

Highly Robust Alginate-based Magnetic Nanosorbents of Pd Catalysts for the 4-Nitrophenol Reduction

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Abstract

This work presents the synthesis of alginate-coated magnetite nanoparticle (MNP) containing amino-enriched moieties for the immobilization of palladium (Pd), and its use as a recyclable catalyst for the reduction of 4-nitrophenol (4NP) in water. The alginate grafted onto the surface of MNP contained carboxylate anions that served as coordination sites for Pd. Additionally, the incorporation of amino-enriched components, such as poly(vinyl amine) (PVAm) and 2-(dimethyl amino)ethyl methacrylate (DMAEMA), onto the alginate-coated MNPs resulted in additional interactions, including the formation of carboxylate-ammonium salts. In this study, the influence of these amino groups on the efficiency of Pd immobilization, catalytic activity and reusability of nanosorbents for 4NP reduction was investigated. The existence of Pd in the nanosorbents was detected by inductively coupled plasma atomic emission spectroscopy, transmission electron microscopy, and energy-dispersive X-ray techniques. The average size of MNPs was approximately 12.3 ± 2.9 nm, and for Pd, it was about 3.9 ± 0.8 nm. It was found that the incorporation of these amino-enriched moieties into the particles significantly enhanced the catalytic activity of the nanosorbents. Notably, MNP containing extended DMAEMA units exhibited excellent tolerance to 4NP reduction, with an insignificant loss of catalytic performance even after 20 consecutive reuses, maintaining a conversion of over 98 %.

Keywords: Magnetite, Alginate, Amino-containing, Polymer, Nanosorbent, Catalyst, Pd, Adsorption

Introduction

Palladium catalyst (Pd) finds extensive use in cross-coupling reactions, facilitating the formation of carbon-carbon bonds and play an important role in synthesizing complex molecules, including natural products, pharmaceuticals, agrochemicals and polymers, owing to its remarkable selectivity and reactivity [1,2]. Nevertheless, the drawbacks of Pd utilization lie in its high cost and the challenges associated with separation and recycling processes [3-6]. Notably, Pd is prone to aggregation, leading to the formation of uncontrollable clusters, primarily due to its high surface energy, expansive specific surface area and inherent instability. These factors can significantly diminish its catalytic activity and selectivity [2]. The immobilization of Pd on the surface of nanosorbents emerges as a promising strategy to lessen these limitations. These nanosorbents included modified cellulose [1], carbon [7], nanocomposite [8-10] and magnetite nanoparticle (MNP) [11-13]. This approach offers an efficient means to address challenges related to separation, recycling and the prevention of catalyst aggregation. Recent attention has been directed towards studies involving magnetite nanoparticle (MNP) as nanosorbents for 2 primary reasons: 1) Their notable magnetic responsiveness, which facilitates the magnetic separation of catalysts and 2) Their high surface area-to-volume ratio, which provided a platform for adsorption of molecules of interest. However, MNP tended to macroscopically aggregate, resulting in a reduction in their surface area. This, in turn, led to a loss of their desirable unique properties and subsequently limits their applications [14-16]. Therefore, 1 efficient strategy to prevent this undesirable agglomeration involved coating MNP with functional polymers, such as poly(acrylic acid) [17] and poly(diethylamino)ethyl methacrylate (PDEAEMA) [18] as well as thermo-responsive polymers, e.g. poly(N-isopropylacrylamide) [19]. Coating MNPs with long-chain polymers on their surface provided steric stabilization, designed to enhance their stability and dispersibility in various media [20-25]. Additionally, these polymer coatings on the particle surface can also serve as a platform for the immobilization of molecules of interest, including noble metals, drugs, aptamers and antibodies.

4NP serves as a common raw material and synthetic intermediate in the production of pesticides, paper and drugs, such as paracetamol [11,12]. The United States Environmental Protection Agency (USEPA) classifies 4NP as a highly toxic pollutant due to its potential exposure to humans through ingestion, inhalation, and skin contact [26]. Consequently, it can lead to cancer in living organisms, impair liver and kidney function and affect the central nervous system [26,27]. Research has shown that catalytic reduction presents a promising method for converting 4NP into the more environmentally friendly 4-aminophenol (4AP), which is commonly used as an intermediate in the production of agrochemicals, dyes and pharmaceuticals [28]. Thus, achieving an efficient catalytic reduction of 4NP to 4AP is of great importance in the research and development of this field.

The reduction of 4NP has been the subject of numerous studies with the use of various catalysts and techniques employed to achieve 4AP as a product. A widely adopted method involves the use of noble metals as catalysts [29-31]. However, these metals present challenges. For example, they need to be immobilized onto a solid support for post-reaction separation. However, common issues include the nano-aggregation of these noble metal nanoparticles, which can diminish the catalyst efficiency, and the potential leaching of the noble metals from the solid support during their uses. To address these challenges, this current study introduced specially designed polymers to anchor Pd, aiming to minimize Pd detachment upon usages and essentially enhance its reuse efficiency.

In this work, alginate-coated MNPs containing amino groups enriched the polymers were first synthesized and then used as nanosorbents for immobilization with Pd (**Figure 1**). These nanocomposites were essentially used as a recyclable catalyst for the 4NP reduction. The amino groups applied to the particle surface were derived from PVAm and DMAEMA. It was hypothesized that the alginate (the “G0” catalyst) applied to the MNP surface would not only improve their dispersibility and stability in water, but also serve as binding sites for Pd due to carboxylate anions. Alginate coated on MNP surface can react with PVAm to create the “G1” catalyst, and further reaction with DMAEMA to form the “G2” catalyst, introducing additional amino groups. It was hypothesized that the addition of the amino groups of PVAm and DMAEMA can somewhat influence the catalytic activity for the reduction of 4NP. In addition, these coating polymers employed in this work were expected to facilitate the even distribution of Pd nanoparticles. Hence, the effects of the amino groups of PVAm and DMAEMA on the Pd immobilization efficiency, catalytic activity and reusability of the nanosorbents for the reduction of 4NP were investigated. The particles were characterized by fourier transform infrared spectrometry (FTIR), thermogravimetric analysis (TGA), vibrating sample magnetometry (VSM), photo correlation spectroscopy (PCS), transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM), energy-dispersive X-ray analysis (EDX), and inductively coupled plasma atomic emission spectroscopy (ICP-OES). The catalytic activity and reusability of Pd for the 4NP reduction were investigated and monitored *via* a UV/visible spectrophotometer.

Materials and methods

Materials

Otherwise stated, all materials were used without purification; $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (99 %, Acros Organics), FeCl_3 (98 %, Acros Organics), PdCl_2 (99 %, Sigma-Aldrich), $\text{Pd}_2(\text{dba})_3$ (97 %, Acros Organic), alginate sodium salt powder (Sigma-Aldrich), glutaraldehyde (25 %, Loba Chemie), *N*-vinylformamide (NVF, 98 %, Sigma-Aldrich), (DMAEMA, 99 %, Acros Organics), ammonium persulfate (APS, 98 %, Bio Basic), 4NP (≥ 99 %, Carlo Erba), NaBH_4 (98+ %, Acros Organics), palladium standard for ICP (999 ± 2 mg/L, Sigma-Aldrich), NH_4OH 30 % (Carlo Erba), paraffin liquid (Kemaus).

