Chemistry Department **Faculty of Science** **Sohag University**

Eco-friendly synthesis of silver nanoparticles using extracts of some medicinal plants and their different applications

A Thesis

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Abstract:

It is well known that silver nanoparticles is a powerful antimicrobial agent with low toxicity, and it has several application in the treatment of burn wounds. The green method was employed to synthesis silver nanoparticles (AgNPs) using medicinal plant extracts such as Flamboyant (*Delonix regia (*DRE)) and *Moringa oleifera (*MOE*)* on reducing of Ag^{+} ions to Ag^{0}, then silver nanoparticles (AgNPs) formation to produce (DREAgNPs) and (MOEAgNPs), respectively. The significance of some synthesis conditions such as: silver nitrate concentration, concentration of the plant extract, time of synthesis reaction, temperature and pH on the particle size of synthesized silver nanoparticles was investigated and optimized. The results of this investigation showed that the optimum conditions of the studied green synthesis process are defined as: 2 mM silver ions concentration, reaction time of 24 hour, pH = 7 and 60 ^{o}C temperature. The synthesized AgNPs were characterized using FT-IR, XRD, TEM, HR-TEM, DLS and UV/visible Spectrophotometry. XRD pattern of AgNPs has a face-centered cubic (FCC) form and crystalline lattice as shown by the peak values at 2θ of 38.12°, 44.3°, 64.45° and 77.42° corresponding to (111), (200), (220), and (311) reflections of the Bragg structure of AgNPs. Based on the transmission electron microscopy image analyses (TEM), size, shape and morphology of the silver nanoparticles were studied. TEM confirmed the formation of spherical AgNPs with particle size range of 5 -55 nm. The HR-TEM images illustrate the highly crystalline behavior of these nano systems. FT-IR spectra indicate the functional groups of phytochemical compounds at *Delonix regia* extract DRE, DREAgNPs, *Moringa oleifera (*MOE*)* extract and MOEAgNPs. DLS showed the distribution of average particle size of AgNPs. The synthesized AgNPs were characterized using a UV/visible spectrophotometry, with maximum absorbance at 450 and 440 nm at (DREAgNPs) and (MOEAgNPs), respectively. Moreover, the prepared AgNPs were screened for their cytotoxic effect against colon carcinoma cells (HCT- 116 cell line), hepatic carcinoma cells (HepG-2 cell line) and breast carcinoma cells (MCF-7 cell line). The cytotoxic effect (IC_{50}) of DREAgNPs against (HCT- 116), (HepG-2) and (MCF-7)

cell line were 6.2, 4.35 and 5.12, respectively and the cytotoxic effect (IC_{50}) of MOEAgNPs against (HCT- 116), (HepG-2) and (MCF-7) cell line were 6.51, 4.75 and 5.54 µg/ml, respectively, these results were compared with the cytotoxic effect (IC_{50}) of Doxorubicin standard drug (5.25, 4.25 and 4.45 µg/ml), respectively. The cytotoxic effect of AgNPs is close to the cytotoxic effect of Doxorubicin standard drug. HepG-2 cell line more sensitive as cell proliferation was inhibited by DREAgNPs and MOEAgNPs with an IC_{50} value were 4.75 and 4.25 µg/ml, respectively. Moreover, the toxicity of the AgNPs was tested against bacterial species such as Gm (+) positive bacteria (*Bacillus subtilis*) and Gm (-) negative bacteria *(Serrati amarcescence and Escherichia coli*) and fungal species such as *Candida albicans, Geotrichm candidum and Aspergillus flavus*, the antimicrobial activity of AgNPs was greater towards Gm (+) positive bacteria compared to Gm (-) negative bacteria. The DREAgNPs and MOEAgNPs showed antibacterial activities close to Ofloxacin standard drug and antifungal activities close to Fluconazole standard drug . In addition, the ability of the prepared AgNPs as a pesticide towards *Spodoptera littorals* was screened. The highest pupal mortality was recorded in group A (45.28%), insignificantly followed by groups F (40.93%) and B (36.00%). The ability of the synthesized AgNPs as a catalyst for $NaBH_4$ reduction of 2,4-Dinitrophenol (2,4-DNP) to 2,4-Diaminophenol (2,4-DAP) under mild reaction conditions was studied. In case of MOEAgNPs as catalyst, new peaks appeared at 294 and 450 nm indicated the formation of 2,4-Dinitrophenolate ion and 2,4-Diaminophenol in the reaction solution. As 2,4-Dinitrophenolate intermediate transformed into 2,4-Diaminophenol, new small characteristic band around 316 nm was formed and the absorption bands of the 2,4-Dinitrophenolate ion was decreased and spectrum became stable indicating the formation of 2,4-Diaminophenol in the reaction solution. In case of DREAgNPs as catalyst, new peaks appeared at 288 and 422 nm indicated the formation of 2,4-Dinitrophenolate ion and 2,4-Diaminophenol in the reaction solution. As 2,4-Dinitrophenolate intermediate transformed into 2,4-Diaminophenol, new small characteristic band around 312 nm was formed and the absorption bands of the 2,4-Dinitrophenolate ion was decreased and spectrum became stable indicating the formation of 2,4-Diaminophenol in the reaction solution.

