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RESEARCH ARTICLE

SYNTHESIS AND INVESTIGATING OF THE NOVEL OF ES-PANI@PDNPSNANOCOMPOSITE

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Abstract

The aim of this research is the synthesize materials Novel of ES-PANI@PdNPs nanocomposites obtained chemically. The synthesis of ES-PANI@PdNPs nanocomposite was prepared by the chemical method using FeCl3 as a redox initiator (insitu) and refluxed for 48 hours at 500C, then dried at 500C for 24 hours, obtained a brown-black solid and no water-soluble.The nanocomposite is characterized by UV-Vis and Fourier transform infrared (FTIR) spectroscopy, the composite shows absorption of Pd(0) nanoparticles along with ES-PANI peaks at 312 nm. FTIR and UV-visible spectra show an interaction between Pd(0) and ES-PANI. This indicated that Pd(0) zero valence had been formed and that internal reduction processes had occurred by imines and amines toward Pd(II) ions.

Introduction:-

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. To permanently maintain the zero valence state of metals, solution polymerization of empty nanoparticles containing polyaniline and polypyrrole has been carried out to obtain “MetalPolymer” or “OrganoMetal” nanocomposites [Athawale et al., 2003], [Marulasiddeshwara, et al., 2015]. 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 [Marulasiddeshwara, et al., 2015]. 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 et al., 2008].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.

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Artificial nanocomposites displaying novel properties can be synthesized by careful selection and appropriate combinations of the two components [Athawale et al., 2006]..Polyanilines are promising because of their ease of synthesis, low-cost environmental stability, doping-induced processability, highly attractive conductivity, and optical properties. As a result, extensive research has been conducted on polyaniline applications in sometimes remote technological domains. Polyaniline anticorrosion coating, and catalytic support. [Dhaouiet al., 2010].The development of nanotechnology in medicine and agriculture (insecticides), sensors, and nano catalytic composites is due to the very unique properties of nanoparticles, nano size, and high surface area ratio compared to metal ions. Metal nanoparticles have been used very widely in the field of chemistry, as special nanocatalysts in the field of organic synthesis, other unique properties can be used repeatedly and are very effective with a high level of accuracy so they are very efficient.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 et al., 2016].The synthesis of 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 [Busroni et al., 2022]. 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 PPy. 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, and Fe is reduced with reducing agents such as sodium citrate, sodium borohydride, hydrazine, polyaniline, and polypyrrole[Patel et al., 2014]. The absorption of ES-PANI peaks at 3600–3000 cm-1 and 3000-2800 cm-1 according to the –N H and –CH PANI stretching vibrations respectively. Bands due to aromatic stretching of CN vibrations appear at 1294 cm-1, while the absorption peaks at 1594 and 1490 cm-1 represent the Quinoid (Q) and Benzenoid (B) structure of the emeraldine salt phase from PANI, however, a comparison of the FT-IR spectra of the samples exposed to unexposed nanocomposites revealed two significant differences.[Athawale et al., 2006]

Material and Methods:-

Material:-

Synthesis Material of ES-PANI@PdNPs; according to Shillin Chen et all., 2020, Ethanol, $PdCl_2$ (Merck), $FeCl_3$ $5H_2O$, Aniline, Chloroform Merck, Acetone 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), and UV-Vis.(GENESYS 10S UV-VIS)

Methods:-

Synthesis of ES-PANI@PdNPsnanocomposites in situ

Preparation of ES-PANI@PdNPs nanocomposite was prepared using the redox method (in situ), 20 mg $PdCl_2$ mixed with 15 mL aniline solution in (ethanol:chloroform =25:25).. The mixture was stirred magnetically for 1 hour at room temperature where a homogeneous solution was obtained. Then a solution of $FeCl_3$ (5 g $FeCl_3$ in 25 mL of ethanol) was added dropwise with constant stirring and refluxed for 48 hours at 50°C, where a brown-black precipitate was obtained. The precipitate was allowed to settle overnight, filtered, and dried at 50°C. for 24 hours

