

Development of Alumina-Supported Pd-Ru Nano-Catalysts for Catalytic Reduction Reactions for Water Pollutants in Aqueous Media

Ezginur GÜLERİŞ, Osman DAYAN*

* Department of Chemistry, Faculty of Science, Çanakkale Onsekiz Mart University, 17020- Çanakkale, Turkey.

This study examines the catalytic efficiency of six materials (EG1-6) synthesized on an Al_2O_3 support material using different PdCl_2 and RuCl_3 precursors. The catalyst EG4 (Ru:Pd 3:2) was determined to be superior because of its synergistic impact. The utilization of XRD, SEM-EDX, and TEM techniques unveiled the existence of Al_2O_3 , RuO_2 , and Pd constituents, exhibiting an average crystal size of around 16 nm. The even distribution of nanoparticles on the Al_2O_3 support is likely to enhance the accessibility of reactants to active sites, leading to an increase in catalytic efficiency.

Keywords: *Water pollutants; nanoparticles, reduction, Ruthenium, Palladium*

Submission Date: 18 January 2024

Acceptance Date: 17 April 2024

*Corresponding author: osmandayan@comu.edu.tr

1. Introduction

Because of the harmful effects of toxic dyes such as azo dyes and nitrophenols, environmental pollution is a major concern, particularly in the textile industry [1]. Currently, synthetic organic compounds are widely used in a variety of industries, including plastics, paper, food, pharmaceuticals, cosmetics, and textiles. The introduction of these pollutants into water systems via wastewater discharges can cause a variety of health problems, including skin irritation, blood disorders, liver and kidney damage, and central nervous system toxicity. Dye-contaminated water can also interfere with photosynthesis, which is necessary for aquatic organisms to survive [2-5]. These toxic dyes not only affect human and aquatic life, but their presence in water can also harm the environment as a whole. Ecosystems can degrade significantly, resulting in decreased biodiversity and overall ecosystem health [6, 7]. Furthermore, the presence of hazardous dyes in water sources can have an economic impact, particularly on industries that rely on clean water for production. To address this issue, industries must adopt sustainable and

environmentally friendly practices, such as using natural dyes and implementing appropriate wastewater treatment technologies [8-12]. Dyes released from industries such as plastics, textiles, leather, printing, and paper pose a threat to human health by accumulating in the environment and polluting water resources [13-15]. To remove these pollutants, a variety of methods are used, including biochemical and electrochemical techniques, ion exchange, and adsorption. However, these methods are frequently ineffective for treating polluted water. We require more advanced technologies to effectively remove these pollutants.[16-19].

From this standpoint, catalytic conversion of organic pollutants provides both economic and environmental benefits [20, 21]. Chemical catalytic conversion methods involving transition metal catalysts can be a strategic solution because they are quick and efficient [22]. Transition metal nanoparticles are utilized as highly effective, expeditious, uncomplicated, and economical catalysts for the degradation of dyes [23]. To improve catalyst efficiency, new nanoparticles of metal salts with catalytic properties are created on a solid support made of inorganic or porous material [24]. While a catalyst with a

large surface area and uniform metal distribution is desirable, the aggregation of metal nanoparticles reduces its effectiveness [25]. Metal complexes, nanoparticles, and solid-supported nanoparticles have received a lot of attention in the scientific literature for their ability to catalyze dye reduction and degradation [26-28].

Catalytic reduction is preferred over other methods due to the wide range of applications for dye reduction products [29]. The surface area/volume ratio of metal nanoparticles and catalytic efficiency are directly proportional.

Alumina, also known as aluminum oxide (Al_2O_3), is a commonly used support material for the preparation of metal nanoparticles [30]. Because of its porous and less dense structure, reactive molecules have easy access to metal nanoparticles. This increases catalytic activity while decreasing the time required for the reduction process [31]. Al_2O_3 oxides are commonly used in the catalytic conversion of organic pollutants due to their low toxicity, chemical stability, and abundance [32, 33].

