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Exploring the Potential of Hydrochar for the Removal of Toxic Metals from Mining-Influenced Waters: A Case Study on Arsenic

Álvaro Amado-Fierro[1], Antonio Luis Marqués Sierra[2], Begoña Fernandez[3], Julia Ayala[4], Teresa A. Centeno[5]

[1]Carbon Science and Technology Institute (INCAR), CISC, Francisco Pintado Fe 26, 33011, Oviedo, Spain, alvaro.af@incar.csic.es, ORCID 0000-0002-2851-2169

[2]Institute of Space Sciences and Technologies of Asturias (ICTEA), University of Oviedo, Independencia 13, 33004 Oviedo, Asturias, Spain, marquesantonio@uniovi.es, ORCID: 0000-0003-4665-4491

[3]University of Oviedo, Gonzalo Gutierrez Quirós, 33600 Mieres, Asturias, Spain, fernandezbegona@uniovi.es, ORCID 0000-0003-1239-4839

[4]University of Oviedo, Gonzalo Gutierrez Quirós, 33600 Mieres, Asturias, Spain, jayala@uniovi.es, ORCID 0000-0002-6404-1296

[5]Carbon Science and Technology Institute (INCAR), CISC, Francisco Pintado Fe 26, 33011, Oviedo, Spain, teresa@incar.csic.es, ORCID 0000-0002-2851-2169

Abstract

The contamination of water sources by potentially hazardous elements (PHEs), especially in mining areas, poses serious environmental and health risks. This study investigates the potential of waste-derived hydrochar – a carbonaceous material produced via hydrothermal carbonisation (HTC – for the removal of arsenic (As) from mining-influenced waters.

Hydrochar's surface chemistry, rich in functional groups, enables the adsorption of various contaminants. Hydrochars derived from different biodegradable feedstocks (e.g., wood waste, green waste, municipal solid waste, grape bagasse) were produced at pilot scale and evaluated for their As adsorption capacity.

Batch experiments using synthetic As solutions assessed the performance of four hydrochars under varying pH conditions. Although none effectively removed As, the results highlighted factors such as surface charge, feedstock type, and pH as critical for adsorption performance.

Despite the limited removal in this preliminary study, hydrochar shows promise as a low-cost, sustainable adsorbent. With further optimisation—such as surface functionalisation—it could be integrated into passive treatment systems (e.g., constructed wetlands or reactive barriers) for remediation of mining-impacted waters.

Keywords: Hydrochar, Potentially Hazardous Elements (PHEs), Arsenic

Introduction

The contamination of water sources by potentially hazardous elements (PHEs) poses a substantial threat to ecosystems and public health, particularly in regions with intensive mining activity. Among these contaminants, arsenic (As) stands out due to its toxicity, mobility in aquatic systems, and longevity in the environment. Its presence in surface and groundwater originates from both natural and anthropogenic sources, including the leaching of mining waste, the oxidation of sulfides, and acid mine drainage (Ramos Ramos *et al.* 2014; Quino Lima *et al.* 2021).

Conventional techniques for PHE removal include physicochemical processes such as chemical precipitation, reverse osmosis, ion exchange, and ultrafiltration. However, these methods often present limitations in terms of operational costs, secondary waste generation, and removal efficiency in complex matrices (Ayala and Fernández 2019a; Sun *et al.* 2022). In this context, the development of sustainable and low-cost adsorbents has gained considerable interest as a viable alternative for remediating contaminated water.

Hydrochar, a carbonaceous material obtained through hydrothermal carbonisation (HTC) of residual biomass, has emerged as a promising solution due to its high porosity and abundance of oxygenated functional groups (carboxyl, hydroxyl, and carbonyl) (Akkari *et al.* 2024; Khanzada *et al.* 2024). This functional group richness is one of the key factors enhancing the adsorption capacity of PHEs. Unlike biochar, which is produced by pyrolysis, hydrochar is obtained at lower temperatures under wet conditions, allowing for better utilisation of high-moisture biomass, such as grape bagasse, municipal solid waste, and discarded wood residues (Nadarajah 2020).

Recent studies have demonstrated that the functionalisation of hydrochar through chemical or physical activation can enhance its adsorption capacity, optimising its performance in the removal of metal contaminants (Nadarajah 2020). In particular, modification with alkaline agents or impregnation with metal oxides has been shown to improve interactions with As species in aqueous solutions (Nadarajah 2020).

This study evaluates the efficiency of hydrochar derived from various biomasses for As removal under laboratory-scale and pilot-scale conditions. The adsorption capacity and As capture mechanisms are analysed, providing a detailed framework for future research on its application in mine water remediation and integration into passive treatment systems such as constructed wetlands and permeable reactive barriers. The results obtained suggest that hydrochar could play a key role in the development of innovative and sustainable strategies for water purification and the mitigation of environmental impacts in mining areas.

