

Catalytic reduction of methylene blue and Congo red dyes using green synthesized gold nanoparticles capped by salmalia malabarica gum

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Abstract Stable gold nanoparticles (AuNPs) were synthesized using salmalia malabarica gum as both reducing and capping agent. It is a simple and eco-friendly green synthesis. The successful formation of AuNPs was confirmed by UV–visible spectroscopy (UV–Vis), Fourier transform infrared spectroscopy (FTIR), X-ray powder diffraction and transmission electron microscopy (TEM). The synthesized AuNPs were characterized by a peak at 520–535 nm in the UV–Vis spectrum. The X-ray diffraction studies indicated that the resulting AuNPs were highly crystalline with face-centred cubic geometry. TEM studies showed that the average particle size of the synthesized AuNPs was 12 ± 2 nm. FTIR analysis revealed that –OH groups present in the gum matrix might be responsible for the reduction of Au^{+3} into AuNPs. The synthesized AuNPs exhibited good catalytic properties in the reduction of methylene blue and Congo red.

Keywords Gold nanoparticles · Salmalia malabarica gum · Methylene blue · Congo red

Introduction

Metal nanoparticles such as platinum, gold, silver, etc., have been playing a significant role in the fields of biomedical, environmental, pharmaceutical, cosmetic, electronics and energy [1–3]. Among the noble metal nanoparticles, gold nanoparticles (AuNPs) show

distinguished surface plasmon resonance (SPR) absorption properties which are strongly related to their size, shape and interparticle distance [4]. AuNPs find applications in various fields viz., manufacture of optical devices, surface-enhanced Raman scattering, catalysis, colorimetric sensors, drug delivery, bioimaging [5–7] and so on.

Organic dyes are widely used in many industries such as textile, paper, pharmaceutical and food industries [8, 9]. But, the excessive use of organic dyes leads to the environmental pollution that occurs from their undesirability, high visibility, recalcitrance and waste water has been a major concern for a long time. For that reason, the control of industrial effluents is an indispensable job which helps in the creation of a harmless and clean environment. Methylene blue (MB) and Congo red (CR) are cationic and anionic dyes, respectively [10]. These dyes are used extensively in textile, paper, rubber and plastic industries and cause serious ecological damage to the environment if they are discharged without proper action. Thus, the development of a simple method for the efficient degradation of dyes has gained greater significance. Due to their relatively large surface-to-volume ratios, metal nanoparticles show enhanced catalytic activity for the degradation of organic dyes [11].

There are several methods synthesize well-defined AuNPs such as chemical reduction, electrochemical, photochemical and sonochemical [12, 13], etc. But, these methods are harmful as they usually require the use of toxic chemicals which lead to the environmental toxicity or biological hazards. To prevent the negative impacts of the chemical reduction methods, researchers were interested to integrate “green chemistry” synthesis of nano materials using plant extracts, bio surfactants, etc., in aqueous medium [14]. Green synthesis of AuNPs has been reported using a variety of polysaccharides, including acacia nilotica leaf extract, xanthan gum, gellan gum, etc. [2, 15].

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Here, green synthesis of AuNPs is attempted using *Salmalia malabarica* gum (SMG) as reducing and stabilizing agent. SMG is a naturally occurring polysaccharide gum extracted from the plant *Bombax ceiba*, a native tree of India. The complete hydrolysis of gum has revealed that it contains a mixture of various sugars such as D-galacturonic acid, D-galactose, L-arabinose [16]. This gum is used in traditional ayurvedic and unani medical preparations for the treatment of anti-inflammatory, hepato-protective, hypotensive ailments and as an antioxidant and is also used for the treatment of asthma and diarrhoea [17, 18].

The present study reports the synthesis of AuNPs with *Salmalia malabarica* gum acting as the reducing and stabilization agent. The synthesized nanoparticles were characterized by UV-visible spectroscopy (UV-Vis), Fourier transform infrared spectroscopy (FTIR), X-ray powder diffraction (XRD) and transmission electron microscopy (TEM) techniques. These AuNPs were also studied for their applications as a catalyst in the reduction of MB and CR in the presence of NaBH₄ in water medium using UV-Vis spectrometry.

