Journal Homepage: - www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH (IJAR)

Article DOI: 10.21474/IJAR01/16358
DOI URL: http://dx.doi.org/10.21474/IJAR01/16358

RESEARCH ARTICLE

THEMIZOROKI HECK REACTION IN AQUEOUS SOLVENTS PROMOTED BY RESIN-SUPPORTED OF NOVEL RPF@PDNPS NANOSPHERES: CATALYTIC REDUCTION TEST

Busroni Busron[1], Suyanta[2] and Chairil Anwar[2]

1. Departement of Chemistry, Faculty of Mathematics and Natural Sciences Jember University, Jl. Kalimantan 37, Jember 681752.
2. Departement of Chemistry, Faculty of Mathematics and Natural Sciences Gadjah Mada University, Jl. Sekip Utara, Yogyakarta 55281.

Manuscript Info

Manuscript History
Received: 31 December 2022
Final Accepted: 31 January 2023
Published: February 2023

Key words:-
RPF (Formaldehyde Phenol Resin), Aldol Condensation, Nanospheres, Catalytic Reduction, Nanoparticle Palladium

Abstract

The aim of the research was to synthesize formaldehyde phenolic resin (RPF) nanospheres using the aldol condensation method. The Novel of RPF@PdNPs Nanospheres that were prepared at that time was used as a reducing agent and stabilizing supported for the synthesis of PdNPs nanoparticles. It turns out phenol replacement led to a significant decrease in nanosphere size and an increase in the surface roughness of the nanospheres, which ultimately increases the specific surface area of the RPF nanospheres. Because of enhanced specific surface area and excellent reducing activity of RPF (Formaldehyde Phenol Resin), prepared RPF nanospheres have a very high amount of PdNPs loading. Therefore, the as-prepared of RPF@PdNPs nanospheres exhibit a highly efficient catalytic capability for the reduction of Cr(VI) toxicity.

Introduction:-

Precious metal NPs have been of great interest stemming from their various useful applications in various fields, such as in sensors, biomedical treatment, energy conversion, catalysis, and so on (Chen et al., 2020). Among all the precious metal NPs, Palladium NPs have attracted considerable attention, as it has great catalytic activity and a remarkable hydrogen adsorption capacity at low temperatures around 50^0C (Li et al., 2009). Therefore, Pd NPs are widely used as effective catalysts for the rapid elimination of organic pollutants and heavy metals by the catalytic transformation of these pollutants. (Han et al., 2016; Veerakumar et al., 2017). In particular, Pd-based catalytic reduction shows high potential in the treatment of wastewater containing hexavalent Cr (VI) chromium, as it can convert the highly toxic Cr(VI) to relatively non-toxic and inert Cr(III) which can be easily removed. from an aqueous system in the form of insoluble hydroxide (Liu Q. et al., 2016). Nanoparticles are widely used as catalysts, antibacterial, and antioxidants, as well as anticancer. The nanoparticle structure is composed of metal, non-metal (organic), or mixed atoms. The nanoparticles are hydrophobic and the surface of the nanoparticles is often coated with a polymer to stabilize the metal. Chemical synthesis of metal nanoparticles was carried out by forming metal atoms from the reduction of metal precursors using chemical reducing agents, such as NaBH4, HCOOH, PANI, and Polypyrrorole. The formed metal atoms will experience nucleation followed by growth which will produce nanoparticles. Nucleation can occur because supersaturated solutions are thermodynamically unstable. Metal nanoparticles have a solid three-dimensional structure. These particles are made by reducing metal ions into zero-valent and uncharged metals. The reaction process for the formation of nanoparticles by means of charged metal ions such as Au, Pt, Ag, Pd, Co, Fe is reduced with reducing agents such as sodium citrate, sodium borohydride,

Corresponding Author:- Busroni Busron
Address:- Departement of Chemistry, Faculty of Mathematics and Natural Sciences Jember University, Jl. Kalimantan 37, Jember 681752.

