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Tallow amphopolycarboxyglycinate-stabilized silver nanoparticles: new frontiers in development of plant protection products with a broad spectrum of action against phytopathogens

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Abstract

Sustainable agriculture calls for minimal use of agrochemicals in order to protect the environment. It has caused an increase in the rate of nanoparticles use, in particular silver nanoparticles (AgNPs) due to their safety for mammals, unique biological activity and a broad spectrum of action against fungal and bacterial pathogens. Until now the use of AgNPs dispersions in the agricultural sector has been essentially limited due to many factors decreased their stability (mixing with other pesticides, presence of electrolytes). We present a versatile synthesis of polyampholyte surfactant (tallow amphopolycarboxyglycinate) stabilized AgNPs. We took a close look at unique aggregation behavior (via dynamic light scattering and UV–vis spectroscopy) and biocidal activity of obtained silver colloids. AgNPs are characterized by exclusively high aggregative stability in the presence of coagulating agents $NaNO_3$ and $NaSO_4$ (up to 1 M), during drying/redispergation, and frost/defrost cycles. The dispersion of AgNPs shows high biocidal activity (EC_{50} is ten times lower than commercial species ones) with respect to *Phytophthora infestans* and phytopathogenic fungi. This points to the possibility of successful application of silver preparations within agriculture with the goal of partial reduction of the use of toxic and expensive synthetic antibiotics and pesticides.

1. Introduction

Silver nanoparticles (AgNPs) and their antibacterial and antifungal action are quickly gaining relevance in human medicine, veterinary medicine and agriculture due to being less toxic to people, animals and plants than cations of silver [1]. The explosive growth in the number of pathogenic microorganisms resistant to the action of antibiotics and pesticides also draws attention to AgNPs; as it stands, the resistance to silver de novo is difficult to acquire [2]. Furthermore, silver compounds have immunomodulating effect [3] and stimulate growth and development of plants [4].

Wide use of AgNPs colloids against pathogenic microorganisms is essentially limited by the inclination of silver sols to coagulate during dilution, action of electrolytes and many other factors [5]. For instance the critical electrolyte concentrations needed for AgNPs to coagulate were ~10 mmol l^{-1} for monovalent ions and ~1 mmol l^{-1} for divalent ions [6–8].

The modification of AgNPs surface by various surfactants is a direct way to increase their stability towards aggregation [5, 9, 10]. There are three known types of stabilization: electrostatic stabilization by a small

molecular weight chelating agent, like citrate and carbonate [11–14]; steric stabilization by polymers like polyvinylpyrrolidone (PVP), dextran [15–19] or non-ionic surfactants like Tween 80 [20, 21]; and electrosteric stabilization by polymers with charged groups (i.e., polyelectrolytes), like branched-polyethyleneimine [11, 20, 22–27]. Of these compounds polyelectrolytes are often used to stabilize nanoparticle dispersions.

An important approach to stabilizing AgNPs is to embed them in a polyelectrolyte multilayers (PEMUs). For example, Zan *et al* reported *in situ* preparation of AgNPs in PEMUs and showed that they exhibited lasting antimicrobial activity [28, 29]. Wei *et al* further studied the stability of AgNPs in the PEMU matrixes [30].

Macromolecules of polyelectrolyte surfactants may be positively or negatively charged (and called polycations and polyanions respectively) which is dictated by how their functional groups are charged. AgNPs covered by positive or negative polyelectrolytes both have a clear inhibitory effect on bacterial growth [31], but they have a small pH range of stability [32].

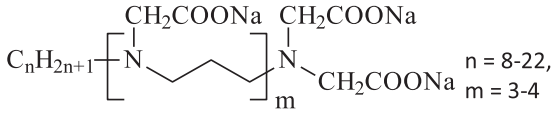
Recently a new class of polymer surfactants for noble metal nanoparticles—polyampholytes—have appeared [33, 34]. The polyampholytes are charged macromolecules carrying both acidic and basic repeat groups at high charge asymmetry (far above or far below the isoelectric pH); these polymers demonstrate polyelectrolyte-like behavior [35, 36]. The metal nanoparticles stabilized with polyelectrolytes can potentially be applied in catalysis, electronic devices, drug delivery devices, etc [34]. It was shown [37–39] that both hydrophobically modified polyampholytes and polyampholyte-modified microemulsions can act simultaneously as reducing and stabilizing agents with respect to formation of gold nanoparticles. The stabilized Au nanoparticles are notable for high catalytic activity and recyclability [40].

