Photocatalytic activity of titanium dioxideand silver nanoparticles on the degradation of alizarin reddye

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ABSTRACT

Photocatalysis has been considered as an effective alternate for the purification of dyes in waste water. The objective of this study focused on the photocatalytic activity of titanium dioxide and silver nanoparticles (AgNPs)on the degradation of alizarin red. Green synthesis of silver nanoparticles using gooseberry extract is investigated. The synthesized nanoparticles are characterized by using UV-Visible and FTIR spectroscopy. The particle size of the AgNPs is determined by XRD analysis. The photocatalytic activities of the nanotitania and the synthesized AgNPs are examined by the degradation of alizarin red under visible light illumination. The rate of photodegradation of 100 ml alizarin redin the presence of 0.01 and 0.05 g of TiO_2 nanoparticles are 1.20 x 10^{-2} sec^{-1} and 1.60 x 10^{-2} sec^{-1} respectively. The absorption kinetics of the dye followed the pseudo-first order mechanism. Results indicate that the TiO_2 nanoparticles act as an efficient photocatalystthan that of AgNPs for the degradation of alizarin red.

Keywords: Gooseberry extract; Titanium dioxide; Silver nanoparticles; Photocatalytic degradation; Degradation efficiency.

Introduction

Alizarin Red is a water soluble anthraquinone dye used for the dyeing of cotton, silk, paper, leather and also in the manufacturing of paints and printing inks. Alizarin red isa durable pollutant, released especially by textile industries in the aquatic ecosystems [1]. It causes several harmful effects, such as gastritis, mal-functioning of lungs, severe headache, painful micturition and methemoglobinemia [2]. Due to this significant health risks to human and fish, it is essential to establish a proper method to remove this dye from water or industrial effluents. Removal of this dye from industrial wastewaters is a crucial process, from both economic and environmental point of view. This dyeis not easily removed by routine wastewater treatment methodologies like chemical coagulation, precipitation and chemical or biological oxidation due to their thermodynamic stability and resistance towards photocatalytical or biological oxidizing agents [3].

There are several methods to remove dyes from waste water such as coagulation [4], reverse osmosis [5], photodegradation [6], ion exchange [7], oxidation [8], biodegradation [9], nanotechnology [10] advanced oxidation process [11] and adsorption [12]. Current research community focuses on technologies for the treatment of polluted air, water or soil that are cost effective and benign. Among all these methods, photocatalytic degradation seems to be quite promising as it can provide a low cost method to solve this problem.

Photocatalysis is a booming field of chemistry due to its numerous potential applications. In this method, semiconductorsare used as photocatalyst and have been considered as an effective alternate for the purification of dye containing wastewater [13]. All semiconductors can be used as photocatalyst due to the characteristic of filled valence band, and an empty conduction band. Many semiconductors have been synthesized and studied as photocatalysts including zinc oxide, titanium dioxide, strontium titanate, iron oxide, cadmium sulfide, tungsten trioxide, zinc sulphide, ilmenite, zirconium dioxide, vanadium oxide, niobium pentoxide, and tin oxide. Of these, TiO_2 has been found most suitable for general environmental remediation [14].

Green synthesis of nanoparticles is an emerging branch of nanotechnology. The synthesis of nanomaterials is of current interest due to their wide variety of applications in fields such as electronics, photonics, catalysis, medicine, etc. Biosynthesis of nanoparticles provides advancement over chemical and physical methods as it is cost effective and environmental friendly method. Recently, biosynthesised silver nanoparticles (AgNPs) are also used as photocatalyst for the degradationon of dyes [15]. Jegadeeswaran *et al*., [16] examined the photocatalytic properties of green synthesised AgNPs on congo red and direct brown 95 under sunlight. Based on the literature survey, the present study concentrates on the photocatalytic degradation of alizarin red dye with nanoparticle of titanium dioxide and silver. The green synthesised AgNPs from gooseberry extract is characterized by UV-Visible spectroscopy and FTIR spectroscopy. The particle size is determined by XRD analysis. The photocatalytic experiments are conducted in the presence of sunlight.

2. Materials and Methods

Fresh and ripened gooseberry fruit were obtained from the local market. The dyealizarin redand $AgNO_3$were procured from Merck. Nano titanium dioxide was purchased from Sigma-Aldrich. The double distilled deionized water was used as a solvent for the synthesis as well as the degradation studies.

