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Experimental study on silver nanoparticles: synthesis, photo-degradation and analysis

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ABSTRACT

The aim of present study was waste water treatment via advanced oxidation process (AOP). Wet chemical precipitation method was used to prepare silver nanoparticles (Ag NPs). The Ag NPs were employed for photo catalytic degradation of Congo red (CR) dye in aqueous medium. The scanning electron microscopy (SEM) investigation shows agglomerated form of Ag NPs. The average sizes of agglomerations are below 600 nm. Energy dispersive X-rays spectroscopy (EDX) and ultraviolet light visible spectroscopy (UV/Vis) also established the formation of Ag NPs. The photo-degradation study reveals that Ag NPs degraded by 73% of CR dye in 480 min. Catalytic dosage study shows the dye degradation was increased vice versa as increased the amount of Ag NPs and then almost level off after 0.025 g of catalyst. In pH study it was observed that degradation of CR dye increased as pH increased. The recovered catalyst study also significantly degraded the CR dye.

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1. Introduction

The pollution of the environment is a global problem, which not only giving threat to humanity but also to other living things. The environmental pollution is due to the increasing global population and industrialization. Among various contaminates, the importance is given to the organic compound removal from waste water and its complete removal becomes necessary because these can also precipitate at low quantities.

Dye compounds are important organic pollutants, which are mainly discharging from textile, leather, cosmetics, and food industries, which are the major sources of pollution and eutrophication [1]. Synthetic dyes approximately about 100,000 are frequently used in industries. Generally, dyes are obtained from coal tar and petroleum intermediates. The overall yearly production of dyes is in excess of 7 x 10^5 tons. These non-decomposable textile dyes, which are around 15% (one thousand tons) per year are released into water bodies via textile waste effluents [2]. These compounds are highly toxic, carcinogenic, mutagenic and non-biodegradable and are harmful for aquatic life and humans [3]. The coloring materials/dyes also absorb sunlight strongly, which slow down photosynthetic activity of aquatic plants, and threatening badly the entire ecosystem [4].

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Nomenclature

AOP	Advanced oxidation process
Ag Nps	Silver nanoparticles
CB	Conduction band
CR	Congo red
EDX	Energy dispersive X-rays spectroscopy
JEOL	Manufacturing company
M	Mole
OH	Hydroxyl
ppm	Parts per million
SEM	Scanning electron microscopy
UV	Ultraviolet light
UV-Vis	Ultraviolet light visible spectroscopy
VB	Valence band

The chirality of industrial products and agro chemicals are big threat to human beings [5], [6]. Various methods widely utilized for the removal of dyes include reverse osmosis, filtration, precipitation, coagulation, flocculation chemical oxidation and adsorption but these methods need additional treatment [7]-[9]. For example, coagulation and adsorption produce huge quantity of waste and sludge that need further treatment for disposal [10]. Recently, advanced oxidation process such as semiconductor based photo-catalysis, Ozonization, Fenton, photo-Fenton have found the most effective methods for the dyes degradation [11]-[15]. Semiconductor based photo-catalysis is gaining more importance, which is carried out an ambient conditions can degraded dyes in the presence of UV visible irradiation [15].

Deferent types of metal and metal oxide nanoparticles, for example tailored TiO_2, ZnO, and carbon-Fe, Fe_2O_3, NiO, Ni/MgO and WO_3 are utilized for photo catalytic degradation of dyes [6],[15]-[20]. When metal or metal oxide nanoparticles expose to light, the excitation of electron occurs from valence to conduction band and as a result positively charged holes are formed in the valence band. The electron-hole pairs react readily with water and oxygen molecules and results hydroxyl and superoxide radicals; the radicals are strong oxidizing agents and responsible for the photo-degradation of organic pollutants [20].

In the present study, wet chemical precipitation method was used to prepare Ag NPs from their precursors. Ag NPs were analyzed by using SEM, EDX and UV/Vis spectrophotometry. The Ag NPs were used as photo-catalyst to degrade Congo red dye in aqueous medium.

2. Experimental

2.1. Materials

The silver nitrate, Congo red dye and nitric acid were supplied by Sigma Aldrich.