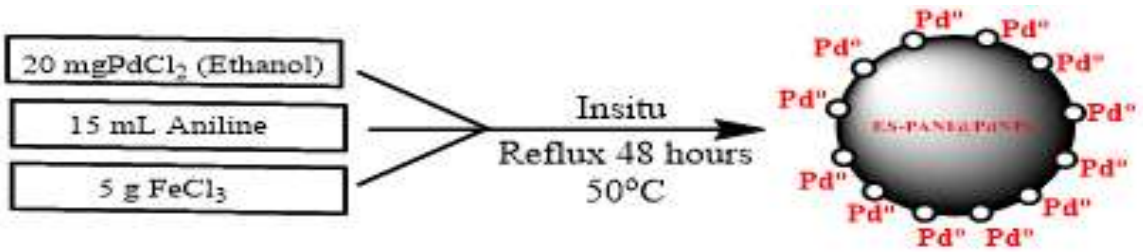

Figure 1:- Scheme representation depicting the preparation of ES-PANI@PdNPs.

Route Mechanism Polymerization of ES-PANI@PdNPs :
Route I. Polymerization of polyaniline :

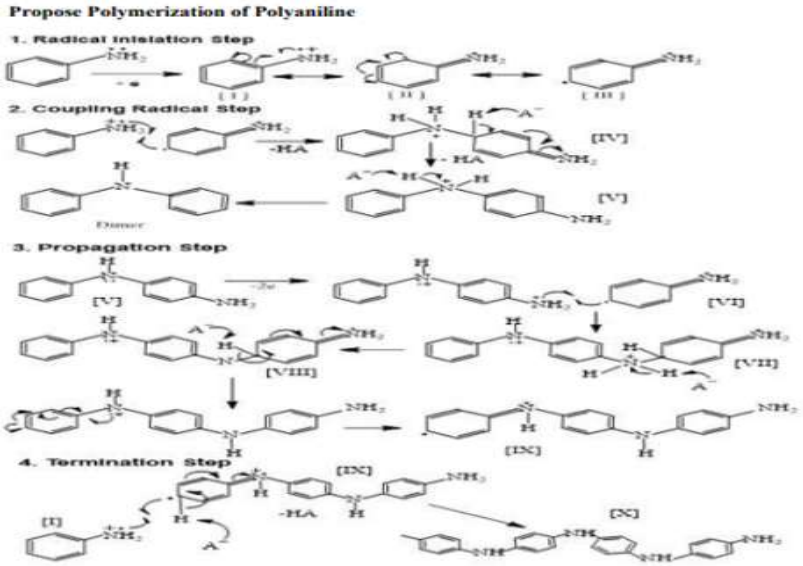

Figure 2:- Proposed Mechanism Polymerization of Polyanilines[Busroni, et al., 2022].

Route II: Synthesis Novel of ES-PANI@PdNPsNanocoppsites (in-situ)
In Figure 5, below ES-PANI@PdNPs absorption due to aromatic stretching of the absorption peaks at 1577,69 and 1494,14 cm^{-1} represent the Quinoid (Q) and Benzenoid (B) structures of the emeraldine salt phase of ES-PANI@PdNPs. However, a comparison of the FT-IR spectra of the samples exposed to the unexposed nanocomposite and the exposed nanocomposite indicated that there were two significant differences from 1577,69 cm^{-1} thus causing an effective reduction effect. in the presence of PdNPs or palladium nanoparticles by converting imine nitrogen into amines, namely a benzene-like structure formed during positive interactions. The reaction is shown in Figure 3 and Figure 4. This is a representative model of the ES-PANI@PdNPs nanocomposite material in the form of a blackish-brown solid identical to Figure 3 below.

