Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Supporting Information

Fractionation and preconcentration of silver nanoparticles at environmentally relevant concentrations through induced eco-corona formation and spICP-MS characterization

Aline Martins de Andrade[a], Anerise de Barros[c], Italo Odone Mazali[c], Marco Aurélio Zezzi Arruda[a,b*]

[a] Spectrometry, Sample Preparation and Mechanization Group - GEPAM, Institute of Chemistry, University of Campinas – Unicamp, P.O. Box 6154, Campinas, SP, Brazil, 13083-970
[b] National Institute of Science and Technology for Bioanalytics, Institute of Chemistry, University of Campinas – Unicamp, P.O. Box 6154, Campinas, SP, Brazil, 13083-970
[c] Laboratory of Functional Materials – LMF, Institute of Chemistry, University of Campinas – Unicamp, P.O. Box 6154, Campinas, SP, Brazil, 13083-970
Corresponding author: *zezzi@unicamp.br

Table S1. Operational parameters for spICP-MS analysis.

Operational parameters	
ICP-MS	
Spray chamber	Cyclonic
Nebulizer	MicroMist™
RF Power	1550 W
Cool flow	14 (L min^{-1})
Auxiliary flow	0.8 (L min^{-1})
Nebulizer flow	1 (L min^{-1})
Cones	Sampler e skimmer - Ni
Peristaltic pump	35 rpm
Sample flow rate	0.372 (mL min^{-1})*
spICP-MS	
Analyte	Silver
Isotope (m/z)	$^{107}Ag^{+}$
Density	10.49 g cm^{-3}
Dwell Time	10 ms
Total Acquisition Time	180 s

*Calculated daily, measuring the water taken up by a peristaltic pump within 1 min (N = 3).

Table S2. Physicochemical analysis for river water.

River water analysis	Results	Uncertainty (%)
Total alcalinity (mg L^{-1})	99.0	3.6
Total organic carbon (mg L^{-1})	6.5	-
Conductivity (µs cm^{-1})	255	20
True color (TCU)	12	12
pH	7.3	1.8
Turbidity (NTU)	15.9	3.4
Oxygen consumption (mg L^{-1})	5.8	-

Table S3. Results for ANOVA of the proposed DoE.

ANOVA					
	SS	df	MS	F	p
1 – HA (L+Q)	1670449	2	835225	32.40	0.03
2 – Shaking time (L)	289180	1	289180	11.22	0.08
3 – Centrifugation time (L)	11476	1	11476	0.4	0.6
1 × 2	182106	1	182106	7.1	0.1
1 × 3	55611	1	55611	2.2	0.3
2 × 3	68635	1	68635	2.7	0.2
Lack of fit	66066	1	66066	2.6	0.3
Pure Error	51553	2	25776		
Total SS	2395077	10			

Table S4. Number of detected NPs for each condition evaluated in the DoE experiments.

HA concentration (mg L-1)	Shaking time (min)	Centrifugation time (min)	Number of detected NPs
1	120	10	356
20	120	10	1732
1	360	10	1405
20	360	10	1814
1	120	40	814
20	120	40	1493
1	360	40	1129
20	360	40	1568
10.5	240	25	1640
10.5	240	25	1947
10.5	240	25	1875

