Green Synthesis of Nanoparticles -A Learning Experience

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ABSTRACT:

Cyclic Voltammetry and Differential Pulse Anodic Stripping Voltammetry were utilized in this experiment to detect phenol with a carbon bi-metallic nanoparticle modified electrode. A green synthesis method using pineapple juice extract assisted in the optimized synthesis of bi-metallic silver (Ag) and palladium (Pd) nanoparticles to enhance the catalytic activity of the electrode to successfully detect phenol. Phenol oxidation is carried out in acidic and basic conditions using Cyclic Voltammetry. Peak potentials are found to be distinct for the pH of acidic substances and the pH of basic substances. The electrochemical oxidation of phenol is possible way to treat the wastewaters containing phenol A method such as this is gaining support and acknowledgement within the scientific community. In electrochemical oxidation, phenol is expected to undergo oxidation on a working carbon electrode versus a modified Ag/Pd nanoparticle carbon electrode. This lab has proven to be gratifying for our students, and it has assisted with education on the uses of novel analytical technology and graphing software.

INTRODUCTION:

There have been several scientific applications for the development of noble metal nanoparticles, built to meet the needs of today's society. Silver and gold nanoparticles which additionally have anti-bacterial capabilities, can be based off of common substances such as vegetable oil. The growing concern for widespread pollution brings to light the need for environmentally safe products that are non-toxic and biodegradable. Such a concern emphasizes the demand for Green Chemistry in the modern world. This study actively engaged into an economical and environmentally friendly (Green) approach for the biosynthesis of nanoparticles to be utilized for future sensors in the detection of chemical imbalances in human health and environmental systems. In contrast to traditional chemical and physical nanoparticle synthesis methods, this **Green** alternative eliminates the use of hazardous chemicals such as surfactants, and chemical reducing and capping agents. With this quality in mind, household substances containing polyphenols which have a strong anti-oxidant effect i.e. coffee, pineapple juice, replace traditional chemical reducing and capping agents. A variety of antioxidant functions and specific structures in these green alternative substances, are qualities that reduce the metal ions (Ag^{+}, Pd^{+2}). For example, pineapple juice contains several unique nutrients such as manganese, vitamin C, phytochemicals, ferulic acid, and chlorogenic acid-all of which inhibit the oxidation process. In this study, green tea, pineapple juice, and coffee were the green household substances described in the former, whose extracts were utilized in the synthesis of silver (Ag) and palladium (Pd) nanoparticles. Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Spectroscopy (EDS) and UV-Vis spectroscopy were the methods used to characterize the green synthesis and confirm that the particles were developed successfully. These nanoparticles were coated onto a carbon electrode surface to enhance its electrocatalytic activity for the detection of specific functional groups such as phenol. Electrochemistry techniques such as Cyclic Voltammetry and Differential Pulse Anodic Stripping Voltammetry were used to study the success of the synthesis of these nanoparticle enhanced electrode surfaces to detect the phenol contaminant.

This research can be challenging for students since it requires the synthesis of nanoparticles to modify the electrode surface with uniform coating. The understanding of the potentiostat and the software on the instrument to overlay the data was required knowledge skills set. The analysis for the laboratory skill exercise required comparison of the bi-metallic nanoparticle modified electrodes' cyclic voltammogram with that of a bare carbon electrode. Cyclic Voltammetry is widely used and is a plot of current at the working electrode versus the potential applied. When the potential is sufficiently "negative" or "positive", the component in the solution being analyzed is oxidized or reduced at the electrode surface respectively. A jump of current is observed when the component is electrolyzed (oxidized or reduced) corresponding to a peak on the graph. The parameters of a cyclic voltammogram are the magnitudes of the peak currents as well as the potentials at which the peaks occur. The cyclic voltammogram of phenol will display irreversible response due to the fact that is solely oxidizes. The electrochemical oxidation of phenol will also be detected by Differential Pulse Anodic Stripping Voltammetry (DPASV) in this lab, in order to show another electrochemical technique with a bi-metallic nanoparticle modified working electrode (carbon). Differential Pulse Anodic Stripping Voltammetry, DPASV is a quantitative method for detection of specific species such as phenol. The phenol analyte of interest is electroplated onto the working electrode at the deposition step. During this deposition step, the species is oxidized from the working electrode through a process referred to as "stripping". The oxidation of the species phenol then becomes a recorded peak in the current versus potential graph. This stripping step was a pulse step with the DPASV.

