Synthesis of stabilized silver nanoparticles exposed to hydrochloric acid

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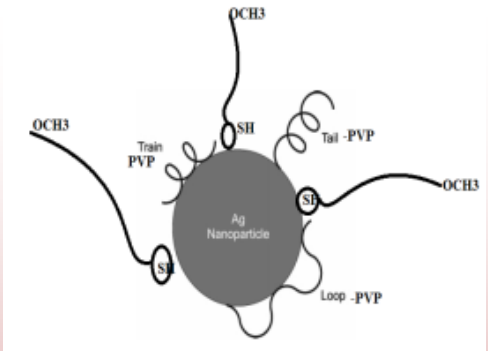
Abstract:

- The bioavailability of ingested silver nanoparticles (AgNPs) depends in large part on initial particle size, shape and surface coating, properties which will influence aggregation, solubility and chemical composition during transit of the gastrointestinal tract.
- In this respect, different types of citrate-stabilized AgNPs coated with poly(vinyl-pyrrolidone) (PVP). Modified thiol derivatives of polyethylene glycol, polyacrylamides were exposed to synthetic human stomach fluid (SSF) (pH 1.5) and changes in size, shape, zeta potential, hydrodynamic diameter and chemical composition were determined during a 1 hr exposure period using Surface Plasmon Resonance (SPR), High Resolution Transmission Electron Microscopy/ Energy Dispersive X-ray Spectroscopy (TEM/EDS), Dynamic Light Scattering (DLS) and X-ray Powder Diffraction (XRD) combined with Rietveld analysis.
- Exposure of AgNPs to SSF produced stabilized SPR peak at 414 nm which changed according to the exposure time and the conditions of preparation of AgNPs. Changes in zeta potential, aggregation and morphology of the particles were also observed as well as production of silver chloride which appeared physically associated with particle aggregates.

Aim of the Work:

1. Silver is a noble metal with an inert chemical reactivity in its bulk form and is listed below hydrogen in the activity series of metals. If the reaction between Ag nanoparticles and HCl can occur, the product will be silver chloride (AgCl), which is an insoluble precipitate.
2. To our knowledge, there have been no reports on the production of chemical stable of Ag nanoparticles toward HCl, whose reaction has been proved impossible for the bulk Ag.
3. Because bioavailability of ingested AgNPs will likely depend on the aggregation state and chemical properties of particles after modification in the acidic environment of the stomach, the primary objective of this preliminary study was to investigate physical and chemical changes that occur during exposure of AgNPs to synthetic stomach fluid (SSF) system and HCl.



scheme 1. Drafts of possible modes of how polymers can be bonded on the silver NP surface.

$3AgNO_3+Na_3C_6H_5O_7$ (sodium citrate)=

$3Ag+C_5H_6O_5$ (3-ketoglutaric acid)$+3NaNO_3+CO_2$ (1)

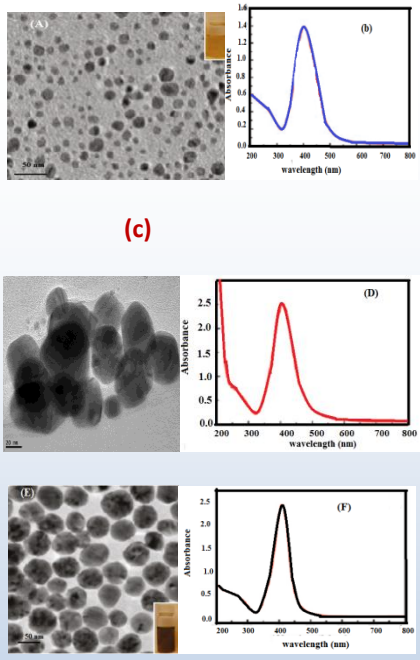
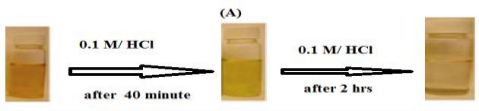


Figure 1. Set of images for silver nanoparticles: TEM image of the citrate AgNP (A) Its UV-vis absorption spectrum (B); TEM image of PVP/PEGSH Ag NPs(C), its UV-vis absorption spectrum(D); TEM image of PEGSH Ag NPs(E) and its UV-vis absorption spectrum(F).



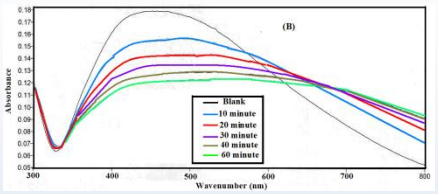


Figure2:Citrate AgNPs a)digital photo b) UV-vis absorption spectra at interval times in 0.1 M HCl.

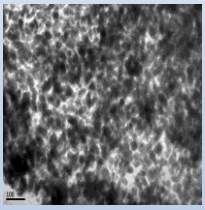
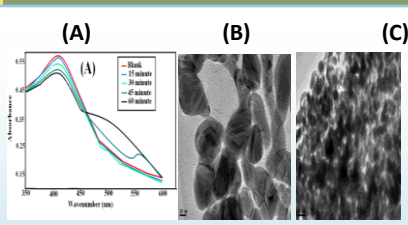


Figure 3:TEM of citrate AgNP after exposure to 0.1M HCl.



PVP/PEGSH AgNPs a) UV-vis absorption spectra at interval times in 0.5 M HCl, b) 10 hrs in 1M HCl and C) 24 hrs in 1M HCl.

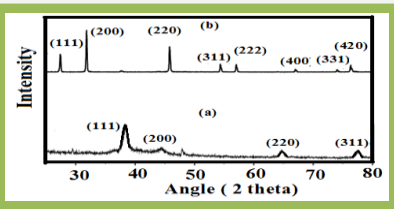
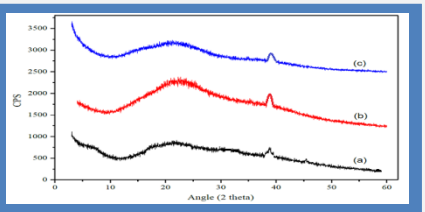


Figure 5: XRD patterns of samples. (a) citrate Ag nanoparticles and (b) the product of AgCl obtained from the reaction of citrate AgNP with hydrochloric acid.



XRD patterns of a)PVP/PEGSH coated Ag, b)after exposure to 0.5M HCl and c) 1M HCl for 10 hrs.

conclusions

- Three kinds of silver nanoparticles (Ag NPs) prepared in this study were citrate AgNP, PEGSH coated AgNP and PVP-PEGSH coated AgNPs used to study the reactivity of AgNPs toward HCl solutions.
- The average particle size of the AgNPs changed from 6 nm to 25 nm and 65 nm by coating AgNPs with PEGSH and PVP/PEGSH, respectively.
- HCl affected the stability of citrate AgNPs which might be attributed to the gradual increase in average particle diameter due to the Ostwald ripening process.
- The overall stability of the PVP/PEGSH coated Ag NPs are better than the citrate NPs under 0.5M aqueous HCl. We supposed that the appearance of a broad band consisting of three peaks implied that a thin layer of silver oxide (Ag_2O) formed on the surface of silver nanoparticles, and the colloids were the mixture of silver nanoparticles with and without silver oxide layers.
- Both of the PVP-coated and citrate coated nanoparticles aggregated, but the aggregates formed from the former were stable in suspension.