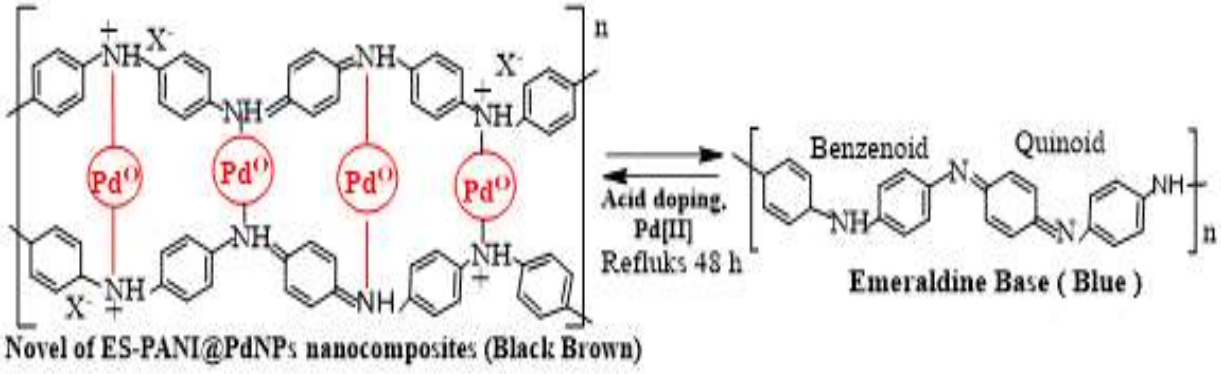

Figure 3:- Proposed Structure Novel of ES-PANI@PdNPsnanocomposites.

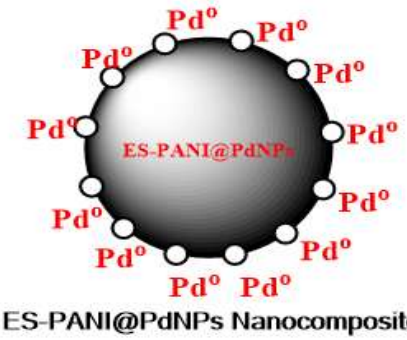

Figure 4:- Proven of Novel of ES-PANI@PdNPs nanocomposites.

Result and Discussion:-

Material of ES-PANI@PdNPs nanocomposite concept to enhance the catalytic reduction of Cr(VI). Base on Figures 3 and 4. illustrates the concept of synthesis of ES-PANI@PdNPs. The nanocomposite was prepared in two steps: a simple hydrothermal process to synthesize ES-PANI@PdNPs nanocomposite and an in-situ reduction method using ES-PANI@PdNPs without external reducing agents.

Investigating of ES-PANI@PdNPs Nanocomposite
Investigating of ES-PANI@PdNPsNanocomposites Using FT-IR

