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Polyaniline Immobilized Palladium: An Efficient Catalyst for Reductive Degradation of Dyes

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ABSTRACT

Water remediation is a very challenging task and a need of the hour. Various industrial pollutants, primarily organic synthetic dyes, mix with ground water and have a negative impact on aquatic life. There are various techniques available to treat the polluted water. Reductive degradation of organic dyes is one of the most commonly used techniques. Herein, the catalytic degradation of a diversified range of dyes (cationic dyes and anionic dyes) using a polyaniline anchored palladium (PANI-Pd) catalyst in the presence of sodium borohydride (SB) is discussed in detail. PANI-Pd is easy to recover and efficiently recycle with minimum loss of activity. It was found in the study that the PANI-Pd $(OAc)_2$ catalyst is highly active in the reductive degradation of both cationic (MB) and anionic dye (MO). Furthermore, reaction time is also very short.

Keywords: *Dye degradation; Polyaniline; Palladium; Heterogeneous; Catalyst*

INTRODUCTION

Synthetic organic dyes liberated into waterbodies by a number of production companies such as clothing material, pulp and paper, pharmaceutical, agrochemicals and processed food are causing damages to aquatic life and in turn harming all other living organisms. Research suggests that most of these dyes are non-biodegradable, highly stable, toxic and carcinogenic. Some even cause reduced photosynthesis in plants (Weerasekara, 2017; Wong *et al.*, 2004; Gupta, 2009).

In view of the adverse effect of water pollution on mankind, pollution control agencies across the nation have enacted stringent legislation to control the permissible limit of such entities in the discharged effluent. To meet these regulatory guidelines, such hazardous chemicals, need to be controlled below a ppm (parts per million) level in the effluent.

Different techniques are employed for the complete or partial removal of these pollutants from the wastewater. These are broadly divided into the following types: physical methods like adsorption, coagulation; chemical methods utilizing both oxidation (by O_2, NaOCl, O_3, H_2O_2etc.) (Singh & Arora, 2011), and reduction (by $Na_2S_2O_4$) (Li *et al.*, 2009), biological methods (Sudarjanto, Keller-Lehmann & Keller, 2006) and photochemical methods (Van der Zee & Villaverde, 2005). Diversified metal based catalysts (e.g. Au, Ag, Pt and Pd) are found to be extremely powerful towards reductive degradation of organic colorant molecules as metal can participate in the electron transfer process between $NaBH_4$ and pigments (Gupta, Singh & Sharma, 2011; Mallick, Witcomb & Scurrell, 2005; Khan, Lee & Cho, 2014).

Heterogeneous palladium-based catalysts demonstrated very efficient reductive degradation of different dye molecules as palladium is inherently highly active in reduction reactions. Moreover, being heterogeneous offers the added advantages of easy recovery and recyclability (Hu *et al.*, 2007; Wang *et al.*, 2009; Li *et al.*, 2015; Patra *et al.*, 2016).

Polyaniline (PANI) which is a conducting polymer, has very interesting properties such as inert nature, easy to prepare from readily available aniline, insolubility in common organic solvents as well as water, extensive N=N and NH-NH functional groups and modular redox nature. All these qualities make PANI a good support for anchoring active metal catalysts (Choudary *et al.*, 2006). By utilizing these properties of PANI, several different metal catalysts were immobilized. PANI and their catalytic properties are explored in various types of coupling reactions as well as oxidation, reduction, etc. (Choudary *et al.*, 2006). Herein, PANI-Pd is explored for the degradation of different organic dyes, e.g. Methylene blue, methyl orange, etc. (Roy *et al.*, 2019) under a reductive environment.

METHODOLOGY

All the chemicals were purchased from commercial sources and used, except Aniline which was distilled before use. Particle size was analyzed by Transmission electron microscopy (TEM) and Pd content of the catalyst was analysed by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Synthesis of Polyaniline Base (PANI)

To a solution containing concentrated H_2SO_4 (30mL) in water (750mL), purified aniline (9.8 g, 106 mmol) was added and the solution was stirred continuously at 0°C. Ammonium persulfate (24 g, 106 mmol) in water (250 mL) was added slowly within 4 h to the solution so obtained. Polyaniline-sulfate salt was recovered by filtration and it was washed with ample water followed by acetone. Then 1000 mL 1N sodium hydroxide solution was added to polyaniline-sulfate salt and stirred for 12 h at 25-30°C. Finally, it was filtered, washed with water, followed by acetone and dried under reduced pressure at 50-60°C to obtain 8.37 g of PANI as black solid powder.

