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# Catalytic Reductions of Organic Dyes Eosin Y and Methylene Blue Using Graphene Oxide Supported With Pd Nanoparticles as Catalyst

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**A B S T R A C T**

Graphene oxide supported Pd nanoparticles was synthesized by adopting simple and an ecofriendly approach. The obtained GO-supported Pd nanoparticles was characterized by Raman spectroscopy, scanning electron microscopy with energy dispersive x-ray analysis (SEM-EDAX) and transmission electron microscopy (TEM) analyses. The synthesized GO-supported Pd nanoparticles were used as catalysts for reductive degradation of organic dyes in an aqueous medium. The reduction reaction was followed by pseudo first order experimental conditions. The reductive degradation product was monitored by UV-Visible spectroscopy. The rate constant values were also calculated. Eosin y dye was found to degrade in a better then the Methylene blue dye.

**Keywords:** Graphene oxide, Pd nanoparticles, catalyst, reduction, Eosin y, Methylene blue

**A R T I C L E I N F O**

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## 1. Introduction

In recent years, chemical conversion was extensively carried out using metal nanoparticles as catalyst [1-4]. Metal nanoparticles have several advantages in the following fields such as electronics, photonics, filters, sensors, catalysis, information storage, and surface enhanced Raman scattering (SERS), because of the low dimensions [5-9]. Small sized particles offer several beneficial effects compared to the bulk catalysts by

providing high surface to volume ratio per particle. The unusual structural modifications and number of active sites variations enhance the catalytic performances. The recent development in the preparation methods of metal nanoparticles show that the, colloidal method of synthesis alters the morphology and size of the nanosized particles extensively in the presence of a stabilizing agent like PVA, PVP and other PEG polymers. Long term usages are limited in nanoparticles because of the lower stability of nanoparticles which tend to agglomeration of nanoparticles. In order to overcome these drawbacks graphene and graphene oxide utilized as support materials for nanoparticles. Graphene is a 2D carbon material with single atomic thickness and with hexagonally arranged sp2 carbon atoms. Carbon based matrix material is one of the promising solution for the next generation due to its low preparation cost, high surface area and unique graphene oxide basal plane showing high conductivity [10-13]. Thus, graphene is considered suitable for the dispersion of catalytically active metal nanoparticles (NPs) and to act as good support for heterogeneous catalytic processes. Graphene supported monometallic NPs composites have been widely studied, and a strong metal-graphene interaction was also revealed and might contribute to the enhanced catalytic performances of supported monometallic nanoparticles [14, 15].

Water contamination by aqueous dye effluents from industries, has become a serious environmental issue since a decade time. Most of the dyes are toxic and carcinogenic, in nature. Also, some of the dye pollutant significantly affects the photosynthetic activity of aquatic life. Dyes are generally resistant to aerobic digestion, and therefore treating wastewaters containing dyes is a complex task [16-19]. Therefore in this present study, the graphene oxide supported Pd nanoparticle as catalysts was synthesized by chemical reduction method and used for the catalytic reductive degradation of organic dyes an aqueous medium. The size and shape of the synthesized Pd nanoparticles are characterized using various techniques. Further Eosin y and Methylene blue as a model dyes are chosen and the kinetics of the reductive degradation was followed.

## 2. Experimental

### Materials

Graphite powder (SRL), Polyvinyl pyrrolidone (SRL), Potassium tetrachloropalladate (Alfa aesar), Methylene blue and Eosin y (SRL), Sodium borohydride (SRL), Ethanol (SRL), Double distilled water were analytical grade of 99% purity and used as received.

**Preparation of graphene oxide supported Pd nanoparticles**: Graphene oxide was prepared from graphite precursors using hummer's method. Typically 60 mg of polyvinylpyrrolidone and 0.05 mM Potassium tetrachloropalladate was added into 5 mg of sonicated (30 minutes) graphene oxide aqueous solution at room temperature. The mixture was continuously stirred for 24 hours at room temperature. Then 0.1mM freshly prepared sodium borohydride was added into the solution by drop wise. Further the reaction was stirred 15 minutes. Finally the solid product from the solution was collected, by washing with water and ethanol. The product was dried in vacuum oven at 70˚C.