hydrazine, polyaniline, and polypyrrole (Wulandari, 2021). Among the reactions catalyzed by palladium, the arylation of alkenes called the Mizoroki–Heck reaction is the most important carbon-carbon bond formation process. Over the last 25 years, a large number of applications have been developed on a laboratory and industrial scale (**Alacid E. and Carmen Nájera**, **2008**), All Chromium valence (VI) compounds are toxic (because of their oxidizing power), and carcinogenic, especially if airborne and inhaled where they can cause lung cancer, and nose and nasal sinus cancer. The use of chromate compounds in manufactured goods is also restricted. Therefore, remediation is needed to reduce the impact on humans and ecosystems. Chromium valence (III) has an octahedral coordination configuration, and its complexes are generally inert. In an aqueous environment, which contains oxygen-based species, chromate complexes (**Omole et al., 2017).**Nanotechnology has become an important research area in the development of engineered materials that can be integrated into technology. The synthesis and selective application of engineered materials are very important for the development of nano-functional devices. Metal-polymer nanocomposite materials are expected to become an important class of materials in nanotechnology. These engineered materials have very different electronic and optical properties from the original nanoparticles. Artificial nanocomposites displaying novel properties can be synthesized by careful selection and appropriate combinations of the two components (Athawale et al., 2006)..The Catalytic activity of the Pd@ZIF-67 The catalytic activity of the Pd@ZIF-67 was evaluated in the aqueous reduction of Cr(VI) to Cr(III) with formic acid (HCOOH). In a typical process, a mixture containing 5.89 mg (2.0 mM) of K2Cr2O7, 173.2 μL (0.45 M) of HCOOH, 312.3 mg (0.45 M) of HCOONa, and 10 mL of Milli-Q water was added into a round-bottom flask, and magnetically stirred at ambient temperature for 15 min, then 2 mg of the Pd@ZIF-67 catalyst was introduced into the flask, and the reduction reaction started (t=0 min) with magnetic stirring. At given time intervals, 100 μL of the reaction solution was withdrawn and diluted to 1.0 mL to monitor the transformation of Cr(VI) to Cr(III) using a UV–vis spectrometer (UV-2450, SHIMADZU**)(Li H.C. et al., 2016**).**Busroni et al., 2022**, reported that the C-4-phenylcalix[4]resorcinarene-nanopalladium compound can be synthesized via several reaction routes in succession: One of the reaction steps for the synthesis of palladium nanoparticles is the reduction process of palladium[II] to palladium[0] in the presence of phenylhydrazine. Several researchers related to the formation of etherification reactions and continued the complexation route between palladium[II] cations and calix[4]resorcinarene derivatives. Most of the transition metal nanoparticles such as palladium, nickel, gold, silver, and platinum have been studied and used for different catalytic applications. The catalytic activity of metal nanoparticles depends on their smaller size with a large surface area ratio and produces very good yields and very efficient reaction times. Palladium nanoparticles are very sensitive to many carbon-carbon coupling reactions such as the Mizoroki-Heck reaction (**Kongor, A., etal., 2016).Athawale (2003) and Marulasiddeshwara, (2015),** reported that the synthesis of Palladium nanoparticles (Pd@NPs) can be synthesized by two different methods namely. reflux and irradiation as well as research related to the stability of the synthesized nanoparticles. Among the various stabilizers added. polyaniline was found to be the most effective. Pd metal was chosen because Pd is an interesting transition metal element from the point of view of magnetism and has very good catalytic activity. In order to permanently maintain the zerovalent state of metals, solution polymerization of empty nanoparticles containing polyaniline and polypyrrole has been carried out to obtain "MetalPolymer" or "OrganoMetal" nanocomposites. Zero valent palladium can catalyze the Mizoroki–Heck, and Suzuki-Miyaura reactions and is the strongest and best synthetic material for forming carbon-carbon bonds in organic syntheses, such as in arylation, alkylation, or vinylation reactions with alkenes through reactions with aryl, vinyl, benzyl or allyl halides in the presence of a base, andthe carbon-carbon joining reaction catalyzed by transition metal nanoparticles of aryl or alkenyl halides with olefins/alkenes is known as the Mizoroki-Heck reaction. This reaction is one of the best methods for the rapid formation of carbon-carbon bonds (**Lin B.L. et al., 2003).**

Experimental

Material:-

Synthesis Material of Novel RPF@PdNPs; according to(Shillin Chen et all., 2020), $K_2Cr_2O_7$, Ethanol, Aquadest, $PdCl_2$ (Merck), HCOOH (Merck)

Instrumentation

The instruments used in this study consist of laboratory glassware, heating, and magnetic stirring analytical scales; Buchii evaporators (R-124),spectrophotometry infrared (FTIR, Genesys) UV-Vis.