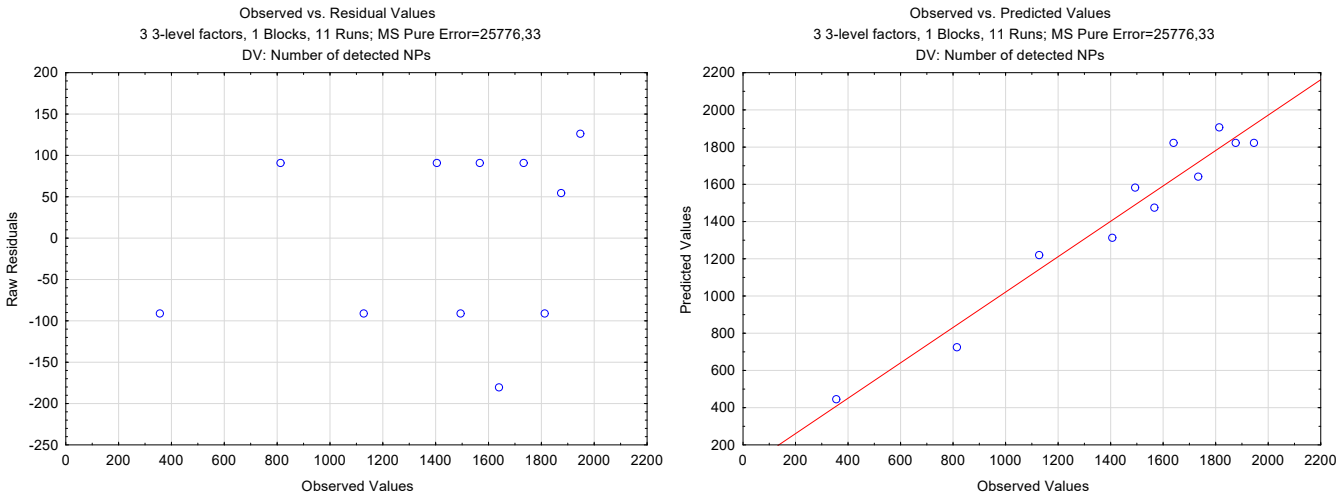

Figure S1. Observed *vs.* Residual values (left) and Observed *vs.* Predicted values (right) of ANOVA results.

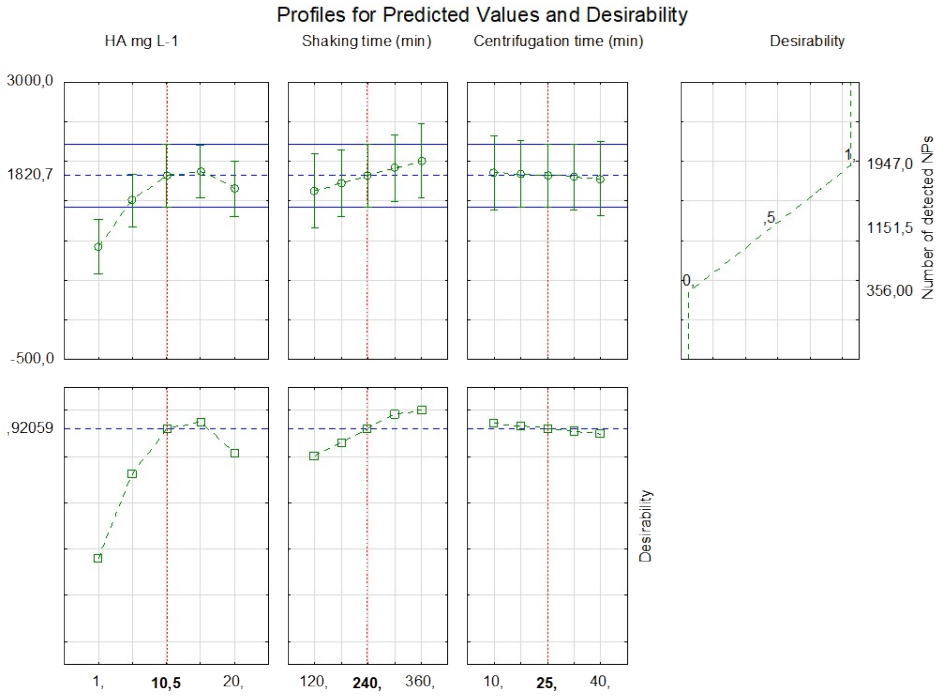

Figure S2. Profile for predicted values and desirability using the ANOVA results. It is possible to notice that the central point is indicated as the suitable condition for the method.

