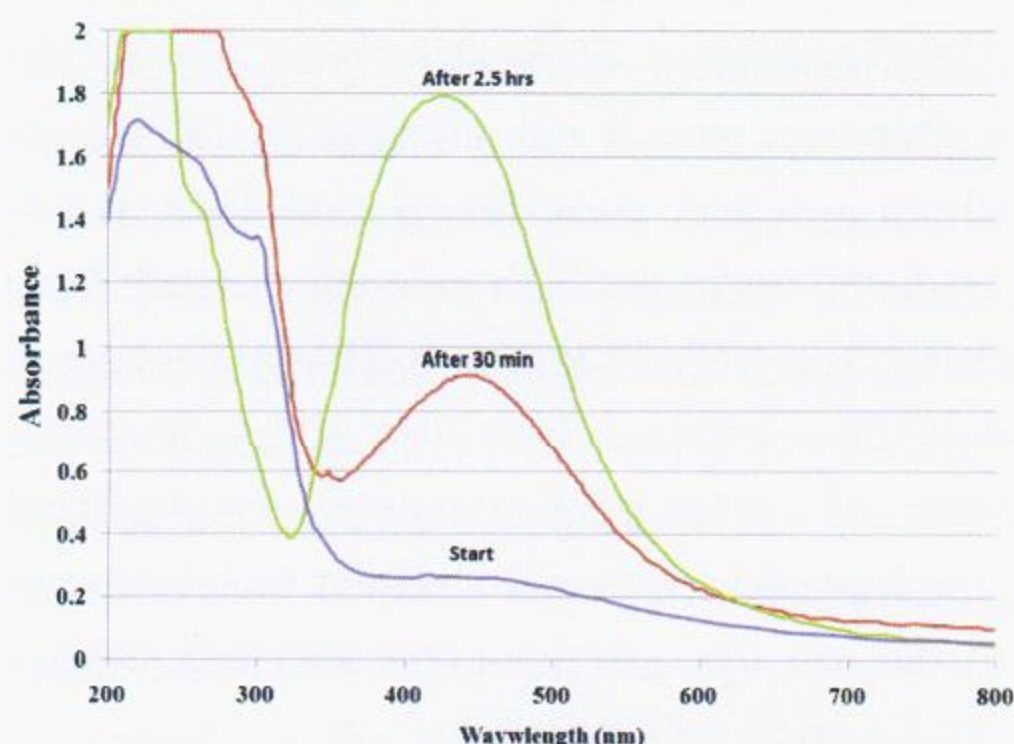


Figure 1. UV-Vis spectra of the irradiated solution at different times.

A blank experiment as a control (in the absence of Preyssler acid) has shown that the formation of nanoparticles is very slow. Moreover, in our previous work, it had been shown that in absence of UV irradiation and using Preyssler acid, formation of silver nanoparticles took place in more than 6 hours. UV irradiation decreased this time to about one half. It also affected the size of synthesized silver nanoparticles. Particle size distribution of Ag NPs in the absence and presence of UV irradiation was