Despite the existence of a great number of scientific articles dedicated to surfactant-stabilized AgNPs the potential use of silver-contained preparations in medicine and agriculture was limited due to their low stability. During our wide ranged study of aqua sols of surfactants stabilized AgNPs [41, 42] we have discovered that the use of polyampholyte alkyl-polycarboxy-amine surfactants allows to obtain extremely stable dispersions of AgNPs. The process of synthesis as well as the properties of the most stable colloidal systems obtained are presented in this brief report.

2. Methods

2.1. Synthesis of AgNPs dispersion stabilized with sodium tallow amphopolycarboxyglycinate

Colloidal solution of AgNPs containing 3 g l^{-1} of silver and 48 g l^{-1} of sodium tallow amphopolycarboxyglycinate



was obtained during a general procedure [42] of silver nitrate (99.9+%, Sigma-Aldrich) reduction by sodium borohydride (98+%, Lancaster) in the presence of sodium tallow amphopolycarboxyglycinate (30% aqueous solution of sodium tallow amphopolycarboxyglycinate, additionally containing up to 10% NaCl, Akzo Nobel) as a stabilizer. Aqueous solution of silver nitrate (10 ml of 11.76 mM) was added drop-wise to the solution of sodium tallow amphopolycarboxyglycinate (100 ml of 0.23 mM) being vigorously stirred. Then the obtained mixture was stirred for 15 min, after that the 90 ml of aqueous solution of sodium borohydride (2.61 mM) and sodium tallow amphopolycarboxyglycinate (0.25 mM) were added drop-wise during vigorous stirring. After the entire amount of the reducing agent has been added, the mixture was stirred for an hour. Concentrations of the solutions were calculated based on the adjusted content of metal and the content of the stabilizer in final dispersion, the ratio Ag:$NaBH_4$ was stoichiometric and corresponded to the following equation:

$$2AgNO_3 + 4NaBH_4 + 7H_2O \rightarrow 2Ag + Na_2B_4O_7 + 2NaNO_3 + 15H_2. \quad (1)$$

2.2. Characterization

To register absorption spectra in the visible region a spectrophotometer JENWAY 6310 (Jenway, Great Britain) was used.

Zeta potential of an AgNPs sol was carried out on a Zetasizer Nano ZS analyzer with an integrated 4 mW He–Ne laser, $\lambda = 633$ nm (Malvern Instruments Ltd, Great Britain). Zeta potentials were measured by applying an electric field across the dispersion of silver NPs using the technique of laser Doppler anemometry. Size distribution of silver AgNPs sol was carried out on a Photocor Complex light scattering unit with an integrated 25 mW diode laser, $\lambda = 650$ nm (Photocor Instruments Russia).

Micrographs of specimens of silver NPs were made on a transmission electron microscope LEO 912 AB OMEGA (Carl Zeiss, Germany) operating at 100 kV. The specimens were prepared by placing of 1–2 μl of dispersion on a formvar-coated copper grid which then was dried in the air.

2.3. Study of prepared colloids' stability

In order to investigate the stability of the AgNPs dispersions and their agglomeration behavior at different ionic strengths, cations and anions, liquid solutions of KCl, $NaNO_3$, Na_2SO_4, $Ca(CH_3COO)_2$, $SrCl_2$, $Ba(NO_3)_2$ were added to aliquots of silver NPs, containing 0.03 g l^{-1} of silver and 0.48 g l^{-1} of sodium tallow amphopolycarboxyglycinate, adjusting molar concentrations of 1, 5, 10, and 100, 200 and 400 mmol l^{-1}. Then the absorption light-spectra of prepared mixtures were recorded. The critical concentration of electrolytes was recorded when the intensity decreased below 90% of the initial value.

2.4. Study of aggregation kinetics of the prepared colloids

For the purpose of Ag colloids' aggregation kinetics investigation time-resolved DLS measurements of aggregating AgNP suspensions were performed using a light scattering unit Photocor Complex (Photocor, Russian Federation). In all tests, the AgNP suspensions used for DLS measurements had a total volume of 2 ml and a AgNP concentration of 15 mg l^{-1}. All DLS measurements were conducted at a scattering angle of 90°. Each autocorrelation function was accumulated over 15 s and the intensity-weighted hydrodynamic diameter was then derived using second-order cumulant analysis (Dynals software). Time-resolved DLS measurements were performed during 1–10 000 s in order to achieve a large enough increase in the hydrodynamic diameter (more than 30%) for accurate derivation of aggregation kinetics.

