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Phyto-crystallization of palladium through reduction process using *Cinnamom zeylanicum* bark extract

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ABSTRACT

In this paper we studied the potential of nanocrystalline palladium particle production using *Cinnamom zeylanicum* bark extract (CBE) as the biomaterial for the first time. We studied the effects of biomaterial dosage, pH and temperature on nanoparticle formation; none of these factors had a major effect on the size and shape of the nanoparticles formed. Transmission electron microscopy (TEM) observations confirmed the synthesis of nano-sized palladium particles. More or less uniformly sized palladium nanoparticles were synthesized with an average size ranging from 15 to 20 nm. It was found that the zeta potential of these formed palladium nanoparticles was negative, and that it increased with an increase in pH. Energy dispersive X-ray (EDX) analysis results confirmed the significant presence of palladium. Of the palladium ions, 60% were reduced to a zero valent form by CBE. Terpenoids are believed to play an important role in palladium nanoparticle biosynthesis through the reduction of palladium ions. Currently, however, the exact mechanism for the synthesis of palladium nanoparticles is unclear. Our protocol for the phyto-synthesis of palladium nanoparticles under moderate pH and room temperature offers a new means to develop environmentally benign nanoparticles.

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1. Introduction

The increased use of precious metals in various applications, including catalysis and electronics, in addition to a paramount increase in their value has instigated a great need in their recovery. In particular, palladium, belonging to the platinum group metals, is widely used in automotive catalytic converters in order to reduce gaseous emissions in vehicle exhausts for the sake of environmental protection [1]. Palladium nanoparticles are widely used as catalysts in various reactions, in addition to being utilized in chemiresistor-type sensing devices [2–4]. A large quantity of palladium is released along with wastewater, which needs to be recovered in order to minimize the overall operational costs for the industries. Chemical treatment techniques, including precipitation, are either not effective at lower metal concentrations or not readily applicable [2]. Chelating ion exchange resins containing polyisothiurea groups have been developed for the recovery of precious metals [5], but the removal of metals from resins has proven to be a very serious problem. Solvent extraction methods are expensive due to the high cost of extractants; furthermore, the extraction rates are generally low. Electrochemical methods proved to be efficient at a lab-scale [2]; however, on an industrial scale, the necessary large electrode surface area is a limiting factor, as it results in high running costs. The recovery of the thin base metal film deposits is an additional negative factor. Recently, Park and Fray [6] developed a new technique for the recovery of various precious metals, including palladium from waste printed circuit boards. Theirs is a consortium of several techniques, including electrochemical, electro-winning, solvent extraction, chemical leaching, etc. The main drawback in this method is an immense use of chemicals and the necessity of many techniques, which in turn results in an increase in the overall treatment cost. Palladium recovery by biosorption was also attempted using various biosorbents such as bacteria, moss [7–9]. The problems with these biosorbents include a low adsorption and desorption capacity and the cost-factor for maintaining aseptic conditions. Bioreduction of palladium is one area which has not been explored in depth; however, it appears to provide very promising technology for the recovery of noble metals. Chemical reduction technologies have been well researched in the past decade, involving extreme operational conditions such as high temperature and pressure, and using numerous toxic chemicals which make the process environmentally destructive. On the other hand, the microbially mediated reduction of precious/noble metallic species has generated more interest among researchers around the world in recent years [2,10–12]. However, microbe-assisted synthesis of noble metal nanoparticles is not industrially feasible, as it

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requires the maintenance of aseptic conditions throughout the process and needs skilled technical labors for the process operation. The phyto-reduction of precious metals is a promising technology which has not been very well researched, expect for in silver and gold [13–15]. Especially for palladium reduction using plant materials, there has been no report to date. For these reasons, in this study we opted for a plant material, *Cinnamom zeylanicum* bark, as the biomaterial used for the reduction of palladium ions to zero valent form. The main aim of the study was to develop a cost-effective and eco-friendly technique for palladium nanoparticle production with non-extreme operational conditions from a palladium salt solution. It is expected that this work could provide the basis for phyto-reduction of palladium from industrial wastewaters. To the best of our knowledge, this is the first successful attempt on Pd nanoparticle synthesis using a plant material as reducing agent.

