Interdisciplinary Research in Medical Sciences Specialty
ISSN: 3062-4401
2023, Volume 3, Issue 2, Page No: 145-156

Galaxy Publication

A Green Chemical Remediation Process Achieving 71% Arsenic and 95% Mercury Extraction from Marine Sediments for Safe Reuse

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Received: 01 August 2023; **Revised:** 04 November 2023; **Accepted:** 14 November 2023

ABSTRACT

Prolonged coastal industrialization has generated persistent pollution in many marine zones, making restoration actions necessary to eliminate hazardous inorganic contaminants. This study introduces a clean-up strategy tailored for marine sediments enriched with arsenic (As) and mercury (Hg). The approach is suitable for movable treatment units and is intentionally designed to reduce secondary impacts on the environment. The procedure was evaluated on two laboratory-spiked sediments and on two field materials originating from highly impacted regions in southern Italy—Augusta Bay and the Gulf of Bagnoli—known for elevated Hg and As levels, respectively. The workflow integrates four sequential operations: alkaline washing with sodium hydroxide (NaOH) to release metals interacting with humic substances; a Fenton system in which α-CycloDextrin (aCD) stabilizes Fe(II) at natural pH and promotes oxidation of As(III) and Hg(0/I); a complexation step involving aCD; and a final treatment with sodium sulfide (Na_2S) to convert Hg into soluble polysulfide complexes. Relative to other approaches described in the literature, this method yields superior extraction efficiencies for both As and Hg, achieving 26–71 % and 57–95 % removal, respectively. Based on the remaining concentrations and the regulatory thresholds imposed by European directives for reuse, the processed sediment can be reintroduced into various civil or industrial applications. The proposed protocol aligns with circular-economy principles, limits further contamination, conserves natural resources, and facilitates the productive reuse of remediated matrices (sediments, soils, and aqueous phases), thereby reducing landfill disposal.

Keywords: Sulfide-based processing, Sediment/soil washing for decontamination, Hg–As elimination, Reuse, Residual waste

How to Cite This Article: Lopes F, Azevedo R, Moreira T. A Green Chemical Remediation Process Achieving 71% Arsenic and 95% Mercury Extraction from Marine Sediments for Safe Reuse. Interdiscip Res Med Sci Spec. 2023;3(2):145-56. https://doi.org/10.51847/KTbxorQY73

Introduction

Diverse human activities—including the manufacture of construction goods, fertilizer production, agricultural operations, forestry work, and unregulated urban growth—have progressively intensified global heavy-metal contamination. Within Europe alone, an estimated 2.8 million locations affected by polluting operations still exhibit significant environmental impacts and therefore necessitate remediation or mitigation procedures [1].

Metal accumulation in sediments is particularly problematic, as these matrices can act both as repositories and as delayed sources of hazardous elements in marine settings. In aquatic systems, metals occur as suspended particles, dissolved species, colloidal forms, or solid-phase constituents [2–11]. Under certain environmental conditions, more than 90 % of released metals may settle into sediments where they can be found bound to Fe/Mn oxyhydroxides or clay minerals, associated with organic matter, incorporated into primary minerals (such as silicates), incorporated into secondary phases (e.g., carbonates or sulfates), or enclosed within amorphous materials [12, 13]. Each fraction exhibits different mobility and toxicity, meaning that abrupt shifts in physicochemical parameters can trigger the release of mobile metal species back into the water column. Once mobilised, these metals can be assimilated by aquatic organisms and eventually reach humans through trophic transfer [14].

Mercury represents a particularly hazardous element and is classified as "possibly carcinogenic to humans" [15]. Major anthropogenic emissions include coal burning, mining activities, chlor-alkali production, and various industrial discharges [16–18]. Following the Minamata Convention, mapping and characterising Hg-impacted coastlines has become a priority for evaluating risks to ecosystems and to public health [19, 20].

Arsenic, a toxic and carcinogenic metalloid, is released to the environment via several human activities such as pharmaceutical and pesticide production, historical mining, leather processing, and the combustion of fossil fuels [21].

