The ratio protein-silver modulates the availability of ionic silver and the potential toxicity of silver nanoparticles: applications for cheaper and more effective consumer products

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Abstract

Because of their biocide properties [1], silver nanoparticles (AgNP) are present in numerous consumer products. During recent years, an increasing number of works demonstrated their toxicity to different microorganisms as bacteria [1-4] or algae [5-8]. Biocide properties of AgNP have been suggested to relate with both the release of ionic silver (Ag^+) and interactions between AgNP and cell membranes [2, 7, 9-11]. The determinant role of dissolved silver ions, in explaining the observed toxicity of AgNP to microorganisms, has been experimentally evidenced by evidenced by the fact that complexation of Ag+ ions by thiol ligands as well as anaerobic conditions prevent toxicity of AgNP [12-15]. These results emphasize the importance for disentangling the contribution of AgNP and Ag^+ to the observed toxicity.

There are only a few works available, focusing on the influence of coatings on ionic silver release from AgNP [17-19].These studies emphasize their role in complexing and storing silver ions suggesting a potential control of silver bioavailability by the coatings. However, desorption and release of ionic silver will ultimately depend on the affinity of membrane transporters to Ag^+. Although some comparative studies with various coatings have indeed reported on differences in AgNP toxicity to aquatic organisms [7, 20, 21] none have systematically examined how coatings influence Ag^+ bioavailability to organisms.

In this study we have assessed the toxicity of nanoparticles presenting different % of casein and silver. These thee products presented 72,5% total Ag, 21,03% and 7,88% of total Ag. Toxicity was measured as the impact of the different compounds on the photosynthetic yield of *Chlamydomonas rehinadrtii.* The amount of ionic silver toxically active was assessed using ultrafiltration and ICP-MS and also by Diffusive Gradients in Thin-films. Cysteine, a strong silver ligand, prevented in all cases the toxicity of silver nanomaterials, demonstrating the key role of ionic silver on the toxicity. Therefore, Effective Concentrations (EC_{50}) were calculated as a function of the ionic silver measured.

Products	Total Ag % (the rest is casein)	EC_{50}	DGT Dissolved Ag % from total Ag	Ultrafiltration
1	72.5	413 nM	0.84	0.35
2	21.03	45 nM	2.1	0.56
3	7.88	274 nM	0.082	0.12

Results, expressed as a function of measured ionic silver, shown that the product containing 21% of silver was 10 times more effective (EC_{50} is ten times smaller) than the nanomaterial presenting 70% of silver. Even if coatings are commonly used to mininimize nanoparticle aggregation in liquids [13, 16], these results shown that coatings may also optimize the delivery of ionic silver from nanomaterials. The final result would be a more effective and cheap consumer product.

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