DOI: 10.1002/aoc.5123

FULL PAPER

WILEY Applied Organometallic Chemistry

Application of palladium nanoparticle-decorated *Artemisia abrotanum* extract-modified graphene oxide for highly active catalytic reduction of methylene blue, methyl orange and rhodamine B

Mirmehdi Hashemi Salehi¹ | Mohammad Yousefi² | Malak Hekmati¹ | Ebrahim Balali¹

¹Department of Organic Chemistry, Faculty of Pharmaceutical Chemistry, Tehran Medical Sciences, Islamic Azad University, Tehran, Iran

²Department of Chemistry, Yadegar-e-Imam Khomeini (RAH) Shahr-e-Rey Branch, Islamic Azad University, Tehran, Iran

Correspondence

Mohammad Yousefi, Department of Chemistry, Yadegar-e-Imam Khomeini (RAH) Shahr-e-Rey Branch, Islamic Azad University, Tehran, Iran. Email: myousefi50@hotmail.com A green palladium-based catalyst supported on *Artemisia abrotanum* extractmodified graphene oxide (Pd NPs/RGO-*A. abrotanum*) hybrid material has been used as a recoverable and heterogeneous nanocatalyst for the catalytic reduction of various dyes, including methylene blue, methyl orange and rhodamine B, in the presence of NaBH₄ as reducing agent in aqueous medium at room temperature. With the help of UV–visible spectroscopy, the catalytic reactions were investigated. According to the results, these reactions followed the pseudo-first-order rate equation.

KEYWORDS

Artemisia abrotanum, dyes, graphene, palladium nanoparticles, reduction

1 | INTRODUCTION

In recent years, the utilization of supports in the process of producing nanoparticles (NPs) has attracted much attention. The supports prevent agglomeration of NPs and increase their stability and efficiency. The resulting heterogeneous catalysts have many advantages over homogeneous metal catalysts, such as ease of handling, simple work-up and recyclability.^[1,2] Therefore, many researchers are trying to develop a simple and green method to produce heterogeneous nanocatalysts.

Graphene oxide (GO) and reduced graphene oxide (RGO) are a new class of promising and efficient supports and catalysts, which have been considered by many scientists.^[3–7] GO is a two-dimensional material derived from graphene sheets with a large number of oxygen-containing functional groups such as epoxy, hydroxyl and carboxylic groups (Figure 1).^[8] GO has useful

properties such as thermal and chemical stability, large specific surface area, high mechanical strength, water solubility and electron conductivity.^[9–11]

The presence of organic dyes in wastewaters provides more chemical oxidation and therefore leads to severe rancidity.^[12] Azo dyes are able to show colour in wastewaters even at small concentrations.^[13] They contain N=N double bonds and belong to the synthetic organic dyes and due to their weak dissociation, high toxicity and long durability are considered as the main pollutants of effluent of the textile, leather, wood, paper and cosmetic industries.^[14] Therefore, degradation of these dyes from wastewater is very important. Adsorption,^[14-18] coagulation^[18-20] and membrane filtration^[21] are some conventional methods for treatment of wastewaters containing azo dyes. The main drawback of these methods is that the nature of the pollutant is maintained after treatment. The prominent point of the method used in 2 of 6 WILEY Organometallic Chemistry



FIGURE 1 TEM image of Pd NPs/RGO-A. abrotanum nanocatalyst

the research reported here (catalytic reaction) is degradation of a dye during a reaction and therefore the nature of the pollutant will change and it is converted to a compound which is not harmful to the environment.

As azo dyes are difficult to degrade into non-toxic compounds, diverse treatment methods have been developed, such as physical and chemical reduction,^[22] adsorption and oxidation. Among all solutions, catalytic reduction has exhibited the highest efficiency. While most catalysts have been nanosized and composed of Ag, Pt, Pd and Au noble metals,^[23] Ag NPs have attracted more attention due to their unique characteristics and applications.

Artemisia abrotanum L. has traditionally been utilized for pharmaceutical purposes in treating certain diseases, like upper airway disorders.^[24] The polyphenols and flavonoids that are contained within *A. abrotanum* mean that this herbal extract has the potential to be used in a wide range of applications.

In terms of multiple features of graphene stated above, we have introduced a simple green synthetic method to a Pd NPs–graphene hybrid with *A. abrotanum* leaf extract as both reductant and stabilizing agent.^[25] Firstly, the extract can effectively reduce GO and adsorb on the RGO surface. Next, the adsorbed *A. abrotanum* leaf biomolecules can additionally reduce Pd ions *in situ* to Pd NPs and cause their stabilization.

