St. Paul's Convent School
SOSeliminator – Synthesis of Nanoselenium, Nanosulphur and Graphene Oxide for Dye Degradation and Hg^{2+} Removal

Introduction

Nowadays, many industries discharge a large amount of dye containing sewage or even contain heavy metals. If this water pollution problem remains untreated, it may bring permanent damage to the ecosystem. In science research papers, we found that nanoparticles have been able to degrade dyes, but the research of using nanoparticles from Group VI elements is scanty. Therefore, our project aims to synthesize nanoselenium, nanosulphur, graphene oxide and sulphur-reduced graphene oxide, and test their effects on degrading dyes, as well as their effect on removing Hg^{2+}.

Objectives

In Part 1, we synthesized selenium nanoparticles by using sodium selenosulphate, 6 different carboxylic acids, and PVA as stabilizing agent. The absorbance of orange-yellow nanoselenium was determined by colorimetry. We have also done a characterization with Dynamic Light Scattering and UV-Visible Spectroscopy to find out the size of the nanoselenium we synthesized. In Part 2, we carried out a green synthesis of sulphur nanoparticles using 2 types of leaves and 2 types of tea as capping and reducing agents. Either hydrochloric acid or citric acid, along with sodium thiosulphate was added to the extracts. We also synthesized graphene oxide and sulphur-reduced graphene oxide nanohybrid. In Part 3, we tested the effectiveness of our nanoparticles on degrading hazardous dyes – methylene blue and gentian violet, as well as their effectiveness in adsorbing Hg^{2+} by gravimetric analysis.

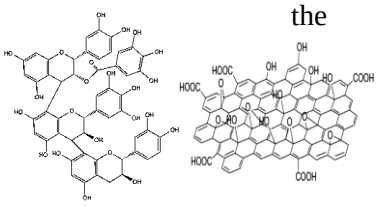
Chemical Principles

Part 1 - Synthesis of Selenium Nanoparticles (SeNPs)

SeNPs can be produced using simple wet chemical method, by employing protic acids such as acetic acid or oxalic acid to synthesize polyvinyl alcohol (PVA)- stabilized SeNPs from aqueous sodium selenosulphate as selenium precursor. This method is capable of producing spherical SeNPs under ambient conditions. The use of carboxylic acid initiates chemical changes for forming SeNPs, thus, different basicity, aromaticity, pH and strength of acids used will affect the yield and size of SeNPs. PVA acts as a stabilizer. The addition of PVA promotes stable suspensions formation due to steric or electrostatic stabilization of solid particles, hence maintaining the nanosize of these SeNPs.

Part 2 - Synthesis of Sulphur Nanoparticles (SNPs), Graphene Oxide (GO) and Sulphur-reduced Graphene Oxide (SRGO)

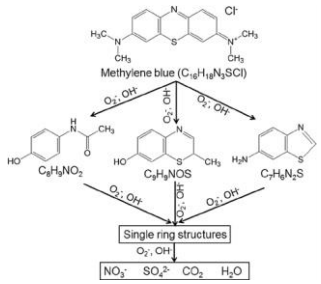
Proanthocyanidines in leaves and polyphenols in tea act as reducing and capping agents in the synthesis of SNPs. GO is made when carbon layers of graphene is oxidized. For the synthesis of SRGO, sodium thiosulphate undergoes a redox reaction with GO to form a slightly more graphitic carbon than GO and initiate the formation of SNPs. These nucleating sites grow further to form SNPs by disproportionation reaction with the use of lemon juice, which contains mainly citric and ascorbic acids.



Proanthocyanidins Catechins

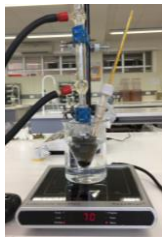
Part 3 - Group VI nanoparticles for removing Dyes and Mercury(II) ions

SeNPs, SNPs and GO act as catalysts. Under ultraviolet light, the dye will undergo photcatalysis. Hydroxyl radicals and peroxyl-radicals are formed. The breakdown of water and oxygen in air into hydrogen peroxide is catalyzed. The dye molecules will then react with the radicals, thus the dye degrades. For the removal of Hg^{2+} removal, SNPs contain major binding sites and can bind effectively with Hg^{2+} due to soft-soft interaction with Hg^{2+}. GO is highly efficient to detect and remove Hg^{2+} due to its two-dimensional carbon shape.



