Yuzuncu Yil University Journal of the Institute of Natural & Applied Sciences, Volume 28, Issue 1 (April), 271-284, 2023

Yuzuncu Yil University
Journal of the Institute of Natural & Applied Sciences
https://dergipark.org.tr/en/pub/yyufbed

Research Article

Catalytic Use of Pd(II) Complex Bearing 2-(thiophen-2-yl)-1*H*-Benzimidazole Ligand for The Reduction / Degradation of Multiple Mixtures Containing 4-NP, RhB and MB Organic Pollutants

Melek TERCAN[*]

Çanakkale Onsekiz Mart University, Faculty of Science, Department of Chemistry, 17100, Çanakkale, Türkiye
Melek TERCAN, ORCID No:0000-0001-7330-6076
* Corresponding author e-mail: melektercan@comu.edu.tr

Article Info

Received: 25.08.2022
Accepted: 19.12.2022
Online April 2023

DOI:10.53433/yyufbed.1167004

Keywords
Catalysis,
Methylene blue,
Pd complexes,
Rhodamine B,
4-Nitro phenol

Abstract: In this study, the catalytic use of $[Pd(L1)_2]Cl_2$ complex is aimed for the reduction / degradation reactions of organic pollutants in water sources which pose a threat to the environment. For this purpose, 2-(thiophen-2-yl)-1*H*-benzimidazole ligand (*L1*) and its Pd(II) complex (*C1*) were synthesized and characterized by FT-IR, ^{1}H-NMR, ^{13}C-NMR, ESI-MS spectroscopic techniques. The catalytic efficiency of the *C1* complex on the reduction of 4-nitro phenol compound (4-NP) and the degradation of rhodamine B (RhB), methylene blue (MB) dyes was investigated in the presence of $NaBH_4$ in aqueous medium. The catalytic performance was examined with single solutions of these substrates (4-NP and RhB, MB dyes) and at the end of 5 minutes, over 92% conversion was observed for all three substrates. In the catalytic trials with 4-NP + RhB + MB triple substrate mixture, 84, 94 and 93% conversion values were obtained, respectively, after 5 minutes. *C1* complex catalyst is very effective in the simultaneous reduction / degradation of these toxic organic compounds from aqueous environments without any competition or selectivity.

2-(tiyofen-2-il)-1*H*-Benzimidazol Ligandı Taşıyan Pd Kompleksinin 4-NP, RhB ve MB Organik Kirleticileri İçeren Çoklu Karışımların İndirgenmesi / Bozunmasında Katalitik Kullanımı

Makale Bilgileri

Geliş: 25.08.2022
Kabul: 19.12.2022
Online Nisan 2023

DOI:10.53433/yyufbed.1167004

Anahtar Kelimeler
Metilen mavisi,
Organik kirleticiler,
Pd kompleksleri,
Rodamin B,
4-Nitro fenol

Öz: Bu çalışmada, çevre için tehdit oluşturan organik kirleticilerin indirgeme / bozunma reaksiyonları ile su kaynaklarından uzaklaştırılması için $[Pd(L1)_2]Cl_2$ kompleksinin katalitik kullanımı amaçlanmıştır. Bu amaçla 2-(thiophen-2-yl)-1*H*-benzimidazole ligandı (*L1*) ve onun Pd(II) kompleksi (*C1*) sentezlenmiş ve FT-IR, ^{1}H-NMR, ^{13}C-NMR, ESI-MS spectroscopic teknikleri ile karakterize edilmiştir. *C1* kompleksinin rhodamine B (RhB) ve methylene blue (MB) boyalarının bozunmasındaki ve 4-nitro phenol (4-NP) bileşiğinin indirgenmesindeki katalitik etkinliği NaBH4 varlığında, sulu ortamda incelenmiştir. Bu substratların (4-NP ve RhB, MB boyaları) tekli çözeltileri ile katalitik performans incelenmiş ve 5 dakikanın sonunda her üç substrat için de 92% üzerinde dönüşüm gözlenmiştir. 4-NP + RhB + MB üçlü substrat karışımı ile yapılan katalitik denemelerde 5 dakikanın sonunda sırasıyla 84, 94 ve 93% dönüşüm değerleri elde edilmiştir. Çevre için oldukça toksik bu organik bileşikleri çoklu olarak içeren sulu ortamlardan bu bileşiklerin aynı anda ayrılmasında ***C1*** kompleks katalizörü oldukça etkindir.

1. Introduction

The wastes of dyes used in industries such as plastic, textile, leather, printing and paper cause bioaccumulation and pose a hazard to human health by being transported to people through the food chain (Joseph et al., 2019). Even very low concentrations of these toxic compounds, phenolics and dyes cause pollution in water resources and become a serious threat to the environment (Rafatullah et al., 2010; Thabet & Ismaiel, 2014; Alouani et al., 2018; Singh et al., 2019). Techniques such as biochemical and electrochemical methods, ion exchange, adsorption are used to remove these pollutants in water, but they have disadvantages such as low efficiency and cost (Robinson et al., 2001; Singh & Arora, 2011; Mokhtar, 2017). For this reason, metal nanoparticles (NPs), supported metal nanoparticles and metal complexes are used as catalysts in reduction / degradation reactions of toxic organic compounds (Kidambi et al., 2004; Wang et al., 2018). In fact, transition metal salts are quite good catalysts for many reactions on their own, but their separation / purification from the reaction environment and reusability problems occur in case of direct use. The metal salt may react with the substrates or dissolve in the reaction solvent causing metal leaching into the reaction medium. For this reason, nanoparticles of the metal salt whose catalytic properties will be utilized are prepared on an inorganic solid support or a porous material. Thus, it is possible to prepare a catalyst with homogeneous metal distribution and large surface area, and to increase the efficiency of the catalyst, by preventing the aggregation and clustering of metal particles. In the catalytic use of metal complexes, the metal is reduced after the first catalytic cycle, but the metal particles are stabilized by electrostatic interactions with the used ligand. That is, they do not agglomerate because they are still surrounded by ligands. Moreover, thanks to the electronic and steric properties of the ligand, the catalyst material can be prepared according to the substrate, thus increasing the catalytic efficiency as a result of the ligand-metal synergistic interaction. In this respect, benzimidazole derivative ligands are indispensable for coordination chemistry because they contain both electron withdrawing and donor groups in their heterocyclic structures and are frequently used in complexation reactions. Pd complexes, Pd nanoparticles and solid supported Pd nanoparticles are widely used in the catalytic reduction / degradation of the dyes in the literature (Nadagouda et al., 2012; Abdelaal & Mohamed, 2013; Hassani et al., 2015; Nguyen et al., 2018; Asadabadi et al., 2019; Wang et al., 2021). Pd metal complexes with improved electronic and chemical properties with appropriate ligand selection are used in catalysis.