The application of the thus produced hybrid material (Pd NPs/RGO-*A. abrotanum*) as an efficient and heterogeneous nanocatalyst was investigated for catalytic reduction of various dyes, namely methylene blue (MB), methyl orange (MO) and rhodamine B (RhB), in the presence of NaBH₄ as reducing agent.

2 | EXPERIMENTAL

2.1 | Preparation of Pd NPs/RGO-A. *abrotanum* nanocatalyst

In order to synthesize Pd NPs/RGO-*A. abrotanum*, the *A. abrotanum* extract was added to GO (100 mg) and sonicated for 20 min. Then, the reaction mixture was refluxed with agitation for 2 h. The colour of the mixture changed from light brown to black, indicating the reduction of GO, which was stable. The RGO was separated via centrifugation, after cooling to ambient temperature. Following rinsing, 30 ml of 0.3 M Na₂PdCl₄ under agitation was added dropwise into the mixture at 100°C for 24 h. The final Pd NPs/RGO-*A. abrotanum* was isolated by centrifugation, and washed three times with deionized water. It was next used for assessment and catalysis research. The amount of Pd in Pd NPs/RGO-*A. abrotanum* was 0.18 mmol g^{-1} as measured using inductively coupled plasma atomic emission spectrometry (ICP-AES).

2.2 | Procedure of reducing organic dyes using Pd NPs/RGO-A. abrotanum nanocatalyst

At first, 2.0 mg of the Pd NPs/RGO-*A. abrotanum* nanocatalyst was added into 5 ml of 10 ppm organic dye (MB, MO or RhB) solution and stirred at room temperature. Then, 1 ml of newly prepared NaBH₄ solution (0.1 M) was added to the reaction mixture. Time-dependent UV-visible spectra of the organic dyes were obtained and the change in absorption intensity was recorded at λ_{max} . After disappearance of the colour of the solution, the catalyst was separated by centrifugation, then washed with EtOH-H₂O, dried and reused.

3 | RESULTS AND DISCUSSION

The Pd NPs/RGO-*A. abrotanum* nanocatalyst was synthesized in one step by reducing Pd(II) ions and GO with the extract of *A. abrotanum* as a stabilizer and reducing agent (Scheme 1). In this study, it is assumed that the presence of phenols and acid compounds in the extract results in bio-reduction and stabilization of Pd NPs without using toxic ingredients and toxic organic solvents.

Transmission electron microscopy (TEM) and energydispersive X-ray (EDX) analysis were used to characterize the nanostructure of Pd NPs/RGO-*A. abrotanum* that was prepared based on our earlier report.^[25] The image corresponding to the nanocatalyst (Pd NPs/RGO-*A. abrotanum*) at 200 nm indicated that the Pd NPs are well distributed on the surface of RGO. The results showed



SCHEME 1 Fabrication pathway of Pd NPs/RGO-*A. abrotanum* nanocatalyst

that the *A. abrotanum* extract plays a key role in enhancing the dispersibility of Pd NPs (Figure 1). Most of the particles are in the range 10–20 nm. Furthermore, the presence of biomolecules of the extract on the surface of graphene and Pd NPs was proved using EDX analysis, which confirmed the existence of C (88.3%), N (1.1%, O (9.4%) and Pd (1.2%) as shown in Figure 2.

After characterizing the prepared Pd NPs/RGO-A. *abrotanum* nanocatalyst, its catalytic efficiency was investigated in the reduction reactions of MB, MO and RhB in the presence of NaBH₄ as reducing agent. To investigate the catalytic reduction reactions, a UV–visible spectrophotometer was used. It is known that organic dye pollutants, for example MB, MO and RhB, are released from various industries and are toxic and dangerous environmental pollutants. Therefore, nowadays the development of efficient and reliable methods for catalytic reduction of these organic dye pollutants is an important requirement.

The Pd NPs/RGO-*A. abrotanum* nanocatalyst was used to catalyse the degradation of organic dyes. The colour of the solution disappeared quickly, indicating the success of the degradation process. The reduction reaction process was monitored using UV-visible spectroscopy. Figure 3 displays the time-dependent UV-visible absorption measurements of azo dye reduction reactions. Determination of the reaction progress was done through recording the reduction of the absorption intensity at λ_{max} of 465 nm (MO), 550 nm (RhB) and 660 nm (MB). The



FIGURE 2 EDX analysis of Pd NPs/RGO-A. abrotanum nanocatalyst

decrease of absorbance at λ_{max} was observed due to decolorization of the dyes. This indicates that functional groups of -N=N- (azo) as the chromophoric group in the organic dyes were reduced to -NH-NH-. The reduction reaction times for the organic dyes were completed at 40, 90 and 140 s for MB, RhB and MO, respectively. The initial concentration of NaBH₄ was high (more than 10³ times) and it remained constant during the reaction. Therefore, pseudo-first-order kinetics can be used for the rate constants the decolorization of these azo dyes and were followed from the kinetic equation: $\ln(C_t/C_0) = -kt$ (or $\ln(A_t/A_0)$), where C_t is the concentration at time *t*, C_0 is the initial concentration and *k* is the apparent rate constant (k_{app}) that was obtained as 0.049, 0.022 and 0.02 s⁻¹ for MB, RhB and MO, respectively.

