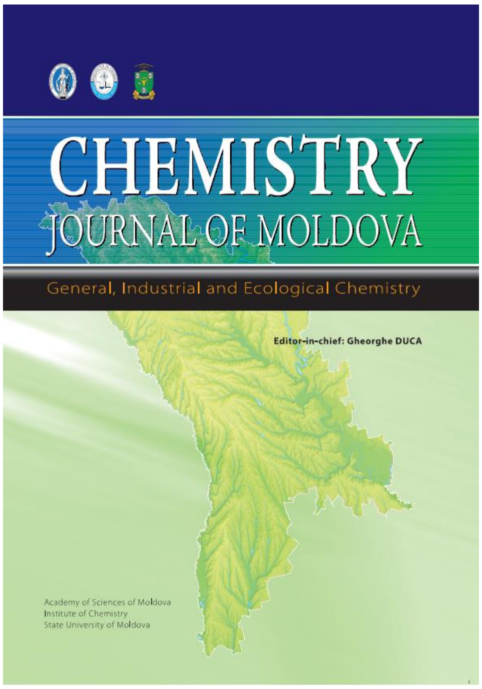

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Abstract. This study examines the potential use of a low-cost biosorbent - chamomile tea residues, as an alternative to traditional adsorbents for removing Pb^{2+} ions from aqueous solutions. The inductively coupled plasma-optical emission spectrometry (ICP-OES) was used to measure the amount of metal before and after the removal, and a scanning electron microscope (SEM) was used to examine the morphology of the residues. To ascertain the optimal operational parameters for effective metal extraction from the aqueous solutions, a range of different concentration levels, as well as the addition of acid in the solutions, was explored. The results show that lead concentration is reduced under optimized conditions, achieving an impressive nearly 50% Pb^{2+} ions removal with just 0.05 g of the waste material. These findings depict chamomile tea residues as promising, affordable, and highly efficient biosorbent in lead removal for environmental remediation.

Keywords: environmental pollution, remediation, biosorption, lead, chamomile residues.

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Introduction

The expression "heavy metal" is typically used to allude to the pollution that these elements cause in the environment, which can have a detrimental effect on both people and the environment [1]. Due to their unique physical and chemical properties, including high conductivity, durability, and catalytic abilities [2] these elements are indispensable in the process industry, playing vital roles in insecticides, batteries, and electronics production [3]. Numerous factors can cause heavy metal pollution, including industrial discharge, agricultural practices, mining, and poor waste management [4]. These metals may survive for very long after being discharged into the environment and can travel great distances by air and water. A variety of harmful environmental outcomes, such as the extinction of aquatic life, agricultural degradation, and other changes to natural environments, can be brought on by heavy metal contamination. Furthermore, exposure to heavy metal pollution can have detrimental impacts on human health, such as cancer, neurological impairment, and other chronic diseases [5]. There are many techniques used to lessen the effects of heavy metal pollution, including adsorption, precipitation, ion exchange, and bioremediation [6]. When it comes to eliminating heavy metals from the environment, biosorption and bioremediation are among the methods that are regarded as being both economical and environmentally responsible.

Biosorption of heavy metals is a process that describes removing these metals either spontaneously or metabolically with various physicochemical pathways, using numerous biological components, such as biomass or microbes [7]. Because it depends on the capacity of many biomolecules, including proteins, carbohydrates, and lipids, to bind and remove heavy metals from water, biosorption can be a successful method for eliminating heavy metals from the environment [8]. For biosorption, a variety of biological materials can be used such as bacteria, fungi, algae, and plant parts [9]. The materials mentioned above can be utilized in their natural state or in a modified one to increase their ability to remove heavy metals or any unwanted substances. Scientists have modified certain bacteria to produce biosorbents that have a high capacity to bind metal. Agricultural waste like straw, rice husks, and banana peels can also be utilized for biosorption, and these low-cost substitutes can be reused again without losing their efficacy [10]. In addition to or instead of more traditional methods such as membrane filtration, ion exchange, and chemical precipitation, biosorption is considered an affordable and sustainable approach to removing heavy metals from aqueous solutions [11]. Chamomile is known for its remarkable efficacy in metal and contaminant removal from water, demonstrating notable adsorption capabilities, particularly concerning heavy metals like lead, cadmium, and copper [12]. This efficacy can be attributed to the presence of specific compounds in chamomile, such as flavonoids and phenolic acids, which have a strong ability for complexing with heavy metals [13].