2.2. Synthesis of Ag NPs

Fig. 1 shows the schematic representation of the experimental setup. 2 M NaOH solution were added drop wise to 150 mL of 0.3 M ($AgNO_3$) in 250 mL flask until a pH value of 10 was attained. The obtained mixture was stirred continuously and heated for 2 hour at 80 °C. Then solution was cooled and the precipitate of Ag NPs was separated through filtration. The Ag NPs were washed several times to remove any attached acid. The Ag NPs were kept in an oven for drying at 100 °C and then stored.

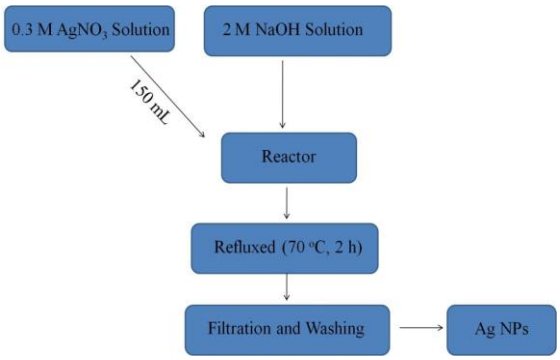


Fig. 1. Schematic representation of experimental work

2.3. Photo-degradation of CR Dye

0.025g of Ag NPs was taken in 25 mL beaker and 10 mL of CR dye (100 ppm) sealed in transparent plastic sheet to penetrate prevent light and evaporation. The mixture was stirred under UV light for a specific irradiation period. After irradiation specific time Ag NPs were centrifuged. UV/Vis spectrophotometer was utilized for photo-degradation of the CR dye. The following equations were utilized to compute the percentage (%) degradation.

$$R_{deg}\ (\%) = \left(\frac{C_0 - C}{C_0}\right) \times 100 \quad (1)$$

$$R_{deg}\ (\%) = \left(\frac{A_0 - A}{A_0}\right) \times 100 \quad (2)$$

R_{deg} is the degradation rate, C_o is initial dye concentration, C denotes dye concentration after UV irradiation, A_o is initial absorbance, and A represents dye absorbance after UV irradiation.

2.4. Instrumentation

Morphological investigations of Ag NPs were carried via JEOL, SEM model JSM-5910. The percentage constituents of synthesized

NPs was analyzed on EDX (Model Inca 200). SEM and EDX are important analytical tools; SEM is used for the study of morphology and size determination while the EDX is used for the determination of percentage composition of the materials.

The confirmation of Ag NPs and Double Beam UV/Vis (Labomed model UVD-2960) was used to investigate photo-degradation of CR. UV/Vis spectroscopy is constructive instrument for the investigation of optical response of metal nanoparticles. The establishment of colloidal metal nanoparticles is quite sensitive owing to the intense surface plasmon resonances technique. In this study, UV/Vis spectrophotometric technique is used to determine Ag NPs synthesis from their precursor salt.

3. Results and Discussion

3.1. SEM and EDX Analysis

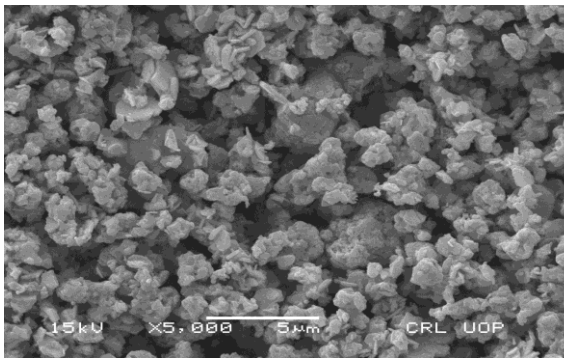
Fig. 2 show the SEM micrographs and EDX spectrum of Ag NPs. The SEM micrograph shown in Fig. 2 (a) of Ag NPs is present in agglomerated form with irregular shape. The sizes of agglomerations were below 600 nm. The EDX spectrum (Fig. 2(b)) shows only silver and minute amount of oxygen. The existence of large quantity of Ag NPs indicates that the NPs are formed successfully from the precursor salt (silver nitrate).

