# Simultaneous Stabilization of Heavy Metals and Organic Carbon in Sediment Using FeS-modified Hydrochar Derived from Waste Chitosan

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## ABSTRACT

Sediment accumulating in lakes and reservoirs is subject to long-term accumulation of arsenic and heavy metals originating from geogenic and anthropogenic sources, posing potential risks to aquatic ecosystems and human health. Stabilization technologies that reduce contaminant mobility and bioavailability in sediment have accordingly been recognized as an essential research area, and recent studies have explored converting waste biomass into hydrochar via hydrothermal carbonization (HTC) and loading it with iron sulfide (FeS) to develop low-cost, environmentally friendly composite stabilizers. In this study, an FeS-modified hydrochar (CA-FeS) was synthesized from waste chitosan discarded after microalgae adsorption in water treatment processes, and its physicochemical properties were characterized by XRD, FT-IR, and SEM/EDS. XRD analysis confirmed diffraction peaks characteristic of pyrite ($FeS_2$) and greigite ($Fe_3S_4$), indicating successful incorporation of FeS onto the hydrochar. CA-FeS was applied to As-contaminated sediment and to heavy-metal-contaminated soil at dosages of 2, 5, and 10 wt%. TCLP-leachable Cd, Cu, and Pb concentrations in the heavy-metal-contaminated soil decreased to near or below the detection limit under the 60-day, 10 wt% treatment condition, and TCLP-leachable As in the As-contaminated sediment decreased by approximately 65% relative to the control. Supernatant analysis indicated that this stabilization was driven by sulfide precipitation rather than pH reduction. In the heavy-metal-contaminated soil, the concentration of dissolved organic matter (DOM) released into the supernatant decreased with increasing reaction time (84.5 mg/L at day 7 to 53.6 mg/L at day 60 for the 10 wt% treatment), whereas organic matter content increased over the same period (7.5% to 8.6%), suggesting that released organic carbon was progressively re-adsorbed and stabilized onto the solid phase. These results demonstrate that CA-FeS is a promising sediment stabilization technology capable of addressing multiple contaminant types through the valorization of waste biomass.

**Keywords**: Hydrochar / FeS / Sediment stabilization / Heavy metals / Organic matter

## 1. INTRODUCTION

Sediment accumulating in lakes and reservoirs is subject to long-term accumulation of arsenic and heavy metals originating from geogenic sources, industrialization, and agricultural activities, significantly affecting the nutrient balance and ecological stability of aquatic ecosystems [1]. Contamination in such sediment can deteriorate water quality through resuspension or leaching and accumulate in organisms, posing potential risks to ecosystems and human health. Stabilization technologies that reduce the mobility and bioavailability of contaminants in sediment have accordingly been recognized as an essential research area requiring continuous management.

Recent studies have actively explored the use of biochar and hydrochar, produced by pyrolysis or hydrothermal carbonization (HTC) of waste biomass, as stabilizing agents. Such carbon-based materials have been reported to be effective soil amendments owing to their high specific surface area, porosity, and abundant surface functional groups. In particular, iron sulfide (FeS) has attracted attention as a material capable of effectively immobilizing a wide range of heavy metals through the formation of low-solubility metal sulfides [2]. Iron sulfide minerals such as pyrite ($FeS_2$) remain stable even under the low-oxygen conditions typical of sediment environments and are effective at adsorbing heavy metals such as arsenic and lead.

However, most existing studies have evaluated stabilization performance for only a single contaminant, and it remains unclear whether a single stabilizer can be effectively applied to different contaminant types (arsenic and heavy metals) within a sediment environment, or how organic matter introduced by the stabilizer behaves within the solid phase [3]. Accordingly, this study applied CA-FeS, an FeS-modified hydrochar synthesized by hydrothermal carbonization of waste chitosan discarded after microalgae adsorption in water treatment processes, to As-contaminated sediment and to heavy-metal-contaminated soil under simulated sedimentary conditions, in order to evaluate whether a single stabilizer can address different contaminant types, while also comprehensively assessing the liquid-to-solid partitioning behavior of organic matter that emerged during the stabilization process.