Selecting an appropriate remediation technique requires a thorough evaluation of the local environmental conditions as well as a comparison of viable technologies. Options for the rehabilitation of metal-contaminated marine sediments include [22, 23]: (i) isolation via in-situ or ex-situ capping; (ii) containment through solidification/stabilisation; and (iii) dredging followed by off-site treatment.

In-situ measures tend to be used for environments with moderate metal levels but show limited effectiveness when contamination is severe [24]. For heavily polluted materials, ex-situ strategies generally provide more reliable outcomes. Many soil-remediation methods can also be adapted to dredged sediments with appropriate consideration of their distinct physical, chemical, and biological properties [24].

A variety of approaches—such as washing of sediments, treatments based on electrochemical reactions, and biosorptive processes—are commonly selected for eliminating metal contaminants from dredged marine materials [24, 25]. Despite their frequent use, these methods generally fail to extract meaningful amounts of Hg or As from marine sediments, particularly when the substrate is fine-textured or exhibits low permeability, where removal performance for these and other hazardous substances becomes notably poor [26].

Within the broader category of physicochemical remediation, chemical separation aims to shift pollutants into an aqueous medium so that they may be collected, concentrated, or transformed [27]. Leaching fluids may consist of acids, alkaline reagents, or chelating solutions. Acidic washes are typically employed to dissolve basic metal-derived solids (hydroxides, oxides, carbonates), while alkaline agents may free certain metals attached to mineral surfaces [27]. Once metals have been solubilised, the treated sediment must be neutralised, and the extract must be clarified to remove particulates. The resulting metal-laden solution then requires additional handling—through ion-exchange media, conversion to stable precipitates, or photocatalytic systems, among other possibilities [28].

Scientific reports indicate that chelator-enhanced washing rarely surpasses ~30 % extraction efficiency for either As or Hg from marine sediments [29, 30]. Oxidation-based separation is another option, where appropriate oxidants convert sediment-bound contaminants into less hazardous or more mobile species [31]. Frequently used oxidants include sodium permanganate, sodium persulfate, ozone, and hydrogen peroxide [32]. These agents can induce rapid elimination of PTEs or partial decomposition of other pollutants, but often come with high operational demands and may generate secondary waste streams that require further intervention [32].

The purpose of this study is to design a new ex-situ oxidation-based remediation sequence for sediments polluted with As and Hg. The investigation uses two synthetic (spiked) sediments and two field samples from heavily impacted coastal zones in southern Italy—Augusta Bay and the Bagnoli area. This work evaluates, for the first time, a combined sequence that incorporates sodium hydroxide to liberate metal species associated with humic matter, α-CycloDextrin to oxidise As(III) and Hg(0/I), and sodium sulfide to convert mercury into polysulfide-soluble forms. The goal is to produce a sustainable, economically favourable multistep method capable of achieving As and Hg removal well above previously documented maxima—namely the 30 % limit reported for both elements [29, 30]. Consideration is also given to the potential adaptation of this approach for full-scale remediation.

Materials and Methods

Reagents included 30 % H_2O_2, $Na_4P_2O_7$, NaOH, and reagent-grade α-cyclodextrin (aCD) from Carlo Erba Reagent (Italy), along with extra-pure $Na_2S \times H_2O$ (60–64 %, Thermo Scientific). Supra-pure HNO_3 (Carlo Erba) was used during preparation and analytical steps.

Collection of samples

The method was tested on both real contaminated sediments and artificially loaded clean materials. Two sites with well-documented pollution histories were chosen. Augusta Bay (SE Sicily, N 37°12.244′, E 15°11.175′), designated AUG, is a semi-enclosed coastal basin impacted by a chlor-alkali industrial facility (Hg-cell process, 1958–2003). This plant discharged more than 500 tons of mercury—both as Hg^0 and as various complexes—into the marine system until regulatory limits were imposed in 1978 [33, 34]. The second site, Bagnoli (Gulf of Pozzuoli, Naples area, N 40°48.691′, E 14°09.755′), referred to as BAG, has been subjected to emissions from numerous industrial operations, including a major steelworks complex (ILVA), resulting in strong contamination by metals and polycyclic aromatic hydrocarbons [35–37]. Two uncontaminated marine sediments from Capo Granitola Coast (western Sicily; N 37°33.895′, E 12°39.626′ and N 37°30.941′, E 12°33.263′) were collected—CG_Sand and CG_Clay—chosen because their grain-size characteristics matched those of the polluted sediments. They were then deliberately enriched with Hg and As.

