



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

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Abstract: This study presents the formulation and application of strippable coatings for the entrapment and removal of heavy metals (HMs) and radio nuclides (RNs). The "green" formulations involve the use of a water-based solution consisting of a synthetic biodegradable polymer, polyvinyl alcohol (PVA), together with a natural polymer (sodium alginate) as the polymer matrix and bentonite as the reinforcing agent with cation exchange capacity. Four chelating agents comprising two classical chelating agents (ethylenediaminetetraacetic acid (EDTA), diethylenetriamine-pentaacetic acid (DPTA)) and two "green" chelating agents (iminodisuccinic acid (IDS), 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC)) were used to evaluate the capacity to remove Cu, Sb, Zn, Sr, Pb, Co, and Hg from the contaminated surfaces. This decontamination method leads to the formation of a solid waste, thus eliminating the need for wastewater treatment. Atomic absorption spectroscopy (AAS), inductively coupled plasma mass spectrometry (ICP-MS), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX), and ultraviolet-visible (UV–Vis) spectroscopy were used to comparatively evaluate the decontamination efficacy. EDX elemental mapping confirmed the entrapment of the contaminants inside the polymeric matrix.

Keywords: decontamination; heavy metals; polymer film; peelable; nanoparticles

# 1. Introduction

Heavy metals (HMs) and radionuclides (RNs) are among the most dangerous, cytotoxic, mutagenic, and carcinogenic contaminants [1]. Modernization and increased industrial activity have caused an increase in the levels of radioactive and toxic metals in the environment. Significant contamination problems have resulted from using RNs or HMs in various industries including the chemical industry, nuclear industry (e.g., nuclear power plants), extractive industries (e.g., mining activities), medicine (e.g., radiotherapy and diagnosis), or the defense and security industries (e.g., manufacturing and loading of ammunition, explosives, firing shooting ranges). Mining-related RN or HM materials can be present in windblown dust. Inhaling these RNs or HMs from dust harms the cells and tissues. <sup>60</sup>Co is utilized for radiotherapy as well as for sterilization processes, while <sup>90</sup>Sr is found in the environment due to nuclear reactor waste, but it is also employed in medicine and industry [2,3]. High concentrations of HMs have been found in shooting ranges, or



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). explosives and ammunition factories due to the decomposition of materials such as mercury fulminate, lead azide, lead styphnate, or other explosives found in the composition of primers and detonators [4,5]. In shooting ranges, lead particles as well as dust and fumes from the lead primer and the fragments of bullets are ejected at high pressure from the gun barrel straight next to the shooter [6]. Consequently, small particles settle out around the firing weapon. Some metals released by firing might have particle sizes in the nanoscale range [5,7,8]. The proximal exposure pathway is through inhalation by the shooter of fine Pb particulates, primarily from the primer. Another route for lead exposure is through the fine and coarse particulates that adhere to the shooter's hands, clothing, and other surfaces from the primer and bullet fragments [6,7]. The utilization of ammunition may also result in high concentrations of other metals and metalloids including copper, antimony, zinc, and arsenic, which could also have adverse health effects [5]. Lead (Pb) and antimony (Sb), two of the metallic components involved, emerge from the bullet, while barium (Ba) and Sb can appear from the primer ignition. Other metals from the case alloys such as copper (Cu), zinc (Zn), and aluminum (Al) are widely used and may result in firing residues. Due to its low environmental abundance, the Sb is thought to be the best firing residue indicator [7].

Thus, anthropogenic RNs and HMs in the environment are mainly related to human activity [9]. Heavy metals can bioaccumulate and enter the food chain because organisms easily absorb them [10]. Eline Vandebroek et al. reported that lead and antimony, both present in ammunition, were found to be in elevated concentrations in the urine and blood of Special Forces staff who participated in weekly shooting training sessions as well as the instructors and maintenance personnel [5]. The central nervous system and kidneys are two organs that may be particularly affected by occupational exposure to mercury (Hg). Skin contact and respiratory systems are potential exposure sources [11].

In the eventuality of contamination incidents, two main paths are involved: detection and identification of the contaminant and decontamination.

For identification of the metallic contaminants, various spectrometric techniques are utilized including FAAS (flame atomic absorption spectrometry), ICP-OES (inductively coupled plasma optical emission spectroscopy), ICP-MS (inductively coupled plasma mass spectrometry), ETA-AS (electrothermal atomic absorption spectrometry), etc. [7]. Many benefits may arise from the sector field inductively coupled plasma mass spectrometer (SF-HR-ICP-MS), which offers a wide dynamic linear range, multi-element evaluation functionality, and remarkably low detection limits [7].

