



Catalytic Reduction of 4-Nitrophenol to 4-Aminophenol using Chitosan Ag-TiO₂ Nanocomposite and its Applications in the Removal of Malachite Green by Photodegradation Technique

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A simple colloidal processing method was used to synthesize chitosan Ag-TiO₂ nanocomposite and its use aimed at the catalytic reduction of 4-nitrophenol to 4-aminophenol in the presence of NaBH₄ as reductant. The nanocomposite catalyst was characterized using different techniques and revealed its better catalytic ability than pure TiO₂. Since the nanocomposites are readily improved from the solution phase without centrifugation or filtration. The catalytic activity trials were examined by changing the catalyst dose, concentration of NaBH₄, amount of nitrobenzene and temperature. The reduction reactions were affected by the temperature of reaction medium and the concentration of NaBH₄. The photodegradation conditions were optimized by changing different parameters such as irradiation time, dosage, pH and initial dye concentration.

Keywords: Chitosan, 4-Nitrophenol, 4-Aminophenol, Nanocomposite, Malachite Green, Photodegradation.

INTRODUCTION

Metal nanoparticles based investigation have prolonged growing care in the current years, because of their use in various fields *e.g.* sensors [1], energy [2], drug delivery [3] and many others [4]. They are also developed as catalysts in highly significant chemical reactions [5-9]. Being cheaper, is one among several compounds which has conventional a great deal of attention for the preparation of micro and nanoparticles [10]. Studies have shown that it is non-toxic, biodegradable [11] and exhibit unique properties, such as biocompatibility, biodegradability, low immunogenicity and non-toxicity [12].

Silver or its composites have been familiar for their broad-spectrum of antimicrobial activities, since they provide non-toxic carriers for drug applications [13]. The antimicrobial properties of silver nanoparticles (AgNPs) are well established, and several mechanisms for their bactericidal effects have been recently proposed [14]. Fabrication of chitosan/nanosilver film and its potential for antibacterial applications were also studied [15]. During the past few years, chitosan nanoparticle has a variety of aquaculture applications [16].

p-Aminophenol is a main intermediate for the manufacture of analgesic and antipyretic drugs, which can be produced by the reduction of *p*-nitrophenol [17,18]. 4-Aminophenol determines its use as a photographic developer, corrosion inhibitor, dyeing agent, *etc.* [19]. Due to the significance of 4-aminophenol, there is a demand for direct catalytic reduction of 4-nitrophenol [20]. Indeed, several research groups [21-29] have investigated the reduction of 4-nitrophenol using a different noble metals nanoparticles as catalysts.

Photocatalytic degradation has a great potential to control aqueous contaminants or pollutants [30]. In recent years, advanced oxidation processes (AOPs) using titanium dioxide have been effectively used to detoxify recalcitrant pollutants present in industrial wastewater [31-34]. Photocatalysis using titania as a catalyst provides a good tool for synthetic dyes decomposition due to its high efficiency, low cost, chemical corrosion inertness and long-term stability against photo-corrosion and chemical corrosion [35]. Hence, in present study, the catalytic activity of Ag co-doped TiO₂ nanoparticles is utilized for the reduction of 4-nitrophenol to 4-aminophenol in the presence of NaBH₄ as reductant. Moreover, in order to enhance the catalytic efficiency, high selectivity and easy recovery of photocatalyst

after photocatalytic degradation of toxic dyes, the surface of photocatalyst TiO₂ has been modified using biopolymer chitosan. The degradation of toxic dyes such as malachite green dye under UV light *via* synthesized chitosan/TiO₂ composite has been carried out in the present work. A systematic study was undertaken in order to exploit the synergistic effect of both chitosan and TiO₂ and to determine the influence of irradiation time, dosage of chitosan/TiO₂ composite, initial dye concentration, pH, coexisting ions, light intensity, dye and removal percentage.

EXPERIMENTAL

Titanium dioxide (TiO₂), malachite green dye, chitosan (m.w. 150,000, 1.5% w/v), silver nitrate, sodium hydroxide and acetic acid were purchased from Sigma-Aldrich Co, USA and used as such.