Sediment spiking

Roughly 500 g of each clean sediment was amended using 3 ml of a 1000 mg/L Hg(II) solution and 45 ml of a 1000 mg/L As(V) solution. The mixture was homogenised for 2 h using a rotary evaporator system, then dried under vacuum. This spiked batch was subsequently blended with an additional 2.5 kg of the same sediment and mixed for 24 h inside a 10-L sealed rotating tank. The resulting composite materials—CG_Clay* and CG_Sand*—were frozen for storage for more than three months.

Sediment characterisation

Particle-size distribution and metal concentrations were determined following the analytical procedures below.

- *Mercury quantification in solids and eluates*

Total Hg in solids and liquids was measured using a DMA-80 Direct Mercury Analyzer (Milestone s.r.l., Italy) with atomic absorption detection, operated according to US-EPA Method 7473. Solid samples were analysed by weighing approximately 20 mg of dry material directly into the sample holder [38, 39]. For eluates, either 50 µl or 200 µl of solution was transferred into the holder, depending on anticipated concentration levels.

- *Heavy metals determination in sediment and eluates*

Quantification of metallic contaminants in both solid sediments and extracted solutions was performed using ICP/MS at two independent facilities: the ICP/MS unit of CNR-IAS (Italy, Tp) and the ENEA analytical laboratory (Italy, Rm). Prior to measurement, samples underwent microwave-assisted mineralisation using concentrated hydrochloric and nitric acids [40, 41], followed by analysis according to EPA-standard protocols [42, 43]. The acid mixture and sediment aliquot were placed inside sealed Teflon digestion vessels [44] and processed in a DISCOVER SP-D80 microwave apparatus (CEM Corporation). Final digests and reagent blanks were analysed using an inductively coupled plasma system equipped with a Q-cell interface (Thermo Fisher iCAP-Q).

- *Grain size procedure*

During preparation for grain-size assessment, organic fractions were removed through treatment with a mixture of 30 w/v % hydrogen peroxide (100 vol%) and distilled water in a 1:4 ratio, allowing oxidation to proceed for 24–48 h. Multiple rinses with deionised water were then applied to eliminate soluble salts, particularly NaCl [45]. Grain-size distributions of samples AUG and CG_Clay were obtained using a Horiba Partica LA-950V2 laser analyser. Measurements were processed through HORIBA LA950 V.5.20 software, which provided statistical parameters and reconstructed distribution curves. Samples BAG and CG_Sand were characterised by mechanical sieving using a vibrating shaker and ASTM sieves spaced at ϕ/2 increments, covering openings from 2 mm (–1ϕ) to 63 µm (4ϕ). The resulting data were processed using the "Fritsch Particle Sizer AUTOSIEB/A20" programme. All materials were classified according to particle-size limits expressed in ϕ, applying the logarithmic Krumbein transformation ($\phi = -\log_2 d$, where d is the particle diameter in mm) [45, 46].

- *Quality control*

Verification of analytical accuracy for Hg, As, and other metals in sediment matrices employed the certified marine sediment reference PACS-3 (NRCC, Canada), analysed after every ten samples for both DMA-80 and ICP/MS performance checks.

For Hg measurements carried out via DMA-80, accuracy and precision ranged between 94–109 % and <7 % RSD across five replicates. Roughly 20 % of all samples were run in duplicate, confirming reproducibility below 7 %.

For liquid-phase Hg (eluates), duplicate analysis of ≈20 % of samples gave reproducibility <15 %, and spike-recovery tests produced accuracy between 85–120 %.

For As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, and Zn measured by ICP/MS, PACS-3 was again used. Estimated accuracy and precision fell within 94–106 %, with precision better than 7 % RSD (three replicates). Duplicate testing on ≈20 % of the dataset provided reproducibility near 94 %.