Synthesis of PANI- Pd(OAc)$_2$

PANI (500 mg) was added to a solution of palladium acetate (500 mg) in acetonitrile (40 mL) and agitated under an inert environment for 2 days. The solid so obtained was filtered and washed with acetonitrile and acetone respectively. Wet catalyst was dried for almost 1 day to afford PANI-Pd(OAc)$_2$ (600 mg). The catalyst was subjected ICP-AES analysis to get the palladium content (Pd 0.35 mmolg^{-1}).

Catalytic degradation of dyes

Estimated quantities of dye, $NaBH_4$, and catalyst were mixed in water and decrease in absorption of the dye was monitored by UV-vis spectrophotometer at the λmax of the dye.

RESULTS AND DISCUSSION

Study of catalytic degradation process

A typical degradation experiment was performed by adding 5 mg of PANI-Pd(OAc)$_2$ and aqueous solution of $NaBH_4$ (2ml, 2×10^{-6} M) rapidly into an aqueous solution of MB (2ml, 1.5×10^{-5} M). The resultant solution was then subjected to UV–vis spectral analysis at ambient temperature. The absorption intensities at λmax664 nm were monitored to estimate the concentrations of methyl orange. At the same time, catalytic degradation of Rhodamine B and MO were also studied by measuring the absorption intensities at λ_{max}550 nm and 465 nm respectively.

Study of catalytic degradation of Methylene Blue (MB)

To explore the catalytic activity of PANI-Pd(OAc)$_2$ in the reduction of dyes, MB was chosen as a representative example because it is widely used as colorant for fabric and related material and cause of wide spread aquatic pollution. Reaction between MB and PANI-Pd(OAc)$_2$ is summarized in figure1.

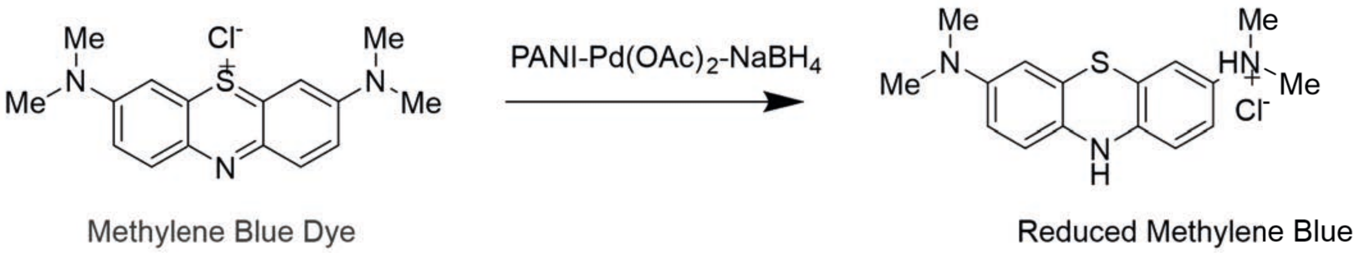

Figure 1: Reduction of MB in presence of PANI-Pd(OAc)$_2$ and SB

Optimization of the reaction condition was carried out by using various concentrations of SB while keeping MB concentration set at 2 x 10^{-6} M. It was found that at higher concentration of SB (1 x 10^{-4} M, 4 x 10^{-5} M, 2 x 10-5 M) and 5 mg of catalyst reaction was very fast and became difficult to follow properly. Finally, the SB concentration was optimized to be 1.5 x 10^{-5} M. Figure-2(a) depicts the decrease of absorption intensity of MB at 664 nm with time. The degradation process was observed to be complete within 8 min.

Control experiments were also carried out using SB or PANI-Pd$(OAc)_2$or PANI alone failed to reduce the dye (Figure-2 (b) , (c) & (d)).

