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Q1 Perspective

2 **Interaction of silver nanoparticles with**
3 **mediterranean agricultural soils: Lab-controlled**
4 **adsorption and desorption studies**

Q3 Q2 **Laura Torrent¹, Eva Marguí¹, Ignasi Queralt², Manuela Hidalgo¹, Mònica Iglesias^{1,*}**

6 1. Department of Chemistry, University of Girona, C/M. Aurèlia Capmany, 69, 17003 Girona, Spain

7 2. Institute of Environmental Assessment and Water Research (IDAEA-CSIC), C. Jordi Girona, 18-26, 08034 Barcelona, Spain

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A B S T R A C T

The production of silver nanoparticles (AgNPs) has increased tremendously during recent years due to their antibacterial and physicochemical properties. As a consequence, these particles are released inevitably into the environment, with soil being the main sink of disposal. Soil interactions have an effect on AgNP mobility, transport and bioavailability. To understand AgNP adsorption processes, lab-controlled kinetic studies were performed. Batch tests performed with five different Mediterranean agricultural soils showed that cation exchange capacity and electrical conductivity are the main parameters controlling the adsorption processes. The adsorption kinetics of different sized (40, 75, 100 and 200 nm) and coated (citrate, polyvinylpyrrolidone and polyethyleneglycol (PEG)) AgNPs indicated that these nanoparticle properties have also an effect on the adsorption processes. To assess the mobility and bioavailability of AgNPs and to determine if their form is maintained during adsorption/desorption processes, loaded soils were submitted to leaching tests three weeks after batch adsorption studies. The DIN 38414-S4 extraction method indicated that AgNPs were strongly retained on soils, and single-particle inductively coupled plasma mass spectrometry confirmed that silver particles maintained their nanoform, except for 100 nm PEG-AgNPs and 40 nm citrate-coated AgNPs. The DTPA (diethylenetriaminepentaacetic acid) leaching test was more effective in extracting silver, but there was no presence of AgNPs in almost all of these leachates.

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50 Introduction

51 During recent years, the use of manufactured nanoparticles
52 (MNPs) for domestic and industrial purposes has grown
53 tremendously (Pulit-Prociak and Banach, 2016; Sajid et al.,
54 2015). The fraction of atoms at the nanoparticle surface is high

because of its nanosize (1–100 nm), thus promoting both the
specific surface area and adsorption capacity. Consequently,
the physicochemical characteristics (electrical conductivity,
mechanical strength, optical or magnetic properties) of nano-
particles are unique, and differ from those of their bulk
counterparts. Among different types of nanoparticles, metallic

* Corresponding author. E-mails: laura.torrent@udg.edu, (Laura Torrent), monica.iglesias@udg.edu. (Mònica Iglesias).

MNPs have experienced substantial growth in the industry, with silver nanoparticles (AgNPs) one of the most produced NPs due to their effective biocidal activity. Their applications are spread across a variety of commercial goods such as foods, textiles, construction, medicines, cosmetics, power, pharmacy, biomedicine, household goods and agriculture (Pulit-Prociak and Banach, 2016; Pachapur et al., 2016; Van Koetsem et al., 2015). As a consequence of the widespread production of AgNPs, these particles are inevitably released through different pathways into the environment (air, water and soil). Soil is the biggest sink of disposal for most of the released MNPs. The main source of entry of these emerging contaminants to soils is through the application of sewage sludge from wastewater treatment plants (WWTPs) to agricultural lands. In WWTPs, AgNPs can undergo different transformations (e.g., dissolution, oxidation or sulfidation), with transformation to silver sulfide in sewage sludge being the main pathway. However, anthropogenic silver nanoparticles can also enter agricultural land directly via unintentional emissions, accidental spills or application of nanopesticides (Li et al., 2017; Pachapur et al., 2016; Azimzada et al., 2017). Soil matrices are relatively complex because they present a solid phase, consisting of organic matter and minerals, and an aqueous phase that contains various amounts of natural colloidal/particulate materials (Peralta-Videa et al., 2011; Tourinho et al., 2012). Consequently, AgNP interactions with soils are difficult to interpret. These interactions lead to processes, such as aggregation/agglomeration, dissolution to metal ions or sorption onto surfaces, which are responsible for their mobility, transport and bioavailability in the environment (Tourinho et al., 2012). Aggregation and agglomeration are associations of particles due to physicochemical processes including Van der Waals forces, electrostatic interactions or Brownian motion. Dissolution of AgNPs into their constituent atoms is governed by diverse phenomena, such as chemical reactions that take place due to the presence of oxygen, chlorine and enzymes (Pachapur et al., 2016). Deposition occurs when particles are retained on a solid surface or when aggregation (both homo- and hetero-aggregation)/agglomeration takes place. Adsorption of nanoparticles onto the solid components of soils is influenced by particle properties (size, shape, surface charge, surface and core chemistry, capping agent, agglomeration state, crystallinity, redox potential, catalytic activity and porosity) as well as soil features (pH, organic matter content, ionic strength, zeta potential and texture) (Darlington et al., 2009; Van Koetsem et al., 2015). The capping agent is one of the main determinant characteristics since it affects the surface charge, which governs attraction/repulsion interactions among particles, and the steric hindrance (Christian et al., 2008; Schultz et al., 2015; Tourinho et al., 2012; McGillicuddy et al., 2017; Lin et al., 2012). Additionally, particle size is another property that strongly influences immobilization on soil surfaces, especially when there is aggregate formation (Darlington et al., 2009; Hoppe et al., 2014; He et al., 2019).

