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Degradation of Disperse Orange 3 -an azo dye by silver nanoparticles

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The degradation of Disperse Orange 3, an azo dye, by silver nanoparticles which has been synthesized using green methodology has been described. These silver nanoparticles have been found to be potential catalysts for the degradation of Disperse Orange 3 in the presence of sodium borohydride ($NaBH_4$). The rate constant (k) for the catalyzed and uncatalyzed reaction has been determined. The spectrum of catalyzed reaction shows a sudden decay in the absorbance value (A) confirming the catalyst effect of Ag nanoparticles. In absence of silver nanoparticles the rate of degradation of dye has been found to be negligible.

Keywords: Catalyst, Degradation, Disperse Orange 3, Azo dye, Green approch, Silver nanoparticles

Azo dyes, which are characterized by one or more azo group (−N=N−) are a predominant class of colourants used in tattooing, cosmetic, foods and consumer products[1,2]. They are well known for their scientific and technological applications such as in laser dyes, photonics, antidiabetics, antibacterial and antitumor[3-7]. Textile dyes in wastewater are a concern not only because they are displeasing aesthetically but are linked to health hazards as well because of their toxicity and carcinogenicity on human and animal life[8, 9]. Dye pollutants can have dramatic effects on the environment. It is, therefore, justified to investigate techniques to remove these harmful pollutants safely. The traditional physical, chemical and biologic methods of wastewater treatment have a little degradation effect on this type of pollutants. On the contrary, the technology of nanoparticles for degradation has been proved to be effective compared with any conventional wastewater treatment techniques. Due to the excellent features of this technology, it appears promising and has attracted the researchers of all over the world[10-13]. In the present work degradation of disperse orange 3 has been analyzed through synthesized silver nanoparticles and rate constant (k) for the catalyzed and uncatalzed reaction have been determined. Disperse Orange 3, being a typical azo dye for the one azo bonds (−N = N−) chromophores in its molecular structure is selected as a model dyeing pollutant to evaluate the catalytic character of the silver nanoparticles. Tannic acid is used here as a reducing agent for silver nanoparticles. It is also known for its capping activity to cap the particles and providing them stability[14,15]. Disperse Orange 3 is an azo dye soluble in water to give intense yellow color, which is extensively used to colour all kind of natural fibres like wool, cotton, polyesters, acrylic and rayon. This is also applied in paints, inks, plastics and leather.

Experimental Section

Materials

All the chemicals used in this study are of analytical regent (AR) grade. Tannic acid, silver nitrate ($AgNO_3$) and sodium borohydride ($NaBH_4$) were obtained from Merck. Disperse orange 3 is purchased from M/S Sigma Aldrich Chemical Company, Inc., USA. All samples were used as it is without any further purification.

Equipment

UV-Visible spectroscopy is a unique analytic technique to decide the color and concentration of a compound. Molecules having non-binding valence electrons, such as *pi*-bonds, have unique properties that emit colour when excited by light. All the spectra are recorded on CAMSPEC-M 550, UV-Visible spectrophotometer at room temperature.

Synthesis of silver nanoparticles by green approach

To 5 mL of tannic acid (1.4×10^{-4} M), 1 mL of 0.05% w/v $AgNO_3$ was mixed to synthesize silver nanoparticles. The mixture was stirred for 1 min to obtain silver nanoparicle at room temperature. The solution changed to yellowish brown indicating the synthesis of silver nanoparticles as shown in Fig. 1a. Such synthesized silver nanoparticles were used as catalyst for the degradation of Disperse Orange 3 through $NaBH_4$.

