UTILIZATION OF SILICON-MODIFIED CORN WASTE BIOCHAR FOR CADMIUM AND LEAD REMOVAL FROM AQUEOUS SOLUTIONS

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Abstract
In this study, we investigated the potential of biochar derived from corn harvest residues, modified with silicon, to enhance the removal efficiency of cadmium and lead ions from aqueous solutions. Our characterization of pristine and silicon-modified biochars using Fourier-Transform Infrared Spectroscopy (FTIR) confirmed the successful incorporation of silicon on the modified biochar's surface, a crucial factor for the enhanced adsorption of metals, especially Cd. The metal residue was quantified by Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES). Our adsorption experiments demonstrated that the silicon-modified biochar exhibited significantly improved adsorption capacity, achieving removal efficiencies exceeding 99% in various pH conditions. This high removal efficiency was achieved with a minimal amount of Si, and in combination with the use of a low-cost and widespread biochar precursor, this approach demonstrates its potential as a cost-effective strategy for the removal of metal contaminants from water.

Introduction
Lead and cadmium are recognized as two of the most toxic and persistent heavy metals in the environment, notorious for their ability to bioaccumulate in living organisms. Their widespread presence primarily results from various anthropogenic activities, including mining, smelting, and waste disposal. Owing to their high persistence, these metals remain in the environment for extended periods, posing a significant and long-term risk to ecosystem integrity and public health [1]. To mitigate this risk, several removal approaches have been proposed. Among these, adsorption is considered one of the most suitable and promising methods for the remediation of heavy metals [2]. Over time, researchers have experimented with various materials as sorbents for adsorption, and each material brings its unique characteristics to the adsorption process. Recently, biochar-based materials have gained attention as innovative and cost-effective options for adsorbing various heavy metals [3].

Biochar is a black, carbon-rich, and porous material, obtained by carbonization of biomass at temperatures higher than 250 °C in an inert atmosphere of nitrogen [4]. These carbonaceous materials possess several advantageous properties, including low density, extensive porosity, and a large surface area, making them highly effective, even in their unmodified state [5]. However, strategic modifications are often employed to enhance their surface chemistry and textural properties, improving targeting efficiency for specific contaminants and enhancing overall removal performance.

Modified biochar can be prepared through various physical, chemical, and microbial methods to improve its performance. Among these, silicon modification has emerged as a particularly effective strategy [6].

This study focuses on biochar produced from corn harvest residues (corn cobs and corn stalks) as adsorbent materials, comparing their pristine forms with silicon-modified variants. The research examines their effectiveness in the removal of cadmium and lead from contaminated water, with the dual objective of evaluating their applicability in water treatment and their potential use as amendments for assisted phytostabilization. This approach aims to identify the samples that exhibit the most promising characteristics for removing lead and cadmium from the media, providing a foundation for future *in situ* investigations.

Experimental

Materials and Methods

The precursor biomass (corn stalks and corn cobs) was collected from an agricultural site near Belgrade, Serbia, following the harvest. The precursor material was modified using an aqueous solution of sodium metasilicate nonahydrate ($Na_2SiO_3 \cdot 9H_2O$), commonly known as water glass. Carbonization was conducted in a horizontal tube furnace, Adamel-Lhomargy CT7, under a nitrogen atmosphere. Cadmium and lead stock solutions (50 ppm) were prepared by dissolving $Cd(NO_3)_2 \cdot 4H_2O$ and $Pb(NO_3)_2$ in deionized water. The initial pH was modified by adding 0.1 M HCl or 0.1 M NaOH to achieve target pH values of 3 and 5, respectively. Concentrations of the analytes after the adsorption process were quantified using a *Thermo Fisher iCAP DUO 7000* inductively coupled plasma optical emission spectrometer (ICP-OES). The surface chemistry of pristine and silicon-modified biochar was characterized by Fourier-transform infrared spectroscopy (FTIR) using a *Thermo Fisher Scientific Nicolet iS5 spectrometer*.

Synthesis of pristine and Si-modified biochar

Biomass was air-dried at room temperature, mechanically ground to a fine powder, and homogenized in a 1:1 mass ratio of corn cobs to corn stalks. The biomass was treated in a horizontal tube furnace under a nitrogen atmosphere for carbonization. The heating rate was maintained at 5 °C per minute until the target temperature of 800 °C was achieved. The temperature was held constant for 2 h to ensure complete carbonization. After the carbonization process, the biochar was subjected to cooling to room temperature inside the furnace, and then ground into a fine powder. The resultant unmodified biochar was labeled NoSi, corresponding to zero additional silicate content.

The synthesis of silicon-modified biochars was carried out using a soaking method. Specifically, biomass samples were impregnated with sodium silicate solution (1.5 g/mL) before carbonization, at three different biomass-to-silicate ratios (4:1, 2:1 and 1:1). The silicon-modified samples were subjected to the same carbonization conditions as the unmodified ones. The resultant modified biochars were labeled LowSi, MedSi, and HighSi, corresponding to the low, medium, and high additional silicate content.