3.2. UV/Vis spectroscopic study of Ag NPs

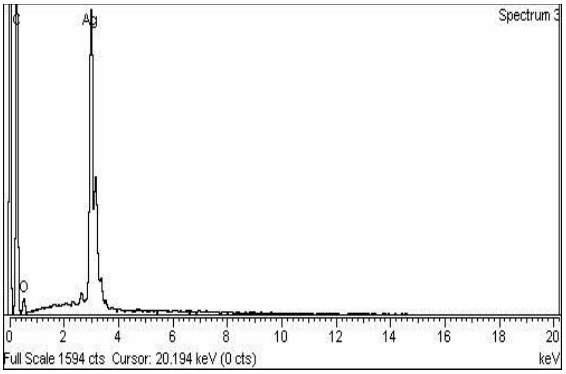
UV/Vis spectrums of Ag NPs are shown in Fig. 3, which gave UV spectrum of Ag colloids within a range of 300 to 750 nm. The absorption spectrum showed formation of Ag colloids because due to the surface plasmon Ag NPs present an absorption peak illustrates the excitation of conduction electrons in a metal). The well-defined peak of Ag NPs around 435 nm was found in the spectrum.

3.3. Photo-degradation Study of CR Dye

The photo-catalytic activity of Ag NPs was assessed by utilizing it for the photo catalytic degradation of CR dye under UV light-irradiation. The CR photo-degradation was measured from the relative intensity of UV/Vis spectra, having maximum absorbance peak at 500 nm. Fig. 4 (a) displays the UV/Vis spectra of CR dye, which presented degradation of dye increased as the irradiation time increased. Fig. 4 (b) illustrated percentage degradation of dye. It was found that Ag NP degraded about 13 and 73 % of dye within 30 and 480 min under UV irradiation, respectively. Furthermore, the digital photographs shown in Fig. 4(c) represent increased decolorization of CR dye as increased the irradiation time, which means photo catalytic degradation of dye occurred in the presence Ag NPs



(a)



(b)