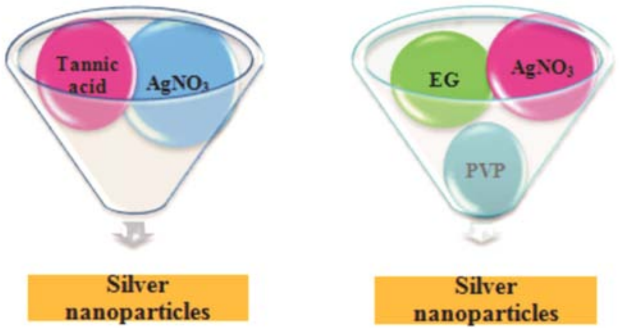

Fig. 1 — Synthesis of silver nanoparticles (a) by green approach; (b) by chemical approach

Synthesis of silver nanoparticles by chemical approach

Polyvinylpyrrolidone (PVP) was dissolved in 5 mL of ethylene glycol (EG). $AgNO_3$ (0.5g) was (0.6g) added into the above solution and then the mixture was stirred vigorously for 10 min. After the start of the reaction, the solution changed to yellowish brown, indicating the formation of silver nanoparticles (Fig. 1b). The silver concentration in the synthesized solutions was 9.5 wt%. Ethanol was added to dilute the solution.

Kinetic study for the degradation of disperse orange 3

To a mixture containing 100 µL of Disperse orange 3 with molar concentration of 1×10^{-3} M and sodium borohydride (0.5% w/v), 50 µL of 0.01% aqueous dispersion of silver nanoparticle was added in a 3.5 mL capacity quartz cuvette. Total volume of the mixture was made up to 3.2 mL by adding the required amount of double distilled water. The reaction was studied in a spectrophotometer cuvette. For the uncatalyzed reaction 50 µL of silver nanoparticles was replaced by an equal amount of double distilled water. The reaction was followed by studying absorbance (A) in a UV-visible spectrophotometer for 20 min and the fall in A with time at desired temperature was noted.

Results and Discussion

Green as well as chemical methodology were applied for the synthesis of silver nanoparticles. The λ_{max} of the prepared silver nanoparticles by green and chemical approach is observed at 410 and 416 nm respectively as shown in. This nature of silver nanoparticles showing λ_{max} at same wavelength is reported in literature[16,17]. This confirms the formation of silver nanoparticles with help of these approaches. In silver nanoparticle the conduction band and valence band lie very close to each other in which electrons move freely. These free electrons give rise to a surface plasmon resonance (SPR) absorption band. When the frequency of the electromagnetic field becomes resonant with the coherent electron motion, a strong absorption takes place, which is the origin of the observed colour[18-20]. The formation of silver nanoparticles can be determined by a change in colour since small nanoparticles of silver are yellow[21]. Here the colour of the prepared silver nanoparticles by both approaches were yellowish brown, indicating the synthesis of silver nanoparticles. After this green methodology was chosen because of its various advantages over the chemical methodology. The synthesized nanoparticles by green route methodology are stable as their λ_{max} value remains constant (max=416) with the time of stirring due to the capping of silver nanoparticles by tannic acid. Tannic acid serves as a reducing agent as well as stabilizer for silver nanoparticles. The nanoparticles so prepared, using tannic acid, were used here as catalyst for the reduction of Disperse Orange 3 with the help of $NaBH_4$. The rate of degradation of DO 3 was analyzed in the presence and absence of silver nanoparticles spectroscopically at a wavelength of 400 nm which is shown in Fig. 2(a and b). It was observed that degradation of Disperse Orange 3 was enhanced in the presence of silver nanoparticles due to electron relay effect. Silver nanoparticles act as an electron relay, aiding in the transfer of electrons from the BH_4^- ions to the dyes, and thereby causing a reduction in the absorption of the dyes[17,22]. Opposite of this, the reduction of Disperse Orange 3 with $NaBH_4$ in absence of catalyst at room temperature is not visible. Sodium borohydride individually was unable to reduce Disperse Orange 3 in absence of catalyst showing the catalytic efficacy of silver nanoparticles. From the graph, a rapid change in the value of absorbance of Disperse Orange 3 in presence of silver nanoparticles was analysed. This phenomenon of degradation of Disperse orange 3 was observed for 20 min. No significant degradation was found in case of uncatalyzed reaction even after 150 min. as depicted (in Fig. 2b). The spectra showing the reduction of DO 3 in the presence of $NaBH_4$ using tannic acid instead of silver nanoparticles showed same pattern (like Fig. 2b). This confirm that silver nanoparticles acts as catalyst and not tannic acid. The degradation of DO 3 obeys first order kinetics. The comparison for catalyzed and uncatalyzed reaction relative to time

