Polyaniline Supported Palladium Catalyzed Reductive Degradation of Dyes Under Mild Condition

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Abstract: Polyaniline supported palladium catalyst was applied in the reductive degradation of organic dyes such as Methylene Blue, Rhodamine B, and Methyl Orange in presence of sodium borohydride as an environmental-friendly approach. Role of pH, catalyst amount, and catalyst support were investigated thoroughly to achieve complete and efficient degradation within few minutes under ambient condition. Heterogeneous nature of the catalyst allowed easy recovery by centrifugation and the catalyst was recycled for five cycles with slightly reduced activity. Recovered catalyst was characterized by ICP-AES and TEM and a slight decrease in the activity of the catalyst was attributed to the agglomeration of the palladium nanoparticles.

Keywords: Polyaniline, palladium, degradation, organic dye, catalyst, reusable.

1. INTRODUCTION

Water pollution has become a major problem worldwide in recent days [1]. Synthetic organic dyes discharged to water bodies by several industries like textile, paper, drug, food processing etc. also contribute to this problem by damaging aquatic life and affecting indirectly other living organisms. Many of these dyes are nonbiodegradable and highly stable owing to their complex structure [2]. Most of these dyes are found to be toxic and carcinogenic [3-5]. Some of these dyes also reduce the efficiency of the photosynthesis of plants [3].

Government legislation for a greener environment is forcing these industries to control their effluents to a standard permissible limit [4, 5]. So it has become a challenge to purify the wastewater from these dye molecules. Different techniques including physical methods such as adsorption, [6-8] coagulation [9], chemical methods utilizing both oxidation (by O₂, NaOCl, O₃, H₂O₂ etc.) [10, 11] and reduction (by Na₂S₂O₄) [10], biological [12] methods as well as photo-chemical [13] methods are available for complete or partial removal of such organic pollutants [14]. However, due to expensive and complex equipment’s requirement, inefficient dye removal capacity, and generation of effluents in the form of sludge make these methods of dye removal not of greater use [10]. Although photocatalytic oxidative degradation of organic dyes is effective and eco-friendly, these processes are also time and high energy consuming [13].

Catalytic reduction being inherently quicker has attracted a lot of attention from the scientific communities for the degradation of organic dyes and pollutants [15]. Currently, catalytic reductive degradation of organic dyes using different metal catalysts (e.g. Au, Ag, Pt and Pd) is explored as an alternative dye degradation means as these reactions are found to be very effective for their involvement in the electron transfer process between NaBH₄ (donor) and dye species (acceptor) [16-18].

Heterogeneous catalysts are always preferable over homogeneous catalysis for its ease of recovery, recyclability of the precious catalysts, longer service life, and all these attributes lead to a more economical and environmentally friendly process. Intrigue by these facts, recently, considerable efforts are seen in the development of an efficient heterogeneous palladium-based catalyst for degradation of various organic dyes due to the high catalytic activity of palladium [19-22] as efficient reusability and recyclability of these catalysts can offset the cost of the expensive palladium.

Polyaniline (PANI, Fig. 1a), one of the most widely studied conducting polymers, is also explored as support for different metal catalysts owing to its environmental stability and interesting red-ox properties [23, 24]. PANI poses several qualities such as easy preparative protocol from non-expensive starting material (aniline), controllable doping levels through an acid doping/base de-doping process, inert nature, and non-solubility in most of the organic solvents and water, which makes it a good candidate as support in heterogeneous catalysis. Earlier, we have successfully demonstrated the catalytic activity of PANI supported different metal catalysts in various types of organic transformations [25]. In recent times, PANI in its various form was utilized for adsorptive removal of cationic and anionic dyes [26]. Moreover, Polyaniline conjugates e.g. PANI-mesoporous silica [27], PANI-chitosan [28] and PANI-Graphene Oxide-
Fe₃O₄ [29] have been used for removal of organic pollutant such as Methyl orange, different sulfonated dyes, fluorides etc. from wastewater. In all the cases, polyaniline was utilized to enhance adsorption capacity of the main adsorbent [30]. But the use of polyaniline as support in catalytic reductive degradation of dyes has not yet reported. We envisaged that the chelating functionalities of PANI can help to adhere the palladium throughout the reaction cycle acting as a macro-ligand [31] and the electron-rich conjugated aromatic system, -NH and -N= bonds will be useful to attract the aromatic dyes through Lewis acid-base interaction, H-bonding or π-electronic interaction and thus facilitate the reduction/degradation of the dyes. In continuation of our recent work on metal-catalyzed reductive degradation of organic dyes [32] herein, we report the polyaniline supported palladium (Fig. 1b) catalyzed reductive degradation of organic dyes. Moreover, to establish the reproducible nature of the catalyst, it was recycled over several cycles.