2.1. Preparation of gooseberry extract

Ripened gooseberry was used for the preparation of the extract. 25 g of this ripened fruit was thoroughly washed with distilled water and cut into small pieces. Grind the pieces by a pestle and mortar and the resulting extract was filtered using Whatmann filter paper. The filtrate was collected and then centrifuged for about 10 minutes at 8,000 rpm. The supernatant extract was collected and used as reducing agent for the synthesis of AgNPs.

2.2 Synthesis of silver nanoparticles from gooseberry extract

1mM aqueous solution of $AgNO_3$ was prepared and used for the synthesis of AgNPs. 10 ml of gooseberry extract was added to 90 ml of 1mM aqueous $AgNO_3$ solution in a 250 ml Erlenmeyer flask and incubated at room temperature. The sample colour changes from colourless to light grey colour within 10 minutes indicate the formation of AgNps. The AgNPs obtained by gooseberry extract were centrifuged at 15,000 rpm for 5 min and subsequently dispersed in sterile distilled water to get rid of any uncoordinated biological materials. The pellet of AgNPs collected at the bottom of the centrifuge tube was collected, dried and stored at - 4°C.

2.3 Instrumentation Techniques

The absorption spectrum of AgNPs and the photodegradation of dye were carried out using Shimadzu UV-1800 spectrophotometer. FT-IR analysis of the dried AgNPs was carried out through the potassium bromide (KBr) pellet (FT-IR grade) method in 1:100 ratio and the spectrum was recorded using Shimadzu IR Affinity-1 FT-IR spectrophotometer with the range of 4000-400 cm^{-1} at the resolution of 4 cm^{-1}.Phase formation of the synthesized nanoparticles was characterized by X-ray diffraction. Diffraction data for thenanoparticles on glass slides were recorded on an X-ray diffractometer (Ultima III, Rigaku, Tokyo, Japan) with Cu Kα radiation (λ = 1.5406 Å) source in the 2θ range of 10°–80° with 4°/minute scanning rate. The particle size was calculated from the width of the XRD peaks using the Scherrer formula.

$$D = 0.94 \lambda / \beta \cos \theta$$

where D is the average crystallite domain size perpendicular to the reflecting planes, λ is the X-ray wavelength, β is the full width at half maximum (FWHM) and θ is the diffraction angle.

2.4 Photocatalytic degradation

0.0365 g of alizarin red was dissolved in 100 ml of double distilled water and was used as a stock solution. This stock solution was further diluted for the degradation studies. The alizarin redshows an absorption maximum at 520 nm. The degradation of alizarin redwas studied by taking 100 ml of 8.0×10^{-6} M of the dye and the catalystin the presence of sunlight. An aliquot of 4.0 ml is taken out from the reaction mixture at regular time intervals and absorbance is measuredat 520 nm. The progress of the photocatalytic reaction was observed by taking optical density at regular time intervals. The decrease in absorbance with increasing time intervals shows the degradation of dye. The degradation efficiency (η) was described by the equation:

$$\eta = (A_0 - A)/A_0 \times 100\%$$

whereA_0 and A was the absorption intensities at the beginning and after photocatalytic reaction for certain time.

3. Results and Discussion

The characterization of AgNPs and the detailed study on the catalytic degradation of alizarin red with nanoparticles of silver and titanium dioxide in the presence of sunlight are reported in this section.

3.1 Absorption spectral analysis of AgNPs

Reduction of silver ions into AgNPs during exposure to the gooseberry extract could be followed by colour change. Silver nanoparticles exhibits light grey colour in aqueous solution due to the surface plasmon resonance phenomenon, which results from collective oscillations of their conduction band electrons in response to electromagnetic waves. Absorption spectra of AgNPs formed in the reaction media after 10 minutes has an absorbance peak at 362 nm, broadening of peak indicated that the particles are polydispersed (**Fig. 1**).

