Synthesis and characterization of SiO2-Chitosan supported AgNPs and its catalytic application for reduction of malachite green

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Designing novel nanocatalysts for the reduction of water borne dyes is a topic of recent research interest. A new composite, SiO2-chitosan supported AgNPs (3-11%), has been synthesized and characterized through FT-IR, XRD, BET and SEM. The catalytic activity of the composites has been investigated through reduction of malachite green as a model reaction in the presence of NaBH4. The reduction is rapid and followed pseudo first order kinetics. Increase of pH increased the rate of reduction compared to low pH, as at a low pH, NaBH4 decomposed directly and rapidly. An increase in NaBH4 content also increased the rate. The results indicate that the reduction can also be extended to other water borne reducible contaminants.

**Keywords**: Silica, Chitosan, AgNPs, Malachite green, Composite, Silica-chitosan/AgNPs

Malachite green (MG) has been used as an organic dye and antimicrobial agent for many years. Traditionally, it is used as a dyestuff for materials such as silk, paper, and leather. Thousands of tons of MG are produced annually. Malachite green is used in the killing of Saprolegnia oomycete, which infects fish eggs in aquaculture. There are several physical and chemical methods for removal of dyes: they include membrane filtration, electrochemical technology, advance oxidation process (AOP) and adsorption process. However, most of these methods suffer from disadvantages such as high operating cost, ultraviolet (UV) irradiation at a required wavelength, long reaction time, scale-up issues, high cost and adding secondary pollution. Among these methods adsorption is considered as the efficient one to remove dye pollutants from industrial effluents due to its comparably easy operation, low cost and insensivity to toxic substances. Recently, the natural polymers, such as chitosan and its derivatives have significantly attracted much research interest for water purification. This is because chitosan is a low-cost and effective adsorbent compared to other adsorbents used in the adsorption of organic or inorganic pollutants. Furthermore, due to the unique structure of chitosan, it has proved to have outstanding removal capacities for dyes. Modified chitosan is also very useful as a support material in heterogeneous catalysis. To improve the properties of chitosan materials for use in catalysis, chitosan has been modified with ceramic alumina, alginate, polyvinyl alcohol, cyclodextrins magnetic nanoparticles, ionic liquids, and silica. Among these supports, silica plays a vital role due to its thermal stability, tunable porosity, physical rigidity, chemical inertness and negligible swelling in aqueous solutions. Silver (Ag) ion has been used for a long time as an antibacterial agent due to its strong inhibiting effect on bacteria. Recently, Ag nanoparticle has attracted considerable attention to provide maximum catalytic property with minimum amount of Ag. In these studies, characterization of SiO2-Chitosan supported AgNPs (SiO2-chitosan/AgNPs) composite by spectroscopic methods and study of the catalytic property of these materials have been investigated. However, chitosan and Ag nanoparticles separately have been studied extensively, but study of combination of all these three materials is only rarely carried out. So, our main objective in this study includes synthesis and characterization of SiO2-Chitosan/AgNPs and study of its catalytic activity towards reduction of MG in the presence of NaBH4.

**Experimental Section**

**Materials**
Reagent grade chemicals of silver nitrate (Kojima, Japan), Chitosan, acetone (SRL, Mumbai), tetraethyl orthosilicate (TEOS) (98%, Acros, USA), NaBH4,
isopropanol, ammonia (28%, SRL, Mumbai) and anhydrous ethanol (99.5%, SRL, Mumbai) were used as received.

Characterization

The Fourier transform infrared (FT-IR) spectra were recorded in the range from 400 to 4000 cm\(^{-1}\) on a Bruker Tensor-27 FTIR spectrophotometer with OPUS software. The Raman spectra were recorded in a Witec Confocal Raman instrument (CRM200) with Ar ion laser (514.5 nm). Ultraviolet–visible (UV–Vis) spectra were recorded at room temperature using a Lambda 35 spectrophotometer. The surface morphology was investigated using HITACHI SU 6600 scanning electron microscope (SEM). Ultra-sonication was done by Cole Palmer sonication bath using single distilled water as a dispersion medium with a frequency of 40 keV. X-ray powder diffraction (XRD) data were collected on PANalytical Instrument.