Highly selective detection and UV–VIS monitoring of mercuric ions in aqueous solutions can be achieved by a colorimetric method, which implies the use of a colloidal silver nanoparticle solution (AgNP) [12,13]. The shape of the nanoparticles significantly impacts the absorption and the color of the colloidal solution, potentially influencing the design of new colorimetric sensors [14].

Since long-term exposure to these dangerous materials (RNs or HMs) can cause severe health and safety issues, minimizing the amount of time spent in contaminated areas is imperative. Furthermore, finding a rapid and effective technique to entrap and remove RN and HM contaminants to limit personnel exposure is crucial. The decontamination methods employed for removing RNs and HMs depend on the type of contaminated substrate (e.g., water, soil, solid surfaces, air decontamination, etc.). For the decontamination of solid surfaces, various techniques are available, mainly consisting of washing formulations [15,16]. Even if it may seem to be the most uncomplicated, removing metallic impurities from solid substrates using liquid media [15] and validating the complete removal of the contaminant may prove challenging.

The advantage of using peelable coatings for surface decontamination resides in the generation of solid waste, which reduces secondary cross-contaminations and its elimination is straightforward [17–19]. The washing procedures can lead to cross-contaminations and generate larger volumes of waste water that require treatment. Thus, through this method, water serves as a delivery medium for the polymer matrix and chelating agents

and by its evaporation, a solid polymer film residue containing the contaminants is formed and no waste water treatment is required.

Poly(vinyl alcohol) (PVA) is a water soluble synthetic polymer that is biodegradable under both aerobic and anaerobic conditions [19–21]. PVA is widely used for the fabrication of plastic items and as an additive in the paper, wood, tannery, paint, and coatings industries. Additionally, PVA has found significant application in agriculture related applications where its application leads to disposal in the soil ecosystems [20]. Sodium alginate is a biodegradable polysaccharide polymer obtained from marine brown algae. It is comprised of  $\alpha$ -D-mannuronic acid and  $\beta$ -L-guluronic acid units [22,23]. The presence of the carboxyl groups permits the chelation of metal cations and leads to a pH-dependent drug release capacity [24]. Sodium alginate has found application in the food additives [25], cosmetics, pharmaceutic [26], paint, and coatings industries [27].

The aim of this paper consisted of the utilization of multiple analytical methods (including a facile UV–Vis screening method employing silver nanoparticles and SEM-EDX) to demonstrate and evaluate the decontamination efficacy of dual-action innovative water-based strippable coatings designed to remove heavy metal contamination from various types of surfaces from firing ranges or specialized laboratories (indoor shooting ranges floors, walls, targets, workbenches, etc.). These "smart" coatings comprise a water-soluble film-forming polymer, a chelating agent that forms stable complexes with heavy metals/radionuclides, a hydrophilic nanoclay, and a plasticizer that ensures the flexibility required for the exfoliation of the polymeric coating. The nanoclay is an adsorbent for the contaminant and acts as a reinforcing agent for the resulting coating.

Our previous studies described the influence of each distinct component (polymeric matrix, nanoclay, chelating agent) of these formulations on the decontamination performances [4,16,28]. The results were then correlated with the data obtained by AAS and ICP-MS. We showed that the interaction of AgNPs with mercuric ions reduced the UV–Vis signal of the colloidal AgNP solution, allowing the colorimetric detection of mercuric ions and their quantification by monitoring the resulting blue shifts. Finally, the maximum of the AgNP absorbance peak and Hg concentration were found to be linearly and inversely proportional [12] in the range of 2.4 ppm–28.3 ppm Hg, which helps estimate the decontamination efficacy of Hg.

Each analytical method utilized in this study to evaluate the decontamination efficacy of "green" strippable coatings for Cu, Sb, Zn, Sr, Pb, Co, and Hg has its particularities, advantages, and limitations.

