Journal of Chemistry and Technologies, 2022, *30*(1), 21-25

Journal of Chemistry and Technologies

pISSN 2663-2934 (Print), ISSN 2663-2942 (Online).

journal homepage: http://chemistry.dnu.dp.ua

UDC 547.54

REDUCTION OF p-NITROANILINE USING PLANT MEDIATED Co-NPs: A GREEN PERSPECTIVE

Ramya Ch.,[1] Murali Krishna Madasu,[2] K. Suresh Kumar,[3] K. V. Pamavathi,[4] M. Padma*[1]

[1]*Department of Engineering Chemistry, AUCE (A), Visakhapatnam, India.*

[2]*Department of Chemistry, S V K P & Dr K S Raju Arts & Sciennce College (A), West Godavari Dist., Andhra Pradesh, India*

[3]*Department of Chemistry, Kakinada, E. Godavari Dist., Andhra Pradesh, India*

[4]*Department of Chemistry, GVP College of Degree & PG Courses, MVP Colony, Visakhapatnam, India.*

Received 7 January 2022; accepted 28 February 2022; available online 27 April 2022

Abstract

Cobalt nanoparticles (Co- NP's) were used as an eco-friendly catalyst in a green approach format in water at room temperature to accomplish an efficient chemoselective reduction of p-nitroaniline. The product of this chemical reduction, p-phenylenediamine, is an attractive intermediate in the preparation of polymers, hair dyes, and rubber products. Hence, there is a great demand to develop effective catalysts for this chemical reduction of p-nitroanilines. The reactions can be recommended for use, since the catalysts are reusable and the reactions are high yielding (around 90 %). Co nanoparticles of different concentrations were synthesized and used as a catalyst in the reduction of p-nitroaniline with NaBH4 to p-phenylenediamine. It was observed that the reaction rate was high with the low concentrated sample compared to other high concentrated samples because of their size. The reusability of 1 mM nanoparticles shows that they are a potential catalyst suitable for industrial reuse.

Keywords: chemo-selective; p-nitroaniline; green approach; reusable; high yielding.

ВІДНОВЛЕННЯ п-НІТРОАНІЛІНА ЗА ДОПОМОГОЮ РОСЛИННИХ СПОЛУЧНИКІВ Co-NPs: ЕКОЛОГІЧНА ПЕРСПЕКТИВА

Рам'я Х.,[1] Муралі Крішна Мадасу,[2] К. Суреш Кумар,[3] К. В. Памаваті,[4] М. Падма*[1]

[1]*Кафедра інженерної хімії, AUCE (A), Вішакхапатнам, Індія.*

[2]*Департамент хімії, S V K P & Dr K S Raju Arts & Sciennce College (A), West Godavari Dist., Andhra Pradesh, Індія*

[3]*Департамент хімії, Какінада, округ Е. Годаварі, Андхра-Прадеш, Індія*

[4]*Кафедра хімії, GVP College of Degree & PG Courses, MVP Colony, Вішакхапатнам, Індія.*

Анотація

Наночастинки кобальту (Co- NP) були використані в якості екологічно чистого каталізатора в межах зеленого підходу в водних розчинах за кімнатної температури для для здійснення ефективного хемоселективноговідновлення п-нітроанилину. Продукт вказаного хімічного відновлення, п-фенілендіамін, є привабливим проміжним продуктом в процесі отримання полімерів, фарб для волоссята гумових виробів. Таким чином, існує велика потреба в розробці ефективних каталізаторів для цього хімічного відновлення п-нітроанілінів. Ці реакції можуть бути рекомендовані до використання, бо каталізатори можуть бути використані повторно, а самі реакції відрізняються високим виходом (около 90 %). Наночастинки Co були синтезовані та використані із зазначеною метою відновлення п-нітроаніліна з допомогою $NaBH_4$ до п-фенілендіаміну. Було відзначено, що швидкість реакції висока за умови використання низькоконцентрованого зразку в порівнянні з висококонцентрованими зразками із-за їх розмірів. Можливість повторного використання наночастинк 1 мМ робить їх потенційним каталізатором, придатним для використання у промисловості.