Ruthenium and palladium nanoparticles are widely used due to their large surface areas, easy fabrication, and catalytic properties [24, 34]. For example, ruthenium nanoparticles on Al_2O_3 demonstrated excellent catalytic activity in the conversion of nitrobenzene to aniline [35, 36]. Furthermore, the superior catalytic performance of ruthenium and palladium nanoparticles allows for lower catalyst concentrations, resulting in cost savings and waste reduction during the reduction process [37, 38]. In this study, a bimetallic catalytic system (Ru-Pd) attached to an Al_2O_3 support was used to investigate the reduction of a real sample-like mixture of dyes.

2. Experimental

Catalyst Preparation (EG1-6)

The catalysts, named EG1-6, were prepared by supporting bimetallic Ru@Pd on $\gamma\text{-Al}_2\text{O}_3$ at a weight percentage of 5%. The Ru:Pd ratio varied for each catalyst, with EG1 having a ratio of 0:5, EG2 having a ratio of 1:4, EG3 having a ratio of 2:3, EG4 having a ratio of 3:2, EG5 having a ratio of 4:1, and EG6 having a ratio of 5:0. To achieve this objective, suitable volumes of aqueous solutions containing $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and PdCl_2 (20 mL) were stirred constantly for a duration of 30 minutes. $\gamma\text{-Al}_2\text{O}_3$ was introduced into the mixture and evenly distributed using an ultrasonic bath for a duration of 1 hour. After the designated period, the mixture underwent centrifugation, followed by washing with distilled water and subsequent drying. The solid underwent calcination in a muffle furnace at a temperature of 500 °C for a duration of 5 hours. The materials prepared in this manner were examined for their catalytic activity. The X-ray diffraction (XRD) technique, specifically using the PANalytical Empyrean instrument,

was employed to determine the structure of EG4 with the highest catalytic activity. Additionally, the scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX) method, utilizing the JEOL SEM-7100-EDX equipment, was utilized for further analysis.

Catalytic reactions

The study examined the catalytic degradation/reduction reactions of pure dyes (2-Nitroaniline, 4-Nitroaniline, Methylene Blue, and Eosin Yellow) in aqueous solutions. The dyes were obtained from commercial sources. The reactions were carried out at room temperature using EG1-6 catalysts and NaBH_4 . In a given reaction, a quantity of 5 milligrams of catalyst and a concentration of 0.02 molar of NaBH_4 were introduced into a 5 milliliter solution containing a substrate with a concentration of 5×10^{-4} molar. At regular intervals, samples of this mixture were collected, and the advancement of the reactions was observed using UV-Vis spectrometry. Catalytic conversions were determined based on the alterations in absorption wavelengths.

3. Results

Catalytic Activity

This work involves the preparation of six materials (EG1-6) by impregnation of varying proportions of PdCl_2 and RuCl_3 precursors on Al_2O_3 followed by calcination at 500 °C. The study investigated the catalytic performance of EG1-6 materials in the reduction/degradation reaction of a sample consisting of a combination of 2-NA, 4-NA, EY and MB substrates in an aqueous medium using NaBH_4 . EG4 (Ru:Pd 3:2) served as a catalyst in the optimization studies. The optimization table (Table 1) presents the catalytic results obtained under various conditions. Following the optimization experiments, condition 2 in the table was identified as suitable for further investigation.

Table 1. The optimization studies for the degradation/reduction reaction of dye mixtures at various concentrations using EG4 (5 mg) catalyst.

| No | C_{Dye}^* | C_{NaBH_4} | Conversion (%) | | | | | | | |
|----|--------------------|---------------------|----------------|-------|------|-------|------|-------|------|-------|
| | | | 2-NA | | 4-NA | | EY | | MB | |
| | | | 5 m. | 10 m. | 5 m. | 10 m. | 5 m. | 10 m. | 5 m. | 10 m. |
| 1 | 5 | 0.01 | 65 | 82 | 56 | 81 | 25 | 31 | 81 | 93 |
| 2 | 5 | 0.02 | 71 | 96 | 86 | 89 | 77 | 93 | 93 | 93 |
| 3 | 5 | 0.04 | 69 | 78 | 56 | 80 | 61 | 87 | 81 | 87 |
| 4 | 10 | 0.01 | 63 | 79 | 63 | 88 | 35 | 42 | 91 | 93 |
| 5 | 10 | 0.02 | 65 | 89 | 61 | 88 | 37 | 68 | 88 | 95 |
| 6 | 10 | 0.04 | 73 | 75 | 71 | 72 | 61 | 90 | 97 | 97 |