Materials and Methods

In this study, four types of hydrochar were produced via hydrothermal carbonisation (HTC) at 200 °C for 4 hours under autogenous conditions in the reactor shown in Fig. 1, located at the Spanish National Research Council (CSIC) facility in COGERSA (Consortium for the Management of Solid Waste in Asturias).

The first, hydrochar from wood with water (MH), was produced from shredded wood waste using water as the reaction medium. The second, hydrochar from wood with whey (LM), was obtained by using whey instead of water to assess the effect of an organic medium on the material's structure. Additionally, bio-stabilised hydrochar (BIOEST) was used, derived from the bio-stabilised organic fraction of municipal solid waste, along with a paper–cardboard hydrochar (PC), generated from paper and cardboard waste previously soaked in water.

The materials were crushed and sieved to obtain particles smaller than 250 µm, ensuring an adequate surface area for adsorption experiments (Ayala & Fernández, 2023).

To evaluate the adsorption capacity of the hydrochars, a synthetic As solution was prepared at a concentration of 900 µg/L As.

Figure 1 Reactor for hydrochar production utilising the residual steam flow from the electricity generation of the hospital waste incinerator at COGERSA (image: Álvaro Amado-Fierro).

This solution was obtained by dissolving $Na_2HAsO_4 \cdot 7H_2O$ in deionised water and adjusting the pH to 3, 4, 5, and 6 by adding H_2SO_4 or NaOH (0.01 and 0.1 M), following standardised protocols for As adsorption studies (Ayala and Fernández 2019b, c).

Each working solution was prepared and stored in sealed glass bottles to prevent pH variations before the adsorption experiments.

The adsorption experiments were conducted in a batch system using 100 mL polyethylene flasks, which were placed on a mechanical shaker to ensure homogeneous mixing of the solution. In each experiment, 10 g/L of hydrochar was added to 50 mL of contaminated solution and left in contact for 24 hours at a temperature of 25 ± 2 °C, with a constant stirring speed of 175 rpm. After the contact time, the samples were filtered, and the supernatant was analysed by ICP-MS to determine the residual metal concentration in solution. This procedure allowed the evaluation of the adsorption efficiency of each hydrochar and its potential application in the remediation of water contaminated with potentially hazardous elements (PHEs) (Nadarajah 2020).

Results and Discussion

Below (Fig. 2) are the results for the final As concentration in solution after the adsorption test with the four types of hydrochar evaluated (Bio-stabilised – BIOEST, Wood with Whey – LM, Wood with Water – MH, and Paper – Cardboard – PC).

The results (Fig. 2) indicates that none of the hydrochars effectively reduced As concentrations below 900 µg/L As. The BIOEST hydrochar exhibited the lowest concentrations; however, these remained above the initial concentration. In contrast, the paper–cardboard hydrochar (PC) displayed the highest final concentrations, reaching 990.43 µg/L at pH 6, suggesting increased desorption. Overall, no clear trend was observed as a function of pH, indicating that desorption is not strongly influenced by this parameter within the studied range.

This behaviour aligns with previous studies demonstrating that the efficiency of hydrochar in PHEs adsorption is highly dependent on its structure, surface chemistry, and working pH (Khanzada *et al.* 2023, 2024). Specifically, some hydrochars have been reported to be not only ineffective in contaminant removal but may also release metals if their surface charge is negative at certain pH values (Khanzada *et al.* 2023).

The results obtained in the As adsorption experiments with hydrochar indicate that none of the materials achieved effective removal, with most exhibiting net desorption, leading to final concentrations exceeding the initial 900 µg/L. This phenomenon may be attributed to several factors, including the surface charge of the hydrochar as a function of pH, the initial composition of the material, and the presence of impurities or functional groups unsuitable for As adsorption (Khanzada *et al.* 2023, 2024). It has been reported that the structure of hydrochar is largely influenced by the type of biomass used and the synthesis conditions, which can significantly affect its capacity to retain PHEs (Akkari *et al.* 2024).

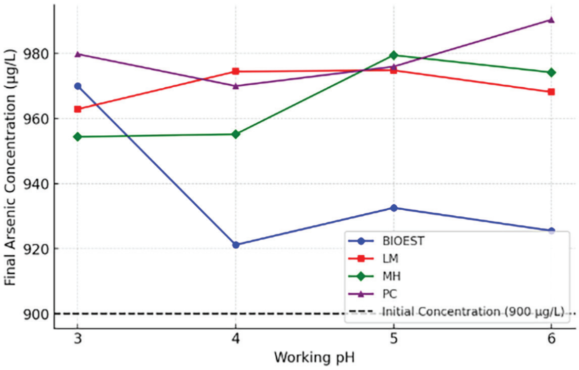

***Figure 2** Final Arsenic Concentration in Solution by Hydrochar Type.*

pH is a critical factor in PHEs adsorption, as it influences both the speciation of metals in solution and the surface charge of the adsorbent. In this study, all hydrochars were evaluated within a pH range of 3 to 6, which may have favoured the desorption of As in its arsenate form (AsO_4^{-3}), particularly if the point of zero charge (PZC) of the material was lower than the working pH (Wang *et al.*, 2018). This is consistent with previous studies indicating that hydrochars with a PZC lower than the system pH tends to repel anionic species rather than adsorb them (Navas-Cárdenas *et al.* 2023; Khanzada *et al.* 2024). Additionally, it has been documented that the presence of competing anions in solution, such as phosphate or sulfate, may further reduce hydrochar efficacy in As adsorption by displacing it from active sites and promoting its release into the aqueous medium (Akkari *et al.* 2024).