The early stage aggregation kinetics of AgNPs can be calculated from the initial rate of change of hydrodynamic diameter, D_h, with time, t, as measured by time-resolved DLS [43]. During the early aggregation stage, the initial aggregation rate constant, k, is proportional to the initial rate of increase of D_h and inversely proportional to the initial primary AgNP concentration in the suspension, C_0 [44]:

$$k \propto \frac{1}{C_0}\left(\frac{dD_h(t)}{dt}\right)_{t\to 0}. \quad (2)$$

A linear least-squares regression analysis of the initial increase of D_h was conducted to obtain $(dD_h(t)/dt)_{t\to 0}$.

The attachment efficiency, α, is used to quantify the aggregation kinetics of AgNPs. It is calculated by normalizing the aggregation rate constant obtained in the solution of interest to the aggregation rate constants under diffusion-limited conditions, k_{fast} [44]:

$$\alpha = \frac{k}{k_{fast}} = \frac{\frac{1}{C_0}\left(\frac{dD_h(t)}{dt}\right)_{t\to 0}}{\frac{1}{(C_0)_{fast}}\left(\frac{dD_h(t)}{dt}\right)_{t\to 0,\ fast}}. \quad (3)$$

Electrolyte ($NaNO_3$, $Ca(NO_3)_2$, $Sr(NO_3)_2$, and $Mg(NO_3)_2$) solutions were prepared and filtered with the help of 0.22 μm Millex membrane syringe filters (Merck Millipore Ltd) before use. All experiments and measurements were performed at pH 7.2 $\pm$ 0.2 (buffered with 0.15 mM $NaHCO_3$).

2.5. Study of biocidal activity of sodium tallow amphopolycarboxyglycinate stabilized dispersion of AgNPs with respect with respect to phytopathogenic fungi and oomycete *Phytophthora infestans*

In this research isolates of *Phytophthora infestans* (Mont.) de Bary and various fungi (table 1) isolated by the authors from affected potato plants were used. An estimation of biocidal properties was carried out on agar pea medium with the addition of test preparation. In order to compare it to traditional preparations with biocidal properties, used for plant protection, fungicide fludioxonil (4-(2,2-difluoro-1,3-benzodioxol-4-yl)-1H-pyrrole-3-carbonitrile 25 g l^{-1}), insectofungicide mixture of imidacloprid ((E)-1-(6-chloro-3-pyridylmethyl)-N-nitroimidazolidin-2-ylideneamine, 140 g l^{-1}), pencycuron (1-(4-chlorobenzyl)-1-cyclopentyl-3-phenylurea, 150 g l^{-1}) and azoxystrobin (methyl (2*E*)-2-(2-{[6-(2-cyanophenoxy)pyrimidin-4-yl]oxy}phenyl)-3-methoxyacrylate, 250 g l^{-1}) were studied under similar conditions. Agar block with mycelium 5 mm in diameter was placed in the center of a Petri dish, which was then sealed with Parafilm®. The dishes were incubated at 23 °C–25 °C (*P. infestans*—at 18 °C) and in daylight. Measurements of the colonies' diameters were carried out at the moment when the diameter of the colony of the control sample—in the agar medium—was around 0.75 of the Petri dish diameter. An estimation of radial growth was carried out in three surfaces. Using averaged values of colonies' diameters, the ratio of the size of colonies on the medium with the preparation to the colony size on the control sample was calculated and then the effective inhibitory concentration EC_{50}—the amount of a preparation in the medium needed to reduce the radial growth of a colony by half—was determined.

Table 1. Biocidal activity of sodium tallow amphopolycarboxyglycinate stabilized dispersion of silver NPs and commercially available fungicides.

