Degradation of Congo red using nanoparticles

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Abstract
Reaction has been carried out in Palladium-silver (Pd-Ag) core nanoparticles using the citrate method. The development of the nanoparticles was examined by the UV-Vis spectroscopy. The catalytic activity of these nanoparticles was demonstrated by the reductive degradation of the congo red dye. In order to transfer electrons from the reducing agent ($NaBH_4$) to the dye molecules, the nanoparticles serve as electron mediators. The effect of reaction parameters on the dye degradation was examined. These results therefore represent a cost effective alternative for environmental protection against water pollution by dyes in the textile industry.

Keywords: Pd-Ag core nanoparticles, Congo red, Catalytic degradation.

Introduction

The gradual decline of clean water resources is a serious threat to humanity. The discharge of industrial wastewater into water bodies results in pollution of the water. The textile industry is considered as one of the primary causes of water pollution and approximately 80×10^4 tons of azo dyes is produced worldwide[7]. Azo dye increases the COD and BOD level of water by altering the pH and inorganic chemical content[4]. A significant amount of research has been put into developing novel materials and innovative water purification methods based on nanoscience and nanotechnology[11]. Nanoparticles can be used as an efficient method for the degradation of congo red dye[8].

A core nanoparticle is made of one material coated with another material. The core nanoparticles exhibit better properties when compared to the simple nanoparticles of individual material. High dispersibility, increased chemical and thermal stability, reduced cytotoxicity and enhanced conjugation with other bioactive molecules are some of the improved properties[12,17]. From an economic perspective, the core nanoparticles are significant. In order to minimize the waste of the precious material, an expensive material can be coated over a low cost material of the same size rather than creating a pure material[2]. The process of dying textiles, paper, plastics, leather are considered to be the main cause of water pollution since it results in effluent that is colored and contains harmful species.

A major concern was raised over the decolorization or detoxification of dyes in wastewater[6]. The textile industry has contributed to water pollution, poses a significant threat to the United Nations' Sustainable Development Goals (SDGs), particularly SDG 6, which aims to ensure safe water and sanitation for all. The primary goal of improving global water quality by 2030 is to reduce pollution, eliminate discharges, decrease the proportion of untreated wastewater and substantially increase recovery and safe recycling of wastewater. Ineffective water management and environmental challenges are leading to water scarcity, impacting 15% of the global population[16].

Bimetallic nanoparticles including Au/Pd, Au/Ag and Au/Pt exhibit better catalytic effects over their monometallic counterparts, they are also of great interest, particularly in the field of catalysis[3]. In recent years, stringent color permission guidelines have been enforced by the Government to safeguard the environment from the adverse effects of dyes in effluent discharged into the water bodies. Based on this motivation, the catalytic activity of Pd-Ag core nanoparticles was studied towards the decolorization and degradation of congo red dye.

Material and Methods

Materials: All chemicals were of analytical quality such as silver nitrate, potassium tetrachloropallidate ($K_2[PdCl_4]$, 99.9%), sodium borohydride ($NaBH_4$,99.0%), Tri-sodium citrate dihydrate and Congo red.

Synthesis of Nanoparticles: The core nanoparticles were prepared by reduction techniques[3]. The citrate reduction technique was used to prepare the Pd-Ag core nanoparticles. There are two stages involved in preparing the Pd-Ag core nanoparticles. The preparation of Pd nanoparticles was the first stage, while the preparation of Pd-Ag core nanoparticles was the second stage. The Pd nanoparticles were prepared as follows: K_2PdCl_4 (0.01 g) and Tri sodium citrate (0.02 g) were continuously stirred with distilled water and added to the sodium borohydride solution.

Following the addition, the solution turned into dark grey colour, indicating the formation of Pd nanoparticles[20]. In the second stage, 20 ml of $AgNO_3$ aqueous solution was mixed with Pd nanoparticles solution. This was followed by the addition of tri sodium citrate. The Pd-Ag core nanoparticles were allowed to cool to room temperature at 10 °C after 1 h of reflux.

Catalytic Effect of the Nanoparticles: The Congo red and $NaBH_4$ (reducing agent) solutions were mixed together and then the core nanocatalyst solution were added in order to

examine the catalytic activity of the freshly prepared core nanoparticles. Next, using spectrophotometry at 496 nm, the reduction of the dye was monitored. $NaBH_4$ solution concentration was maintained a minimum of 100 times higher than the dye concentration. The reaction mixture consisted of distilled H_2O, Congo red dye solution, $NaBH_4$ solution and the nanocatalyst solution. Following the addition of nanocatalyst into the reaction mixture, the kinetics measurements were initiated instantly. The measurements were carried out repeatedly until no further decrease in absorbance was recorded.