Experimental section

Materials

Chloroauric acid (HAuCl₄·3H₂O) was purchased from Sigma Aldrich, Mumbai, India, and sodium borohydride (NaBH₄), MB and CR were procured from Himedia Laboratories, Mumbai, India. *Salmalia malabarica* gum was obtained from Girijan Cooperative Society, Hyderabad, India. All the solutions were prepared in double distilled water.

Synthetic procedure for gold nanoparticles

All the glass ware was washed thoroughly with aquaregia to avoid any residual chemical contamination carried along with glassware. In a typical experiment, 1 mL of 1 mM HAuCl₄·3H₂O and 3 mL of 1 % gum solution were added into a boiling tube for the synthesis of SMG capped AuNPs. The mixture was subjected to autoclaving at 121 °C and 15 psi for 15 min. The colour of the resultant solution was changed from pale yellow to red indicating the formation of the AuNPs from Au⁺³. The synthesis of nano particles was further confirmed by UV-Vis, FTIR, TEM and XRD techniques.

Characterization techniques

The resulting SMG capped AuNPs solution was analysed by UV-Vis absorption spectrophotometer (Model:

Shimadzu UV-Vis 3600, Shimadzu Corporation, Japan) in the range of 200–800 nm. FTIR analysis was carried out on the aqueous solution of synthesized AuNPs using FTIR Spectrophotometer (Model: IRAffinity-1, Shimadzu Corporation, Japan) in the scanning range of 650–4000 cm⁻¹. XRD analysis was conducted on a Rigaku-Miniflex method with CuK α radiation. TEM analysis was performed using a transmission electron microscope (Model: 1200EX, JEOL Ltd., Japan). The presence of elemental gold was determined using a scanning electron microscope (Model: EDX Zeiss Evo 50, Carl Zeiss AG, Germany). The samples were dried at room temperature and then analysed for composition of the synthesized NPs.

Procedure for reduction of dyes

The reduction of MB and CR using sodium borohydride in the presence of AuNPs was carried out to demonstrate the catalytic activity of the prepared AuNPs. 1 mL of 10 mM sodium borohydride solution was mixed with 1.5 mL of 1 mM MB and the mixture was made up to 10 mL using double-distilled water and then stirred for 5 min. 1 mL of 10 mM NaBH₄ solution was mixed with 1.5 mL of 1 mM CR, and the solution mixture was made up to 10 mL using doubled distilled water and then stirring was continued for 5 min. To both these solutions, sufficient quantities of synthesized AuNPs were added separately and the UV-Vis spectra were recorded at regular intervals of time.

Results and discussion

UV-Vis spectroscopy

The UV-Vis spectroscopy is one of the most important and widely used simple and sensitive technique for determining the formation as well as size of the metal nanoparticles [19]. UV-Vis spectra of the AuNPs are presented in Fig. 1. The absorbance maximum was observed in the range of 523–535 nm, which is characteristic of gold surface plasmon resonance (SPR). To optimize the synthesis of nanoparticles, the influence of parameters such as concentration of gum and concentration of chloroauric acid was studied. Figure 1 shows the UV-Vis spectra of the synthesized AuNPs with different concentrations of gum (0.1–1 %) with 1 mM HAuCl₄ and 15 min of autoclaving time. After autoclaving, the reaction mixture with a red colour was observed from which it is evident that the AuNPs were formed by the reduction of chloroauric acid with gum. It also reveals that the formation of nanoparticles increases with increasing concentration of gum. Figure 2 shows the UV-Vis spectra of the synthesized AuNPs at different concentrations of chloroauric acid (0.1–1 mM)

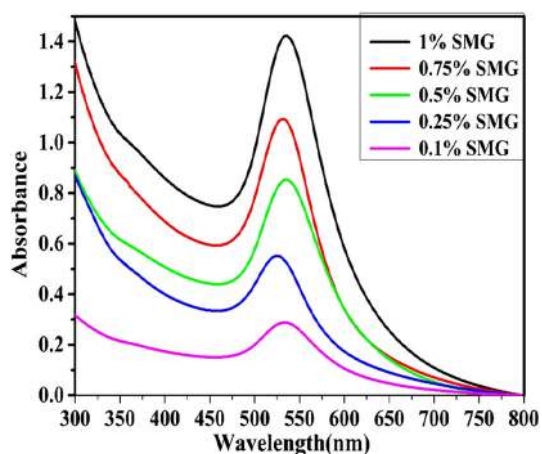


Fig. 1 UV–Vis absorption spectra of gold colloid suspensions showing different concentrations of gum SMG solutions at 1 mM HAuCl₄ concentration