Remediation method

The remediation protocol was executed using a four-position magnetic stirring system and follows a sediment/soil washing concept incorporating reagents associated with ISCO-style oxidation and complexation. It was developed to maximise the extraction of total As and Hg from the tested sediments. The design was informed by insights from a mercury selective extraction procedure (SEP) previously applied to Augusta Bay sediments [47], which indicated that Hg exists mainly as Hg(0) plus Hg(I) (≈80–95 %) and as Hg(II) (≈4–19 %) relative to total Hg (THg). Hg(0) and Hg(I) correspond to elemental emissions from the chlor-alkali facility, whereas Hg(II) is linked to HgS [48].

Key operating principles included:

i) maintaining solution pH above 7 to protect carbonate minerals, and

ii) applying sediment-to-solution ratios between 1:1 and 1:2 to limit the amount of eluate requiring post-treatment before disposal.

iii) Preliminary washing tests using both distilled and saline water were performed on the spiked materials to confirm that the introduced As and Hg were stable; no measurable release occurred, indicating their association with humic and sulfur-bearing phases.

iv) The final method consisted of four treatment stages applied to ≈25 g of each sediment type (AUG, BAG, CG_Clay, CG_Sand) using 25 ml of the chosen reagents. After each reaction period, solid and liquid phases were separated by centrifugation at 4500 rpm for 10 min. The supernatant was transferred for Hg and As determination, while the solid was resuspended with fresh reagent using a vortex mixer and stirred again magnetically. This process was repeated three consecutive times.

First step – Separation of humic substances

A 25 g portion of each sediment was left in contact overnight with 25 ml of a mixed alkaline solution (NaOH 1 M and $Na_4P_2O_7$ 0.5 M), adjusted to pH 14, to mobilise soluble species and extract humic acids from the matrix [49]. After this incubation, the solid phase was isolated through centrifugation at 4500 rpm for 10 min and rinsed twice with 1 M NaOH, each wash lasting roughly 2 min and assisted by a vortex mixer. All rinsates were combined for subsequent determination of As and Hg. This initial stage was included to eliminate metal fractions bound to humic substances and to limit the consumption of H_2O_2 required for mercury oxidation in the following phase.

Second step – Oxidative conversion

Sediments carried over from step one underwent a modified Fenton-type procedure, where naturally occurring Fe(II/III) acted as the catalyst, and α-cyclodextrin was used as a stabilising ligand at near-neutral pH (≈7.5). The material was mixed with 25 ml deionised water containing 0.1 M α-cyclodextrin (aCD), followed by periodic addition of 2 ml H_2O_2 (30% v/v) every 30 min over a total duration of ~3 h. At the end of the reaction, liquid and solid were separated by centrifugation, and the collected solutions (approximately 25 ml for each interval) were analysed individually for As and Hg. This stage was intended to convert reduced As and Hg phases into more soluble oxidised forms.

Third step – aCD complexation wash

The remaining solid was then resuspended and rinsed three consecutive times with 25 ml of 0.1 M aCD to extract Fe complexes and any additional metal species.

Fourth step – Treatment with Na_2S

The final remediation stage employed sodium sulfide as a complexing agent to generate soluble Hg-polysulfide species (HgS_x). Prior studies indicate that Hg polysulfides form when sulfide is abundant, and the redox potential is below −200 mV [50]. Sediments were stirred for 30 min in the reagent, and the liquid fraction was separated via centrifugation and combined in a clean tube. The residual material was contacted again with 25 ml Na_2S 1 M for a further 30 min. Each of the three recovered solutions was analysed individually to quantify As and Hg.

Results and Discussion

Grain size, pH, and Eh characteristics

Table 1 summarises the grain size distribution based on six independent measurements. AUG and CG_Clay contain predominantly fine particles (silt + clay accounting for approximately 99.14% and 93.37%, respectively), whereas CG_Sand and BAG are characterised mainly by sandy fractions (about 98.96% and 97.36%). pH and redox potential were determined prior to grain-size testing and are listed in **Table 1.**

Table 1. Grain size data (mean ± standard deviation, %), along with pH and Eh.