Synthesis of three different types of SiO\(_2\)-Chitosan composite

Three different types of SiO\(_2\)-Chitosan composite were prepared by fixing the weight ratio of SiO\(_2\) and chitosan as 1:1, 1:2, and 2:1. Initially, SiO\(_2\)-Chitosan (1:1) composite was prepared by taking 4.5 mL of TEOS as silica source and 1.22 g of Chitosan. 4.5 mL of TEOS was taken in a 100 mL RB and to this 1.2 g of chitosan was added, and stirred with 2 mL of 2% acetic acid. It resulted in a pale yellow viscous solution. Then 10 mL of NH\(_3\) was added to it to catalyze the condensation reaction. The resulting white suspension was vigorously stirred for 24 h at room temperature. The obtained white precipitate was centrifuged and dried at 80°C for 5 h. Similarly, the other two composites were also prepared using 9.0 mL of TEOS and 1.22 g of chitosan for SiO\(_2\)-Chitosan (2:1), and 4.59 mL of TEOS and 2.44 g of chitosan for SiO\(_2\)-Chitosan (1:2).

Synthesis of SiO\(_2\)-Chitosan/AgNPs composites

Five different types of SiO\(_2\)-Chitosan/AgNPs composites were prepared by fixing the weight ratio of SiO\(_2\)-Chitosan composite as constant and varying the silver load as 3, 5, 7, 9 and 11%. Briefly, 500 mg of SiO\(_2\)-Chitosan composite (1:2) was dispersed in 40 mL of DD water and to that 50 mL of isopropanol, 0.054 g of AgNO\(_3\), 1.27 mL of NH\(_3\) were added and stirred for 15 min. 5 mL of 0.1M NaBH\(_4\) was added and the color of the solution changed from colourless to dark brown. Then the mixture was stirred for 2 h with a magnetic stirrer. The solid particles formed were recovered by filtration, washed with ethanol and dried. Similarly, the remaining four different types SiO\(_2\)-Chitosan/AgNPs composites were prepared by varying the amount of AgNO\(_3\) as 0.093, 0.126, 0.162 and 0.198 g, and they were labelled as SiO\(_2\)-chitosan/AgNPs (3%), SiO\(_2\)-chitosan/AgNPs (5%), SiO\(_2\)-chitosan/AgNPs (7%), SiO\(_2\)-chitosan/AgNPs (9%) and SiO\(_2\)-chitosan/AgNPs (11%), respectively.

Catalytic reduction experiments

The catalytic activity of SiO\(_2\)-chitosan composite and five different composites were evaluated separately under same the condition using reduction of malachite green as a model reaction. The catalytic experiments were carried out in a 100 mL glass beaker containing 10 mg/L solution of malachite green, 0.1 g of the respective catalyst and 0.01 mL of NaBH\(_4\) (0.1M). The progress of reduction was monitored at different time intervals and measured the absorbance of the supernatant through UV-Vis spectrophotometer. The absorbance of the supernatant liquid was measured periodically using UV-Vis spectrophotometer at the wavelength of 615 nm, which is due to Malachite Green. The decreased intensity of MG absorbance against the time was
periodically monitored until the complete reduction of MG. Then by monitoring the decrease of intensity of MG absorbance, the pseudo-first order rate constant ($k_{obs}$) was calculated using the formula:

$$-kt = \ln \frac{C_t}{C_0}$$

where, $C_0$-initial absorbance, $C_t$-absorbance at time “t”.

