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Photochemical Detoxification of Arsenic- and Mercury-Contaminated Soils: Geochemical Mechanisms and Pathways

Sunakbaeva Dilara[1], S. Ravichandran[2, *]

Abstract

This study evaluates the geochemical aspects of soil detoxification in areas contaminated with arsenic (As) and mercury (Hg), emphasizing sustainable strategies for improving soil health and ensuring safe crop production. The research provides an ecological and toxicological assessment of regional soils and classifies them base on the concentration and mobility of toxic elements. Although the current levels of As and Hg do not yet present a critical risk to agricultural productivity, the steady increase in heavy metal accumulation due to industrial and agricultural activities necessitates effective remediation measures. To address this issue, a geochemical barrier composed of recycled poultry manure, marble chips ($CaCO_3$), and calcium peroxide (CaO_2) was designed and tested. The composite system functions as a multifunctional sorbent that stabilizes soil pH, enhances aeration, and reduces the bioavailability of heavy metals. Adsorption isotherm experiments demonstrated that mercury sorption capacity increased with higher CaO_2 content, while arsenic removal was strongly dependent on pH, reflecting distinct mechanisms of metal–sorbent interaction. The experimental results confirm that the proposed barrier effectively immobilizes toxic elements and transforms them into less mobile forms, contributing to soil detoxification and ecological restoration. The approach offers an environmentally friendly and economically viable solution for improving soil quality in contaminated regions. Overall, this study supports the integration of geochemical barrier technologies into sustainable land management and agricultural practices.

Keywords: Arsenic, bioavailability, calcium peroxide, mercury, soil

INTRODUCTION

Soil contamination with heavy metals such as arsenic (As) and mercury (Hg) has become a critical environmental issue worldwide, primarily driven by industrial emissions, mining activities, and agricultural intensification (1). In many developing regions, including Central Asia, these pollutants threaten soil fertility, ecosystem stability, and human health through food-chain accumulation. Therefore, understanding the geochemical behavior and detoxification mechanisms of As and Hg in soils is essential for achieving sustainable land management and ensuring food security (2).

***Author for Correspondence**
S. Ravichandran
E-mail: drravichandran.chemistry@spiher.ac.in

[1]Head of Faculty, Department of Ecology and Chemistry, Faculty of Natural Sciences, Khoja Akhmet Yassawi International Kazakh-Turkish University, Turkestan, Kazakhstan.
[2]Professor in Chemistry, Tagore Institute of Engineering and Technology, Salem, Tamilnadu, India.

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Numerous remediation technologies have been proposed to address heavy-metal pollution, including chemical stabilization, phytoremediation, and the use of biochar and metal-oxide nanoparticles. However, many of these approaches face limitations such as high cost, low field efficiency, or the risk of secondary contamination. Integrating low-cost sorbents of natural and waste origin therefore represents a promising alternative for sustainable remediation. Modern materials developed for this purpose include biochar derived from agricultural and wood waste, which exhibits a high sorption capacity for As and Hg (3); metal-oxide nanoparticles such as Fe_3O_4, ZnO, and TiO_2, which possess a large specific surface area and strong chemical reactivity that enhance toxic-element adsorption (4); and composite sorbents combining organic and mineral components, such as mixtures of recycled poultry manure with $CaCO_3$ and CaO_2, which stabilize soil pH, improve aeration, and reduce metal bioavailability (5).

Furthermore, phytoremediation using plants capable of accumulating and transforming heavy metals can complement these chemical stabilization methods, providing an integrated approach to reducing soil toxicity (6).

One innovative approach involves the creation of geochemical barriers within soil systems to immobilize toxic elements and prevent their migration into the root zone (Khan et al., 2019). However, this study focuses only on arsenic and mercury, which represent a limited subset of potential soil contaminants. Other toxic elements such as lead, cadmium, and chromium were not included, which restricts the generalizability of the findings to broader heavy-metal pollution contexts. Such barriers can be designed using composite sorbents that combine organic and inorganic components. In this study, a mixture of recycled poultry manure, marble chips ($CaCO_3$), and calcium peroxide (CaO_2) was selected due to its synergistic properties—pH stabilization, improved aeration, and strong metal-binding capacity (7).

MATERIALS AND METHODS

Study Objects

The study focused on regional gray and Chernozem soils. The investigated heavy metals included arsenic (As) and mercury (Hg). The sorbents used were recycled poultry manure, marble chips ($CaCO_3$), and calcium peroxide (CaO_2). In some experiments, bentonite, biocarbon, and Fe_3O_4 nanoparticles were also incorporated.