Ключові слова: хемоселективний; п-нітроанілін; зелений підхід; багаторазове використання; високий вихід.

**Corresponding author: e-mail: mpenggchem@gmail.com*

doi: 10.15421/jchemtech.v30i1.250883

Introduction

The reduction of nitro composites with an excess amount of Sodium Borohydride has been often utilized as a model reaction in the literature [1]. Chirea et al., for example, looked into the catalysis of p-nitroaniline reduction using gold nanowire particles [2]. According to Kundu et al., small globular gold nanoparticles have higher catalytic activity in p-nitroaniline reduction than large globular gold nanoparticles [3]. P-phenylenediamine, an attractive intermediate in the productionof polymers, hair dyes, and rubber products, is the result of this chemical reduction [4–5]. It's also employed as a developing agent in the production of color photographic film. Earlire numerous methodologies (such as flocculation, membrane filtration, adsorption, hydrothermal, advanced oxidation processes, biological, and catalytic reduction) have been utilized for the treatment of nitroaromatic pollutants. As a result, there is a high demand for effective catalysts to aid in the chemical reduction of p-nitroaniline [6–16].

Transition metal nanoparticles have a unique position among other nanosized particles from the point of view of the development of new technologies. They are of significant interest due to the unique catalytic, magnetic, mechanical, optical, electrical, and biological properties that they possess [17–27]. The catalytic capability of the synthesized Co-NPs nanoparticles was been established here [28]. In the presence of sodium borohydride in a water medium, the catalytic conditioning of synthesized nanoparticles was investigated for the reduction of p-nitroaniline to p-phenylenediamine.

Materials and methods

P-nitroaniline and sodium borohydride ($NaBH_4$), purchased from Fisher Scientific India.

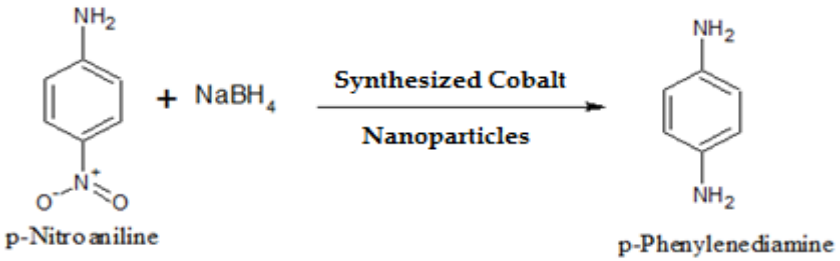
Synthesis of Cobalt Nanoparticles using the *Asparagus racemosus* roots Extract

The aqueous root extract of *Asparagus racemosus* was mixed in a 1 : 5 ratio with 10 mM cobalt acetate solution and incubated on a heated plate at 60 °C for 90 minutes until color change [28]. A comparison of UV-Vis spectra indicated that nanoparticles were formed as a result of the synthesis.

p-Nitroaniline catalysis

100 µL of 1 mM p-nitroaniline, 100 µL of 10 mM $NaBH_4$, and the synthesized colloidal samples of Co-NPs 10 µL were mixed in a typical catalytic reaction (keeping nearly the same amount of synthesized nanoparticles in all cases). To reduce the dilution impact, different amounts of deionized water were added to the reaction admixture. To study the chemical reduction of p-nitroaniline, an UV-visible spectrophotometer was used, using quartz cuvettes with a path length of 1 cm and newly prepared data.

The synthesized nanoparticles were separated from the admixture by centrifugation at 10000 rpm after the reduction process was completed, rinsed three to four times with de-ionized water, and reused for further cycles. The treatment was performed up to four times in total.