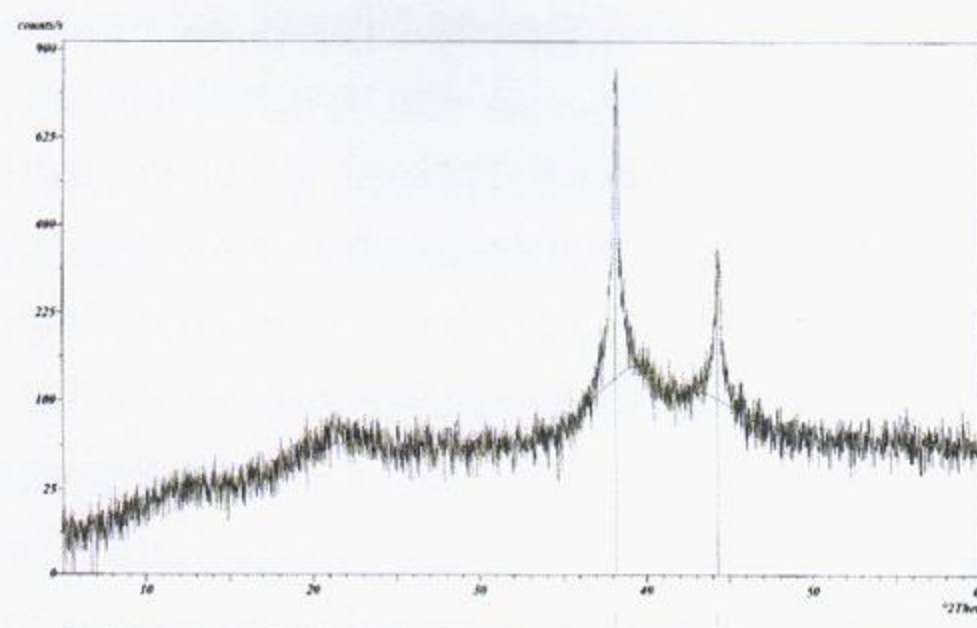


Figure 3. XRD pattern of the synthesized Ag NPs.

quantitatively displayed in a histogram shown in Figures 2a and 2b, respectively. These figures indicate that UV irradiation decreased the size of silver nanoparticles from about 11 nm to 6 nm. Photocatalytic activity of Preyssler acid under UV irradiation increases the rate of reaction, leading smaller and more uniform nanoparticles. As it shown in Figure 2, by using UV irradiation, more than 75% of nanoparticles are ranged between 5.5 to 8.5 nm.

X-ray diffraction (XRD) pattern of Ag NPs is shown in Figure 3. The reflection peaks indicate that silver nanoparticles are well crystallized. Moreover, The transmission electron microscopy (TEM) image of