Phenols are a group of common environmental contaminants found in dyes, polymers, drugs, and other organic substances. Phenol compounds enter the ecosystem as a result of drainage of industrial sewage to surface water. They are also used in pesticides and can be generated from the decomposition of organic matter. Phenols are hematoxic, hepatoxic, and carcinogenic to humans and living organisms. Phenols have been listed as a priority of pollutants according to the US EPA reports, due to their harmful effects on aquatic organisms.

SEM shows the successful synthesis of these bi-metallic nanoparticles using Green Chemistry principles.

Experimental:

Safety/Hazards: All solution preparations were carried out under the fume hood. Phenol is harmful upon contact with tissue or if digested. Sulfuric acid heat evolves when mixing with water and proper laboratory caution should be taken. Sodium hydroxide is harmful upon contact with tissue or if digested. All waste was disposed in the proper waste containers with labels. Silver nitrate and palladium chloride very hazardous take precautions in case of skin contact, eye contact or inhalation thus used under the hood for synthesis. Protective garment, goggles, and gloves were worn at all times. All MSDS information can be found at www.sigmaaldrich.com for all products.

Procedure and Apparatus: All electrochemical measurements were carried out on a Bioanalytical Systems Epsilon. The auxiliary electrode was a platinum wire, and a reference electrode was an Ag/AgCl/ 3M NaCl.The working electrode consisted of a modified carbon electrode with bi-metallic Ag/Pd electrode. The Cyclic Voltammetry and Differential Pulse Anodic Stripping Voltammetry (DPASV) was carried out on the Bioanalytical Systems Epsilon instrument.

The Glassy Carbon electrode was polished with alumina suspensions (1 µm and then 0.5 µm size from Bioanalytical Systems), washed with water and finally sonicated in water for 5 minutes. Cyclic voltammograms were recorded at potentials scanning from 0.0 V to 1000 mV with 100 mV/s. DPASV experiments were carried out in the potential range of 0.0 to 2500 mV with the following parameters: scan rate 20 mV/s; pulse amplitude 50 mV, pulse width 500 ms and sample width 50 ms. All measurements were performed at room temperature (25^0C).

Preparation of *Ananas Comosus* based Ag and Pd nanoparticle samples.

Three pineapples (Dole brand) were purchased from the local supermarket (Kroger Beavercreek, Ohio). The pulpy fruit was cut into pieces to fit into a blender and was blended to a pulpy (liquid) solutions. The juice was extracted form the puply sample by method of filtration, utilizing coffee filters. The pineapple juice was stored in a refrigerator. An aqueous solution of 0.1M $AgNO_3$ was prepared. Pineapple juice was added to $AgNO_3$ at the volumetric ratio of 1mL pineapple extract to 10mL $AgNO_3$. A mixture of $AgNO_3$ and pineapple juice was created at the volumetric ratio of 2ml pineapple extract to 10ml $AgNO_3$. In a similar manner, Pd nanoparticles were prepared with an initial solution containing 1mL pineapple extract:10mL $PdCl_2$ and a second solution with a heightened ratio for 2ml pineapple extract :10ml $PdCl_2$. A color change was observed within approximately 5 minutes of the creation of each of the ratio solutions.

Preparation of ratio mixture (Ag:Pd) *Ananas Comosus* based nanoparticle samples.

For 1mL Ag :1mL Pd ratio: 1ml of the previously made 2mL pineapple extract:10mL $AgNO_3$ solution was added to 1mL of the previously made 1mL pineapple extract:10mL $PdCl_2$ solution, creating a 1:1 volumetric ratio solution of Ag nanoparticles to Pd nanoparticles.