Instrument

Microwave (ETHOS UP Milestone) was used in the Pd synthesis by holding the temperature at 110 °C for 2 min. FTIR was conducted using Spectrum GX, Perkin Elmer, with ATR mode. The remaining %weight was investigated using TGA (Thermo Plus TG8120, Rigaku) at temperatures of 25 - 620 °C and a heating rate of 20 °C/min under N_2 atmosphere. Saturation magnetization was analyzed *via* VSM (Standard 7403 Series, Lakeshore) with a magnetic moment in the range of $\pm 10,000$ G. The lattice diffraction patterns of Fe_3O_4 and Pd were analyzed using X-ray diffraction (XRD) with a Bruker D2 Phaser X-ray diffractometer. Surface morphologies were carried out using FESEM (AperoS, Thermo Fisher Scientific) with 20 kV accelerating voltage. The dried particles were adhered onto an aluminum stub and coated with gold before the measurements. Particle size and its distribution were studied *via* TEM (Techi 20, Phillip) at 120 kV equipped with Gatan model 782 CCD camera. The dispersion of the particle in deionized water was sonicated and then dropped onto a carbon-coated copper grid. The water was allowed

to slowly evaporated at room temperature. Elemental analyses (C, N, O, Fe and Pd) were performed on energy-dispersive X-ray spectroscopy (EDX) (Oxford Instruments, Oxford). For the quantitative measurement of Pd, all samples were treated with 20 mL of concentrated nitric acid for 20 min at 150 °C. Subsequently, they were diluted with a 1 % nitric acid solution. The palladium content in these solutions was then analyzed using ICP-OES (AVIO 500, Perkin Elmer). Hydrodynamic size and zeta potential were analyzed *via* PCS (Nano ZS4700, Malvern). The particles were dispersed in deionized water and the dispersion was sonicated for 20 min before each measurement without filtration. The reduction reactions of 4NP were monitored *via* UV/Visible spectrophotometer (UV/Vis, Specord 210 plus, Analytic Jena) with the wavelength ranging from 200 to 600 nm.

Syntheses

Synthesis of magnetite nanoparticles (MNP)

MNP was synthesized by a co-precipitation between Fe^{2+} and Fe^{3+} salts [32]. $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (1.0 g, 5×10^{-3} mol) and FeCl_3 (1.66 g, 1×10^{-2} mol) were dissolved in distilled water (40 mL) in a round bottom flask. NH_4OH solution (20 mL) was added into the mixture and stirred at 400 rpm for 30 min to obtain MNP as black powder. The as-synthesized MNP was magnetically separated from the dispersion and repeatedly washed with distilled water.

Synthesis of alginate-coated MNP (G0) and alginate-co-PVAm-coated MNP (G1)

Alginate (0.1792 g, 4.5×10^{-4} mol of the repeating unit) was dissolved in distilled water (8 mL) with stirring at 70 °C and under N_2 atmosphere, followed by an addition of NVF (63 μL , 9×10^{-4} mol) and APS (0.002 g, 9×10^{-6} mol) as a radical initiator and continuously stirring for another 60 min (**Figure 1**). After the polymerization of poly(*N*-vinyl formamide) (PNVF), MNP (200 mg) was added and the mixture was sonicated for 5 min. The dispersion was slowly dropped into paraffin liquid (30 mL), followed by an addition of glutaraldehyde (3 mL), and the dispersion was stirred for another 60 min at room temperature. The proposed reaction of glutaraldehyde with alginate coated on MNP is shown in the supporting information (**Figure S1**).

The particles were magnetically separated and washed with hexane for 3 times to remove paraffin liquid and then distilled water for 3 times to remove unreacted alginate. PNVF coated on the particles was then hydrolyzed with NaOH solution (10 mL, 9×10^{-2} M) at room temperature for 3 h to gain PVAm. The base hydrolysis of PNVF to obtain PVAm is shown in the Supporting information (**Figure S2**). The as-synthesized alginate-co-PVAm-coated MNP, so called “G1”, was magnetically separated from the mixture, washed with distilled water, and dried *in vacuo*. “G0” nanosorbents, as a control catalyst, was synthesized in a similar fashion without the use of PNVF in the synthesis; G0 particles had no PVAm in the structure (**Figure 1**).

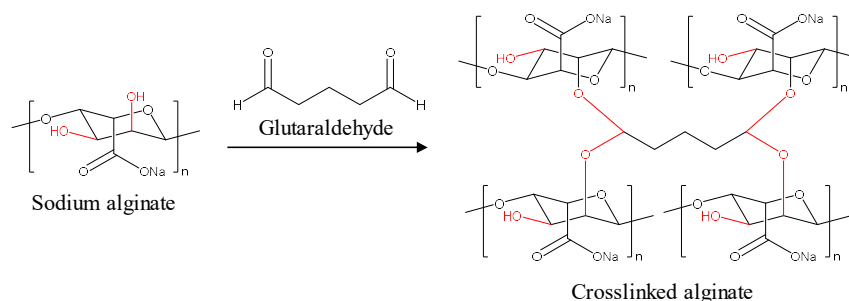


Figure S1 Schematic of the crosslinking of sodium alginate with glutaraldehyde.

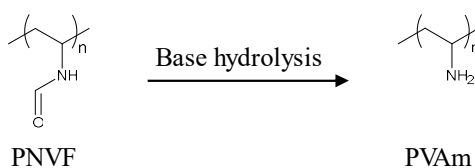


Figure S2 Schematic of the base hydrolysis of PNVF to obtain PVAm.

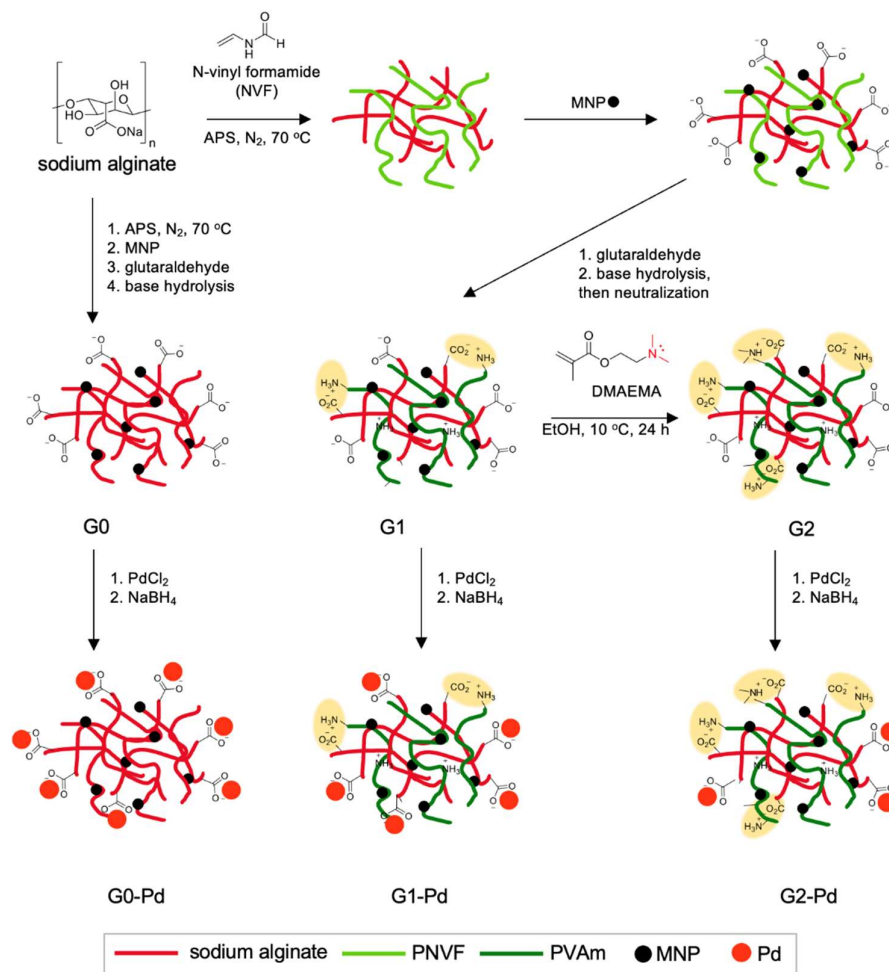


Figure 1 Schematic of the synthesis of Pd-immobilized nanosorbents.