## 2. METHODOLOGY

### *2.1 Hydrochar preparation*

Waste chitosan (CA) discarded after microalgae adsorption in a water treatment process was used as the biomass feedstock. CA was converted into hydrochar via hydrothermal carbonization (HTC) using a stainless-steel hydrothermal autoclave reactor. Specifically, 5 g of CA, 45 mL of 0.2 M $FeCl_3$ solution, and 45 mL of 0.6 M NaHS solution were loaded into the reactor and reacted in an oven at 200 °C for 6 h. Following the reaction, the solid product was separated by vacuum filtration, washed with distilled water, and dried at 65°C for 24 h under a nitrogen atmosphere to obtain the FeS-modified waste-chitosan hydrochar (CA-FeS). The physicochemical properties of the synthesized hydrochar were characterized by FT-IR, SEM/EDS, and XRD analyses.

### *2.2 Sediment stabilization experiments*

CA-FeS was added to As-contaminated sediment and to heavy-metal-contaminated soil at dosages of 2, 5, and 10 wt%. Both samples were reacted at a solid-to-deionized-water ratio of 1:10 to simulate submerged sedimentary conditions, for 1, 7, and 30 days (As-contaminated sediment) or 7, 14, 30, and 60 days (heavy-metal-contaminated soil). The background contamination levels of the two matrices are summarized in Table 1. After the reaction, the supernatant was analyzed for pH and metal concentrations by ICP-OES, while the stabilized solid samples were oven-dried and subjected to pH measurement and the toxicity characteristic leaching procedure (TCLP). For the heavy-metal-contaminated soil, the supernatant was additionally analyzed for dissolved organic matter (DOM), and the organic matter content of the stabilized solid was determined by loss-on-ignition (LOI).

**Table 1.** Background contamination levels of the As-contaminated sediment and heavy-metal-contaminated soil (mg/kg).

| | pH | As | Cd | Cu | Pb |
|---|---|---|---|---|---|
| Sediment | 6.90 | 102 | 5 | 20 | 67 |
| Soil | 7.64 | 337 | 387 | 2740 | 1520 |
| Korea Concerning Level | | 25 | 4 | 150 | 200 |

*Note.* Korea Concerning Level refers to the Soil Contamination Concern Level (Region 1) specified in the Enforcement Rule (Annex 3) of the Soil Environment Conservation Act of the Republic of Korea.

## 3. RESULTS AND DISCUSSION

XRD analysis revealed diffraction peaks characteristic of iron sulfide minerals, pyrite ($FeS_2$) and greigite ($Fe_3S_4$), newly appearing in CA-FeS, confirming that FeS had been successfully incorporated onto the hydrochar. Based on this, stabilization experiments showed that TCLP-leachable Cd, Cu, and Pb concentrations in the heavy-metal-contaminated soil decreased to near or below the detection limit relative to the control (421.8, 588.9, and 420.3 mg/kg, respectively) under the 60-day, 10 wt% CA-FeS treatment condition, while TCLP-leachable As in the As-contaminated sediment decreased from a

control value of 2.4 mg/kg to as low as approximately 0.8 mg/kg with CA-FeS addition, corresponding to a reduction of roughly 65%. Although supernatant pH decreased slightly with increasing CA-FeS dosage, metal concentrations decreased concurrently, supporting the interpretation that the observed stabilization was driven not by pH reduction but by sulfide precipitation (e.g., formation of CdS, PbS, and CuS). Meanwhile, in the heavy-metal-contaminated soil, under a fixed dosage condition, the concentration of dissolved organic matter (DOM) released into the supernatant decreased with increasing reaction time (84.5 mg/L at day 7 versus 53.6 mg/L at day 60 for the 10 wt% treatment), whereas the organic matter content (based on loss-on-ignition; 7.5% at day 7 versus 8.6% at day 60) increased over the same period (Figure. 1). Because these two metrics differ in what they represent (dissolved organic matter concentration in the liquid phase versus organic matter mass fraction in the solid phase), their absolute values cannot be directly compared. Nonetheless, the opposing temporal trends between the liquid and solid phases suggest that a portion of the organic carbon initially released may have been re-adsorbed and stabilized onto the solid phase over time.