C, concentration (Molar, when calculating the concentration of the dye mixture, equal molar number of each component was taken.) *, $\times 10^{-4}$ M;, m: minutes, Each experiment was repeated three times.

Next, we examined the catalytic efficiency of EG1-6 materials in the reduction/degradation process of 2-NA, 4-NA, EY, and MB substrates using NaBH_4 in optimized

conditions. The results are displayed in Table 2. Figure 1 displays the UV-visible spectra that vary with time.

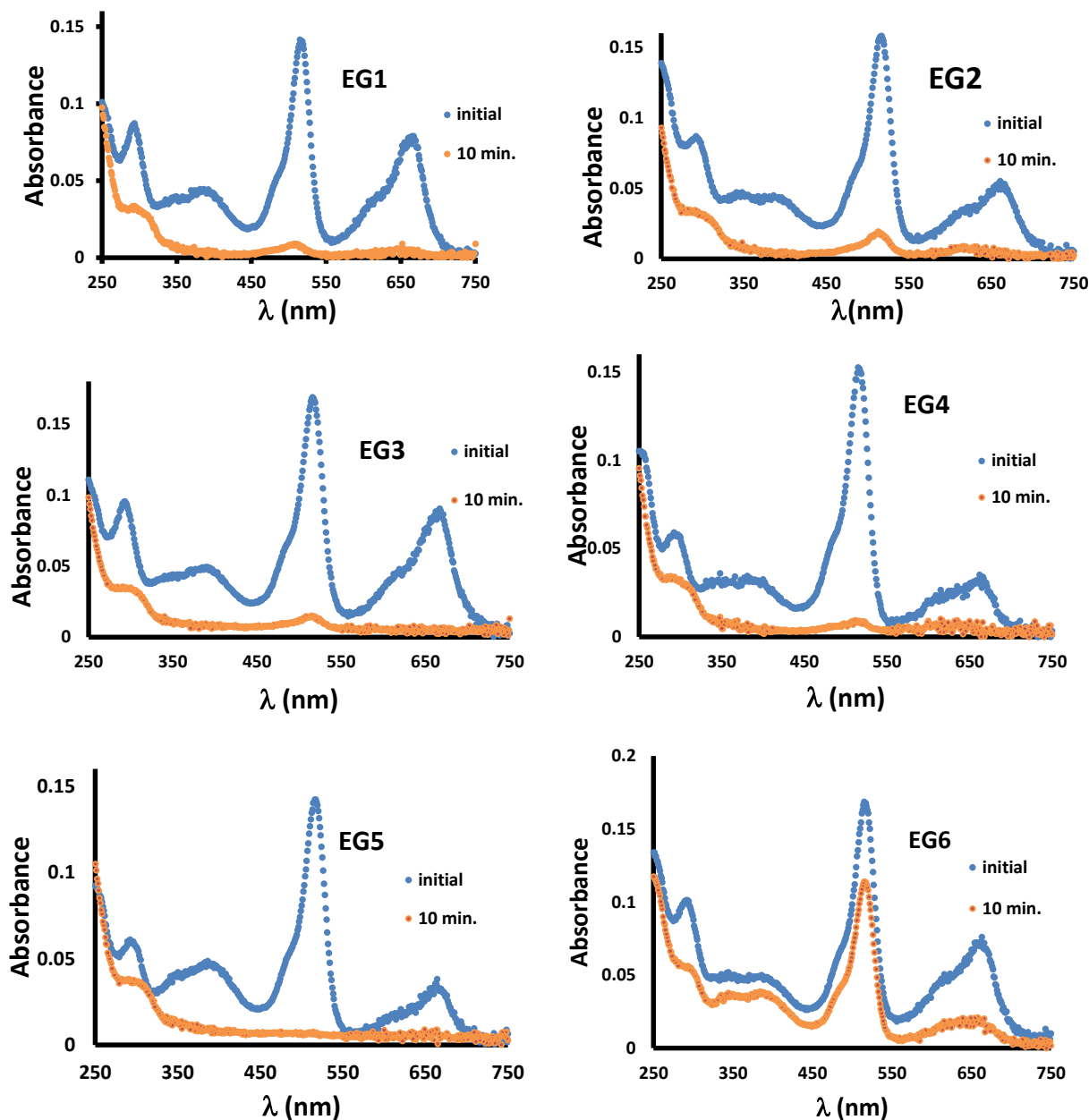


Figure 1. Time-dependent UV-visible spectra of the reduction/degradation reaction of the dye mixture obtained with a mixture of 2-NA, 4-NA, EY and MB substrates under optimized conditions in the presence of NaBH_4 using EG1-6 materials

Table 2. The substrate conversions (%) were determined after 10 minutes of catalytic reduction/degradation reactions using the optimized conditions.

| Cat. | Conversion (%) | | | |
|------|----------------|------|----|----|
| | 2-NA | 4-NA | EY | MB |
| EG1 | 81 | 85 | 94 | 97 |
| EG2 | 89 | 88 | 90 | 90 |
| EG3 | 78 | 76 | 89 | 91 |
| EG4 | 96 | 89 | 93 | 93 |
| EG5 | 80 | 83 | 97 | 85 |
| EG6 | 29 | 28 | 32 | 75 |

Based on the information presented in Table 2, it was observed that under the optimized conditions, all of the prepared materials exhibited catalytic activity in the reduction/degradation reaction of the dye mixture. The catalyst consisting solely of Ru exhibits significantly lower catalytic activity compared to the catalyst consisting solely of Pd. When comparing EG4 (Ru: Pd; 3:2) with the catalyst that only contains Pd, it can be concluded that EG4 is the superior catalyst for all dye components. This can be ascribed to the synergistic impact.

