

# One-pot synthesis of gelatin-based, slow-release polymer microparticles containing silver nanoparticles and their application in anti-fouling paint



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## ABSTRACT

Gelatinous polymer matrix microparticles containing silver nanoparticles (AgNPs) were prepared by a novel method to obtain quasi non-swelling anti-fouling paint additives with slow-release characteristics. A w/o type dispersion were elaborated with the aqueous phase of gelatin, urea, silver-nitrate and formaldehyde dispersed in linseed oil. Gelatin was cross-linked by formaldehyde, together with urea for limiting the swelling of the product. Silver-nitrate was reduced with the assistance of gelatin and formaldehyde into homogenously dispersed AgNPs. The microparticles and embedded AgNPs were visualized by scanning and transmission electron microscopy. Encapsulated AgNPs with ~18 nm crystallite size were identified by X-ray powder diffraction. Characterization of gelatin-urea-formaldehyde polymer matrices was carried out by attenuated total reflectance FTIR spectroscopy. Silver dissolution from microparticles and paints with AgNP-containing microparticles was measured by inductively coupled plasma spectrometer and resulted in highly sustained release, compared to unmodified gelatin microparticles and paints containing unencapsulated silver salts. A 7-month-long fouling experiment run in natural sweetwater media showed that solvent-based acrylic paint with AgNPs-containing gelatinous microparticles as additives offered resistance against biofouling at low Ag-release ratio.

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## 1. Introduction

After centuries of questionable and not reliable usage, during the last few decades silver is about to be involved into scientific fields of antibacterial, biocidal applications. Biocide effect of silver which is assigned to its ionic and metallic nanoparticle form (herein AgNP) either, is expressed against certain lifeforms due to catalytic oxidative reactivity, disruption of electron transfer, prevention of DNA unwinding, etc. [1].

Today AgNPs or Ag<sup>+</sup> ions as biocide agent are being investigated for numerous applications like water filter membranes [1], fabrics [2–5] thin layers [6–9], anti-fouling thick coatings [10–14], dental materials and devices [15,16], surface modified implants [17–21],

catheters and bone cements [22]. In the surgery they have major role as disinfectants in burn wound dressings [23–25].

AgNPs immobilized in certain biopolymeric carrier structures are quite in sight of interest in the last decade. AgNPs are embedded in- or fixed on the surfaces of hydrogel beads [26,27] or fibers [28,29] of nano/micron range. General criteria toward them are the homogenous distribution of AgNPs in the polymer matrix or on the surface and the accessibility for aqueous media.

General incidence of biopolymers in nature, low cost, biocompatibility, biodegradability makes biomaterials apparent to use as host material for AgNPs. Biopolymers such as peptide-based (gelatin [28,30–35], glutathione [36], keratin [37]) or polysaccharide-based (alginate [26,27,38–41], chitosan [32,34,42–47], starch [48]) polymers are good capping agents for silver ions [38,49,50]. Amine groups, oxygen atoms present in ring or –OH groups stabilize Ag<sup>+</sup>s via complexation and ensure

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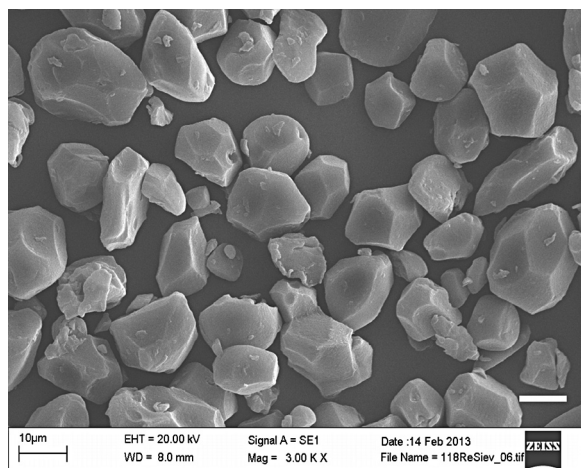


Fig. 1. SEM micrograph of AgNPs@GMPs. The white scale bar represents 10  $\mu\text{m}$ .

homogenous distribution of later reduced AgNPs within the polymer solution or matrix. Biopolymer-driven reduction of metal ions into stabilized AgNPs without further reducing agents is also being investigated [28,51,52].

The preparation methods of AgNPs in micro/nano-biopolymers consist of four major steps in various orders depending on their purpose. The steps are the following: polymer shaping (fibers: spinning/extrusion, microspheres: mostly emulsification in w/o systems); cross-linking polymeric chains (precipitation in another liquid phase (e.g. alginates) or with linking agents (e.g. aldehydes); silver incorporation into polymer (swelling in  $\text{Ag}^+$ -containing solution); silver ion reduction to metallic AgNPs. Depending on the circumstances, the mentioned steps might be changed or combined. Combination of polymer shaping and silver incorporation ( $\text{Ag}^+$  or  $\text{Ag}^0$ ) is general, it is followed by reduction and cross-linking. It is even usual that silver incorporation follows the shaping and cross-linking of host polymer.