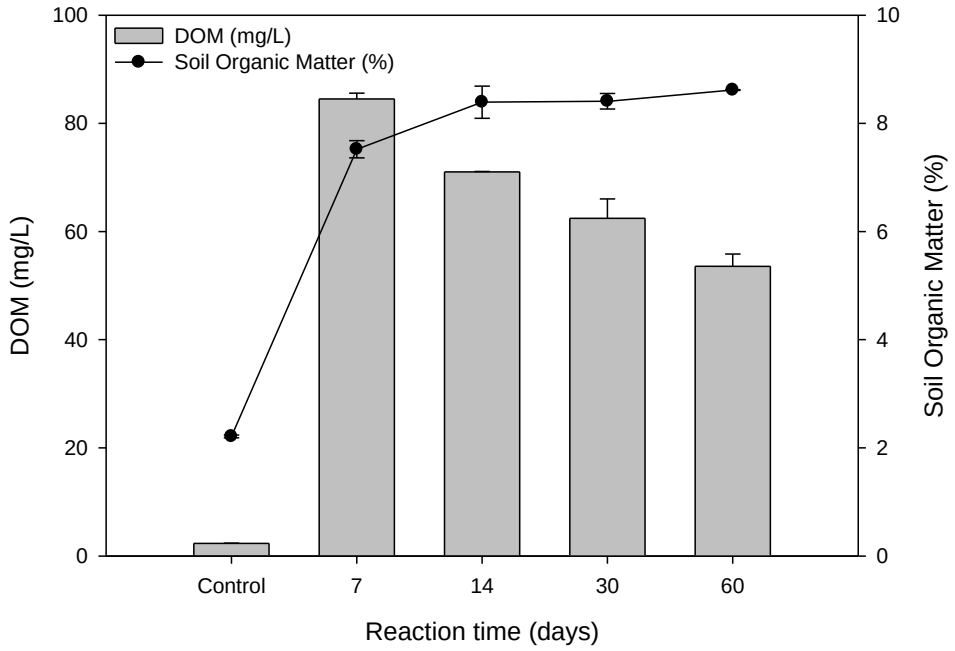


**Figure 1.** Changes in supernatant dissolved organic matter (DOM) concentration and organic matter content (loss-on-ignition) with reaction time in the heavy-metal-contaminated soil treated with 10 wt% CA-FeS.

## 4. CONCLUSIONS

Based on laboratory experiments and data analysis in this study, some conclusions were drawn as follows:

1. XRD analysis confirmed the appearance of diffraction peaks characteristic of iron sulfide minerals (pyrite and greigite) in CA-FeS, indicating successful incorporation of FeS onto the CA surface.

2. CA-FeS treatment effectively reduced TCLP-leachable heavy metals (Cd, Cu, Pb) in the heavy-metal-contaminated soil and arsenic in the As-contaminated sediment, with reductions reaching near or below the detection limit and approximately 65%, respectively.

3. Changes in supernatant pH and metal concentration indicated that the observed stabilization was attributable to sulfide precipitation rather than pH reduction.

4. Organic carbon initially released into the liquid phase decreased over time, while organic matter content increased, suggesting that the released organic carbon was progressively re-adsorbed and stabilized onto the solid phase.

5. CA-FeS demonstrates potential as a sediment stabilization technology capable of addressing multiple contaminant types while also promoting beneficial redistribution of organic matter, supporting its value as a waste-biomass-derived remediation material.

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