Results and Discussion

The FE-SEM image of SiO$_2$ nanoparticles, Fig. 1a, showed dense aggregates carrying large pores. The origin of pores is due to evaporation of water and alcohol through the matrix during the formation of silica. There were no characteristic morphological features. The FE-SEM image of SiO$_2$-Chitosan composite also showed aggregates (Fig. 1b) without specific morphology. The SiO$_2$-chitosan/AgNPs composite, Fig. 1c, showed mostly spherical particles, with each one of them as an aggregate$^{16}$. But a wide distribution in size was noted. Very small nanoparticles were very much aggregated, but the nanoparticles of large size remained isolated. The EDAX results are presented in Fig. 2. It confirms the presence of the main elements in the matrix of the composites.

The XRD pattern of SiO$_2$-Chitosan/AgNPs composite showed reflections characteristic of AgNPs (Fig. 3b-f). The peaks at 38.09°, 44.31°, 64.51° and 77.46° (2θ) are due to (111), (200), (220), and (311), respectively. Similar reflections were also reported in the literature$^{17}$. The peaks due to chitosan generally appear around 9.3° and 22.56° (2θ)$^{18}$. But in this spectrum the lower angle peak was not observed and the higher angle peak retained, but it was slightly shifted to a higher angle. This shift is due to compression of chitosan by both silica and silver nanoparticles. The absence of lower angle peak is ascribed to false scattering of its diffracted ray by both the silica and AgNPs. The envelope occurred around 22.56° is due to silica (Fig. 3a). With the increase in the loading of AgNPs, the intensity of the peaks also increased, evidencing increase of the size of the nanoparticles.

The FT-IR spectra of SiO$_2$-chitosan/AgNPs composite is shown in Fig. 4. The broad band in the

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt %</th>
<th>At %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CK</td>
<td>43.25</td>
<td>54.25</td>
</tr>
<tr>
<td>NK</td>
<td>05.06</td>
<td>05.45</td>
</tr>
<tr>
<td>OK</td>
<td>34.89</td>
<td>32.86</td>
</tr>
<tr>
<td>SiK</td>
<td>12.86</td>
<td>06.90</td>
</tr>
<tr>
<td>AgL</td>
<td>03.93</td>
<td>00.55</td>
</tr>
<tr>
<td>Matrix</td>
<td>Correction ZAF</td>
<td></td>
</tr>
</tbody>
</table>

Table 1 — EDAX elemental analysis

Fig. 2 — EDAX results SiO$_2$-Chitosan/AgNPs composite (11%)

Fig. 3 — XRD Pattern of (a) SiO$_2$, (b-f) SiO$_2$-Chitosan/AgNPs composite (3-11%)

Fig. 4 — FT-IR spectra of (a-e) SiO$_2$-Chitosan/AgNPs composite (3-11%)
high energy region is due to –O-H and –N-H stretching vibration of chitosan\(^\text{19}\). This band is broad and intense with the increase in the percentage of AgNPs loading. It favours much entrapment of water. Presence of much water is also confirmed by its bending vibration at 1630 cm\(^{-1}\). The intensity of this peak increased with the increase in AgNPs loading. The intense peak between 1400 and 1000 cm\(^{-1}\) is due to asymmetric Si-O-Si stretching\(^\text{20}\). The symmetric stretch occurred at 802 cm\(^{-1}\). It’s bending mode yielded a peak at 471 cm\(^{-1}\). The alcoholic C-O stretch generally occurs around 1050 cm\(^{-1}\), but in this spectrum, it is masked by asymmetric Si-O-Si stretch. With the increase in AgNPs loading the Si-O-Si and alcoholic C-O stretching vibrations are broadened towards high and low energy side, illustrating interaction with AgNPs.

The nitrogen adsorption isotherms of SiO\(_2\) and SiO\(_2\)-Chitosan/AgNPs composite (11\%) are shown in Fig 5. The isotherm of SiO\(_2\) showed more than one type of micropores, as at least two steps one close to 0 p/p\(_0\) and the other at 1.0 p/p\(_0\) were seen and it is also supported by FE-SEM images. The composite showed type (I\(V\)) adsorption isotherm, but presence of mesopores was not clearly evident, though its micropores are confirmed by the appearance of capillary condensation between 0 and 1p/p\(_0\)\(^\text{21}\). Fig. 6 illustrates pore size distribution in SiO\(_2\) and composite. The SiO\(_2\) is verified to have only one type of micropore, less than 20\(\text{Å}\). But the composite showed presence of both micropores less than 20\(\text{Å}\)and mesopores around 30\(\text{Å}\).