Synthesis of alginate-co-PVAm-coated MNP and then modified with DMAEMA (G2)

To the G1 dispersion in ethanol, DMAEMA was added to increase the number of amino groups in the nanosorbents and the proposed reaction is shown in the Supporting information (**Figure S3**). G1 (100 mg) was redispersed in ethanol (3 mL), followed by a slow addition of DMAEMA (215 μ L, 2.52×10^{-3} mol) to the dispersion at 10 °C for 24 h. The as-synthesized alginate-co-PVAm MNP modified with DMAEMA, so called “G2”, was magnetically separated from the dispersion and washed with ethanol 3 times (**Figure 1**).

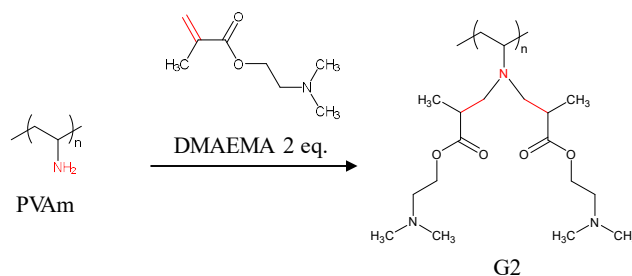


Figure S3 Schematic of synthesis of alginate-co-PVAm-coated MNP and then modified with DMAEMA (G2).

Immobilization of Pd onto G0, G1 and G2 nanosorbents

Pd was immobilized onto G0, G1 and G2 nanosorbents by reducing Pd^{2+} to Pd^0 using PdCl_2 as a Pd precursor [33]. G0, G1 or G2 (100 mg) was redispersed in distilled water (3 mL) and stirred for 10 min. PdCl_2 solution (16.75 mg in 7 mL of distilled water) was then added into the MNP dispersion. Next, HCl solution (20 μL of 0.1 M HCl) was added into the dispersion to complete the dissolution of PdCl_2 , and it was stirred for another 1 h at room temperature. NaBH_4 solution (35 mg, 9×10^{-4} mol, in 5 mL of distilled water) was added to the mixture and the Pd reduction was allowed for 2 h. The particles were magnetically separated and washed with distilled water to obtain G0-Pd, G1-Pd and G2-Pd (**Figure 1**).

In addition to the synthesis at room temperature, the microwave-assisted synthesis of Pd-immobilized nanosorbents was also of great interest in this work. Therefore, the use of $\text{Pd}_2(\text{dba})_3$ instead of PdCl_2 as a Pd precursor was also performed. The advantages of this approach over the use of PdCl_2 were that 1) There was no need of acidic solution to completely dissolve the Pd precursor and 2) It was a rapid process. The mixture of $\text{Pd}_2(\text{dba})_3$ (44.35 mg, 4.2×10^{-4} mol) and G1 or G2 (100 mg) was dispersed in toluene (5 mL), sonicated for 10 min, and then heated to 110 $^\circ\text{C}$ with a microwave for 2 min. After magnetic separation, the Pd-immobilized nanosorbents were washed 3 times with dichloromethane and dried *in vacuo* to obtain G1-Pd* and G2-Pd*.

The reduction reaction of 4NP in the presence of Pd-immobilized nanosorbent catalysts

The catalytic activity of Pd-immobilized nanosorbents was investigated using the 4NP reduction in water as a model reaction with the use of NaBH_4 as a reducing agent to form 4AP as a product (**Figure S4** in the Supporting information) [12]. The reaction was monitored *via* UV/Visible spectrophotometer at 200 - 600 nm wavelengths. The 4NP solution (4 mL, 2.50×10^{-4} M) and NaBH_4 solution (2 mL, 0.125 M) were mixed in a quartz cuvette with continuously stirring, followed by adding Pd-immobilized nanosorbents with 1, 3 or 5 %mol of Pd (0.015 - 0.14 mg of the nanosorbents depending on the Pd content in each sample). The reaction progress was monitored from the decrease of the absorbance intensity of 4NP at 400 nm. In the recycling procedure, the nanosorbents were magnetically separated and washed with DI water before reused in the next cycle.

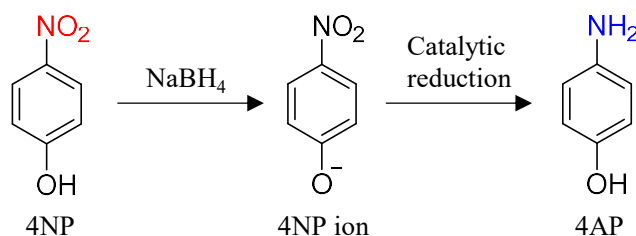


Figure S4 Schematic for the 4NP reduction catalyzed by Pd-immobilized nano-adsorbents.

Results and discussion

In this work, alginate-coated MNP (G0), alginate-co-PVAm-coated MNP (G1), and those further modified with DMAEMA (G2) were synthesized and used as nanosorbents of Pd. The alginate coating on the MNP not only imparted excellent water solubility and prevented uncontrolled aggregation of the catalysts but also provided abundant carboxylate anions for interaction with Pd [34,35]. Moreover, additions of the amino-containing polymers including PVAm and DMAEMA to the particles were of great interest in this study because they had the potential to form ionic interactions with the carboxylate groups present in the alginates. It was expected that this interaction would have some influence on the Pd immobilization efficiency, catalytic activity and the reusability of the nanosorbents. The catalytic performance of as-synthesized the Pd-immobilized nanosorbents was investigated using the 4NP reduction as a model reaction.

Characterization of Pd-immobilized nanosorbents

FTIR spectra of G0, G1, G2 and their precursors, namely bare MNP, alginate, are shown in **Figures 2(a)** and **2(b)**. A characteristic absorption peak corresponding to the Fe-O stretching of the MNP core at 536 cm^{-1} is clearly evident in all samples [36-38]. The spectra of alginate display characteristic absorptions, including the symmetric and asymmetric vibrations of carboxylate groups at 1590 and 1394 cm^{-1} , a broad signal corresponding to O-H stretching at 3194 cm^{-1} , and the C-O stretching at 1000 cm^{-1} [39]. Upon coating MNP with alginate, the spectra exhibit characteristic signals consistent with those of alginate,

confirming the presence of alginate in the nanosorbents, as shown in **Figures 2(c) - 2(e)**. Interestingly, in the spectrum of G2, a signal at 1204 cm^{-1} , attributed to the C-N stretching, was prominently observed [40,41]. This can be attributed to the additional reaction of DMAEMA with G1.