This research aims to investigate substitutes for the traditional application of activated carbon in water purification procedures and to find environmentally friendly materials that are both affordable and easily incorporated into real-world applications. The study aims to tackle these issues by examining novel methodologies that conform to the tenets of green chemistry. Consequently, this investigation was designed to examine the chamomile tea residues from New York City, United States, as potent biosorbents in lead removal. The results highlight the potential of Chamomile tea residues as a cost-effective and highly efficient biosorbent for environmental remediation. Moreover, the results suggest that due to its economic and widespread availability, chamomile tea residues are a cost-effective and accessible alternative to conventional adsorbents like activated carbon.

Experimental

Reagents

All reagents used in this investigation were of high analytical grade purity. Initially, a standard solution of lead with a concentration of 2000 mg/L was prepared from $Pb(NO_3)_2$ (Merck, Germany) in a 2 L volume. For investigation purposes, a dilution of this substance was done with distilled deionized water. The argon gas utilized for the ICP-OES spectrometer boasted a purity level of 99.99%.

Instrumentation and method

Lead was determined by ICP optical emission spectrometer (Perkin Elmer, Optima 2100DV ICP-OES). Morphological analysis was carried out by scanning electron microscopy (JSM-6010LA, JEOL. USA) [14].

Adsorption experiments

This study conducted a batch adsorption experiment to evaluate chamomile residue effectiveness in removing lead from aqueous solutions. Lead concentrations, ranging from 40 to 1000 mg/L, were tested with 20 mL of a metal solution. Chamomile residues were treated with either 0.4 M HNO_3 for acid-sorbent or 0.4 M NaOH for base-sorbent conditions, washed with deionized water, and dried. The adsorbent mass was constant at 0.05 g, and experiments were conducted at a consistent temperature of 23°C. The sorbent was in contact with 20 mL lead solutions of various concentration samples for 15 minutes, and then the solution was filtered with a 0.45 mm HPLC filter paper. A volume of 2.00 mL of the filtered solution was mixed with 2.00 mL of 4% nitric acid for the atomic emission measurements.

The amount of Pb^{2+} adsorbed Q (mg/g) was calculated using Eq.(1).

$$Q = \frac{(C_i - C) * V}{m} \quad (1)$$

where, C_i is the initial Pb^{2+} concentration (mg/L),
C is the left Pb^{2+} concentration (mg/L),
V is the volume of Pb^{2+} solution used (L),
m is the mass of adsorbent used (g).

In contrast, the Pb^{2+} percent removal was calculated by applying Eq.(2).

$$Removal\ (\%) = \frac{(C_i - C) * 100}{C_i} \quad (2)$$

Results and discussion

The study aims to examine chamomile tea residues as a cost-effective biosorbent for the removal of lead from aqueous solutions, investigating operational parameters and demonstrating its potential as an efficient environmental remediation tool. The SEM images of the finely ground chamomile tea before lead ion adsorption are shown in Figure 1. Figure 2 shows the SEM of the adsorbent when the metal was adsorbed into it.

The SEM analysis of chamomile residues provides valuable insights into the surface characteristics and microstructure. The chosen working distance of 11 mm contributed to optimal imaging conditions, ensuring a balance between depth of field and resolution. Understanding these features is crucial for comprehending the composition and potential applications of chamomile in various fields, including the adsorption of lead metal in this case.

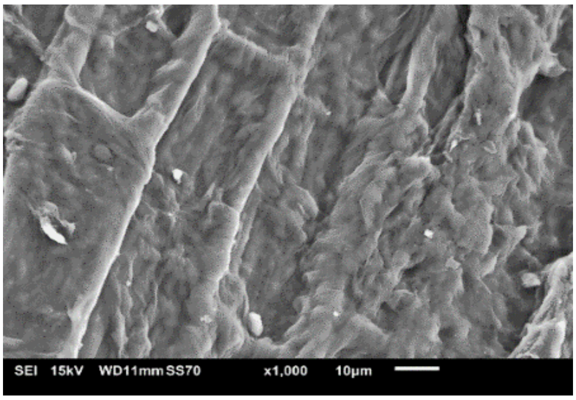

Figure 1. SEM images of the biosorbent before metal adsorption.