Adsorption experiments

The obtained materials were immersed in a 50 ppm mixed solution of cadmium and lead salts, which was adjusted to two different pH values and agitated using an orbital shaker at 180 rpm for 24 h. Upon completion of the adsorption experiment, the solutions were filtered and analyzed using ICP-OES. The adsorption efficiency was evaluated based on the residual metal concentration, where the lowest concentration indicated the highest adsorption capacity.

Results and discussion

FTIR analysis

FTIR spectra of the analyzed samples are presented in Figure 1. The characteristic vibrational peak at region 3300 cm^{-1} is assigned to ^{-}OH stretching vibrations of free or intercalated water. The peak at 1620 cm^{-1} may be assigned to C=C bonds. Two vibrational peaks at 470 cm^{-1} and 1110 cm^{-1} are assigned to Si-O-Si or Si-O stretching vibrations [7]. These two peaks confirm the successful binding of silicon to the surface of the materials carbon structure. An increase in the intensity and peak area at 1110 cm^{-1} is also visible, which is increasing in samples with a higher Si content, which is an additional confirmation of the successful modification of the biochar.

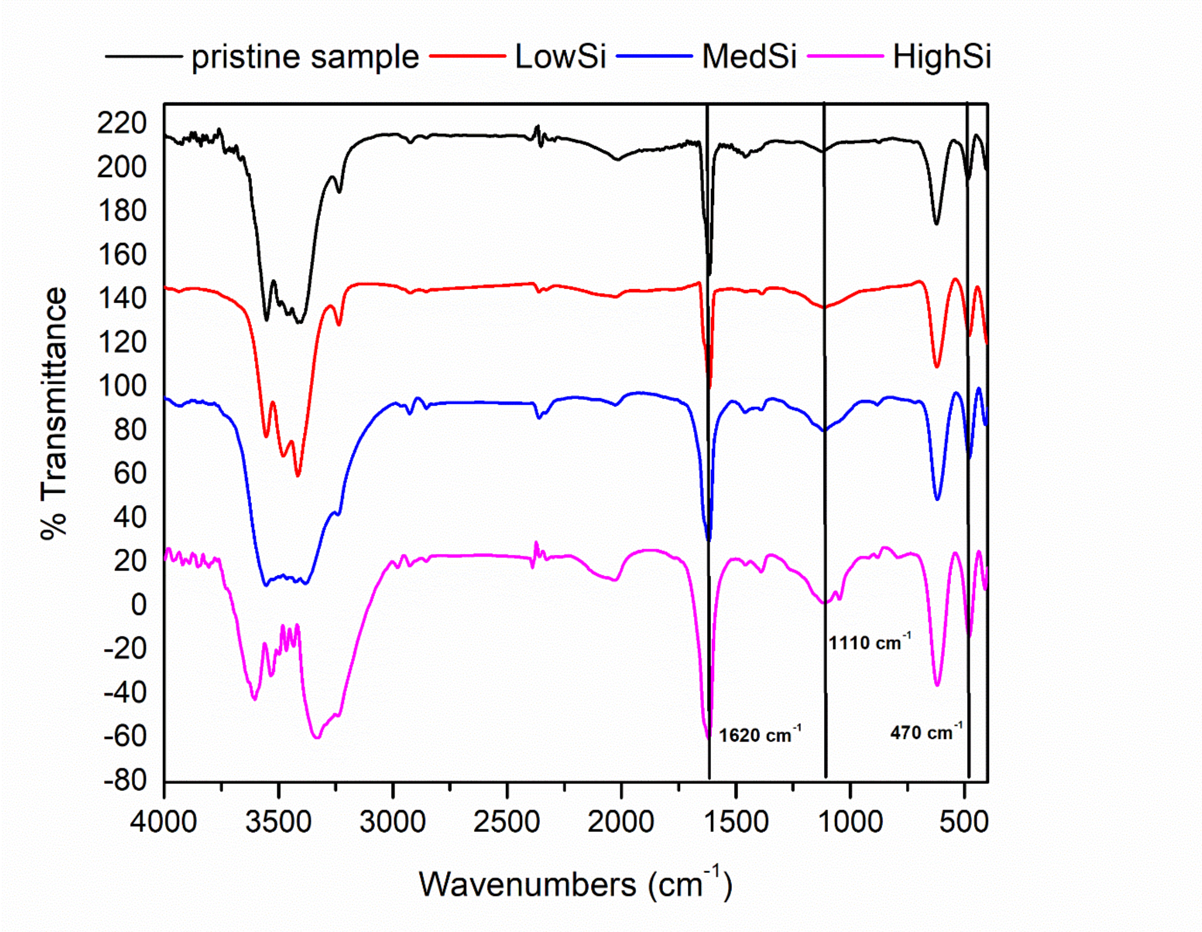

Figure 1. FTIR spectrum of synthesized samples with different ratios of silicon

Adsorption study

The adsorption of Cd and Pb was investigated at pH 5 and pH 3, a range selected to prevent metal precipitation, which typically occurs at higher pH values. The adsorption trends for the different biochar samples at each pH are presented in Figure 2. At pH 5, complete removal of Pb is observed for the pristine and LowSi samples. For samples with higher Si content, the percentage removal slightly decreases up to 90% for the HighSi sample, but it is still a very high percentage of Pb removal. In Cd adsorption, the pristine sample shows a low removal efficency of 64%, while the Si modified samples show drastically better adsorptive characteristics, from 99% for the LowSi sample to 91% for the HighSi sample. Even in the case of Cd adsorption, a slight decrease