2. RESULTS AND DISCUSSION

2.1. Catalyst Preparation and Characterization

Detail preparation and characterization of PANI supported palladium catalyst are reported in the literature [25].

2.2. Catalytic Degradation of Methylene Blue (MB)

MB, a cationic dye and widely used in textile industries was chosen to investigate the catalytic activity of PANI-Pd(OAc)₂ towards the reductive degradation reaction as shown in Scheme 1.

The reaction condition was optimized for various SB concentrations keeping MB concentration fixed at 2 x 10⁻⁶ M. It was observed that at higher concentration of SB (1 x 10⁻⁴ M, 4 x 10⁻⁵ M, 2 x 10⁻⁵ M) with 5 mg of catalyst, the reaction was too fast to be monitored. The SB concentration was finally optimized as 1.5 x 10⁻⁵ M. Fig. (2a) shows how the absorption intensity of MB at 664 nm decreased with time. The degradation was found to be completed within 664 nm decreased with time. The degradation was found to be completed within 8 min.

Fig. (2b) shows the absorption pattern of MB treated with SB (1.5 x 10⁻⁵ M) without PANI-Pd(OAc)₂. It was evident from the spectra that SB alone cannot degrade the dye even after 180 min. When MB was treated with PANI-Pd(OAc)₂ in absence of SB (Fig. 2c), no appreciable loss of absorption intensity of MB was observed. It rules out the possibility of noncatalytic background absorption of the MB in the PANI.

It became very clear neither the SB nor the catalyst alone is able to carry out the degradation of the dye molecule. Again it was also clarified whether there is any role of PANI-Base itself (due to adsorption phenomenon) towards the decrease in intensity of the colour of the dye. Fig. (2d) shows there is no diminishing of intensity of the peak even by using 25.0 mg of PANI-Base.

To compare the catalytic activity of homogeneous Pd(OAc)₂, acetonitrile solution (2.0 ml) containing 0.08 mg of Pd(OAc)₂ (i.e. equivalent to 5.0 mg of PANI-Pd(OAc)₂) was added to MB solution and treated with SB under standard reaction condition. Degradation of MB was completed within 5.0 min but the catalyst could not be recovered. Further, when the reaction mass after completion of the degradation of MB was reacted with a fresh stock solution of MB and SB, degradation of MB became very sluggish and complete degradation was not achieved even after 180.0 min. This is may be due to agglomeration of palladium particles to form catalytically inactive species.

Under similar reaction condition, MB was treated with 5.0 mg of commercial 5% Pd on Carbon and it was observed that the complete disappearance of the absorption maxima at 664 nm took 30.0 min in comparison to 8.0 min by PANI-Pd(OAc)₂. The enhanced activity of the PANI-Pd(OAc)₂ underlines the role of the support PANI which can help in electron transfer process involving BH₄⁻, palladium and dye being a conductive polymer as well help to attract the dye in the vicinity of the palladium by Lewis acid-Lewis base interaction, H-bonding or π-electronic interaction. It requires more experimentation to fully understand the exact role of the PANI.

2.3. Effect of Catalyst Amount

In order to investigate role of the amount of catalyst, three experiments were performed using 3.0 mg, 5.0 mg and 10.0 mg of catalysts keeping the ratio of MB and SB fixed (2 X 10⁻⁶ : 1.5 X 10⁻⁵) and temperature was maintained at 25°C and the rate of degradations was monitored by observing a decrease in intensity of the absorption band of MB at 664 nm. Results are summarized in (Table 1). An observed

![Fig. (1). a) Structure of Polyaniline and b) PANI-Pd(OAc)₂.](image)
Scheme 1. Reduction of MB in presence of PANI-Pd(OAc)₂ and SB.

Fig. (2). a) Degradation of MB in presence of PANI-Pd(OAc)₂ and SB; b) Degradation of MB with SB only; c) Degradation of MB with PANI-Pd(OAc)₂ only; d) Degradation of MB with SB and PANI-Base.

increase in the degradation efficiency of a higher amount of catalyst is probably due to the availability of higher number of active catalytic sites.