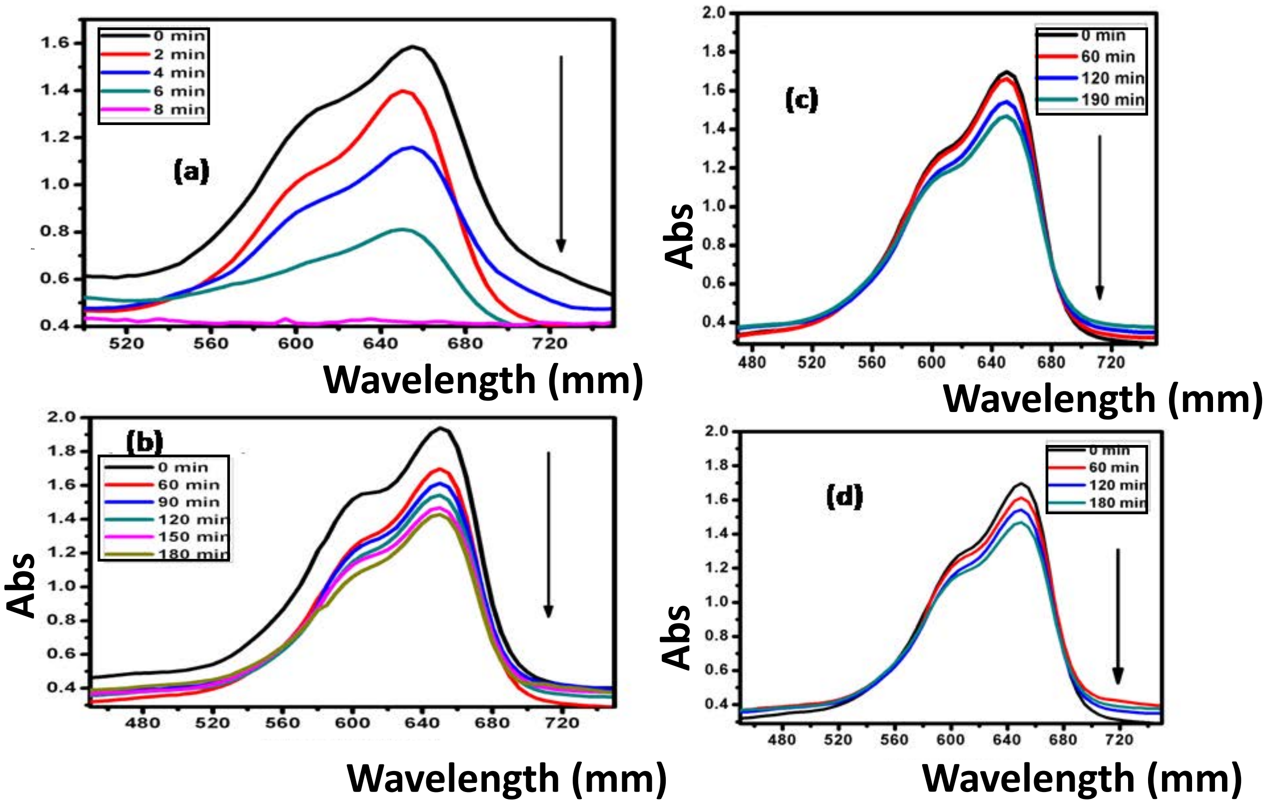

Figure 2: a) Degradation of MB in presence of PANI-Pd$(OAc)_2$ and SB; b) Degradation of MB with SB only; c) Degradation of MB with PANI-Pd$(OAc)_2$ only; d) Degradation of MB with SB and PANI-Base

The efficiency of the catalyst was also compared with homogeneous counterpart i.e. Pd$(OAc)_2$. It took five minute for the degradation of MB when treated with Pd$(OAc)_2$ (0.08 mg, corresponding to 5.0 mg PANI-Pd(OAc_2). In the process precious palladium became non recoverable. Moreover, addition of another lot of MB and SB to the reaction mass lead to very slow degradation of MB and it was incomplete even after 3h. Agglomeration of Pd particles to form inactive palladium black could be the reason behind this phenomenon.

MB was also reacted with 5% Pd/C (50% wet, 5.0 mg) keeping all the reaction condition same. The absorption of MB measured at λmax 664 nm ceased to zero after 30 min where as it took only 8.0 min for the PANI-Pd$(OAc)_2$. Superior catalytic efficiency of PANI-Pd$(OAc)_2$ over Pd$(OAc)_2$ or Pd/C highlights the positive effects of PANI by facilitating the e^- transport between borohydride, Pd and MB with the help of its elaborative π-elctron network. Moreover, its extended –NH=N- functional moieties as well as quinoid-benzenoid structure might be helping to bring all the reacting species such as MB, $NaBH_4$ and Pd in close enough required for the reaction by H-bonding and or acid-base interaction. Detailed studies are needed to comment on the precise function of the PANI in the catalytic system.