2. Materials and methods

2.1. Preparation of C. zeylanicum bark extract (CBE)

The raw material, *C. zeylanicum* bark, was purchased from a local market and washed to remove any possible remaining impurities. It was then chopped into small pieces and later dried under sunlight for a week to completely remove the moisture. The small dry pieces were then ground in a mixer into a powder and poured through a 20-mesh sieve in order to get uniformly sized pieces. Then, 2.5 g of the sieved powder was added to 100 mL of sterile distilled water in a 500 mL Erlenmeyer flask, and then boiled for 1 min to get extract.

2.2. Biosynthesis of nanocrystalline palladium particles

Palladium chloride ($PdCl_2$) was purchased from Kojima Chemicals Co., Ltd., Japan. For the synthesis of palladium nanoparticles with CBE, 0.5, 1.0, 2.5 and 5 mL of extract was added separately to 50 mL of 1 mM aqueous $PdCl_2$ solution in a 250 mL Erlenmeyer flask. The flasks were then incubated in a rotary shaker at 160 rpm in the dark at a temperature of 30 °C. The reactions between the extract (CBE) and the palladium ions were allowed to occur for a period of 72 h and the reaction product was collected by separating it using centrifugation at 10,000 rpm for 15 min.

To study the effect of pH on formation of palladium nanoparticles, the experiments were conducted at various initial pHs ranging from 1 to 11. To study the effect of temperature, experiments were conducted at various temperatures ranging from 20 to 60 °C.

2.3. Characterization of palladium nanoparticles

TEM samples of the aqueous suspension of platinum nanoparticles were prepared by placing a drop of the suspension on carbon-coated copper grids. The films on the TEM grids were allowed to stand for 2 min, after which the extra solution was removed using a blotting paper and the grid was allowed to dry prior to measurement. TEM observations were performed using a HITACHI-JP/H7600 instrument (Japan) operated at an accelerating voltage of 100 kV. The size distribution of the resulting nanoparticles was estimated on the basis of TEM micrographs with the assistance of SigmaScan Pro software (SPSS Inc, Version 4.01.003). Energy dispersive X-ray (EDX) analyses were performed using a JEOL JSM-6400 microscope (Japan) fitted with Oxford-6506 EDX analyzer (England). The zeta potential (ELS-6000) of the produced nanoparticles was analyzed in order to understand the surface charge of the nanoparticles. The remaining metal ion concentration after bioreduction was analyzed using an ICP (Agilent 7500), and FTIR analysis was done using a Shimadzu 8201PC.