Experiment

Part 1 - Synthesis of Selenium Nanoparticles (SeNPs)

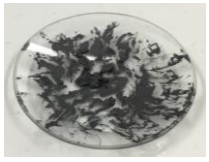


0.5 g of Se were heated with 10 g of Na_2SO_3(s) in 100 cm^3 of water at 70°C under reflux for 7 hours to prepare 0.25 M Na_2SeSO_3(aq). 4 cm^3 of Na_2SeSO_3(aq) was diluted to 100 cm^3 (diluted 25 times) to give 0.01 M Na_2SeSO_3(aq). 6.0 cm^3 of 0.01 M Na_2SeSO_3(aq) was then mixed with 8.0 cm^3 0.2 M ethanoic acid and 2.0 cm^3 of 0.05% PVA. The procedures were repeated by using different volumes of Na_2SeSO_3(aq), replacing 0.05% PVA with 0.01% and 0.1% PVA, or replacing ethanoic acid with oxalic, citric, benzoic, salicylic and aspartic acid to test the effect of Na_2SeSO_3(aq), PVA concentration and different carboxylic acids on the synthesis of SeNPs respectively. The absorbance of various SeNPs mixtures was taken by a colorimeter using a blue filter (490nm).

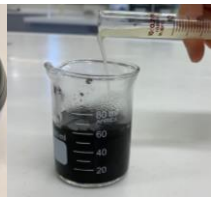
Part 2 - Synthesis of Sulphur Nanoparticles (SNPs), Graphene Oxide (GO) and Sulphur-reduced Graphene Oxide (SRGO)



4.0 g of leaf A (White Champak) were cut into small pieces and grinded with mortar and pestle. The pieces of leaf A were immersed in 100 cm^3 of hot water for 15 minutes. The mixture was then filtered using a Buchner funnel to collect the filtrate. 80 cm^3 of leaf A extract were added to 2.48 g of $Na_2S_2O_3$(s) in a beaker, followed by adding 10 cm^3 of 2 M citric acid to the mixture drop by drop with constant stirring. The mixture was centrifuged for 30 minutes and the solid deposited in the centrifuge tubes, that is the SNPs synthesized, were transferred onto watch glasses and dried by an oven. The procedures were repeated by using leaf B (Chinaberry), red tea and green tea. Then, repeated using 20 cm^3 of 0.2 M hydrochloric acid instead of citric acid for leaf A, leaf B, red tea and green tea. Mass of SNP synthesized was then weighed with an electronic balance.

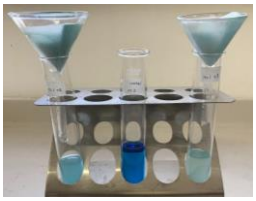
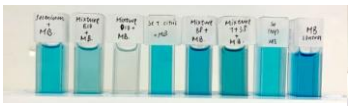
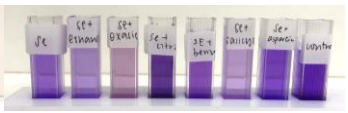



For the synthesis of GO using the Tour method, 1 g of graphite fine powder, 0.59 g of KNO_3, 2.16 cm^3 of H_2SO_4 and 2.4 cm^3 of H_3PO_4 were added into a conical flask and put it into an ice bath under constant stirring for 10 minutes. The solution was kept below 5°C. Then, 3 g of $KMnO_4$ was slowly added into the conical flask. The suspension was allowed to react for 2 hours and then stirred for 1 hour. The conical flask was transferred to a 40°C water bath with constant stirring for 1 hour and heated up to 98°C. The solution was kept stirring for 65 minutes while adding deionized water continuously until the solution volume reaches 80 cm^3. 3 cm^3 of H_2O_2 was added into the solution. The reaction product was filtered and the GO synthesized was collected as residue. The GO was washed with deionized water and 1 M hydrochloric acid repeatedly. Finally, the GO was scrapped onto a watch glass and dried in the oven. The GO was then weighed using an electronic balance.