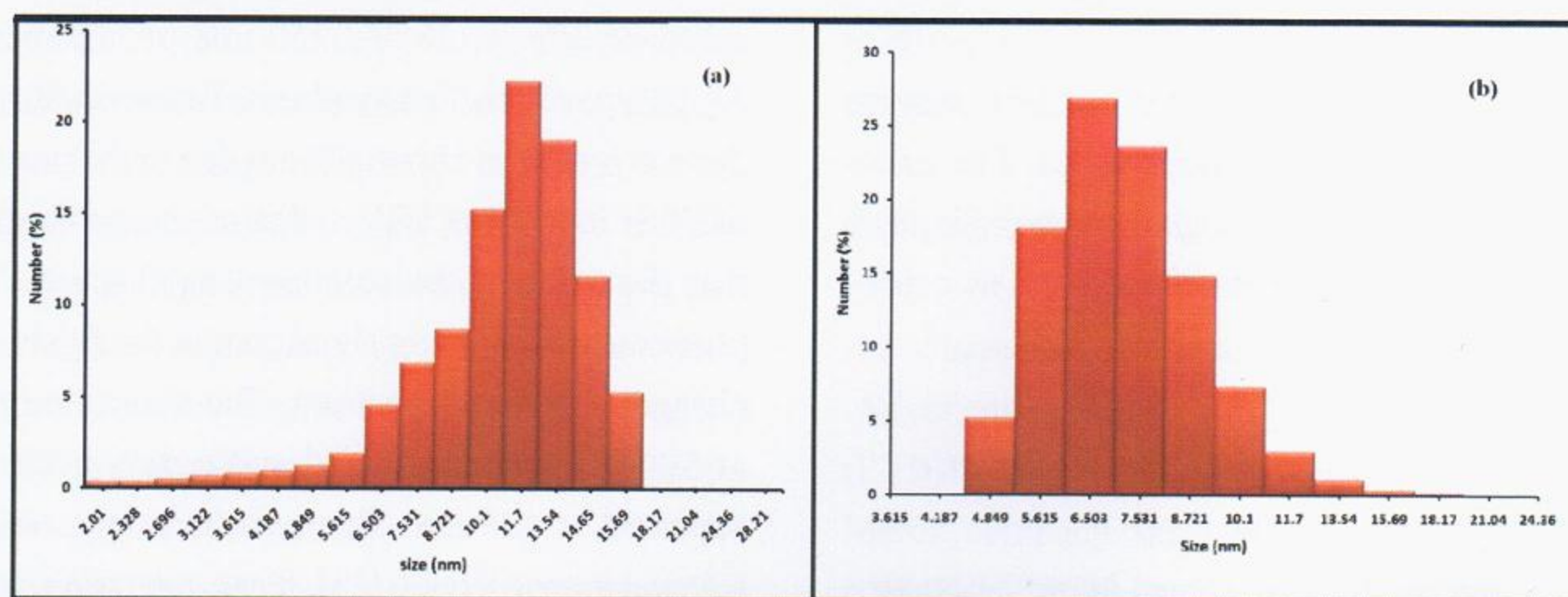


Figure 2. Particle size distribution of the synthesized Ag NPs, (a) in the absence of UV irradiation, (b) under UV irradiation.

these nanoparticles is shown in Figure 4. The representative TEM image shows that the Ag NPs have nearly spherical structure. Also, particle size distribution of the synthesized nanoparticles indicates uniformity of synthesized NPs (Figure 2b).