Synthesis of chitosan/Ag-TiO₂ composite (Ag/TiC): Chitosan (0.2 g, dissolved in 20 mL of 1% v/v CH₃COOH), 0.05 g of TiO₂ and 2% of 20 mL of AgNO₃ was mixed by constant stirring for 30 min. The reaction mixture solution was then added dropwise into a 2% NaOH solution. After 15 min, a yellow-brown spheres were obtained. The spheres were collected and washed two times with 30 mL double distilled water to remove residual alkali and left for dry at room temperature.

RESULTS AND DISCUSSION

UV- visible studies: The UV-visible absorption spectrum of chitosan Ag-TiO₂ nanocomposite sphere was recorded using a Hitachi U-2900 spectrophotometer in the range of 250-800 nm. Fig. 1 shows that chitosan possesses a characteristic spectrum at 280 nm while Ag/TiO₂ nanoparticles also has an absorption band at 380 nm. A peak shown in UV-visible indicated the existence of Ag/TiO₂ nanoparticles embedded in the chitosan spheres.

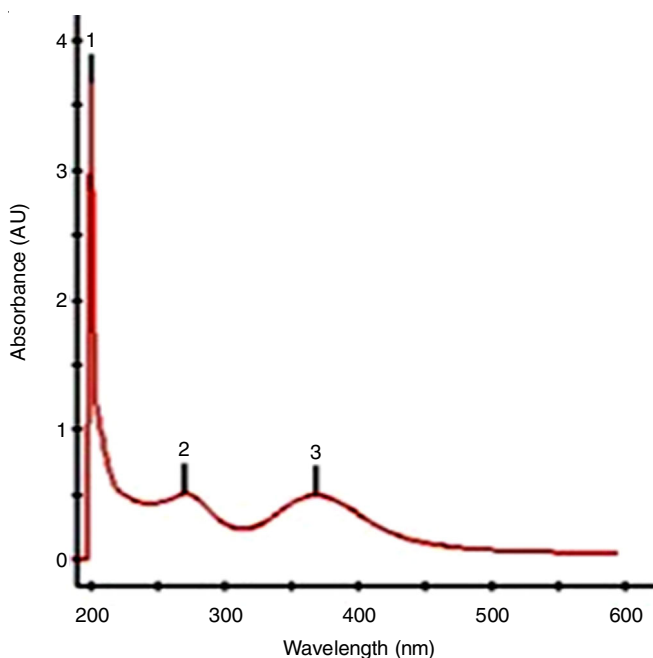


Fig. 1. UV-vis spectrum of chitosan TiO₂/Ag composite

FTIR studies: The FTIR spectrum of chitosan Ag TiO₂ nanocomposite sphere in the frequency range of 4000-500 cm⁻¹ is shown in Fig. 2. The synthesized nanocomposite exhibit the peaks corresponding to the stretching vibration of O-H and bending vibrations of adsorbed water molecules around 3400-3200 and 1600 cm⁻¹, respectively. Furthermore, the broadening of ~3400 cm⁻¹ O-H stretching vibration the formation of a different -OH group, and most probably as Ti-OH surface group. A broad intense band in the range of 700-450 cm⁻¹ is due to the Ti-O stretching and Ti-O-Ti bridging stretching modes.