Fig. 2. Ag NPs (a) SEM images (b) EDX spectrum

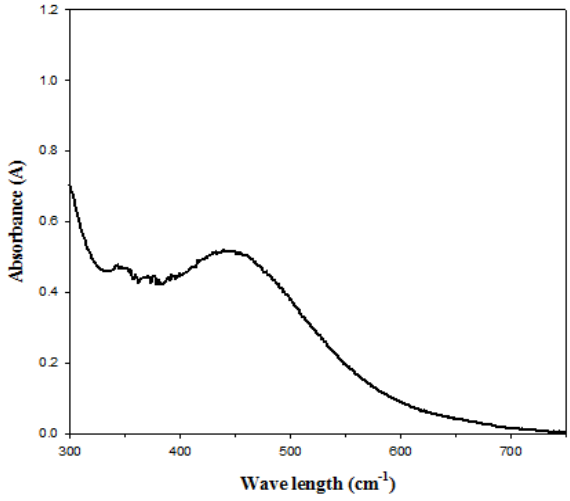


Fig. 3. UV visible spectrum of Ag NPs

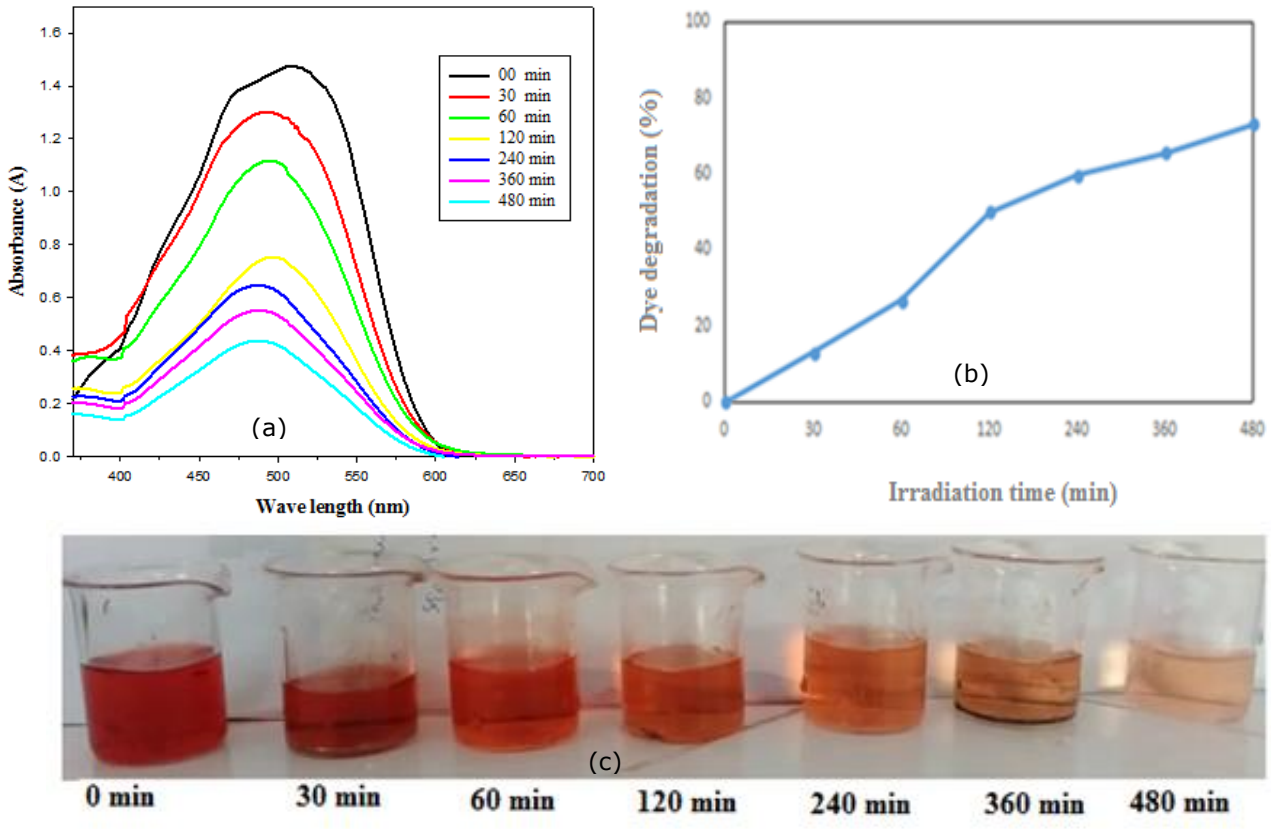


Fig. 4. Photo-degradation of CR dye by Ag NPs photo-catalyst under UV-light irradiation versus time; (a) UV/Vis absorbance spectra, (b) % degradation, and (c) digital photographs of CR dye degraded by GNPs/Ag.

3.4. Recycled Photo-catalyst Analysis

The recycled catalyst efficiency was assessed under the same experimental conditions as function of irradiation time. Fig. 5 shows comparison of percentage degradation of CR dye by fresh and recycled Ag NPs. Results represent fresh Ag NPs degraded about 73 % dye in 480 min while recycled Ag NPs degraded about 58% dye in the same irradiation time. It means that the recycled Ag NPs degraded the CR dye significantly in aqueous medium. However, it shows less photo-catalytic activity compared to the fresh photo-catalyst because of the blocking of active sites by dye molecules.

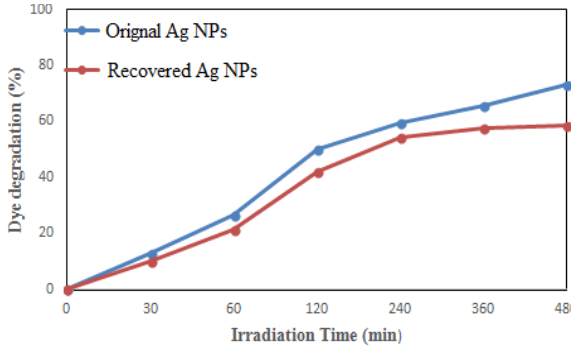


Fig. 5. Comparison of percentage degradation of CR by fresh and recycled Ag NPs.