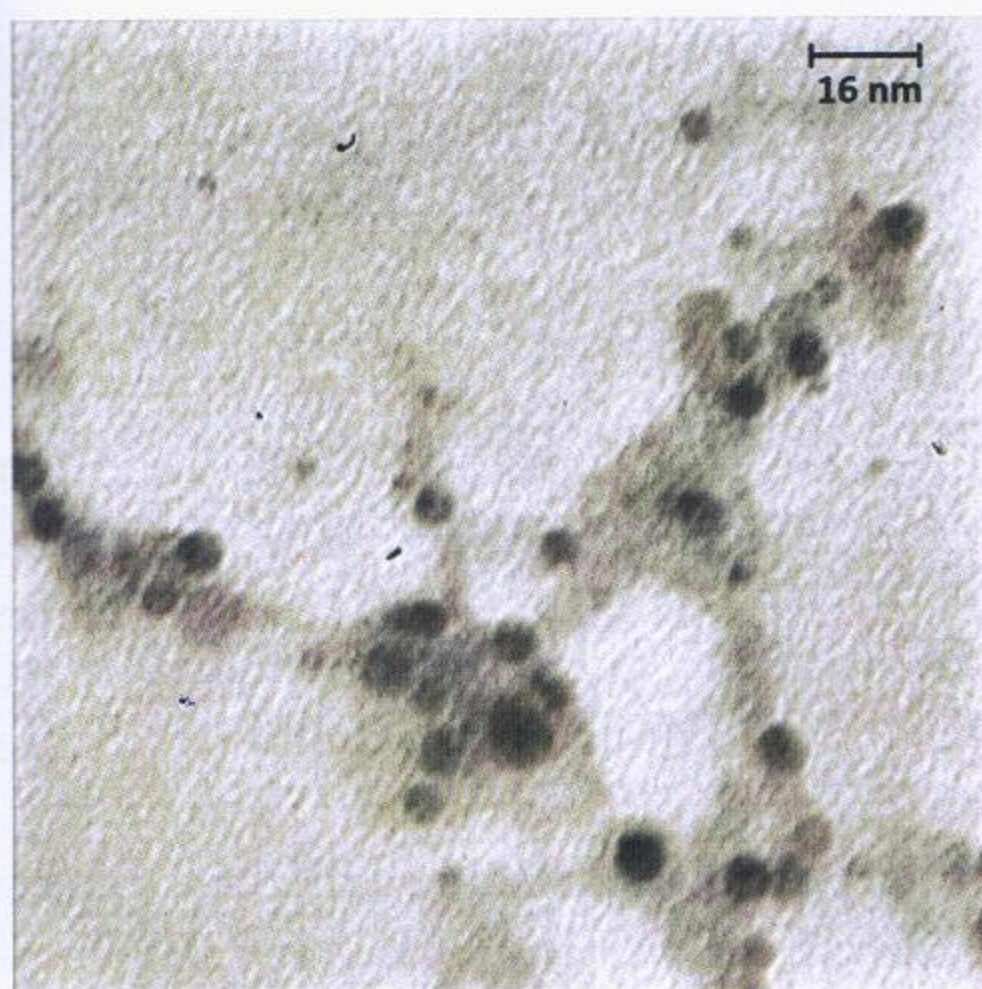


Figure 4. TEM images of synthesized Ag NPs after 150 min UV irradiation

3.2. Photocatalytic activity of synthesized NPs in photodegradation of MeO

The photodegradation of MeO as an azo dye model was performed in our photo-reactor as a test reaction to estimate the photocatalytic activity of these silver nanoparticles. We have checked the intensity changes of UV band in MeO solution. The degree of MeO decolorization was used as a indication for photocatalytic activity measurement.

The photodegradation of 30 μ M MeO solution with various amounts of nano catalyst were analyzed. The absorbance of the solution was monitored at specific time interval. The UV results of a sample with 3×10^{-3} g silver nanoparticles are shown in Figure 5. This figure shows that MeO solution can

be degraded under UV light in the presence of Ag NPs as a catalyst. After 30 min, the total absorption of methyl orange was decreased and 98% decolorization was obtained.

The pseudo-first order rate constant were calculated from the plot of $\ln(A_t/A_0)$ versus time (Figure 6). The first-order decolorization constants, obtained from three experiments by using different amounts of silver nanoparticles, are listed in Table 1. It can be found from this study that speeding the photodegradation rate by increasing the catalyst amount, is obviously due to the higher number of photocatalytic active sites. There are several other factors that can also affect the photocatalytic activity. Literature in photocatalysis research reveals that photocatalytic activity can be strongly dependent on the crystallographic structure, morphology, and size of the particles [24, 25].

Table 1. The rate constants for photodegradation of MeO in different amounts of the nano catalyst.

Ag NPs (gr)	10^{-3}	2×10^{-3}	3×10^{-3}
k (s^{-1})	0.065	0.083	0.103

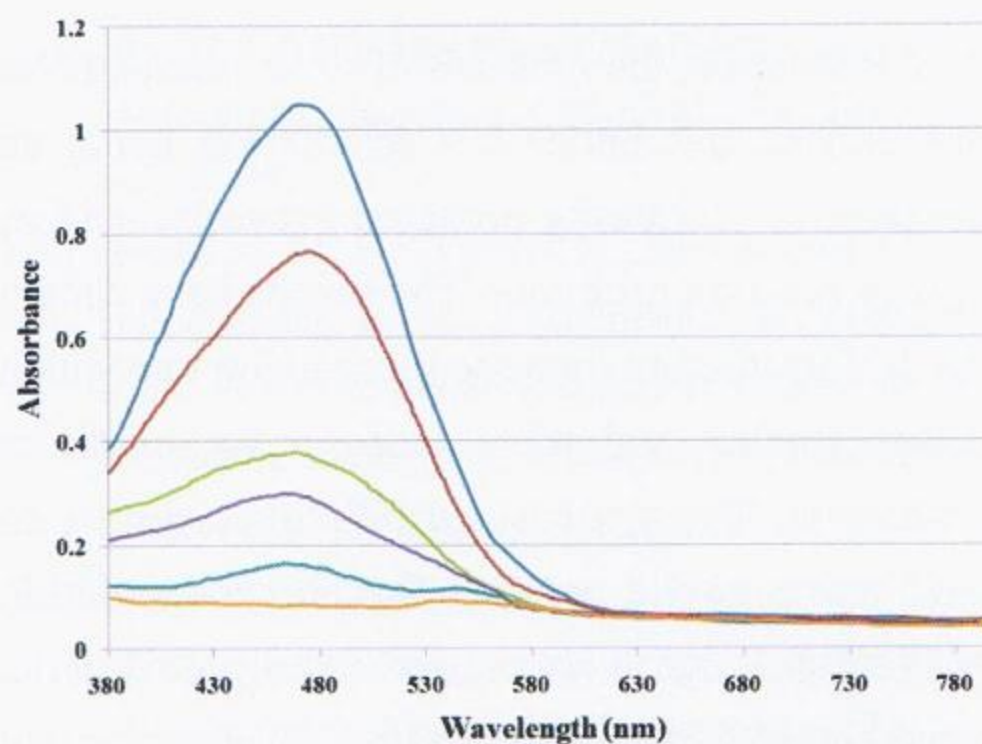


Figure 5. Catalytic photodegradation of MeO in the presence of Ag NPs at different times.

