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# Impact of density of coating agent on antibacterial activity of silver nanoparticle impregnated plasma treated activated carbon

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## ABSTRACT

To use stabilized nanoparticles (NPs) in water as disinfectants over a very long period, the amount of coating agent (for NP stabilization) needs to be optimized. To this end, silver nanoparticles (Ag-NPs) with two different coating densities of tri-sodium citrate (12.05 and 46.17 molecules/nm<sup>2</sup>, respectively), yet of very similar particle size (29 and 27 nm, respectively) were synthesized. Both sets of citrate capped NPs were then separately impregnated on plasma treated activated carbon (AC), with similar Ag loading of 0.8 and 0.82 wt.%, respectively. On passing contaminated water (containing 10<sup>6</sup> CFU *Escherichia coli*/mL of water) through a continuous flow-column packed with Ag/AC, zero cell concentration was achieved in 22 and 39 min, with Ag-NPs (impregnated on AC, named as Ag/AC) having lower and higher coating density, respectively. Therefore, even on ensuring similar Ag-NP size and loading, there is a significant difference in antibacterial performance based on citrate coating density in Ag/AC. This is observed in lower coating density case, due to both: (i) higher Ag<sup>+</sup> ion release from Ag-NP and (ii) stronger binding of individual Ag-NPs on AC. The latter ensures that, Ag-NP does not detach from the AC surface for a long duration. TGA-DSC shows that Ag-NPs with a low coating density bind to AC with 4.55 times higher adsorption energy, compared to Ag/AC with a high coating density, implying stronger binding. Therefore, coating density is an important parameter for achieving higher antibacterial efficacy, translating into a faster decontamination rate in experiments, over a long period of flow-column operation.

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## Introduction

Silver nanoparticles (Ag-NPs) are well established as one of the most efficient water disinfecting agents (Biswas and Bandyopadhyaya, 2016a, 2016b; Sondi and Salopek-Sondi, 2004). The particles are impregnated in a host matrix to prevent their aggregation and to also avoid their leaching into the environment. However, in most cases, antibacterial performance of only free NPs are tested in the batch mode (Li, 2012), whereas for water disinfection applications, it is more appropriate and essential to assess the performance in a continuous flow system.

Conventionally, different coating agents have been used for stabilizing and controlling the growth of Ag-NPs during nanoparticle synthesis and its impregnation. The effect of different coating agents like, sodium dodecyl sulfate (SDS), polyvinylpyrrolidone (PVP), polysorbate 80 (Tween 80), polyethylene glycol (PEG), citrate etc. in the aggregation kinetics and stability of NPs was already reported in previous works (Kvítek et al., 2008; Tejamaya et al., 2012). Tri-sodium citrate was extensively used as both a reducing and a coating agent during Ag-NP synthesis, since it is non-toxic and considered safe for drinking water applications (Biswas and Bandyopadhyaya, 2016a; Srinivasan et al., 2013). To the best of our knowledge, the effect of coating

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density of citrate on Ag-NPs, on the antibacterial activity has not been extensively investigated.

Toxicity of Ag-NPs to bacterial cells is primarily because of the release of Ag<sup>+</sup> ion, via the dissolution of Ag-NPs (Jung et al., 2008; Li, 2012; McShan et al., 2014). Now, coating agent is used primarily for stabilizing the NPs and controlling their size during the Ag-NP synthesis. However, the coating agent also affects the surface chemistry and thereby the ion release kinetics, during cell-killing.

Therefore, in the present work, antibacterial activity of citrate coated Ag-NPs of same particle size and of same loading percentage in activated carbon (AC) (as Ag/AC), but having different coating densities of citrate have been assessed in a continuous flow-column. The performance has been evaluated in terms of both release of Ag<sup>+</sup> ion and detachment of Ag-NPs from the AC surface, for assessing the effect of coating density on the water disinfection performance during long term water disinfection.

## 1. Materials and methods

### 1.1. Synthesis of Ag-NPs with different coating density

For synthesizing Ag-NPs, silver nitrate (AgNO<sub>3</sub>, Qualigens, India) was used as a precursor and tri-sodium citrate (Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>·2H<sub>2</sub>O, Qualigens, India) as a reducing as well as capping agent. In the first method, typically, 70 mL, 0.01 mol/L AgNO<sub>3</sub> was mixed with 7 mL, 0.01 mol/L trisodium citrate and the reaction mixture was placed in a ultraviolet (UV) chamber (365 nm wavelength) for 12 hr, to form Ag-NPs (Appendix A. Fig. S1a). In the second method, 100 mL, 7 mmol/L tri-sodium citrate of pH 11.1 was prepared (adjusted by addition of NaOH) and heated at 100°C. Subsequently, 1.0 mL, 0.1 mol/L AgNO<sub>3</sub> was added dropwise to the reaction mixture and maintained at a mixing speed of 500 r/min and a temperature of 100°C for 1 hr. The color of reaction mixture changes from colorless to yellow, then turbid, indicating the completion of reaction (Appendix A. Fig. S1b).