Scheme 1: Reduction of p-Nitroaniline using Metal NP's: Co-NP's

Results and discussion

The reduction of p-nitroaniline with $NaBH_4$ in aqueous solutions originating from pure metal nanoparticles (Co-NPs) results in the synthesis of p-phenylenediamine, as shown in Scheme 1. UV-visible spectroscopy was used to track the synthesis of p-phenylenediamine in the presence of metal nanoparticles in real time. In the absence of metal nanoparticles, a blank experiment was carried out for the reduction of p-nitroaniline with $NaBH_4$. After one day, the characteristic absorbance of p-nitroaniline at 358 nm slowly decreased.

Figure 1 shows the reaction in the presence of above synthesized cobalt nanoparticles, with the absorbance peak at 355 nm gradually decreasing,

the absorbance peak at 227 nm shifting, and a new absorption peak developing at 310 nm. This suggests that the metallic Co-NPs obtained in the presence of $NaBH_4$ accelerated the reduction of p-nitroaniline to p-phenylenediamine. Since $NaBH_4$ was utilized in considerable excess compared to p-nitroaniline, the reduction rate of this reaction can be considered independent of its concentration (see Materials and Methods). As a result, the kinetics of this chemical reduction is first order.

Our results show that the reaction rate was high when using a Co-NPs sample made from 1 mM of cobalt acetate as a catalyst, medium when using the cobalt sample made from 5 mM of cobalt acetate as a catalyst, and slow when using the cobalt sample made from 10 mM of cobalt acetate as a catalyst. Figure 2 shows a graphic representation of all of these findings. In the presence of the 1 mM nanoparticle metal sample, 92.6 % of p-nitroaniline was converted to p-phenylenediamine, 90.0 % in the presence of the 5 mM nanoparticle metal sample, and 86.8 % in the presence the 10 mM nanoparticle metal sample. By comparing the spectral data the 10 mM nanoparticle metal sample, the obtained product was validated.

The amount of nanoparticles present in the reaction mixture, as well as the availability of active surface area for reactant adsorption, determine the change in reaction rate or catalytic efficiency. We used varying amounts of metal solutions to fix nearly the same number of metal nanoparticles in all reaction mixtures in our study. As a result, the variance in reaction rate or catalytic efficiency is mostly determined by the available surface area for reactant absorption. The electron transfer from BH_4 to the p-nitroaniline occurs in the current reduction via metal nanoparticles.

Numerous parameters, including particle size and shape, as well as the molecules wrapped around the nanoparticles, have been shown to influence the surface area accessible for reactant absorption [9–10]. It was previously observed that large gold nanoparticles exhibit stronger steric interactions with BH_4 and p-nitroaniline than small gold nanoparticles [29–30], owing to the larger number of molecules wrapped around the surface of large gold nanoparticles.

Perhaps this blend of cobalt nanoparticles has a lower effective surface area for catalysis than the quasi-sphere nanoparticles. Thus, the reaction rate is slower in the cobalt sample prepared with 10 mM cobalt acetate than in the cobalt sample prepared with 5 mM cobalt acetate. At this point, it is not sufficient to explain the precise cause of these rate changes. Additional research is required to fully comprehend this catalytic process. The reduction of p-nitroaniline was accomplished in all cases within two hours. The metal nanoparticles synthesized from 1mM of the respective precursors require less than one hour to complete the reduction of p-nitroaniline to p-phenylenediamine, which is less or slightly more than the time required for chemically synthesized gold nanoparticles, and also the chemicals used previously (auric chloride) are more expensive than the present catalysts [1–3].

Additionally, we investigated the reusability of these nanoparticles formed from 1 mM metal used as a catalyst for the reduction of p-nitroaniline with $NaBH_4$. The reusable catalytic characteristics of metal nanoparticles formed from 1mM are shown in Fig. 3. After four reuse processes, it was discovered that p-nitroaniline could still be converted to p-phenylenediamine in the presence of $NaBH_4$ with a conversion rate of 86.8 %. As a result, the produced metal nanoparticles are very effective reusable nanocatalysts for industrial applications.