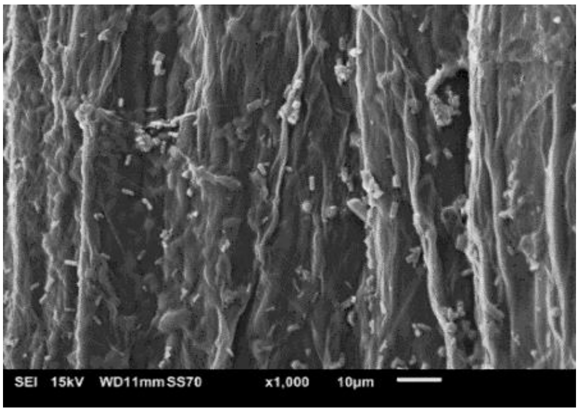

Figure 2. SEM images of the biosorbent after metal adsorption.

The 15 kV accelerating voltage provided enhanced resolution, allowing for a comprehensive examination of the chamomile residue microstructure. The micrographs captured at 70x magnification showcased the unique morphology of chamomile residues. The Secondary Electron Imaging mode effectively highlighted surface topography, revealing fine details at a spatial scale of 10 micrometres per unit. The adsorption of lead ions was studied with acid, neutral (non-treated), and base-treated chamomile.

In this study, lead metal removal was investigated using chamomile tea. The data on Table 1 reveals the varying adsorption capacities (Q) and percentage removal (%), corresponding to different initial concentrations (C_i) of lead in milligrams per litre (mg/L).

The data presented in Table 1 illustrates the effectiveness of lead removal under acidic and neutral media conditions. At a lower initial lead concentration of 40 mg/L, the chamomile tea exhibited notable efficiency with a high percentage of lead adsorption (40.32%) and a significant quantity adsorbed per gram (6.45 mg/g). However, as the initial lead concentration increased, respectively to 100, 200, 500, and 1000 mg/L, the efficiency of lead adsorption diminished, as reflected in decreasing percentages to 9.18%, 6.32%, 5.73%, and 8.83%.

On the contrary, better adsorption capabilities are observed in neutral media, where the initial concentration of 40 mg/L led to 46.66% of lead removed. This resulted in a residual concentration of 21.34 mg/L, equivalent to 7.46 mg/g of lead adsorbed into the biosorbent. As the concentration of lead increased to 100 mg/L, the adsorption capacity improved to 22.2 mg/g, resulting in a final concentration of 44.5 mg/L. Further elevating the metal concentration to 200 mg/L led to a remaining concentration post-adsorption of 111.49 mg/L, with a removal efficiency of 44.25%, equivalent to 35.4 mg/L of lead adsorbed. Continuing the trend, at a higher metal concentration of 500 mg/L, approximately 17.6% of the metal was adsorbed, resulting in a concentration left of 411.99 mg/L of lead, with 35.21 mg/L of metal adsorbed. The final experiment, conducted at an initial concentration of 1000 mg/L, displayed a removal efficiency of 12.92%, adsorbed 51.68 mg/L of lead, with the remaining concentration at the end recorded as 870.81 mg/L.

As evident, the concentration of Pb^{2+} influences the adsorption capacity, supporting findings from research studies that underscore different factors governing the adsorption of heavy metals onto biosorbents, notably concentration [15].

Table 1

Results of Pb^{2+} adsorption ions in biosorbent.