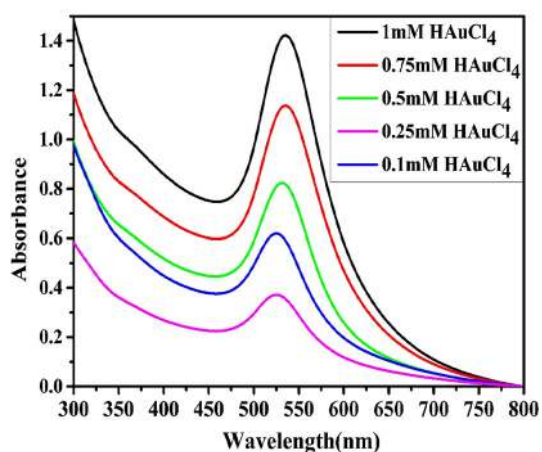


Fig. 2 UV–Vis spectra of the AuNPs obtained at various concentrations of HAuCl₄ solutions and at 1 % gum acacia concentration

containing 1 % of gum with an autoclaving time of 15 min which demonstrates that the formation of nanoparticles increases with increase in the concentration of chloroauric acid.

FTIR

The identification of the possible functional groups involved in the reduction and the stabilization of green-synthesized AuNPs can be achieved by the FTIR spectroscopy. The major frequencies that are found in the FTIR spectrum of SMG are 3421, 2929, 2125, 1729, 1629, 1427, 1240 and 1017 cm⁻¹ (Fig. 3a). The broad band peak observed at 3421 cm⁻¹ could be assigned to stretching vibrations of –OH groups in gum. The bands at 2929 cm⁻¹ correspond to asymmetric stretching vibrations of methylene group. The broad band at 1729 cm⁻¹ could be

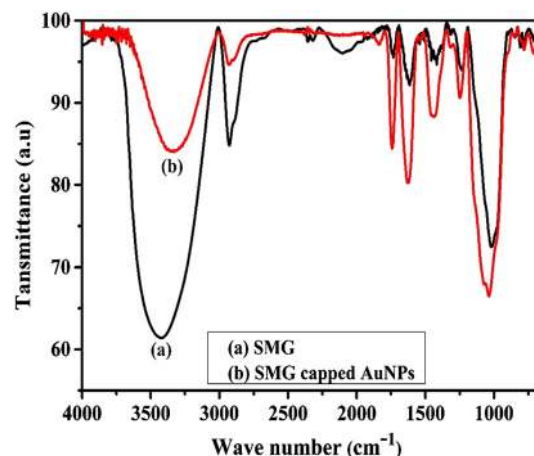


Fig. 3 FTIR spectra of the pure **a** SMG and **b** SMG capped AuNPs

assigned to carbonyl stretching vibrations in ketones, aldehydes and carboxylic acids. The sharp band found at 1629 cm⁻¹ could be assigned to characteristic asymmetrical stretch of carboxylate group. The stronger band found at 1427 cm⁻¹ could be assigned to characteristic bending of –C–H group. The peak at 1240 cm⁻¹ was due to the C–O stretching vibrations of polyols and alcoholic groups. While the IR spectrum of SMG capped AuNPs showed (Fig. 3b) characteristic absorbance bands at 3332, 2927, 2123, 1842, 1741, 1627, 1439, 1242 and 1029 cm⁻¹, respectively, in the IR spectrum of nanoparticles, a shift in the absorbance peaks was observed from 3421 to 3332, 1729–1741, 1629–1627 and 1427–1439 cm⁻¹. The extra shoulder peak observed at 1830 cm⁻¹ indicates the attachment of COO⁻ to the surface of the AuNPs. FTIR spectral studies suggest that the carbonyl and hydroxyl groups have a stronger affinity to bind with metal and facilitate the formation of a coat over the nanoparticles and favour in stabilizing the AuNPs against agglomeration.