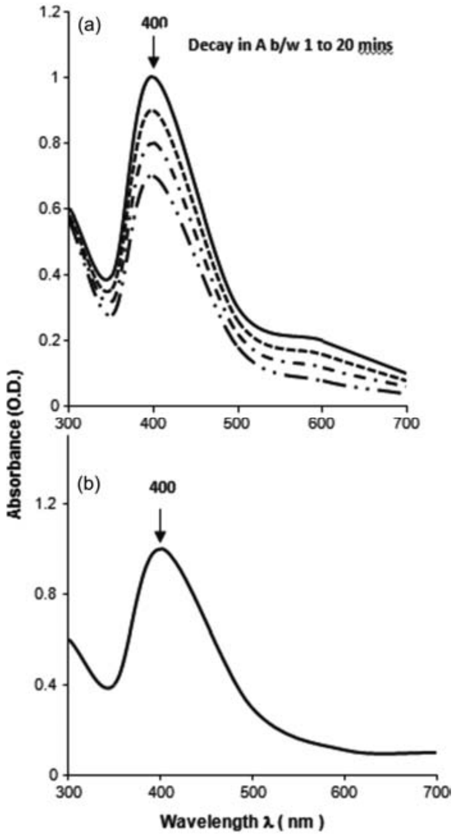

Fig. 2 — Degradation of disperse orange 3 in presence of $NaBH_4$ with and without Ag nps: (a) catalyzed reaction and (b) uncatalyzed reaction

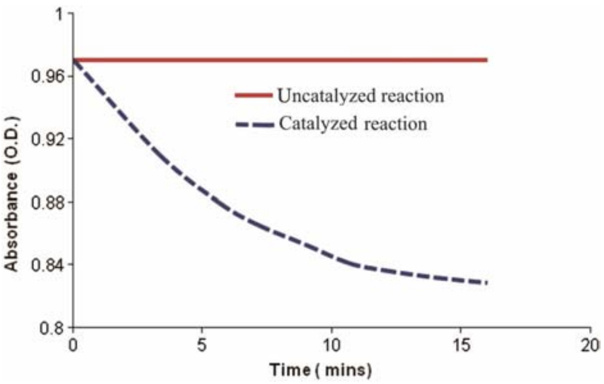

Fig. 3 — Comparison of plot of decrease in absorbance versus time

has been shown in Fig. 3. The rate constant (k) has been calculated for catalyzed reaction as 0.01 min^{-1} and for uncatalyzed reaction is found negligible as presented in Table 1. Therefore it is concluded that silver nanoparticles degrade the Disperse Orange 3 rapidly. The reduction of DO 3 with the help of $NaBH_4$ in absence of catalyst is favourable thermodynamically but kinetically difficult process. Metal nanoparticles give a different path for the reaction by reducing the activation energy resulting in reduction of kinetic barrier. Therefore, these make reaction favourable thermodynamically as well as kinetically. So, these studies can be utilized by industries to get rid of harmful dyes by the use of nanotechnology.

Table 1—Comparison of rate constant (k) for the catalyzed and uncatalyzed reaction

Conc. of Catalyst	Conc. of DO 3	Conc. Of $NaBH_4$	Temp. (°C)	Rate Constant (k) (min^{-1})
50 µL of 0.01% Ag nps solution	100 µL of 1×10^{-3} M	100 µL of 0.5%	20	0.01
Absence of catalyst	100 µL of 1×10^{-3} M	100 µL of 0.5%	20	Negligible

Conclusion

The synthesis of silver nanoparticles using green methodology has been discussed. These synthesized Ag nanoparticles have been used for the catalytic degradation of Disperse Orange 3 in the presence of $NaBH_4$ and their catalytic activity has been determined by measuring the rate constant k. The rate of degradation of colour of dye by $NaBH_4$ is monitored in the presence and absence of Ag nanoparticles spectrophototometrically. In is the absence of silver nanoparticles the rate of degradation of azo dye has been found extremely slow. But on the addition of silver nanoparticles into the azo dye and $NaBH_4$ mixture, the rate of azo dye degradation enhanced significantly indicating the catalytic behavior of silver nanoparticles.

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