Batch experiments are commonly used in order to understand the retention and transport of contaminants in soils. This approach allows one to examine the retention under well-defined conditions in an easier and faster way compared to column experiments (Treumann et al., 2014; Plassard et al., 2000). However, as stated in different reports, nanoparticle dispersions are thermodynamically unstable and their

behavior cannot be described as an equilibrium process. Despite this fact, batch tests can still provide valuable information on nanoparticle attachment/detachment kinetics (Praetorius et al., 2014; Cornelis, 2015). For example, Cornelis et al. (2012) concluded from batch tests that adsorption of polyvinylpyrrolidone (PVP) coated AgNPs (negatively charged) on iron and aluminum oxides and mineral clay edges may be important in retention processes in soils. An additional batch retention experiment using sterically stabilized AgNPs determined that immobilization of nanosilver depends on soil properties such as clay content, pH and calcium content (Hoppe et al., 2014). Furthermore, organic matter content is also relevant in adsorption of AgNPs onto silt particles, as stated by Klitzke et al. (2015).

Scarce information on the desorption of AgNPs from soil particles to the liquid phase exists in the published literature (Coutiris et al., 2012; Navarro et al., 2014). To evaluate the potential mobility and bioavailability of metals in polluted soils, leaching tests are frequently used (Hoppe et al., 2015), which gives information related to soil-plant transfer of pollutants and their migration in a soil profile that is connected with groundwater (Rauret, 1998). More recently, some leaching tests have been used to evaluate the bioaccessibility of AgNPs from soils in the human gastrointestinal tract (Dang et al., 2018).

Common analytical tools for quantitative determination of AgNPs in liquid extracts are inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). These analytical techniques allow the determination of total metal content, hindering the ability to distinguish the metallic AgNPs from other silver (Ag) species present in the solution (Koopmans et al., 2015). However, in recent years the use of single-particle ICP-MS (SP-ICP-MS) to detect and characterize MNPs at trace levels in environmental samples has increased (Mitrano et al., 2014; Montañó et al., 2014). Analysis with SP-ICP-MS requires nanoparticle suspensions that have been sufficiently diluted and a short dwell time to ensure that a maximum of one particle is measured in each integration time. Once injected into the plasma, the discrete particle is vaporized, atomized and ionized, producing a burst of ions that can be measured as a single pulse (Laborda et al., 2013; Tuoriniemi et al., 2012; Yang et al., 2014). This analytical technique allows differentiation between nanosilver and soluble silver species and also can give information about the size distribution (Majedi and Lee, 2016).

In this work, batch experiments and leaching tests were carried out in order to understand the adsorption and desorption processes of AgNPs with soils. The goal of this study was to determine the adsorption kinetics of AgNPs with different soils, using different particle sizes and coatings, and assessing the desorption of these particles by leaching tests. Furthermore, the possible AgNP transformations during the studied interaction processes were evaluated by analyzing the samples by the SP-ICP-MS technique. To our knowledge, few research papers exist involving the adsorption and desorption of AgNPs from soils that test nanoparticles with different physicochemical properties. In addition, none of them employ SP-ICP-MS for AgNP detection after the adsorption and desorption processes.

1. Materials and methods

1.1. Chemicals, materials, apparatus and instrumentation

ICP-OES standard solutions were prepared from a silver stock solution (silver nitrate (AgNO_3) in nitric acid (HNO_3)) of (1000 ± 2) mg/L from Merck (Germany). High purity water from a Milli-Q purification system (Millipore Corp., Bedford, MA) was employed for the leaching experiments (DIN 38414-S4 extraction method). It was also used to dilute stock solutions and soil leachates (supernatants). Triethanolamine (TEA) (Sigma-Aldrich, Germany), diethylenetriaminepentaacetic acid (DTPA) (Panreac, Spain) and calcium chloride dehydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, Panreac, Spain) were utilized to prepare the extracting solution for the DTPA leaching test.

Batch adsorption experiments and leaching tests were performed employing LD-76 rotary mixers (Dinko, Spain). In order to break down the possible agglomerates of AgNPs, an ultrasonic bath (J.P. Selecta, Spain) was used. A Rotofix 32A centrifuge (Hettich-Zentrifugen, Germany) was utilized to separate the soil and the soil extract after kinetic adsorption tests and leaching tests.

Total silver content in aqueous suspensions from adsorption and leaching experiments was determined using an ICP-OES Vertical Dual View 5100 system (Agilent Technologies, Japan), with calibration curves ranging between 5 and 350 $\mu\text{g/kg}$ silver concentration. SP-ICP-MS for silver nanoparticle detection in aqueous leachates was performed using a quadrupole-based ICP-MS Agilent 7500c system (Agilent Technologies, Japan) equipped with Octapole Reaction System (ORS) technology. The instrumental characteristics and measurement conditions of the two instruments are summarized in Appendix A Table S1. Histograms of the results were calculated and plotted using Microsoft Excel software.