#### 2. Materials and Methods

#### 2.1. Materials

Poly(vinyl alcohol) (PVA, 98–99% hydrolysis degree, DP  $\approx$  1700–1800, Mw  $\approx$  115,000 Da, Loba Chemie, Mumbai, India), sodium alginate (Alg, Special Ingredients®, Garlenda, Savona, Italy), ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA, for analysis, ACS reagent, Sigma Aldrich, St. Louis, MO, USA), diethylenetriamine-pentaacetic acid calcium trisodium salt hydrate (DTPA, 97.0%, Sigma Aldrich, St. Louis, MO, USA), iminodisuccinic acid (IDS, BAYPURE® CX 100 solid G, Lanxess, Cologne, Germany), 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC, BAYHIBIT® AM, Lanxess, Cologne, Germany) (see Figure S1 for the chemical structures), bentonite (BT, nanoclay, hydrophilic bentonite, Nanomer<sup>®</sup> PGV, Sigma Aldrich, St. Louis, MO, USA), glycerol (Gly, anhydrous for synthesis, Sigma Aldrich, St. Louis, MO, USA), silver nitrate (299.0%, Sigma Aldrich, St. Louis, MO, USA), tri-sodium citrate dihydrate (Sigma Aldrich, St. Louis, MO, USA), sodium borohydride (299.0%, Sigma Aldrich, St. Louis, MO, USA), and mercury(II) chloride (ACS reagent,  $\geq$ 99.5%, Sigma Aldrich, St. Louis, MO, USA) were used as received. The HAc-NaAc buffer (pH 5.6) was prepared from sodium acetate (ACS reagent,  $\geq$ 99.0%, Sigma Aldrich, St. Louis, MO, USA) and acetic acid (glacial, ACS reagent, ≥99.7%, Sigma Aldrich, St. Louis, MO, USA).

# 2.2. Methods2.2.1. SynthesisDecontamination Solution Synthesis

The water-based decontamination solutions, designed for the entrapment and removal of heavy metal contaminants, were synthesized through these sequential steps: the first step consisted of the dissolution of the chelating agents (EDTA, DTPA, PBTC, or IDS) in double-distilled water, followed by the dispersion of the hydrophilic bentonite nanoclay with an ultrasonic processor (Sonics<sup>®</sup> Vibracell VCX750W). The following step consisted of the dissolution of PVA and Alg, at 60 °C, with the aid of a high-speed dispersing instrument (IKA T18 digital ULTRA-TURRAX<sup>®</sup>) set at 15,000 rpm. The addition of glycerol was the final step, followed by another 30 min of magnetic stirring. Thus, we obtained four distinct decontaminating formulations with the compositions indicated in Table 1.

Sample Code	Chelating Agent [wt.%]	PVA [wt.%]	Alg [wt.%]	BT [wt.%]	Gly [wt.%]
DS1—EDTA	1	5	0.7	1	3
DS2—DTPA	1	5	0.7	1	3
DS3—PBTC	1	5	0.7	1	3
DS4—IDS	1	5	0.7	1	3

Table 1. Formulation of the decontamination solutions.

Silver Nanoparticles (AgNPs) Synthesis

Silver nanoparticles (AgNPs) were prepared according to [13,29]. A trisodium citrate solution (5 wt.%, 2 mL) was added to a silver nitrate solution (0.5 mM AgNO<sub>3</sub>, 100 mL). This solution was maintained under vigorous stirring with an ultrasonic liquid processor (Sonics, Vibra-cell<sup>TM</sup>, 750 Watts), and a sodium borohydride diluted solution (0.1 wt.%, 2 mL) was subsequently added. The solution was maintained for another 15 min under vigorous stirring (with the above-mentioned ultrasonic liquid processor) and one hour under magnetic stirring at 80 °C. The nanoparticles obtained were stored overnight in a refrigerator (4 °C).

# 2.2.2. Controlled Contamination Procedure

The working protocol for the controlled contamination followed the basic principles of NATO Standard—AEP-58—Combined operational characteristics, technical specifications, test procedures, and evaluation criteria for chemical, biological, radiological, and nuclear decontamination equipment [30]. Stainless steel coupons were subjected to controlled contamination. Each metallic coupon was contaminated with 1 mL stock solution, placed in the middle of the plate, leading to a uniform distribution due to the wetting properties of the formulation. The stock solution contains a blend of all the heavy metal (HM) solutions: Cu, Sb, Zn, Sr, Pb, Co, and Hg (c<sub>HM</sub> = 1000 mg/L). Contamination was performed in triplicate for each type of solution. In addition, for the UV–Vis investigations on the efficacy of Hg removal, two supplementary concentrations were employed for contamination ( $c_{Hg} = 2 \text{ g/L}$  and  $c_{Hg} = 3 \text{ g/L}$ ). Sr and Co served as simulants for the radioactive isotopes <sup>90</sup>Sr and <sup>60</sup>Co. The other metallic species used in this study were selected because they are the most frequently encountered contaminants generated in shooting ranges. The contaminated metallic coupons were placed in an oven (40 °C) overnight.