3.5. Effect of Photo-catalyst Dosage

The influence of photo catalyst dosage on photo-catalysis of CR was evaluated by loading increasing amount of Ag NPs (0.015, 0.020, 0.025, 0.030 and 0.035 g). Fig. 6 (a) illustrates UV/Vis spectra of CR dye and the constant irradiation time using different amount of Ag NPs photo-catalyst. The results shows dye degradation increased as the amount of Ag NPs increased, which might be due to the availability of large amount of Ag NPs. Fig. 6 (b) presents the percentage degradation of CR dye, which indicated that about 74 % of dye was degraded by 0.035 g of NPs at constant irradiation time (120 min) and dye concentration.

3.6. Effect of pH on Photo-degradation

The pH also plays a vital role in aqueous medium for degradation of organic pollutants. Table 1 presents the % degradation CR dye by Ag NPs at different pH values. Degradation of dye increases with increasing pH of the medium. The results show that more than 55 % of dye was degraded at pH value of 2 and up to 81% at pH value of 10 at same irradiation period (120 min) and dye concentration.

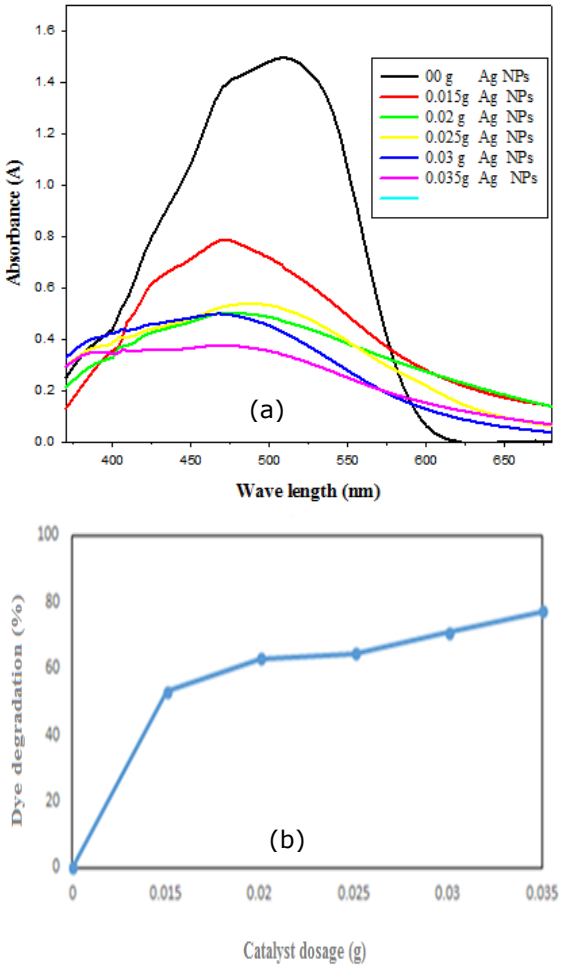


Fig. 6. Comparison of percentage degradation of CR dye in aqueous medium for different catalyst dosage of Ag NPs

Table 1. CR dye degradation at different pH

pH	% Degradation of CR
2	55.45
4	62.21
6	68.38
8	75.89
10	81.69

The pH has large effect on decolorizing the CR dye and high pH of the medium (basic medium) is favorable for photo-degradation of CR dyes. The high degradation rate of the dye might be because of the formation of large number of hydroxyl radicals in basic medium. An independent study [21] also reported the increased photo-degradation of CR dye at high pH value.

4. Conclusion

An experimental study on the synthesis, photo-degradation and analysis of silver nanoparticles has been presented. The SEM investigations showed that Ag NPs are present in agglomerated form and average sizes of agglomerations are below 600 nm. The EDX confirmed formation of Ag NPs and UV/Vis spectroscopy. The photo catalytic degradation study showed both fresh and recycled Ag NPs significantly degraded the CR dye in aqueous medium. It was established that the basic medium is favorable for the degradation of CR dye.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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