Sample	Sand %	Silt %	Clay%	pH	Eh
CG_Clay	0.86 ± 0.17	42.28 ± 0.99	56.86 ± 0.91	7.35	−160 mV
CG_Sand	98.96 ± 0.05	1.04 ± 0.05		7.55	+96 mV
AUG	6.63 ± 0.40	57.43 ± 0.73	35.94 ± 0.76	7.45	−290mV
BAG	97.36 ± 0.22	2.64 ± 0.22		8.10	+6 mV

Heavy metals in sediment matrices

Trace metals were quantified in ten replicates from each sediment type (AUG, BAG, CG_Sand, CG_Clay, CG_Sand*, CG_Clay*) prior to applying any remediation procedure. **Table 2** reports mean values ± standard deviation and is summarised below.

i) AUG shows concentrations comparable to uncontaminated sediments of similar composition (CG_Clay), except for Cr, Cu, Ni, and Hg, which are markedly elevated (92.8, 45.2, 46.5 mg/kg, respectively). Mercury levels (9.2 mg/kg) are more than two orders of magnitude higher than those of CG_Clay. Cr, Ni, and Hg all exceed marine sediment quality thresholds in Italian legislation (D. Lgs 172/2015 – **Table 2**). The elevated Hg confirms an anthropogenic source associated with the local chloro-alkali facility [19, 33, 34, 51–54].

ii) BAG samples, relative to clean sandy material (CG_Sand), contain increased Mn, As, Pb, Zn, and Hg. Lead (133.6 mg/kg) surpasses the regulatory limit (D.Lgs 172/2015 – **Table 2**). Mean Mn, As, Pb, and Zn values (996.3, 95.1, 133.6, 234.6 mg/kg) notably exceed those measured in Augusta sediments (317.4, 17.4, 28.4, 92.4 mg/kg).

iii) CG_Clay vs. CG_Sand: the clay fraction retains metal concentrations roughly one order of magnitude higher than the sand for nearly all analytes (Mn being the exception), consistent with the higher sorptive capacity of clay minerals.

iv) Spiked materials (CG_Clay and CG_Sand)** show Hg contents consistent with the added dose (about 1.2 and 1.1 mg/kg). The As levels (36.7 and 31.8 mg/kg) exceed the expected spike concentration because sediments already contained natural As (**Table 2**). Other metals were also quantified to evaluate possible competitive interactions with As and Hg and to identify additional species affected during remediation.

Table 2. Metal concentrations in dried sediments prior to treatment (mean ± standard deviation, mg/kg). Values in parentheses refer to pre-spike As and Hg content.

	AUG	BAG	CG_Clay*	CG_Sand*	GES
As	17.4 ± 1.04	95.1 ± 8.32	36.7 ± 2.11 (20.4)	31.8 ± 2.25 (14.5)	12.00
Hg	9.2 ± 1.08	0.14 ± 0.01	1.2 ± 0.03 (0.044)	1.05 ± 0.07 (0.004)	0.30
Mn	317.4 ± 45.55	996.3 ± 87.04	263.1 ± 28.66	275.2 ± 20.41	
Cd	0.21 ± 0.03	0.29 ± 0.04	0.21 ± 0.03	0.08 ± 0.02	0.30
Co	17.2 ± 1.42	6.7 ± 0.57	9.8 ± 0.61	1.6 ± 0.08	
Cr	92.8 ± 14.21	19.8 ± 1.57	78.5 ± 6.95	9.1 ± 1.88	50.00
Cu	45.2 ± 2.02	11.2 ± 0.74	16.5 ± 0.92	1.1 ± 0.08	
Ni	46.5 ± 4.84	6.7 ± 0.72	27.1 ± 2.42	2.3 ± 0.33	
Pb	28.4 ± 1.67	133.6 ± 12.26	30.5 ± 1.99	3.9 ± 0.42	30.00
V	96.3 ± 5.36	92.4 ± 3.76	123.2 ± 9.29	15.2 ± 1.68	
Zn	92.4 ± 8.74	234.5 ± 16.86	79.6 ± 7.80	7.9 ± 0.60	
Fe^a	3.7 ± 0.23	8.1 ± 0.67	3.5 ± 0.15	0.5 ± 0.07	

a values in percentage; GES = Good Environmental State.