#### 2.2.3. Decontamination Procedure

Every stainless-steel coupon was placed on a different Petri dish for the decontamination procedure. Successively, the decontamination solution was poured onto the contaminated surface. The decontaminating aqueous formulations covered each metallic plate entirely. The samples were allowed to dry overnight at room temperature. The next day, the strippable nanocomposite coatings obtained were gently removed by peeling. The decontaminated surfaces were subsequently introduced in 100 mL of double-deionized water and placed in an ultrasonic bath for 30 min. These were further subjected to successive dilutions, following the specific requirements of the analytical methods (AAS, ICP-MS, UV–Vis) employed to evaluate the remnant HMs. Experiments were performed in triplicate, and the mean values were reported.

#### 2.2.4. Evaluation of the Decontamination Efficacy

The decontamination efficacy (DE<sub>HM</sub>[%]) was calculated according to the following formula: DE<sub>HM</sub>[%] =  $100 \times (c_0 - c_f)/c_0$ , where  $c_0$  represents the initial concentration of the contaminant placed on the stainless steel coupons and  $c_f$  stands for the final concentration of HMs found on the decontaminated plate. In addition, the peeled nanocomposite films were subjected to SEM-EDX to demonstrate the presence of the contaminants inside the polymeric film.

#### 3. Results and Discussion

# 3.1. Basic Principles of HM/RN Decontamination with Nanocomposite Peelable Coatings

Decontamination is defined as the process of removing hazardous materials from contaminated surfaces to reduce local or systemic exposure to a contaminant [31]. Among the existent decontamination methods designed for contaminated surfaces, peelable coatings present multiple advantages in removing the HMs/RNs: they can incorporate chelators, it is an affordable method of decontamination, it is a fast method, the film-forming blends can be easily applied on larges surfaces, they may ensure high decontaminations efficiencies, etc. [32]. Figure 1 explains the basic principles of a decontamination process involving nanocomposite peelable coatings. As illustrated in Figure 1, this decontamination method implies first (1) applying a liquid solution comprising active ingredients on the contaminated surface; (2) allowing it to interact with the contaminants while curing; (3) removing the polymeric film after the complete evaporation of the solvent; (4) re-establishing the operability of the decontaminated surface; and (5) securely disposing of the small amount waste generated by this process.



Figure 1. Basic principles of a decontamination process involving nanocomposite peelable coatings.

# 3.2. Decontamination Mechanism Analysis

In this study, besides the polymeric matrix, bentonite and distinct chelating agents were introduced in the decontamination formulations under investigation. When the chelating agent and the nanoclay were combined in the same decontamination solution, the contaminant was more likely to be retained in the polymeric composite coating due to the following two distinct routes: chemical interaction (complexation) and physical interaction (adsorption), respectively.

The bentonite employed in this study was a hydrophilic layered nanoclay composed of octahedral sheets sandwiched between two tetrahedral silica sheets (Figure 2). Bentonite has a net negative surface charge, which allows for a higher yield of cation removal (Figure 2) [33]. In addition, bentonite was selected for this application because of its small particle sizes and because it possesses one of the largest internal and external surface areas for cation exchange (Figure 2) among mineral clays [33].



**Figure 2.** Cation exchange steps: (1) Bentonite before hydration; (2) swelling of bentonite; (3) hydration of the exchangeable cations; (4) the contaminant replaces the interlayer exchangeable cations.

Even if bentonite enhances the decontamination efficacy [4], chelating agents are essential [16] in the decontamination of metallic species (HMs or RNs). Figure 3 illustrates a typical complexation scheme executed by one of the chelating agents employed in this study (EDTA). The other chelating agents (DTPA, PBTC, IDS) used in this study exhibited analogous complexation mechanisms (Figure S1).



**Figure 3.** Schematic illustration of the interaction of the heavy metal cation and EDTA chelating agent.

The chelating ability of sodium alginate is also a factor that may positively influence the decontamination performances. However, the influence of sodium alginate on the decontamination efficacy is still not as visible as the one with the chelating agents or bentonite [29,34]. Nevertheless, the alginate aids by improving the mechanical properties of the peelable film.