Subsequently, an investigation was conducted to assess the reusability of the EG 4 catalyst. To achieve this objective,

the catalyst was subjected to centrifugation, precipitation, washing, and drying after each catalytic reaction. Following that, it was employed in the novel catalytic reaction. During the experiments, it was noted that the catalyst experienced a significant decrease in its activity during the third repetition, after 10 minutes, under the optimized conditions. The obtained results are presented in Table 3.

Table 3. Reusability of EG4 as a catalyst in catalytic reduction/degradation reactions of dye mixture under optimized conditions.

| Repetition | Conversion (%) | | | |
|------------|----------------|------|----|----|
| | 2-NA | 4-NA | EY | MB |
| 1. | 96 | 89 | 93 | 93 |
| 2. | 42 | 32 | 58 | 92 |
| 3. | 42 | 31 | 41 | 85 |

Characterization

EG4 was subjected to XRD, SEM-EDX, and TEM analyses in order to ascertain its structure. These analyses revealed that EG4 possesses exceptional catalytic activity in comparison to the other materials that were prepared. Figure 2 displays the X-ray diffraction (XRD) pattern of the material. Figure 2 data indicates that the material is composed of Al_2O_3 , RuO_2 , and Pd components. The spectral peaks detected in these components corresponded to the established patterns recorded in the ICDD database. The existence of these constituents in the substance was verified through SEM-EDX analysis. The X-ray diffraction (XRD) analysis indicated the existence of a crystalline arrangement in the material. The material exhibited a crystalline structure with an average crystal size of approximately 16 nm.