Results and Discussion

UV-Vis Absorption Spectra: Noble metal nanoparticles have significant light absorption in the visible range of spectrum because of the localized surface Plasmon resonance (LSPR) effect. At a particular resonance wavelength of the incident light, this LSPR corresponds to charge density oscillation within the nanoparticles and the development of a strong electromagnetic field confinement around the nanoparticles[5]. The local refractive index, geometry and type of material surrounding nanoparticles determine the position, intensity and type of LSPR[18]. The peak position represents the mean particle size[10].

Figure 1 shows the UV/Visible absorption spectra of Pd-Ag nanoparticles in aqueous solution. The spectrum of Pd-Ag contains a strong absorption peak at 400 nm and shifting of absorption band from 400 to 450 nm. This might be characterized by the bimetallic core nanoparticles nanostructure effect.

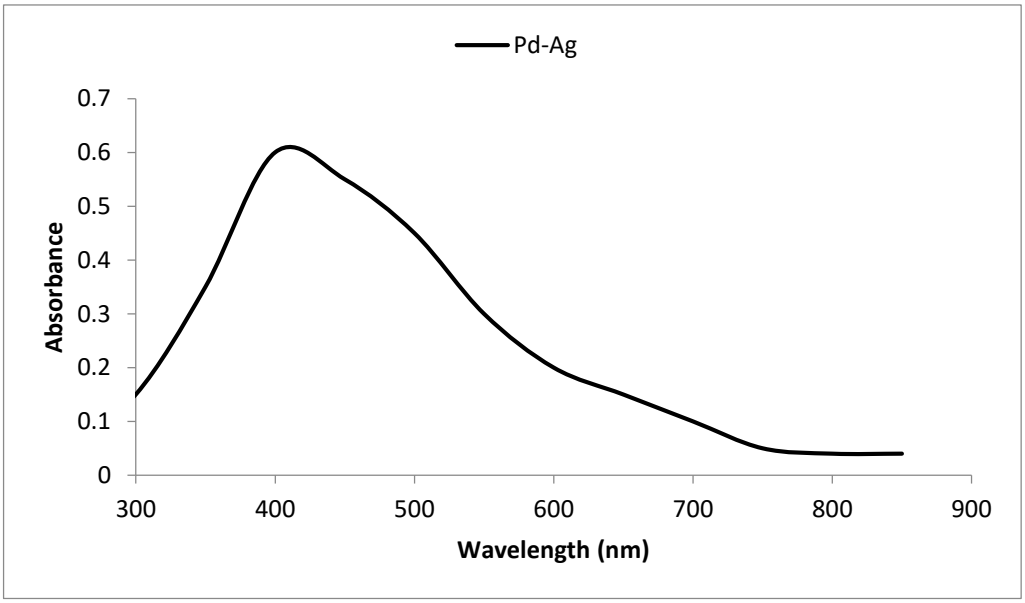

Fig. 1: UV/Visible absorption spectra of Pd-Ag nanoparticles

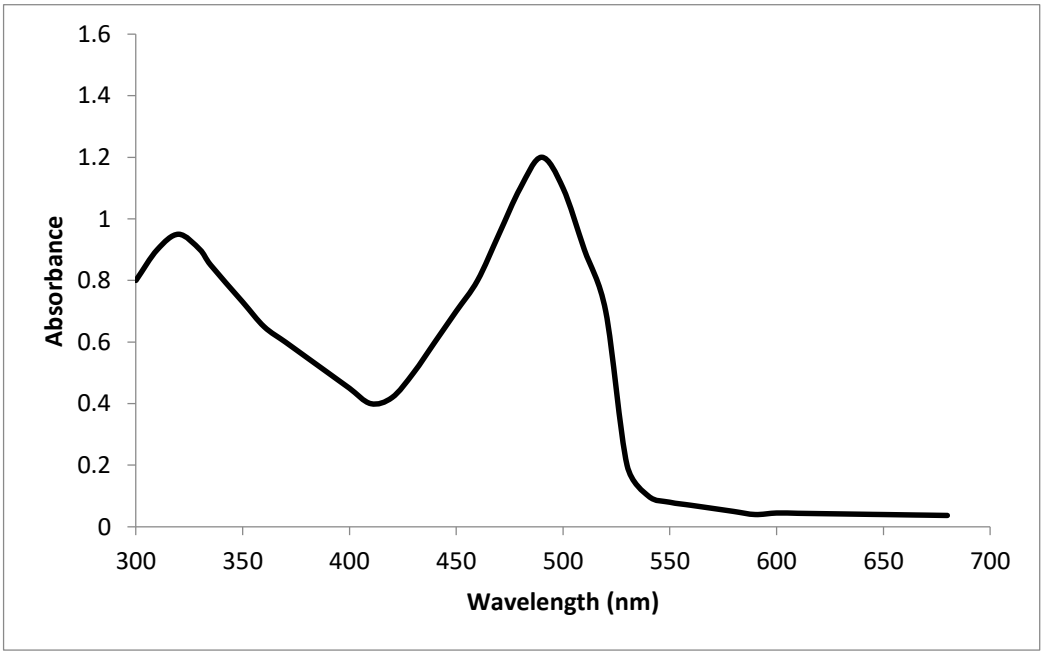

Fig. 2: Absorbance of Congo red dye in the presence of Pd-Ag nanoparticles

Kinetics of Dye Reduction: Congo red was selected for this study due to its extensive use in the textile industry as a colorant. It shows an absorption peak at 480 nm. As $NaBH_4$ was reduced in the presence of the nanocatalysts, the peak gradually decreased with time as shown in figure 2. The dissociation of the -N=N- bond of the dye molecules resulted in the formation of aromatic amine products.

Effect of Dye Concentration: The correlation between the initial concentration of the congo red dye and the reaction rate in the presence of Pd-Ag nanocatalyst and the reducing agent are presented in table 1. At a dye concentration of 5 x 10^{-5} mol/1, the rate initially increased to reach a maximum and then decreased at the higher dye concentration.

Due to the extensive availability of active sites on the catalyst surface, which can accommodate the small number of dye molecules that migrate from solution to the surface, the reaction rate initially increases at low dye concentrations. However, it is also possible to explain the decrease in reaction rate caused by the high dye concentration by considering that the catalyst receives a limited quantity of dye molecules to degrade.