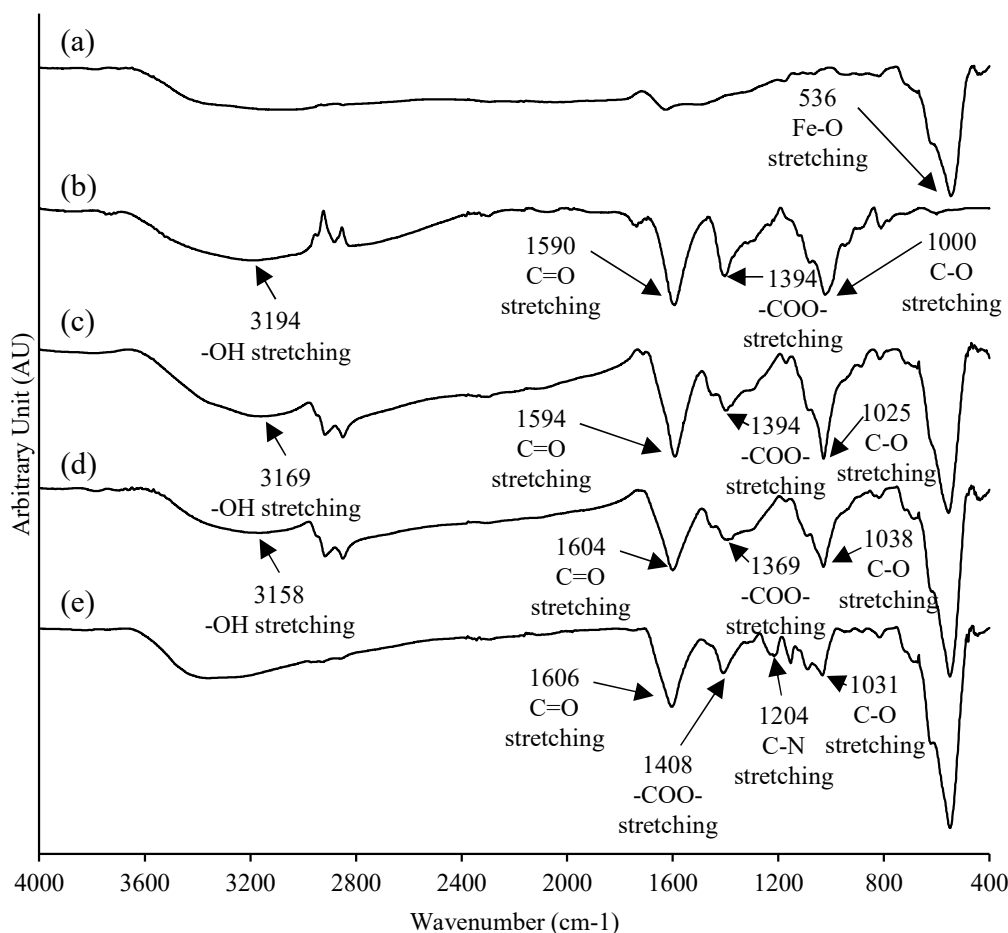


Figure 2 FTIR spectra of (a) bare MNP, (b) alginate, (c) G0, (d) G1 and (e) G2.

Hydrodynamic size (D_h) and zeta potential values of G0, G1 and G2 were determined using the PCS technique (**Figure 3(a)**). The D_h of the nanosorbents tended to decrease from approximately 480 nm (G0 and G1) to 390 nm (G2) after the extended reaction with DMAEMA. This decrease can be attributed to the improved water dispersibility of the particles due to the presence of additional amino groups from DMAEMA, resulting in a reduction in D_h . Interestingly, the zeta potential values indicated a decrease in the degree of negative charges from -33 eV (G0) to -28 eV (G1) and a further decrease to -22 eV (G2) when PVAm and DMAEMA moieties were incorporated into the nanosorbents (**Figure 3(b)**). This reduction in negative charges might be attributed to the existence of additional amino groups, which could facilitate the formation of carboxylate-ammonium salts, essentially leading to a decrease in the net negative charge.

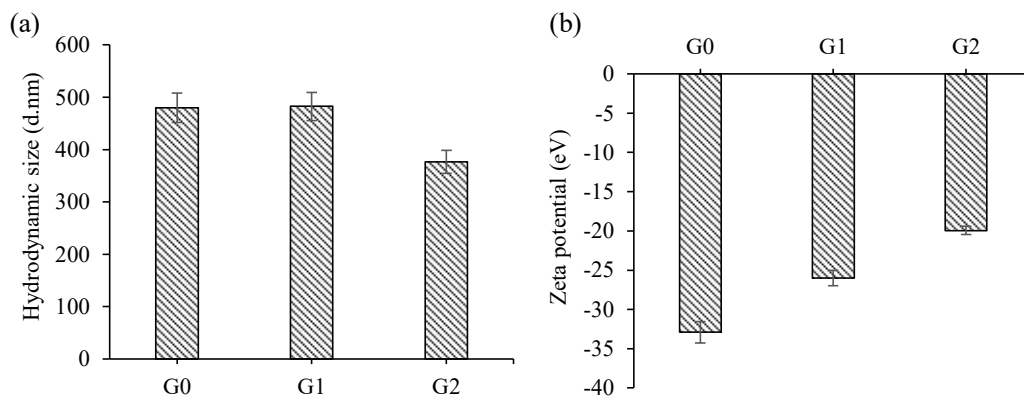


Figure 3 Hydrodynamic size (D_h) and zeta potential values of G0, G1 and G2.

The determination of %weight remaining for bare MNP, G1 and G2 was conducted using the TGA technique within the temperature range of 20 - 620 °C (**Figure 4(a)**). This analysis aimed to investigate the compositions of organic and iron oxide contents within these nanosorbents. Bare MNP exhibited a weight loss of approximately 15 %, which was attributed to trace water molecules adsorbed on the MNP surface. These losses were taken into consideration for estimating the organic/inorganic composition in the nanosorbents. The organic components in G1 and G2 were found to be 20 and 25 %, respectively, while the iron oxide content was 65 % for G1 and 60 % for G2. The increase in organic components from 20 % in G1 to 25 % in G2 resulted from the addition of DMAEMA to G1. Magnetic responsiveness of bare MNP, G1 and G2 was analyzed *via* the VSM technique (**Figure 4(b)**). The saturation magnetization (M_s) value of G1 was 55 emu/g and that of G2 was 52 emu/g, and these values were slightly lower than that of bare MNP (71 emu/g). The decrease of in M_s values was attributed to the increased presence of non-magnetic components, including PVAm, alginate and DMAEMA, within the nanosorbents. Nevertheless, both G1 and G2 demonstrated a good response to an external magnet, allowing them to be effectively separated from the dispersion.

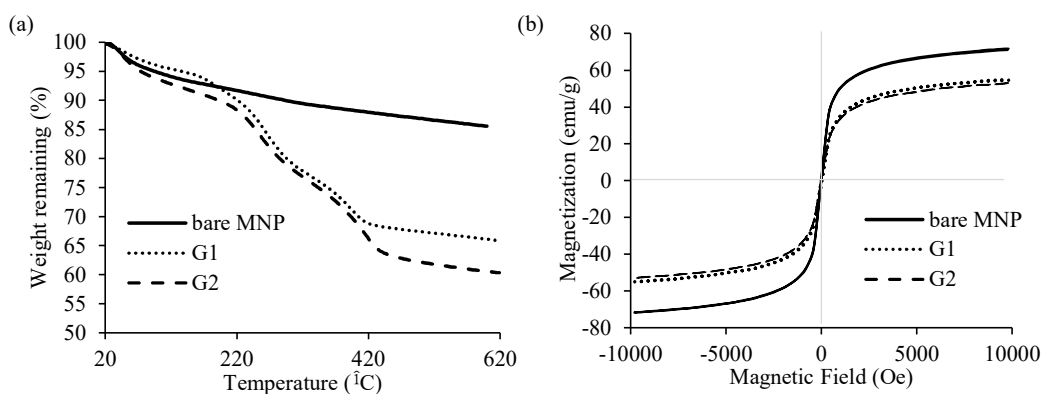


Figure 4 (a) TGA thermograms and (b) VSM plots of bare MNP, G1 and G2.