# 3.3. SEM—EDX

SEM-EDX analysis was employed to investigate the morphology of the strippable polymeric nanocomposite films and to evaluate the entrapment of the contaminants (HMs) inside these films. As can be observed from Figures 4–8, the nanocomposite polymeric films exhibited a relatively flat surface and a slightly porous inner structure. The EDX mapping revealed the presence of the HM contaminants inside the polymeric matrix. The back-side view shown is the part of the polymeric film, which was in direct contact with the heavy metals, and EDX displayed their homogeneous distribution along the coating. The cross-section view offers evidence of the in-depth entrapment of the contaminants inside the polymeric matrix and also a uniform distribution of the contaminants along the cross-section. Thus, all of the metallic elements captured by the nanocomposite coating were visible in the cross-section view of the EDX-mapping. However, it is worth mentioning that no significant differences in the distribution of the entrapped elements were observed when changing the chelating agents. This means that all the chelating agents were uniformly distributed in the polymer matrix.



**Figure 4.** SEM-EDX survey of the strippable coating (DS4) after removal (back-side view). (**a**) SEM image of the peeled coating; (**b**) EDX mapping of the peeled coating; (**c**) energy dispersive X-ray analysis (EDX) spectrum.



Sb

Figure 5. Cont.



**Figure 5.** EDX mapping of the elements entrapped inside the polymeric strippable coating DS4 (back-side view).



**Figure 6.** SEM image of the peeled coating (DS4, cross-section view) employed for Cu, Sb, Zn, Sr, Pb, and Co decontamination.



**Figure 7.** SEM-EDX survey of the strippable coating (DS4) after removal (cross-section view): (**a**) SEM image of the peeled coating; (**b**) EDX mapping of the peeled coating; (**c**) energy dispersive X-ray analysis (EDX) spectrum.



SD

Figure 8. Cont.



**Figure 8.** EDX mapping of the elements entrapped inside the polymeric strippable coating (DS4, cross-section).

Thus, this first type of investigation confirms the entrapment of the contaminants. Still, it is essential to highlight that the SEM-EDX method was only used as a qualitative screening method. The data obtained via SEM-EDX was valuable as an initial stage in this research.

# 3.4. AAS

Supplementary investigations, with higher accuracy, were further used to quantify the contamination/decontamination efficacies, established following the guidelines in NATO Standard AEP-58 [30]. The concentration of heavy metals before and after decontamination was calculated using atomic adsorption spectrometry (AAS). The decontamination efficacy of each solution for each metal was assessed using the information obtained from the AAS analysis (Figure 9). The concentration of residual metal cations found on the decontaminated surface (Figure 9a) was correlated with the initial concentration of each contaminant, thus obtaining decontamination efficacies in the range of 99.3–99.5% (Figure 9b). According to the AAS results, two of the most notorious heavy metals, lead and mercury, were more efficiently removed by the decontaminating formulations containing EDTA or PBTC. The solution containing DTPA exhibited the lowest decontamination efficacies (DE > 99.4%) for all the HM tested. In the case of Sr and Co, the two elements employed as simulants for the <sup>90</sup>Sr and <sup>60</sup>Co radionuclides, two of the chelating agents, EDTA and IDS, provided the best results for Sr. In contrast, PBTC and IDS supplied the best results for Co.



Figure 9. AAS assessment of the decontamination efficiency.

#### 3.5. ICP-MS

ICP-MS was employed as a complementary investigation to evaluate decontamination efficacy with higher accuracy. AAS is considered less accurate, less beneficial, and extra time-consuming, but far more cost-effective than the ICP-MS technique. AAS is less expensive than ICP-MS, but it can only evaluate the concentration of the elements one by one. To measure multiple atoms, ICP-MS is more accurate, advantageous, faster, and far less time-consuming [35]. However, ICP-MS is not as cost-effective as AAS. Figure 10 illustrates the results obtained from the ICP-MS investigations. The pattern of the decontamination efficiencies was relatively similar for analogous samples, however, higher values for DE were obtained when employing the ICP-MS technique (99.4–99.8%). According to the ICP-MS analysis, for each type of chelating agent used, the decontamination efficiency was the highest for Sr. Almost all of the results obtained via ICP-MS are in accordance with the ones obtained via the AAS technique. Still, few discrepancies appeared for Hg and Pb for DS1-EDTA and DS2-DTPA, respectively.