1.2. Nanoparticles

Silver nanoparticles of different sizes and coatings were tested in this work. Two suspensions of silver nanoparticles stabilized with sodium citrate (citrate-AgNPs) of 40 and 100 nm were obtained from Sigma-Aldrich (USA) and one of 200 nm from NanoComposix (USA). Polyvinylpyrrolidone-coated silver nanoparticles (PVP-AgNPs) of 75 and 100 nm and polyethyleneglycol-coated silver nanoparticles (PEG-AgNPs) of 100 nm were purchased from NanoComposix (USA). The principal difference between these nanoparticles was the zeta potential, which depends on the capping agent and is related to the surface charge. The most negative zeta potential at pH 7 was found for citrate-AgNPs and the least negative for PEG-AgNPs, which was almost neutral (NanoComposix. Standard Capping Agents, 2018). Detailed information about the characteristics of the studied AgNPs can be found on the manufacturers' webpages.

1.3. Soils studied

Five Mediterranean agricultural soils with different physicochemical properties were tested in order to evaluate their influence in AgNP adsorption processes. The five studied soils

were sampled at different locations from Barcelona and Girona provinces (NE Spain): Soil 1 and Soil 2 (Vallcebre), Soil 3 (Castellbisbal), Soil 4 (Gavà) and Soil 5 (La Tallada d'Empordà). These soils were selected to cover the variety of soils along this Mediterranean region. Composite and representative surface soil samples were obtained by combining several subsamples per location. They were collected using a polypropylene shovel and subsequently transferred to clean polypropylene bags. In the laboratory, soil samples were dried at room temperature, sieved (2 mm) and stored in polypropylene containers.

The particle size distribution (Appendix A Table S2) revealed strong differences regarding the smallest sizes, <0.125 mm, ranging from near 4% for Soil 3 to around 50% for Soil 4. Soil mineralogy was determined by X-ray diffraction (XRD), following randomly oriented powder methodology for bulk composition and the oriented aggregate method for the identification of clay minerals. From the results, (Appendix A Table S3) studied soils could be classified as marly soils, characterized by the prevalence of carbonates (mainly calcite, CaCO_3) and quartz. Soils from the Vallcebre area (Soil 1 and Soil 2) differed in the type of carbonate, dolomite (MgCaCO_3) for Soil 1 and a noticeable content of gypsum for Soil 2. Dealing with the content of clay minerals, Soils 1 and 2 were characterized by the presence of swelling clays of the smectite group, with a minor amount of kaolinite, whereas the rest of the soils exhibited different clay assemblages, illite-kaolinite for Soil 3 and chlorite-illite for Soils 4 and 5. Clay mineralogy is the key factor in the cation exchange capacity (CEC) of soils. Pure smectite has a CEC from 80 to 150 $\text{mEq}/100$ g, with illite and chlorite ranging from 10 to 40 $\text{mEq}/100$ g and kaolinite from 3 to 15 $\text{mEq}/100$ g. Minor quantities of feldspars and hematite were also detected in the XRD runs.

The physicochemical properties of these studied soils are shown in Table 1. As can be expected from the mineralogy, the pH of the soil samples was neutral to slightly basic. The cation exchange capacity, around three times higher in Soils 1 and 2, was directly related to the presence of smectite. The electrical conductivity was very high in Soil 2 due to the presence of gypsum, exhibiting a wide variety for the rest of the soils, and the organic matter was nearly constant (5%–6%), except for Soil 5 that had the lowest content.

1.4. Adsorption studies

Batch adsorption experiments were performed in order to investigate the interaction between AgNPs and soil in lab-

Table 1 – Physicochemical characteristics of studied soils.

	pH (in H_2O)	Moisture (%)	O.M. (%)	CEC ($\text{meq}/100$ g)	EC ($\mu\text{S}/\text{cm}$)	
Soil 1	8.0	13.3	6.5	20.1	105.1	t1.5
Soil 2	7.4	13.05	5	18.9	2460	t1.6
Soil 3	7.6	9.3	5.7	6.5	276.5	t1.7
Soil 4	7.4	3.7	6.1	7	427.3	t1.8
Soil 5	7.1	0.5	1.8	5.3	87.3	t1.9
O.M.: organic matter content. CEC: cation exchange capacity. EC: electrical conductivity.						t1.10 t1.12

controlled conditions. For this purpose, 0.5 g of soil was weighed into polystyrene tubes. Then, 20 mL of a 1 or 10 mg/L aqueous suspension of AgNPs was added followed by agitation with a rotary mixer at 35 r/min.

Afterwards, samples were removed in duplicate at specific times (10 min, 20 min, 30 min, 1 hr, 2 hr, 4 hr or 6 hr) and centrifuged at 3500 r/min for 8 min. Finally, the supernatant was transferred to a new polystyrene tube and stored overnight at 4°C until analysis.

Prior to analysis by ICP-OES, liquid samples were ultrasonicated for 5 min to break down the possible agglomerates of silver nanoparticles present in the aqueous suspension. Then, samples were shaken vigorously for 1 min and filtered through a 0.45 µm cellulose acetate filter (Whatman, Filterlab, Spain) to remove suspended soil particles. Finally, the samples were analyzed by ICP-OES and the total silver content was quantified using an ionic silver (Ag⁺) calibration curve. All experiments were carried out in duplicate.

1.5. Leaching studies: DIN 38414-S4 and DTPA extraction

In order to study the possible release of AgNPs from soils, two leaching tests named DIN 38414-S4 (German Standard legislation, 1984) and DTPA (Quevauviller, 1998) were performed. These leaching tests were selected to allow the evaluation of the mobility and bioavailability of metals in the environment. The DIN 38414-S4 leaching test gives information about the more mobilized metals and the DTPA leaching method predicts the bioavailability of metals to plants (Rauret, 1998; Kosson et al., 1996). To this aim, soils containing known amounts of adsorbed AgNPs were tested 21 days after the adsorption experiment.