Procedure:-

Synthesis ofPhenol Formaldehyde Resin (RPF) nanospheres

Synthesized formaldehyde phenolic resin (RPF) nanospheres using the aldol condensation methodwere prepared following a modified method (Shilin et. al., 2020). Specifically, 0.12 g of phenol, 0.28 g of 37% formaldehyde solution, and 0.04 g of NaOH are weighed and then mixed sufficiently in 28 mL of aqueous ethanol solution (8 mL of ethanol and 20 mL of distilled water). The prepared solutions were then heated at 75℃ for 2 hours and 90°C for 30 minutes, respectively. Thereafter, the solution was transferred into and heated at 120 ℃ for 1 hour, followed by natural cooling to room temperature. The solid product was collected by centrifugation and washed several times with distilled water and ethanol respectively. Finally, the thermo-setting RPF nanospheres were obtained by drying in a vacuum oven at 30 ℃ for 24 h.

Synthesis of RPF@PdNPsnanospheres by (Shilin Chen, 2020)

Typically, 60 mg asprepared PRF nanospheres were dispersed into 20 mL deionized water, then 20 mg PdCl2 was added and the mixture was stirred using a magnetic stirrer at 80℃ for 7 hours. After continuous stirring, the initial pale yellow solution progressively white-darkened, suggesting the formation of the PdNPs. The products were collected by centrifugation or filtered and washed with ethanol and deionized water three times, respectively, and followed by drying at 50 ℃ overnight to obtain RPF@PdNPs nanospheres. For comparison purposes, RPF@PdNPs nanospheres were also prepared using the same procedure as followed for RPF@PdNPs.The residue was air dried for 24 hours to produce an initial pale yellow to white darkened powder of RPF@PdNPs nanocomposite containing zero-valence palladium. The results of the RPF@PdNPs nanospheres as a catalyst were characterized using Figure 1. FTIR spectra, and Figure 2. UV-Vis spectra. Figure 3. Structure of RPF@PdNPs nanospheres, solid white-darkened.

Catalytic Reduction Test

Potassium dichromate ($K_2Cr_2O_7$) was chosen as one of the representative Cr(VI) compounds for catalytic reduction experiments. It is known that the characteristic absorption peak of Cr(VI) centered at 350 nm (Shilin C. et al., 2020) is caused by a ligand-to-metal charge transfer transition. Thus, in the RPF@PdNPs nanospheres for the catalytic reduction process, it was observed that after the addition of the RPF@PdNPs. Decreased in color from orange to white at 30 minutes, accompanied by a color change from yellow to colorless, this indicates that there has been a reduction of Cr(VI). The reduction reaction is considered complete when the main absorption peak at 350 nm disappears or the absorption peak of Cr(VI) ions becomes Cr(III) or Cr(VI) becomes zero-valence Cr(0)(Shilin Chen, 2020)