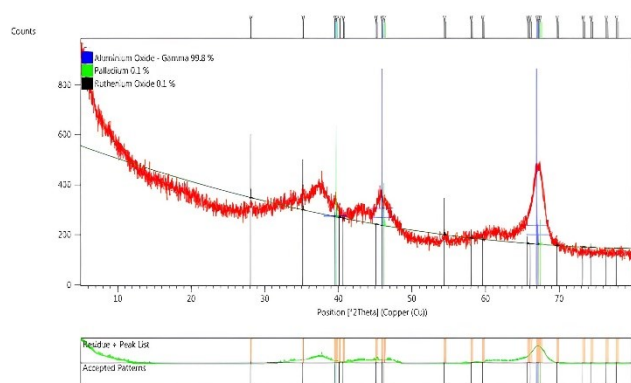


Figure 2. X-ray diffraction pattern of EG4

Figure 3 depicts the scanning electron microscopy (SEM) image and energy dispersive X-ray (EDX) analysis of EG4. The SEM image demonstrates that the particles are uniformly dispersed throughout the material. The scanning electron microscopy (SEM) image of the Al_2O_3 support

material confirms the findings reported in the literature. The EDX analysis indicates that the material consists mainly of aluminum, thereby confirming the existence of ruthenium and palladium. The potential relationship between the percentages of Ru and Pd and the specific crystallization type is remarkable. Furthermore, the EDX analysis revealed the existence of supplementary elements, including minute quantities of carbon within the material. The presence of these small quantities can be ascribed to the process of preparing the sample.

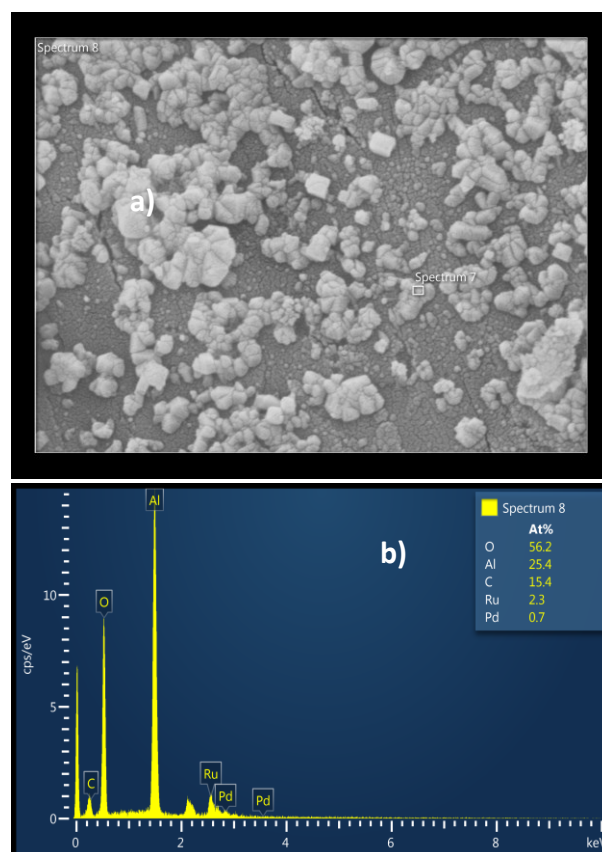


Figure 3. The EG4 catalyst is characterized by a) a scanning electron microscope (SEM) image and b) an energy-dispersive X-ray (EDX) analysis.

Figure 4 displays a transmission electron microscopy (TEM) image of EG4. Figure 4 depicts the homogeneous dispersion of RuO_2 and Pd nanoparticles on the Al_2O_3 substrate. The nanoparticles possess dimensions that are less than 50 nm. The nanoparticles display distinct boundaries and are uniformly dispersed on the support.