3. Results and discussion

3.1. Effect of biomaterial dosage in the crystallization of palladium

Biomaterial dosage is an important criterion in the crystallization of palladium, as they are the main reductants that determine the outcome of the net result. Fig. 1 shows a representative TEM picture recorded from the drop-coated films of the palladium nanoparticles that were synthesized by treating palladium chloride with CBE for 72 h at 30 °C. Pd nanoparticle formation was also noticed from 24 h onwards, but the productivity was high at 72 h beyond which no significant palladium nanoparticle formation was noticed. Thus 72 h was considered as optimum reaction time for all the further studies. The densely arranged palladium nanoparticles, even at lower biomaterial dosages, show the capability of CBE for high nanoparticle productivity by reducing the number of palladium ions. No definite agglomeration of the nanoparticles was noticed, which represents the polydispersity of the formed nanoparticles. The particles were predominantly more or less spherical in shape (Fig. 1). For any particular application of the nanoparticles, homogeneity in shape plays a very important role. Considering this factor, the nanoparticles produced in this present study would be more suitable for application and this substantiates the utilization of CBE as a biomaterial for palladium nanoparticle synthesis. Variation in the initial concentration of biomaterial (CBE) dosage did not affect the shape and size of the nanoparticles formed. Huang et al. [15] reported a vast difference in the size and shape of the silver nanoparticles synthesized using various initial dosages of sun-dried *Cinnamomum camphora* leaf powder. Palladium nanoparticles synthesized using *Desulfovibrio desulfuricans* had an average size of 50 nm [2]. The major disadvantage in that case was asymmetrical crystal structures, which would limit their application. In addition, as described earlier, the application of bacteria for the synthesis of metal nanoparticles is industrially disadvantageous, especially due to high running and maintenance costs. The density of the formed particles increased with an increase in the initial CBE dosage, which can be attributed to the higher concentration of reductive material at higher CBE dosages. Fig. 2 shows the histogram of palladium nanoparticle size distribution at 30 °C and pH 3, which revealed that most of the produced nanoparticles ranged from 15 to 20 nm. The EDX spectroscopy results confirmed the significant presence of palladium (Fig. 2). The optical absorption peak was observed approximately at 3 keV, which is typical for the absorption of metallic silver nanocrystallites due to the surface plasmon resonance [2]. The XRD studies also confirmed the presence of crystalline palladium, which was coherent with previous reports [2] (Fig. 3). The prepared NPs showed two peaks in the cubic palladium phase (JCPDS No. 05-0681), at 48.2 and 66.5, and a small peak due to some impurity from the biomaterial at 56.8. The slight shift in the peak positions indicated the presence of strains in the crystal structure, which is a characteristic of nanocrystallites.

3.2. Effect of pH on the crystallization of palladium

The solution pH normally plays a major role in all bio-chemical reactions. Therefore, the effect of pH on the crystallization of palladium using CBE was studied using various pHs ranging from 1 to 9. At the pH above 5, a mild precipitation was noticed in the solution; thus, the results using pH 5 and above may not be that reliable. Despite this, the effect of pH was studied as planned. No big difference was noticed in the shape of the nanoparticles produced at various pHs. Similarly, no agglomeration was noticed at any pH. We found that the pH had a mild effect on the size of the particles produced. An increase in pH increased the size of the nanoparticles to a small extent. At pH <5, the maximum number of particles ranged from 15 to 20 (Fig. 4), whereas in samples at pH >5, the maxi-