XRD

The crystalline nature of green-synthesized AuNPs was confirmed by XRD analysis. Diffraction peaks were observed at 38.21°, 44.24°, 64.31° and 77.46° (Fig. 4) which can be indexed as (111), (200), (220) and (311), respectively, and the planes of face-centred cubic (fcc) AuNPs. The existence of diffraction peaks were matched to the standard data files (the JCPDS card No. 04-0784) for all reflections. No extra peaks were found in XRD-spectrum, indicating the synthesized AuNPs were purely crystalline. Crystallite size of AuNPs was determined using the Scherer's formula from the XRD pattern and was found to be around 13.2 nm. The observations from the XRD analysis can very well be correlated with the values obtained from TEM images.



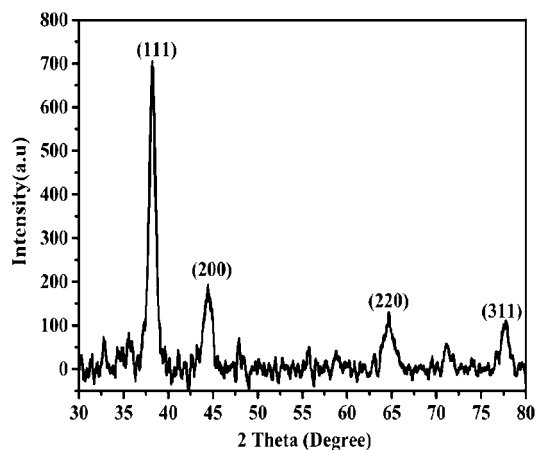
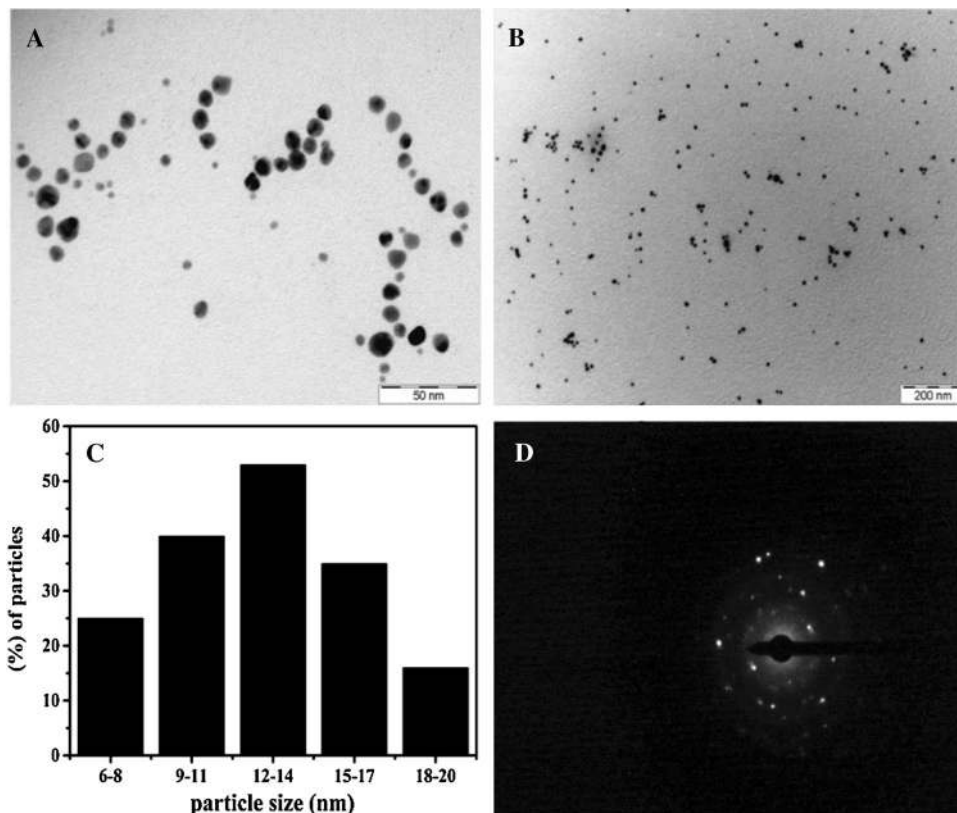


