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PHOTOCATALYTIC ACTIVITY OF NANO TITANIA AND SILVER NANOPARTICLES ON THE DEGRADATION OF MALACHITE GREEN

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Abstract-Photocatalysis is a booming field of chemistry due to its numerous potential applications. Using light as an energy source to drive a reaction in a desired direction has resulted in chemistry, which is much more 'green'. Photocatalysis has been considered as an effective alternate for the purification of dye containing waste water. Therefore, this study focused on the photocatalytic activity of titanium dioxide nanoparticles and silver nanoparticles (AgNPs)on the degradation of malachite green. Green synthesis of silver nanoparticles using gooseberry extract is investigated. This extract acts as a reducing and stabilizing agent for the production of silver nanoparticles. The formation of silver nanoparticles is primarily detected within 15 minutes by the change of colour from colourless to reddish-brown. The synthesized nanoparticles are characterized by using UV-Visible and FTIR spectroscopy. The photocatalytic activities of the nano titania and the synthesised silver nanoparticle are examined by the degradation of malachite green under visible light illumination. The rate of photodegradation and degradation efficiency of malachite green using silver nanoparticles is 1.18 x 102 sec-1 and 69.23 %. The rate of photodegradation and degradation efficiency of malachite green in nanoparticles of titanium dioxide is 0.74 x 102 sec-1 and 50.00 %. The absorption kinetics of the dye followed the pseudo-first order mechanism. Results indicate that the silver nanoparticles act as an efficient photocatalyst compared to that of nano titania for the degradation of malachite green.

Keywords: Gooseberry extract; Silver nanoparticles; Nano titania; Photocatalytic degradation; Degradation efficiency.

Introduction

A dye is a coloured substance which has a tendency to get attached to the substance on which it is being applied. In most of the cases, the application of dye is in the form of aqueous solutions. All the dye wastes, which are produced from various industries, might have harmful impacts on microbial inhabitants and even fatal to mammals.Dyes can have acute and/or chronic effects on exposed organisms depending on the exposure time and dye concentration.

Malachite Green is a triphenylmethane dye that is used extensively in the textile and fish farming industries as a biocide [1]. Malachite Green is most commonly used for the dyeing of cotton, silk, paper, leather and also in manufacturing of paints and printing inks.Malachite green is an unsafe dye which not only possesses extremely toxic properties affecting the cells of mammals but also is a major cause of creating tumour in liver. The dye discharged in water bodies without being treated properly, hampers the life-cycle of aquatic animals and plants by obstructing the penetration of sunlight [2].Scientific evidence indicated that malachite green and especially its reduced form, leucomalachite green, might persist in edible fish tissues for extended periods of time [3]. Due to this significant health risks to human and fish, it is essential to establish a proper method to remove this substance from water or industrial effluent.

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 waste water [13].Using light as an energy source to drive a reaction in a desired direction has resulted in chemistry, which is much more 'green'. It also helps to eliminate the need for harsh reactants, which are often toxic and unrecoverable.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].Titanium dioxide is a non-toxic semiconductor photocatalyst, possess

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prominent role in the degradation and decolorization of dyes. Titanium dioxide has been intensively investigated as a photocatalyst since HondaandFujishimadiscovered the photocatalytic splitting of water on TiO_2 electrodes in 1972 [15].Titanium dioxide has multiple crystallographic phases such as rutile and anatase phase.Tanaka et al. [16] reported that catalytic activity of the anatase is much higher than the catalytic activity of the rutile. Besides crystalline structure the catalytic activity of TiO_2can be also influenced by its particle size. Xu et al. [17] observed an increased degradation rate as theparticle size of TiO_2 decreased.

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 [18]. Green synthesised AgNPs are commonly utilized nanomaterials due to specific surface area is relevant for catalytic reactivity, high electrical conductivity, and unique optical properties that could be usedin various applications.Jegadeeswaran et al., [18] examined the photocatalytic properties of green synthesised silver nanoparticles by using dye solutions of congo red and direct brown 95 under sunlight. The results clearly shows that seaweed mediated silver nanoparticles have good activity for the degradation of Congo red and Direct brown 95.

Based on the literature survey, this study concentrates on the photocatalytic degradation of malachite green dye with nanoparticle of titanium dioxide and silver. The green synthesised AgNPsfrom gooseberry extract is characterized by UV-Visible spectroscopy and FTIR spectroscopy.The photocatalytic experiments are conducted in the presence and absence of light with and without catalyst.

2. Materials and Methods

Fresh and ripened gooseberry fruit were obtained from the local market.The dyemalachite greenand $AgNO_3$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 8,000 rpm for about 10 minutes. The supernatant extract was collected and used as reducing agent for the synthesis of AgNPs.