Result and Discussion:-

Investigation with FTIR Novel of RPF@PdNPsnanospheres

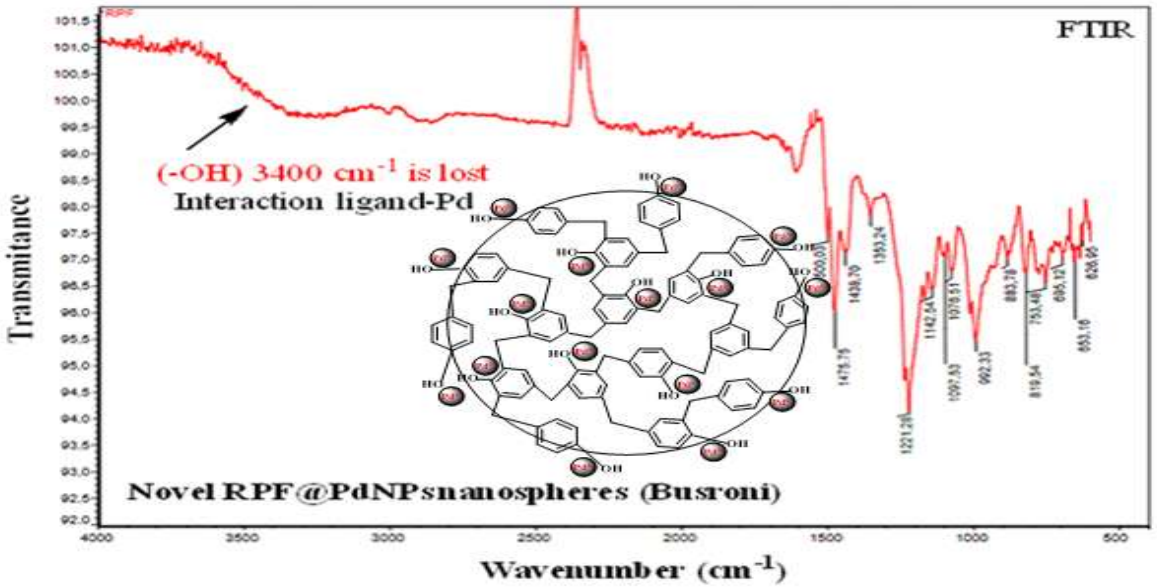

Figure 1:- Spectra FTIR of Novel RPF@PdNPs nanospheres.

However, a comparison of the FT-IR spectra of samples exposed to nanospheres and exposed Palladium(II) ions indicated that there were two significant differences in the absorption area of 3000 - 3500 cm^{-1} where there was interaction with Pd(II) resulting in the reduction of Pd(II) ions. to Pd(0), this can be indicated from the results of the investigation that there was a change in the color of the Phenol Formaldehyde Resin (RPF) in which the yellow or pale yellow solid turned into a white-black or white-darkened color. A literature study by Busroni et al., 2022 and Shilin et al., 2020, that black is a Palladium color with zero valences. While the white-dark color is zero valent palladium which interacts with OH ligands or OH groups in the nanospheres form of RPF@PdNPs or palladium nanoparticles in the presence of hydroxy groups in Phenol Formaldehyde Resin during the interaction. The reaction interaction model is shown in Figure 2 UV-Vis analysis is bellow.

Investigation with UV-Vis Novel of RPF@PdNPsnanospheres

Investigation using UV-vis spectroscopy to track the occurrence of changes in Pd(II) to Pd(0), based on the results of this study that the RPF@PdNPs nanosphereswere used by the research group to synthesize palladium nanoparticles. To this knowledge, no one has reported the use of RPF@PdNPs nanospheres as reducing and stabilizing agents to synthesize nanoparticles, in particular, PdNPs or palladium nanoparticles. Herein have been prepared PdNPs using palladium chloride and RPF in water without the use of external reducing agents or stabilizers. Thus, dispersible in water, RPF@PdNPs nanospheres are formed by chemical reduction in one method. The morphology of the formed nanoparticles was investigated by UV-Vis spectroscopy. The addition of palladium chloride to the hot RPF (Formaldehyde Phenol Resin) solution appeared at 80^0C and showed a color change from pale yellow to white-dark after stirring for 8 hours. After 8 hours previously confirmed the formation of colloidal RPF@PdNPs nanospheres as catalysts. The UV–vis spectrum was taken to monitor and investigate the maximum absorption of the analysis results using the UV-Vis material RPF@PdNPs formed. The maximum absorption was obtained at a wavelength at 291 nm in Figure 3. Palladium chloride solution gives a broad maximum absorption band of 400-600 nm which refers to the presence of Pd(II).Lostof band at 450 nm ($PdCl_2.5H_2O$)(Busroni et al., 2022). it was found that due to the reduction of Pd(II) to Pd(0) the oxidation state confirmed as a comparison of the formation of PdNPs there was an absorption change of around 250 nm as Pd(0) based on the results of the research of Panchal et al., 2018, $PdCl_2.5H_2O$ the aqueous solution was added to the same volume of hot water solution $PdCl_2.5H_2O$. Theresulting mixture was kept under vigorous stirring and heated at 80^0C for 6 hours. The reduction of palladium was confirmed by a color change from pale-yellow to white-darkened, meaning that there was a change in absorption of Pd(II) to Pd(0). There was a change in absorption from 450 to 291 nm, confirmed using UV-Vis spectroscopy as water-insolubleRPF@PdNPs nanospheres and reduced Pd(0) zero valence in RPF@PdNPs.Thus the results of RPF@PdNPs are then used to carry out the catalytic test process. UV-Visible spectroscopy was mainly used to evaluate the formation of RPF@PdNPs and the different color changes from pale-yellow to white-darkened, confirming the formation of RPF@PdNPs in Figure 2, according to the results of research by (Kongor et al., 2016 and Panchal, et al., 2018)