	EC_{50}, mg l^{-1}			
Plant pathogenic fungi	Silver NPs	Fludioxonil	Pencycuron	Azoxystrobin
Phytophthora infestans (Mont.) de Bary	3.1 ± 0.3	145 ± 5	>500	0.05 ± 0.01
Sclerotinia sclerotiorum (Lib.) de Bary	3.9 ± 0.3	—[a]	—[a]	—[a]
Alternaria solani Sorauer	7.7 ± 0.5	1.2 ± 0.1	5 ± 1	562 ± 1
Alternaria alternata (Fr.) Keissl.	28 ± 1	1.2 ± 0.1	140 ± 1	970 ± 1
Fusarium solani (Mart.) Sacc.	8.3 ± 0.5	>100	>100	>100
Colletotrichum coccodes (Wallr.) S Hughes	6.6 ± 0.3	—[a]	>100	0.05 ± 0.01
Helminthosporium solani Durieu & Mont.	10 ± 0.7	>100	>100	—[a]
Rhizoctonia solani J G Kühn	0.4 ± 0.1	0.1 ± 0.05	0.1 ± 0.05	>100

[a] A study was not carried out.

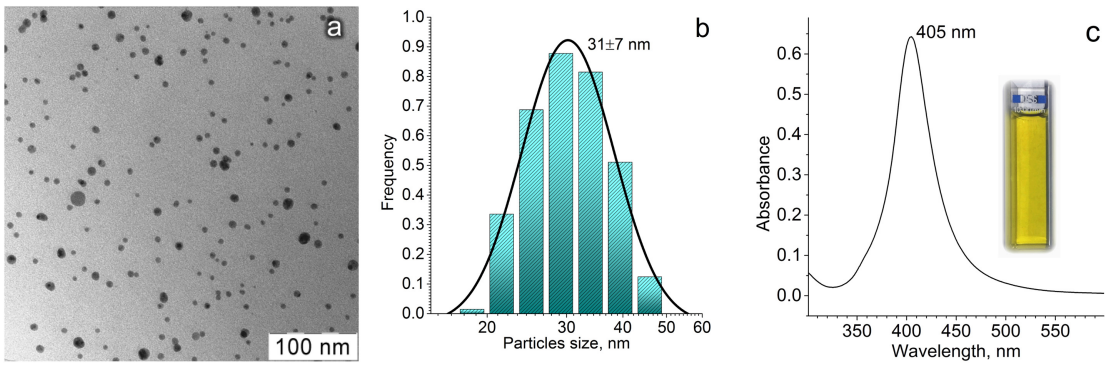


Figure 1. TEM image of particles (a); hydrodynamic radius distribution histogram (b); UV–visible absorbance spectrum (c) of sodium tallow amphopolycarboxyglycinate stabilized silver sol.

3. Results and discussion

3.1. Synthesis of silver nanoparticles

During the first step of synthesis the sol of AgCl is formed after the addition of a silver nitrate solution to the solution of sodium tallow amphopolycarboxyglycinate, additionally containing NaCl. After that the particles of AgCl are reduced using sodium borohydride followed by formation of dispersions of metal AgNPs.

Silver colloidal solution obtained according to TEM images of dried samples (figure 1(a)) and dynamic light scattering data (see figure s1, ESI) is a dispersion of crystalline AgNPs mainly of a spherical shape, an average diameter of particles being 31 ± 7 nm (figure 1(b)). Sols have the russet color, on a UV–visible absorbance spectrum there is an intensive plasmon resonance region of AgNPs with a peak at 405 nm (figure 1(c)).

Dispersion particles are negatively charged, the zeta potential determined by dynamic light scattering equals −54 ± 1 mV. The dispersion of AgNPs is stable with respect to aggregation during, at least, 4 months after the synthesis, which agrees with the sufficiently high value of the zeta potential.

Sodium tallow amphopolycarboxyglycinate stabilized silver sol shows extreme aggregative stability. First, this dispersion is stable even with a high content of silver—3 g l^{-1} (see table s1, ESI), which is not achievable for dispersions stabilized with surfactants and polymers used before. For comparison an average concentration of silver in a typical synthesized sol is 10–100 mg l^{-1} [32]. Besides that, the sodium tallow amphopolycarboxyglycinate stabilized colloidal silver solution maintains aggregative stability in the presence of monovalent metal salts up to a concentration of 0.4 mol l^{-1} for KCl, $NaNO_3$, Na_2SO_4 (see figure 2). Other polyelectrolytes-stabilized colloidal silver solutions have lower stability amid high ionic strength (up to 0.1 mol l^{-1}) [32, 45, 46]. Increasing the charge of anions of Na_2SO_4 compared to $NaNO_3$ (see figure 2) does not have a significant effect on aggregative stability of the colloidal silver solution.