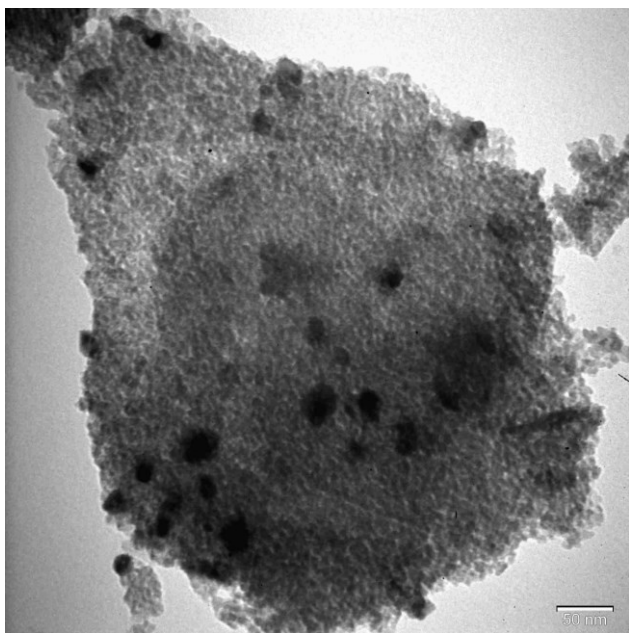


Figure 4. Transmission electron microscopy (TEM) photograph of EG4

4. Conclusion

In this paper, six materials (EG1-6) were prepared on Al_2O_3 support material with varying ratios of PdCl_2 and RuCl_3 precursors. The catalytic performance of EG1-6 materials was investigated in the reduction/degradation reaction of a sample of 2-NA, 4-NA, EY, and MB substrates in an aqueous medium with NaBH_4 . EG4 (Ru:Pd 3:2) served as a catalyst in the optimization studies. Under optimal conditions, all prepared materials were discovered to be active catalysts in the dye mixture's catalytic reduction/degradation reaction. However, the catalyst containing only Ru demonstrated significantly lower catalytic activity than the catalyst containing only Pd. EG4 (Ru:Pd; 3:2) was identified as the better catalyst in terms of all dye components due to the synergistic effect. XRD, SEM-EDX, and TEM analyses were used to determine the structure of EG4, which had higher catalytic activity than other materials. The XRD pattern revealed the presence of Al_2O_3 , RuO_2 , and Pd components, with an average crystal size of approximately 16 nm. The SEM image and EDX analysis revealed that the material has a uniform appearance and is primarily made of aluminum, confirming the presence of ruthenium and palladium. The TEM photograph of EG4 revealed a uniform distribution of RuO_2 and Pd nanoparticles on the Al_2O_3 support with sizes smaller than 50 nm. These findings suggest that the superior catalytic activity of EG4 is due to the synergistic effect of the Al_2O_3 support, RuO_2 , and Pd nanoparticles. The uniform distribution of nanoparticles on the support material most likely increases reactant accessibility to active sites, resulting in increased catalytic efficiency.

Acknowledgement

We would like to thank TUBITAK 2209/A University Students Research Projects Support Program Unit for their contribution.

References

- [1] S.M. Albukhari, M. Ismail, K. Akhtar, E.Y. Danish, Catalytic reduction of nitrophenols and dyes using silver nanoparticles @ cellulose polymer paper for the resolution of waste water treatment challenges, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 577 (2019) 548-561.
- [2] M. Yusuf, Synthetic Dyes: A Threat to the Environment and Water Ecosystem, *Textiles and Clothing* 2019, pp. 11-26.
- [3] F. Akarşlan, H. Demiralay, Effects of textile materials harmful to human health, *Acta Physica Polonica A* 128(2B) (2015).
- [4] V. Selvaraj, T. Swarna Karthika, C. Mansiya, M. Alagar, An over review on recently developed techniques, mechanisms and intermediate involved in the advanced azo dye degradation for industrial applications, *Journal of Molecular Structure* 1224 (2021) 129195.
- [5] B. Çoban, *Tekstilde kullanılan çeşitli kimyasalların ve boyarmaddelerin iş sağlığı ve güvenliği açısından incelenmesi*, Fen Bilimleri Enstitüsü, 2019.
- [6] A. Tkaczyk, K. Mitrowska, A. Posyniak, Synthetic organic dyes as contaminants of the aquatic environment and their implications for ecosystems: A review, *Sci Total Environ* 717 (2020) 137222.
- [7] M. Berradi, R. Hsissou, M. Khudhair, M. Assouag, O. Cherkaoui, A. El Bachiri, A. El Harfi, Textile finishing dyes and their impact on aquatic environs, *Heliyon* 5(11) (2019) e02711.
- [8] A. Erkuş, E. Oygün, M. Türkmenoğlu, A. Aldemir, Boya endüstrisi atıksularının karakterizasyonu, *Yüzüncü Yıl Üniversitesi Fen Bilimleri Enstitüsü Dergisi* 23(3) (2018) 308-319.
- [9] J. Erkmen, E. KAVCI, M. ADIGÜZEL, Üretim planlaması yapılarak su bazlı boyaların üretimi esnasında oluşan su kirliliğinin ve boya kaybının önlenmesi, *Journal of the Institute of Science and Technology* 9(1) (2019) 57-65.
- [10] J. Sharma, S. Sharma, V. Soni, Classification and impact of synthetic textile dyes on Aquatic Flora: A review, *Regional Studies in Marine Science* 45 (2021) 101802.
- [11] L. Pereira, M. Alves, Dyes—environmental impact and remediation, *Environmental protection strategies for sustainable development* (2012) 111-162.
- [12] A.P. Periyasamy, Recent Advances in the Remediation of Textile-Dye-Containing Wastewater:

Prioritizing Human Health and Sustainable Wastewater Treatment, *Sustainability* 16(2) (2024) 495.

[13] S. Khan, A. Malik, Environmental and Health Effects of Textile Industry Wastewater, in: A. Malik, E. Grohmann, R. Akhtar (Eds.), *Environmental Deterioration and Human Health: Natural and anthropogenic determinants*, Springer Netherlands, Dordrecht, 2014, pp. 55-71.

[14] R. TÜRKSOY, G. TERZİOĞLU, İ.E. YALÇIN, Ö. TÜRKSOY, G. DEMİR, Removal of heavy metals from textile industry wastewater, *Frontiers in Life Sciences and Related Technologies* 2(2) (2021) 44-50.

[15] C. Valli Nachiyar, A.D. Rakshi, S. Sandhya, N. Britlin Deva Jebasta, J. Nellore, Developments in treatment technologies of dye-containing effluent: A review, *Case Studies in Chemical and Environmental Engineering* 7 (2023) 100339.

[16] M. Ahmed, M.O. Mavukkandy, A. Giwa, M. Elektorowicz, E. Katsou, O. Khelifi, V. Naddeo, S.W. Hasan, Recent developments in hazardous pollutants removal from wastewater and water reuse within a circular economy, *npj Clean Water* 5(1) (2022) 12.

[17] P. Yadav, R.P. Singh, G. Singh, H. Verma, S.K. Singh, P. Dahiya, A. Kumar, Chapter Eleven - Contamination removal from waste water using electrochemical approaches, in: A. Kumar, M. Bilal, L.F.R. Ferreira (Eds.), *Advances in Chemical Pollution, Environmental Management and Protection*, Elsevier2024, pp. 261-273.

[18] V. Kumar, M. Sharma, S. Sondhi, K. Kaur, D. Sharma, S. Sharma, D. Utreja, Removal of Inorganic Pollutants from Wastewater: Innovative Technologies and Toxicity Assessment, *Sustainability* 15(23) (2023) 16376.

[19] V. Vinayagam, K.N. Palani, S. Ganesh, S. Rajesh, V.V. Akula, R. Avoodaiappan, O.S. Kushwaha, A. Pugazhendhi, Recent developments on advanced oxidation processes for degradation of pollutants from wastewater with focus on antibiotics and organic dyes, *Environmental Research* 240 (2024) 117500.

[20] Y.I. Matatov-Meytal, M. Sheintuch, Catalytic abatement of water pollutants, *Industrial & engineering chemistry research* 37(2) (1998) 309-326.

[21] G. Centi, P. Ciambelli, S. Perathoner, P. Russo, Environmental catalysis: trends and outlook, *Catalysis Today* 75(1-4) (2002) 3-15.

[22] D. Wang, D. Astruc, The recent development of efficient Earth-abundant transition-metal nanocatalysts, *Chemical Society Reviews* 46(3) (2017) 816-854.