Following the immobilization of the nanosorbents with Pd, TEM techniques were employed to investigate the size and size distribution of both MNP and Pd (as depicted in **Figures 5(a)** and **5(b)**). The diameter of MNP ranged from 7.6 to 19.0 nm, with an average size of approximately 12.3 ± 2.9 nm, while those of Pd ranged from 3.4 to 5.0 nm, with an average size of around 3.9 ± 0.8 nm. Notably, **Figure 5(a)** reveals the presence of a polymer layer coating on the surface of MNP. The visible (111) planes ($d = 0.23$ nm) of Pd, along with those of MNP ((220) planes, $d = 0.28$ nm), were observed on the nanosorbents, as shown in **Figure 5(b)** [4,39]. Additionally, **Figure 5(c)** provides confirmation of the presence of Pd embedded within the nanosorbents, as indicated by the characteristic peak of Pd in the EDX spectrum. The EDX mapping shows the Fe and Pd homogeneous distribution in G2-Pd (**Figure S5** in the supporting

information). **Figure 5(d)** presents a representative FESEM image of G2-Pd, displaying an agglomerated morphology of spherical clusters with diameters ranging from 28.0 to 72.7 nm, and an average size of approximately 48.5 ± 11.9 nm. The XRD spectra of G0-Pd, G1-Pd and G2-Pd are shown in **Figure S6** in the Supporting information. The XRD patterns can be used to confirm the species of Fe present in the samples. According to the XRD spectrum from the standard magnetite (Fe_3O_4) powder diffraction data (ICSD No. 01-075-0449) and previously reported papers [20,42], the XRD patterns of the nanosorbents synthesized in this work aligned well with those of magnetite, indicating the formation of Fe_3O_4 (magnetite) as a major product in the current work (**Figure S6** in the supporting information). The spectra show the specific angles (crystal planes) of magnetite at 30.1° (220), 35.7° (311), 43.1° (400), 53.7° (422), 57.4° (511) and 62.7° (440), and those of Pd at 40.2° (111), 46.6° (200) and 68.3° (220).

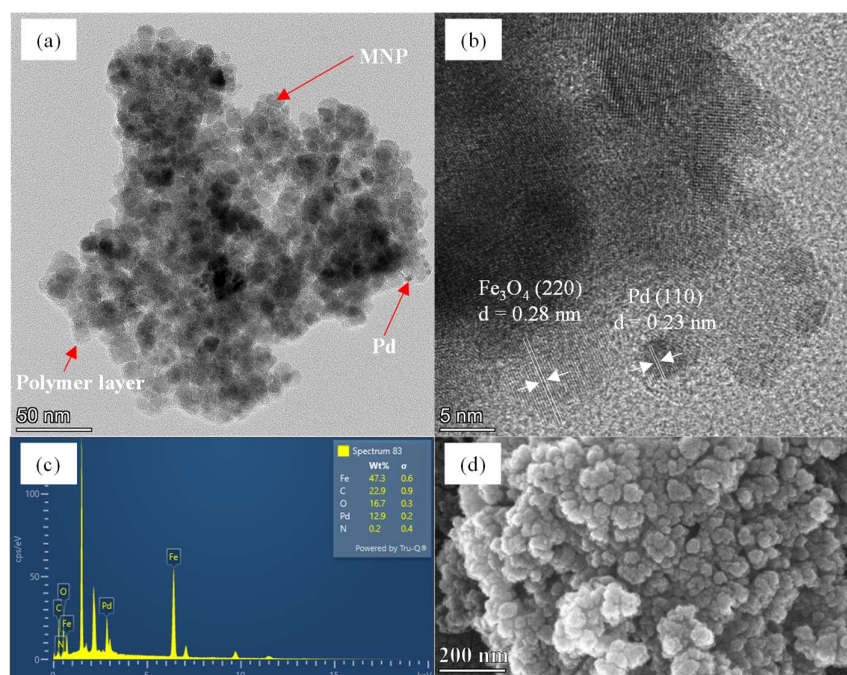


Figure 5 (a and b) TEM images, (c) an EDX spectrum and (d) an SEM image of G2-Pd.

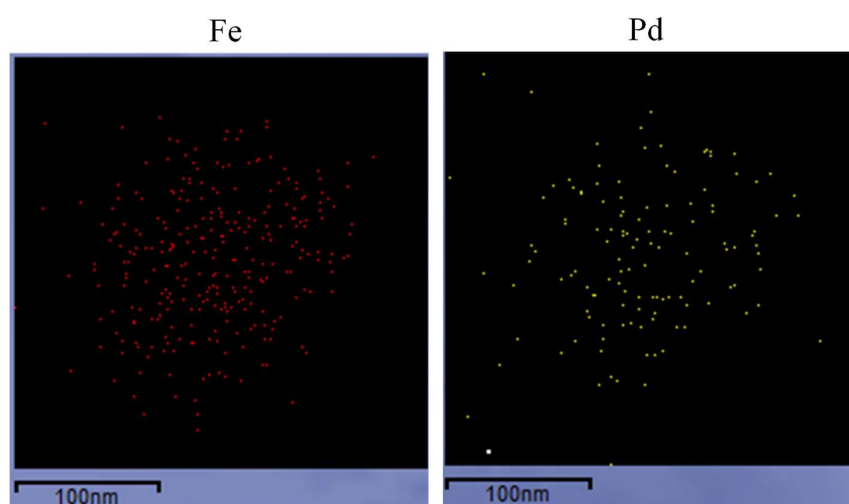


Figure S5 The EDX mapping showing the Fe and Pd homogeneous distribution in G2-Pd.

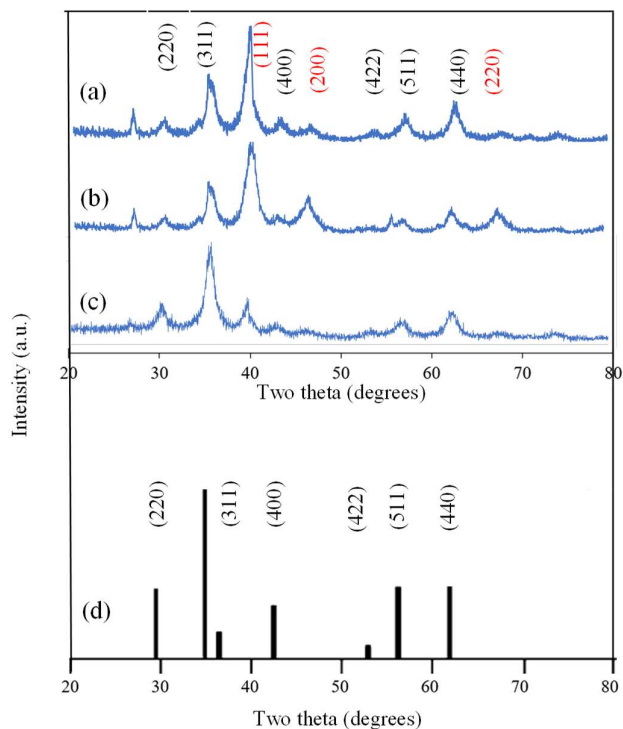


Figure S6 The XRD spectra of (a) G0-Pd, (b) G1-Pd, (c) G2-Pd and (d) the standard Fe_3O_4 powder diffraction data (ICSD No. 01- 075-0449).

The quantitative analysis of Pd of the nanosorbents was determined *via* ICP-OES technique. The efficiency of the Pd immobilization process was analyzed from %Pd content, Pd loading and %Pd incorporation values, which were calculated using Eqs. (1) to (3);

$$\% \text{Pd content} = \frac{\text{weight of Pd immobilized on nanosorbent} \times 100}{\text{weight of nanosorbent}} \quad (1)$$

$$\text{Pd loading} = \frac{\text{mol of Pd immobilized on nanosorbent}}{\text{weight of nanosorbent}} \quad (2)$$

$$\% \text{Pd incorporation} = \frac{\text{weight of Pd immobilized on nanosorbent} \times 100}{\text{weight of Pd precursor}} \quad (3)$$

As indicated in **Table 1**, the Pd loading of the nanosorbents prepared from PdCl_2 (G0-Pd, G1-Pd and G2-Pd) ranged from 0.36 to 0.66 mmol/g, corresponding to Pd contents of 3.82 and 7.05 %. For those prepared from $\text{Pd}_2(\text{dba})_3$ (G1-Pd* and G2-Pd*), the Pd loading ranged between 0.24 and 0.36 mmol/g, corresponding to Pd contents of 2.60 and 3.88 %.

Table 1 %Pd content, Pd loading and %Pd incorporated of the nanosorbents synthesized in this work.