For the DIN 38414-S4 extraction procedure, 5 mL of Milli-Q water was added to 0.5 g of loaded soil and the mixture was submitted to rotation with a rotary mixer (35 r/min) for 24 hr at room temperature (22°C). In the case of the DTPA extraction test, 5 mL of DTPA solution (0.005 mol/L DTPA, 0.01 mol/L TEA, 0.5 mol/L CaCl₂·2H₂O adjusted to pH 7.3) was agitated (35 r/min) with 0.5 g of loaded soil for 2 hr at room temperature (22°C).

After these contact times, samples were centrifuged for 8 min at 3500 r/min, after which the supernatants were transferred to new polystyrene tubes and stored overnight at 4°C until analysis by ICP-OES and SP-ICP-MS techniques.

1.6. Evaluation of the presence of Ag as AgNPs by SP-ICP-MS analysis

SP-ICP-MS was used to confirm the presence of AgNPs in the stripping solutions. To obtain good results in SP-ICP-MS, the Ag concentration in the form of AgNPs should be very low to afford a solution that has at maximum one particle in the volume aspirated during the dwell time (10 msec). For this reason, the Ag concentration of the samples was determined by the ICP-OES technique before SP-ICP-MS analysis to determine which dilution was needed to obtain a final solution of approximately 0.8 µg/L. Previous to the ICP-OES analysis, in order to remove the suspended soil particles, samples were filtered through a cellulose acetate filter of 0.45 µm after being ultrasonicated for 5 min and shaken for 1 min to avoid the possibility of agglomerates. Finally, the

samples were analyzed by SP-ICP-MS to determine if silver was present in the leachate solution (supernatant) in nanosilver form. In the case of DTPA solutions, the stability of AgNPs had been previously verified. The presence of nanoparticles was confirmed in this media for 100 nm AgNPs with the three different coatings after 2 hr of agitation.

2. Results and discussion

2.1. Stability and storage of AgNP solutions

Some recent publications have highlighted the potential alteration of the dispersion state of nanoparticles by laboratory procedures (Simonet and Valcárcel, 2009). For this reason, previous to the soil adsorption studies, some experiments were carried out in order to evaluate the stability of silver nanoparticle suspensions submitted to different treatments and storage conditions. Specifically, various times of storage (<6 hr and 6 days) at different temperatures (around 4°C and around -20°C) were evaluated. Moreover, the effect of filtration of these suspensions was also tested. Results can be observed in Appendix A Fig. S1.

Good recoveries of fresh suspensions (95%–100%) assessed using an ICP-OES system and silver standard solutions for quantification purposes confirmed the good performance of the analytical procedure.

It can be seen that the storage of aqueous silver nanoparticles suspensions during 6 days caused a 40% decrease in their recovery with respect to the ones stored for <6 hr for all types of AgNPs tested (significant statistical differences by Student's t-test, $t_{critical} < t_{experimental}$). Nevertheless, a recovery of (104.6% ± 1.2%) was obtained from an aqueous suspension of citrate-coated silver nanoparticles (100 nm) after being stored 24 hr at 4°C (data not shown in the bar chart). No significant statistical differences were observed (Student's t-test, $t_{critical} > t_{experimental}$) between storing the samples at 4 or at -20°C. Finally, it was shown that the filtration of fresh samples does not cause any effect on the recovery of AgNPs (no significant statistical differences by Student's t-test, $t_{critical} > t_{experimental}$). Moreover, the supernatant solution had no effect on silver recovery (94.6% ± 1.3%) of 100 nm PVP-AgNPs after filtration. However, the filtration process caused an important decrease in the AgNP concentration when silver nanoparticles aqueous suspensions had been stored at -20°C (significant statistical differences by Student's t-test, $t_{critical} < t_{experimental}$). Some aggregation processes have been reported for nanoparticles suspension under these low temperatures (Sigfridsson et al., 2013). These aggregations can produce a loss of particles when they are subjected to filtration afterwards. Taking into account all these results, the adsorption studies could be carried out analyzing the samples after storage for a maximum of 24 hr at 4°C and subjecting the samples to a filtration process if necessary.

2.2. Adsorption of AgNPs in agricultural soils: Kinetic studies

Some preliminary experiments were performed in order to determine the appropriate amount of soil and the volume and concentration of silver nanoparticle suspensions. The aim of

these experiments was to establish the conditions that permitted the evaluation of the adsorption of AgNPs onto soil surfaces. For this purpose, 2, 1 and 0.5 g of soil were put in contact with 20 mL of a 1 mg/L citrate-AgNPs (100 nm) suspension (Appendix A Fig. S2). Likewise, 10, 15 and 20 mL of 75 nm PVP-AgNP suspensions (1, 5 and 10 mg/L concentrations) were mixed with 0.5 g of soil (Appendix A Fig. S3). In both cases the soil and nanoparticle suspensions were stirred under rotary agitation conditions (35 r/min) for 2 hr. Afterwards, the silver concentration in the supernatant was determined by ICP-OES analysis. Results showed that a smaller amount of soil (0.5 g) and greater volume of solution (20 mL) gave higher Ag concentrations in the supernatant suspensions, indicating slower kinetics in comparison with that obtained using high soil amounts. This is favorable for detection of the differences in adsorption kinetics of different types of AgNPs. Therefore, it was decided to use 0.5 g of soil and 20 mL of a 10 mg/L silver nanoparticle suspension (PVP-AgNPs 75 nm) only for testing the influence of soil properties on AgNP adsorption. For the other tests (coating and size effects), 0.5 g of soil and 20 mL of 1 mg/L AgNP suspensions were used due to the low concentration of the stock solutions available (20 mg/L). Using these conditions, a kinetic study was undertaken.