Abstract

Thermodynamic parameters such as (ΔH*), (ΔS*) and ΔG* (Gibb's free energy) for the reduction of 2,4-Dinitrophenol were 34.1 kJ mol^{-1}, -157.5 J $mol^{-1}K^{-1}$ and 81.02 kJ mol^{-1}, respectively for MOEAgNPs catalyst, also (ΔH*), (ΔS*) and ΔG* (Gibb's free energy) for the reduction of 2,4-Dinitrophenol were 29.2 kJ mol^{-1}, -177.02 J $mol^{-1}K^{-1}$ and 82.01 kJ mol^{-1}, respectively for DREAgNPs catalyst. This reaction will not proceed spontaneously at any temperature since (ΔH*) > 0 and (ΔS*) < 0. The opposite reaction, however, is kinetically inhibited. The negative value of (ΔS*) indicate the decrease in randomness. The 2,4-DNP reduction process is clearly endothermic. The Cu^{2+} ions adsorption process was studied by (AgNPs). The Cu^{2+} ions removal efficiency (R. E.) is 88.4 % at initial concentration 15 ppm. Removal efficiency (R. E.) decreases as the Cu^{2+} ions concentration increases. As the increase in adsorbent dosage, the metal ions removal efficiency increases. Cu^{2+} ions removal efficiency was lowest value (74.4 %) obtained with 25 mg and highest value (88.4 %) with 300 mg of AgNPs adsorbent. The R. E. % was very low 67.66 % when a larger particle size (500 nm) was used, and this was probably due to smaller surface area of the adsorbent. It was observed that the R. E. % was higher (88.4 %) when smaller particle nano size (20 nm) was used. The Cu^{2+} ions removal efficiency increased with an increase in a contact time. The Cu^{2+} ions removal efficiency at different initial concentrations (15, 30, 50 mg/L) by AgNPs increases while the temperature is increasing until a certain value that varies around 40 °C. Furthermore, thermodynamic studies confirmed that the biosorption process was endothermic and the positive value of ΔG* is quite common when an ion-exchange mechanism applies in the biosorption. The Positive value of ΔS* suggested an increase in randomness during the biosorption. The Freundlich isotherm has a good fit with the experimental data (R^2 = 0.99) compared to Langmuir isotherm (R^2 = 0.90). This study shows that AgNPs are available, low cost, effective and environment friendly bio sorbent for the removal of Cu^{2+} ions from aqueous environment. These activities of the synthesized AgNPs could be promised to use it as adsorbent for the heavy metals, catalyst, pesticide, antimicrobial and anticancer agent in medical applications.

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