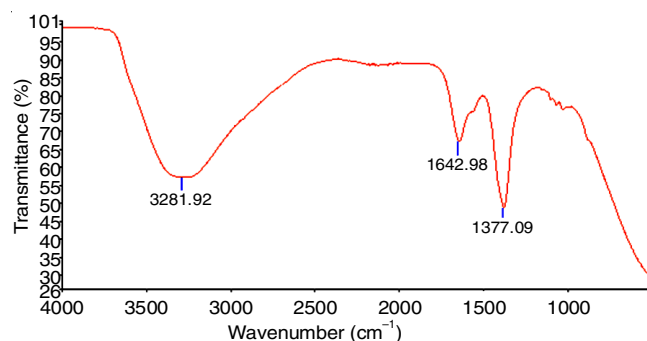


Fig. 2. FTIR spectrum of chitosan Ag/TiO₂

XRD studies: The XRD patterns of well-ordered chitosan and chitosan/Ag-TiO₂ is given in Fig. 3. The well-ordered chitosan film shown the typical peaks at $2\theta = 10.67^\circ$ and 21.8° [36] given to (0 2 0) and (1 1 0) reflections of chitosan. However, four peaks at $2\theta = 25.2^\circ$, 37.7° , 47.9° and 54.0° were clearly visible, corresponding to the crystal planes (1 0 1), (0 0 4), (2 0 0) and (1 0 5) of TiO₂, respectively. This revealed the successful formation of nanosized chitosan/Ag-TiO₂ complex [37].

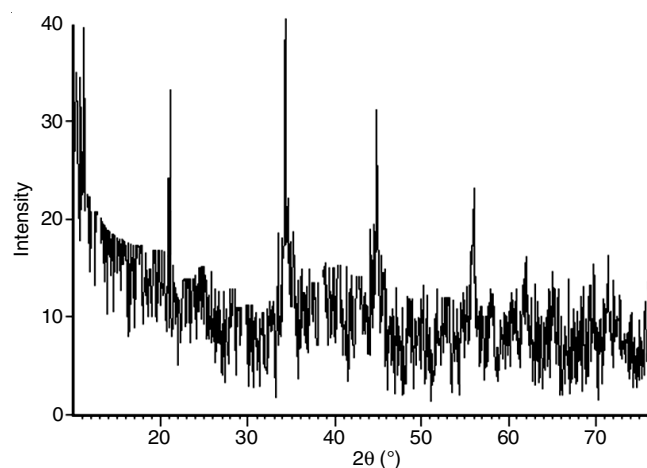


Fig. 3. XRD spectrum of chitosan Ag/TiO₂ composites

Photocatalytic activity: The reduction of 4-nitrophenol to 4-aminophenol by excess amount of sodium borohydride is the model reaction for the evaluation of catalytic performances of metal nanoparticles. On the catalytic reduction of nitrobenzene was investigated under the optimum experimental conditions (1 mmol nitrobenzene, 5 mL of NaBH₄, 1.0 wt.% catalyst) (Fig. 4). The reaction is based on the principle of the generation of 4-nitrophenolate ions after the addition of NaBH₄

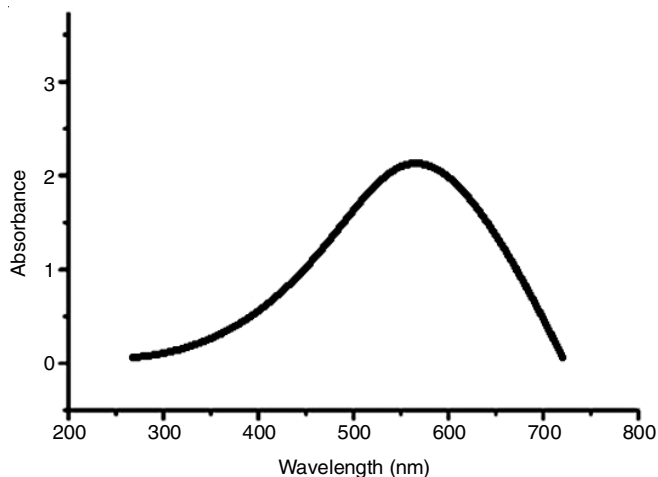


Fig. 4. UV-visible spectrum of nitrobenzene

as a reductant into 4-nitrophenol solution showing an absorption peak at 580 nm. The UV-visible absorption peak of 4-nitrophenol shifts from 580 to 360 nm, thus the colour of solution changes from light yellow to dark yellow by the addition of NaBH_4 . The changes indicate the formation of 4-nitrophenolate ions in the reaction environment. Unfortunately, the peak at 580 nm remains unaltered but decreased for a long period despite the excess amount of NaBH_4 . It could be explained by the kinetic barrier arose from large potential difference between 4-nitrophenolate and BH_4^- ions. Chitosan-Ag-TiO₂ nanoparticle as a plasmonic catalyst serves as an electronic relay system to pass through the kinetic barrier, thus has capability to catalyze the formation of 4-aminophenol effectively.