The study was conducted with all the soils described in Section 1.3 (for details of soil characteristics see Appendix A Tables S2 and S3). The results obtained using AgNPs of 75 nm coated with PVP are shown in Fig. 1a. As can be seen, the adsorption rates obtained for all tested soils after 4 hr of rotation were high (80% of adsorption). Soil 2 showed the fastest adsorption rate, reaching almost 100% adsorption in less than 10 min. The main characteristics of this soil are its high electrical conductivity and cation exchange capacity. This fact agrees with different works that point out the increase of AgNP adsorption on soils with increasing ionic strength (Anjum et al., 2013). Thus, both homo- and hetero-aggregation processes could be responsible of this adsorption. On the other hand, Soil 3 after half an hour of the kinetic adsorption study presented the slowest adsorption rate (75%). This soil had one of the lowest cation exchange capacity values; however, its electrical conductivity was higher than that of Soil 1, which shows a higher rate of adsorption. After 4 hr of the kinetic study, the slowest adsorption rate was obtained for Soil 5, which had the lowest cation exchange capacity and electrical conductivity. The size distribution of soil particles seems not to have a great influence in the adsorption rate, although the soils with a lower adsorption rate (Soils 3, 4 and 5) were those with greater amounts of small soil particles. Cornelis et al. (2013) determined a correlation between clay content and AgNP retention by natural soils. This correlation seems to be explained by the heterocoagulation of AgNPs with colloids naturally present in soils.

Using these results, an approximate value for the affinity coefficient, α , could be calculated following the methodology developed by Barton et al. (2014). For removal of AgNP suspensions at time t , $r(t)$ was calculated as $r(t) = (C_0 - C_t)/C_0$, with C_0 ($\mu\text{g/L}$) being the initial AgNP mass concentration and C_t ($\mu\text{g/L}$) the AgNP mass concentration in the supernatant suspension at time t (min). Afterwards, $\ln(rC_0/C_t + 1)$ vs time was plotted

Fig. 1 – Percentage of adsorption of different silver nanoparticles in agricultural soils (0.5 g of soil and 20 mL of nanoparticle suspension). (a) Comparison of agricultural soils with different physicochemical properties using a suspension of 10 mg/L of 75 nm ϕ polyvinylpyrrolidone (PVP) coated AgNPs. (b) Comparison of different coatings (PVP, polyethyleneglycol (PEG), citrate) of 100 nm ϕ nanoparticles using Soil 3 and a solution of 1 mg/L of total silver. (c) Comparison of different sizes of citrate silver nanoparticles using Soil 3 and a solution of 1 mg/L total silver concentration.

and a linear portion was obtained for these plots (between 10 and 60 min) except for Soil 2, which showed very fast adsorption (Appendix A Fig. S4). The values of the slope of this linear portion correspond to the product $\alpha\beta B$, which is a measure of the relative affinity of the nanoparticles for soil. β and B are the collision frequency and the concentration of soil particles respectively, which in this case were constant. From these calculations the

values of α_B determined were 6.42×10^{-4} , 4.88×10^{-4} , 3.21×10^{-4} and 2.16×10^{-4} for soils 1, 3, 4 and 5 respectively. These affinity coefficients thus obtained are in agreement with the soil adsorption kinetics, because Soil 1 is one of the soils with the fastest AgNP adsorption kinetics and its affinity coefficient is the highest, meanwhile Soil 5 shows the slowest AgNP adsorption kinetics and its affinity coefficient is the lowest.

2.3. Effect of the coating and size of AgNPs in soil adsorption

Soil 3 was chosen to study the adsorption behavior of different types of nanoparticles (surface and size) because, as observed previously, this soil had an intermediate affinity toward AgNPs among all the studied soils.

First of all, the adsorption kinetics of different coated silver nanoparticles (PVP, PEG and citrate) onto Soil 3 was compared using AgNPs of $\varnothing$ 100 nm. For comparison purposes, the adsorption kinetics of silver ions (added as AgNO_3) was also examined. Results are depicted in Fig. 1b.

As can be observed, Ag^+ showed a faster adsorption rate than silver nanoparticles, reaching 100% of adsorption in 15 min. In fact, different works underline the high capacity of Ag^+ to be adsorbed by soils, either by thiol groups or to colloidal particles (Anjum et al., 2013). The different types of AgNPs showed quite fast and similar adsorption rates, achieving a steady-state concentration in less than 60 min. Nevertheless, AgNPs with a citrate surface coating were less adsorbed (80%) than PEG- and PVP-coated nanoparticles, which reached almost 100% adsorption under the present conditions. For citrate particles an additional value was determined at 6 hr (data not shown), which was very similar to the adsorption value obtained at 4 hr. The lower adsorption rate of citrate-AgNPs respect to PEG-AgNPs and PVP-AgNPs could be due to their zeta potential, which is controlled by the pH of the solution. Zeta potential, which is the charge at the surface of the electrical double layer, is a key indicator of the stability of colloidal dispersions. Usually, capping of the particles with highly negative zeta potential indicates the increase of particle stabilization. As detailed by the manufacturer, citrate-AgNPs present a highly negative zeta potential (negatively charged) in comparison to PVP-AgNPs and PEG-AgNPs. Thus, citrate-AgNPs are more stable and their aggregation tendency is lower due to higher repulsion with negatively charged soil surfaces in comparison to other tested AgNPs (Tech Note: Zeta/pH Curves and Isoelectric Point Data for Standard Nanocomposix Silver Citrate and PVP Nanoparticle Dispersions, 2012; Prathna et al., 2011; Hoppe et al., 2015).