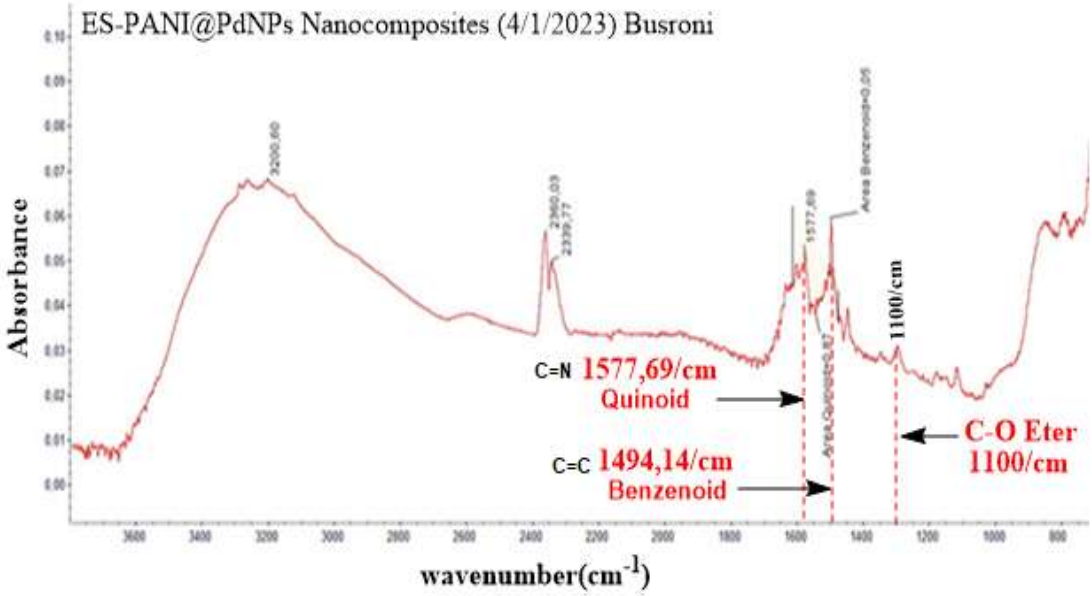

Figure 5:- Spectra FTIR of ES-PANI@PdNPs Nanocomposites.

In Figure 5, the FT-IR spectrum, the anti-prostate, and cancer MCF-7 compound is a complex of [Pd(en)(8HQ)]NO3, according to the results of research by [Wulandari et al., 2021], that palladium ions can form a complex compound with ethylenediamine in complex of [Pd(en)(8HQ)]NO3. The results of investigations with FTIR obtained absorption peaks at 1110, 2920, 3020, and 3414 cm-1 associated with absorption peaks C−O ether, C−H aromatic, C-H aliphatic, N-H amines, and absorption peaks at 1500 and 1600 cm-1 are related to C=C aromatic, and C=N imine. In this research, and the investigations of the complex of ES-PANI@PdNPs nanocomposites obtained absorption broad peaks at 3200-3400; 1577.69; 1494.14 cm-1 related to absorption peaks N-H, C=N imine (Quinoid), C=C aromatic (Benzenoid) respectively. Meanwhile, the results of the ES-PANI@PdNPs nanocomposites [Mazzeu et al., 2016]

Investigating of ES-PANI@PdNPsNanocomposites Using UV-Vis

Investigating 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 novel material of ES-PANI@PdNPs nanocomposites was used by the research group to

synthesize palladium nanoparticles. To this knowledge, no one has reported the use of ES-PANI@PdNPs nanocomposites as reducing agents and stabilizers to synthesize nanoparticles, in particular, PdNPs or palladium nanoparticles. Herein have prepared PdNPs using palladium chloride and ES-PANI insitu in waters without the use of reducing agents or external stabilizers. Investigating using UV-Vis spectroscopy found absorption at 312 nm in Figure 6, indicating that there has been a reduction process of Pd(II) ions to Pd(0) zero valence, and the absorption at 450 nm has been lost in Figure 7, due to the presence of the C=N imine (Quinoid), and amine groups in the ES-PANI@PdNPs nanocomposites compound. Thus, dispersible inwater. ES-PANI@PdNPs nanocomposites are formed by chemical reduction with the reflux method. The morphology of the formed nanoparticles was analyzed by UV-Vis spectroscopy in Figure6, and Figure 7, below:

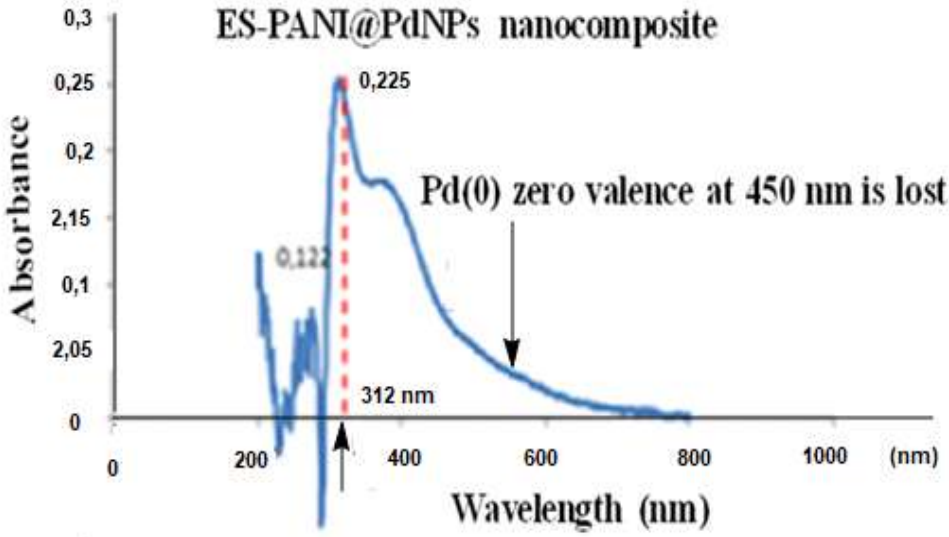

Figure 6:- Spectra UV-Vis analysis of ES-PANI@PdNPs,

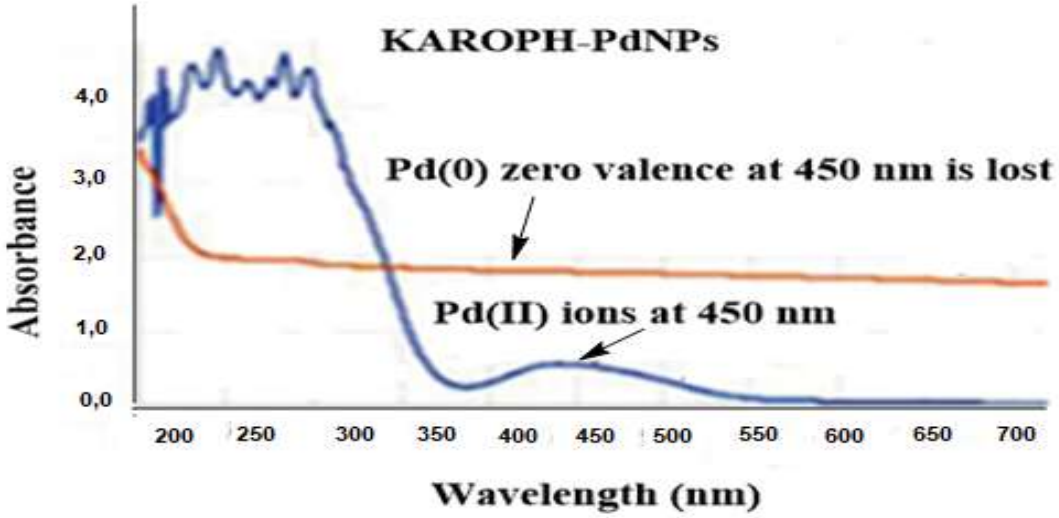

Figure 7:- Spectra UV-Vis analysis of KAROPH-PdNPs(Busroni et al., 2022).

Based on the UV-Vis analysis of the Pd(II) ion solution, the results of the analysis using UV-Vis obtained the maximum absorption at 450 nm and Pd(0) in the KAROPH-PdNPs material in Figure 7 the results of the analysis using UV-Vis obtained absorption at 200-250 nm, meaning that there had been a reduction process by the hydrazine group and absorption at 450 nm had disappeared[Busroni et al., 2022; Boeva et al., 2014], while for the composite material on ES-PANI@PdNPsnanocomposites, Figure 6 the results of the analysis used UV-Vis obtained the maximum absorption at 312 nm, meaning that there had been lost. The addition of palladium chloride solution to the ES-PANI solution insitu and heated to 500C showed a color change from yellow to dark brown. After one hour the