In the presence of tri- and divalent metal salts the sodium tallow amphopolycarboxyglycinate stabilized colloidal silver solution has shown the same low stability (see table s2, ESI) as the other stabilized colloidal silver solution [32, 44, 47, 48]. In particular 5 mmol l^{-1} Ca^{2+} causes instantaneous coagulation of AgNPs that was verified by the change in their absorption light-spectra (see figure 2).

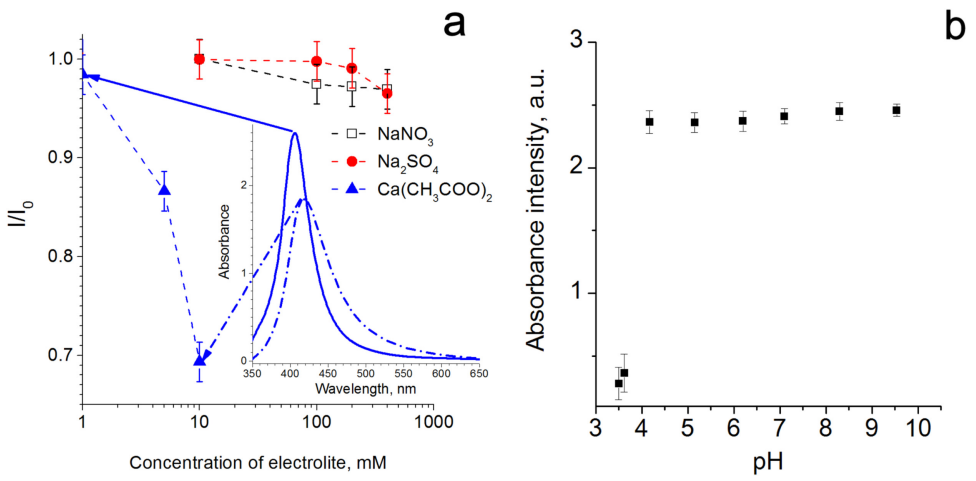


Figure 2. Dependence of AgNPs peak absorbance relative intensity on (a) the concentration of electrolytes ($NaNO_3$, Na_2SO_4 and $Ca(CH_3COO)_2$) and (b) pH.

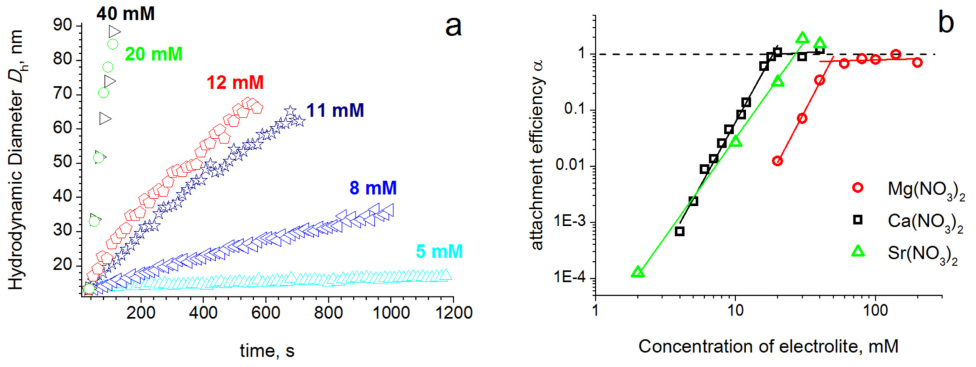


Figure 3. (a) Time-dependences of the AgNPs hydrodynamic diameter in the presence of various $Ca(NO_3)_2$ concentrations; (b) attachment efficiency of AgNPs in the presence of various electrolyte concentrations ($Mg(NO_3)_2$, $Ca(NO_3)_2$, and $Sr(NO_3)_2$).

The coated tallow amphopolycarboxyglycinate AgNPs can redisperse in an aqueous medium even after complete drying and without ultrasonic treatment. Up until this redispersion of AgNPs have been reported only in nonpolar solvents [49]. Also the sodium tallow amphopolycarboxyglycinate stabilized colloidal silver solution stands for more than 20 frost/defrost cycles, while major dispersions of AgNPs stabilized by other surfactants can only stand for 2–3 frost/defrost cycles without stability loss [50]. Moreover the prepared AgNPs colloids are stable amid a wide range of pH (4–9, see figure 2(b)), unlike polyelectrolyte stabilized AgNPs—for example, branched polyethyleneimine [32].