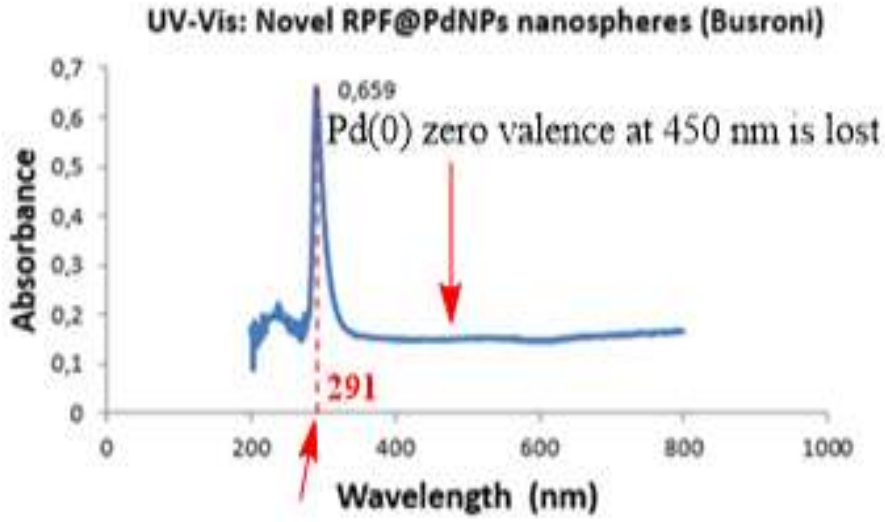

Figure 2:- UV-Vis Analysis of RPF@PdNPs nanospheres.

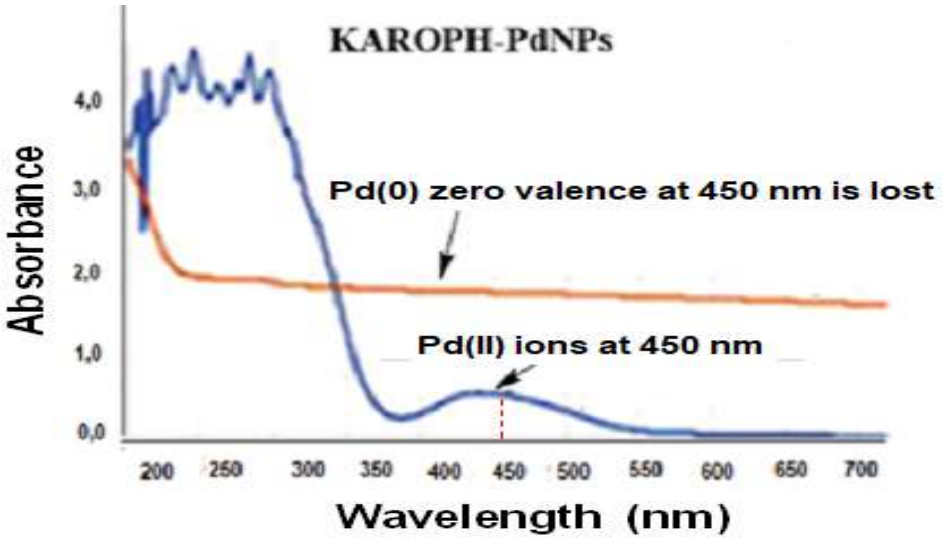

Figure 3:- Spectra UV-Vis analysis of KAROPH-PdNPs (Busroni et al., 2022).