Figure 10. ICP-MS assessment of the decontamination efficiency.

#### 3.6. Silver Nanoparticles Characterization

Before the UV–Vis investigations, colloidal silver nanoparticles were obtained and characterized. Thus, the formation of spherical nanosized silver particles was confirmed via TEM-EDX analysis (Figure 11).

The color of the colloidal solutions is influenced by the shape and dimension of the nanoparticles [14]. Usually, the mean size of the spherical particles in yellow solutions, with UV–Vis absorbance maxima in the range of 380–420 nm, is approximately 25 nm [14]. TEM analysis revealed that the AgNPs synthesized for the UV–Vis survey described below had a mean diameter of approximately 25 nm.



Figure 11. Silver nanoparticles (AgNPs)—TEM image and EDX spectrum.

# 3.7. UV-Vis

The last analytical technique employed for the comparative evaluation of the decontamination efficacy was UV–Vis spectroscopy. This method implies using a colloidal AgNP solution to quantify the decontamination performances for Hg. UV–Vis is highly selective for Hg detection via AgNPs [13]; thus, the results calculated from the UV–Vis data imply only Hg contamination/decontamination. Therefore, after their synthesis (as described in the *Synthesis* Section 2.2.1), colloidal AgNPs were subjected to UV–Vis scans, displaying a typical peak around 410 nm. In addition, 300 µL of HAc-NaAc buffer (pH 5.6), an appropriate amount of distilled water, a different volume of Hg solution, and 390 µL of AgNP solution were introduced via a 5 mL centrifuge tube (the combined solution had a total volume of 3 mL). Since Hg (II) ions can interact with the AgNP solution prepared by sodium borohydride, this led to visible changes in the UV–Vis spectra (Figure 12). One explanation could be that the remnant sodium borohydride from the AgNP colloidal solutions could also reduce Hg(II) to Hg (0). These mercury atoms may cover the surface of the silver nanoparticles, generating an aggregate [13], thus leading to a blue shift of the maximum in the UV–Vis peaks (Figures 12 and 13).



**Figure 12.** UV–VIS for the AgNP colloidal solutions—blue-shift with the gradual addition of Hg: (1) 0 ppm Hg; (2) 1.18 ppm Hg; (3) 2.37 ppm Hg; (4) 4.71 ppm Hg; (5) 7.08 ppm Hg; (6) 9.45 ppm Hg; (7) 23.67 ppm Hg; (8) 25.87 ppm Hg; (9) 28.28 ppm Hg; (10) 30.69 ppm Hg; (11) 32.89 ppm Hg; (12) 33.10 ppm Hg; (13) 35.30 ppm Hg.



**Figure 13.** Image illustrating the color change in accordance with the absorption spectra of AgNPs in the absence and the presence of Hg(II) (1) 0 ppm Hg; (2) 1.18 ppm Hg; (3) 2.37 ppm Hg; (4) 4.71 ppm Hg; (5) 7.08 ppm Hg; (6) 9.45 ppm Hg; (7) 23.67 ppm Hg; (8) 25.87 ppm Hg; (9) 28.28 ppm Hg; (10) 30.69 ppm Hg; (11) 32.89 ppm Hg; (12) 33.10 ppm Hg; (13) 35.30 ppm Hg.

Therefore, based on these UV–Vis assays, we intended to find a cost-effective, fast, simple, and highly selective method to evaluate the decontamination efficiency for Hg. The intensity of the AgNP absorption peak observed was interdependent of the concentration of Hg added. Different concentrations of mercury were blended with a constant amount of nanoparticles to obtain an absorption intensity dependent on the Ag nanoparticles versus Hg concentration. A linear and inversely proportional relationship was found between the absorbance intensity of the Ag nanoparticles and the concentration of Hg(II) ions over the range from 2.4 ppm to 28.3 ppm. Thus, this method is not suitable at concentrations of Hg higher than 28 ppm due to the diminution of the AgNP peak until its complete disappearance. Thus, the concentration of Hg in the samples collected from the decontaminated surfaces was established based on the equation (Figure 14) obtained for AgNPs and the association of these data with the UV–Vis maxima shifts.



Figure 14. Correlation between the intensity of AgNPs absorbance and Hg concentration.