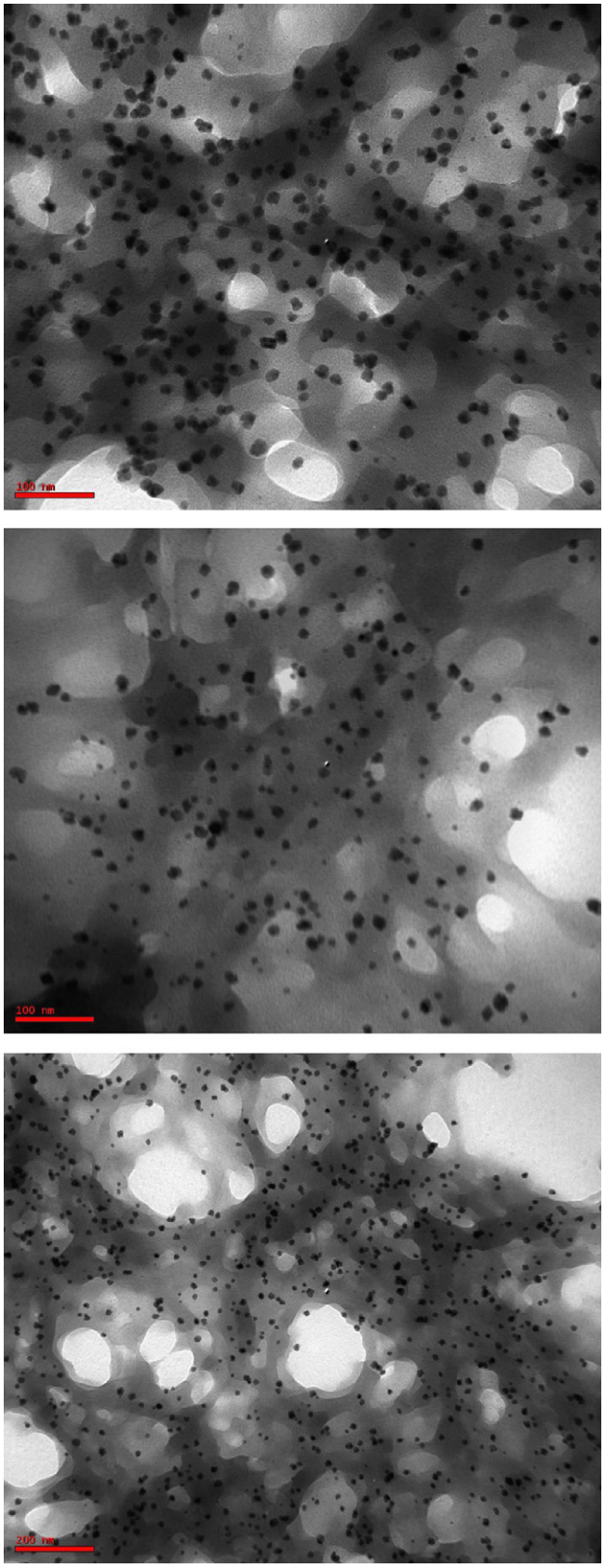

Fig. 1. TEM image of palladium nanoparticles produced by CBE at 30 °C and pH 5.

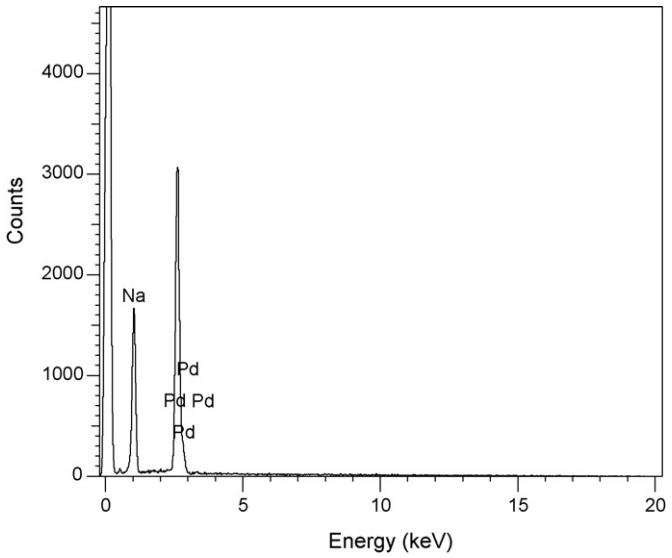

Fig. 2. EDX spectra of palladium nanoparticles produced by CBE at 30 °C and pH 5.

mum number of particles ranged from 20 to 25. A similar effect was reported by Yong et al. [2] for the bioreduction of Pd(II) by *Desulfovibrio desulfuricans*. However, our results showed that CBE was able to synthesize palladium nanoparticles to a much smaller size. The average size of palladium nanoparticles reported by Yong et al. [2] was 50 nm. Andreescu et al. [16] reported a similar pH effect, in addition to the rapid and complete reduction of the silver species at elevated pHs.

3.3. Effect of temperature on the crystallization of palladium

Temperature had a major effect on palladium nanoparticle production. In the temperature range studied (20–60 °C), an increase in temperature increased the productivity of palladium nanoparticles. In all of the temperatures studied, the particles were mostly spherical in shape; no other shape was noticed.