Fig. 4 XRD pattern of gold nanoparticles stabilized by gum SMG. Conditions: 1 % (w/v) gum SMG, 1 mM HAuCl₄ autoclaved for 15 min at 15 psi

EDX

The green synthesis of AuNPs by SMG was further characterized by EDX analysis, which gives the additional evidence for the reduction of HAuCl₄ to elemental gold. The synthesized nanoparticles showed a strong peak of Au along with a weak carbon and oxygen peaks, which may originate from the gum that were bound to the surface of

Fig. 5 EDX analysis of gold nanoparticles synthesized with 1 % (w/v) gum SMG and 1 mM HAuCl₄, autoclaved for 15 min at 15 psi



the AuNPs (Fig. 5). The peak of Cu is also observed which could originate from the carbon coated Cu grid.

TEM

The size, shape, morphology and distribution of the AuNPs were analysed using TEM. The TEM images (Fig. 6a, b) shows that the particles are predominantly spherical. The spherical nanoparticles were formed with diameters ranging from 5 to 20 nm and are of highly mono-dispersed in nature. The average particle size was found to be 12 ± 2 nm and the particle size distribution histogram (Fig. 6c) was constructed by counting the size of 150 particles. The selected-area electron diffraction pattern was shown in Fig. 6d.

Catalytic activity of gold nanoparticles

Catalytic degradation of methylene blue

A potential application of synthesized AuNP catalytic activity was the reduction of aqueous MB to Leuco MB in the presence of excess NaBH₄. The reaction was monitored by UV–Vis spectrophotometry in the wavelength range between 450 and 750 nm at room temperature. In aqueous medium, MB shows the absorption peaks at 664 and

Fig. 6 TEM images of gold nanoparticles synthesized with 1 % (w/v) gum SMG and 1 mM HAuCl_4 , autoclaved for 15 min, at 15 psi. **a** 50 nm scale, **b** 200 nm scale, **c** the corresponding size distribution histogram and **d** corresponding SAED pattern

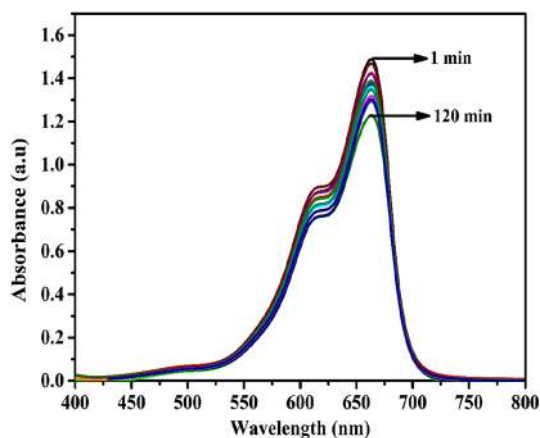
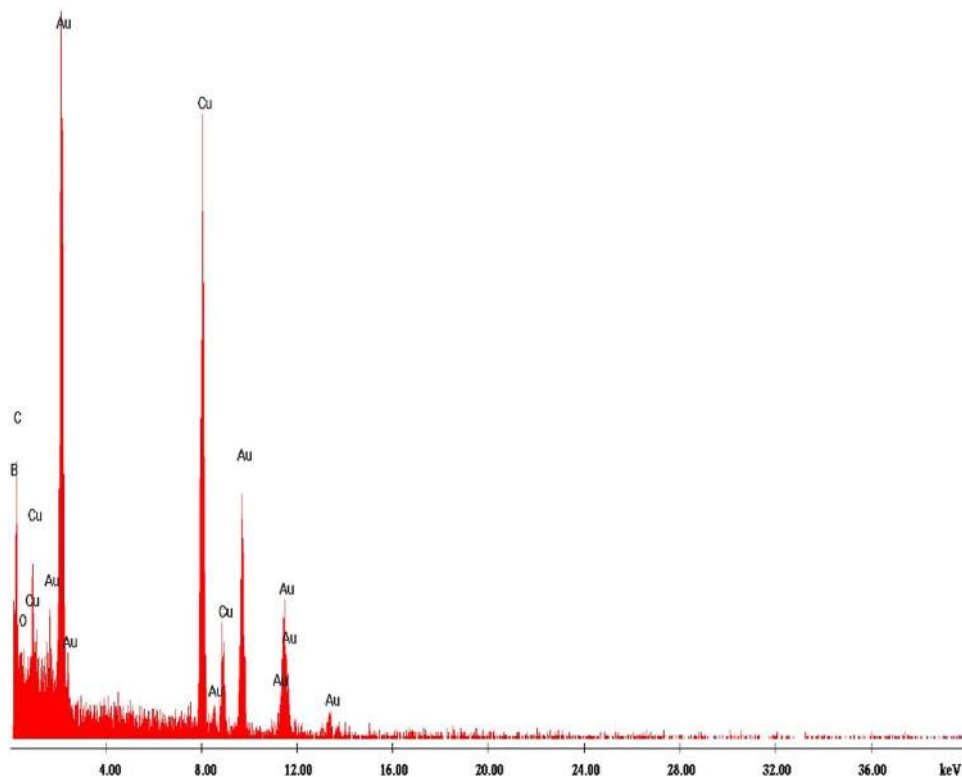