Based on the UV-Visible investigation of the Pd(II), the results of the investigation using UV-Vis obtained the maximum absorption Pd(0) at 450 nm in the KAROPH-PdNPs(Busroni et al., 2022), the results of the analysis using UV-Vis obtained absorption at 200-250 nm (Boeva et al., 2014) meaning that there had been a reduction process by the hydrazine group and absorption at 450 nm had disappeared [Busroni et al., 2022), while the composite of RPF@PdNPsnanospheres, Figure 3 the results of the analysis used UV-Vis obtained the maximum absorption at 291 nm, meaning that there had been lost. The addition of Pd(II) ion solution to the RPF@PdNPssolution in situ and heated to 50^0C showed a color change from pale-yellow to white-darkened. After six hours the previously confirmed formation of the RPF@PdNPs colloid or suspension. The UV–vis spectrum was taken to monitor and verify the formed RPF@PdNPs nanospheres as a catalyst. Palladium chloride solution gives a broad maximum absorption band around 400-600 nm which refers to the presence of Pd(II). The loss of the band at 450 nm in Figure 3 according to the results of UV-Vis investigation in Figure 3(Busroni et al., 2022), was found due to the reduction of Pd(II) to Pd(0) the oxidation state confirmed the formation of PdNPs changes absorption around 291 nm as Pd(0) in Figure 3. Then the presence was compared based on the results (Torshizi et al., 2016), and an aqueous solution of $PdCl_2.5H_2O$ was added to the same volume of hot water solution of $PdCl_2.5H_2O$. The resulting mixture was kept under vigorous stirring and heated at 80^0C for 6 hours.

CatalyticReduction Test

Potassium dichromate ($K_2Cr_2O_7$) was chosen as one of the representative Cr(VI) compounds for catalytic reduction experiments. It is known that the characteristic absorption peak of Cr(VI) centered at 350 nm (Shilin C., et al., 2020) is caused by a ligand-to-metal charge transfer transition. Thus, in the RPF@PdNPs nanospheres as a catalytic reduction process, it was observed that after the addition of the RPF@PdNPs as the catalyst, the absorption peak intensity at 350 nm changed (Figure 2. UV-Vis decreased in color from orange to yellow-green with increasing reaction time accompanied by a color change from yellow to colorless, this indicates that there has been a reduction of Cr(VI). The reduction reaction is considered complete when the main absorption peak at 350 nm disappears or the absorption peak of Cr(VI) ions decreases to Cr(III) or Cr(VI) to zero valences Cr(0) according to the research results of Shilin Chen, 2020. The interaction model for the catalytic reduction reaction is shown in Figure 4 below