Table 1

Catalytic efficiency of Co nanoparticles with catalyst loading (x mol %)

Sl. no	Catalyst loading (x mol %)	Time for complete the reduction (min)	p-nitroaniline conversion (%)
1	01 mm	55	86.6
2	05 mm	49	90
3	10 mm	45	93

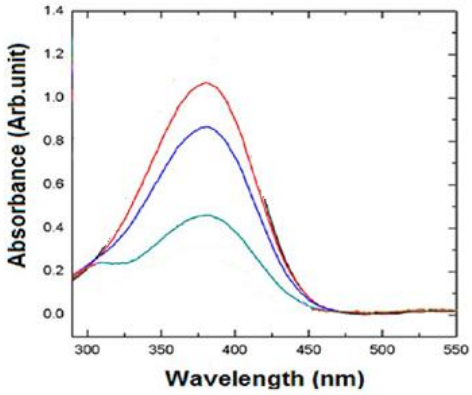


Fig. 1. UV-visible spectra for the successive chemical reduction of p-nitroaniline with $NaBH_4$ catalyzed by cobalt nanoparticles and plots of concentration versus time for the reduction of p-nitroaniline (Red line – initial reduction; blue line – at the middle of reduction; green line – final reduction).

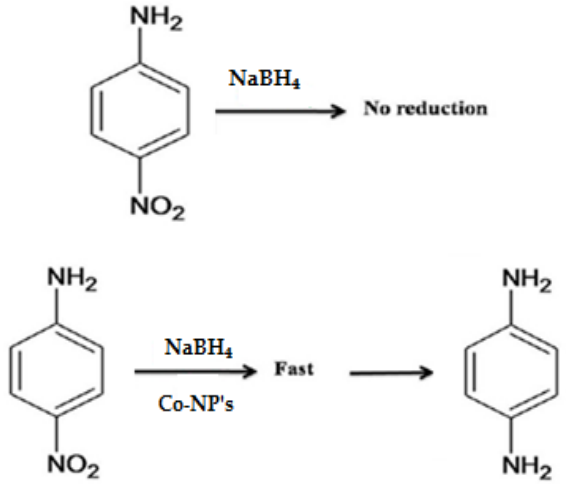


Fig. 2. Schematic drawing of the metal nanoparticles and catalysis of p-nitroaniline in the presence of nanoparticles as catalysts.

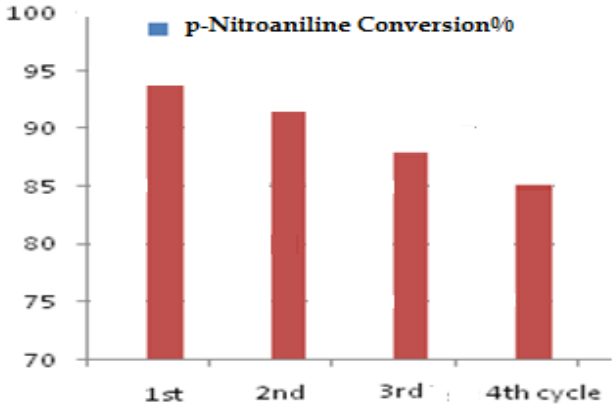


Fig. 3. Recyclability of the metal nanoparticles Co-NPs obtained from 1 mM as a catalyst for the reduction of p-nitroaniline with $NaBH_4$.

Conclusion

Co nanoparticles of different concentrations were synthesized and used as a catalyst in the reduction of p-nitroaniline with $NaBH_4$ to p-phenylenediamine. It was observed that the reaction rate was high when using the low-concentrated sample compared to the other high-concentrated samples due to their size. As the particle size decreases the surface area increases. It was also observed that the reaction rate was high with 1 mM in comparison with the other samples produced from 5 mM and 10 mM as a catalyst. This is because the nanoparticles of 1 mM have a larger effective surface area and possess less steric hindrance for p-nitroaniline and $NaBH_4$ when compared to nanoparticles of 5 mM and 10 mM due to their shape. The reusability of 1 mM nanoparticles shows that it is

a potential recyclable catalyst for industrial applications.