	Acid media			*Neutral media*		
C_i (mg/L)	*C (mg/L)*	*Q (mg/g)*	*Removal (%)*	*C (mg/L)*	*Q*	*Removal (%)*
40	23.87	6.45	40.32	21.34	7.46	46.66
100	90.82	3.67	9.18	44.5	22.2	55.5
200	187.36	5.06	6.32	111.49	35.4	44.25
500	471.37	11.45	5.73	411.99	35.21	17.6
1000	911.71	35.31	8.83	870.81	51.68	12.92

The results indicate that with the increase in the concentration of Pb^{2+} for the same amount of adsorbent, the scale of adsorption will decrease. This happens because there are more active binding sites on the sorbent at lower concentrations [16] allowing for more efficient adsorption, hence a reduction in the adsorption of the Pb^{2+}. Moreover, stronger binding affinity between the sorbent and substance may occur at lower concentrations, therefore leading to increased adsorption [17].

The addition of acid onto the solution where the adsorption is happening might lead to the protonation process, with the carboxyl, hydroxyl, and amino groups that are presented in biosorbent [18]. The act of adding a proton (H^+) to these functional groups changes the surface charge of the biosorbent. This protonation process of functional groups tends to decrease the biosorbent's electrostatic affinity for metal ions, including lead ions (Pb^{2+}). This is because protons compete with metal ions for binding sites on the surface of the biosorbent under acidic media. Under acidic pH values, the biosorbent may therefore show decreased lead ion adsorption ability [19].

Similar research was conducted in base media (the results are not presented in the paper) showing a significant decrease in Pb^{2+} concentration, leading to an adsorption efficiency of nearly 96%. This reduction of concentration can be primarily attributed to the phenomenon where Pb^{2+} ions undergo precipitation at pH levels greater than 7. The increase in adsorption at higher pH values is consistent with the principle that, under alkaline conditions, lead ions tend to form insoluble precipitates, reducing their concentration in the solution.

As it was noted, the obtained results verify that the neutral media provide better conditions for the adsorption of lead ions to be removed from aqueous solutions in chamomile residues. The functional groups of the biosorbent are less likely to become excessively protonated in neutral media, preserving a more appropriate surface charge for the efficient adsorption of lead ions. The ideal circumstances for the biosorbent to interact with lead ions and facilitate their removal from the solution are promoted by this pH-neutral environment.

It's crucial to understand that every substance behaves differently when it comes to adsorption. Each material has its specific patterns of behaviour during adsorption, and these patterns can be influenced by factors like pH, temperature, the presence of other ions, and more [20].

There are several forms of heavy metals found in water resources, such as ionic, soluble organic or inorganic complexes, particles, or trapped in organic or mineral colloids, sediments, and biota. For all these types of heavy metals presented in the environment, knowing the pH value is very important. It underscores that pH [21] not only impacts the adsorption efficiency but also influences the surface chemistry of the biosorbent and the specification of metal ions in the solution.

It was shown that pH significantly affects the dissociation of the sites on the biomass surface and the chemical behaviour of toxic metals in the solution [22]. Consequently, establishing and maintaining an appropriate pH level is essential for optimizing the efficacy of biosorption in heavy metal removal processes [23]. Subsequently, with a further rise in pH, the onset of metal precipitation occurs, attributed to the formation of metal hydroxides or hydroxide anionic complexes [24].

According to the results presented in the study, it is evident that the adsorption of lead in chamomile tea residues was consistently higher in neutral media compared to acidic conditions across all the initial concentrations. In neutral media, the chamomile tea residues performed better performance, characterized by higher percentages and quantities of lead adsorbed.

The more favourable pH environment in neutral conditions likely enables interactions in the surface between the chamomile tea residues and lead ions, leading to increased adsorption efficiency. On the contrary, in acidic media, the presence of additional protons may compete for available binding sites on the residues, potentially blocking the adsorption process [25].

Based on the experimental findings, it is evident that the concentration of Pb^{2+} ions is reduced in aqueous solutions. This study establishes that the waste derived from the tea residues can be effectively used as a substitute for activated carbon.

This approach can be applicable in water bodies characterized by elevated lead pollution levels, especially near industrial zones, a context fitting for Kosovo, renowned for its abundance of this metal. In instances where water is contaminated with lead, the effectiveness of isolation of Pb^{2+}, as demonstrated in this study, can be achieved by utilizing the waste byproduct.