Fig. 7 Reduction of methylene blue dye in the presence of NaBH_4 and absence of AuNPs

614 nm [20]. Figure 7 shows the reduction of MB by NaBH_4 in the absence of gold nano catalyst for a time period of 120 min. A small decreasing trend of the absorption maximum indicates the reduction of MB, but in a slow pace. The UV–Vis spectrum of the reduction of MB by NaBH_4 in the presence of catalytically active AuNPs is shown in Fig. 8. The reduction process was found to be accelerated in the presence of gold nano colloids which showed a rapid decrease in the absorption intensity of MB solution. AuNPs help in the electron relay from BH_4^- (donor) to MB (acceptor). BH_4^- ions are nucleophilic, while

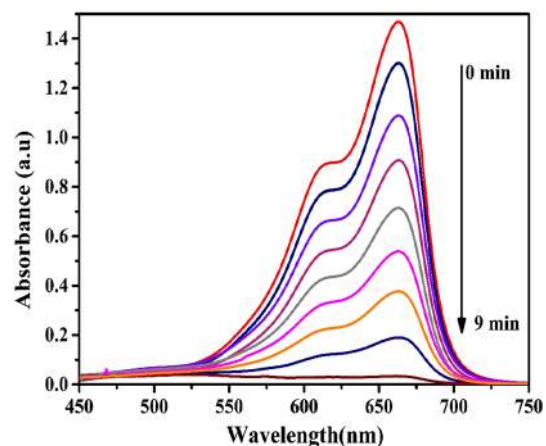


Fig. 8 Time-dependent UV–Vis spectra for the catalytic reduction of methylene blue to leuco methylene blue by NaBH_4 in the presence of AuNPs. Conditions: $[\text{MB}] = 1 \text{ mM}$; $[\text{NaBH}_4] = 10 \text{ mM}$; gold nanoparticles obtained from 1 mM of chloroauric acid and 1 % of gum SMG

MB are electrophilic in nature with respect to AuNPs, where the AuNPs accept electrons from BH_4^- ions and conveys them to the MB (Fig. 9) [21]. The absorption spectrum showed the decreasing peaks in intensity for MB dye at different time intervals. Initially, the absorption peak at 664 nm for MB dye was found to decrease only gradually with the increase in the reaction time indicating that the dye has been degraded slowly [22]. The linear