For 2mL Ag :1mL Pd ratio: 2mL of the previously made 2mL pineapple extract: 10mL $AgNO_3$ solution was added to 1mL of the previously made 1mL pineapple extract:10mL $PdCl_2$ solution, creating a 2:1 volumetric ratio solution of Ag nanoparticles to Pd nanoparticles.

For 3mL Ag :1mL Pd ratio: 3mL of the previously made 2mL pineapple extract: 10mL $AgNO_3$ solution was added to 1mL of the previously made 1mL pineapple extract:10mL $PdCl_2$ solution, creating a 3:1 volumetric ratio solution of Ag nanoparticles to Pd nanoparticles. Catechol and ascorbic acid were prepared and diluted appropriately with sulfuric acid.

Results and Discussion:

The phenol detection was successfully carried out with the modified bi-metallic Ag/Pd nanoparticle carbon electrode utilizing Cyclic Voltammetry and DPASV. The phenol molecule undergoes electrooxidation and oxidized to phenoxy radical which is pH dependent as shown below:

$$C_6H_5OH \rightarrow C_6H_5O\bullet + H^+ + e-$$

The radical intermediate undergoes polymerization thus formation of a film on the electrode surface. Figure 2 and Figure 3 illustrate the phenol peak occurring around 0.55 V and agrees well with reported literature Garcia et al.

Figure 1 illustrates the unsuccessful detection of phenol at a bare carbon electrode utilizing Cyclic Voltammetry compared to Figure 2 where the detection of phenol was successful with a bi-metallic Ag/Pd carbon electrode compared to the bare carbon electrode (overlay graph). Figure 2 and Figure 3 illustrate how pH of the phenol is a factor on where the oxidation peak will appear. The results of the electro-oxidation of phenol revealed as the pH is increased the oxidation peak potential shifts cathodically thus indicator that the oxidation is facilitated. Thus increase the pH (pH=2 vs. pH=8) facilitated the abstraction of the H^+ from phenol. Figure 4 displays how DPASV can be used to detect phenol successfully as well with the Ag/Pd nanoparticle electrode. Figure 5 illustrates the successful SEM of bi-metallic nanoparticles Ag/Pd onto the carbon electrode surface which enhanced the catalytic activity of the electrode surface to detect phenol. The Ag and Pd nanoparticles were found to be spherical and sizes ranged from 5 to 100 nm depending if coffee, tea or pineapple juice were used to form. Our most successful synthesis results utilized pineapple juice for the development of the bi-metallic nanoparticles onto the carbon electrode.

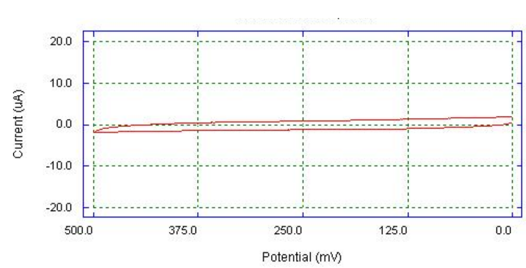

Figure 1. Cyclic Voltammogram of 0.005 M Phenol in acidic conditions

(sulfuric acid; pH=2) with bare carbon electrode.

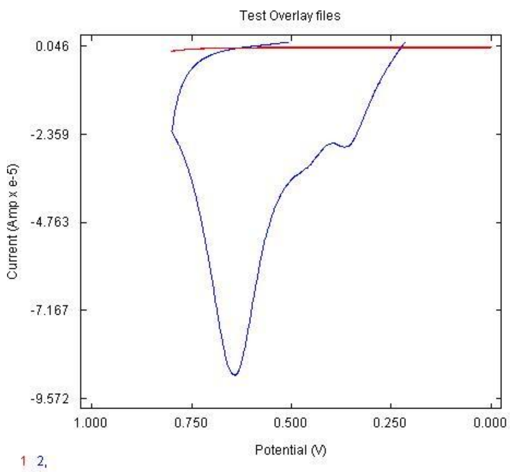

Figure 2. Cyclic Voltammogram of 0.005 M Phenol in acidic conditions (sulfuric acid; pH=2) with bare carbon electrode 1) and 2) Ag/Pd nanoparticle carbon electrode.