Sample	%Pd content (%w/w)	Pd loading (mmol/g)	%Pd incorporated (%)
G0-Pd	7.05	0.66	70.54
G1-Pd	4.62	0.43	46.17
G2-Pd	3.82	0.36	38.20
G1-Pd*	2.60	0.24	26.04
G2-Pd*	3.88	0.36	38.82

When examining the results for G0-Pd, G1-Pd and G2-Pd, the addition of amino groups, such as PVAm (in G1-Pd) and DMAEMA (in G2-Pd), to the nanosorbents appeared to decrease Pd loading. This decrease was likely a consequence of the presence of PVAm and DMAEMA amino groups on the particles, leading to the formation of carboxylate-ammonium salts (**Figure 1**). This reduction in free carboxylate anions in the alginate coating on the particles affected their ability to coordinate with Pd, resulting in a decrease in Pd immobilization efficiency (**Table 1**). This explanation aligns well with the findings from the PCS technique (**Figure 3(b)**), which indicated a reduction in negative charges after the addition of PVAm and DMAEMA to the particles. Consequently, G0-Pd, G1-Pd and G2-Pd were chosen for further experiments to investigate the effects of Pd distribution within the polymers on the catalytic activity and recyclability of the nanosorbents.

Catalytic activity of Pd-immobilized nanosorbents for the reduction of 4NP

The catalytic activity of G0-Pd, G1-Pd and G2-Pd was investigated using the reduction of 4NP in water at room temperature as a model reaction. Neutral 4NP exhibited its maximum absorbance at 317 nm in UV/Visible spectrophotometry. In an alkaline solution, the maximum absorbance shifted to 400 nm due to the formation of the 4NP anion. This shift could be visualized by the change in solution color, transitioning from bright yellow to deep yellow. Upon adding Pd-immobilized nanosorbents to the 4NP ion solution, the absorbance at 400 nm steadily decreased, while a new peak representing the product, 4AP, emerged at 330 nm as the reduction progressed. It is noteworthy that the solution turned colorless when the absorbance at 400 nm disappeared, signifying the completion of the 4NP reduction. Consequently, the progress of the 4NP reduction was monitored by observing the decrease in the absorbance of 4NP ions at 400 nm over time. The rate constant (k) for the 4NP reduction was calculated using the pseudo 1st order equation (Eq. 4), employing the plots of $\ln(A_t/A_0)$ versus reaction time [5].

$$\ln(A_t/A_0) = -kt \quad (4)$$

Turnover frequency (TOF) and %conversion of Pd-immobilized nanosorbents were calculated from Eqs. (5) and (6).

$$TOF = (\text{mol of } 4AP / \text{mol of Pd used}) / t \quad (5)$$

$$\%Conversion = ((A_0 - A_t) / A_0) \times 100 \quad (6)$$

where A_t and A_0 were the absorbance intensity of 4NP ions at a given time and the initial time, respectively, t was the reaction time (s) and k was the rate constant of the 4NP reduction.

Pd at concentrations of 1, 3 and 5 %mol (with mol of Pd being 2.5×10^{-6} , 7.5×10^{-6} and 12.5×10^{-6} mol, respectively) was used for the catalytic activity studies of the 3 catalysts (G0-Pd, G1-Pd and G2-Pd). **Figure 6(a)** presents examples of the UV/Visible spectra for the reduction of 4NP using 3 %mol Pd of G2-Pd as a catalyst, while the remaining spectra can be found in the Supporting information (**Figure S7 - S9**). **Figures 6(b) to 6(d)** show the k values calculated from the slopes of the linear plots of $\ln(A_t/A_0)$ versus the reaction time using these catalysts. All plots exhibit a linear relationship between $\ln(A_t/A_0)$ and the reaction time, indicating pseudo-1st-order kinetics behavior. Increasing the percentage of Pd appeared to enhance the k values. Interestingly, G2-Pd demonstrated superior catalytic activity compared to the other 2 catalysts, as evidenced by its higher %conversion, TOF and k values at the same catalyst concentrations. This improved catalytic activity of G2-Pd, in contrast to G0-Pd and G1-Pd, can be attributed to the enhanced distribution of Pd on the MNP surface, a result of the additional salt formation between the carboxylate groups of alginate and the ammonium groups of PVAm/DMAEMA (**Figure 7**).

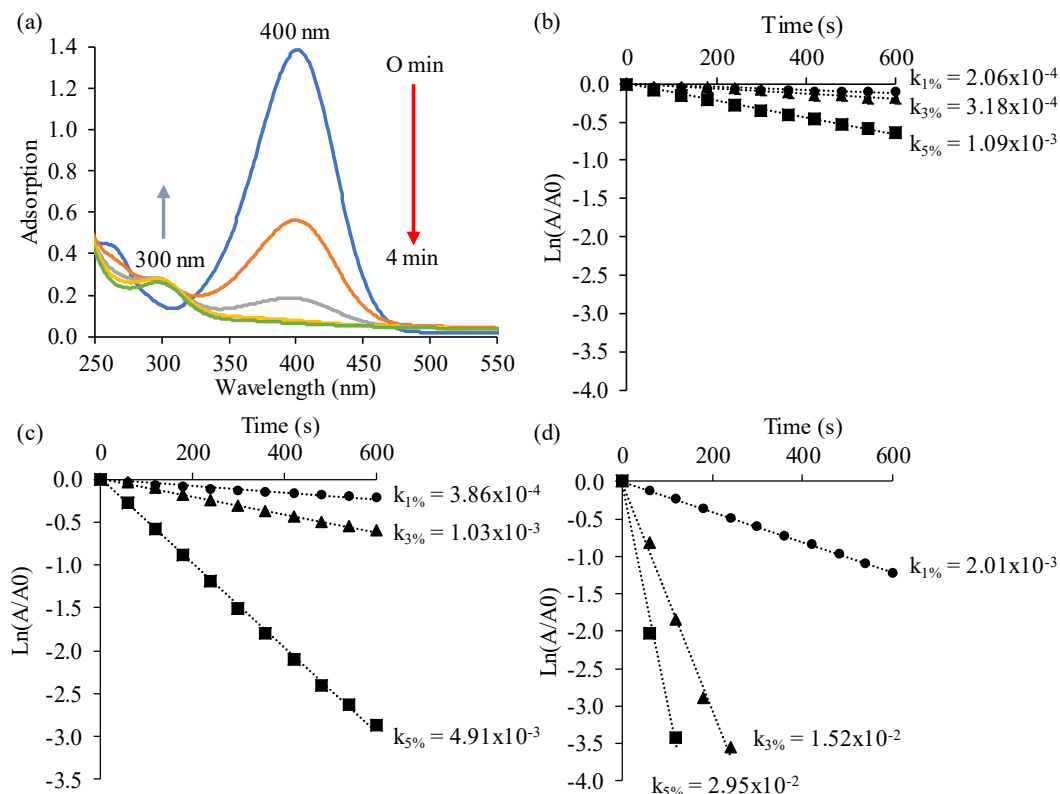


Figure 6 (a) UV/Visible spectra of the 4NP reduction using 3 %mol Pd of G2-Pd as a catalyst, the plots of $\ln(A/A_0)$ versus time (s) of (b) G0-Pd, (c) G1-Pd and (d) G2-Pd using (●) 1 %, (▲) 3 % and (■) 5 %mol of Pd.