Study of catalyst loading

The effect of the catalyst concentration was thoroughly checked by means of three experiments using

3.0 mg, 5.0 mg and 10.0 mg of catalysts maintaining fixed proportion of MB and SB (2×10^{-6}: 1.5×10^{-5}) at ambient temperature (~25°C). Degradation of MB was monitored spectroscopically by intensity drop in the absorption at λmax 664 nm (Table-1). Higher loading of catalyst afforded faster degradation which could be attributed to the availability of more active palladium molecules.

Table 1: Consequence of different concentration PANI-Pd(OAc)$_2$ on reduction of MB in presence of SB

Quantity of PANI-Pd(OAc)2 (mg)	Time taken for complete degradation (sec)
3	1800
5	480
10	60

Study of pH

At different pH values the degradation of MB was studied using the MB at 2×10^{-6} M, and SB at 1.5×10^{-5} M at room temperature ~ 25°C. pH of the reaction mixture was maintained with controlled addition of HCl (0.1 N) and NaOH (0.1 N) respectively. Without any interference pH of the reaction mass was recorded to be 8.7. Figure-3 clearly shows the variation of degradation rate with pH (Choi *et al.*, 2016).

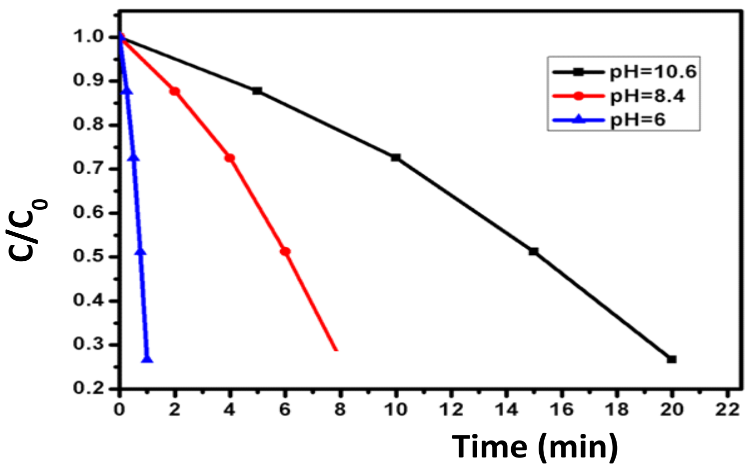

Figure 3: Degradation of MB with PANI-Pd(OAc)$_2$ and SB at various *p*H

Study of reductive degradation of methyl orange (MO)

The degradation of anionic dye using PANI-Pd(OAc)$_2$ catalysts was also investigated (figure 4) (Mondal, Adhikary & Mukherjee, 2015).

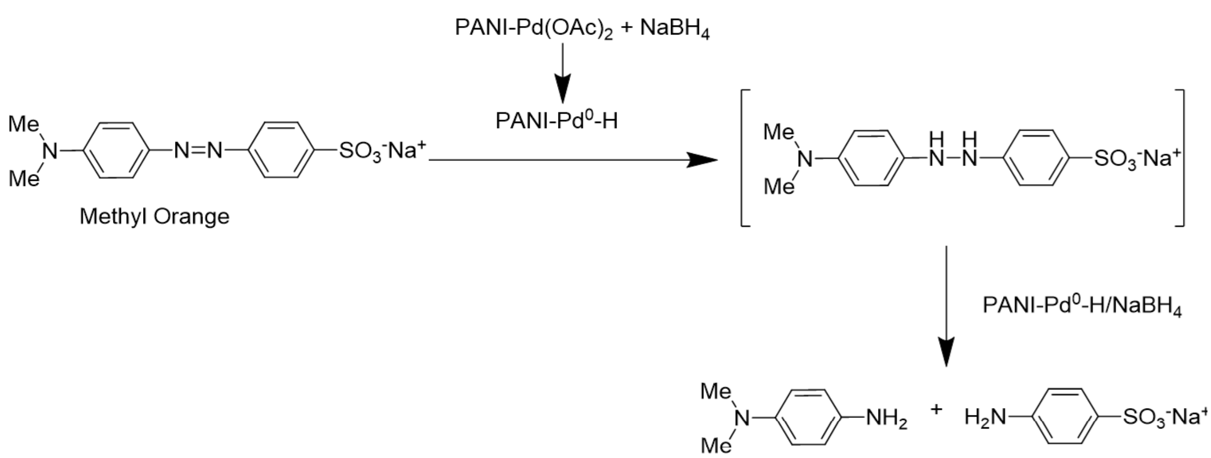

Figure 4: Reduction of MO using PANI-Pd(OAc)$_2$ and NaBH$_4$

MO was chosen for this purpose as it has wide application as indicator in acid-base chemistry as well as colorant mainly for wool and silk. As the degradation of MO was very fast under identical condition for MB, concentration of SB was reduced significantly (2 X 10^{-6}) to capture the entire UV-picture of the degradation of MO. Decrease in the absorption of MO over time is depicted in Figure 5.