We only used the DS4-IDS for the UV–Vis survey because this decontaminating formulation demonstrated the ability to remove all the tested HMs efficiently. In addition, IDS ensured high Hg decontamination efficiency. The samples collected from the decontaminated surfaces were mixed with AgNP solutions. The resulting solutions were subsequently subjected to UV–Vis analysis; the data obtained were correlated with the equation describing the dependence of the absorbance of AgNPs with the concentration of Hg, and the results for DE are illustrated in Figure 15. Finally, the decontamination efficacies obtained for Hg were comparable and nearly independent of the initial contamination level.



Figure 15. Decontamination efficacies of Hg obtained via UV-Vis.

The entrapment of mercury inside the polymeric matrix was also confirmed via SEM-EDX analysis (Figures 16 and 17). Cross-section EDX elemental mapping (Figure 17) revealed the uniform distribution of the contaminant inside the peeled coating.



**Figure 16.** SEM image of the peeled coating (**a**) cross-section view (**b**) top view employed for Hg decontamination.

Figure 18 summarizes the results obtained for the decontamination formulation DS4-IDS. Compared with the other decontaminating formulations, DS4-IDS demonstrated a remarkable decontamination efficacy for all the HMs tested. Thus, all the samples collected from the surfaces decontaminated with DS4-IDS were analyzed via AAS and ICP-MSA. In addition, the UV–Vis technique was utilized to investigate the Hg-containing samples. In the end, it was shown that each analytical method used for evaluating DE(%) has its particularities, benefits, and constraints.



**Figure 17.** EDX mapping of Hg entrapped inside the polymeric strippable coating (cross-section view).



**Figure 18.** Comparative evaluation between the AAS, ICP-MS, and UV–Vis results regarding DS4-IDS decontamination efficacy DE(%).

As it was comparatively shown in Figure 18, the DE(%) values obtained from the ICP-MS analysis were slightly higher than those obtained from AAS, probably due to its higher accuracy. However, one unit lower DE(%) values were obtained with the UV–Vis technique. Thus, we can affirm that each of these three methods can provide fairly accurate results, even if minor differences still exist. The discrepancies probably originate

from the different accuracy of each instrument, the interpretation of the results, or sample preparation (successive filtrations, dilutions, human inaccuracies, etc.).

Hg concentrations obtained from the correlation with the blue shift of the AgNP colloidal solutions, monitored via UV–Vis, seems a straightforward method due to the ease of application. Still, its major constraint is that it only applies to Hg [13]. Nevertheless, analytical techniques such as AAS or ICP-MS remain the most viable for other types of heavy metals.

In Figure 18, it can also be easily observed that the DE(%) pattern obtained for Pb and Hg through AAS correlated well with the results obtained from ICP-MS. The differences between the results obtained for DE(%) through AAS vs. ICP-MS were slightly higher for Sb, Zn, Sr, Co, or Cu. However, the outcomes of this study align with the NATO Standards [30,36], which stipulate that the decontamination method applied must lead to a decontamination efficacy of at least 90% to be considered adequate.

#### 4. Conclusions

This study comprises a comparative study that evaluated the decontamination efficacy of four types of "green" strippable coatings for Cu, Sb, Zn, Sr, Pb, Co, and Hg contaminants. EDTA, DTPA, PBTC, and IDS were the chelating agents used to remove the above-mentioned contaminants from the stainless-steel coupons. Controlled contamination was performed first, followed by applying the decontaminating solutions on the contaminated surfaces. These formulations possess the ability to capture the contaminants through adsorption and complexation mechanisms, entrapping them inside the polymeric matrix while curing. After peeling the resulting strippable nanocomposite coatings, the decontaminated surfaces were subjected to an extraction procedure to capture the residual contaminants in an aqueous solution that can be further analyzed via AAS, ICP-MS, or UV–Vis (only for Hg).

Summarizing the results, we can affirm that the classical chelating agents, EDTA and DTPA, ensured higher decontamination efficacies for Hg and Sr, respectively. Moreover, from the two 'green' chelating agents employed in this study, PBTC rendered better results for Pb, while IDS seemed to be the only one ensuring high DE(%) values for all the tested contaminants.

Even though the decontamination efficacies obtained through the AAS correlated relatively well with the results obtained from ICP-MS, Hg quantification via UV–Vis based on the blue shift of the AgNP colloidal solutions seems a more straightforward process.

**Supplementary Materials:** The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/w15050982/s1, The following supplementary materials include: Material description for AAS and ICP-MS techniques; Figure S1: Chemical structures of the chelating agents used in the study and the description of the characterization methods.

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