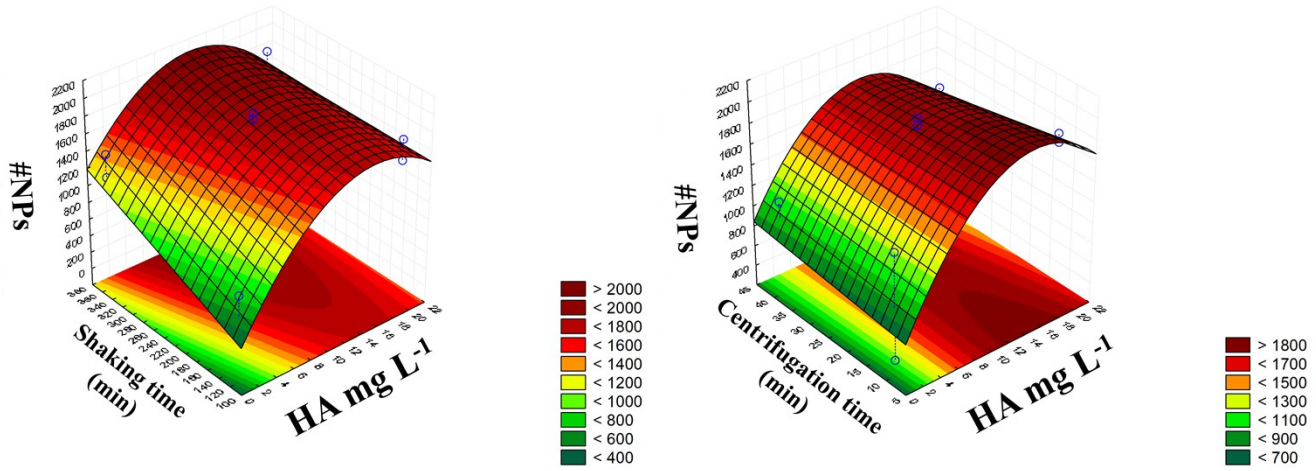

Figure S3. Response surface for ANOVA results obtained with a factorial experiment design (2^3), with humic acid concentration, shaking time, and centrifugation time as factors.

The SEM-FEG using the mode S-TEM is performed by an auxiliary accessory, as illustrated in Figure S4. Figure S4(a) correspond to the sample preparation scheme, and Figure S4(b) correspond to the equipment SEM-FEG250 photo. Figure S4(c) illustrates the holder sample accessory used in the S-TEM and the chamber of microscopy, where the sample is inserted. Figure S4(d) shows a schematic illustration containing the main scanning electron microscopy components. Briefly, an aliquot of 10 µL sample is dropped onto a carbon-copper grid using a micropipette and repeated one more time; then, the sample is dry to room temperature (Figure S4(a)). Then, the grid with AgNPs-HA deposited is allocated to the sample holder, as indicated in Figure S4(c). Subsequently, the chamber is closed, and a pump is pressed to make a vacuum until 8×10^{-3} Pa. The micrographs are then collected. Figure 4(d) corresponds to the schematic illustration of the main components of scanning electron microscopy, in which an electron gun is responsible for ejecting electrons from the tungsten filament and then the electron beam is driven to the sample by the anode and magnetic lens. After the interaction of electrons and the sample, the backscattered electrons are driven to the detector. The micrographs obtained using high-energy backscattered electrons provide different information, i.e. in addition to contrast based on relief, it is possible to obtain contrast based on the atomic number of the chemical elements present in the analysed sample, where the lighter regions of the image represent heavier chemical elements.