3.2. Study of aggregation kinetics of prepared colloids

Time-dependences of the AgNPs hydrodynamic diameter in the presence of different concentrations of calcium nitrate are presented in figure 3(a). With the increase of the concentration the slope of the initial stage (<30 nm) D_h dependence also increases. But beyond the respective critical coagulation concentrations (CCCs) this dependence reaches its limit. According to [44, 51], such behavior corresponds with the classic DLVO theory. At low electrolyte concentrations, reaction limited (slow) aggregation occurs due to the antagonism between the negatively charged tallow amphopolycarboxyglycinate-coated AgNPs. At electrolyte concentrations above the respective CCCs, diffusion-limited (fast) aggregation takes place as the surface charge on the AgNPs is sufficiently screened to eliminate the energy barrier for aggregation.

Above described aggregation model well illustrated at figure 3(b). For $Mg(NO_3)_2$ and $Ca(NO_3)_2$ electrolytes the CCCs are 48 and 18 mM respectively; beyond these concentrations the attachment efficiency reaches 1. These values are several times higher than what other polymer-stabilised silver nanoparticles like PVP [44] or bare silver nanoparticles show [6].

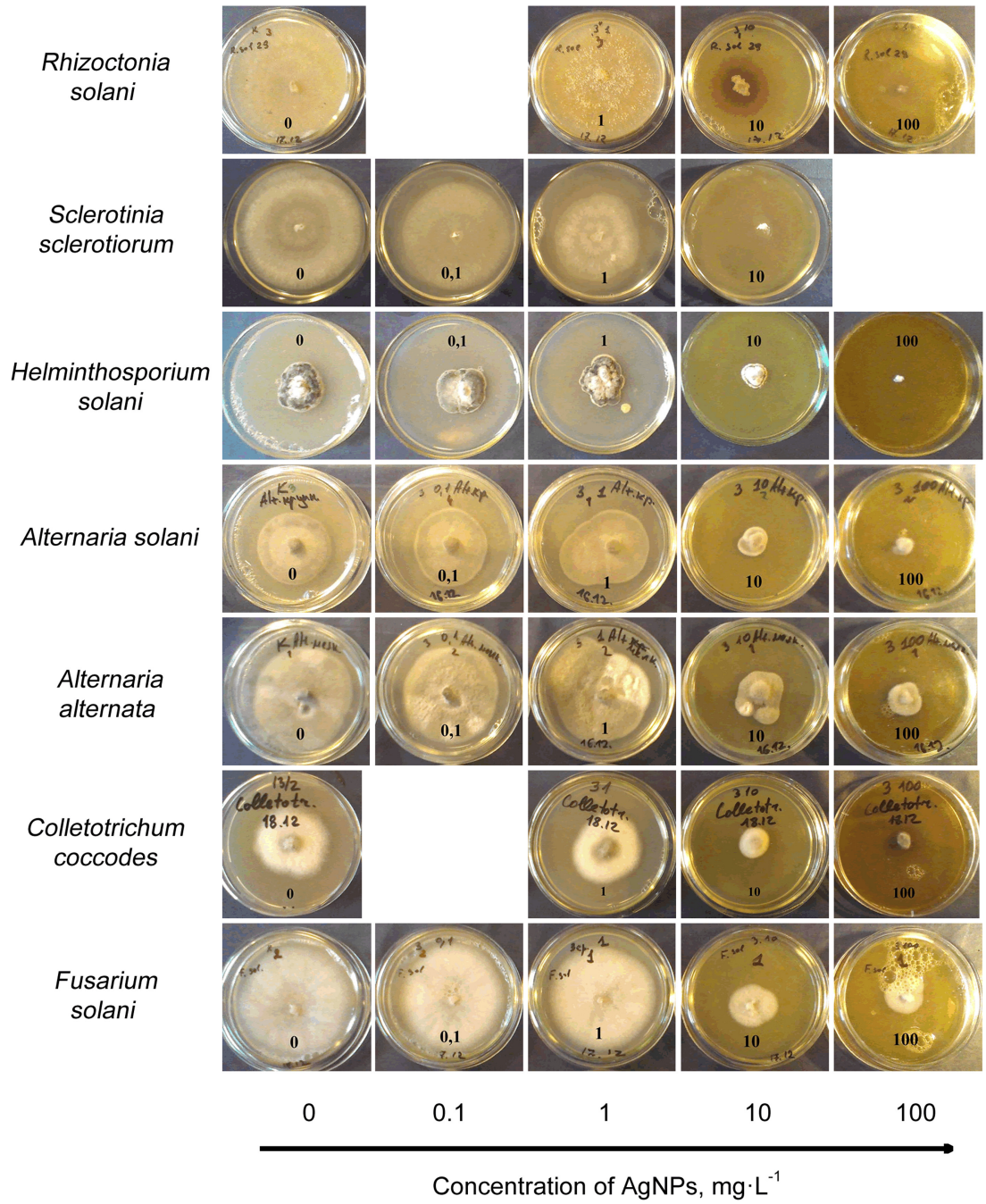


Figure 4. Direct antifungal activity of tallow amphopolycarboxyglycinate capped AgNPs with various concentration (1–100 mg l^{-1}) on different fungi on Petri dishes.

Exposed to $NaNO_3$ the hydrodynamic diameter of AgNPs (concentration up to 1 M) has not changed in an hour. This observation can be explained using the DLVO theory, according to which the ratio of CCCs of singly and doubly charged ions is 1:64 (Schulze-Hardy rule) [52]. In our case this concentration exceeds 1 M (18 * 64 mM). It should be noted that the DLVO theory can only be applied to diluted solutions; steric repulsion may also cause such high AgNPs colloids' stability compared to electrostatic interactions.

3.3. Biocidal activity of pesticides and the sodium tallow amphopolycarboxyglycinate stabilized dispersion of AgNPs with respect to plant pathogenic bacteria

The results of studies of biocidal activity of the obtained silver sol compared to commercially available fungicides used for pre-plant treatment of tubers and plant treatment during vegetation with respect to *P. infestans* are given in table 1 and figure 4. In [53–55] we can find the EC_{50} values of dispersions of AgNPs stabilized with polymers containing polyvinylpyrrolidone units, with respect to *R. solani*—6 mg l^{-1} [53], fungi of *Fusarium*