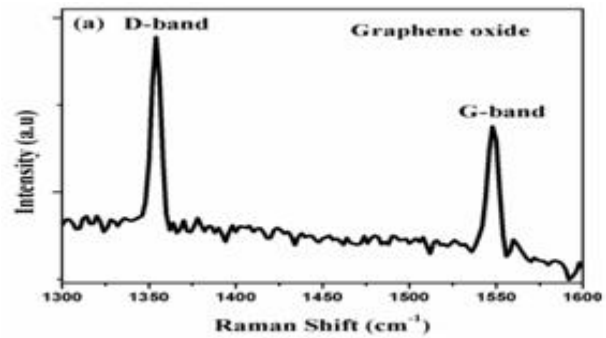


**Figure 1a:** Raman spectrum of Graphene oxide

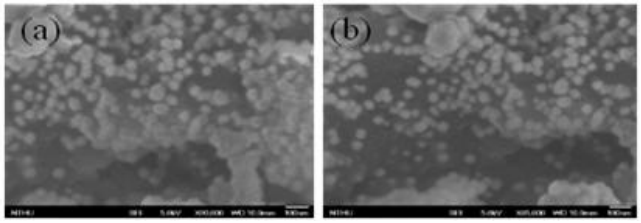


**Figure 2a, b:** SEM images of GO-Pd nanoparticles

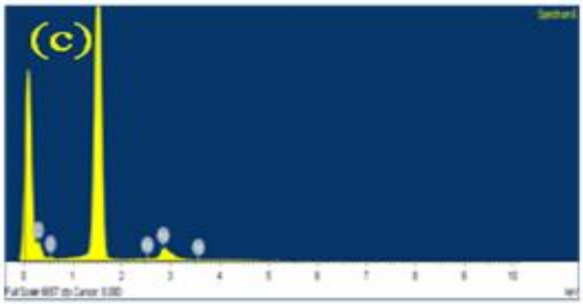


**Figure 2c:** EDAX spectrum of GO-Pd nanoparticles

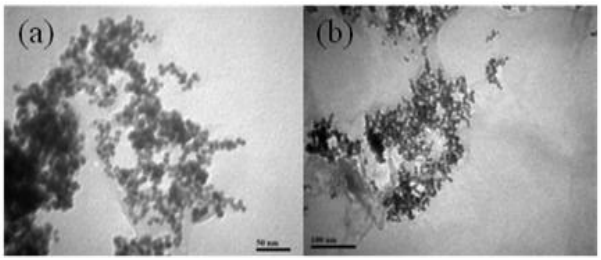


**Figure 3a, b:** TEM images of GO-Pd nanoparticles

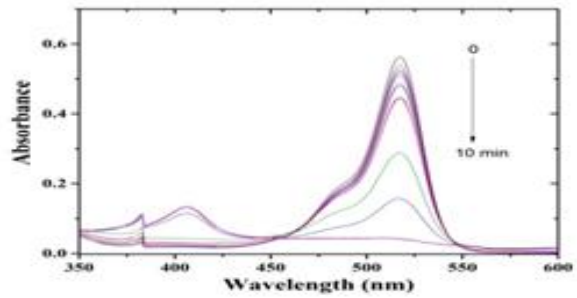


**Figure 4a:** Reductive degradation of Eosin y using GO-Pd nanoparticles at $25^0$ C

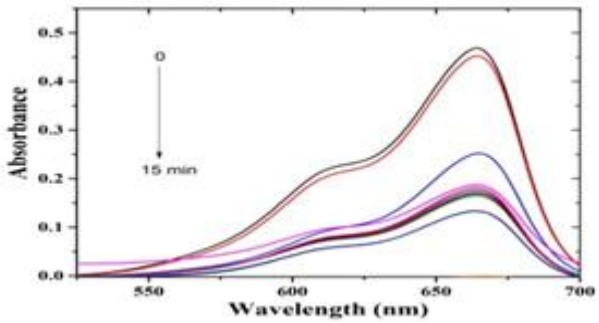


**Figure (4b):** Reductive degradation of Methylene blue using of GO-Pd nanoparticles at $25^0$ C

**Table 1:** the overall pseudo first order rate coefficient values for the Eosin y reductive degradation by GO-Pd NPs in various cycles of reactions

| Catalyst | Kobs x $10^{-3}S^{-1}$ |
|---|---|
| GO-Pd NPs | 4.23 |
| 1st cycle | 3.75 |
| 2nd cycle | 3.57 |
| 3rd cycle | 3.25 |