To synthesize SRGO, 0.06 g of $Na_2S_2O_3$ and 0.04 g of GO were dissolved in 100 cm^3 of water. The mixture was then sonicated for 1 hour. 10 cm^3 of citrus lemon juice was added to the mixture. The mixture was allowed to react for 30 minutes. The solid formed, that is the SRGO nanohybrid synthesized, was washed with propanone and put into the 50°C oven for 2 days. The nanohybrid was weighed with an electronic balance.

Part 3 - Group VI nanoparticles for removing Dyes and Mercury(II) ions

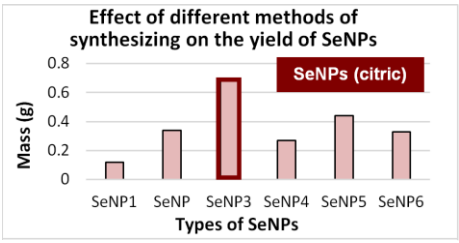





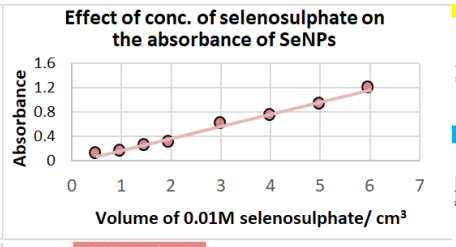
To test the effects of the nanoparticles on dye degradation, 0.01% methylene blue and gentian violet were prepared by diluting 2.5 cm^3 of 0.1% methylene blue and 25.0 cm^3 of 0.01% gentian violet to 250.0 cm^3 with deionized water. 0.02 g of each photocatalyst was mixed to 20 cm^3 of 0.01% methylene blue and 0.01% gentian violet, the mixtures were then stirred for 2 hours using magnetic stirrers. The mixtures were filtered or centrifuged to obtain clear filtrates. The filtrates were then transferred into cuvettes and absorbance readings were taken with a colorimeter. A 590 nm filter and a 580 nm filter were used for methylene blue and gentian violet respectively.

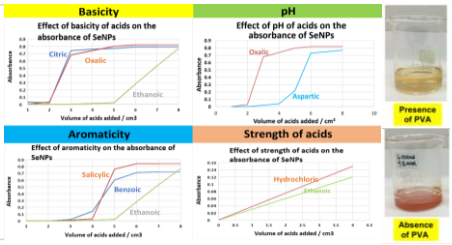

To test the effectiveness of the nanoparticles on Hg^{2+} adsorption, 20 cm^3 of 0.1 M $HgCl_2$(aq) was mixed with 0.2 g of each of the adsorbents and the mixtures were stirred for 2 hours using magnetic stirrers. The mixtures were filtered to obtain the filtrates. 10 cm^3 of 1 M Na_2CO_3(aq) was added to the filtrates to precipitate out the Hg^{2+}(aq) as $HgCO_3$(s). For SNPs synthesized with aspartic acid, 20 cm^3 of 0.2 m KI(aq) was added to the filtrate to precipitate out Hg^{2+}(aq) as HgI_2(s). Precipitates were filtered out from the mixtures and dried by standing overnight and reweighed.

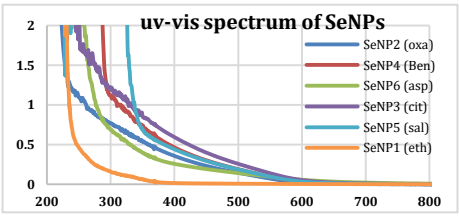
Results

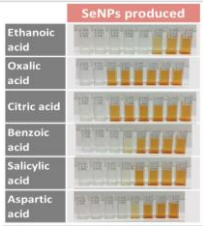
Part 1 - Synthesis of Selenium Nanoparticles (SeNPs)