previously confirmed formation of the ES-PANI@PdNPs nanocomposites suspension. The UV–vis spectrum was taken to monitor and verify the formed ES-PANI@PdNPs nanocomposites. 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 6 according to the results of UV-Vis analysis in Figure 8[Busroni et al., 2022; Boeva et al., 2014; Dhaoui et al., 2010 and Omole et al., 2017] was found due to the reduction of Pd(II) to Pd(0) the oxidation state confirmed the formation of PdNPs changes absorption around 312 nm as Pd(0) in Figure 6.Then the presence was compared based on the research results[Panchal et al., 2018; Patel 2t al, 2014; andTorshizi et al., 2016], and an aqueous solution of PdCl2.5H2O was added to the same volume of hot water solution of PdCl2.5H2O. The resulting mixture was kept under vigorous stirring and heated at 800C for 6 hours. The reduction for palladium was confirmed by a color change from yellow to blackish brown, meaning that there was a change in absorption of Pd(II) to Pd(0). There had been a change in absorption from 400 nm to around 260 nm confirmed using UV-Vis spectroscopy as ES-PANI@PdNPs nanocomposite insoluble in water and reduced Pd(0) zero valence in ES-PANI@PdNPs nanocomposite. Thus the results of ES-PANI@PdNPs nanocomposites. UV-Vis spectroscopy was mainly used to evaluate the formation of ES-PANI@PdNPs nanocomposites and the different color changes from yellow to blackish brown confirming the formation of Emeraldine Salt-PANI@PdNPs or ES-PANI@PdNPs materials. nanocomposite in Figure 6, according to the research results of [Kongor et al., 2016; Kebiche et al., 2020, and Torshizi et al., 2016]. Based on the research results [Kebiche et al., 2020], it was reported that the UV-Vis spectrum of the synthesized PdNPs nanoparticles was recorded on a spectrophotometer in the wavelength range of 200–600 nm showing the UV-Vis spectrum of the untreated reaction mixture containing absorption Pd(II) ions at the peak of 465 nm observed in the spectrum representing the absorption to Pd(II) ions. On the other hand, a strong maximum absorption appeared at 324 nm, indicating that a reduction of Pd(II) ions by polyaniline had occurred and the formation ofpalladium nanoparticles had occurred. The absence of a peak corresponding to Pd(II) ions in the sol nanoparticles indicates that the conversion has occurred completely from Pd(II) ions to the zero valent Pd form, a color change from yellow to black has occurred. Analysis using the UV-Vis spectrum of PANI in basic form is dominated by two absorption bands, one at 330 nm (LB), fixed on the benzenoid ring, and the other on the visible band. The region, 630 nm (IQ), is linked to the quinoid ring.[Mazzeu et al., 2016] and the UV–Vis of the Pd-PANI nanocomposite spectrum, show the presence of two peaks in each sample (reflux and irradiation), one observed at 411 nm and 393 nm, and a broad peak at 560 nm respectively corresponding to the pernigraniline phase. However, the presence of Pd nanoparticles is indistinguishable in the nanocomposites as the peaks for the Pd nanoparticles were found to overlap with the polymer.[Athawale et al., 2003, Kebiche et al., 2020].

Conclusion:-

It has been confirmed that Emeraldine-Salt-PANI can reduce Pd(II) ions to Pd(0) zero valence. The success of ES-PANI can be reduced internally, because the composition of ES-PANI can be reduced internally, because the composition of ES-PANI has groups that act as reducing agents, namely the C=N imine (Quinoid) group and the N-H amine group can form complexes with metal cations. ES-PANI's success in reducing Pd(II) ions to Pd(0) has been proven by the results of investigations using UV-Vis and FTIR. The results of the investigation with UV-Vis showed that there was a maximum absorption for palladium zero valence at 312 nm and absorption of palladium ions at 450 nm had disappeared while investigations with FTIR obtained the presence of C=N imine (Quinoid) groups and N-H amine groups. Both of these groups have an important role as reducing groups for metal cations, in research they can reduce Pd(II) ions to Pd(0) zero valence.

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