The remaining dye molecules will continue to stay in the bulk solution until the molecules that were previously bonded to the surface are degraded. Such successive dye degradation process results in the reduction of active sites within the catalyst and eventually the rate reduces[13]. An additional explanation for this phenomenon could be that as the initial dye concentration is raised, an increasing number of dye molecules are adsorbed on the Pd-Ag nanocatalyst surface. Large quantities of adsorbed dye prevent direct interaction with the active sites, which may limit dye degradation[1,15].

The following equation was used to calculate the degradation efficiency with time in order to show the progress of the reaction[9,14,19].

$$\% \text{ Efficiency} = \frac{C_0 - C_t}{C_0} \times 100$$

where C_o and C_t represent the initial concentration of the dye and its concentration at time t, respectively. The percentage of dye degradation varies with time as a function of the initial dye concentration in the presence of nanocatalysts as shown in table 2.

When the initial dye concentration increased, the percentage of degradation reduced, but it increased with contact period of time. Furthermore, in the presence of Pd-Ag core nanocatalyst, a sharp increase in the percentage of dye degradation at the early stages of reaction (within 5 min) was observed. For the initial concentration of the dye (3×10^{-5} mol l^{-1}), the percentage of dye degradation was 95%, exhibiting the high catalytic efficiency.

Conclusion

Under the operating parameters tested, the Pd-Ag core nanoparticles showed effective nanocatalysis for the degradation of congo red in an aqueous medium. As the concentrations of the nanocatalyst and $NaBH_4$ increased, the rate of reaction also increases. Regarding the influence of dye concentration, the rate increased at low dye concentrations, reaching a maximum and then decreased at increasing dye concentrations. This method can be extended to wastewater treatment since it makes reasonable to use it to remove other dyes from aqueous solutions as well.

Table 1
Relation between the initial concentration of the congo red dye and the reaction rate

S.N.	Dye concentration (10^{-5} mol / l)	Reaction rate (mol / l. min)
1	3	0.07
2	4	0.1
3	5	0.11
4	6	0.105

Table 2
Dye degradation percentage

S.N.	Time (min)	Dye degradation (%)			
		Dye concentration (3 x 10^{-5} mol/1)	Dye concentration (4 x 10^{-5} mol/1)	Dye concentration (5 x 10^{-5} mol/1)	Dye concentration (6 x 10^{-5} mol/1)
1	1	45	40	35	30
2	3	75	60	60	55
3	5	80	80	80	75
4	7	90	85	85	80
5	9	95	90	90	85

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(Received 12th June 2025, accepted 17th August 2025)