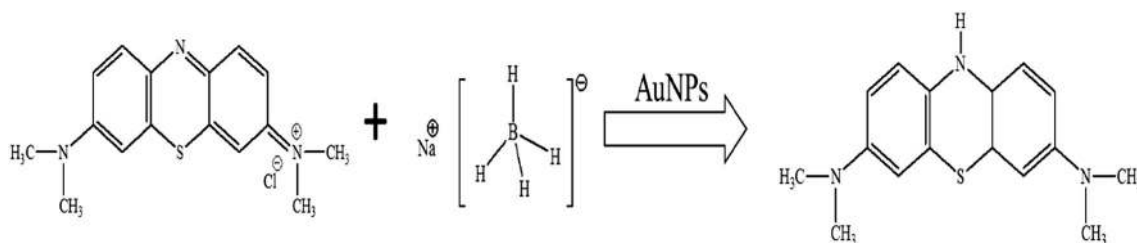


Fig. 9 Reduction reaction of MB to LMB

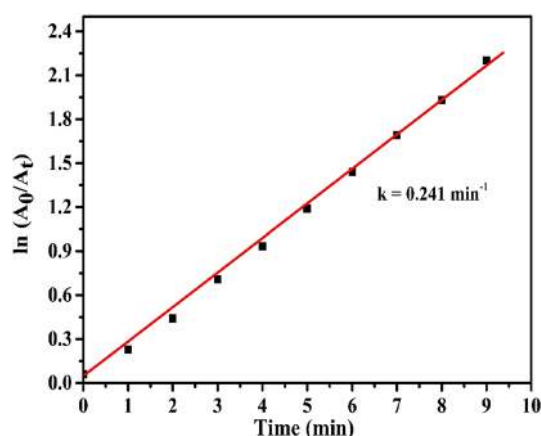


Fig. 10 The plot of $\ln(A_0/A_t)$ versus time for the reduction of methylene blue

correlation between $\ln(A_t/A_0)$ versus reduction time in minutes (Fig. 10) indicates that the reduction follows a pseudo-first-order reaction kinetics with respect to MB as the concentration of NaBH_4 (10 mM), was relatively larger than that of MB (1 mM). The rate constant is calculated from the slope of this graph and is found to be 0.241 min^{-1} .

Catalytic degradation of congo red

The prepared AuNPs could be effectively used to catalyse the decolorization of CR, a kind of azo dye with two $-\text{N}=\text{N}-$ bonds as shown in Fig. 11. It is an anionic dye widely used in textiles, paper, plastic and rubber industries.

Fig. 11 Structure of Congo red

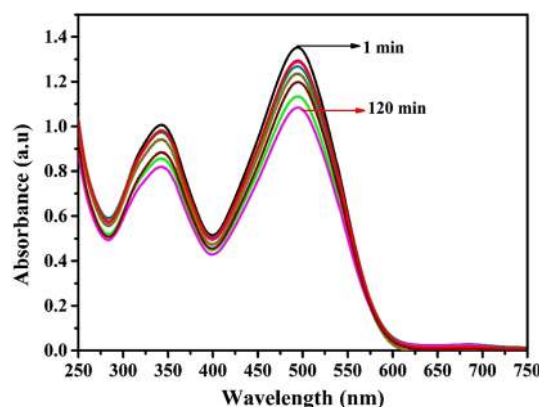
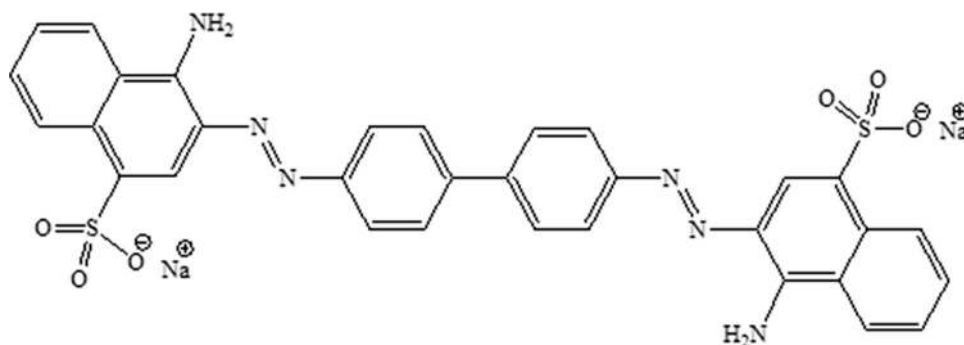


Fig. 12 Reduction of Congo red dye in the presence of NaBH_4 and absence of AuNPs