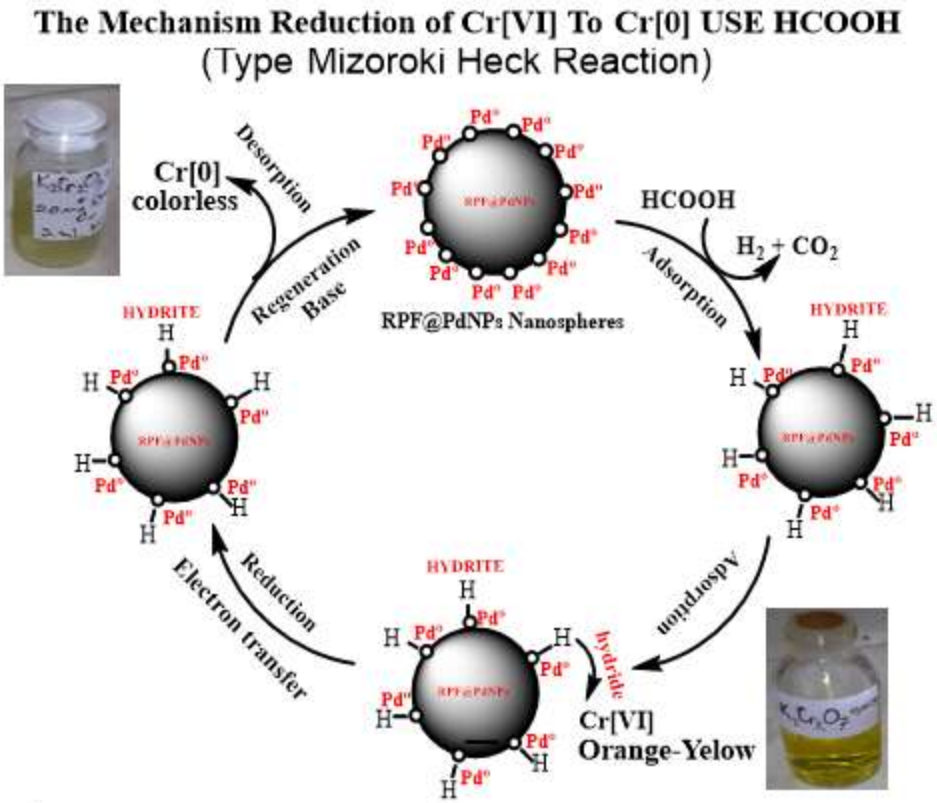

Figure 4:- Catalytic Reduction Test of Novel RPF@PdNPs onto $K_2Cr_2O_7$Using HCOOH.

Conclusion:-

A methodology has been developed for the synthesis of RPF@PdNPs nanospheres, and subsequent reduction of PdNPs without the addition of reducing agents or stabilizers. The catalytically active PdNPs nanoparticles dispersed well on the surface of the RPF nanospheres. Incorporation of Formaldehyde in Phenol Resin results in the surface of RPF nanospheres. The incorporation of Formaldehyde in Phenol Resin results in an increase in surface roughness, which increases the specific surface area of the RPF nanospheres. In addition, the formed RPF nanospheres inherited the reducing activity of the hydroxy ligands, which further increased the number of PdNPs nanoparticles. Thus, the novel catalyst RPF@PdNPs exhibits highly efficient catalytic activity in the reduction process of the toxic and hazardous Cr(VI). In addition, RPF@PdNPs nanospheres and excellent reusability in reducing Cr(VI). Therefore, the high catalytic and reusable of RPF@PdNPs nanospheres, together with the relatively easy reduction preparation, demonstrates the excellent potential of this functionalized material in catalytic and wastewater treatment applications

References:-

[1]. Athawale, A. A., Bhagwat, S.V., Prachi P. Katre, P.P., 2006, Nanocomposite of Pd–polyaniline as a selective methanol sensor, Sensors and Actuators, Vol 114, pp. 263-267

[2]. Athawale, A.A., Bhagwat, S.V., Katre, P.P., Chandwadkar A.J., Karandikar P., 2003, Aniline as a stabilizer for metal nanoparticles, Materials Leters, 57, pp. 3889 – 3894

[3]. Ayad, M. M., Amer, W.A., Mohammed G. Kotpa, M. G., 2017, Magnetic polyaniline-chitosan nanocomposite decorated with palladium nanoparticles for enhanced catalytic reduction of 4- nitrophenol, Molecular Catalysis, vol 439, pp 72-80

[4]. Alacid E., and Carmen Nájera C., 2008, The Mizoroki-Heck reaction in organic and aqueous solvents promoted by a polymer-supported Kaiser oxime-derived palladacycle, ARKIVOC, (viii) pp. 50-67

[5]. Busroni B., Handayani, A.T.W., Irawan, E.D., and Anwar C., 2022, Synthesis and Characterizationof Novel Basketing of C-4-Phenyl-octa(phenylhydrazide)-calix[4]resorcinarenePdNPs, JCC, 020032-1 sd 020032-8

[6]. Busroni, Putra M.J., Hanafi S.A., , Ummami R., Piluharto B., and Sjaifullah A., 2022, Dopant, Immersion Time Effect, AND Hydrolysis Onto Polyaniline-BC Composites: Conductivity Studies, IJAR, 10(09), pp. 853-862