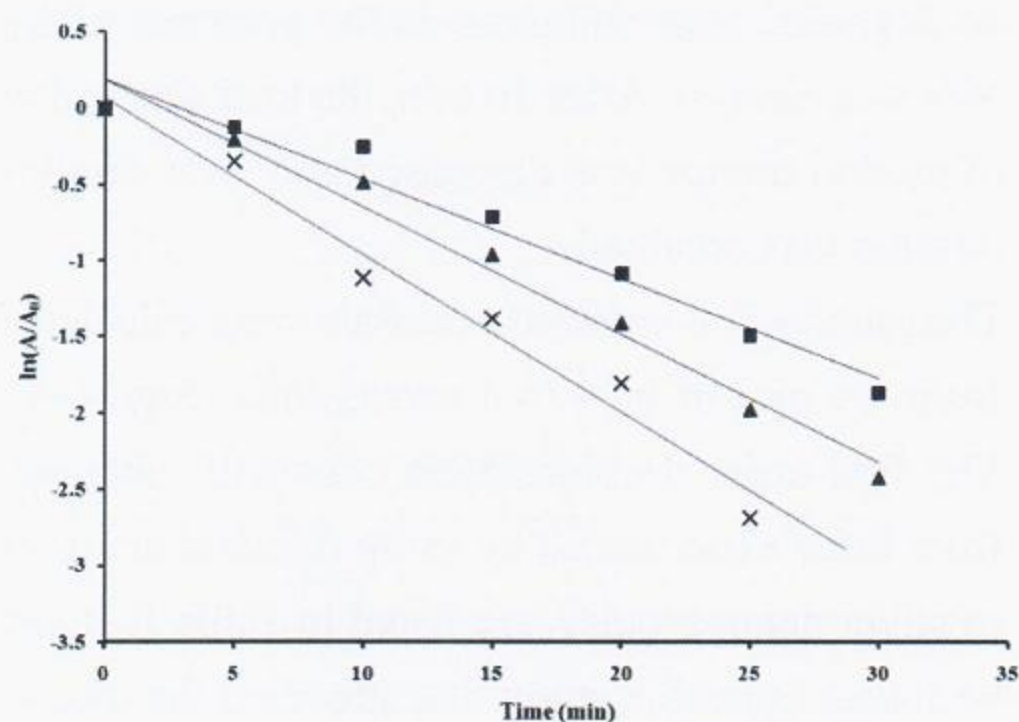


Figure 6. Plot of $\ln A/A_0$ versus time for MeO photodegradation using various amount of Ag NPs, (\square) 10^{-3} g, (\blacktriangle) 2×10^{-2} g, (\times) 3×10^{-3} g.

As the control experiments, we have also studied the MeO photodegradation reaction in the absence of Ag nanocatalyst, oxidant, and UV-illumination. In the absence of nanocatalyst the reaction was very slow and the reaction did not have any progress without hydrogen peroxide. Also, the degradation of methyl orange in the absence of UV-illumination did not change significantly.

4. Conclusions

In this research, the synthesis of silver nanoparticles was carried out under UV irradiation using an inexpensive and easily prepared Preyssler acid as a green reaction promoter. The results have shown that UV irradiation increase the reaction rate which causes smaller and more uniform nanoparticles production. The synthesized NPs have shown an excellent catalytic activity for photodegradation of MeO azo dye with pseudo-first-order kinetic. Increasing Ag NPs was resulted an enhancement of photodegradation rate.

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