A peak intensity at 580 nm in the UV-vis spectra shown in Fig. 5 was found to be gradually decreasing with respect to time. The reaction was completed in 30 min. Figs. 5 and 6 show the absorbance in absence and presence of the prepared catalyst with respect to the time.

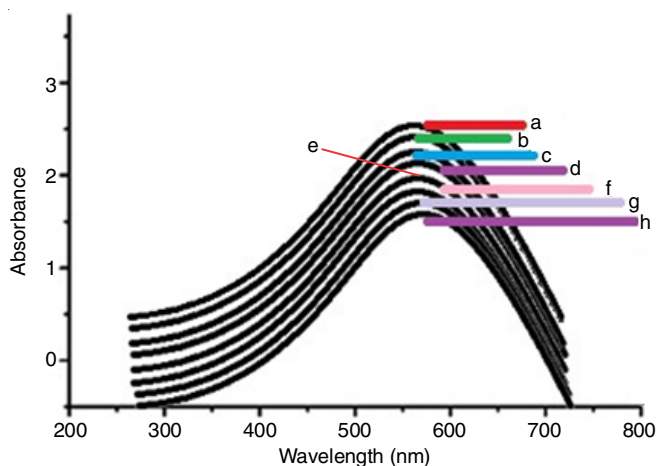


Fig. 5. UV-visible spectra of nitrobenzene + sodium borate after (a) 10 min, (b) 20 min, (c) 30 min, (d) 40 min, (e) 50 min, (f) 60 min, (g) 70 min, (h) 80 min

Optimum conditions of photocatalytic degradation of dye: The photocatalytic dye degradation efficiency of chitosan/Ag-TiO₂ was determined. The degradation was conducted before

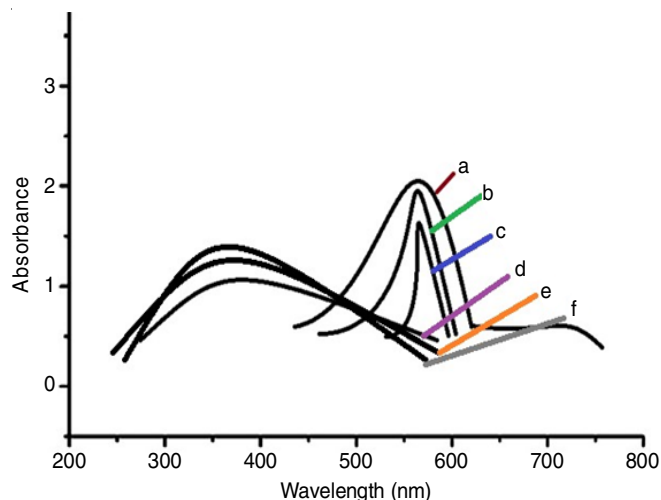


Fig. 6. UV-visible spectra of nitrobenzene + sodium borate + CTS addition of CTS after (a) 10 min, (b) 20 min, (c) 30 min, (d) 40 min, (e) 50 min, (f) 60 min

before and after 320 nm ultraviolet light irradiation under the doses of 5, 10, 15 and 20 mg of the prepared catalyst mixed in 100 mL aqueous solution of malachite green (10 mg/1000 mL). The prepared reaction suspension was permissible to react at ambient condition under constant stirring. After irradiation, the catalyst was separated by centrifugation and the absorbance of malachite green was measured using a UV-visible spectrophotometer at 664 nm. The percentage photocatalytic activity was calculated using the following formula:

$$\text{Dye degradation (\%)} = \frac{C_0 - C}{C_0} \times 100$$

where C_0 is the initial concentration of dye solution at 0 min (before photocatalytic reaction), and C is the concentration of dye solution at a certain time (after photocatalytic reaction).