In this paper we extend the preparation and characterization of our former work [53] presenting in details the one-pot synthesis of AgNPs-containing gelatin–urea microparticles cross-linked with formaldehyde (herein AgNPs@GMP) as well as their application in solvent-based anti-fouling paint.

The aim of our work was to prepare hydrophilic polymer particles of 10–20  $\mu\text{m}$  diameter with the ability of releasing ionic silver into aqueous media. As we tend to use the particles as additives for underwater paints or coatings, their diameter is limited to the

mentioned size. The polymer particles should contain homogeneously distributed AgNPs embedded without higher agglomeration. The last criterion was that the hydrophilic microparticles should not swell significantly in aqueous neither in organic media. Swelling of the microparticles may cause inner strains in the applied coating which leads to disintegration. Indifference toward organic solvents is also important because the particles would be stored in solvent-based ship paints.

In order to fulfill all these criteria we have realized a one-step process in which the reduction of  $\text{Ag}^+$  ions and the polymer cross-linking run parallelly in time. To reduce the swelling of gelatin (which could happen even in cross-linked form) we copolymerized it with another biocompatible material, urea. The method was water-in-oil dispersion polymerization where the aqueous phase contained the matrix materials (gelatin, urea), the silver source (silver-nitrate) and the cross-linking + reducing agent (formaldehyde).

## 2. Experimental

### 2.1. Materials

#### 2.1.1. Chemicals used for preparation of microparticles and coatings

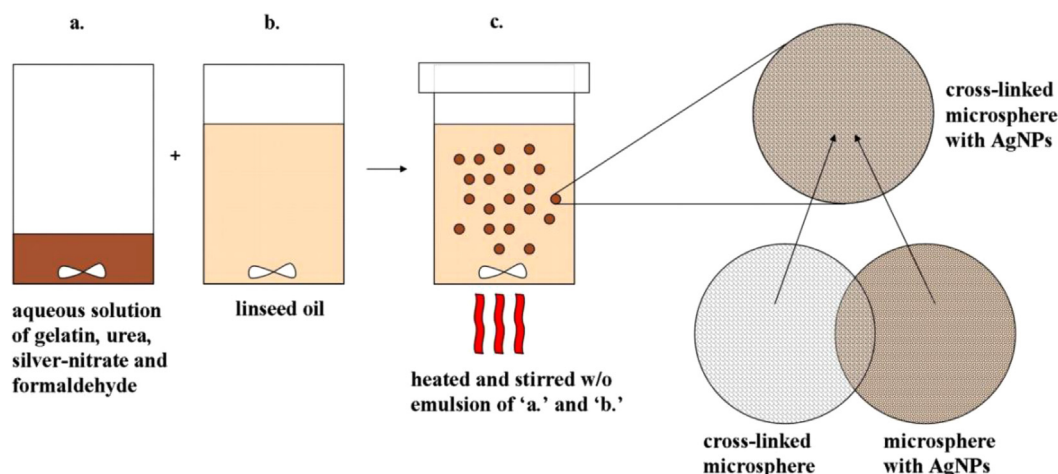
Urea (Fluka, p.a.); gelatin (Reanal, purum); formaldehyde (Sigma-Aldrich, purum, 37% aqueous sol.); silver-nitrate (Reanal, a.r.); silver-carbonate (Reanal, puriss.); linseed oil (Aldrich, purum); toluene (Carlo Erba, a.r.); anti-fouling paint without commercial anti-foulant: dry matter ~50% acrylate resin, solvents: isobutyl acetate 3–12% and methoxypropyl acetate 20–45% (Dunaplast Anti-fouling from Dunaplast Ltd., 'DPL'); natural sweet-water from Lake Balaton.

#### 2.1.2. Chemicals used at sampling

Sample preparation for inductively coupled plasma spectrometer (ICP) measurements: nitric acid 65% (Spektrum 3D, a.r.), hydrogen-peroxide 30% (Molar Chemicals Ltd., a.r.); solvent mixture as paint model: isobutyl acetate–methoxypropyl acetate at a mass ratio of 6:40; biofilm fixation: ethanol (Molar Chemicals Ltd., a.r.); biofilm visualization: 0.01% acridine orange in ethanol.

### 2.2. Preparation of AgNPs@GMPs

The dispersion polymerization method (Scheme 1), was based on our previous work [53]: in 15 mL distilled water 2.0 g gelatin, 3.0 g urea, 0.45 g silver-nitrate were dissolved at 40 °C and then



Scheme 1. Preparation scheme of AgNPs-containing gelatin–urea–formaldehyde microparticles.

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