With the aim of measuring the time required for the completion of nanoparticle formation, absorbance of NP suspension was measured using an UV-vis spectrophotometer (Lambda 35, Perkin Elmer, USA). For checking the mechanism of formation of Ag-NPs for both the Ag-NPs, time dependent imaging and measurement of particle size was performed using field emission gun-transmission electron microscopy (FEG-TEM) (JEM-2100F, JEOL, Japan) and dynamic light scattering (DLS) (Zetasizer Nano ZS, Malvern Instruments, UK). Samples were collected after 3, 6, 12 and 14 hr and 10, 30, 60 and 80 min for Ag-NP with low and high citrate coating densities, respectively. Size distribution was generated from images of Ag-NPs by measuring at least 500–600 particles from both the synthesis methods, by measuring 200 particles from each synthesis run.

### 1.2. Measurement of coating density of citrate for both the Ag-NPs

The synthesized Ag-NP suspension contains citrate coated Ag-NPs and excess free citrate. For ensuring complete removal of excess citrate from the Ag-NP suspension, the NP suspension was dialyzed using cellulose dialysis tubing (molecular weight cut off — 14,000, approximate pore size of 1.4 nm, Sigma, India).

The 25 mm diameter dialysis tubes were filled with Ag-NP suspension and immersed in a 5 L milli-Q water container and a mixing speed of 300 r/min was maintained using a magnetic stirrer. The dialysis membrane allows permeation of excess citrate (molecular weight of 258.06 g/mol) and prevents the out flow of Ag-NPs (having average diameter of 27 and 28 nm). Mixing ensures faster removal of citrate molecules by preventing accumulation of citrate near the dialysis membrane. Initially the milli-Q water was changed after every 6 hr and subsequently, after 10 days water was changed after an interval of 12 hr (as the release of citrate molecule decreases over time). The dialysis was continued for 21 days for complete removal of all the excess citrate. Therefore, all the citrate molecules present in the suspension were adsorbed on the Ag-NPs. Subsequently, the suspension was dried at 80°C in a vacuum drier for preparing Ag-NP powder, which is suitable for further thermo gravimetric analysis (TGA) (STA 409 PS, NETZSCH, Germany).

The mass of the citrate molecules adsorbed on the Ag-NPs was measured by performing TGA (Appendix A. Fig. S2). Subsequently, the coating density ( $\sigma$ ) of citrate on the Ag-NP was calculated using Eq. (1) (Benoit et al., 2012)

$$\sigma = \frac{\text{wt.\%}_{\text{shell}} \times \rho_{\text{core}} \times \frac{4}{3} \pi r_{\text{core}}^3 \times N_A}{\text{wt.\%}_{\text{core}} \times \text{MW}_{\text{polymer}} \times 4 \pi r_{\text{core}}^2} \quad (1)$$

where, wt.%<sub>shell</sub> is the relative mass of citrate (measured from TGA data), wt.%<sub>core</sub> is the residual mass of the pure Ag-NPs (measured from TGA data),  $\rho_{\text{core}}$  is the density of bulk silver,  $r_{\text{core}}$  is the average radius of Ag-NPs,  $N_A$  is the Avogadro's number, and  $\text{MW}_{\text{polymer}}$  is the molecular weight of tri-sodium citrate. The diameter of the particle was measured from multiple FEG-TEM images of Ag-NPs. The zeta potential (Zetasizer Nano ZS with zeta potential measurement cell, Malvern Instruments, UK) of both the samples was measured.

### 1.3. Impregnation of Ag-NPs on plasma treated activated carbon (AC)

Both the Ag-NPs were separately impregnated on plasma treated activated carbon (AC) (with a size range of 420–840  $\mu\text{m}$ ) by wet impregnation method. Typically, 5 g of plasma treated AC was added in 77 mL of Ag-NP (with low citrate coating density) suspension and 2.5 g of plasma treated AC was added to 100 mL of Ag-NP (with high citrate coating density). The mixture was maintained at 300 r/min overnight using a magnetic stirrer. Subsequently, both the granules were filtered using ash-less whatman filter paper (2  $\mu\text{m}$  pore diameter) and dried at room temperature for its further use. The granules were imaged in FEG-SEM (JSM-7600F, JEOL, Japan). For measuring the Ag loading, the samples were immersed in concentrated nitric acid for 72 hr and the acidic samples were analyzed in an inductively coupled plasma atomic emission spectroscopy (ICP-AES) (ARCOS, SPECTRO Analytical Instruments GmbH, Germany).

### 1.4. Cell-killing experiments in a continuous flow-column

Batch mode cell-killing experiments were performed using 4, 6 and 8 mg/mL of hybrids (Appendix A. Section S3). Based on the contact time required in batch mode experiments the flow rate

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