2.2 Synthesis of silver nanoparticles from gooseberry extract

2mM aqueous solution of $AgNO_3$ was prepared and used for the synthesis of silver nanoparticles. 10 ml of gooseberry extract was added to 90 ml of 2mM aqueous $AgNO_3$ solution in a 250 ml Erlenmeyer flask and incubated at room temperature. The sample colour changes from colourless to reddish-brown colour within 10 minutes indicate the formation of AgNps. Ninety-five percent of the bioreduction of Ag^+ ions occurred within 1 hour. 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. FTIR analysis of the dried AgNPs was carried out through the potassium bromide (KBr) pellet (FTIR grade) method in 1:100 ratio and the spectrum was recorded using Shimadzu IR Affinity-1 FTIR spectrophotometer with the range of 4000-400 cm^{-1} at the resolution of 4 cm^{-1}.

2.4 Photocatalytic degradation

0.0365 g of malachite green was dissolved in 100 ml of doubly distilled water so that theconcentration of dye solution was 1.0×10^{-3} M. It was used as a stock solution. This stock solution was further diluted for the degradation studies. The malachite green shows an absorption maximum at 620 nm.

The degradation of malachite green was studied by taking 50 ml of 8.0×10^{-6} M of the dye and 0.5 g of nano titania in the presence and absence of light. Similarly, photochemical degradation of malachite green was also studied with 0.1 g of AgNPs. For photodegradation the mixture was exposed to a 200 W tungsten lamp (Philips) of 60.0 $mWcm^{-2}$ light intensity. The pH was maintained at 7.5. A water filter was used to cut off thermal radiation just to ensure illumination by visible light. The progress of the photocatalytic reaction was observed by taking optical density at regular time intervals. The pH of the solution was measured by a digital pH meter (Systronics Model).

The concentration of malachite green was monitored by the change of the absorption (A) at 620 nm in the photocatalytic reaction process. The degradation efficiency (η) was described by the equation:

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

where A_0 and A was the absorption intensities at the beginning and after photocatalytic reaction for certain time.

3. Resultsand Discussion

The characterization of the silver nanoparticles and the detailed study on the catalytic degradation of malachite green with nanoparticles of silver and titanium dioxide in the presence and absence of light are reported in this section.

3.1 Absorption spectral analysis of AgNPs

Reduction of Ag^{+}into Ag^{0} during exposure to the gooseberry extract could be followed by colour change. The synthesised AgNPs exhibitsbrown 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 silver nanoparticles formed in the reaction media after 10 minutes has an absorbance peak at 429 nm, broadening of peak indicated that the particles are polydispersed (**Fig. 1**). Similar results are also obtained for the green synthesis of silver nanoparticles from *Euphorbia hirta*L and *Cissus Quadrangularis* [19].

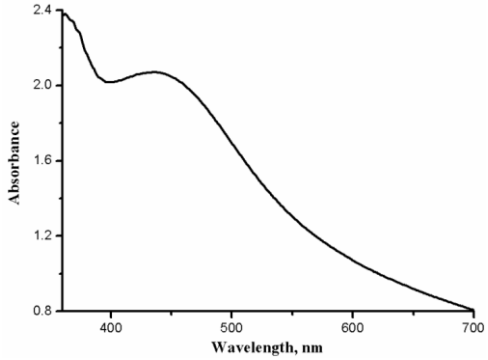

Fig. 1 Absorption spectrum of AgNPs

3.2. FTIR analysis of AgNPs

The FTIR spectrum of the synthesised AgNPs shows a prominent band at around 3261 cm^{-1} signified the O–H stretching of alcohols or phenols. Absorption band at 1745 cm^{-1} is due to C=O stretching modes of esters present in ascorbic acid. The vibration band at 1240 cm^{-1} of fruit extract which is the characteristic signal of C–O group of polyols is almost disappeared in the reaction solution. The polyols in gooseberryextract reduces Ag+ ions to metallic silver, and the polyols got oxidized to unsaturated carbonyl groups rendering a broad peak at 1745 cm^{-1}. Here, the ascorbic acids present in the plant extract take a significant role for the reduction of Ag^{+} to Ag^{0} at room temperature. The absorption bands at around 1060 cm^{-1} is due to the bending vibration of C–OH groups and the asymmetric stretching band of C–O–C groups of carbohydrates. The bands in the range of 500–650 cm^{-1} are assigned to the out-of-plane bending vibrations of C–H groups. These bands became less intense inthe reaction solution which indicated that AgNPs are capped with the organic moieties of the gooseberry extract. Thus, the ascorbic acid present in the gooseberry extract may act as reducing as well as stabilizing agent for the formation of AgNPs.