Experimental Procedures

Sorbents were added to the soils in various ratios ($CaCO_3$: CaO_2 : poultry manure = 4 : 0.5 : 0.1). The sorption capacity of each component and their mixtures was evaluated by constructing adsorption isotherms for As and Hg at pH values ranging from 4 to 8. Metal extraction was carried out using an ammonium acetate buffer (pH 4.8) three days after sorbent application, and the metal content was determined by ICP-MS (8). The obtained adsorption isotherms were used to determine the optimal sorbent ratios and to visualize the efficiency of metal removal.

As shown in Figure 1, the bentonite–calcium peroxide mixture at a 4 : 0.5 ratio exhibited the highest adsorption capacity for mercury and was therefore selected for subsequent experiments. The results also indicated that equilibrium in the system was reached within 10–20 minutes, which is a favorable indicator under industrial and field conditions. The steep increase in the mercury adsorption isotherm suggests a high availability of both internal and external sorbent surfaces for binding heavy metals.

Figure 2 and 3 presents the data that allow assessment of the dependence of sorption processes on the pH of the medium from which heavy metals are extracted. The obtained results are consistent and can be explained by the chemical speciation of arsenic and mercury in aqueous systems under varying pH conditions. As pH increased from 4 to 7, mercury uptake by plants decreased approximately fivefold. This may be attributed to the formation of carbonate precipitates, accumulation of $HgOH^+$ and $Hg(OH)_2$ hydroxo complexes in solution, or reduced activity of free Hg^{2+} ions due to partial complexation into ion pairs., or a decrease in the activity of free Hg2+ ions due to their partial binding into ion pairs.

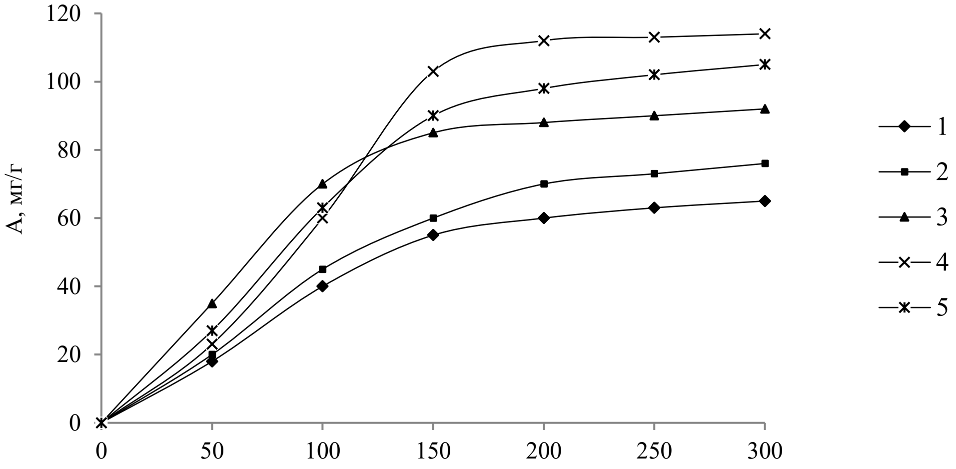

Figure 1. Adsorption isotherm of Hg by a mixture of bentonite and CaO_2 at different component ratios.

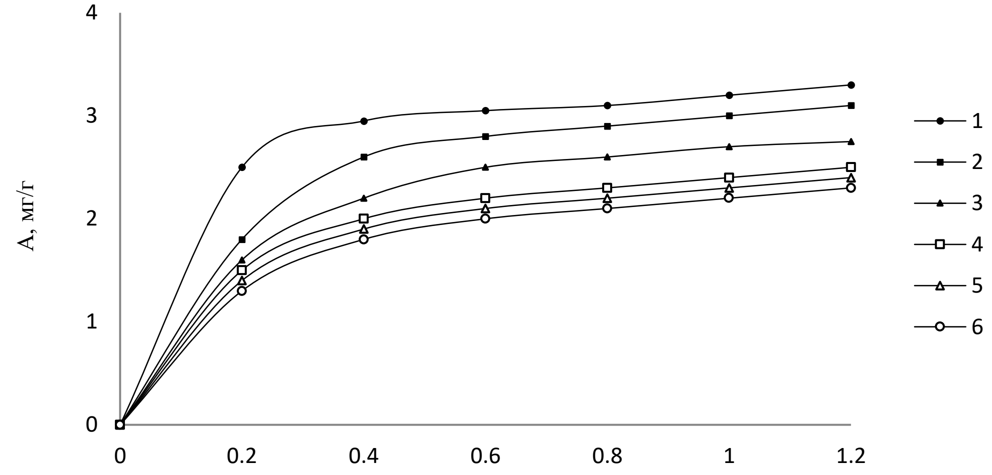

Figure 2. Adsorption isotherms of Hg by a bentonite-calcium peroxide mixture (4: 0.5) at different pH values.

