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EVALUATION OF WASTE MATERIALS FOR CADMIUM REMOVAL: COMPARATIVE STUDY OF SORPTION CAPACITY AND STABILITY

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ABSTRACT – Cadmium (Cd) is a toxic metal requiring effective immobilization strategies. This study evaluated fly ash, rice husk ash, red mud, and treated bovine bones for Cd removal, comparing their performance to commercial products (ion exchange resin, activated carbon, calcium carbonate, and zeolite). Red mud and treated bones showed removal efficiency comparable to or better than commercial products across varying Cd concentrations. Sequential extraction revealed that treated bones ensured long-term Cd immobilization, with most Cd retained in the residual fraction. These findings emphasize the potential of using waste-derived materials as cost-effective alternatives for the remediation of Cd in water and soil.

Keywords: Cadmium, Separation, Immobilization, Waste materials, Sequential extraction.

INTRODUCTION

Cadmium (Cd) is one of the most mobile and bioavailable elements, which requires special attention due to the high risk of water and soil contamination, bioaccumulation, biomagnification in the food chain, and adverse health effects [1]. While geological weathering is a key natural source of Cd in soil and water, industrial emissions, mining, smelting, wastewater irrigation, agrochemicals, and improper waste disposal are primary anthropogenic inputs. The estimated ratio of anthropogenic to natural emissions of Cd is approximately 7:1 on a global scale [2].

The need for effective and affordable materials for separating Cd from aqueous media increased dramatically, particularly in low-income countries [3]. Furthermore, the remediation of Cd in contaminated soil has become a task of paramount importance [4]. Regardless of the soil properties, increasing levels of Cd contamination are characterized by the most notable increase of relative Cd amounts in the exchangeable fraction, which is easily accessible and mobile [5].

This study examined waste materials from food processing, metallurgy, and electric utilities as agents for Cd removal and immobilization. Their effectiveness was compared to commonly used water treatment and soil remediation products. Additionally, the

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distribution of Cd within the spent waste-derived sorbents was further investigated to assess the nature of the bonds between Cd and the materials studied.

EXPERIMENTAL

Waste and commercial materials

Several abundant waste materials with different chemical and mineralogical compositions were selected. Rice husk ash (RHA), sourced from "Agrino", Greece, is a byproduct of the combustion of rice hulls and serves as a source of amorphous reactive silica [6]. Animal bones are a valuable biogenic calcium phosphate (apatite) resource. For this study, the bovine bones were prepared through chemical oxidation using hydrogen peroxide (BBH) and thermal treatment at 400°C (BBT) [7]. Red mud (RM) was sourced from the tailings pond of the "Alumina" factory in Zvornik, Bosnia and Herzegovina. This waste sludge generated from the Bayer process during bauxite ore processing comprises various components, mainly oxides of iron, aluminum, and silica [8]. Lastly, fly ash (FA), a common byproduct of coal combustion, was considered. The sample supplied from a thermal power plant in Kostolac, Serbia, is characterized by a high content of silica and lesser amounts of iron and aluminum oxides [9]. All materials were finely ground using a ceramic mortar.

The following products, commonly used for soil remediation and the treatment of water and wastewater, were examined for comparison: calcium carbonate ($CaCO_3$) from Merck; zeolite ("Zeokop", Serbia) denoted as ZEOL; activated carbon (AquaSorb®HS) referred to as AC, and a mixed bed ion exchange resin (Resinex™ MX-11) referred to as IER, both sourced from Jacobi Group.

Determination of Cd removal efficiency and stability of resulting residues

Solutions with a range of Cd concentrations ($5 \cdot 10^{-6}$, 10^{-3} and 10^{-2} mol/L), and initial pH 5.5, were prepared from $Cd(NO_3)_2 \times 4H_2O$ (Merck, p.a.) and deionized water. The powdered materials and Cd solutions were mixed at a 1:20 (g/ml) soil-to-solution ratio using an overhead laboratory shaker (10 rpm). The experiments were conducted at room temperature (21±1°C) for 24 h to ensure equilibrium conditions. After centrifugation and filtration through 0.45 μm membrane filters, residual Cd concentrations were measured by an Inductively Coupled Plasma Mass Spectrometer (ICP-MS, model iCAP Q, Thermo Scientific). Final pH values were measured using the InoLab WTW pH meter.

The solid residues obtained after mixing the waste materials with 10^{-3} mol/L Cd solution were analyzed to determine the speciation of Cd in five operationally defined fractions: ion-exchangeable (F1), bound to carbonates/acid soluble (F2), bound to iron and manganese oxides/reducible (F3), bound to organic matter/oxidizable (F4), and residual (F5). For that purpose, a Tessier sequential extraction procedure [10] was applied and modified according to Marković et al. [5].