genus—from 9 to 55 mg l^{-1} [54] and fungi of *Colletotrichum* genus—from 8 to 100 mg l^{-1} depending on species [55]—are given. It should be noted that such polymers do not have their own apparent fungicidal activity.

It appears that the biocidal activity of sodium tallow amphopolycarboxyglycinate stabilized nanosilver with respect to most serious potato pathogen *P. infestans* (late blight disease of the potato agent) and plant pathogenic fungi (with the exception of *R. solani*), exceeds the activity of wide spread traditional synthetic pesticides and already known dispersions of AgNPs. The amount of the dispersion stabilizer sodium tallow amphopolycarboxyglycinate in a sol, with the silver content diluted in order to correspond with the EC_{50} values obtained, does not have an apparent fungicidal effect with respect to tested phytopathogens.

High aggregative stability of dispersion allows it to show antimicrobial activity even when added to the solid agar medium which causes momentary coagulation with the loss of activity of many other silver colloidal solutions. As compared to commercially tested available fungicides the sodium tallow amphopolycarboxyglycinate stabilized dispersion of AgNPs is a more versatile substance—it shows the comparable efficiency when used against *R. solani* and is much more effective against other sufficiently aggressive potato pathogens.

4. Conclusions

The dispersion of silver AgNPs stabilized with tallow amphopolycarboxyglycinate obtained for the first time by the authors shows extremely high aggregative stability with respect to the action of singly charged coagulating agents (up to 1 M in the presence of $NaNO_3$). In the presence of doubly charged coagulating agents ($Mg(NO_3)_2$ and $Ca(NO_3)_2$) the aggregation behavior has been confirmed to be in accordance with the classic DLVO theory and CCCs have been calculated (48 and 18 mM correspondingly). Compared to the tested commercially available fungicides the sodium tallow amphopolycarboxyglycinate stabilized dispersion of AgNPs is a more versatile substance—it has the comparable efficiency when used against *R. solani* ($EC_{50} \sim 0.4$ mg l^{-1} versus 0.1 mg l^{-1}), but is much more effective against other sufficiently aggressive potato pathogens ($EC_{50} \sim 10$ mg l^{-1} versus 100 mg l^{-1}). This points to the possibility of successful application of silver preparations in agriculture with the goal of reduction of the use of toxic and expensive synthetic antibiotics and pesticides.

Acknowledges

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