4-NP is a carcinogenic and mutagenic compound frequently used in the pharmaceutical, synthetic dye industry (Wang et al., 2013; Naraginti et al., 2015; Mejia & Bogireddy, 2022; Shu et al., 2022). RB is a biological fluorescence molecule used in bacterial staining studies (Rahman et al., 2013; Jabeen et al., 2021; Olagunju et al., 2021; Al-Buriahi et al., 2022; Zhou et al., 2022). On the other hand, MB is a toxic, heterocyclic cationic dye molecule that is widely used as a textile dye (Sahiner et al., 2015; Kumar et al., 2021; Saputra et al., 2022). Organic dyes are molecules that are resistant to biodegradation and have high stability to heat and light. Many N-containing organic dyes, especially RhB and MB, undergo natural degradation, by yielding potentially carcinogenic aromatic amines. Therefore, the degradation of these toxic molecules by chemical catalysis are important. In the presented study, benzimidazole ligand derivative 2-(thiophen-2-yl)-1*H*-benzimidazole ligand (*L1*), which is very important for coordination chemistry due to its N-donor nitrogen atom and ease of operation, was synthesized and its Pd(II) complex (*C1*) was prepared (Tadokoro & Nakasuji, 2000). The prepared *L1* ligand and *C1* complex were characterized by FT-IR, ^{1}H-NMR, ^{13}C-NMR, ESI-MS spectroscopic techniques. Then the catalytic efficiency of *C1* complex in the reduction reaction of 4-nitro phenol (4-NP) and the degradation reactions of rhodamine B (RhB) and methylene blue (MB) dyes in the presence of $NaBH_4$ as a reducing agent was investigated. In general, removal of pollutants from water source studies should be done in samples containing multiple pollutants, but examination of the catalytic reduction / degradation reaction is important to estimate the overall behavior. For this purpose, catalytic studies were carried out with substrate solutions containing single and triple mixtures of 4-NP compound and RhB, MB dyes used as model compounds, and high conversion values above 90% were obtained for both single and triple substrate solutions.

2. Material and Methods

2.1. Materials

o-phenylenediamine (99%, Sigma Aldrich), 2-thiophenecarboxaldehyde (98%, Sigma Aldrich) and sodium bisülfite (95%, Acros Organics) that used in the ligand (*L1*) synthesis were provided commercially. $PdCl_2$ (59% Pd, Merck) and HCl (37%, Merck) were used in the preparation of Pd(II) complex (*C1*). All solvents used in ligand and complex synthesis were commercially available and used without purification. 4-nitrophenol (99%, Merck), rhodamine B (99%, Sigma Aldrich) and methylene blue (98%, Sigma Aldrich) were used as toxic dye source for catalytic studies. Sodium borohydride ($NaBH_4$, 98%, Merck) was used as reducing agent in catalytic reduction / degradation studies. Perkin Elmer Spectrum One FT-IR/ATR and Jeol JNM-ECX400II NMR spectrometer were used in the characterization of the *L1* and *C1* compounds. LC-MS chromatograms of *L1* and *C1* were recorded by Shimadzu LC/MS 8040 spectrophotometer in a range 100-2000 m/z and electron impact (EI) ionization technique. XRD pattern of *C1* complex was obtained by PANalytical Empyrean X-ray diffractometer. The catalytic studies were monitored by Perkin Elmer Lambda 35 UV-Vis Spectrometer.

2.2. Synthesis of 2-(Thiophen-2-yl)-1*H*-benzimidazole ligand, *L1*

A mixture of 2-thiophenecarboxaldehyde (0.96 mL, 10.00 mmol) and $NaHSO_3$ (11.45 g, 11.0 equiavelent) were refluxed in water (30 mL) overnight. A solution of *o*-phenylenediamine (1.08 g, 10.00 mmol) in water (10 mL) was added dropwise to the mixture and refluxed until the solution became transparent yellow. After the completion of the reaction, the mixture was cooled to the room temperature and the residue was filtered off. The obtained yellowish solid was washed with water twice and dried (Kim et al., 2020). (1.36 g, 68% yield) m.p: 333-335 ^{o}C.

2.2.1. Data for *L1*

FT-IR (ATR/cm^{-1}): 3009, 2525, 1622, 1569, 1476, 1450, 1417, 1338, 1314, 1275, 1234, 1147, 1093, 1073, 1003, 944, 851, 763, 740, 701.
^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 12.92 (s, 1H), 7.80 (d, *J* = 3.63 Hz, 1H), 7.69 (d, *J* = 5.01 Hz, 1H), 7.58-7.47 (m, 2H), 7.22-7.11 (m, 3H).
^{13}C NMR (100 MHz, DMSO-d_6) δ ppm 147.54, 144.27, 135.23, 134.23, 129.30, 128.82, 127.21, 123.03, 122.36, 119.07, 111.66.
Positive ESI–MS (m/z): 201 $[M]^+$, (calculated: 200.26).

2.3. Synthesis of $[Pd(L1)_2]Cl_2$ complex, *C1*

2-(Thiophen-2-yl)-1*H*-benzimidazole ligand (200 mg, 1.0 mmol) was dissolved in a small amount of ethanol and added dropwise to the $[PdCl_4]^{2-}$ solution that obtained by completely dissolving the $PdCl_2$ salt (89 mg, 0.5 mmol) in 50 mL of 20 mM HCl solution. The complex was precipitated as an orange solid in the reaction media after heating in the 60 ^{o}C water bath. Thus obtaining $[Pd(L1)_2]Cl_2$ complex was filtered off, washed with ethanol and dried under vacuo (Ramadan et al., 2004). (0.208 g, 72% yield) m.p: > 360 ^{o}C.

2.3.1. Data for *C1*

FT-IR (ATR/cm^{-1}): 3159, 3077, 1622, 1601, 1563, 1480, 1456, 1436, 1379, 1319, 1234, 1223, 1150, 1100, 1047, 1006, 971, 852, 800, 746, 714.
^{1}H NMR (400 MHz, DMSO-d_6) δ ppm13.83 (t, *J* = 11.3 Hz, 2H), 8.72 (dd, *J* = 8.13 Hz, 1H), 8.38 (dd, *J* = 5.51 Hz, 1H), 8.21-8.14 (m, 2H), 8.02 (dd, *J* = 5.34, 1H), 7.79 (dd, *J* = 3.95, 1H), 7.57-7.52 (m, 2H), 7.46-7.32 (m, 5H), 7.24-7.17 (m, 1H).
^{13}C NMR (100 MHz, DMSO-d_6) δ ppm147.12, 140.39, 133.20, 133.02, 132.35, 132.06, 131.63, 131.51, 131.21, 129.77, 129.36, 128.94, 128.80, 128.49, 125.16, 124.97, 124.33, 123.84, 122.99, 119.64, 118.92, 118.34, 112.71, 112.51.

Positive ESI–MS (m/z): 578 $[M]^+$, 596 $[M+H_2O]^+$, (calculated: 577.85).