References

[1] Kundu, S., Lau, S., Liang, H. J. (2009). Shape-Controlled Catalysis by Cetyltrimethylammonium Bromide Terminated Gold Nanospheres, Nanorods, and Nanoprisms, *Phys. Chem*. C, 113, 5150−5156. https://doi.org/10.1021/jp811331z

[2] Chirea, M., Freitas, A., Vasile, B. S., Ghitulica, C., Pereira, C. M., Silva, F. (2011). Gold nanowire networks: synthesis, characterization, and catalytic activity, *Langmuir*, 27, 3906−3913. doi: 10.1021/la104092b

[3] Kundu, S., Wang, K., Liang, H. J. (2009). Size-Selective Synthesis and Catalytic Application of Polyelectrolyte Encapsulated Gold Nanoparticles Using Microwave Irradiation, *Phys. Chem. C*, 113, 5157−5163.

[4] Franco, C. (1996). On the polymerization of P-phenylenediamine, *Eur. Polym. J*, 32, 43−50.

[5] Hsiao-Shu, L., Yu-Wen, L. (2009), Permeation of Hair Dye Ingredients, p-Phenylenediamine and Aminophenol Isomers, through Protective Gloves. *Ann. Occup. Hyg*., 53, 289−296. https://doi.org/10.1093/annhyg/mep009

[6] Revathi, K., Shajesh. Palantavida, Baiju Kizhakkekilikoodayil, V., (2019). Effective Reduction of p-Nitroaniline to p-Phenylenediamine Using Cu-CuO Nanocomposite. *Materials Today: Proceedings, 9*(3), 633−638. https://doi.org/10.1016/j.matpr.2018.10.386

[7] Edison, T. N. J. I., Sethuraman, M. G., Lee, Y. R. (2016). $NaBH_4$ reduction of ortho and para-nitroaniline catalyzed silver nanoparticles synthesized using Tamarindus indica seed coat extract. *Research on Chemical Intermediates*, *42*(2), 713−724.

[8] Din, M. I., Khalid, R., Hussain, Z., Najeeb, J., Sahrif, A., Intisar, A., Ahmed, E., (2020). *RSC Advances*, 32, 18543−19133.

[9] Naseem, Kh., Begum, R., Farooqi, Z. H. (2017). Catalytic reduction of 2-nitroaniline: a review. *Environ Sci Pollut Res Int., 24*(7), 6446−6460. doi: 10.1007/s11356-016-8317-2

[10] Qureshi, A., Verma, V., Kapley, A., Purohit, H. J. (2007). Degradation of 4-nitroaniline by Stenotrophomonas strain HPC 135. *Biodeterior. Biodegrad.*, 60, 215−218.

[11] Li, K., Li, Y., Zheng, Z., Hazard, J. (2010). Batch and Flow-Through Column Studies for Cr(VI) Sorption to Activated Carbon Fiber. *Mater., 178*, 55−−559.

[12] Din, M. I., Najeeb, J., Hussain, Z., Khalid, R., Ahmad, G. (2020). Critical review on the chemical reduction of nitroaniline. *Inorg. Nano-Met. Chem.,* 10, 19041−19058

[13] Din, M. I., Tariq, M., Hussain, Z., Khalid, R. (2020). *Inorg. Nano-Met. Chem.*, 1−6.

[14] Lee, D. S., Park, K. S., Nam, Y. W., Kim, Y.-C., Lee, C. H. (1997). Hydrothermal decomposition and oxidation of p-nitroaniline in supercritical water. *J. Hazard Mater., 56*, 247−256.

[15] Regan, M. R., Banerjee, I. A., (2006). Critical review on the chemical reduction of nitroaniline. *Scr. Mater., 54*, 909−914.

[16] Das, P., Ghosh, S., Baskey (Sen), M. (2019). Heterogeneous catalytic reduction of 4-nitroaniline by RGO-Ni nanocomposite for water resource management J. of Materials Science: Materials in Electronics, 30, 19731−19737.