Notably, the paper–cardboard hydrochar (PC) exhibited the highest desorption, with a final As concentration of 990.43 µg/L at pH 6. This may be attributed to the presence of residual compounds in its matrix, such as modified lignin, inks, or other additives, which alter its surface chemistry and reduce its affinity for As (Khanzada *et al.*, 2024). Similarly, the wood hydrochar produced with whey (LM) showed high final As concentrations across all pH values tested, suggesting that the manufacturing process involving whey may have induced structural modifications that negatively affected its adsorption capacity. Previous studies have demonstrated that certain agro-industrial residues may generate hydrochars with low affinity for PHEs if the conversion process is not optimized (Adebisi 2017).

Conversely, the bio-stabilised hydrochar (BIOEST) exhibited the lowest desorption levels, though it still failed to retain As efficiently. This suggests that while bio-stabilisation may provide a more stable structure, it does not necessarily confer the appropriate functional groups required for As retention in solution (Navas-Cárdenas *et al.*, 2023). The optimisation of such materials through chemical modifications, such as acid or base activation, metal doping, or nanoparticle functionalisation, has been reported as an effective strategy to enhance PHEs adsorption (Akkari *et al.*, 2024).

The literature suggests that certain modifications can improve hydrochar adsorption capacity for PHEs, including chemical activation with acids or bases, the introduction of specific functional groups, and the incorporation of nanoparticles to enhance metal interactions (Khanzada *et al.*, 2024; Akkari *et al.*, 2024). These strategies have been successfully applied to hydrochars derived from agricultural and agro-industrial residues, yielding substantial improvements in contaminant retention in aqueous environments (Akkari *et al.*, 2024).

Conclusions

The results obtained in this study indicate that none of the four hydrochars evaluated achieved effective As adsorption in solution; in fact, a desorption effect was observed in several cases. These findings clearly demonstrate that, under the tested conditions, the selected hydrochars are not suitable for As removal. However, this does not rule out the broader potential of hydrochar as an adsorbent material. Instead, it underscores the need for systematic optimisation of its physicochemical properties to improve its performance in the remediation of waters contaminated with potentially hazardous elements (PHEs) (Navas-Cárdenas *et al.*, 2023; Khanzada *et al.*, 2024).

The efficacy of hydrochar in PHE adsorption is known to be influenced by its chemical structure, the presence and nature of surface functional groups, its point of zero charge (PZC), and the competition with other anions in solution, such as phosphate and sulfate (Saber *et al.*, 2018; Saba *et al.*, 2024; Zhang *et al.*, 2024). In this study, the bio-stabilised hydrochar (BIOEST) exhibited the lowest As desorption, suggesting that the stabilisation process may provide certain structural advantages, though clearly insufficient to ensure effective As retention.

Conversely, the paper–cardboard hydrochar (PC) showed the highest desorption, likely due to residual compounds such as modified lignin, inks, or additives that adversely affect its surface chemistry and affinity for As. Similarly, hydrochars derived from wood with whey (LM) and wood with water (HW-A) also exhibited poor performance, indicating that the interaction between biomass type and the reaction medium plays a crucial role in determining the resulting material's adsorption capacity (Pasipanodya *et al.*, 2024).

Since adsorption performance can be significantly enhanced through surface modification and controlled synthesis, future research should prioritise optimisation strategies such as chemical activation, pH adjustment, or impregnation with selective agents (Navas-Cárdenas *et al.*, 2023; Akkari *et al.*, 2024).

A limitation of this preliminary study is the absence of advanced physicochemical characterisation of the hydrochars, such as FTIR for functional group identification, SEM and EDS mapping for surface morphology and elemental distribution, and BET analysis for specific surface area determination. These analyses will be essential in future work to correlate structural properties with adsorption behaviour and to guide the optimisation of hydrochar production for targeted contaminant removal.

Although the present findings reveal significant limitations, hydrochar derived from biomass waste remains a promising candidate for future development as an environmentally responsible treatment material. Its valorisation supports circular economy principles and aligns with the Sustainable Development Goals (SDGs), particularly SDG 6 (clean water and sanitation), SDG 12 (responsible consumption and production), and SDG 13 (climate action).

Accordingly, the hydrochars evaluated here open new avenues for research in material engineering. Their future optimisation and possible integration into passive treatment systems, such as permeable reactive barriers and constructed wetlands, could enable their effective deployment in the long-term management of PHE contamination and contribute to the implementation of clean technologies for protecting water resources in mining-affected environments (Khanzada *et al.*, 2024; Akkari *et al.*, 2024).

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