

Introduction

The pathway of wastewater combines silver nanoparticles (AgNP) from different sources, e.g. clothes. High quantities of redundant AgNP are removed from wastewater into sludge, which can become incorporated into soil upon sludge amendment. The objectives of the study are:

- to provide a methodical approach to evaluate the mobility of AgNM-300k (polymer stabilized silver nanoparticles, OECD standard, Fig. 1) in soils
- to test the developed method
- to investigate upon the mobility of silver ions (Ag⁺) and AgNM-300k in the same soil samples

Materials and methods

- Adsorption isotherms for Ag⁺ (added as AgNO₃) derived via batch tests (Utermann et al., 2005)

- Batch test by water to soil ratio of 5 l/kg
- Equilibration time 24 h (end over end shaker, 10 rpm)
- Analysis after centrifugation and filtration (0.45 µm)

- Methodical adaption for AgNM-300k

- Substitution of plastic tubes to glass vessel
- H₂O₂/HNO₃ digestion of soil solution

- Analytics of serial dilution and soil solution

- Ag_{total} after digestion via ICP-OES and ICP-MS
- Particle size via Dynamic Light Scattering
- Support by REM and EDX

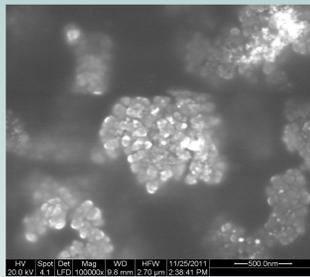


Fig. 1: AgNM-300k after drying

Characterisation of AgNM-300k

- Serial dilution (AgNM-300k, dilution 0.4-15 mg/l) analysed after 24 h batch tests (reference batch without soil material)

- Results are reproducible and indicate high recovery rates of Ag_{total} ranging from 83 % to 89 % (Fig. 2)
- Electric conductivity is low and raises with increasing Ag_{total} content (Fig. 3), pH values are stable over dilution
- Difficulties with particle size measurements due to high polydispersity (average PDI=0.43) and generally if Ag_{total} content is smaller than 1 mg/l (Fig. 4)

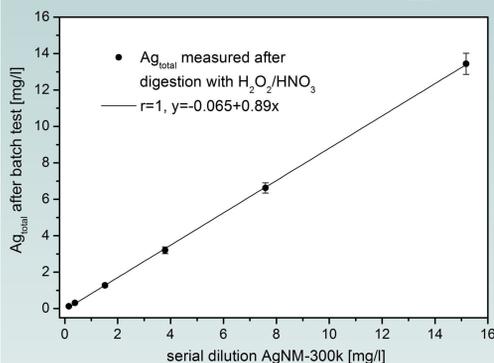


Fig. 2: Ag_{total} recovery after 24 h batch test

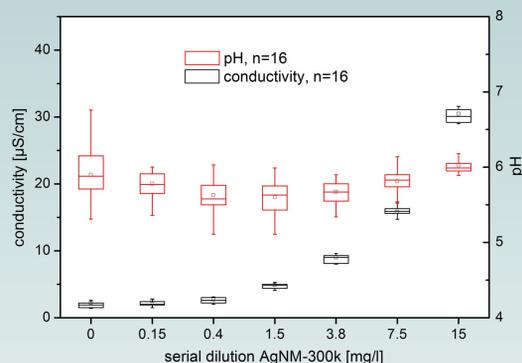


Fig. 3: Conductivity and pH after 24 h batch test

Batch tests with soils

- Repeatable results for analysis with soils and AgNM-300k (Fig. 5)

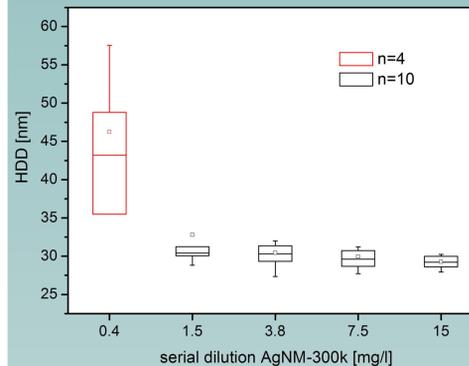


Fig. 4: Particle size (hydrodynamic diameter (HDD) obtained by cumulant analysis) in serial dilution after 24 h batch test