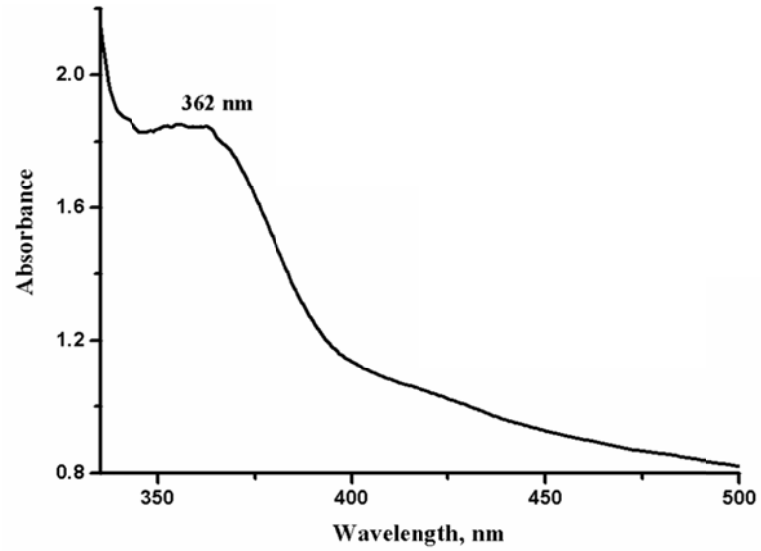


Fig. 1 Absorption spectrum of AgNPs

3.2. FT-IR analysis of AgNPs

The FT-IR spectrum of the synthesized AgNPs (**Fig. 2**) shows absorption bands at 3424, 2918, 2864, 1691, 1651, 1582, 1535, 1457, 1022, 906 and 680 cm^{-1}. The prominent band around 3424 cm^{-1} signified the O-H stretching of alcohols. The presence of weak band at 2918 and 2864 cm^{-1} corresponds to the C-H stretching of alkene. Absorption band at 1691 cm^{-1} is due to C=O stretching modes of esters present in ascorbic acid. IR spectrum exhibits weak bands at 1651, 1582 and 1457 cm^{-1} due to the stretching vibration of C=C bond.

The weak band at 1022 cm^{-1} is assigned for the C-O stretching of primary alcohols. C-H bending vibrations occur at 906 and 680 cm^{-1} respectively. The mechanism of the reduction of Ag^{+} ions to Ag^{0} may be due to the presence of water-soluble antioxidative substances like ascorbic acid which is present in the gooseberry extract. Ascorbic acid acts asa reducing agent leading to the formation of ascorbate radical and an electron. This free electron reduces Ag^{+} ions to Ag^{0} (**Scheme 1**).

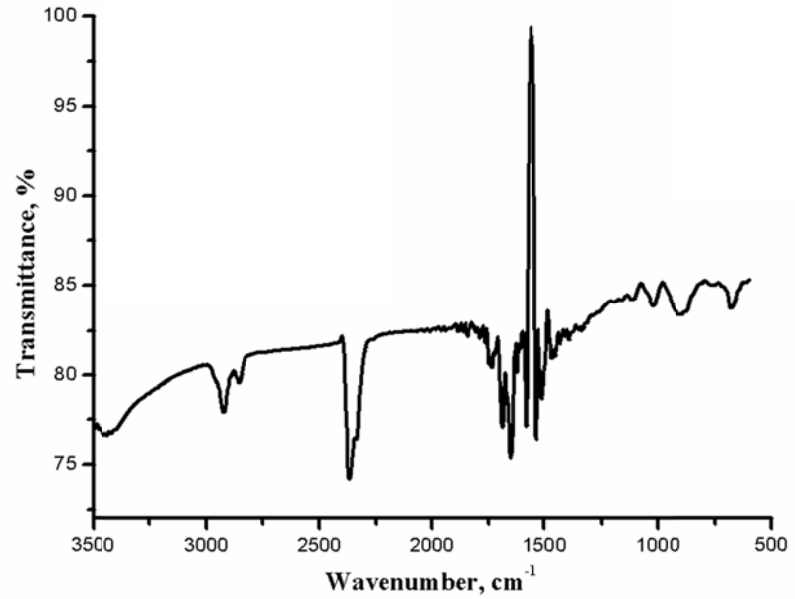
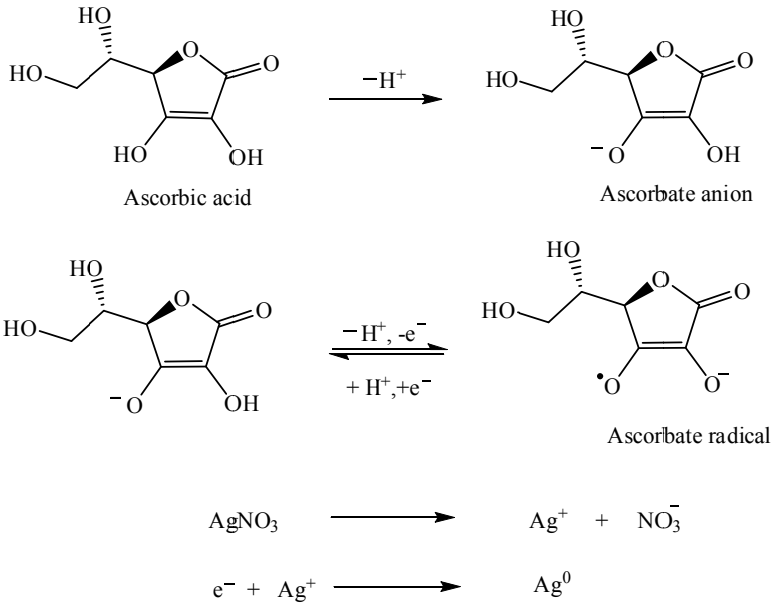