2.4. Catalytic studies

The catalytic efficiencies of the prepared Pd(II) complex, *C1*, in the reduction / degradation reactions of 4-NP, RB and MB substrates were investigated in the presence of $NaBH_4$ in aqueous media. For this purpose, the optimum reaction conditions were determined first by scanning the amount of $NaBH_4$, the substrate concentration and the amount of catalyst. 4-NP substrate, which is frequently used in catalytic studies as model compound, was used for optimization studies. Catalytic trials were made with 0.1, 0.2, 0.3, 0.4 and 0.5 mmol of $NaBH_4$ to be used as a hydrogen source in catalyst-free environment, and it was observed that the use of $NaBH_4$ above 0.2 mmol did not provide a significant difference in reduction of 4-NP substrate. For this reason, the appropriate amount of $NaBH_4$ for catalytic studies was determined as 0.2 mmol (Selvi et al., 2020). Then, the reduction reactions of 10 mL of 0.01, 0.1 and 1.0 mM aqueous solutions of 4-NP in catalyst- free media in the presence of 0.2 mmol $NaBH_4$ was followed by UV-Vis spectroscopy and the percent conversion values were calculated according to Equation 1 (A_0: Initial absorption).

$$Conversion\ (\%) = [(A_0 - A) / A_0]\ x\ 100 \tag{1}$$

Table 1. Catalytic conversion values for the reduction / degradation of 10 mL of 0.01, 0.1, 0.5 and 1.0 mM aqueous solutions of 4-NP substrate in catalyst-free media in the presence of 0.2 mmol $NaBH_4$

4-NP concentration (mM)	Conversion (%)
0.01	44
0.1	21
0.5	20
1.0	6

The percent conversion values obtained after 5 minutes for 0.01, 0.1 and 1.0 mM 4-NP substrate solutions in the presence of 0.2 mmol $NaBH_4$ are 44, 21 and 6%, respectively (Table 1). For the reduction of 0.01 M 4-NP solution with only $NaBH_4$ in a catalyst-free media, 44% conversion is a high value while 6% conversion value observed for 1.0 mM 4-NP is not suitable for comparison on the efficiency of the catalyst. 20% conversion was obtained for the reduction of 0.5 mM 4-NP which was scanned as the mean value of 0.1 and 1.0 mM substrate concentration and 21% conversion for 0.1 mM 4-NP solution. Thus, 0.5 mM concentration for 4-NP was chosen as the optimum substrate concentration and the same substrate concentration was used for all catalytic experiments. Then, in order to examine the effect of catalyst amount, the reduction of 0.5 mM 4-NP solution in the presence of 0.2 mmol $NaBH_4$ with changing amounts of *C1* complex catalyst were investigated. For the reduction of 4-NP substrates with 2.5, 5 and 7.5 mg of *C1* complex catalyst, the percent conversion values after 5 minutes were observed as 92, 95 and 99%, respectively. Considering that almost all 95%) of the catalytic reduction of 4-NP is completed in the presence of 5 mg of *C1* complex catalyst and the use of catalysts containing a small amount of metal is more environmentally friendly, the optimum amount of catalyst to be used in catalytic studies has been determined as 5 mg (Table 2). Finally, catalytic experiments were carried out in triplicate for single and triple mixtures of 4-NP, RhB and MB substrates under optimum reaction conditions.

Table 2. Catalytic conversion values for the reduction / degradation of 10 mL of 0.5 mM aqueous solutions of 4-NP substrate in the presence of 0.2 mmol M $NaBH_4$ with changing *C1* catalyst amounts

Time (min)	**Conversion (%)**		
	2.5 mg catalyst	5 mg catalyst	7.5 mg catalyst
1	45	52	64
2	62	78	88
3	74	91	98
4	85	93	99
5	92	94	99

3. Results

3.1. Structural characterization

The use of the synthesized *C1* complex as a catalyst in the reduction / degradation reactions of 4-nitrophenol, methylene blue and rhodamine B toxic organic compounds in the presence of $NaBH_4$ in aqueous medium was investigated. The schematic representation of the synthesis of the 2-(thiophen-2-yl)-1*H*-benzimidazole ligand (*L1*) and its Pd^{2+} complex, $[Pd(L1)_2]Cl_2$ is given in Figure 1. The chemical structures of the synthesized *L1* ligand and the *C1* complex were clarified by FT-IR, ^{1}H-NMR, ^{13}C-NMR and LC-MSMS spectroscopic methods.

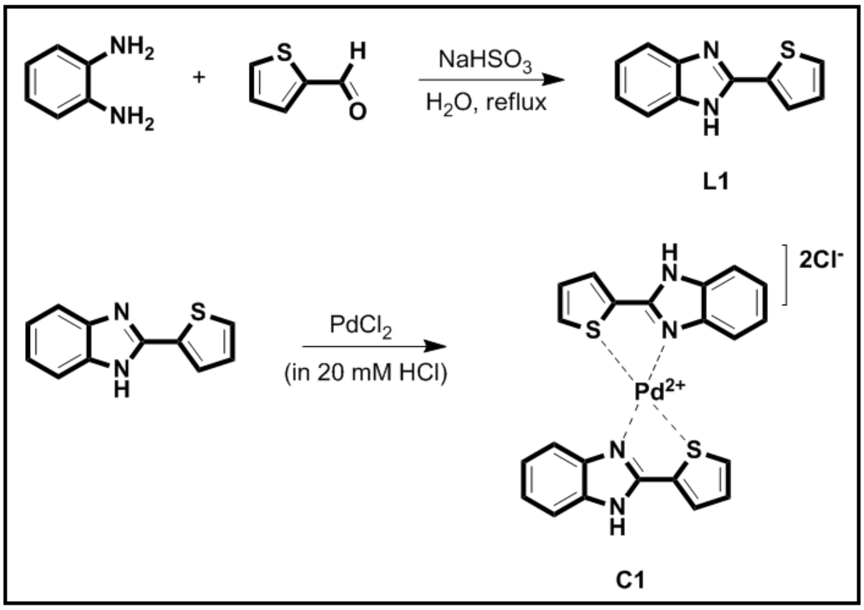

Figure 1. Schematic representation for the synthesis of 2-(thiophen-2-yl)-1*H*-benzimidazole ligand (*L1*) and its Pd^{2+} complex (*C1*).

When the FT-IR spectrum of the *L1* ligand was examined, it was observed that the N-H stretching peak could not be observed due to the intramolecular H-bond, as in the other benzimidazole compounds (Figure 2). The broad peak observed at 2525 cm^{-1} is the aromatic S-H stretching peak observed as a result of intramolecular H-bonding of benzimidazole N-H and thiophene ring sulphur. The stretching peak of C=N double bond was observed at 1622 cm^{-1}. As seen in the ^{1}H-NMR spectrum of *L1*, an aromatic N-H proton was observed at 12.92 ppm. While thiophene ring aromatic protons were observed at 7.80 and 7.69 ppm, other aromatic protons were observed in the range of 7.58-7.11 ppm (Figure 3). The $[M]^+$ peak observed at 201 ppm (calculated: 200.26) in the mass spectrum of *L1* also proves the structure. When the FT-IR spectrum of the dimeric Pd complex (*C1*) of *L1* ligand was examined, it was observed that the intramolecular H-bond was disappeared with the complexation and the N-H stretching peak was observed at 3159 cm^{-1}. This proves the coordination of *L1* ligand to Pd metal occurs via benzimidazole ring nitrogen atom and thiophene ring sulfur atom. For this reason, the S-H stretching peak that observed at 2525 cm^{-1} in the FT-IR spectrum of the *L1* ligand was disappeared in the FT-IR spectrum of the *C1* complex as a result of complexation. It was seen that the N-H protons of the *C1* complex were shifted to 13.83 ppm in the ^{1}H-NMR spectrum. Due to the dimeric structure of the complex, the aromatic doublet and triplet peaks of the two 2-(thiophen-2-yl)-1*H*-benzimidazole ligands were observed to be identical. In the mass chromatogram for the *C1* complex, the $[M]^+$ peak was observed at 578 (calculated: 577.85) and the $[M+H_2O]^+$ peak obtained by attaching the structure one water molecule was observed at 596 (calculated: 595.85).