Adsorption rates of AgNPs with different sizes should also be compared. To this aim, citrate-coated AgNPs of 40, 100 and 200 nm diameters were used. From the results (Fig. 1c) it can be observed that silver nanoparticles with a size of 200 nm were adsorbed faster in comparison to 40 nm AgNPs. In addition, the largest AgNPs were almost totally adsorbed (90%) in 1 hr of contact time; meanwhile, the smallest AgNPs (40 nm) reached a value of 50%, achieving a 75% after 4 hr. It must be taken into account that in this work, we compared suspensions with the same Ag mass concentration but different particle number concentrations. The smaller the nanoparticle size, the higher the particle number concentration for the same Ag mass concentration. So, there were more particles able to be

adsorbed in the 40 nm AgNP solution than in 100 nm or in 200 nm ones. These results agree with those obtained by He et al. (2019) and seem to indicate that no dissolution process is taking place for AgNPs. On one hand, smaller nanoparticles are reported to dissolve more quickly. On the other hand, silver ions are more quickly retained in soils. Both facts point in the opposite direction as the behavior observed.

Finally, the adsorption rates of all types of nanoparticles using the five soils considered in this study were compared. In all cases the concentration of silver in the supernatant solution was determined after two hours of rotation (35 r/min) at 22°C. Higher concentrations of silver in the supernatant indicated lower adsorption degree on the soil. Results are depicted in Fig. 2.

As can be seen in this figure, the lowest adsorption was obtained for 100 nm citrate-coated nanoparticles in comparison to 100 nm PVP-AgNPs and PEG-AgNPs, observing significant statistical differences, except for Soil 2 (Student's t-test, $t_{\text{critical}} < t_{\text{experimental}}$). AgNPs with PVP and PEG surfaces (100 nm) showed similar results and higher adsorption than citrate-coated nanoparticles (no significant statistical differences by Student's t-test, $t_{\text{critical}} > t_{\text{experimental}}$), except for Soil 5, where significant statistical differences were observed (Student's t-test, $t_{\text{critical}} < t_{\text{experimental}}$). This different behavior of Soil 5 could be due to its lower organic matter content. Hoppe et al. (2014) stated that citrate-stabilized AgNP adsorption processes in soils are related to the soil organic matter content, which tends to be negatively charged and may hamper access to positively charged groups (Ketterings et al., 2007). Thus, the low organic matter content of Soil 5, in comparison to other studied soils, indicates that the particles of this soil may contain less negative charges, favoring the adsorption of citrate-AgNPs (highly negatively charged).

Significant statistical differences were also observed between small citrate nanoparticles (40 nm) and the big ones (100 nm) in all the tested soils (Student's t-test, $t_{\text{critical}} > t_{\text{experimental}}$) except for Soil 1 (Student's t-test, $t_{\text{critical}} > t_{\text{experimental}}$), showing a lower adsorption than the small ones. As stated above, the reason for this phenomenon can be the presence of more particles in the 40 nm AgNP solution than in the 100 nm one.

When comparing the behaviors of the soils, again Soil 2 showed a higher adsorption degree for all types of AgNPs in comparison to the other studied soils in this work (significant statistical differences by Student's t-test, $t_{\text{critical}} > t_{\text{experimental}}$). As stated above, the most important difference of this soil compared to the others is its high electrical conductivity derived from the presence of gypsum, which is related with the ionic strength (Torrent et al., 2016), and also the synergic presence of smectite clays, acting as an additional AgNP trapping agent due to its surface properties and CEC features (Solé et al., 1992). Several authors have pointed out that high ionic strength favors nanoparticle adsorption when electrostatic repulsion is present (Dwivedi et al., 2015).

2.4. Recovery of AgNPs from soils using DIN 38414-S4 and DTPA leaching procedures

To evaluate the mobility and bioavailability of different sized and coated AgNPs retained in agricultural soils, two leaching

Fig. 2 – Silver supernatant concentration after 2 hr adsorption in different soils (0.5 g of soil and 20 mL of nanoparticle suspension with 1000 µg/L total silver concentration).

procedures were carried out after 3 weeks of being adsorbed. DIN 38414-S4 and DTPA leaching procedures were applied to Soil 3 to gain information on the potential risks associated with these pollutants. Results can be observed in Table 2. In this table, $\mu\text{g Ag}_{\text{initial}}$ is the total silver amount in the initial suspension, which was put in contact with Soil 3 under rotary agitation (35 r/min) for 2 hr and after this time, the suspension was centrifuged and the supernatant was separated, filtered and analyzed. The $\mu\text{g Ag}_{\text{supernatant}}$ is the total silver amount in the supernatant. After the separation from the supernatant, the soil was dried and kept at room temperature for 3 weeks. Finally, a DIN 38414-S4 or a DTPA leaching procedure was carried out and the silver concentration of this leachate was determined. From these values the total amount of silver in each case was determined ($\mu\text{g Ag}_{\text{leached}}$).