Conclusion

In summary, this investigation highlights the capability of chamomile tea residues as a sustainable biosorbent for lead removal in water samples. The concentration of the metal solution shows a clear correlation between solution concentration and metal extraction observed.

The study reveals that the lowest metal concentration yields the highest removal, and conversely.

The research also highlights that optimal metal adsorption occurs under neutral conditions, emphasizing the advantage of using these waste materials without the need for additional substances to increase the adsorption efficacity. These results show the considerable capacity of chamomile tea residues as an eco-friendly biosorbent, providing applications in sustainable lead removal. Proper application methods and the identification of optimal working parameters are key to realizing the full benefits of chamomile tea residues in this context.

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References

1. Hazrat, A.; Ezzat, K.; Ikram, I. Environmental chemistry and ecotoxicology of hazardous heavy metals: environmental persistence, toxicity, and bioaccumulation. Journal of Chemistry, 2019, 6730305, pp. 1–14 DOI: https://doi.org/10.1155/2019/6730305
2. Tchounwou, P.B.; Yedjou, C.G.; Patlolla, A.K.; Sutton, D.J. Heavy metal toxicity and the environment. Springer: Basel, 2012, 101, pp. 133–164. DOI: https://doi.org/10.1007/978-3-7643-8340-4_6
3. Julander, A.; Lundgren, L.; Skare, L.; Grandér, M.; Palm, B.; Vahter, M.; Lidén, C. Formal recycling of e-waste leads to increased exposure to toxic metals: An occupational exposure study from Sweden. Environment International, 2014, 73, pp. 243–251. DOI: https://doi.org/10.1016/j.envint.2014.07.006
4. Tripathi, M.; Singh, P.; Singh, R.; Bala, S.; Pathak, N.; Singh, S.; Chauhan, R.S.; Singh, P.K. Microbial biosorbent for remediation of dyes and heavy metals pollution: A green strategy for sustainable environment. Frontiers in Microbiology, 2023, 14, pp. 1–9. DOI: https://doi.org/10.3389/fmicb.2023.1168954
5. Caffo, M.; Caruso, G.; Fata, G.; Barresi, V.; Visalli, M.; Venza, M.; Venza, I. Heavy metals and epigenetic alterations in brain tumors. Current Genomics, 2014, 15(6), pp. 457–463. DOI: https://doi.org/10.2174/138920291506150106151847
6. Qasem, N.A.A.; Mohammed, R.H.; Lawal, D.U. Removal of heavy metal ions from wastewater: a comprehensive and critical review. npj Clean Water, 2021, 4, 36, pp. 1–15. DOI: https://doi.org/10.1038/s41545-021-00127-0
7. Shamim, S. Biosorption of heavy metals. IntechOpen, 2018, pp. 21–49. DOI: https://doi.org/10.5772/intechopen.72099
8. Michalak, I.; Chojnacka, K.; Witek-Krowiak, A. State of the art for the biosorption process - a review. Applied Biochemistry and Biotechnology, 2013, 170(6), pp. 1389–1416. DOI: https://doi.org/10.1007/s12010-013-0269-0
9. Misra, M.; Ghosh Sachan, S.; Chattopadhyay, S. Remediation of heavy metals from wastewater treatment plants using bacteria and algae. Elsevier, 2021, pp. 525–558. DOI: https://doi.org/10.1016/B978-0-12-822965-1.00021-0
10. Liu, Y.; Serrano, A.; Villa-Gomez, D. Biological treatment of mine-impacted waters in the context of metal recovery. The Future of Effluent Treatment Plants, Elsevier, 2021, pp. 499–522. DOI: https://doi.org/10.1016/b978-0-12-822956-9.00026-x
11. Beni, A.A.; Esmaeili, A. Biosorption, an efficient method for removing heavy metals from industrial effluents: A Review. Environmental Technology and Innovation, 2020, 17, 100503. DOI: https://doi.org/10.1016/j.eti.2019.100503
12. Pourzare, A.; Ziarati, P.; Mousavi, Z.; Faraji, A.R. Removing cadmium and nickel contents in basil cultivated in pharmaceutical effluent by chamomile (*Matricaria chamomilla L.*) tea residue. Journal of Scientific Discovery, 2017, 1(1), jsd17006, pp. 1–11. DOI: https://doi.org/10.24262/jsd.1.1.17006
13. Chen, S.; Lin, R.; Lu, H.; Wang, Q.; Yang, J.; Liu, J.; Yan, C. Effects of phenolic acids on free radical scavenging and heavy metal bioavailability in *kandelia obovata* under cadmium and zinc stress. Chemosphere, 2020, 249. DOI: https://doi.org/10.1016/j.chemosphere.2020.126341
14. American Society for Testing and Materials, ASTM E1321-18, Standard test method for determining material ignition and flame spread properties. ASTM International, USA, 2018. https://www.astm.org/e1321-18.html
15. Al-Saeedi, J.Y.; Akbar, M.M.; Al-Qarooni, I.H. Removal of Pb (II) and Ni (II) ions from aqueous solution by sea snail shells. Journal of Biodiversity and Environmental Sciences, 2019, 14(3), pp. 17–23. https://www.innspub.net/wp-content/uploads/2022/04/JBES-V14-No3-p17-23.pdf
16. Wang, J.; Chen, C. Biosorption of heavy metals by *Saccharomyces cerevisiae*: A review. Biotechnology Advances, 2006, 24(5), pp. 427–451.