The effect of temperature on the catalytic performance was investigated for the reduction of MB, MO and RhB at 25, 40 and 50°C, for which k_{app} was obtained (MB: 0.049, 0.058 and 0.072 s⁻¹; MO: 0.022, 0.03 and 0.042 s⁻¹; RhB: 0.02, 0.27 and 0.039 s⁻¹, respectively).

The possible mechanism of organic dye reduction using the Pd NPs/RGO-A. abrotanum nanocatalyst is described with an electron relay system. The Pd NPs start the catalytic reduction by relaying electrons from the donor BH_4^- to the organic dye molecules, where the nanocatalyst accepts electrons from BH_4^- ions and transports them to the dye molecules. In fact, when NaBH₄ is added to the reaction mixture, the hydride (H⁻) from BH_4^- may be surrounded by Pd NPs and adsorbed on their surface and it then transfers its electron to the Pd NPs. The hydrogen atom (H^{*}) formed from BH_4^- after electron transfer to the Pd NPs subsequently attacks a nearby dye molecule, and then electron transfer induced hydrogenation of the dye occurs spontaneously (Scheme 2).

Experiments to test the catalyst recyclability of the Pd NPs/RGO-*A. abrotanum* nanocatalyst were conducted to investigate its stability. So, the catalyst was separated by centrifuging from the reaction mixture. It showed no appreciable loss of catalytic performance during six cycles of the degradation of dyes. The yield of reaction after six uses was MB, 99 to 98%; MO, 99 to 97%; RhB, 99 to 97%. The amount of Pd in the reused Pd NPs/RGO-*A*.



FIGURE 3 UV-visible absorption spectral changes for the reduction process of (a) MB, (b) RhB and (c) MO by NaBH₄ in the presence of Pd NPs/RGO-*A. abrotanum* nanocatalyst and corresponding plots of rate constant



SCHEME 2 Possible mechanism of organic dye reduction catalysed by Pd NPs/RGO-A. abrotanum nanocatalyst in the presence of NaBH₄

abrotanum catalyst was 0.175 mmol g^{-1} (for fresh catalyst it was 0.175 mmol g^{-1}), which was measured using ICP-AES. These results show that the synthesized hybrid catalyst is a stable, effective and recoverable catalyst.

For an evaluation of the performance of the prepared catalyst, we have compared the apparent rate constant (k_{app}) for Pd NPs/RGO-*A. abrotanum* with those of some literature reports for the reduction of organic dyes MB,

TABLE 1Comparison of catalytic efficiency of Pd NPs/RGO-A. abrotanum catalyst with previous literature for the reduction of MB, RhBand MO

Organic dye	Catalyst	$k_{\rm app}~({ m s}^{-1})$	Ref.
MB	Ni/CPM-1 (0.5 wt% Ni, r.t.)	9.51×10^{-3}	[26]
MB	Fe ₃ O ₄ @polydopamine (1 wt% Ag, r.t.)	7.16×10^{-3}	[27]
MB	NiNTAs (33 mg l^{-1} , r.t.)	3.7×10^{-4}	[28]
MB	Pd NPs/RGO-A. abrotanum (0.18 mmol g^{-1} Pd, r.t.)	4.9×10^{-2}	This work
RhB	PVP-Au/PVPPANI/Fe ₂ O ₃ (0.13 mg ml ⁻¹ , r.t.)	1.6×10^{-3}	[29]
RhB	Ag-Fe ₃ O ₄ (0.74 mg ml ⁻¹ , r.t.)	7×10^{-3}	[30]
RhB	Ni/CPM-1 (0.5 wt% Ni, r.t.)	7.85×10^{-3}	[26]
RhB	Pd NPs/RGO-A. abrotanum (0.18 mmol g ⁻¹ Pd, r.t.)	2.2×10^{-3}	This work
МО	$MnFe_2O_4@SiO_2@Ag (0.24 mg ml^{-1}, r.t.)$	4×10^{-2}	[31]
МО	Fe_3O_4 @His@Ag (0.24 mg ml ⁻¹ , r.t.)	4.2×10^{-3}	[32]
МО	Ag-γ-Fe ₂ O ₃ @CS (0.67 wt% Ag, r.t.)	0.6×10^{-3}	[33]
МО	Pd NPs/RGO-A. abrotanum (0.18 mmol g ⁻¹ Pd, r.t.)	2×10^{-2}	This work

RhB and MO (Table 1). It can be seen that the Pd NPs/RGO-*A. abrotanum* catalyst leads to a rapid reduction reaction compared to the other catalysts considered.