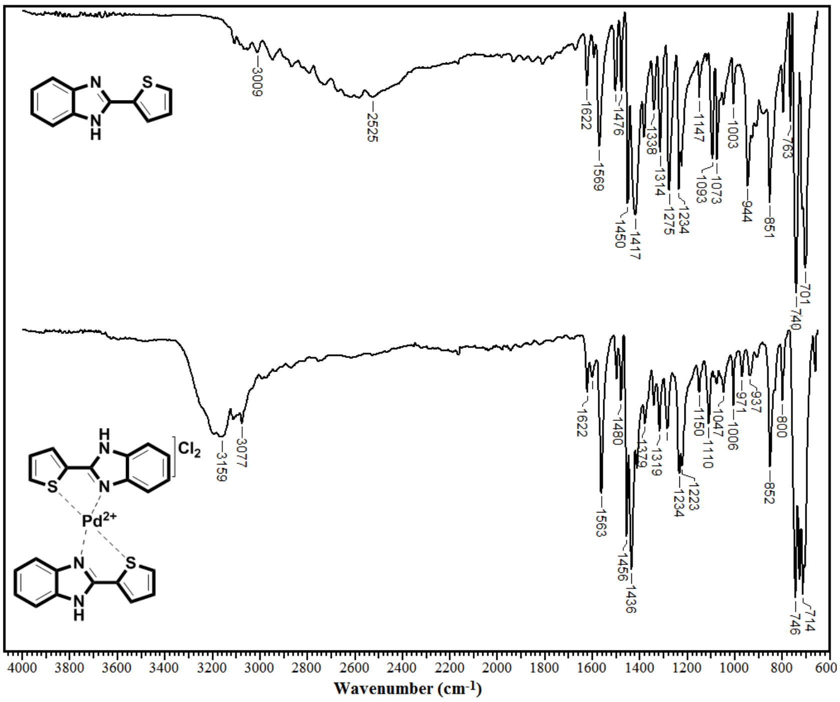

Figure 2. The overlapped FT-IR spectra of *L1* ligand and *C1* complex.

XRD measurents were monitored to investigate the structural ordering of the *C1* complex that used as catalyst in reduction / degradation reactions of the 4-NP, RhB and MB substrates. It is known that the crystal structures are well observed for systems in the ligand phase while semi-crystalline structures occur for the metal complexes of these ligands (Cuerva et al., 2017; Nasrollahzadeh et al., 2019; Gao et al., 2022). In the XRD diffractogram of *C1* complex, 3 different peaks at 39.04°, 43.25° and 55.30° ϴ angles were observed which indicate the presence of Pd metal in the structure (Figure 4).

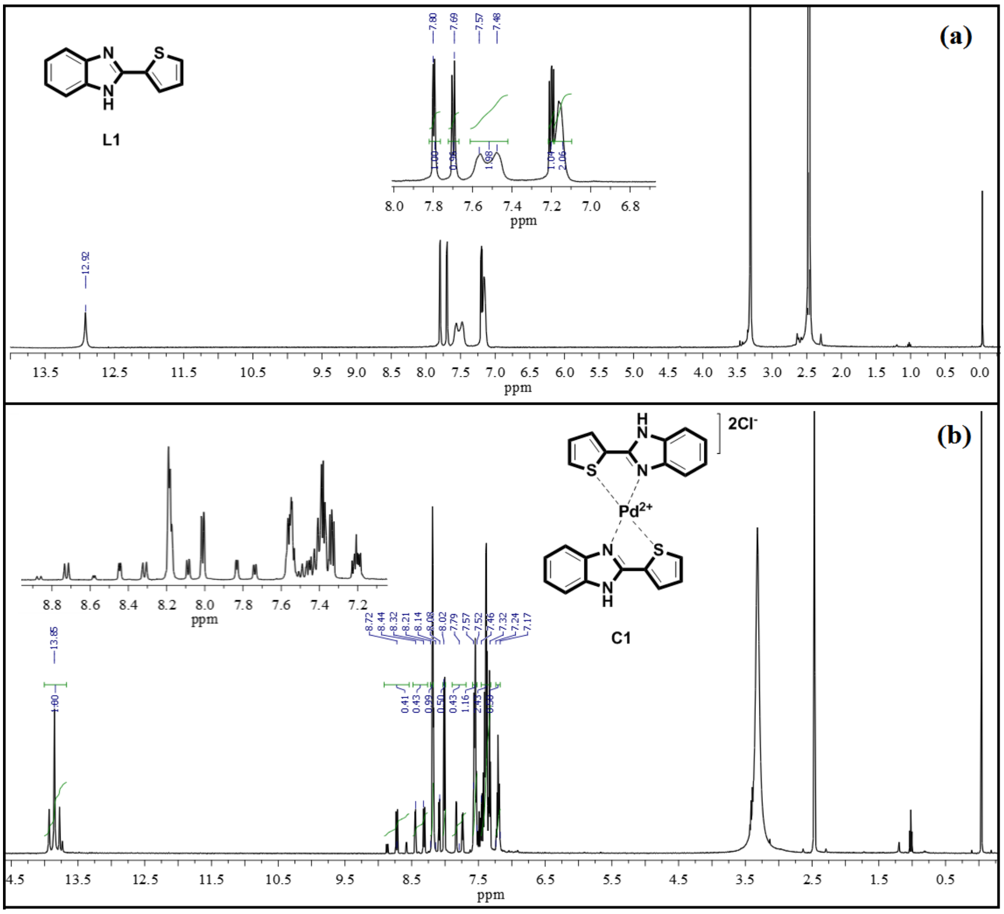

Figure 3. ^{1}H-NMR spectra of *L1* ligand (a) and *C1* complex (b).

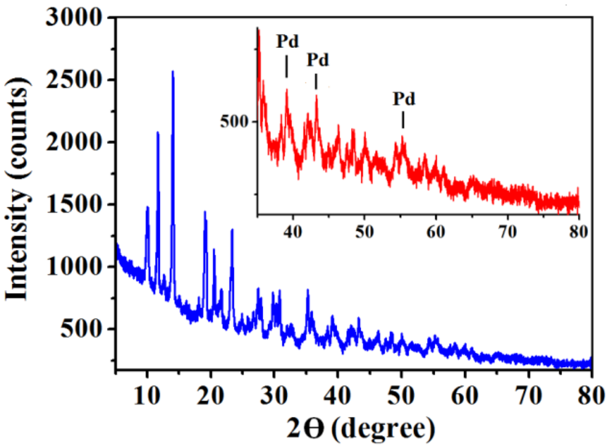

Figure 4. The XRD pattern of [Pd(*L1*)$_2$](Cl$_2$) complex, *C1*.

3.2. Catalytic performance of [Pd(*L1*)$_2$]Cl$_2$ complex, C1

In the present study, the catalytic efficiency of the *C1* complex in the catalytic reduction / degradation reactions of 4-NP, RhB and MB toxic organic compounds was investigated. For this purpose, the reaction conditions were standardized first with the catalytic trials by different NaBH$_4$ amounts, substrate concentrations and catalyst amounts. In the catalytic experiments to determine the optimum reaction conditions with 4-NP substrate, the conversion value was observed as 20% in the presence of 0.2 mmol NaBH$_4$ for 0.5 mM (10 mL) 4-NP substrate in catalyst-free media. This low conversion value indicates that completion of the reduction / degradation of toxic dyes requires the use of active catalysts. Again, as a result of the trials carried out in the presence of 0.5 mM 4-NP substrate, 0.2 mmol $NaBH_4$ and different amounts of *C1* complex catalyst, it was observed that the catalytic conversion was completed with 5 mg *C1* catalyst to a large extent (95%). Since the low metal content of the catalyst to be used is an environmentally friendly approach, the optimum catalyst amount was chosen as 5 mg *C1* complex catalyst. Thus, the catalytic experiments were carried out in 0.5 mM, 10 mL of substrates that containing 5 mg catalyst material and 0.2 mmol $NaBH_4$ as the optimum reaction conditions.