**Table 2:** the overall pseudo first order rate coefficient values for the Methylene blue reductive degradation by GO-Pd NPs in various cycles of reactions

| Catalyst | Kobs x $10^{-3}S^{-1}$ |
|---|---|
| GO-Pd NPs | 4.07 |
| 1st cycle | 3.54 |
| 2nd cycle | 3.25 |
| 3rd cycle | 3.07 |

## 3. Results and Discussion

The Fig.1a shows the Raman spectra of graphene oxide with the D band around 1354 $cm^{-1}$ and G band around 1549 $cm^{-1}$ graphene oxide was confirmed. The surface morphology of GO supported Pd nanoparticles has been investigated by scanning electron microscopy is shown in Fig.2 (a, b). It is clearly seen that Pd nanoparticles are deposited uniformly over the graphene oxide. Fig.2c shows the EDAX spectrum of GO-Pd nanoparticles which also confirms the presence of nanoparticles and stabilizing agent. The EDAX results shows 74.14 wt% of Pd, 18.46 wt% of C, 7.40 wt% O were present in the prepared catalyst. The C and O in the EDAX spectrum confirm the presence of PVP and graphene oxide. PVP act as a stabilizing agent for the nanoparticles to control the agglomeration. The TEM images of GO supported Pd nanoparticles with low and high magnifications are shown in Fig.3 (a, b) respectively. The images clearly show that the GO-Pd nanoparticles are evenly coated on graphene oxide. A further TEM images shows the GO supported Pd nanoparticles are spherical shape and the nanoparticles size is around 10 nm. The Fig.3 (a, b) results are in good agreement with TEM images for the formation of GO supported Pd nanoparticles.

**Reaction Catalysis:**

The synthesized graphene oxide supported Pd nanoparticles further examined for the catalytic reductions of organic dyes in the presence of sodium borohydride in an aqueous medium. The reduction reaction was monitored using UV-visible spectroscopy. Fig 4a shows the UV-Visible spectrum of reductive degradation of Eosin y in the presence of GO-Pd catalyst at various time intervals, there was a gradually decrease with 10 minutes the intensity of absorption peak maximum observed at 530 nm due to reduction of Eosin y dye. Fig. 4b shows the UV-Visible spectrum of reductive degradation of methylene blue in the presence of GO-Pd catalyst the intensity of the absorption peak gradually decreased within 15 minutes at 664 nm shown in Fig 4b. These results observed the dyes are completely reduction only in the presence of graphene oxide supported Pd nanoparticles catalyst. The observed overall rate constant for the reduction reaction for Eosin y is presented in table 1 and for Methylene blue in table 2**.** Finally the recyclability of graphene oxide supported Pd nanoparticles catalyst also evaluated and the rate constant of the reaction was found to be almost equal and given in table 1 Eosin y and table 2 Methylene blue. Therefore, the synthesized graphene oxide supported Pd nanoparticles are potent recyclable nanocatalyst for the environmentally pollutant degradations applications.

## 4. Conclusion

We have successfully synthesized the graphene oxide supported Pd nanoparticles as catalyst by simple chemical reduction method. The synthesized of GO-Pd nanoparticle catalyst were characterized by Raman analysis, SEM-EDAX and TEM techniques. The GO-Pd nanoparticles catalyst show more efficient and excellent catalytic activity towards the reductions of organic dyes in aqueous medium. After several cycles of reaction the catalyst possess the same activity. Therefore GO-Pd nanoparticles catalyst is more efficient for the reduction of environmental pollutant.

## 5. Acknowledgment

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