Extraction of As and Hg from marine sediments

Concentrations of the metals detected in the solutions obtained from each treatment stage and cycle are summarised in **Table 3**, which reports the mean values from three repeated experiments.

Table 3. As and Hg released from each sediment type per extraction step (µg). n.d. = not detected.

Extraction method	AUG soil		BAG soil		CG_Sand soil		CG_Clay soil	
	As (µg)	Hg (µg)	As (µg)	Hg (µg)	As (µg)	Hg (µg)	As (µg)	Hg (µg)
1. Alkaline extraction (NaOH)	104.0	3.2	297.1	3.2	247.8	0.3	267.8	1.5
2. Oxidative treatment (H_2O_2/Fe)	13.4	54.9	27.0	0.9	17.1	34.0	7.8	
3. α-Cyclodextrin complexation								
αCD – Fraction I	5.2	15.3	7.0	0.5	2.5	0.1	9.9	1.7
αCD – Fraction II	1.9	4.7	7.0	n.d.	0.9	n.d.	6.9	0.4
αCD – Fraction III	1.5	2.6	4.1	n.d.	0.1	n.d.	5.2	n.d.
αCD – Overall	8.6	22.6	18.1	0.5	3.5	0.1	22.0	2.1
4. Sodium sulfide complexation								
Na_2S – Fraction I	0.9	37.0	0.8	1.0	0.7	14.4	5.0	n.d.
Na_2S – Fraction II	0.9	17.5	1.8	2.0	0.8	8.5	0.8	5.6
Na_2S – Fraction III	0.4	10.1	1.2	0.2	0.3	6.3	0.5	4.9
Na_2S – Overall	2.2	64.6	3.8	3.2	1.8	29.2	6.3	10.5
Total amount extracted (µg)	128.2	145.3	346.0	7.8	270.2	29.6	330.1	21.9

In the first stage—extraction using 1 M NaOH—arsenic was consistently mobilised more efficiently than mercury across all matrices **(Table 3; Figure 1)**. Approximately 25 ml of eluate contained 104.0, 297.1, 247.9, and 267.8 µg of As for AUG, BAG, CG_Sand*, and CG_Clay*, respectively. Corresponding Hg amounts were 3.2, 3.2, 0.3, and 1.5 µg.

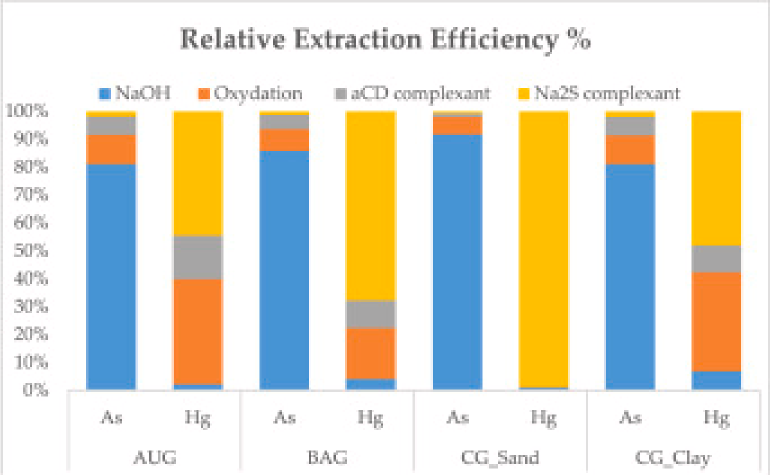

Figure 1. Relative extraction efficiencies (%) for each remediation stage.

During this alkaline extraction, humic substances were removed from all samples exhibiting elevated As, implying the formation of soluble As–humic complexes. One exception was AUG, where As release was roughly half that of the other sediments, likely reflecting its lower initial As content. BAG would likely require more sequential alkaline treatments to fully mobilise its As load.