4 | CONCLUSIONS

Pd NPs/RGO-*A. abrotanum* can be applied as an effective and heterogeneous nanocatalyst for reduction of various dyes, namely MB, MO and RhB, in the presence of $NaBH_4$ as reducing agent.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial and other support of this research provided by Tehran Medical Sciences, IslamicAzad University and Yadegar-e-Imam Khomeini (RAH) Shahr-e-Rey Branch, Islamic Azad University, Tehran, Iran.

ORCID

Mohammad Yousefi https://orcid.org/0000-0002-5609-2640

Malak Hekmati D https://orcid.org/0000-0003-0790-569X

REFERENCES

- M. Nasrollahzadeh, M. Atarod, S. M. Sajadi, *Appl. Surf. Sci.* 2016, 364, 636.
- [2] a) S. Hemmati, A. Rashtiani, M. M. Zangeneh, P. Mohammadi, A. Zangeneh, H. Veisi, *Polyhedron* 2019, 158, 8; b) G. Shaham, H. Veisi, M. Hekmati, *Appl. Organometal. Chem.* 2017, 31, e3737; c) M. Shahriary, H. Veisi, M. Hekmati, S. Hemmati,

Mater. Sci. Eng. C 2018, 90, 57; d) H. Veisi, S. Razeghi, P. Mohammadi, S. Hemmati, Mater. Sci. Eng. C 2019, 97, 624; e)
H. Veisi, S. B. Moradi, A. Saljooqi, P. Safarimehr, Mater. Sci. Eng. C 2019, 100, 445; f) H. Veisi, M. Ghorbani, S. Hemmati, Mater. Sci. Eng. C 2019, 98, 584; g) H. Veisi, N. Hajimoradian Nasrabadi, P. Mohammadi, Appl. Organometal. Chem. 2016, 30, 890; h) H. Veisi, P. Safarimehr, S. Hemmati, Mater. Sci. Eng. C 2019, 96, 310; i) K. Zomorodian, H. Veisi, S. M. Mousavi, M. Sadeghi Ataabadi, S. Yazdanpanah, J. Bagheri, A. Parvizi Mehr, S. Hemmati, H. Veisi, Int. J. Nanomed. 2018, 13, 3965.

5 of 6

Organometallic Chemistry

- [3] a) S. Hemmati, L. Mehrazin, H. Ghorban, S. H. Garakani, T. H. Mobaraki, P. Mohammadi, H. Veisi, *RSC Adv.* 2018, *8*, 21020;
 b) M. Yazdankhah, H. Veisi, S. Hemmati, *J. Taiwan Inst. Chem. Eng.* 2018, *91*, 38.
- [4] A. H. Qusti, R. M. Mohamed, M. A. Salam, *Ceram. Int.* 2014, 40, 5539.
- [5] M. Ebrahimi, A. Zakery, M. Karimipour, M. Molaei, Opt. Mater. 2016, 57, 46.
- [6] a) H. Veisi, M. Kavian, M. Hekmati, S. Hemmati, *Polyhedron* 2019, *161*, 338; b) S. Hemmati, L. Mehrazin, M. Pirhayati, H. Veisi, *Polyhedron* 2019, *158*, 414.
- [7] H. Veisi, N. Mirzaee, Appl. Organometal. Chem. 2018, 32, e4067.
- [8] D. R. Dreyer, S. Park, C. W. Bielawski, R. S. Ruoff, *Chem. Soc. Rev.* 2010, *39*, 228.
- [9] L. Liu, H. Bai, J. Liu, D. D. Sun, J. Hazard. Mater. 2013, 261, 214.
- [10] J. M. Lee, I. Y. Kim, S. Y. Han, T. W. Kim, S.-J. Hwang, *Chem. Eur. J.* 2012, 18, 13800.
- [11] Y. Han, Z. Luo, L. Yuwen, J. Tian, X. Zhu, L. Wang, *Appl. Surf. Sci.* 2013, 266, 188.
- [12] F. I. Hai, K. Yamamoto, K. Fukushi, Crit. Rev. Environ. Sci. Technol. 2007, 37, 315.
- [13] V. K. Gupta, J. Environ. Manage. 2009, 90, 2313.
- [14] M. Rafatullah, O. Sulaiman, R. Hashim, A. Ahmad, J. Hazard. Mater. 2010, 177, 70.