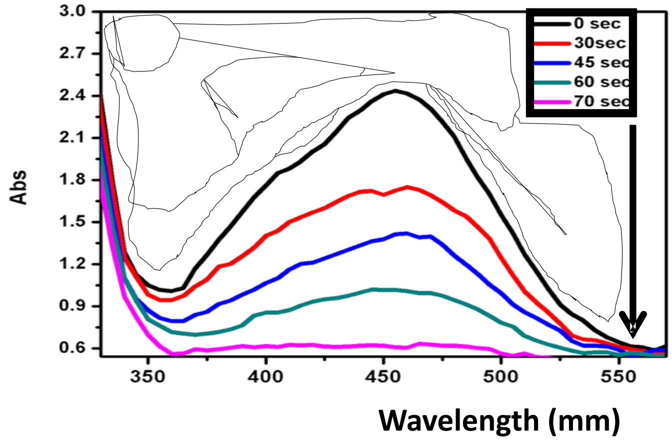

Figure 5: Degradation of MO in with PANI-Pd(OAc)₂ and SB

Study of catalyst recovery and recyclability

PANI-Pd$(OAc)_2$ catalyst was recovered by simple centrifugation technique after completion of reaction. It was then thoroughly washed with water followed by acetone and dried in air. Five consecutive cycles were performed using used catalyst obtained after each cycle and the result is shown in Table-2.

Table 2: Reusability of PANI-Pd(OAc)₂ in reductive degradation of MB

No of use	Time taken for complete degradation (min)	Palladium concentration (mmolg^{-1})
1st	8	0.35
2nd	15	0.33
3rd	17	n.d.*
4th	17	0.32
5th	28	n.d.*

** n.d.: Not determined.*

Catalytic activity after the first cycle was decreased and then it remained constant for the next three cycles. Finally, after the fourth cycle, the activity was found to be considerably reduced. Leaching of active Palladium was found to be nominal (From ICP-AES analysis, it is evident there is a decrease in palladium content by 5% for the used catalyst after 1st compared to the fresh catalyst) and the filtrate obtained after first use did not exhibit any catalytic activity towards reduction of MB after addition of SB. TEM analysis (Figure 6) of the recovered catalysts showed the formation of Pd-nanoparticles and repeated use led to agglomeration of the same (20-25 nm vs.>40 nm after the 4th cycle). Reduction in the catalytic activity probably due to different nature of palladium in fresh (Pd(II)) and recycled catalyst(Pd(0)). Moreover, agglomeration of Pd-nanoparticles along with deposition of B related materials and or degraded dye compounds on the catalytically active Pd made the catalyst less effective after the 4th recycle.

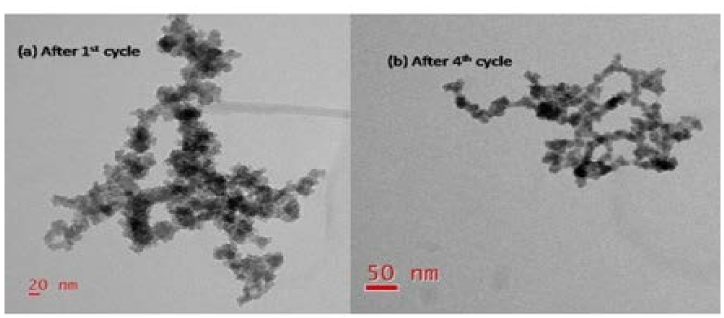

Figure 6: TEM photograph of PANI-Pd after first and fourth use

CONCLUSION

The PANI-Pd$(OAc)_2$ catalyst was discovered to be extremely active in the reductive degradation of both cationic (MB) and anionic dye (MO). In addition, the reaction was completed within a very small span of time, e.g., less than a few minutes. Easy recovery and recyclability offer further opportunities for larger applications.

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