As can be seen, the DIN 38414-S4 procedure gave very low recovery values for total silver, with ionic silver being the most retained silver form together with 100 nm PVP-AgNPs (no significant statistical differences by Student's t-test, $t_{\text{critical}} > t_{\text{experimental}}$). From the results of PVP and citrate coatings, it can be concluded that small nanoparticles show a lower tendency to be adsorbed and a higher trend toward desorption than larger ones, especially 40 nm citrate-AgNPs with respect to 100 and 200 nm, because significant statistical differences were observed (Student's t-test, $t_{\text{critical}} > t_{\text{experimental}}$). Significant statistical differences (one-way ANOVA test, $F_{\text{critical}} < F_{\text{experimental}}$) on leaching recoveries for the differently coated AgNPs tested can be also observed. In the leaching tests, fewer 1PVP-AgNPs were leached, observing statistical differences (Student's t-test, $t_{\text{critical}} > t_{\text{experimental}}$), in comparison to citrate-AgNPs and

Table 2 – DIN 38414-S4 and DTPA leaching tests of Soil 3 after adsorption of AgNPs.

Leaching method	AgNPs	$\mu\text{g Ag}_{\text{initial}}$	$\mu\text{g Ag}_{\text{supernatant}}$	$\mu\text{g Ag}_{\text{leached}}$	Recovery (%)
DIN 38414-S4	PVP 75 nm	19.7	0.6 (0.1)	0.16 (0.02)	0.8 (0.1)
	PVP 100 nm	20.0	0.4 (0.2)	0.08 (0.02)	0.4 (0.1)
	PEG 100 nm	18.6	1.1 (0.5)	0.21 (0.02)	1.2 (0.2)
	Citrate 40 nm	20.3	9.8	0.5	4.6
	Citrate 100 nm	20.2	5 (2)	0.165 (0.003)	1.1 (0.1)
	Citrate 200 nm	20.3	1.6 (0.5)	0.14 (0.03)	0.8 (0.2)
	Ag ⁺	20.6	0.160 (0.008)	0.09 (0.01)	0.4 (0.1)
DTPA	PVP 75 nm	19.7	0.6 (0.2)	0.10 (0.02)	0.5 (0.1)
	PVP 100 nm	20.0	0.6 (0.2)	0.8 (0.1)	3.9 (0.5)
	PEG 100 nm	18.6	1.0 (0.3)	0.47 (0.04)	2.7 (0.2)
	Citrate 40 nm	20.3	9.6	0.05	0.5
	Citrate 100 nm	20.2	5 (1)	0.11 (0.09)	0.7 (0.6)
	Citrate 200 nm	20.3	1.4 (0.1)	0.28 (0.06)	1.5 (0.3)
	Ag ⁺	20.6	0.135 (0.003)	1.60 (0.02)	7.8 (0.1)

DTPA: diethylenetriaminepentaacetic acid.

Values expressed as mean, $n = 2$ (standard deviation), except for nanoparticles of 40 nm with citrate surface ($n = 1$).

PEG-AgNPs. Therefore, PVP-AgNPs were more strongly retained than the other types of AgNPs tested in Soil 3. The DTPA leaching procedure gave higher recovery values than the DIN 38414-S4 extraction method, except for the smaller particles (40 and 75 nm). Surprisingly, the tendencies were completely opposite to those observed using the DIN 38414-S4 procedure: smaller AgNPs gave lower recovery values than bigger ones and ionic silver was the most leached silver form, showing significant statistical differences with respect to tested AgNPs (one-way ANOVA test, $F_{\text{critical}} < F_{\text{experimental}}$). Similarly, for different coated AgNPs, opposite trends were observed. Significant statistical differences (Student's t-test, $t_{\text{critical}} < t_{\text{experimental}}$) were observed between citrate-AgNPs and PVP-AgNPs and PEG-AgNPs, indicating that citrate-AgNPs were the least leached. The complexing capacity of DTPA for Ag^+ could partially explain

these results (Anderegg et al., 2005). As well, organic matter content could have played a role in the stabilization of some of the AgNPs (Klitzke et al., 2015; Liang et al., 2013). Some differences in the leaching capability of these extraction procedures were also observed for samples with different characteristics (Marguí et al., 2004).

2.5. AgNP presence in leaching solutions by SP-ICP-MS

The interaction of nanoparticles with soils can lead to transformations that alter their form and consequently their behavior in the environment (Dwivedi et al., 2015). In order to determine if silver nanoparticles maintain their nano-form after the adsorption and desorption processes onto soils, leachates from DIN 38414-S4 and DTPA tests were also

Fig. 3 – SP-ICP-MS histograms and time-resolved signal plots for polyethyleneglycol silver nanoparticles 100 nm (a, b), citrate silver nanoparticles 100 nm (c, d), polyvinylpyrrolidone silver nanoparticles 100 nm (e, f) from Soil 3 DIN 38414-S4 leachates.

analyzed with SP-ICP-MS. As mentioned above, this analytical technique allows differentiating between nanoparticulate silver and dissolved silver.