**Catalytic reduction experiments**

The catalytic reduction of MG was carried out in the presence of SiO\(_2\)-Chitosan/AgNPs composite (3-11\%) as a catalysts with NaBH\(_4\) as the reducing agent in aqueous medium. The concentration of reagents, MG and conditions are shown in Table 2. The reaction was monitored in a UV Vis spectrophotometer. The absorbance of malachite green gradually decreased with the increase in time for all the five catalysts. The spectra of decrease of absorbance with time for SiO\(_2\)-Chitosan/AgNPs (11\%) composite for the aliquots collected at different time intervals of the reaction mixture is shown in Fig. 7. A separate plot of absorbance vs time, for all the catalysts, shown in Fig. 8, depicted a rapid decrease in absorbance in the beginning and a slow decrease thereafter. Among the catalyst, SiO\(_2\)-Chitosan/AgNPs (11\%) composite showed a rapid decrease in rate compared to other catalysts. So, to study the influence of reaction parameters on the rate of the reaction only SiO\(_2\)-Chitosan/AgNPs (11\%) composite was used. From the initial rapid decrease of absorbance, C\(_0\) at t=0 and Ct at t were taken from the plot of SiO\(_2\)-Chitosan/AgNPs (11\%) composite, and plugged in pseudo first order rate equation to obtain the rate constant. The pseudo first order rate constant was equal to 6.9 sec\(^{-1}\). When NaBH\(_4\) and MG were

![Fig. 5 — N\(_2\) adsorption-desorption isotherms of SiO\(_2\)-Chitosan/AgNPs composite (11\%) and SiO\(_2\)](image)

![Fig. 6 — Pore size distribution of the SiO\(_2\)-Chitosan/AgNPs composite (11\%) and SiO\(_2\) (inset)](image)

<table>
<thead>
<tr>
<th>Catalyst amount</th>
<th>NaBH(_4)</th>
<th>MG</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>30mg</td>
<td>4x10(^{-6})</td>
<td>2x10(^{-4})</td>
<td>7</td>
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</table>
directly mixed in the absence of catalyst the rate of decrease of absorbance was insignificant, hence, the reduction of MG to leuco base is exclusively catalysed by AgNPs: it decomposes NaBH₄ to form hydrogen and electron and both are transferred to MG during reduction.

To study the effect of NaBH₄ on the rate of reduction, its concentration was varied as 4×10⁻⁶, 8×10⁻⁶ and 1.2×10⁻⁵ M. The results are presented in Table 3. The absorbance decreased rapidly with the increase in the concentration of NaBH₄. A separate plot of absorbance vs time was made as shown in the Fig. 8, and from the plot C₀ and Ct, derived at the initial rapid decrease in absorbance, were substituted in the pseudo first order rate equation to obtain the rate constant. The rate constants, shown in Table 3 are nearly same. Hence NaBH₄ is verified to have no direct reaction with MG.

To study the influence of the concentration of MG on the rate of reduction, its concentration was varied as 4×10⁻⁶, 8×10⁻⁶ and 1.2×10⁻⁵ M. The results are presented in Table 4. The rate of reduction increased with the increase in the concentration of MG as shown in Fig. 9. Therefore decomposition of NaBH₄ on AgNPs might be higher than the rate of reduction of MG. The decrease of absorbance for each concentration is separately plotted against time, as shown figure. From the C₀ and Ct obtained from each plot at the initial decrease in absorbance were used to calculate the pseudo first order rate constant, and the values are presented in Table 4. The rate constants

