water

MDPI

Supporting information

Comparative Study on the Decontamination Efficacy of Peelable Coatings for Heavy Metals Removal

Gabriela Toader [1,†], Daniela Pulpea [1,†], Aurel Diacon [1,2], Edina Rusen [2,*], Raluca Elena Ginghina [3,*], Traian Rotariu [1], Alice Ionela Podaru [1,2], Andreea Elena Moldovan [1], Maria Gavrilescu [4], Ana-Mihaela Gavrila [5] and Bogdan Trica [5]

[1] Military Technical Academy "Ferdinand I", 39-49 George Cosbuc Boulevard, 050141 Bucharest, Romania
[2] Faculty of Chemical Engineering and Biotechnologies, University' POLITEHNICA' of Bucharest, 1-7 Gh. Polizu Street, 011061 Bucharest, Romania
[3] Research and Innovation Center for CBRN Defense and Ecology, 225 Oltenitei Ave., 041327 Bucharest, Romania
[4] Department of Environmental Engineering and Management, Faculty of Chemical Engineering and Environmental Protection, Gheorghe Asachi Technical University of Iasi, 700050 Iasi, Romania
[5] National Institute for Research & Development in Chemistry and Petrochemistry ICECHIM, Advanced Polymer Materials and Polymer Recycling Group, Spl. Independentei 202, 6th District, 060021 Bucharest, Romania
* Correspondence: edina.rusen@upb.ro (E.R.); ginghinaraluca@gmail.com (R.E.G.).
† These authors contributed equally to this work.

Materials and Methods

Materials

For AAS and ICP-MS analyses, the following reagents were employed: Double deionized water (Milli-Q Millipore, 18,2 MΩ cm resistivity at 25°C, Merck, Rahway, New Jersey, United States) was used for dilutions, Single component standard solutions suitable for ICP-MS calibrations (from Merck, Rahway, New Jersey, United States): Copper Standard for ICP-MS Trace**CERT**® (1000 mg/L), Antimony Standard for ICP-MS Trace**CERT**® (1000 mg/L), Zinc Standard for ICP-MS Trace**CERT**® (1000 mg/L), Strontium Standard for ICP-MS Trace**CERT**® (1000 mg/L), Lead Standard for ICP-MS Trace**CERT**® (1000 mg/L), Cobalt Standard for ICP-MS Trace**CERT**® (1000 mg/L), Mercury Standard for ICP-MS Trace**CERT**® (1000 mg/L). Single component standard solutions suitable for AAS calibrations (from Sigma-Aldrich, St. Louis, Missouri, United States): Copper Standard for AAS Trace**CERT**® (1000 mg/L), Antimony Standard for AAS Trace**CERT**® (1000 mg/L), Zinc Standard for AAS Trace**CERT**® (1000 mg/L), Strontium Standard for AAS Trace**CERT**® (1000 mg/L), Lead Standard for AAS Trace**CERT**® (1000 mg/L), Cobalt Standard for AAS Trace**CERT**® (1000 mg/L), Mercury Standard for AAS Trace**CERT**® (1000 mg/L). Stainless steel coupons (20 mm × 50 mm × 0.4 mm, 18/8 stainless steel) were utilized for decontamination experiments.