Table 1. Effect of amount of PANI-Pd(OAc)₂ on the degradation of MB using SB.

<table>
<thead>
<tr>
<th>Amount of Catalyst (mg)</th>
<th>Complete Degradation Time (min)</th>
</tr>
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<tbody>
<tr>
<td>3</td>
<td>30</td>
</tr>
<tr>
<td>5</td>
<td>8</td>
</tr>
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<td>10</td>
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2.4. Effect of pH

The degradation of MB was studied at different pH values keeping the MB and SB concentration fixed value (2 X 10⁻⁶ : 1.5 X 10⁻⁵) and the temperature fixed at 25°C. The pH of the aqueous solution was adjusted by adding requisite amounts of HCl (0.1 N) and NaOH (0.1 N). The pH of the original solution was found to be 8.7. Fig. (3) shows how degradation rate varies with pH. The rate of degradation increases as pH of the solution decreases which can be explained by faster hydrolysis of BH₄⁻ to active neutral borane species at lower pH and thus accelerating the catalytic activity. This requirement of spontaneous hydrolysis of borohydride before its catalytic activation by metal nanoparticles was extensively investigated by Choi et al. [33].

2.5. Catalytic Reduction of Rhodamine B

To check the effectiveness of the developed catalyst, PANI-Pd(OAc)₂ was used in the degradation of Rhodamine B another cationic dye under the optimized condition. Complete degradation of Rhodamine B was observed within 7.5 min. The results are shown below (Fig. 4).

2.6. Catalytic Reduction of Methyl Orange (MO)

After getting an impressive result in reductive degradation of a cationic dye (MB), PANI-Pd(OAc)₂ catalysts were explored (Scheme 2) [32] towards the degradation of anionic dyes to boost the scope of the catalyst. MO an anionic azo dye, widely used as an acid-base indicator as well as colorant mainly for wool and silk was chosen for this purpose. To our surprise under similar conditions as applied for MB, com-
plete degradation of MO was achieved within a few seconds. To obtain a complete UV profile for degradation of MO, the concentration of SB was further reduced to $2 \times 10^{-6}$ M and the time-dependent degradation pattern is shown in Fig. (5).

![Graph](image1)

**Fig. (3).** Degradation of MB in presence of PANI-Pd(OAc)$_2$ and SB at different pH.

![Graph](image2)

**Fig. (4).** Degradation of Rhodamine B using PANI-Pd(OAc)$_2$ and SB.

### 2.7. Catalyst Separation and Reusability

Easy separation and reusability of a catalyst are very important in terms of cost-effectiveness as well as environmental point of view. PANI-Pd(OAc)$_2$ was easily separated from the reaction mixture by simple centrifugation and reused after washing several times with water followed by acetone and air drying. The activity of the catalyst was checked for five consecutive cycles and the result is shown in Table 2.

It was noticed that the activity of the catalyst after 1$^{st}$ cycle reduced to some extent then it became constant for the next three cycles and once again reduced after the fourth cycle. ICP-AES analysis for the fresh catalyst and the used catalyst after 1$^{st}$ cycle show a decrease in palladium content by 5%. Moreover, the filtrate after the first cycle was treated with MB and SB in absence of any fresh catalyst. Even after 180.0 min, no appreciable decrease in the absorption of MB at 664 nm was observed. To get further insight into the reduced activity of the recovered catalyst, catalyst after 1$^{st}$ cycle and 4$^{th}$ cycle was analyzed by TEM (Fig. 6). TEM analysis of the recovered catalyst after the first cycle showed the presence of Pd-nano particles of average size of 20-25 nm. The decrease in the catalytic activity of the catalyst after first cycle may be attributed mainly to the different nature of the active catalytic species of fresh (e.g. Pd(II)) and recovered (e.g. Pd(0)) catalyst species. The catalyst after the 4$^{th}$ cycle showed considerable agglomeration of the palladium particles (40 nm). The decrease in the activity of the catalyst after 4$^{th}$ cycle can be explained by the palladium agglomeration, small amount of active metal leaching along with catalyst poison by boron species/reduced MB deposition on the active metal sites and it needs more investigation.