The second stage—a modified Fenton-type oxidation—was aimed at converting As(III), Hg(0), Hg(I), or organically complexed species into more soluble oxidised forms. Redox monitoring confirmed the reaction progress: Eh values began at < −200 mV and exceeded +400 mV after ~3 h. Following this step, ~25 ml of eluate contained 13.41, 27.0, 17.1, and 34.0 µg of As, and 54.9, 0.9, <0.1, and 7.8 µg of Hg for AUG, BAG, CG_Sand*, and CG_Clay*, respectively.

As predicted, a notable fraction of sedimentary Hg was present in reduced states—likely Hg(0) **(Figure 1)**—consistent with earlier findings that elemental Hg dominates in marine deposits [47]. The relatively small As removal indicates that As(III) comprises only a limited portion of the total As inventory.

For the third stage—α-cyclodextrin (aCD) washing—the summed As in the ~25 ml eluates were 8.6, 18.1, 3.5, and 22.0 µg for AUG, BAG, CG_Sand*, and CG_Clay*, respectively. Extracted Hg reached 22.6, 0.5, 0.1, and 2.1 µg.

As shown in **Figure 1**, total As and Hg recovered here were minor, suggesting aCD has weak complex-forming behaviour toward both elements.

The fourth stage—complexation using Na_2S—was designed primarily for mercury removal through formation of soluble polysulfide complexes. After this stage, the total As extracted from ~25 ml solutions was 2.2, 3.8, 1.8, and 6.3 µg for AUG, BAG, CG_Sand*, and CG_Clay*, while Hg amounts were 64.6, 3.2, 29.2, and 10.5 µg, respectively.

As anticipated, this step primarily targeted Hg, producing the largest Hg releases **(Table 3; Figure 1).** Under reducing conditions, sulfide readily reacts with mercury—often initially precipitated as cinnabar—to form soluble polysulfide complexes [55].

When summing all treatment stages **(Table 3)**, total extracted As was 128.2, 346.0, 270.2, and 330.1 µg, whereas total Hg recovered reached 145.3, 7.8, 29.6, and 21.9 µg for AUG, BAG, CG_Sand*, and CG_Clay*, respectively. The percentage contributions of each stage **(Table 3; Figure 1)** are as follows:

1. NaOH extraction:
    - As: 81–92%
    - Hg: 1–7%
2. H_2O_2/Fe oxidation:
    - As: 6–10%
    - Hg: 18–38%
3. aCD complexation:
    - As: 1–7%
    - Hg: 9–15% (≈0.1% in CG_Sand*)
4. Na_2S complexation:
    - As: 0.7–2%
    - Hg: 44–98% (CG_Sand* showed ~98% removal)

These findings indicate that most As (81–92%) is released during the alkaline step, suggesting strong interactions with humic or other soluble organic constituents [56]. The small As amount extracted during oxidation (6–10%) supports the conclusion that As(III) is a minor redox species in these samples. Similarly, the negligible extraction with aCD (1–7%) and Na_2S (0.7–2%) reflects As's poor solubility under these conditions.

Conversely, Hg removal is dominated by the Na_2S stage (44–98%), consistent with formation of aqueous Hg-polysulfides [50, 57]. The exceptionally high efficiency (98%) in CG_Sand*—spiked with Hg(II)—likely reflects the stronger affinity of Hg(II) for sulfide. The oxidation step also contributed substantially (18–38%), whereas NaOH and aCD mobilised only trace amounts, indicating that Hg was not significantly associated with humic material or with aCD-binding domains.

Remediation efficiency

Following the completion of the extraction steps, the processed sediment specimens were dried and examined to determine the remaining levels of As, Hg, and the additional metals. By comparing average concentrations before and after treatment, the proportion of each element removed was calculated and is summarised in **Table 4**. The remediation approach achieved removal of total As and Hg in the intervals 26.4–71.2 % and 57.1–95.2 %, respectively. With respect to the other metals, the method yielded:

i) for the AUG sample, approximate reductions of 6.6 % (Co), 41.8 % (Cu) and 5.2 % (V);
ii) ii) for the BAG sample, decreases of around 59.8 % (Mn), 16.7 % (Co), 18.9 % (Ni) and 64.3 % (Zn);

iii) iii) for CG_Clay*, removals of roughly 48.5 % (Cu), 15.1 % (Pb) and 40.7 % (V);
iv) iv) for CG_Sand*, reductions of close to 15.0 % (Cd) and 8.2 % (Zn).