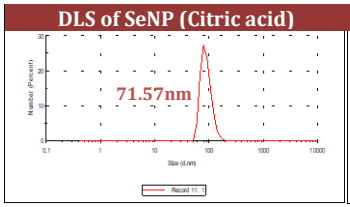


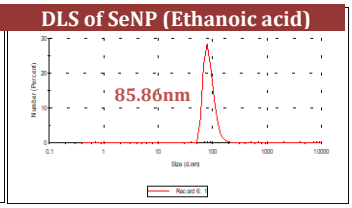




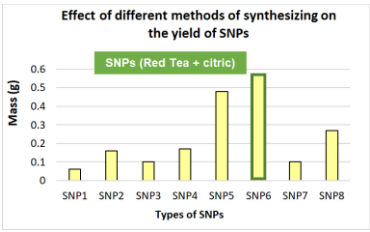


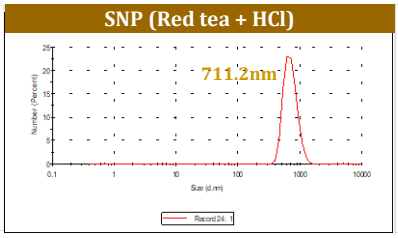


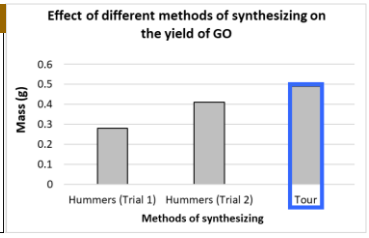


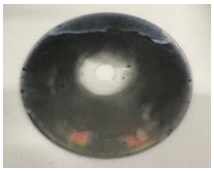


Part 2 - Synthesis of Sulphur Nanoparticles (SNPs), Graphene Oxide (GO) and Sulphur-reduced Graphene Oxide (SRGO)



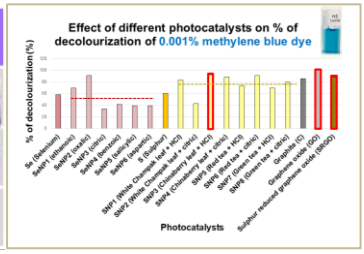


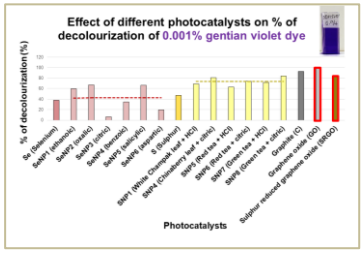


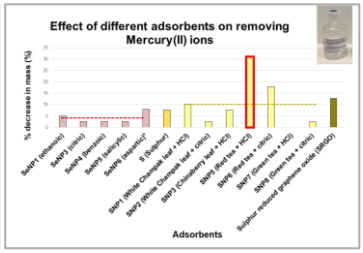


SRGO

Part 3 - Group VI nanoparticles for removing Dyes and Mercury(II) ions







Discussion

In part 1, we found that the concentration of nanoselenium increases with the concentration of Na_2SeSO_3 proportionally. Basicity, pH, aromaticity and strength of acids are all contributing factors that affect the yield. PVA was found to be an efficient and essential stabilizer. Also, results of Dynamic Light Scattering and UV-Visible Spectroscopy indicate that our nanoselenium resembles a size range of 80nm and has absorbance similar to the literature value.

In part 2, by comparing the yield of 8 different nanosulphur, we can conclude that red tea is the best in synthesizing the greatest amount of nanosulphur with the addition of HCl. Results of Dynamic Light Scattering indicates that our nanosulphur synthesized resembles a size range of 300-700nm. As for the synthesis of graphene oxide, tour method gives GO of greatest yield and higher hydrophilic degree. We have also successfully synthesized SRGO using the combined effect of polyphenolic compounds and acids in lemon juice.

In part 3, for dye degradation, among the 19 photocatalysts, GO is most effective in degrading dyes. SNPs perform better than SeNPs, and SRGO is also effective. For mercury(II) ions removal, among the 18 adsorbents, SNPs synthesized with red tea have the best effects, and SNPs have better effect than SeNPs in general. Additionally, SRGO nanohybrid had also brought about desirable results. By incorporating the small, scattered SNPs onto the GO sheets, SRGO have a synergistic effect at adsorbing toxic Hg^{2+} ions. When contaminated water flow past sheets of SRGO, it could possibly provide a filtering effect in removing Hg^{2+} ions.

Conclusion

GO performs best in degrading dyes, and SNPs perform better than SeNPs in general. SNPs synthesized by red tea performs best in Hg^{2+} removal. SRGO also gave desirable results in both dye degradation and Hg^{2+} removal.