During the catalytic reduction / degradation reactions, 0.2 mL was taken from the reaction mixture, diluted to 4 mL with water and filtered into a UV cuvette. Then the changes in absorbance values were monitored by UV-Vis spectrophotometer at 400 nm for 4-NP compound, 553 nm for RhB and 665 nm for MB dyes. The catalytic performance of the prepared Pd(II) complex, *C1*, was measured in triplicate for single and triple substrate mixtures. The catalytic conversion values of the reaction solutions containing a single substrate were observed as 92 ± 6.6 % for 4-NP, 92 ± 2.4 and 93 ± 1.7% for RhB and MB under optimum conditions (Figure 5 (a)). These conversion values observed over 90% for each substrate show that the catalyst is quite effective. 5 mg of *C1* catalyst used in catalytic trials contains 8.7×10^{-3} mmol of Pd (0.9 mg Pd) metal. In other words, it is sufficient for the catalyst to contain 0.9 mg of Pd metal to complete the reduction / degradation reaction of the 0.5 mM substrate mixture. Direct use of metal salt in catalytic reactions is not preferred because it will cause the metal to react with the substrate or it will dissolve in the reaction solution and cause metal leaching. However, in order to understand whether the ligand-metal interaction provides catalytic superiority, the reduction / degradation reactions of 0.5 mM 4-NP, RB and MB substrates were studied in the presence of $PdCl_2$ catalyst (1.5 mg $PdCl_2$) which containing Pd metal equivalent to the amount of Pd metal in the 5 mg *C1* complex. In the presence of 1.5 mg $PdCl_2$, 90, 88 and 81% conversion were observed for the 4-NP aromatic compound, RB and MB dyes, respectively. As expected, higher percent conversion values were obtained with the $[Pd(L1)_2]Cl_2$ catalyst containing equivalent amount of Pd as a result of the synergistic interaction of the ligand and the Pd metal. In Figure 5 (b) the catalytic conversion values of the reaction mixture containing all three substrates were shown as 84 ± 4.3, 94 ± 1.7 and 93 ± 0.8% for 4-NP, RhB and MB, respectively, under optimum reaction conditions. In fact, for mixtures containing multiple toxic compounds, reduction / degradation reaction catalytic conversion values per component are expected to decrease comparing the single ones. However, it was observed that the conversion value, which was 92% in the catalytic experiments with solution containing a single RhB substrate, was preserved with 94% in the triple substrate mixture (4-NP + RhB + MB). Again, the conversion of 93% for MB single substrate was conserved to be 93% for the triple substrate mixture, only the conversion value of 4-NP decreased from 92% to 84% in the triple substrate mixture. The prepared catalyst with low Pd metal content catalyzed the reduction / degradation reaction not only for a single substrate but also for all three substrates. It can be said that the catalytic efficiency is superior for RhB and MB dyes in single and triple substrate mixtures.

The variation of the $\ln(C/C_0)$ values of the catalytic reduction / degradation reactions of 4-NP, RhB and MB substrates in the presence of ***C1*** complex over time is given in Figure 6. As indicated by the changes in substrate concentrations, the reduction / degradation reactions were almost completed after 5 minutes in both single substrate solutions and triple substrate mixtures.

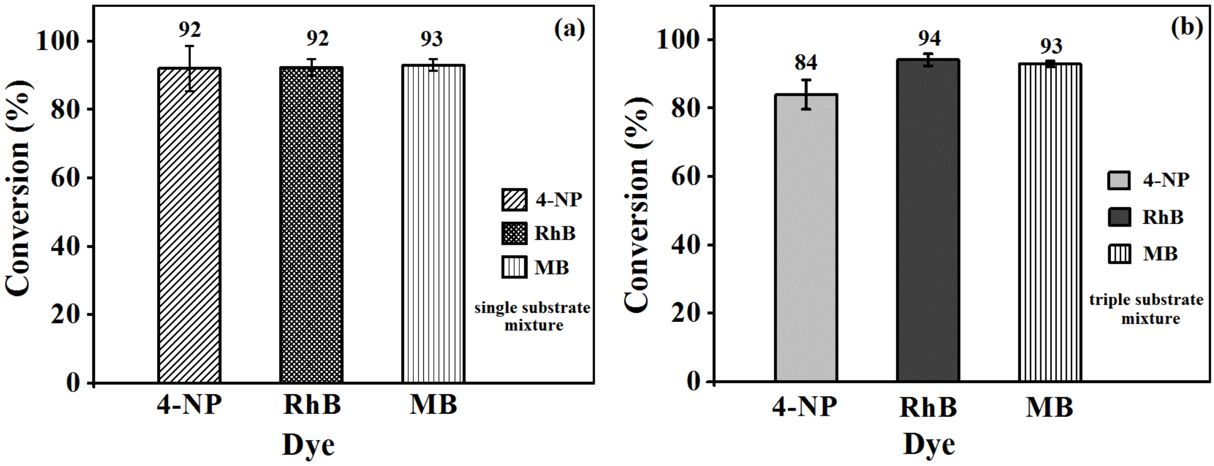

Figure 5. Comparison of the conversion percentage of single substrate mixtures (a) and triple substrate mixtures (b) catalyzed by *C1* complex catalyst in the presence of 0.02 mmol $NaBH_4$ at 5 min reaction time.

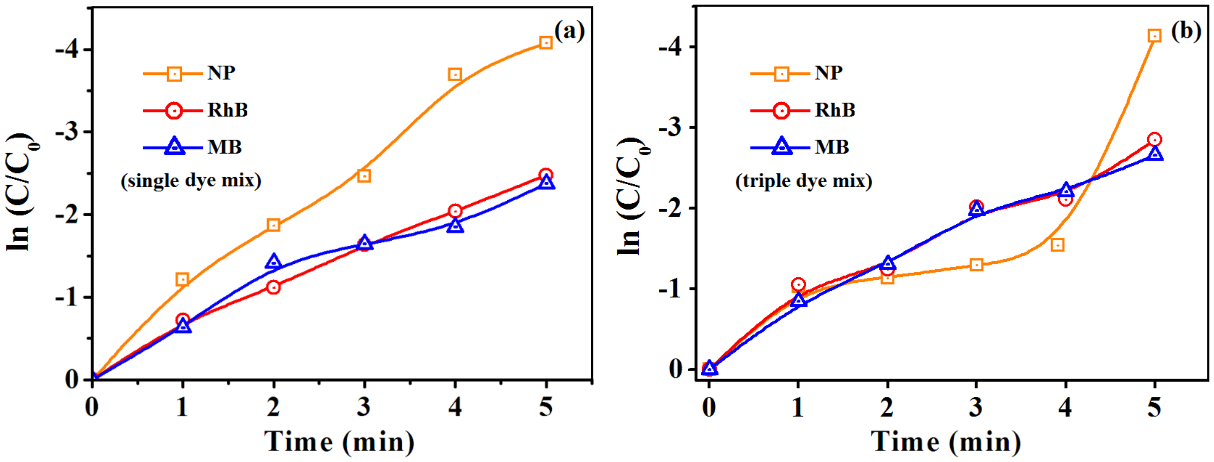

Figure 6. The reduction in conversion percentage of each substrate in single (a) and triple substrate mixtures (b) catalyzed by *C1* complex catalyst in the presence of 0.02 mmol $NaBH_4$ at the end of 5 min.