Table 4. Percentage removal efficiencies of As, Hg, and the remaining metals.
n.c.: negligible variation.

	AUG %	**BAG %**	**CG_Clay* %**	**CG_Sand* %**
As	59.9	26.4	71.2	55.9
Hg	76.3	57.1	92.4	95.2
Mn	n.c.	59.8	n.c.	n.c.
Cd	n.c.	n.c	n.c.	15.0
Co	6.6	16.7	n.c.	n.c.
Cr	n.c.	n.c.	n.c.	n.c.
Cu	41.8	n.c.	48.5	n.c.
Ni	n.c.	18.9	n.c.	n.c.
Pb	n.c.	n.c.	15.1	n.c.
V	5.2	n.c.	40.7	n.c.
Zn	n.c.	64.3	n.c.	8.2

The outcome verifies the strong performance of the proposed chemical treatment for extracting As and Hg from CG_Clay*, CG_Sand*, and AUG sediments, irrespective of whether the matrix is clay-rich or sand-dominant. Conversely, the process is noticeably less effective for the BAG material, likely due to its elevated contents of Fe and highly stable As species. Although the extracted As quantity for BAG resembles that of the other sites (**Table 3**), extending the duration or increasing the number of 1 M NaOH washing steps would probably enhance As recovery. The substantial Fe abundance in BAG, combined with its strong reactivity with sulfide, consumes a large share of the supplied Na_2S, leaving insufficient sulfide to form soluble Hg-polysulfide complexes. Therefore, raising the sulfide dose in step 4 would likely improve Hg extraction.

At the end of the procedure, all sediment types exhibited pH ≈ 12 and Eh ≈ –400 mV, values attributable to the surplus sulfide remaining after treatment. Introducing an additional rinse with water would lower the pH and raise the Eh by removing excess sulfide.

Conclusion

The remediation strategy demonstrated substantial capability for extracting As and Hg from contaminated sediments. The observed removal ranges—56–72 % for As and 76–95 % for Hg—surpass those previously reported in the literature, where maximum recoveries near 30 % have been documented [29, 30, 36]. The BAG sediment constitutes an exception, as its unusual chemical composition (notably high As and Fe) necessitates a customised approach.

Although developed at laboratory scale, the treatment can be scaled up using standard equipment such as mechanical mixers to ensure proper reagent interaction, hydrocyclones for separating sandy fractions from fines and eluates, and centrifuges to isolate clay from the liquid phase. These devices are already in use within soil and sediment washing facilities, as well as in in-situ and ISCO remediation systems, supporting the feasibility of scaling. Owing to the comparable characteristics of soils and marine sediments, the technique can also be transferred to soil remediation.

Employing Na_2S as the Hg-complexing reagent confirms that even strongly bound Hg phases, including forms akin to cinnabar, can be mobilised by forming soluble polysulfide species under sulfur-rich conditions. Considering the low residual As and Hg concentrations following treatment, and in alignment with European regulatory criteria, the remediated sediments are suitable for reuse in industrial or civil applications, contributing to sustainable resource management.

Further work is currently underway to test large-scale implementation using a soil-washing installation operating at 1 ton of sediment per hour, along with an assessment of economic viability.

Acknowledgments: None

Conflict of Interest: None

Financial Support: This research has been conducted within the framework of the Marine Hazard project 416(PON03PE_00203_1). In Italian language: *Ministero dell'Istruzione, dell'Università e della Ricerca (MIUR) – PON "Ricerca & Competitività" 2007–2013 – Decreto Direttoriale 713 Ric. Del 29 ottobre 2010 – Titolo III Creazione di nuovi distretti e/o Aggregazioni Pubblico-Private.*

Ethics Statement: None

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