6 of 6 WILEY Organometallic

- [15] M. Chen, Y. Chen, G. Diao, J. Chem. Eng. Data 2010, 55, 5109.
- [16] K. R. Ramakrishna, T. Viraraghavan, Water Sci. Technol. 1997, 36, 189.
- [17] X. Luo, L. Zhang, J. Hazard. Mater. 2009, 171, 340.
- [18] J. W. Lee, S. P. Choi, R. Thiruvenkatachari, W. G. Shim, H. Moon, *Dyes Pigm.* **2006**, *69*, 196.
- [19] B. Shi, G. Li, D. Wang, C. Feng, H. Tang, J. Hazard. Mater. 2007, 143, 567.
- [20] V. Golob, A. Vinder, M. Simonič, Dyes Pigm. 2005, 67, 93.
- [21] a) T. H. Kim, C. Park, S. Kim, J. Clean. Prod. 2005, 13, 779; b)
 S.-M. Hao, M.-Y. Yu, Y.-J. Zhang, Y. Abdelkrim, J. Qu, J. Colloid Interface Sci. 2019, 545, 128; c) P. Shao, J. Tian, X. Duan, Y. Yang, W. Shi, X. Luo, F. Cui, S. Luo, S. Wang, Chem. Eng. J. 2019, 359, 79; d) S.-M. Hao, J. Qu, Z.-S. Zhu, X.-Y. Zhang, Q.-Q. Wang, Z.-Z. Yu, Adv. Funct. Mater. 2016, 26, 7334; e) Z.-S. Zhu, J. Qu, S.-M. Hao, S. Han, K.-L. Jia, Z.-Z. Yu, ACS Appl. Mater. Interfaces 2018, 10, 30670.
- [22] K. R. Reddy, K. V. Karthik, S. B. Benaka Prasad, S. K. Soni, H. M. Jeong, A. V. Raghu, *Polyhedron* 2014, 120, 169.
- [23] a) M. Amir, U. Kurtan, A. Baykal, J. Ind. Eng. Chem. 2015, 27, 347; b) H. Veisi, S. Azizi, P. Mohammadi, J. Clean. Prod. 2018, 170, 1536; c) H. Veisi, A. Rashtiani, V. Barjasteh, Appl. Organometal. Chem. 2016, 30, 231; d) H. Veisi, M. Pirhayati, A. Kakanejadifard, P. Mohammadi, M. R. Abdi, J. Gholami, S. Hemmati, ChemSelect 2018, 3, 1820.
- [24] G. Joerg, B. Thomas, J. Christof, M. Mukesh, Medical Economics Company, Montvale, NJ 2000 319.

- [25] M. Hashemi Salehi, M. Yousefi, M. Hekmati, Polyhedron 2019, 165, 132.
- [26] P. Veerakumar, S. M. Chen, R. Madhu, V. Veeramani, C. T. Hung, S. B. Liu, ACS Appl. Mater. Interfaces 2015, 7, 24810.
- [27] Y. Xie, B. Yan, H. Xu, J. Chen, Q. Liu, Y. Deng, H. Zeng, ACS Appl. Mater. Interfaces 2014, 6, 8845.
- [28] X.-Z. Li, K.-L. Wu, Y. Ye, X.-W. Wei, CrystEngComm 2014, 16, 4406.
- [29] X. Zhang, X. Zhang, R.-p. Feng, L.-h. Liu, H. Meng, Mater. Chem. Phys. 2012, 136, 555.
- [30] L. Ai, C. Zeng, Q. Wang, Catal. Commun. 2011, 14, 68.
- [31] U. Kurtan, M. Amir, A. Yıldız, A. Baykal, *Appl. Surf. Sci.* 2016, 15, 16.
- [32] M. Amir, U. Kurtan, A. Baykal, J. Ind. Eng. Chem. 2015, 27, 347.
- [33] M. Kaloti, A. Kumar, ACS Omega 2018, 3, 1529.

How to cite this article: Hashemi Salehi M, Yousefi M, Hekmati M, Balali E. Application of palladium nanoparticle-decorated *Artemisia abrotanum* extract-modified graphene oxide for highly active catalytic reduction of methylene blue, methyl orange and rhodamine B. *Appl Organometal Chem.* 2019;e5123. https://doi.org/10.1002/aoc.5123