Figure 7. shows the UV-Vis spectra of the reduction / degradation reactions of 4-NP, RhB and MB substrates singly (a, b, c) and the 4-NP + RhB + MB triple mixture (d) in the presence of ***C1*** complex catalyst. It is clearly seen from the UV-Vis spectrum that the absorbance values observed at 665 nm for MB, 553 nm for RhB and 400 nm for 4-NP decrease over time as a result of reduction / degradation.

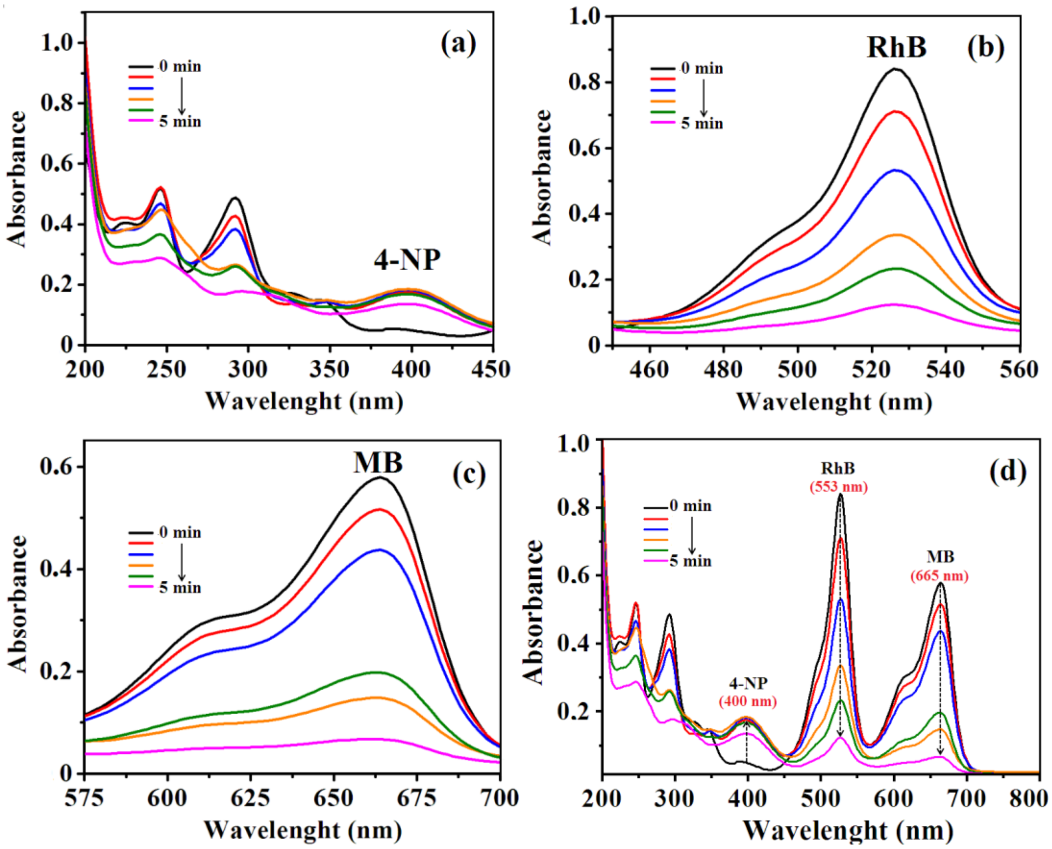

Figure 7. The change in the UV-Vis absorption spectrum of the 4-NP (a), RhB (b), MB (c) substrates and 4-NP + RhB + MB triple substrate mixture with time for the catalytic reduction / degradation reaction catalyzed by *C1* complex catalyst.

The turn-over frequency (TOF) values of *C1* complex-catalyzed reduction / degradation reactions of 4-NP, RhB and MB compounds were calculated using Equation 2 and the results are given in Table 3. TOF values of around 640 h^{-1} were obtained for single and triple substrate mixtures. Accordingly, the high conversion and TOF values obtained by *C1* complex catalyst for single and triple substrate mixtures showed that the prepared *C1* complex catalyst can be used in the removal of polluting organic dyes from water. In addition, the catalyzed reduction / degradation reactions of 4-NP, RhB and MB substrates with other Pd-based catalysts are compared in Table 4. *C1* complex catalyst also showed superiority in reducing all three substrates simultaneously with high efficiency.

$$TOF = \textit{moles of consumed reactant} / (\textit{mole of catalyst x time (h)}) \tag{2}$$

Table 3. Conversion percentages and TOF values for catalytic reduction / degradation reactions of 4-NP, RhB and MB substrates catalyzed by *C1* catalyst

Substrate mixtures	**Molecules**	**Conversion[1] (%)**	**TOF[1] (h^{-1})**
4-NP	4-NP	92.1 ± 6.6	641.2 ± 19.8
RhB	RhB	92.4 ± 2.4	643.4 ± 7.2
MB	MB	93.1 ± 1.7	648.2 ± 5.1
4-NP + RhB + MB	4-NP	84.0 ± 4.3	584.9 ± 12.9
4-NP + RhB + MB	RhB	94.2 ± 1.7	655.8 ± 5.1
4-NP + RhB + MB	MB	93.0 ± 0.8	647.5 ± 2.4

[1] Catalytic reduction / degradation reactions were monitored by UV-Vis spectrophotometer for 10 mL substrate solutions containing 5.0 mmol dye (4-NP, RhB, MB) in the presence of 0.2 mmol $NaBH_4$ and 8.7 µmol Pd complex catalyst. All catalytic trials were performed in triplicate in aqueous media, at room temperature.

Table 4. Comparison for the reduction / degradation reactions of 4-NP, RhB and MB substrates with other Pd-based catalysts

Catalyst	Substrate	Catalyst amount	Time (min)	Conversion (%)	TOF (h^{-1})	Ref.
Fe_3O_4@Triazole-CS@NNN-Pd	4-NP	80 mg	5	98	1176	Rafiee&Rezaee, 2022
BBCP@PhenTet@Pd	4-NP	0.75 mmol	50	95	4.5	Ariannezhad et al., 2022
ZnO/Au/Pd	MB	5 mg	180	97	-	Lee et al., 2019
Pd-rGO	RhB	0.025 mg	0.5	92	-	Bhat et al., 2020
Pd@BTC-CONH	RhB	50 mg	6	99	-	Selim et al., 2020
$[Pd(\mathit{L1})_2]Cl_2$	4-NP	5 mg	5	92	641.2	This work
$[Pd(\mathit{L1})_2]Cl_2$	RhB	5 mg	5	92	643.4	This work
$[Pd(\mathit{L1})_2]Cl_2$	MB	5 mg	5	93	648.2	This work