The reaction was monitored by UV–Vis spectrometry in the wavelength range between 250 to 700 nm at room temperature. In aqueous medium, CR shows an absorption band at 498 nm ($\pi \rightarrow \pi^*$) and 350 nm ($n \rightarrow \pi^*$), transition associated with the azo group [23]. AuNPs act as an electron relay, and electron transfer take place via AuNPs from BH_4^- (donor) to CR (acceptor) molecules. In spite of adding NaBH_4 to dye solutions, no considerable colour change was observed for a long time. Figure 12 suggests that the reduction of CR proceeded very slowly in the presence of the strong reducing agent NaBH_4 [24]. On the other hand, after the addition of the AuNPs to a mixture of dye and BH_4^- ions, the reaction mixture was swiftly decolorized indicating the remarkable catalytic effect of

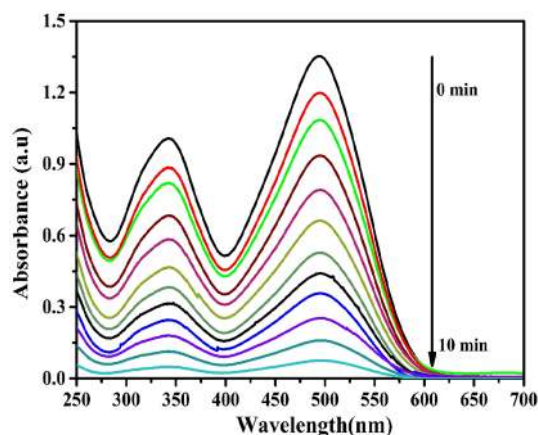


Fig. 13 Time-dependent UV-Vis spectra for the catalytic reduction of Congo red by NaBH_4 in the presence of AuNPs. Conditions: $[\text{CR}] = 1 \text{ mM}$; $[\text{NaBH}_4] = 10 \text{ mM}$; gold nanoparticles obtained from 1 mM of chloroauric acid and 1 % of gum SMG

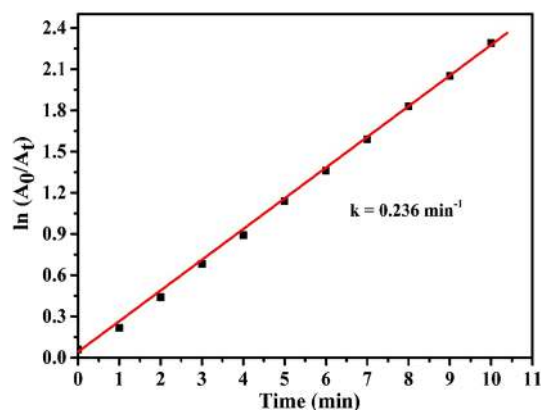


Fig. 14 The plot of $\ln(A_0/A_t)$ versus time for the reduction of CR

AuNPs in the degradation of CR. Figure 13 shows the UV-Vis absorption spectrum of CR dye showing a gradual decrease in peak intensity due to the reduction by NaBH_4 in the presence of AuNP catalyst. The rate constant (k) was determined from the linear plot of $\ln(A_0/A_t)$ versus reduction time in minutes (Fig. 14). The degradation reaction follows a pseudo first order reaction kinetics with respect to CR because the concentration of NaBH_4 (10 mM), is larger than that of CR (1 mM). The reaction rate constant was calculated and was found to be 0.236 min^{-1} .

Conclusion

A facile, non-hazardous, cost-effective and a green approach for the synthesis of AuNPs was developed through the reduction of aqueous HAuCl_4 solution using SMG as reducing and stabilizing agent. The synthesized nanoparticles were characterized by XRD which confirmed

the face-centred cubic crystalline phase. TEM results revealed that the average size of synthesized AuNPs was around $12 \pm 2 \text{ nm}$. The examination of AuNPs by UV-Vis spectroscopy demonstrates that the AuNPs formed are nanosized and the absorption peak range is 520–530 nm. The hydroxyl functional groups present in the gum were found to be responsible for the formation of AuNPs. The green-synthesized AuNPs were proven as efficient catalysts with enhanced rates of reduction of MB and CR dyes.

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