3.4. Determination of crystallized palladium

To check the amount of palladium ions reduced to nanoparticles, after the reduction experiment the sample was centrifuged at 10,000 rpm for 10 min and the supernatant collected was analyzed for palladium ion concentration in ICP. The results revealed that

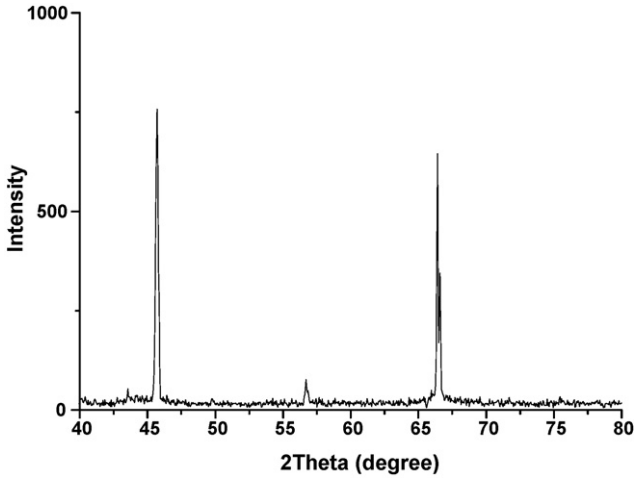

Fig. 3. XRD spectra of palladium nanoparticles produced by CBE at 30 °C and pH 5.

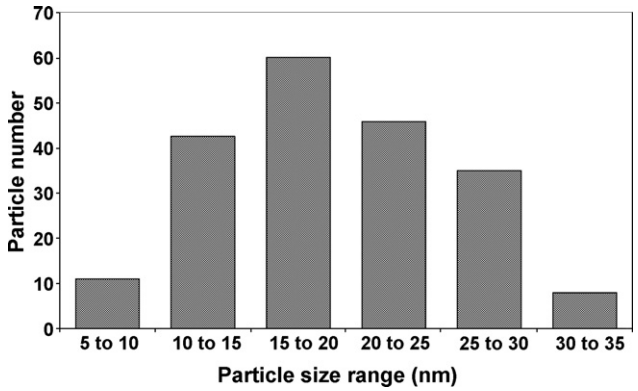

Fig. 4. Histogram of palladium nanoparticle size distribution produced by CBE at 30 °C and pH 5.

60% of the palladium ions were reduced to nanoparticles, with an initial biomaterial concentration of 5 mL/50 mL for a 1 mM initial $PdCl_2$ solution (Fig. 5). On industrial point of view, the remaining 40% of the palladium ions which were not reduced can be used for the next cycle of crystallization.

3.5. Zeta potential studies

The zeta potential results in this study revealed the absolute negative charge on the surface of palladium nanoparticles synthesized using CBE. An increase in pH increased the absolute negative zeta potential value, which is an indirect representation of higher palladium nanoparticle production at a higher pH (Fig. 6). An increase

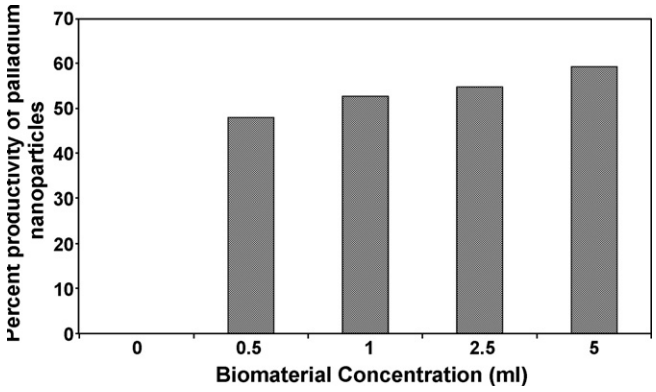

Fig. 5. Percent productivity of palladium nanoparticles from 1 mM $PdCl_2$ at various biomaterial dosages.

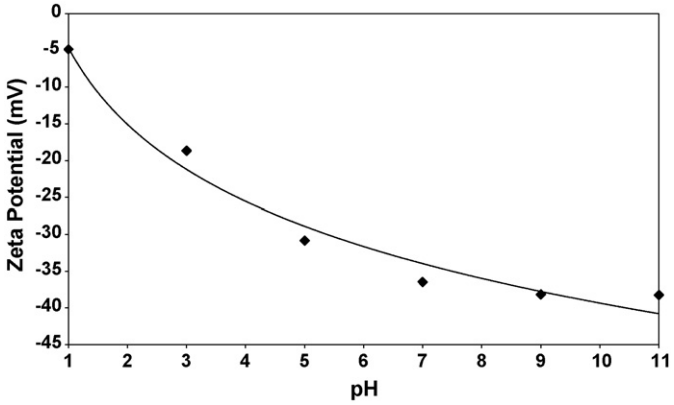

Fig. 6. Zeta potential of palladium nanoparticles synthesized at various pH levels.