RESULTS AND DISCUSSION

Figure 1 displays the Cd removal efficiency of tested materials and the corresponding equilibrium pH values. Under equivalent experimental conditions, all materials

completely removed Cd from $5 \cdot 10^{-6}$ mol/L solution (Figure 1, a), resulting in residual Cd quantities below the detection limit (LOD; 0.05 µg/L). For comparison, the maximum permissible Cd concentration (MPC) in drinking water set by the World Health Organization (WHO) is 3 µg/L [11].

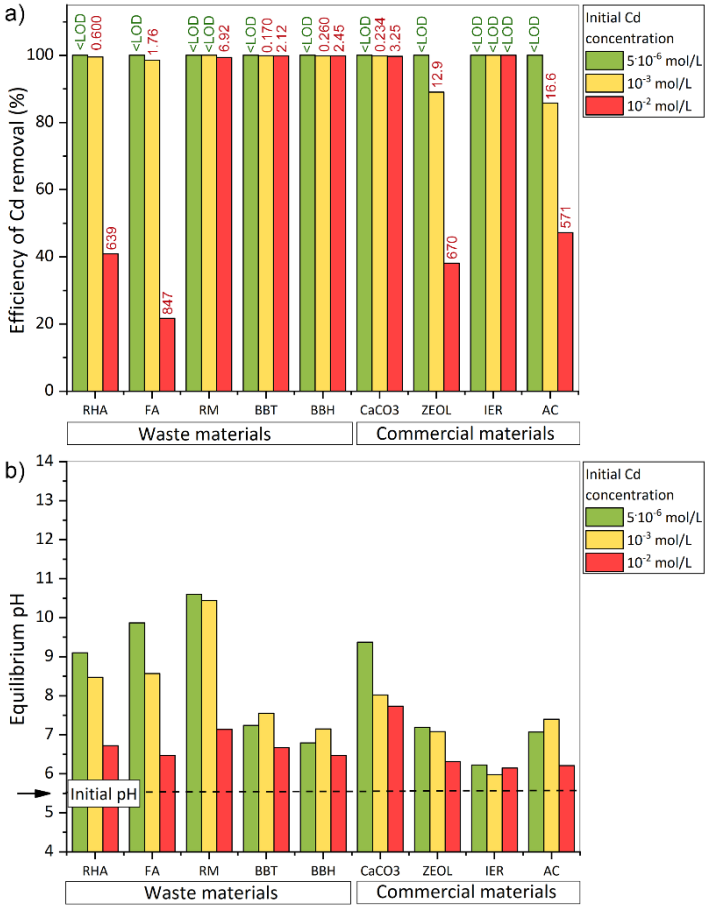

Figure 1 (a) Cadmium removal efficiency by waste and commercial materials (numbers above bars indicate the residual Cd concentration in mg/L; LOD = 0.05 µg/L) and (b) equilibrium pH values

As the initial concentration of Cd increased to 10^{-3} mol/L, the removal efficiencies of RHA (99.5%), FA (98.5%), ZEOL (89.0%), and AC (85.8%) declined compared to other materials that maintained efficiencies above 99.9%. Using a 10^{-2} mol/L concentration, RHA, FA, ZEOL, and AC capacities dropped significantly to 40.9%, 21.7%, 38.1%, and 47.2%, respectively. In contrast, RM removed 99.4%, $CaCO_3$ 99.7%, and bone-derived materials 99.8%, while the IER could still remove Cd completely. The results indicate that

silicate-rich wastes RHA and FA are particularly affected by increases in Cd concentration, leading to a notable loss in their removal efficiencies.

These results are further analyzed by observing the equilibrium pH values (Figure 1, b). The hydrolysis of Cd ions starts at pH > 8, leading to an increase in the percentage of $Cd(OH)^+$ species, whereas $Cd(OH)_2$ precipitation occurs in the pH range of 10-12. RHA, FA, and RM are alkaline wastes that provided high equilibrium pH values but displayed a significant decrease in equilibrium pH with increased Cd concentration. Judging by the equilibrium pH values, sorption and ion exchange of $Cd(OH)^+$ may be the operating mechanism of RHA, FA, and RM for Cd concentrations of $5 \cdot 10^{-6}$ and 10^{-3} mol/L. A substantial pH decline associated with the highest initial concentration of 10^{-2} mol/L implies Cd ions sorption through inner-sphere complex formation with the surface (S-OH) groups following the reaction:

$$Cd^{2+} + S\text{-}OH \leftrightarrows S\text{-}OCd^{+} + H^{+} \quad (1)$$

In carbonate-rich environments, otavite ($CdCO_3$) precipitates at a pH of around 7.0 to 8.0, explaining the high efficacy of $CaCO_3$. Similarly to ZEOL, IER, and AC, the removal of Cd by bone-derived BBH and BBT occurred at near-neutral pH but with superior efficiency. Surface complexation, ion exchange with Ca ions in apatite lattice, and dissolution/precipitation are possible mechanisms of Cd removal by BBH and BBT.