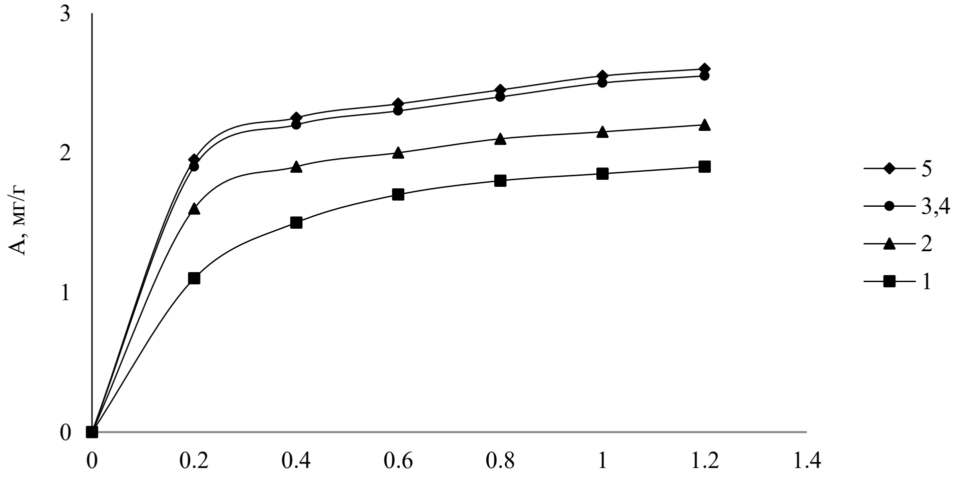

Figure 3. Adsorption isotherms of As by a bentonite-calcium peroxide mixture (4: 0.5) at different pH values.

RESULTS AND DISCUSSION

The adsorption isotherms demonstrated that the sorption capacity of bentonite–CaO_2 mixtures depends on both the component ratio and the pH of the medium. Comparative analysis of Hg and As adsorption revealed distinct interaction mechanisms between each metal and the sorbent.

Mercury (Hg) Adsorption

An increase in the proportion of CaO_2 in the mixture significantly enhanced Hg adsorption. The primary sorption mechanisms include physical adsorption on the bentonite surface and chemical interaction with calcium peroxide, leading to the formation of insoluble mercury compounds. At low CaO_2 content, Hg adsorption is limited by the number of active sites on the bentonite surface. The addition of CaO_2 increases both surface area and chemical activity, thereby enhancing Hg binding. These results are consistent with previous studies showing that oxide additives to clay minerals improve heavy metal adsorption efficiency (9).

However, the long-term stability of the bentonite–CaO_2 barrier and its resistance to environmental degradation were not assessed in this study. Further investigations are required to evaluate potential aging effects, structural transformations, and the possible release of bound metals under fluctuating redox and pH conditions.

Arsenic (As) Adsorption

Arsenic sorption was primarily pH-dependent, increasing under alkaline conditions. The binding mechanism for As differs from that of Hg and involves the formation of hydroxo-arsenate complexes on the surfaces of CaO_2 and bentonite. Compared to Hg, As adsorption was less sensitive to increasing CaO_2 content, highlighting the importance of pH optimization for achieving maximum arsenic removal (10).

Comparative Analysis

The bentonite - CaO_2 mixture exhibited high sorption activity for both Hg and As, although the optimal conditions for maximum adsorption differ: Hg adsorption improves with higher CaO_2 content, whereas pH control is crucial for As removal. Combining a clay mineral with calcium peroxide provides flexibility in adjusting sorption properties depending on the metal. Additionally, CaO_2 may impart partial oxidative effects, stabilizing heavy metals in less mobile and less toxic forms. It should be noted that the experiments were conducted under laboratory-controlled conditions. The absence of field validation limits the ability to predict the effectiveness of the proposed barrier in real contaminated soils, where environmental factors such as moisture, temperature, and microbial activity could alter sorption dynamics (11–15).

CONCLUSION

Bentonite – CaO_2 mixtures demonstrated high efficiency in removing Hg and As from aqueous solutions. Sorption efficiency depends on both the composition of the mixture and the pH of the medium, allowing the process to be adapted to specific contamination conditions. The ecological and biological implications of using these materials were not evaluated. Possible secondary effects on soil biota, plant health, and nutrient balance should be considered in future studies to ensure environmental safety of the remediation approach. These findings confirm the potential application of bentonite–CaO_2 composites in the phytoremediation and rehabilitation of contaminated soils and water bodies, offering a selective and environmentally friendly approach to heavy-metal removal. Since the experiments were based on regional gray and Chernozem soils of Central Asia, the results may not be directly applicable to other soil types or climatic zones. Further testing across diverse environmental conditions would help establish broader applicability of the proposed technology.

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