Figure 7 — Catalytic degradation of MG using SiO₂-Chitosan/AgNPs (11%) composite

Figure 8 — Linear plots of the effect of [NaBH₄] (a) 4×10⁻⁶, (b) 8×10⁻⁶ and (c) 1.2×10⁻⁵ Min the reduction of MG with SiO₂-Chitosan/AgNPs composite (50 mg)

Table 3 — Consolidated kₜₐₙ values for the effect of [NaBH₄] in the reduction of MG with SiO₂-Chitosan/AgNPs composite (50 mg)

<table>
<thead>
<tr>
<th>S. No</th>
<th>[NaBH₄]</th>
<th>kₜₐₙ × 10⁻⁴ sec⁻¹</th>
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<tbody>
<tr>
<td>1.</td>
<td>4×10⁻⁶</td>
<td>6.89</td>
</tr>
<tr>
<td>2.</td>
<td>8×10⁻⁶</td>
<td>6.90</td>
</tr>
<tr>
<td>3.</td>
<td>1.2×10⁻⁵</td>
<td>6.90</td>
</tr>
</tbody>
</table>

Table 4 — Effect of [substrate] on the reduction of MG in the presence of SiO₂-Chitosan/AgNPs composite (50 mg)

<table>
<thead>
<tr>
<th>S. No</th>
<th>[Substrate]</th>
<th>kₜₐₙ × 10⁻⁴ min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>2×10⁻²</td>
<td>6.90</td>
</tr>
<tr>
<td>2.</td>
<td>2×10⁻³</td>
<td>6.93</td>
</tr>
<tr>
<td>3.</td>
<td>2×10⁻⁴</td>
<td>6.91</td>
</tr>
</tbody>
</table>

Figure 9 — Linear plots of the effect of [substrate] (a) 2×10⁻⁴, (b) 2×10⁻³ and (c) 2×10⁻² M in the reduction of MG with SiO₂-Chitosan/AgNPs composite (50 mg)
were same irrespective of the concentration of MG. Thus confirming the pseudo first order.

To study the influence of catalyst loading on the rate of reduction of MG, its content was varied as 30, 40 and 50 mg. The rate of reduction of MG increased with increase in the content of the catalyst. It is due to increase in the rate of decomposition of NaBH₄ on AgNPs and subsequent reduction of MG. The plot of decrease of absorbance vs time is shown Fig. 10. From the plots C₀ and Ct were found for each catalyst loading at the initial rapid decrease in absorbance, the same were substituted in the pseudo first order rate equation. The calculated rate constants, presented in Table 5, remained the same irrespective of the content of the catalyst.

To study the influence of pH on the rate of reduction of MG, the reaction was carried out at pH 5, 7 and 11. The results are presented in Table 6. The rate increased with the increase in pH. At low pH, the rate of decomposition of NaBH₄ to form molecular hydrogen is high. It actually retarded the rate of the reaction. Such loss of NaBH₄ as molecular hydrogen is minimum at higher pHs. So, the rate of reduction increased with the increase in pH. The plot of absorbance vs time for each pH is shown Fig. 11. C₀ and Ct obtained from each curve at the initial rapid decrease in absorbance were used to calculate the pseudo first order rate constant, and the values are presented in Table 6. The rate constants remained the same irrespective of pH.

**Conclusion**

The SiO₂-chitosan/AgNPs composite at five different loading of AgNPs have been synthesized and characterized. Their catalytic activity is examined for the reduction of MG in the presence of NaBH₄. Although NaBH₄ is used as the hydrogen source, it is not much hazardous. The catalyst, SiO₂-chitosan/AgNPs (11%) composite, show higher activity than the other catalysts. The same catalyst can also be exploited for the reduction of any other water borne dyes. It is a non-hazardous, cheap catalyst, and can be easily prepared. The product, leuco base is also non-hazardous. Though the reduction rate was high at higher pHs, at the neutral pH too, the rate is high enough to use in dye reduction.

**References**