4. Discussion and Conclusion

In the presented study, benzimidazole derivative 2-(thiophen-2-yl)-1*H*-benzimidazole ligand (*L1*) and its Pd(II) complex (*C1*) was prepared. The catalytic efficiency of *C1* complex in the catalytic reduction / degradation reactions of 4-NP, RhB and MB toxic organic compounds was investigated. Catalytic reduction / degradation reactions were carried out with substrate solutions containing 5 mmol of 4-NP, RhB and MB dyes in the presence of 5 mg *C1* complex catalyst and 0.2 mmol $NaBH_4$ as reducing agent. Catalytic trials were studied in triplicate for single and triple mixtures of 4-NP, RhB and MB substrates, in aqueous medium and room temperature, and the reaction was monitored by UV-Vis spectrophotometer. Percent conversion values of over 90% were obtained for each of the 4-NP, RhB and MB substrates. It was observed that these high percent conversion values were maintained without any competition or selectivity for the triple substrate mixture containing 4-NP, RhB and MB. TOF values of around 640 h^{-1} were obtained for single and triple mixtures of 4-NP, RhB and MB substrates. As a result, it can be said that the *C1* complex can be used as a catalyst in the elemination of organic toxic compounds or their multiple mixtures from water sources, and it is an environmentally friendly alternative with its low Pd metal content (0.9 mg).

References

Abdelaal, M. Y., & Mohamed, R. M. (2013). Novel Pd/TiO_2 nanocomposite prepared by modified sol–gel method for photocatalytic degradation of methylene blue dye under visible light irradiation. *Journal of Alloys and Compounds*, 576, 201-207. doi:10.1016/j.jallcom.2013.04.112

Al-Buriahi, A. K., Al-Gheethi, A. A., Kumar, P. S., Mohamed, R. M. S. R., Yusof, H., Alshalif, A. F., & Khalifa, N. A. (2022). Elimination of rhodamine B from textile wastewater using nanoparticle photocatalysts: A review for sustainable approaches. *Chemosphere*, 287(2), 132162-132175. doi:10.1016/j.chemosphere.2021.132162

Alouani, M. E., Aleyhen, S., Achouri, M. E., & Taibi, M. (2018). Removal of cationic dye – methylene blue- from aqueous solution by adsorption on fly ash-based geopolymer. *Journal of Materials and Environmental Science*, 9(1), 32-46. doi:10.26872/jmes.2018.9.1.5

Ariannezhad, M., Pourmorteza, N., Yousefi, A., & Esperi, M. (2022). Catalytic reduction of nitroarenes and Suzuki-Miyaura reactions using Pd complex stabilized on the functionalized polymeric support. *Chemical Physics Letters*, 793, 139431-13945. doi:10.1016/j.cplett.2022.139431

Asadabadi, A. Z., Hoseini, S. J., Bahramia, M., & Nabavizadeh, S. M. (2019). Catalytic applications of b-cyclodextrin / palladium nanoparticle thin film obtained from oil/water interface in the reduction of toxic nitrophenol compounds and the degradation of azo dyes. *New Journal of Chemistry*, 43, 6513-6522. doi:10.1039/C8NJ06449K

Bhat, S. A., Rashid, N., Rather, M. A., Bhat, S. A., Ingole, P. P., & Bhat, M. A. (2020). Highly efficient catalytic reductive degradation of Rhodamine-B over Palladium-reduced graphene oxide nanocomposite. *Chemical Physics Letters*, 754, 137724-137731. doi:10.1016/j.cplett.2020.137724

Cuerva, C., Campo, J. A., Cano, M., & Schmidt, R. (2017). Nanostructured discotic Pd(II) metallomesogens as one-dimensional proton conductors. *Dalton Transactions*, 46, 96-105. doi:10.1039/C6DT03521C

Gao, S., Hu, S., Luo, G., Sun, S., & Zhang, X. (2022). 2,2′-bipyridine palladium(II) complexes derived N-doped carbon encapsulated palladium nanoparticles for formic acid oxidation. *Electrochimica Acta*, 413, 140179-140187. doi:10.1016/j.electacta.2022.140179

Hassani, R., Jabli, M., Kacem, Y., Marrot, J., Prim, D., & Hassine, B. B. (2015). New palladium–oxazoline complexes: Synthesis and evaluation of the optical properties and the catalytic power during the oxidation of textile dyes. *Beilstein Journal of Organic Chemistry*, 11, 1175-1186. doi:10.3762%2Fbjoc.11.132

Jabeen, S., Khan, M. S., Khattak, R., Zekker, I., Burlakovs, J., Rubin, S. S., Ghangrekar, M. M., Kallistova, A., Pimenov, N., Zahoor, M., & Khan, G. S. (2021). Palladium-supported Zirconia-based catalytic degradation of rhodamine-B dye from wastewater. *Water*, 13(11), 1522-1534. doi:10.3390/w13111522

Joseph, A., Vellayan, K., González, B., Vicente, M. A., & Gil, A. (2019). Effective degradation of methylene blue in aqueous solution using Pd supported Cu-doped Ti-pillared montmorillonite catalyst. *Applied Clay Science*, 168, 7-10. doi:10.1016/j.clay.2018.10.009

Kidambi, S., Dai, J., Li, J., & Bruening, M. L. (2004). Selective hydrogenation by Pd nanoparticles embedded in polyelectrolyte multilayers. *Journal of American Chemical Society*, 126(9), 2658-2659. doi:10.1021/ja038804c

Kim, J., Lee, S., Kim, S., Jung, M., Lee, H., & Han, M. S. (2020). Development of a fluorescent chemosensor for chloride ion detection in sweat using Ag^+ benzimidazole complexes. *Dyes and Pigments*, 177, 108291-108296. doi:10.1016/j.dyepig.2020.108291

Kumar, A. P., Bilehal, D., Tadesse, A., Kumar, D. (2021). Photocatalytic degradation of organic dyes: Pd-g-Al_2O_3 and PdO-g-Al_2O_3 as potential photocatalysts. *Royal Society of Chemistry Advances*, 11, 6396–6406. doi:10.1039/D0RA10290C

Lee, S. J., Jung, H. J., Koutavarapu, R., Lee, S. H., Arumugam, M., Kim, J. H., & Choi, M. Y. (2019). ZnO supported Au/Pd bimetallic nanocomposites for plasmon improved photocatalytic activity for methylene blue degradation under visible light irradiation. *Applied Surface Science*, 496, 143665-143674. doi:10.1016/j.apsusc.2019.143665

Mejia, Y. R., & Bogireddy, N. K. R. (2022). Reduction of 4-nitrophenol using green-fabricated metal nanoparticles. *Royal Society of Chemistry Advances*, 12, 18661–18675. doi:10.1039/D2RA02663E

Mokhtar, M. (2017). Application of synthetic layered sodium silicate magadiite nanosheets for environmental remediation of methylene blue dye in water. *Materials*, 10(7), 760-773. doi:10.3390/ma10070760

Nadagouda, M. N., Desai, I., Cruz, C., & Yang, D. J. (2012). Novel Pd based catalyst for the removal of organic and emerging contaminants. *Royal Society of Chemistry Advances*, 2, 7540–7548. doi:10.1039/C2RA20562A

Naraginti, S., Stephen, F. B., Radhakrishnan, A., & Sivakumar, A. (2015). Zirconium and silver co-doped TiO_2 nanoparticles as visible light catalyst for reduction of 4-nitrophenol, degradation of methyl orange and methylene blue. *Spectrochimica Acta A: Molecular and Biomolecular Spectroscopy*, 135, 814-819. doi:10.1016/j.saa.2014.07.070