in the absolute negative zeta potential value after pH 7 was meager compared to an acidic pH. Xu et al. [4] reported a similar result for the production of palladium nanoparticles using D-glucose. The measurement of the zeta potential of the as-prepared palladium nanoparticles also demonstrates the presence of the pH-dependent equilibrium between –OH and $–O^-$ on the surface of the palladium nanoparticles. This equilibrium shifting was determined by the pH value relative to the pK value of the hydroxylated surface of the Pd nanoparticles. In other words, when the pH was below the pK value, –OH was predominant; conversely, $–O^-$ is predominant when the pH was above the pK value. Therefore, based on the measurement of the zeta potential, the surface of the Pd nanoparticles should have –OH at pH < 6.5 and $–O^-$ at pH > 6.5 [4]. In the case of biomaterial dosage, an increase in dosage increased the absolute negative zeta potential value. Similarly, an increase in temperature increased the absolute negative charge, representing the higher nanoparticle production at higher temperatures.

Palladium nanoparticles produced using CBE were observed to be very stable in the solution, even after 3 months of their synthesis, which validates the application of CBE as a biomaterial for the synthesis of nanocrystalline palladium nanoparticles. *C. zeylanicum* bark is rich in terpenoids, including linalool, eugenol and methyl chavicol, and in chemicals, including cinnamaldehyde, ethyl cinnamate and β-caryophyllene, which contribute to its distinct aroma [17–19]. In addition, some protein is also present in the bark. Terpenoids are believed to play an important role in palladium nanoparticle biosynthesis through the reduction of palladium ions. Shankar et al. [13] reported the possibility of using terpenoids from geranium leaves in the synthesis of nano-sized Ag particles. Polyols such as terpenoids, flavones and polysaccharides in the dried *C. camphora* leaf were reported to be the main cause of the bioreduction of silver and chloroaurate ions [15]. Proteins bind to the nanoparticles, either through free amine groups or cysteine residues in the proteins, and chlorophyll could be capping the particles [13,20]. A similar mechanism may play a role in this study, where the proteins extracted from the *C. zeylanicum* bark capped the palladium nanoparticles, thereby stabilizing them. However, it is not yet clear which compounds/proteins are responsible for the reduction and capping of the palladium nanoparticles. To summarize these results, the water-soluble fractions composed of complex polyols in the biomass are believed to have played a major role in the bioreduction of palladium ions [21,22].

4. Conclusion

In this study we analyzed, for the first time, the possibility of reducing palladium ions to nano-scale palladium particles using an extract of plant material, *C. zeylanicum* bark. This is an ultra low cost technique for the production of palladium nanoparticles, as it does not involve any extreme operation conditions such as high pressure or temperature. In addition, the biomaterial is very cheap. In this experiment, *C. zeylanicum* bark powder was boiled in distilled water for 1 min, which was followed by vacuum filtration to obtain the bark extract and incubation at 30 °C on an incubator-shaker for 5 days with a 1 mM $PdCl_2$ solution. Transmission electron microscopy (TEM) and XRD observations confirmed the synthesis of nano-sized palladium particles. The presence of well-dispersed palladium nanoparticles ranging from 15 to 20 nm was detected using TEM. We found that the zeta potential of the thus formed palladium nanoparticles was negative, and that it increased with an increase in pH. The studies have also revealed that the nanoparticle production was best at high pHs. High temperatures favored a higher productivity of definite sized and shaped nanoparticles. This protocol of palladium nanoparticle biosynthesis under a

moderate pH and room temperature offers a new means to develop environmentally benign nanoparticles.

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