3.3 Photodegradation of malachite green

The experiments are conducted in dark as well as in light. An aliquot of 4.0 mlis taken out from the reaction mixture at regular time intervals and absorbance is measured spectrophotometrically at 620 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 malachite green with and without catalyst are mentioned in the **Tables 1-3**. A plot of 1 + log A versus time is linear and follows pseudo-first order kinetics (**Fig. 2**), where A is the absorbance of the medium at a particular time t. The rate constant is measured by following expression:

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

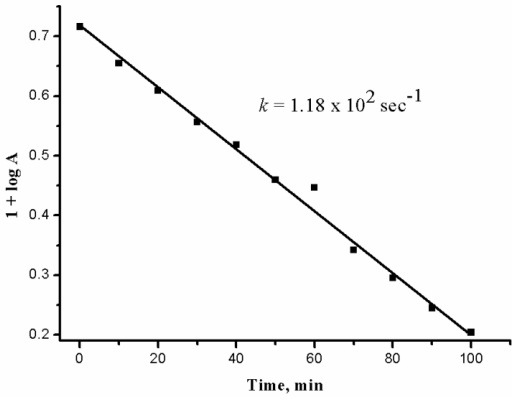

Fig. 2 Plot of 1 + log A vs time for malachite green with AgNPs in the presence of light

Table 1 Degradation of malachite green in the absence and presence of light

Table 2 Degradation of malachite green with AgNPs in the presence and absence of light

Time (min)	Absorbance (A) in dark	Absorbance (A) in light	(1 + log A) in dark	(1 + log A) in light
0.0	0.52	0.52	0.7160	0.7160
10	0.50	0.49	0.6989	0.6901
20	0.50	0.49	0.6989	0.6901
30	0.49	0.47	0.6901	0.6721
40	0.48	0.43	0.6812	0.6334
50	0.47	0.42	0.6721	0.6232
60	0.46	0.41	0.6627	0.6127
70	0.45	0.38	0.6532	0.5797
80	0.44	0.37	0.6434	0.5682
90	0.43	0.35	0.6334	0.5440
100	0.42	0.34	0.6232	0.5314

Time (min)	Absorbance (A) in dark	Absorbance (A) in light	(1 + log A) in dark	(1 + log A) in light
0.0	0.52	0.52	0.7160	0.7160
10	0.50	0.45	0.6989	0.6532
20	0.49	0.40	0.6901	0.6020
30	0.46	0.36	0.6627	0.5563
40	0.43	0.33	0.6334	0.5185
50	0.42	0.30	0.6232	0.4771
60	0.41	0.28	0.6127	0.4471
70	0.39	0.22	0.5910	0.3424
80	0.37	0.18	0.5682	0.2552
90	0.35	0.17	0.5440	0.2304
100	0.34	0.16	0.5314	0.2041

Table 3 Degradation of malachite green with nano titania in the presence and absence of light

20	0.49	0.46	0.6901	0.6627
30	0.46	0.45	0.6627	0.6532
40	0.43	0.43	0.6334	0.6334
50	0.42	0.39	0.6232	0.5910
60	0.41	0.37	0.6127	0.5682
70	0.39	0.32	0.5910	0.5051
80	0.37	0.30	0.5682	0.4771
90	0.35	0.28	0.5440	0.4471
100	0.34	0.26	0.5314	0.4149

The rate of degradation of malachite green without catalyst in dark as well as in light is 0.21 x 10^2 sec^{-1} and 0.43 x 10^2 sec^{-1}. This result shows that the malachite green degrades at a faster rate in the presence of light than that of dark. The rate of degradation of malachite green in the presence of TiO_2 nanoparticles (0.5 g) is 0.49 x 10^2 sec^{-1} (dark) and 0.74 x 10^2 sec^{-1}(light) respectively. The rate of photodegradation in the presence of AgNPs (0.1 g) is 0.49x 10^2 sec^{-1} (dark) and 1.18 x 10^2 sec^{-1} (light). The degradation efficiency (η) of malachite green in dark as well as in light without catalyst is 19.23 % and 34.62 %. The η of malachite green withTiO_2 nanoparticles is 34.62 % (dark) and 50 % (light) respectively. Theη of malachite green with AgNPs is 34.62 % (dark) and 69.23 % (light) respectively.From these results it is clear that the AgNPs at low concentration undergo a faster degradation than that of TiO_2 nanoparticles in the presence of light. Thus, the AgNPs synthesised from gooseberry extract act as an efficient photocatalyst compared to that of TiO_2 nanoparticlesfor the degradation of malachite green.

Conclusion

The present investigations deals about the photocatalytic activity of titanium dioxide nanoparticles and AgNPson the degradation of malachite green. The green synthesised AgNPs from gooseberry extract are characterized by UV-Visible and FTIR spectral analysis. The reduced AgNPs show a characteristic absorption peak at 429 nm due to the surface plasmon resonance phenomenon. The FTIR examination of the samples confirms the involvement of ascorbic acid in the reduction and stabilization of the AgNPs.The rate of photodegradation and degradation efficiency of malachite green in AgNPs is 1.18 x 10^2 sec^{-1} and 69.23 %. The rate of photodegradation and degradation efficiency of malachite green in nanoparticles of titanium dioxide is 0.74 x 10^2 sec^{-1} and 50 %. The absorption kinetics of the dye followed the pseudo-first order mechanism.Results indicate that both the photocatalyst can be employed for the degradation of malachite green dye. But from the kinetic studies and degradation efficiencies the biosynthesised AgNPs act as an efficient photocatalyst for the degradation of malachite green. Thus, the photodegradation mechanisms of AgNPs proposedin this study may shed some light on future applications of the technology for the decolouration of dyes due to cost-effective and eco-friendly.

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