The photocatalytic degradation depends on the amount catalyst, *i.e.* an rise in the number of active sites on the catalytic surface rises the degradation [37]. The order of the photocatalytic efficiency of the catalysts at various dosages is shown in Fig. 7a. Likewise, the photocatalytic degradation of dye was studied in UV irradiation for 120 min for catalyst chitosan/Ag-TiO₂. Fig. 7b shows the absorption spectra of aqueous malachite green in the effect of the chitosan/Ag-TiO₂ catalysts for various time interval. The chitosan/Ag-TiO₂ catalyst showed an absorbance of 69.03% in 90 min. Later 90 min of UV irradiation, no substantial change in dye degradation found. The order of the photocatalytic efficiency of the catalysts for difference irradiation times is shown in Fig. 7b.

Fig. 7c displays the dye degradation efficiency of chitosan/Ag-TiO₂ at acidic, neutral and basic pH values. At pH 12, the catalyst chitosan/Ag-TiO₂ displayed an absorbance of about 98.21% in 90 min. Therefore, the effect of alkaline pH 12, at 90 min of irradiation for 10 mg catalyst chitosan/Ag-TiO₂ caused in the greatest photocatalytic degradation of malachite green.

UV analysis of malachite green dye degradation: The degradation of malachite green dye was calculated with and without the catalyst in ultraviolet light irradiation. The degradation of the dye by the catalyst was carried out at various time

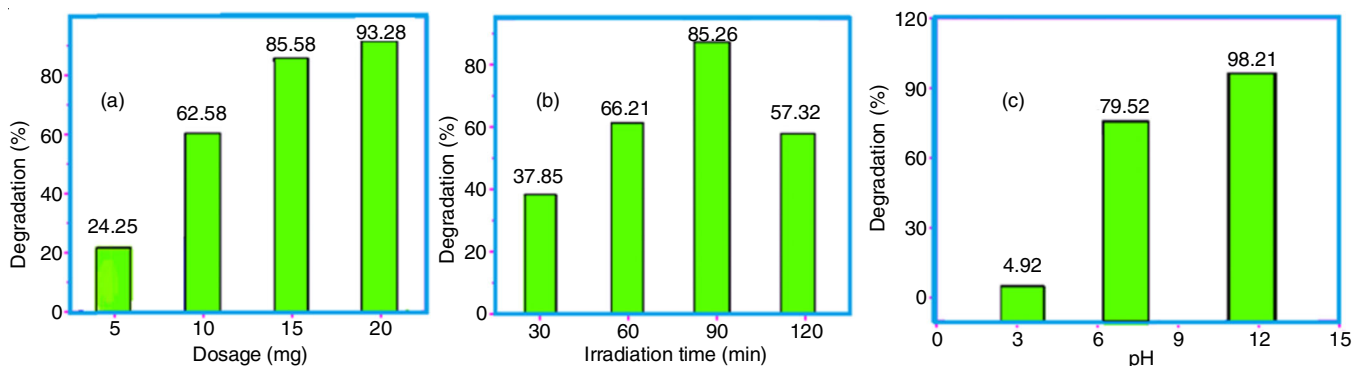


Fig. 7. The photocatalytic efficiency of the catalysts at different (a) dosages, (b) irradiation times and (c) pH

intervals in a dark room. The catalyst showed no variation in the dye degradation rate and the detected adsorption curves are displayed in Fig. 8. Though the catalyst was exposed to UV light irradiation at various catalyst doses, different medium pH and different durations, degradation was detected. The degradation efficiency of about 92.38% for malachite green was attained at with a 20 mg dose of chitosan/Ag-TiO₂ as shown in Fig. 9.