### 2.8. Plausible Mechanism of the Reduction of the Dyes

As the recovered catalysts are showing presence of palladium (0) nanoparticles and can be useful in the reduction in next cycle, it is presumed that initially Pd(OAc)$_2$ gets reduced to Pd(0) in presence of NaBH$_4$ and water. Simultaneously due to $\pi - \pi$ stacking interactions of MB/MO and $\pi$-conjugation of PANI support, the local concentration of MB/MO near PANI supported Pd (0) nanoparticles as well as the proximity of MB/MO and active catalyst increases. Due to electron relay effect, BH$_4^-$ supplies high electron density to polyamine which in turn increases the electron density around palladium nanoparticles and facilitates the electron transfer to MB/MO and help to degrade the same via reduction [21] (Scheme 3). To establish the exact pathway of hydride or electron transfer, further investigation is required.

![Scheme](image3)

**Scheme 2.** Reduction of MO using PANI-Pd(OAc)$_2$ and NaBH$_4$. 

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3. MATERIALS AND METHODS

3.1. Materials

Pd(OAc)₂ was purchased from Aldrich and used as received. Aniline and other solvents were distilled before use. 5% Pd/C (50%) wet) procured from Hindustan Platinum. All other chemicals were procured from commercial sources and used as such without further purification.

3.2. Methods

The UV-vis absorption spectra were measured at room temperature on INTECH spectrophotometer using solutions in 1 cm quartz absorption cell. The particle size of the Pd(0) samples was observed on a JEOL JEM-2100 transmission electron microscopy (TEM). ICP-AES analyses are performed using an IRIS Intrepid II XDL ICP-AES (Thermo Electron Corporation).

4. EXPERIMENTAL

4.1. Preparation of Polyaniline Base (PANI)

Freshly distilled aniline (9.8 g, 106 mmol) was added to water (750 mL) containing concentrated H₂SO₄ (30 mL) and the solution was kept under continuous stirring at 0°C. To this solution, ammonium persulfate (24 g, 106 mmol) in water (250 mL) was added drop-wise over 4 h. The precipitated polyaniline-sulfate salt was recovered by filtration, and the precipitate was washed with a copious amount of water followed by acetone. Thus obtained polyaniline-sulfate salt was stirred for 12 h at ambient temperature with 1 N sodium hydroxide solution (1000 mL) and filtered, washed with water, followed by acetone and dried under vacuum at 50-60°C to afford de-protonated polyaniline base (8.37 g, PANI).

4.2. Preparation of PANI-Pd(OAc)₂

PANI-Pd(OAc)₂ was synthesized according to a published report [25].

PANI (500 mg) was charged into a round-bottomed flask containing an acetonitrile solution (40 mL) of palladium acetate (500 mg) and stirred under a nitrogen atmosphere for 48 h. The resultant catalyst was filtered off and washed with acetonitrile followed by acetone. The residue was dried in air for 24 h to afford the black catalyst (600 mg). The amount of palladium was measured by ICP-AES (Pd 0.35 mmolg⁻¹).

4.3. Catalytic Degradation Process

In a representative degradation experiment, 5 mg of PANI-Pd(OAc)₂ and an aqueous solution of NaBH₄ (2 ml, 2 × 10⁻⁶ M) were rapidly added one by one into an aqueous solution of MB (2 ml, 1.5 × 10⁻⁵ M). The whole mixture was then subjected to UV-vis spectral analysis at room temperature. The concentrations of MB were quantified by...
measuring the absorption intensities at $\lambda_{\text{max}}$ 664 nm. Similarly, catalytic degradation of Rhodamine B and MO was performed and monitored the absorption intensities at $\lambda_{\text{max}}$ 550 nm and 465 nm, respectively.

**CONCLUSION**

Polyaniline supported palladium catalyst showed excellent catalytic activity in the reductive degradation of cationic dye (MB, Rhodamine B) as well as an anionic dye (MO) in presence of SB. Degradation was achieved within a few minutes under an ambient condition which makes this process labour and energy efficient. The catalyst can be easily separated from the reaction medium and recycled for several cycles with slightly diminished activity mainly attributed to the catalyst agglomeration which again attributes to the cost-effectiveness of the process. A better activity of the PANI-Pd(OAc)$_2$ in comparison with commercially available palladium on carbon indicative of the fact that the role of polyaniline is not merely confined to securely holding the palladium but also participate in the catalytic cycle. This opens the opportunity to develop polyaniline supported palladium as an industrially viable option for wastewater treatment.

**CONSENT FOR PUBLICATION**

Not applicable.

**CONFLICT OF INTEREST**

The authors declare no conflict of interest, financial or otherwise.

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