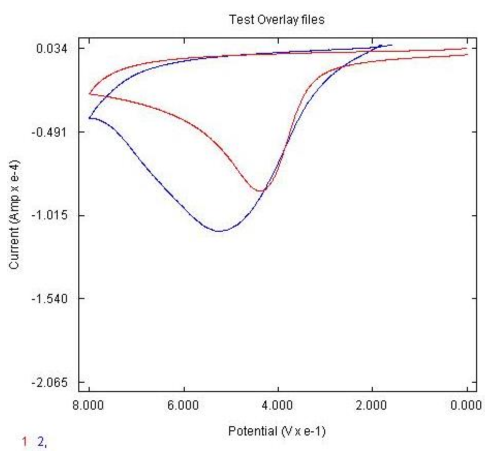

Figure 3. Cyclic Voltammogram of 0.005 M Phenol in basic conditions conditions (pH=8) with bare carbon electrode 1) and 2) Ag/Pd nanoparticle carbon electrode.

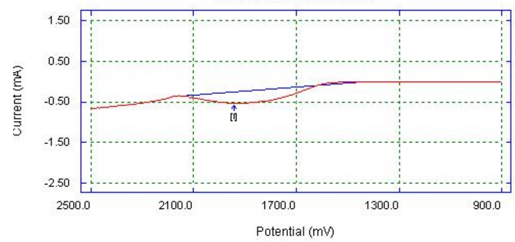

Figure 4. DPASV of 0.005 M phenol with Ag/Pd bi-metallic nanoparticle synthesized by pineapple juice on carbon electrode.

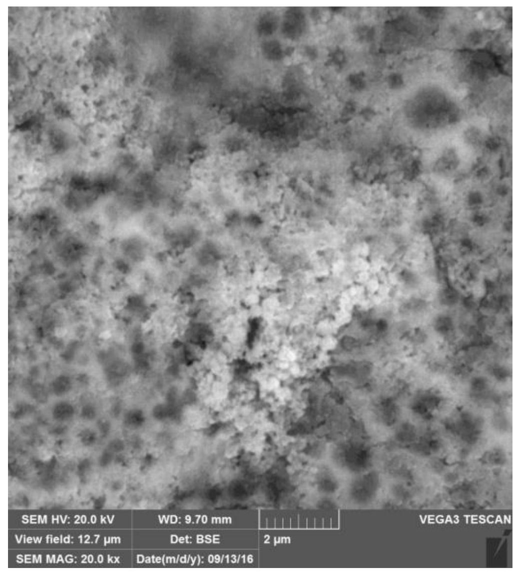

Figure 5. SEM of Ag/Pd nanoparticle synthesized using pineapple juice.

Conclusion:

This lab has allowed our undergraduate students to learn more about the importance of developing electrochemical sensors to detect organic pollutants like phenol in aqueous solution. The instrumentation capable of performing the DPASV, and Cyclic Voltammetry has expanded our undergraduate students' content knowledge in electrochemistry and the research should be valuable to further work in analytical aspects where the processes of the fundamental electrode are of interest. Moreover, this lab experience has allowed our students to expand their lab skills in making solutions, synthesizing nanoparticles, and learning about green chemistry techniques.

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References:

1. A. Shah, L. Rahman, R. Qureshi, Z. Rahman, Synthesis, *Review on Advanced Material Research Science Journal*, **30** 133-149 (2012).

2. M. Nadagouda, and R. Varma, *Green Chemistry*, **10**, 859-862 (2008).

3. N. Ahmad, S. Sharma, *Green and Sustainable Chemistry*, **2**, 141-147 (2012).

4. S. Lunsford and S. Tolias *Chemical Educator*, Nov.13, (2017) accepted.

5. S.E. Manahan, *Environmental Chemistry*, 5th ed., (Lewis Publishers Inc., Chelsea, USA), (1991).

6. C. Spradlin, M. Sullivan, S. Tolias, and S. Lunsford, *Chemical Educator*, **20**, 39-41 (2015).

7. C.D. Garcia &P.I. Oritz, *Anal. Sci*., **15**, 461-465 (1999).