As can be seen in the time-resolved signal plot obtained from SP-ICP-MS analysis of PEG-AgNPs DIN 38414-S4 leachates (Fig. 3b), the baseline counts were shifted to higher values (around 400 counts) and the signal was practically constant, indicating the presence of dissolved silver (Laborda et al., 2014). Although the presence of some peaks above the baseline was observed, they were not enough to confirm the presence of nanosilver. Therefore, during the adsorption or desorption processes, PEG-AgNPs were mainly dissolved. However, the presence of citrate-AgNPs in DIN 38414-S4 leachates was confirmed due to the large number of peaks present above the baseline, which is around 40 counts, indicating that there was also a small amount of dissolved silver (Fig. 3d). In addition, the histogram obtained from this measurement confirmed the presence of AgNPs, because two distributions could be observed (Fig. 3c). The distribution at low pulse intensity represents the dissolved silver, and that at higher pulse intensity values represents the nanoparticles. So, citrate-AgNPs maintained their nanoform after adsorption and desorption processes. Similarly, PVP-AgNPs of 100 nm size also maintained their form after the DIN 38414-S4 leaching procedure (Fig. 3e–f).

In the DIN 38414-S4 leachates of 200 nm citrate-AgNPs, the presence of nanosized particles was also confirmed, as shown in Fig. 4c–d. However, for citrate-AgNPs with dimension of 40 nm, no nanoparticles were present (Fig. 4a–b). Therefore, it

seems that smaller sized AgNPs are more prone to dissolution in soil adsorption and desorption processes in comparison with larger sized nanoparticles. These results agree with some other results found in the literature (Dwivedi et al., 2015), which mentioned a higher rate of dissolution for smaller nanoparticles than for bigger ones due to the larger fraction of surface atoms or the lower redox potentials of smaller AgNPs.

The leachates of 200 nm citrate-AgNPs for the five soils studied were also analyzed in order to determine if there were some differences in the AgNP forms caused by the physico-chemical properties of the soils. In Fig. 5, it can be seen that for Soils 1, 3 and 4, the silver nanoparticles maintain their form after adsorption and desorption experiments. However, for Soils 2 and 5, the presence of nanoparticles cannot be confirmed (Fig. 5b and e). These two soils have a lower amount of organic matter than the rest. Some studies have related the presence of organic matter to the colloidal stability of NPs due to electrostatic and steric interactions (Dwivedi et al., 2015; Pachapur et al., 2016).

For the DTPA leaching procedure, the results obtained by SP-ICP-MS analysis of leachates of different types of coated AgNPs, different AgNPs sizes and different tested soils indicated that silver was dissolved in all cases, except for 75 nm PVP-AgNPs and 100 nm PEG-AgNPs leachates that seem to contain some nanoparticles, due to the presence of some peak pulses above the baseline (Appendix A Fig. S5). Even in these two cases, the number of particles is very small, as can be observed in the histograms (Appendix A Fig. S6). The presence of mainly dissolved silver in all the DTPA leachates

Fig. 4 – SP-ICP-MS histograms and time-resolved signal plots for citrate silver nanoparticles 40 nm (a, b) and 200 nm citrate silver nanoparticles (c, d) from Soil 3 DIN 38414-S4 leachates.

Fig. 5 – SP-ICP-MS time-resolved signal plots for 200 nm citrate silver nanoparticles obtained from DIN 38414-S4 leaching experiments using Soil 1 (a), Soil 2 (b), Soil 3 (c), Soil 4 (d) and Soil 5 (e).

could be due to the complexation capacity of DTPA, which could leach silver ions (Ag^+) strongly attached to soils, as was already observed (Table 2).

3. Conclusions

The interaction of AgNPs with soils and their transformations depend on several factors, including the physicochemical characteristics of the soil, the clay mineralogy, as well as the size and coating of the nanoparticles. The goal of the present work was to study the parameters that control the kinetic adsorption processes of AgNPs, including both those related to soil features and those affected by nanoparticle characteristics. The results showed that cation exchange capacity and electrical conductivity, which are related to soil clay mineralogy, are the main soil features affecting these processes. On the other hand, highly negatively charged citrate-coated AgNPs were retained less than almost neutral polyethyleneglycol-coated AgNPs and negatively charged polyvinylpyrrolidone-coated

AgNPs for most of the soils, organic matter content being one of the factors that hampers their adsorption. Citrate-coated AgNPs of different sizes showed slower retention of smaller nanoparticles (40 nm) than bigger ones (100 and 200 nm) in one of the soils.

Soils were submitted to the leaching procedures 3 weeks after the adsorption process. The results derived from the analysis of the leachates confirmed the low mobility and bioavailability of AgNPs. Only a small fraction of the nanoparticles (<5%) was leached from soils. The smallest nanoparticles used in this work (40 nm) were more easily eluted than larger ones (100 and 200 nm) with DIN 38414-S4, being transformed to soluble forms. It is also interesting to remark that both the capping agent of the nanoparticle and soil physicochemical characteristics seemed to have an effect on the dissolution process of AgNPs. PEG-coated nanoparticles were more easily dissolved than citrate- or PVP-coated ones, and organic matter seemed to stabilize the nanoparticles, avoiding their dissolution. Although this work clarifies some aspects of AgNP adsorption and desorption behavior in soils,

more work is needed in order to completely understand these processes.

Declaration of conflicts of interest

None.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jes.2019.03.018>.

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