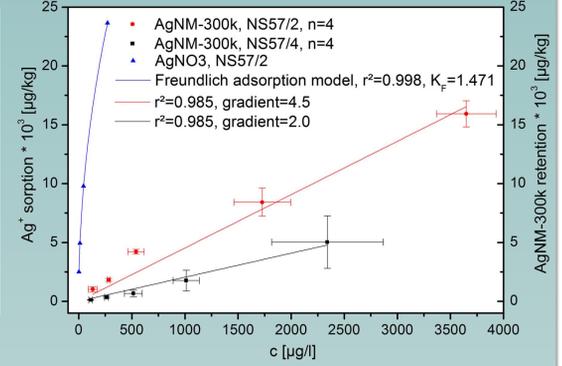


Fig. 5: Topsoil and subsoil of a cambisol tested for adsorption of Ag⁺ and batch retention of AgNM-300k

- Non equilibrium retention of AgNM-300k specified with a linear function, sorption of Ag⁺ specified with the Freundlich model
- High sorption capacity for Ag⁺ in 24 soils, low retention of AgNM-300k in 18 soils (group 1), high retention of AgNM-300k in 6 soils (group 2) (Fig. 6)
- Figure 7 indicates that Ag⁺ sorption is controlled by soil organic matter (SOM), however, also clay content and pH controlling Ag⁺ sorption
- Retention of AgNM-300k shows no statistical relation to SOM and to other soil characteristics like pH and electrical conductivity

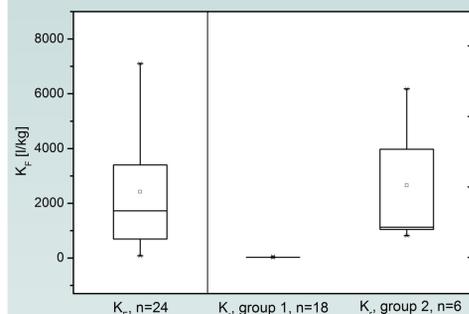


Fig. 6: Boxplots of K_F values for sorption of Ag⁺ (left boxplot), K_d values for retention of AgNM-300k (middle and right boxplot)

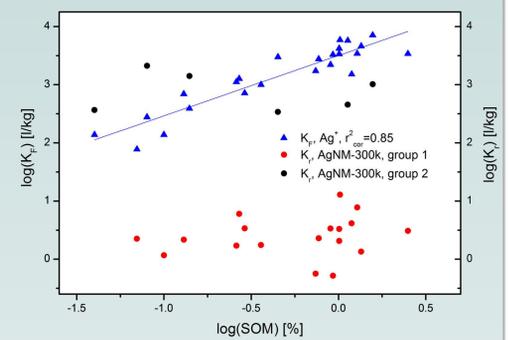


Fig. 7: SOM correlated with K_F values and K_r values

Conclusion

- Method is stable and reproducible for the investigated soils
- Most cropping soils show a small batch retention of AgNM-300k, which is in good agreement with findings conducted by Coutris et al. (2012)
- All topsoil samples show a high sorption capacity for Ag⁺
- Some cropping soils (n=6) show a strong retention of AgNM-300k:
 - in topsoil samples (n=3, pH>7) Ca²⁺ may provoke aggregation
 - in subsoil samples (n=3, pH<5.1) acidity may cause disruption of the surface modifier

References

Coutris, C., Joner, E. J. and Oughton, D. H. Aging and soil organic matter content affect the fate of silver nanoparticles in soil. Science of the Total Environment, 420: 327-333, 2012.
Utermann, J., Meyenburg, G., Altfelder, S., Gäbler, H.-E., Duijnsveld, W., Bahr, A. and Streck, T. Entwicklung eines Verfahrens zur Quantifizierung von Stoffkonzentrationen im Sickerwasser auf der Grundlage chemischer und physikalischer Pedotransferfunktionen. Endbericht, BMBF-Forschungsvorhaben 02WP0206, 2005.

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