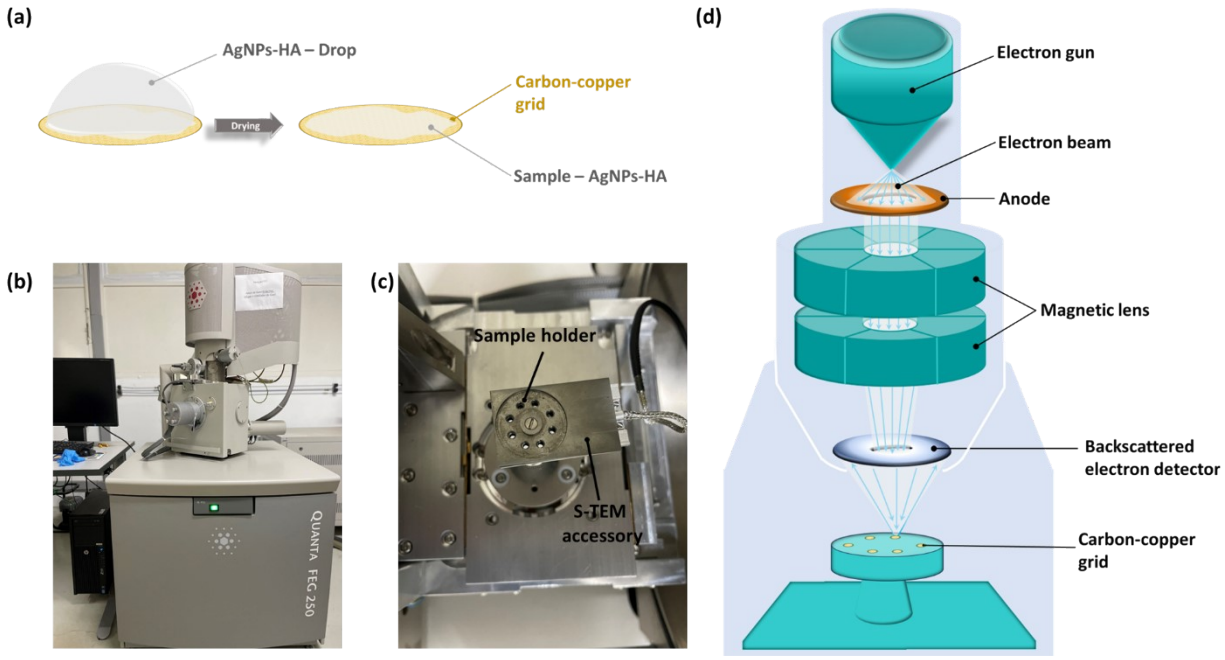

Figure S4. (a) Scheme of AgNPs-HA deposition onto carbon-copper grid; (b) Scanning electron microscopy equipment (SEM); (c) S-TEM auxiliary accessory used as sample holder; (d) schematic representation of SEM components.