[7]. Boeva, Zh, A., and Sergeyev, V.G., 2014, Polyaniline: Synthesis, Properties, and Application, Polymer Science, Vol. 56, No. 1, pp. 144–153
[8]. Chen, S., Wang, G., Sui, W., Parvez, A.M., Dai, L., Si, C., 2020, Novel lignin-based phenolic nanosphere supported palladium nanoparticles with highly efficient catalytic performance and good reusability, Industrial Crops & Products, Vol 145, pp 1-9
[9]. Dhaoui W., Hasik M., Djuradoc D., Bernasik A., and Pron A., 2010, Redox behaviour of polyaniline–palladium catalytic system in the presence of formic acid, Synthetic Metals, Vol. 160 pp. 2546–2551
[10]. Giri, S., Raghunath Dasa, Chris van der Westhuyzen, Arjun Maity a,c*,---, An efficient selective reduction of nitroarenes catalyzed by reusable silver adsorbed waste nanocomposite, Applied Catalysis B: Environmental.
[11]. Kongor A., Panchal M., Mehta V., Bhatt K., Bhagat D., Tipre D., Jain, V. K., 2016, Arabian Journal of Chemistry, Article In Press
[12]. Kebiche, H., Epaillard, F. P., Haddaoui, N., and Debarnot,/ D., 2020, A route for the synthesis of polyaniline-based hybrid nanocomposites, J. Mater Sci
[13]. Lin, B.L., Liu, L., Fu, Y., Luo, S.W., Chen, Q., and Guo, Q.X., 2004, Comparing Nickel- and Palladium-Catalyzed Heck Reactions, Organometallics, Vol. 23, pp. 2114-2123
[14]. Marulasiddeshwara, M.B., Kumar P.R., 2015, Synthesis of Pd(0) nanocatalyst using lignin in water for the Mizoroki–Heck reaction under solvent-free conditions, International Journal of Biological Macromolecules, Vol. 83, pp. 326–334
[15]. Mazzeu M.A.C, Faria, L.K., Baldan M.R., Rezende M.C., and Gonçalves E.S., 2016, Brazilian Journal of Chemical Engineering, Vol. 35, No. 01, pp. 123 – 130
[16]. Omole M.A., K'Owino I.O., Omowunmi A. Sadik O. A., 2017, Palladium nanoparticles for catalytic reduction of Cr(VI) using formic acid, Applied Catalysis, Vol. 76, pp.158–167
[17]. Panchal M., Kongor A., Mehta V., Vora M., Bhattb K., and Jain V., 2018, Heck-type olefination and Suzuki coupling reactions using highly efficient oxacalix[4]arene wrapped nanopalladium, Journal of Saudi Chemical Society, Vol. 22, pp 558-568
[18]. Patel, H.A., Patel, A.L., and Bedekar, A. V., 2014, Polyaniline-anchored palladium catalyst mediated Mizoroki–Heck and Suzuki–Miyaura reactions and one-pot Wittig–Heck and Wittig–Suzuki reactions, Applied Organometallic Chemistry, vol. 29, pp 1-6
[19]. Torshizi H.M., Elham Rezaei E., Kamranfar F., and Majd M.H., 2016, Investigating the Apoptosis Ability of Ethylenediamine 8- Hydroxyquinolinato Palladium (II) Complex, Adv Pharm Bull, Vol.6, no. 3, pp. 449-453
[20]. Wulandari D. A., Safaat M. 2021, REVIEW: PERAN NANOPARTIKEL DALAM MENGHAMBAT PERTUMBUHAN PARASIT Plasmodium PENYEBAB MALARIA, Vol. 8, no. 1, pp124-136
[21]. Lemke W. M., Kaner R. B., and Diaconescu P. L., 2014, A mechanistic study of cross-coupling reactions catalyzed by palladium nanoparticles supported on polyaniline nanofibers,Inorganic Chemistry Frontiers. DOI: 10.1039/c4qi00130c
[22]. Omole M.A., K'Owino I.O., Omowunmi A. Sadik O. A., 2017, Palladium nanoparticles for catalytic reduction of Cr(VI) using formic acid, Applied Catalysis, Vol. 76, pp.158–167
[23]. Panchal M., Kongor A., Mehta V., Vora M., Bhattb K., and Jain V., 2018, Heck-type olefination and Suzuki coupling reactions using highly efficient oxacalix[4]arene wrapped nano palladium, Journal of Saudi Chemical Society, Vol. 22, pp 558-568.