Nasrollahzadeh, M., Issaabadi, Z., & Safari, R. (2019). Synthesis, characterization and application of Fe_3O_4@SiO_2 nanoparticles supported palladium(II) complex as a magnetically catalyst for the reduction of 2,4-dinitrophenylhydrazine, 4-nitrophenol and chromium(VI): A combined theoretical (DFT) and experimental study. *Separation and Purification Technology*, 209, 136-144. doi:10.1016/j.seppur.2018.07.022

Nguyen, C. H., Fu, C. C., & Juang, R. S. (2018). Degradation of methylene blue and methyl orange by palladiumdoped TiO_2 photocatalysis for water reuse: Efficiency and degradation pathways. *Journal of Cleaner Production*, 202, 413-427. doi:10.1016/j.jclepro.2018.08.110

Olagunju, M. O., Zahran, E. M., Reed, J. M., Zeynaloo E., Shukla, D., Cohn, J. L., Surnar, B., Dhar, S., Bachas, L. G., & Knecht M. R. (2021). Halide effects in $BiVO_4$/BiOX heterostructures decorated with Pd nanoparticles for photocatalytic degradation of rhodamine B as a model organic pollutant. *American Chemical Society Applied Nano Materials*, 4(3), 3262-3272. doi:10.1021/acsanm.1c00481

Rafatullah, M., Sulaiman, O., Hashim, R., & Ahmad, A. (2010). Adsorption of methylene blue on low-cost adsorbents: A review. *Journal of Hazardous Materials*, 177(1-3), 70-80. doi:10.1016/j.jhazmat.2009.12.047

Rafiee, F., & Rezaee, M. (2022). Catalytic reduction of nitroarenes and degradation of dyes at room temperature by an efficient NNN pincer palladium catalyst based on the magnetic amino-triazole-modified chitosan. *Reactive and Functional Polymers*, 172, 105208-105220. doi:10.1016/j.reactfunctpolym.2022.105208

Rahman, Q. I., Ahmad, M., Misra, S. K., & Lohani, M. (2013). Effective photocatalytic degradation of rhodamine B dye by ZnO nanoparticles. *Materials Letters,* 91, 170–174. doi:10.1016/j.matlet.2012.09.044

Ramadan, R. M., El-Medani, S. M., Ali, O. A. M., & Mohamed H. A. (2004). Spectroscopic and thermal studies of some palladium complexes with certain heterocyclic nitrogen ligands. *Journal of Coordination Chemistry*, 57(5), 373-379. doi:10.1080/00958970410001680363

Robinson, T., McMullan, G., Marchant, R., & Nigam, P. (2001). Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. *Bioresource Technol*ogy, 77(3), 247-255. doi:10.1016/S0960-8524(00)00080-8

Sahiner, N., Sagbas, S., & Aktas, N. (2015). Very fast catalytic reduction of 4-nitrophenol, methylene blue and eosin Y in natural waters using green chemistry: p(Tannic acid)–Cu ionic liquid composites. *The Royal Society of Chemistry*, 5, 18183-18195. doi:10.1039/C5RA00126A

Saputra, E., Prawiranegara, B. A., Sugesti, H., Fadli, A., Heltina, D., Utama, P. S., Azis, Y., Manawan, M., Wang, S., & Oh, W. D. (2022). High performance magnetic carbonaceous materials as a photo Fenton-like catalyst for organic pollutant removal. *Journal of Water Process Engineering*, 47, 102849-102859. doi:10.1016/j.jwpe.2022.102849

Selim, A., Kaur, S., Dar, A. H., Sartaliya, S., & Jayamurugan, G. (2020). Synergistic effects of carbon dots and palladium nanoparticles enhance the sonocatalytic performance for rhodamine B degradation in the absence of light. *American Chemical Society Omega*, 5, 22603−22613. doi:10.1021/acsomega.0c03312

Selvi, G., Tercan, M., Ozdemir, N., & Dayan, O. (2020). The preparation of new palladium(II) complexes with Schiff base type ligands and its impregnated Al_2O_3 materials: As the catalysts for degradation/reduction of organic dyes. *Applied Organometallic Chemistry*, 34(12), 6009-6019. doi:10.1002/aoc.6009

Shu, F., Wu, J., Jiang, G., Qiao, Y., Wang, Y., Wu, D., Zhong, Y., Zhang, T., Song, J., Jin, Y., Jiang, B., & Xiao, H. (2022). A hierarchically porous and hygroscopic carbon-based catalyst from natural wood for efficient catalytic reduction of industrial high-concentration 4-nitrophenol. *Separation and Purification Technology*, 300, 121823 - 121923. doi:10.1016/j.seppur.2022.121823

Singh, K., & Arora, S. (2011). Removal of synthetic textile dyes from wastewaters: A critical review on present treatment technologies. *Critical Reviews in Environmental Science and Technology*, 4(9), 807-878. doi:10.1080/10643380903218376

Singh, J., Kumari, P., & Basu, S. (2019). Degradation of toxic industrial dyes using SnO_2/g-C_3N_4 nanocomposites: Role of mass ratio on photocatalytic activity. *Journal of Photochemistry and Photobiology A: Chemistry*, 371, 136-143. doi:10.1016/j.jphotochem.2018.11.014

Tadokoro, M., & Nakasuji, K. (2000). Hydrogen bonded 2,2′-biimidazolate transition metal complexes as a tool of crystal engineering. *Coordination Chemistry Reviews*, 198(1), 205-218. doi:10.1016/S0010-8545(99)00223-4

Thabet, M. S., & Ismaiel, A. M. (2014). Sol-Gel γ-Al_2O_3 nanoparticles assessment of the removal of eosin Yellow using: adsorption, kinetic and thermodynamic parameters. *Journal of Encapsulation and Adsorption Science*, 6(3), 71-90. doi:10.4236/jeas.2016.63007

Wang, Y., Zhang, Y., Zhao, G., Wu, M., Li, M., Li, D., Zhang, Y., & Zhang, Y. (2013). Electrosorptive photocatalytic degradation of highly concentrated *p*-nitroaniline with TiO_2 nanorod-clusters / carbon aerogel electrode under visible light. *Seperation and Purification Technology*, 104, 229-237. doi:10.1016/j.seppur.2012.11.009

Wang, Z., Zhang, H., Li, L., Miao, S., Wu, S., Hao, X., Zhang, W., & Jia, M. (2018). Polyacrylonitrile beads supported Pd-based nanoparticles as superior catalysts for dehydrogenation of formic acid and reduction of organic dyes. *Catalysis Communi*cations, 114, 51-55. doi:10.1016/j.catcom.2018.06.004

Wang, W., Dai, G., Yang, H., Liu, X., Chen, X., Meng, Z., & He, Q. (2021). Highly efficient catalytic reduction of 4-nitrophenol and organic dyes by ultrafine palladium nanoparticles anchored on CeO_2 nanorods. *Environmental Science and Pollution Research*, 29, 8242-8252. doi:10.1007/s11356-021-16276-1

Zhou, P., Dai, Z., Lu, T., Ru, X., Ofori, M. A., Yang, W., Hou, J., & Jin, H. (2022). Degradation of rhodamine B in wastewater by Iron-loaded attapulgite particle heterogeneous fenton catalyst. *Catalysts*, 12(6), 669-688. doi:10.3390/catal12060669