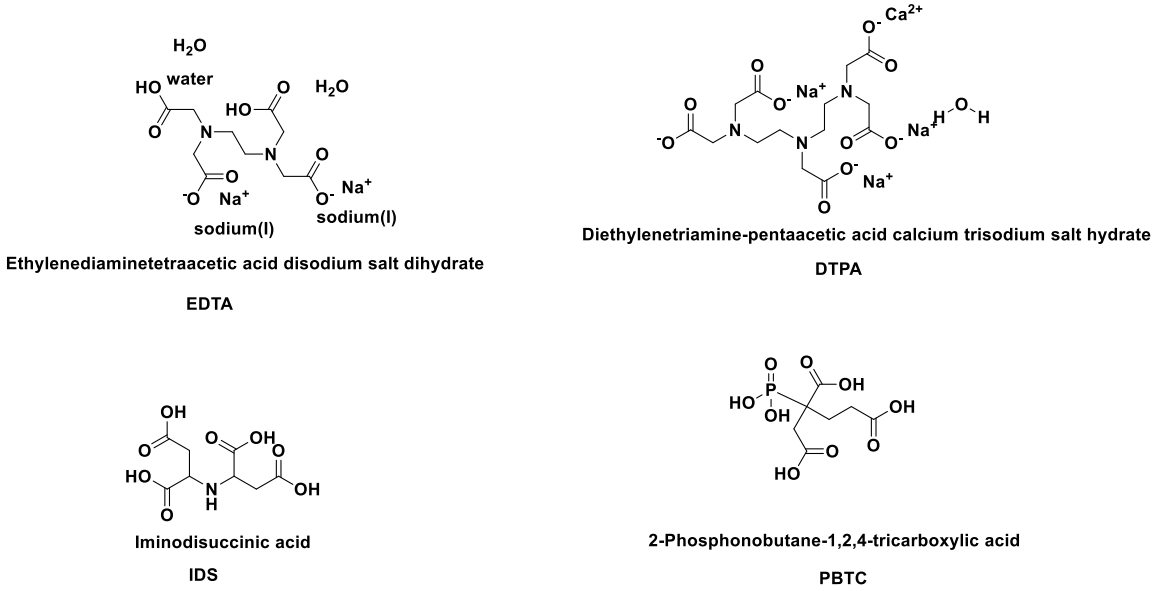

Figure S1. *Chemical structures of the chelating agents used in the study*

Methods

Characterization

SEM imaging was acquired by using a Tescan Vega II LMU microscope. Elemental mapping was assessed by EDX technique (Bruker Quantax XFlash 6/10 energy dispersive X-ray). Before SEM-EDX analysis, the samples were sputter-coated with a thin layer of Au/Pd (80/20) under Argon plasma.
TEM-EDX imaging of the silver nanoparticles was obtained with a TECNAI F30 G2STWIN instrument, Fei Company, Oregon, USA, at 300 kV acceleration voltage and 1 Å resolution.
An atomic absorption spectrometer PerkinElmer AAnalyst™ 800 (Waltham, MA, USA), was utilized to evaluate the removal efficiency for HMs. This instrument is provided with WinLab32 software (Perkin Elmer, Waltham, MA, USA) for AA. External standard calibrations were performed for Cu, Sb, Zn, Sr, Pb, Co, and Hg as follows: standard solution preparation, acquiring analytical signals, and specific mathematical calculations [1]. Finally, all the samples collected from the decontaminated surfaces were subjected to successive dilutions and filtrations steps and subjected to AAS analysis. Triplicate analyses were conducted to reduce uncertainty (discrepancies due to the human factor, dilutions, filtrations, instrument, etc.), and the measured average value was reported.
ICP-MS analysis was performed utilizing a PerkinElmer SCIEX - ELAN® DRC-e instrument supplied with Dynamic Reaction Cell™ (DRC™) technology that eliminates polyatomic interferences. The Smart-Tune™ wizard automatically adjusts the vital operating parameters for optimum performance. An auto-optimization process was used to adjust argon flows, the RF power, the torch position, the lenses, the mirror, and the detector voltages. Nebulizer argon (flow 0.9 L/min) directs the sample through the center of the plasma. The argon plasma (15 L/min), between the outer and intermediate quartz tubes; Auxiliary argon (1.2 L/min), between the outer and intermediate tubes of the torch; RF power - 1.55 kW; Gas flow rates: H_2 - 90 mL/min, He - 120 mL/min, Ar - 10 mL/min; Mixed standard solutions containing the following seven elements: Cu, Sb, Zn, Sr, Pb, Co, and Hg were prepared as blank reagent solutions. The interferences were corrected by subtraction of blank signals. After suitable dilution, the solutions obtained from the samples collected from the decontaminated surfaces were analyzed by ICP-MS with external standards for calibration, which considered five points on the curve and one for quality control. Scandium (^{45}Sc), rhodium (^{103}Rh), and rhenium (^{185}Re) served as internal standards.
UV-Vis spectrums of the pristine colloidal silver nanoparticles and Hg(II) – AgNPs solutions were collected in the 300 – 800 nm range, with a resolution of 5 nm, using a GBC Cintra 101 UV-Vis

spectrophotometer with Cintra Software. The same dilution for the AgNPs was ensured for each measurement.

1. Carter, J.A.; Barros, A.I.; Nóbrega, J.A.; Donati, G.L. Traditional Calibration Methods in Atomic Spectrometry and New Calibration Strategies for Inductively Coupled Plasma Mass Spectrometry. *Frontiers in Chemistry* **2018**, *6*, doi:10.3389/fchem.2018.00504.