in adsorption efficiency is observed in modified samples, around 9%. The trends of decrease in the efficiency of Pb and Cd removal in samples with a higher Si content, as well as the reduced removal percentage of Cd in the pristine sample, can probably be explained by the saturation of the material surface and active sites in the HighSi sample, which reduces the availability of active sites for binding other metals. Further research will give a more detailed and complete answer to this very interesting phenomenon.

Adsorption at pH 3 showed a similar trend with a slight decrease in removal efficiency of both Pb and Cd for the HighSi sample compared to at pH 5. Pristine sample at pH 3 shows a low removal efficiency for Cd, only 37%, which can be explained by the fact that in acidic conditions, there is competition between metal ions and H^+ ions, leading to reduced adsorption of the target analyte [7]. Consequently, achieving an optimal degree of modification is crucial for utilizing the full potential of Si-functionalization as a targeted strategy for biochar enhancement.

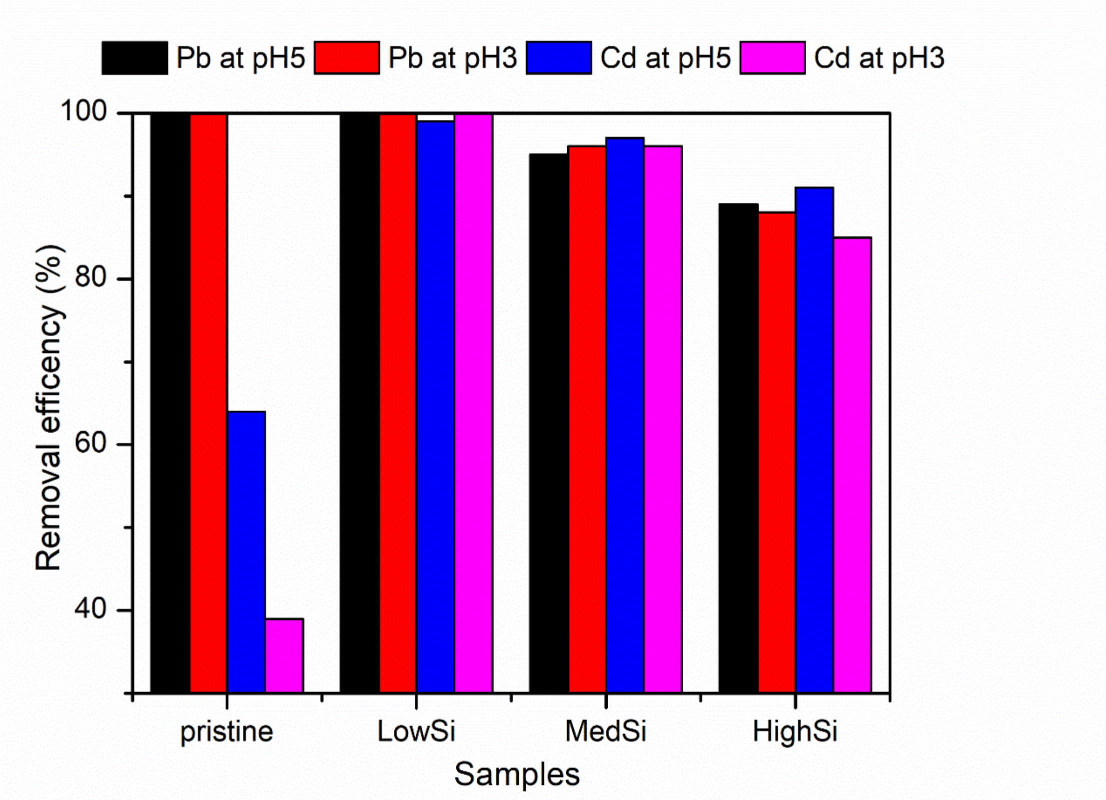

Figure 2. Removal efficiency for Pb and Cd at pH 3 and pH 5

Conclusion

FTIR analysis confirmed the successful modification of pristine biochar with different silicon content. All silicon-modified biochars exhibited excellent heavy metal removal capabilities, especially the sample with low Si content, which demonstrated exceptional efficiency (>99%) for both Pb and Cd across distinct pH conditions. The study highlights the importance of optimal silicon dosage, as the lowest silicate modification (4:1 ratio) achieved better results while minimizing material costs. Combined with abundant agricultural waste biomass, this approach presents a highly cost-effective strategy for the remediation of heavy metal-contaminated media. In future research, the mechanism of silicon binding to the biochar surface during modification and the mechanism of metal adsorption onto biochar will be thoroughly examined.

Acknowledgements
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