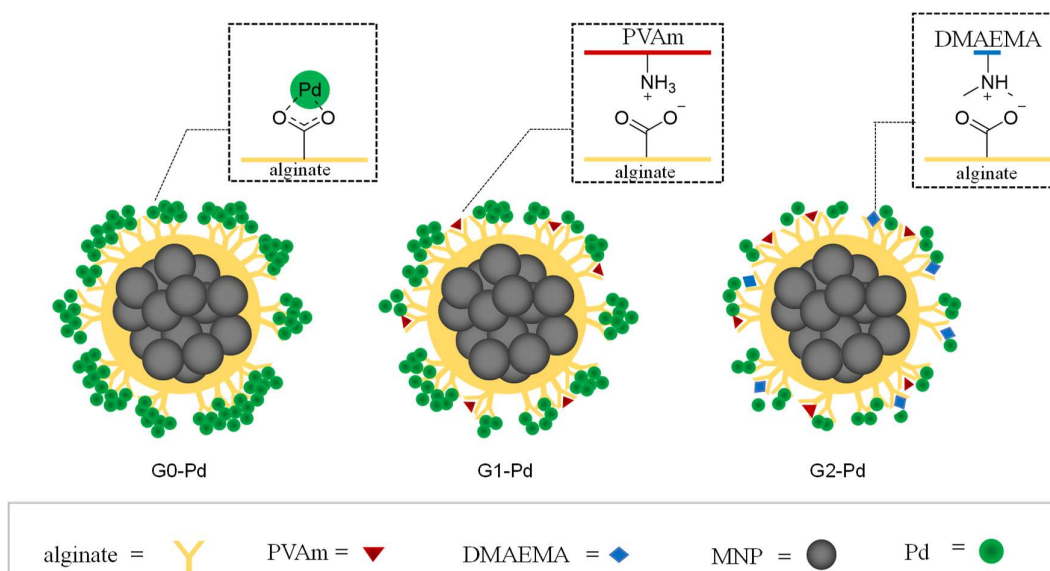


Figure 7 The proposed mechanism for the formation of the carboxylate-ammonium salts after incorporation of PVAm (G1) and DMAEMA (G2) to alginate-coated MNP (G0), resulting in the improved distribution of Pd on the MNP surface.

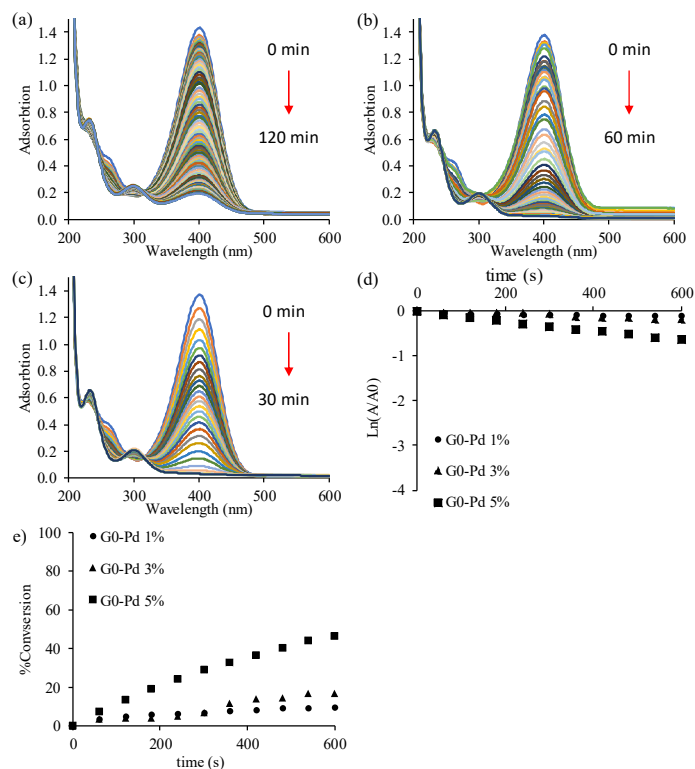


Figure S7 Adsorption spectra of 4NP reduction using (a) (●) 1%, (b) (▲) 3%, and (c) (■) 5%, (d) graph of $\ln(A/A_0)$ versus time (s), and (e) %conversion of G0-Pd.

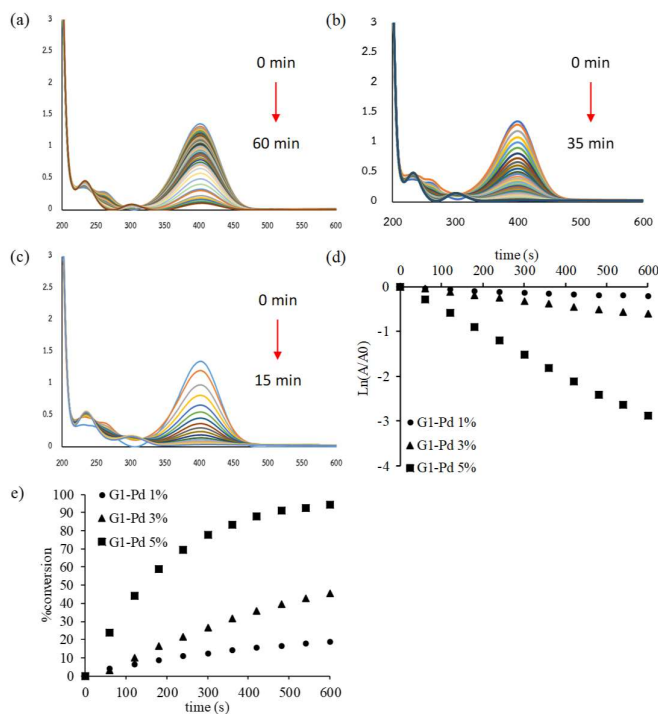


Figure S8 Adsorption spectra of 4NP reduction using (a) (●) 1%, (b) (▲) 3%, and (c) (■) 5%, (d) graph of $\ln(A/A_0)$ versus time (s), and (e) %conversion of G1-Pd.

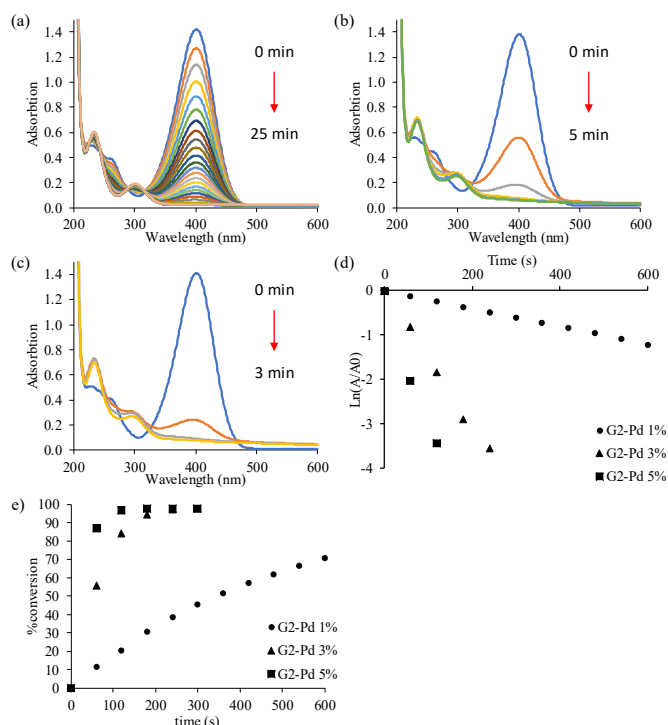


Figure S9 Adsorption spectra of 4NP reduction using (a) (●) 1%, (b) (▲) 3%, and (c) (■) 5%, (d) graph of $\ln(A/A_0)$ versus time (s), and (e) %conversion of G2-Pd.