Fig. 2 FT-IR spectrum of AgNPs



Scheme 1 Ascorbic acid reduction of Ag^{+} to Ag^{0}

3.3 XRD Analysis

The diffractogram of AgNPs (**Fig. 3**) has been compared with the standard powder diffraction card of JCPDS, silver file No. 65-2871. Four peaks at 2θ values of 37.947, 44.219, 64.240 and 77.257 degree in the experimental diffractogram have been identified due to silver metal and the corresponding (hkl) values are (111), (200), (220) and (311). The particle size of AgNPs is 25 nm. The XRD study thus confirmed face centered cubic geometry for AgNPs.

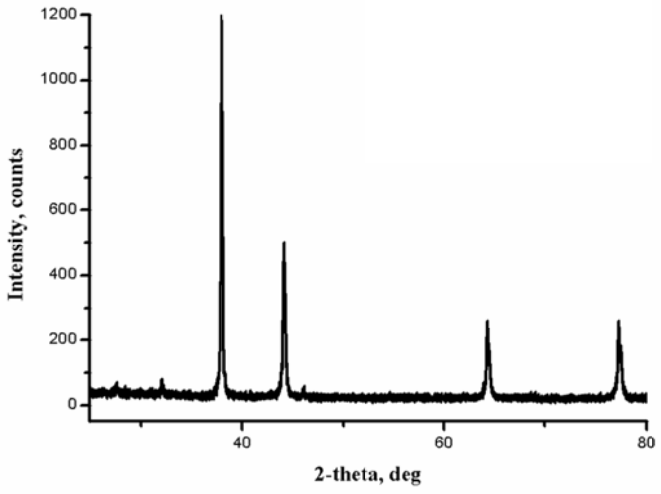


Fig. 3 XRD pattern of AgNPs

3.3 Photodegradation of alizarin red

An aliquot of 4.0 mlis taken out from the reaction mixture at regular time intervals and absorbance is measured spectrophotometrically at 520 nm. It is observed that the absorbance of the solution decreases with increasing time intervals showing thereby that the concentration of the dyes decreases with increasing time of exposure. The results for the degradation of alizarin redwith and without catalyst are mentioned in the **Tables 1-5**. A plot of 1 + log A versus time is linear and follows pseudo-first order kinetics (**Fig. 4**), where A is the absorbance of the medium at a particular time t. The rate constant is measured by following expression:

$$k = -2.303 \times \text{Slope}$$

Table 1 Degradation of alizarin red without catalyst in light

Time (min)	Absorbance (A)	1 + log A
0.0	0.27	0.4313
10	0.28	0.4471
20	0.28	0.4471
30	0.28	0.4471
40	0.28	0.4471
50	0.28	0.4471
60	0.26	0.4149
70	0.25	0.3979
80	0.26	0.4149
90	0.23	0.3617
100	0.25	0.3979

Table 2 Degradation of alizarin red with 0. 01g of nano TiO_2

Time (min)	Absorbance (A)	1 + log A
0.0	0.29	0.4623
10	0.26	0.4149
20	0.24	0.3802
30	0.20	0.3010
40	0.19	0.2787
50	0.17	0.2304
60	0.14	0.1461
70	0.13	0.1140
80	0.12	0.0791
90	0.11	0.042
100	0.10	0