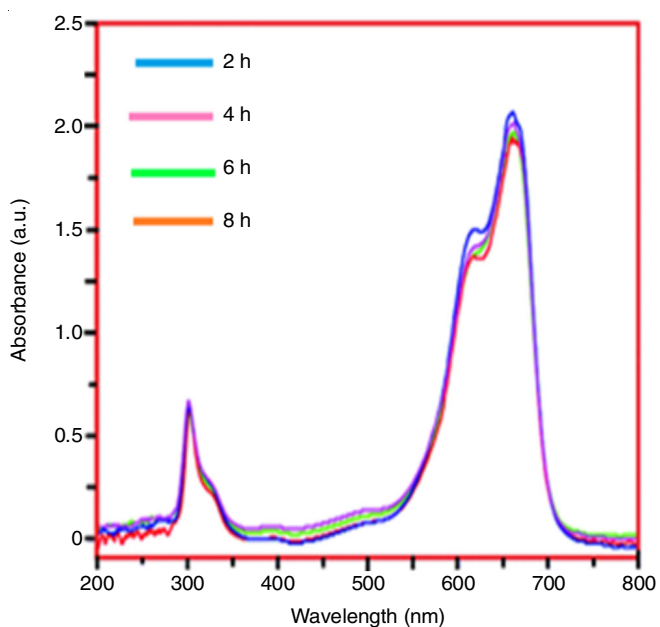


Fig. 8. Malachite green dye degradation by chitosan/Ag-TiO₂ catalysts in dark

Conclusion

The catalytic performance of newly synthesized chitosan Ag-TiO₂ nanocomposite for the reduction of 4-nitrophenol to 4-aminophenol was tested as a model reaction in excess NaBH₄. Consequently, the reduction rates can be observed as being independent of the concentration of NaBH₄. After adding NaBH₄ into the aqueous solution of 4-nitrophenol, the colour of the solution improved from light yellow to dark yellow due to the formation of 4-nitrophenolate ion. Then, the colour of 4-nitrophenolate ions faded with time after the addition of chitosan Ag-TiO₂ nanocomposite. The progress of the reaction could be monitored by UV-Vis spectroscopy. The characteristic peak of 4-nitrophenol at 580 nm decreased, while at 360 nm a new peak appeared, which was assigned to 4-aminophenol. The reaction was finished within 60s at room temperature. The reaction did not proceed in this period in the absence of chitosan Ag-TiO₂ nanocomposite or with undoped TiO₂ alone. The degradation of malachite green at various irradiation times with the catalyst exhibited that the optimum time was 90 min with 85.26% for chitosan/Ag-TiO₂. The catalyst exhibited the best degradation of malachite green with 20 mg of chitosan/Ag-TiO₂ resulting in 93.28% degradation in basic medium revealed the best photocatalytic degradation of malachite green dye at pH 12 of about 98.21% for chitosan/Ag-TiO₂.

CONFLICT OF INTEREST

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

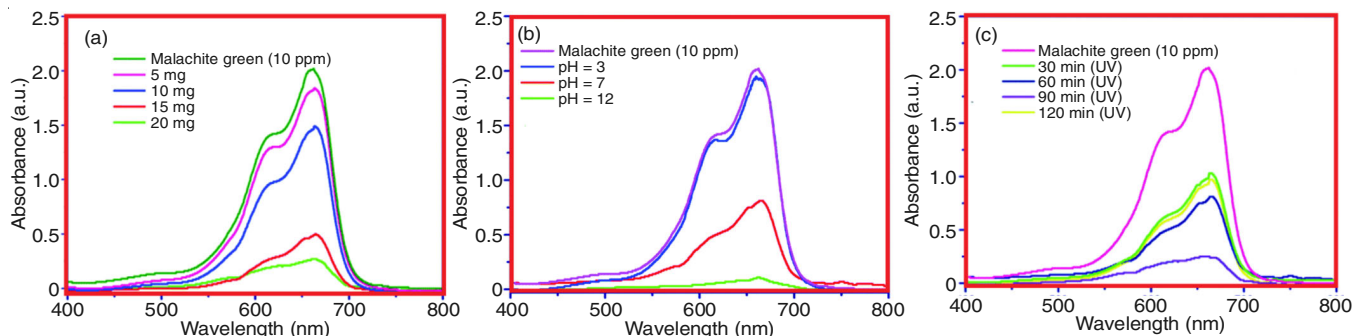


Fig. 9. Photocatalytic degradation of malachite green using biopolymer chitosan/Ag-TiO₂ with respect to (a) catalyst dosage, (b) pH variation and (c) irradiation time

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