To analyze the stability of sorbed Cd, residues with sorbed Cd amounts ranging from 2.307 mg/g to 2.341 mg/g were subjected to a sequential extraction protocol (Figure 2). The recovery of Cd across all five extraction fractions ranged from 95% to 118%.

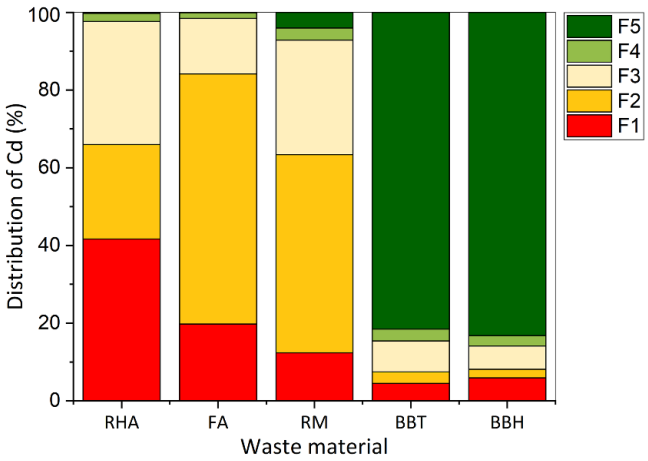

Figure 2 Distribution of Cd in various fractions of waste materials (F1- ion-exchangeable, F2 - bound to carbonates/acid soluble, F3 - bound to iron and manganese oxides/reducible, F4 - bound to organic matter/oxidizable, F5 – residual)

Considering the RHA, FA, and RM, Cd was found mainly in mobile fractions, with respectively 42%, 20%, and 12% in the ion-exchangeable (F1) phase and 24%, 64%, and

54% in the carbonate/acid soluble (F2) phase. Quite the contrary, BBT, and BBH hold most of the sorbed Cd (81% and 83%) in the residual (F5) fraction, which can be liberated only by the action of concentrated mineral acids, i.e., in conditions never encountered in the environment. A small portion was found in F1 (4-5%) and F2 (3-3%) fractions, which supports the dissolution of apatite and precipitation of poorly soluble Cd phosphate as the main mechanism of Cd removal. The presented results have implications for the stability of spent sorbents upon disposal, possible regeneration of sorbents, and their application in soil remediation.

Distribution of Cd in RHA, FA, and RM indicates the release of Cd in conditions of increased acidity and/or concentration of other cations. This suggests potential negative impacts on landfills for waste disposal while also indicating the relatively straightforward regeneration of sorbents and recovery of Cd. Sorbents derived from animal bones tightly bind Cd, establishing strong chemical bonds, which is a valuable performance in terms of spent sorbent stability and soil remediation.

The primary route for human exposure to cadmium (Cd) is through the consumption of vegetables [12]. This raises significant concerns, particularly in areas with cadmium-enriched farmland soil [4]. The forms of Cd that are considered mobile and potentially available for plant uptake include water-soluble, exchangeable, carbonate-bound, and those bound to iron and manganese oxides [4]. As a result, various techniques are employed to reduce Cd content in the labile fractions of contaminated soil, including chemical elution, electro-kinetic remediation, phytoremediation, stabilization and solidification, as well as combined remediation strategies [4]. Applying bone-derived materials to Cd-contaminated soil shows promise for *in situ* immobilization of Cd by enhancing the transfer of the pollutant from soluble and mobile fractions to a more stable residue fraction, effectively reducing their mobility and bioavailability.

CONCLUSION

Valuable minerals found in the waste materials studied can help mitigate Cd pollution. This approach addresses significant issues commonly faced in wastewater treatment, such as the high consumption of precipitating agents and the problems related to sludge formation. Depending on the level of Cd contamination, treatments using RHA, FA, and RM can be highly effective. However, the equilibrium pH of the treated water may exceed permissible discharge values, and monitoring is necessary for the potential leaching of trace impurities from the waste. Bone-derived materials have demonstrated superior efficiency in removing Cd under near-neutral conditions and have a high potential for long-term Cd immobilization, making them promising candidates for soil remediation. Further investigation is necessary to examine how wastewater composition and other factors impact the performance of studied materials.

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