Table 3 Degradation of alizarin red with 0.05 g of nano TiO_2

Time (min)	Absorbance (A)	1 + log A
0.0	0.27	0.4313
10	0.26	0.4149
20	0.24	0.3802
30	0.17	0.2304
40	0.15	0.1760
50	0.12	0.0791
60	0.10	0
70	0.09	-0.0457
80	0.08	-0.0969
90	0.07	-0.1549
100	0.05	-0.3010

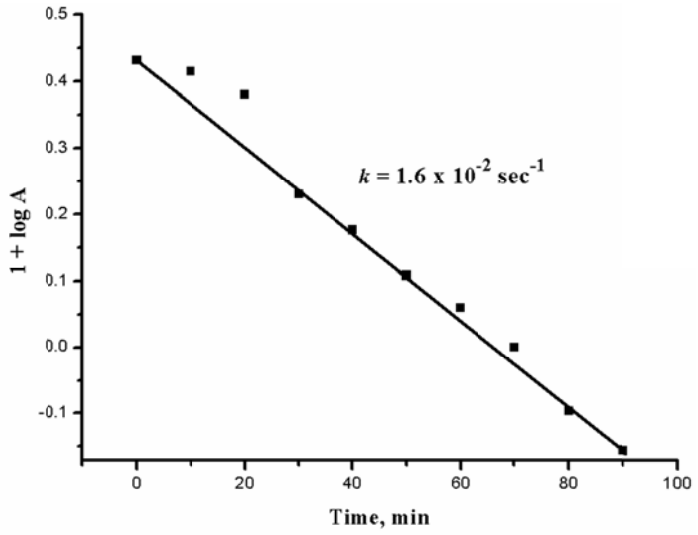


Fig. 4 Plot of 1 + log A*v*s time for alizarin red with 0.05 g of n**a**no TiO_2

Table 4 Degradation of alizarin red dye with 0.01 g of AgNPs

Time (min)	Absorbance (A)
0.0	0.31
10	0.34
20	0.36
30	0.37
40	0.38
50	0.42

Table 5 Degradation of alizarin red dye with 0.05 g of AgNPs

Time (min)	Absorbance (A)	1 + log A
0.0	0.34	0.5315
10	0.35	0.5440
20	0.25	0.3979
30	0.24	0.3802
40	0.27	0.4314
50	0.27	0.4314
60	0.26	0.4150
70	0.28	0.4471
80	0.27	0.4314
90	0.28	0.4471
100	0.30	0.4853

The rate of degradation and degradation efficiency of alizarin red in the presence of 0.01 g of TiO_2nanaoparticle is 1.20 x 10^{-2} sec $^{-1}$ and 31.03 %, and for 0.05 g of TiO_2nanaoparticle is 1.60 x 10^{-2} sec $^{-1}$ and 50.73 %. The irradiation of alizarin red dye with 0.01 and 0.05 g of AgNPs in the presence of sunlight is noted at regular time intervals, the absorbance of the solution first decreases and then increases with increasing time intervals showing thereby that the concentration of the dye increases with increasing time of exposure (**Tables 4 and 5**). These results reveal that only the TiO_2 nanaoparticles acts as a catalyst for the degradation of alizarin red. The AgNPs is not a suitable catalyst for the degradation of alizarin red dye.

Conclusion

The present investigation deals about the photocatalytic activity of titanium dioxide nanoparticles and AgNPs on the degradation of alizarin red. The green synthesized AgNPs from gooseberry extract are characterized by UV-Visible and FT-IR spectral analysis. The particle size of synthesised AgNPs obtained from XRD analysis is 25 nm. The absorption kinetics of the dye followed the pseudo-first order mechanism. The rate of degradation and degradation efficiency of alizarin red in the presence of 0.05 g of TiO_2 nanaoparticle is 1.60 x 10^{-2} sec $^{-1}$ and 50.73 %. Results indicate that the TiO_2 nanaoparticleacts as aphotocatalyst for the degradation of alizarin red dye. Thus, the photodegradation mechanisms proposed in this study may shed some light on future applications for the degradation of dyes.

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