Recycling studies for the 4NP reduction of Pd-immobilized nanosorbents

Owing to their high catalytic activity, as presented in **Table 2**, G1-Pd and G2-Pd were chosen as representatives for the recycling studies, aimed at investigating their reusability and stability in the 4NP reduction. The recycling studies were conducted over a period of 10 min to reach their maximum reaction conversions, as illustrated in **Figure 8(a)**. After 20 cycles, G2-Pd exhibited excellent catalytic activity, with a %conversion rate ranging from 98 to 99 %. This result indicates the high stability of Pd in the nanosorbents, which is further confirmed by the negligible Pd leaching (< 1.2 ppm of Pd in total) (**Table S1** in the Supporting information). In the case of G1-Pd, the %conversion remained between 98 and 99 % during the first 17 cycles of reuse but appeared to decrease to 85 % by the 20th cycle. This decrease in stability for G1-Pd can be attributed to a less favorable distribution of Pd on the nanosorbent compared to G2-Pd. G2-Pd seemed to be less prone to Pd aggregation, resulting in improved stability upon reuse. This explanation regarding the reduced Pd aggregation after adding DMAEMA to the particles aligned well with the decrease in %Pd content observed through ICP-OES analysis (**Table 1**) and the enhanced catalytic activity (**Table 2**). HRTEM images of G2-Pd after multiple reuses reveal insignificant changes in both particle distribution and morphology. Notably, the visible (111) planes with $d = 0.23$ nm of Pd, and the (220) planes with $d = 0.28$ nm of MNP were consistently observed in the nanosorbents (**Figures 8(b)** and **8(c)**) [13].

Table 2 The %conversion, TOF and rate constant (k) values of the 4NP reduction after 3 min of the reactions using G0-Pd, G1-Pd and G2-Pd as catalysts.

Type of catalyst	%mol of Pd	%conversion	TOF (h^{-1})	rate constant (k) ($1/\text{s}$)
G0-Pd	1 %	6	120	2.06×10^{-4}
	3 %	4	28	3.18×10^{-4}
	5 %	19	76	1.09×10^{-3}

Type of catalyst	%mol of Pd	%conversion	TOF (h ⁻¹)	rate constant (k) (1/s)
G1-Pd	1 %	9	175	3.86×10^{-4}
	3 %	17	111	1.03×10^{-3}
	5 %	59	236	4.91×10^{-3}
G2-Pd	1 %	31	615	2.01×10^{-3}
	3 %	94	630	1.52×10^{-2}
	5 %	97	390	2.95×10^{-2}

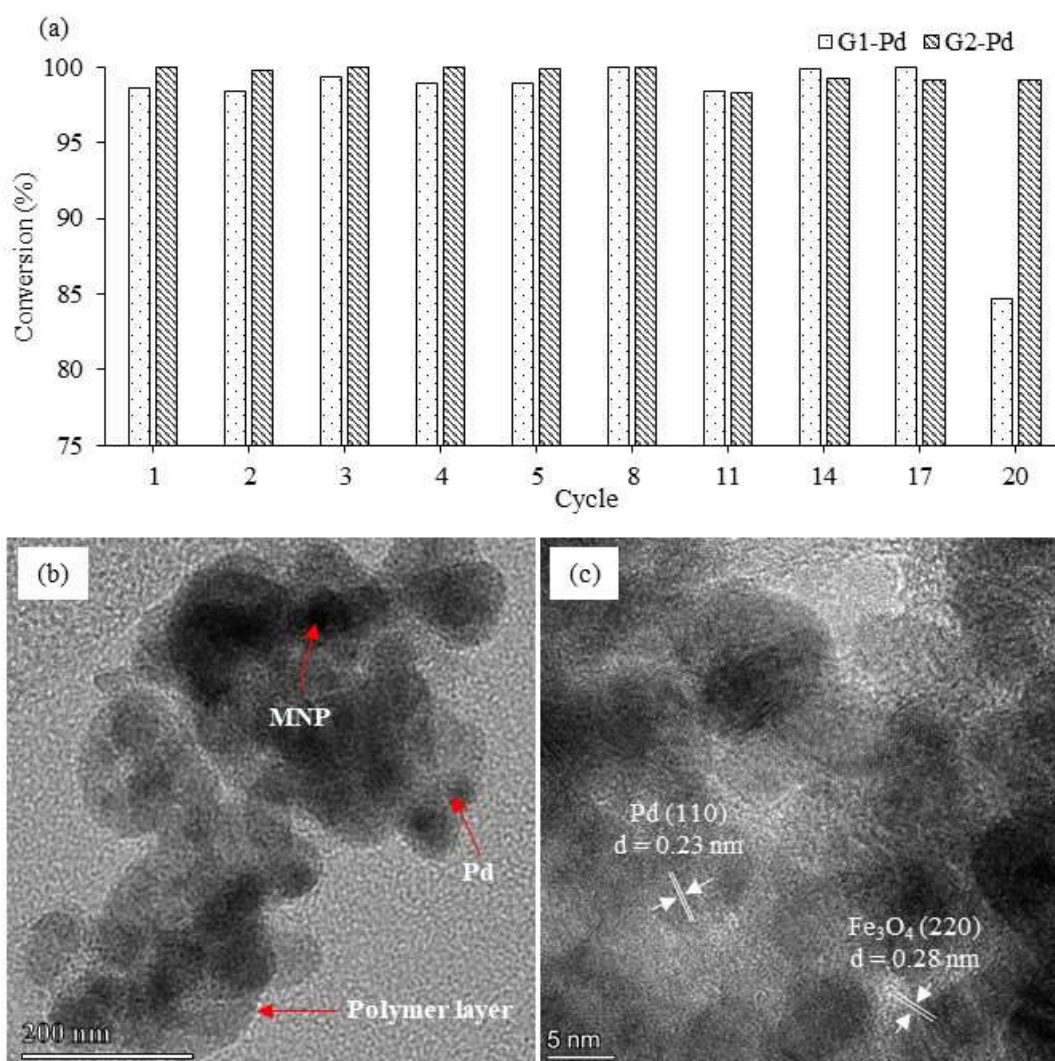


Figure 8 (a) The plot showing %conversion after 10 min of the 4NP reduction using G1-Pd and G2-Pd, (b and c) HRTEM images of G2-Pd after reusing for 20 cycles.

Table S1 Pd leaching of G1-Pd and G2-Pd after the reuse for the 4NP reduction.

Cycle	Pd leaching (ppm)	
	G1-Pd	G2-Pd
1	0.0763 ± 0.0067	0.0163 ± 0.0024
2	0.1054 ± 0.0068	0.1253 ± 0.0202
3	0.0541 ± 0.0030	0.1817 ± 0.0271
4	0.0789 ± 0.0096	0.1566 ± 0.0340
5	0.0396 ± 0.0016	0.1045 ± 0.0145
8	0.1668 ± 0.0164	0.2277 ± 0.0154
11	0.0247 ± 0.0116	0.0416 ± 0.0094
14	0.0483 ± 0.0076	0.0844 ± 0.0040
17	0.0630 ± 0.0080	0.1246 ± 0.0159
20	0.0704 ± 0.0261	0.1070 ± 0.0028
Total	0.7274 ± 0.0973	1.1699 ± 0.1456

Conclusions

Alginate-coated MNP ($ca. 12.3 \pm 2.9$ nm in diameter) was synthesized and employed as the nanosorbent for Pd ($ca. 3.9 \pm 0.8$ nm in diameter). The incorporation of amino-enriched components, including PVAm and DMAEMA, onto the alginate-coated MNP resulted in beneficial interactions, e.g. the formation of carboxylate-ammonium salts. This led to improved dispersibility of Pd and significantly reduced the degree of Pd aggregation on the particle surface. The best condition for the catalytic 4NP reduction in this work was the use of 5 mol% Pd of G2-Pd giving rise to $TOF = 390 \text{ h}^{-1}$ and $k = 2.95 \times 10^{-2} \text{ s}^{-1}$. Consequently, the surface modification of the particles with these amino-containing moieties yielded catalysts with high catalytic performance for the 4NP reduction in water and exhibited highly robust properties with excellent reusability for up to 20 cycles, with insignificant changes in their performance ($> 98\%$ conversion).

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