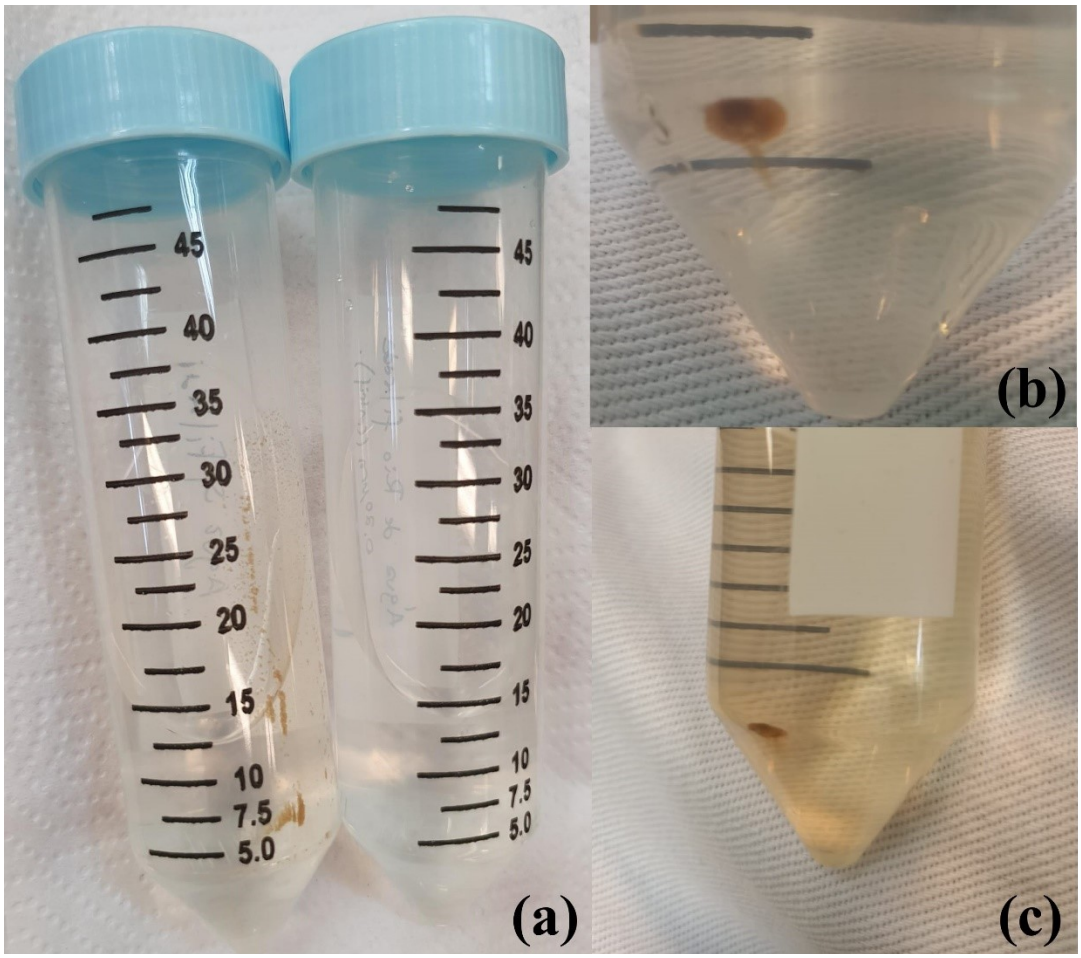

Figure S5. Centrifugation test with river water without AgNPs addition, on left unfiltered, and on right filtered with 0.20 µm (a), river water filtered (0.20 µm) + HA (10.5 mg L^{-1}) (b); and river water filtered (0.20 µm) + AgNPs (8 ng L^{-1}) + HA (10.5 mg L^{-1}) (c). Conditions: 25 min at 14,000 *g* (accel and brake equal to 1).

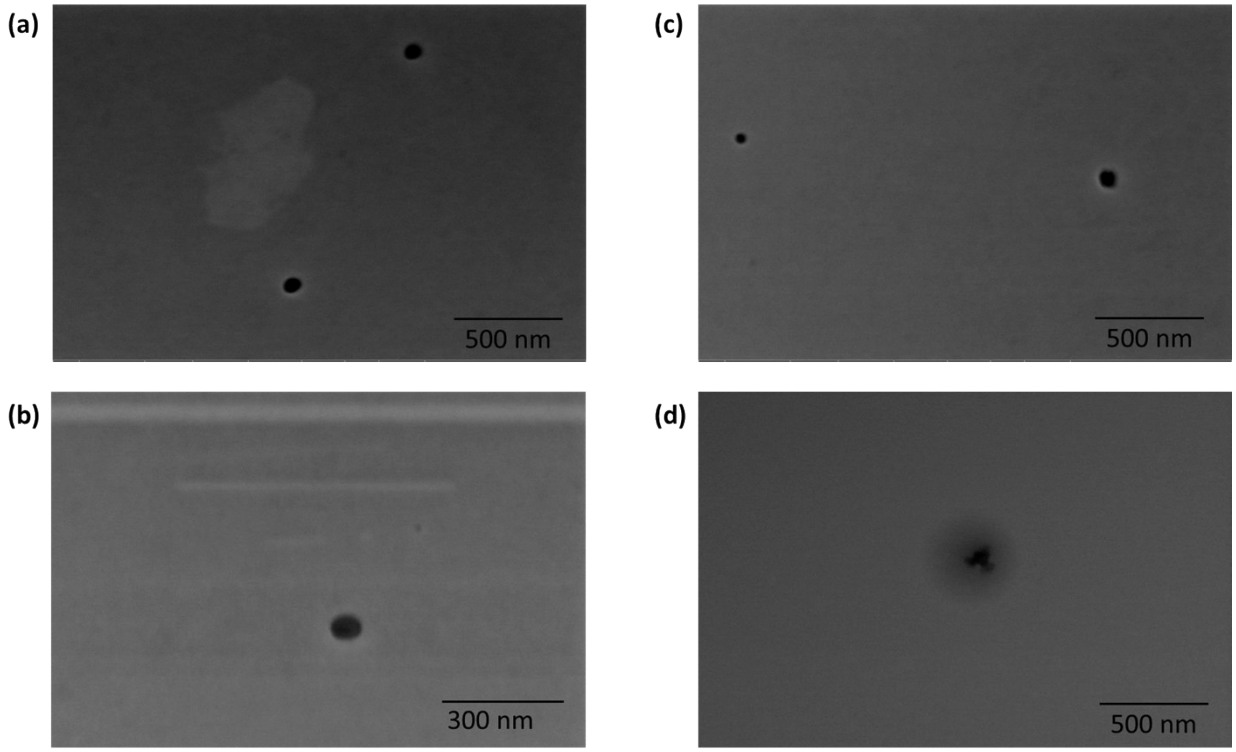

Figure S6. (a-d) S-TEM micrographs of humic acid incorporated on AgNPs in ultrapure water.