[17] Liu, X., Ruiz, J., Astruc, D. (2018). Compared Catalytic Efficiency of Click-Dendrimer-Stabilized Late Transition Metal Nanoparticles in 4-Nitrophenol. J. Inorg. Organomet. Polym., 28, 399−406. doi: 10.1007/s10904-017-0666-x

[18] Peng, G., Mavrikakis, M. (2015). Adsorbate Diffusion on Transition Metal Nanoparticles. Nano Lett. 15, 629−634. https://doi.org/10.1021/nl504119j

[19] Kim, Y., Torres, D. D., Jain, P. K. (2016). Activation Energies of Plasmonic Catalysts. *Nano Lett., 16*, 3399−3407. https://doi.org/10.1021/acs.nanolett.6b01373

[20] Vijayaprasath, G., Murugan, R., Mahalingam, T., Ravi, G., Mater, J. (2015). Structural, optical and photoluminescence properties of copper and iron doped nanoparticles prepared by co-precipitation method. *Sci. Mater. Electron., 26,* 7205−7213. doi: 10.1007/s10854-016-5190-1

[21] Wobbe, M. C. C., Zwijnenburg, M. A. (2015). Chemical trends in the optical properties of rocksalt nanoparticles. *Phys. Chem. Chem. Phys., 17*, 28892−28900.

[22] Hu, Y., Ji, C., Wang, X., Huo, J., Liu, Q., Song, Y. (2017). The structural, magnetic and optical properties of $TMn@(ZnO)_{42}$ (TM = Fe, Co and Ni) hetero-nanostructure. *Sci. Rep. 7*, 16485.

[23] Anandha babu, G., Ravi, G. (2016). Magnetic evolution in transition metal-doped $Co^{3+}xMxO_4$ (M = Ni, Fe, Mg and Zn) nanostructures. *Appl. Phys. A, 122*, 177. doi:10.1007/s00339-016-9710-x

[24] Willing, S., Lehmann, H., Volkmann, M., Klinke, C. (2017). Metal nanoparticle film–based room temperature Coulomb transistor. *Sci. Adv., 3,* 1603191. doi: 10.1126/sciadv.1603191

[25] Quan, C., Qin, Z., Zhu, Y., Wang, Z., Zhang, J., Mao, W., Wang, X., Yang, J., Li, X., Huang, W. (2017). Graphene biosensors for bacterial and viral pathogens. *J. Mater. Sci. Mater. Electron., 28*, 3278−3284.

[26] Jawoor, S. S., Patil, S. A., Kumbar, M., Ramawadgi, P. B. (2018). Synthesis and characterization of Rosa canina-mediated biogenic silver nanoparticles for anti-oxidant, antibacterial, antifungal, and DNA cleavage activities, *J. Mol. Struct., 1164*, 378−385. https://doi.org/10.1016/j.heliyon.2019.e02980

[27] Khusnuriyalova, A. F., Caporali, M., Hey-Hawkins, E., Sinyashin, O. G., Yakhvarov, D. G. (2021). Preparation of Cobalt Nanoparticles. *Eur. J. Inorg. Chem.* 3023−3047. https://doi.org/10.1002/ejic.202100367

[28] Varaprasad, T., Boddeti, Govindh, B., Venkateswara, R. (2017). Green Synthesized Cobalt Nanoparticles using Asparagus racemosus root Extract & Evaluation of Antibacterial activity. *International Journal of ChemTech Research, 10*(9), 339−345.

[29] Kundu, S., Wang, K., Liang, H. (2009). Size-Selective Synthesis and Catalytic Application of Polyelectrolyte Encapsulated Gold Nanoparticles Using Microwave Irradiation. *J. Phys. Chem. C, 113*, 5157−5163. https://doi.org/10.1021/jp9003104

[30] Reddy, V., Torati, R. S., Sunjong, Kim, C. G. (2013). Fe_3O_4/TiO_2 core/shell nanocubes: Single-batch surfactantless synthesis, characterization and efficient catalysts for methylene blue degradation. *Ind. Eng. Chem. Res., 52*(2), 556−564.