[23] U. Shanker, V. Jassal, M. Rani, Catalytic removal of organic colorants from water using some transition metal oxide nanoparticles synthesized under sunlight, *RSC advances* 6(97) (2016) 94989-94999.

[24] M.J. Ndolomingo, N. Bingwa, R. Meijboom, Review of supported metal nanoparticles: synthesis methodologies,

advantages and application as catalysts, *Journal of Materials Science* 55(15) (2020) 6195-6241.

[25] S. Wang, Q. Zhao, H. Wei, J.-Q. Wang, M. Cho, H.S. Cho, O. Terasaki, Y. Wan, Aggregation-free gold nanoparticles in ordered mesoporous carbons: toward highly active and stable heterogeneous catalysts, *Journal of the American Chemical Society* 135(32) (2013) 11849-11860.

[26] A. Alshammari, V.N. Kalevaru, A. Martin, Metal nanoparticles as emerging green catalysts, DOI 10(63314) (2016) 1-33.

[27] H.M. Ali, F.A. Roghabadi, V. Ahmadi, Solid-supported photocatalysts for wastewater treatment: Supports contribution in the photocatalysis process, *Solar Energy* 255 (2023) 99-125.

[28] T. Parandhaman, M.D. Dey, S.K. Das, Biofabrication of supported metal nanoparticles: exploring the bioinspiration strategy to mitigate the environmental challenges, *Green chemistry* 21(20) (2019) 5469-5500.

[29] M.I. Din, R. Khalid, Z. Hussain, T. Hussain, A. Mujahid, J. Najeeb, F. Izhar, Nanocatalytic assemblies for catalytic reduction of nitrophenols: a critical review, *Critical reviews in analytical chemistry* 50(4) (2020) 322-338.

[30] N. Qiao, Y. Nong, N. Liu, Y. Liang, Heterogeneous catalyst of porous anodic aluminum oxide with Al substrate supported metal nanoparticles, *Materials Chemistry and Physics* 225 (2019) 458-463.

[31] S. Said, S. Mikhail, M. Riad, Recent processes for the production of alumina nano-particles, *Materials Science for Energy Technologies* 3 (2020) 344-363.

[32] D.K. Koli, G. Agnihotri, R. Purohit, A review on properties, behaviour and processing methods for Al-nano Al₂O₃ composites, *Procedia Materials Science* 6 (2014) 567-589.

[33] G.K. Özgür, G. Dervisoglu, F.A. Özdemir, N. Özdemir, Z. Serbetçi, O. Dayan, Catalytic and biological properties of palladium(II) complexes with bidentate Schiff base ligands, *Applied Organometallic Chemistry* 38(2) (2024).

[34] C. Morisse, The structure/activity relationship of nitrobenzene hydrogenation over Pd/alumina catalysts, University of Glasgow, 2015.

[35] S. Dayan, F. Arslan, N.K. Ozpazan, Ru (II) impregnated Al₂O₃, Fe₃O₄, SiO₂ and N-coordinate ruthenium (II) arene complexes: Multifunctional catalysts in the hydrogenation of nitroarenes and the transfer hydrogenation of aryl ketones, *Applied Catalysis B: Environmental* 164 (2015) 305-315.

[36] H. Cheng, W. Lin, X. Li, C. Zhang, F. Zhao, Selective Hydrogenation of m-Dinitrobenzene to m-Nitroaniline over Ru-SnO_x/Al₂O₃ Catalyst, *Catalysts* 4(3) (2014) 276-288.

- [37] A. Chen, C. Ostrom, Palladium-based nanomaterials: synthesis and electrochemical applications, *Chemical Reviews* 115(21) (2015) 11999-12044.
- [38] M.R. Axet, K. Philippot, Catalysis with colloidal ruthenium nanoparticles, *Chemical reviews* 120(2) (2020) 1085-1145.
- [39] S.S. Panda, S.C. Jain, Synthesis of 2-Arylbenzimidazoles in Water, *Synthetic Commun* 41(5) (2011) 729-735.