DOI: https://doi.org/10.1016/j.biotechadv.2006.03.001

17. Bakry, A.M.; Awad, F.S.; Bobb, J.A.; El-Shall, M.S. Multifunctional binding sites on nitrogen-doped carboxylated porous carbon for highly efficient adsorption of Pb(II), Hg(II), and Cr(VI) ions. American Chemical Society Omega, 2020, 5(51), pp. 33090–33100. DOI: https://doi.org/10.1021/acsomega.0c04695
18. Basnet, P.; Gyawali, D.; Ghimire, K.N.; Paudyal, H. An assessment of the lignocellulose-based biosorbents in removing Cr(VI) from contaminated water: A critical review. Results in Chemistry, 2022, 4, pp. 1–16. DOI: https://doi.org/10.1016/j.rechem.2022.100406
19. Zafar, M.N.; Nadeem, R.; Hanif, M.A. Biosorption of nickel from protonated rice bran. Journal of Hazardous Materials, 2007, 143(1-2), pp. 478–485. DOI: https://doi.org/10.1016/j.jhazmat.2006.09.055
20. Chen, X.; Hossain, M.F.; Duan, C.; Lu, J.; Tsang, Y.F.; Islam, M.S., Zhou, Y. Isotherm models for adsorption of heavy metals from water - A review. Chemosphere, 2022, 307(1), 135545. DOI: https://doi.org/10.1016/j.chemosphere.2022.135545
21. Maslova, M.; Mudruk, N.; Ivanets, A.; Shashkova, I.; Kitikova, N. The effect of pH on removal of toxic metal ions from aqueous solutions using composite sorbent based on Ti-Ca-Mg phosphates. Journal of Water Process Engineering, 2021, 40, 101830, pp. 1–13. DOI: https://doi.org/10.1016/j.jwpe.2020.101830
22. Nikiforova, T.E.; Kozlov, V.A.; Telegin, F.Y. Chemisorption of copper ions in aqueous acidic solutions by modified chitosan. Materials Science and Engineering: B, 2021, 263, 114778, pp. 1–11. DOI: https://doi.org/10.1016/j.mseb.2020.114778
23. Cruz-Lopes, L.P.; Macena, M.; Esteves, B.; Guiné, R.P.F. Ideal pH for the adsorption of metal ions Cr^{6+}, Ni^{2+}, Pb^{2+} in aqueous solution with different adsorbent materials. Open Agriculture, 2021, 6(1), pp. 115–123. DOI: https://doi.org/10.1515/opag-2021-0225
24. Ali Redha, A. Removal of heavy metals from aqueous media by biosorption. Arab Journal of Basic and Applied Sciences, 2020, 27(1), pp. 183-193. DOI: https://doi.org/10.1080/25765299.2020.1756177
25. Schiewer, S.; Patil, S.B. Modeling the effect of pH on biosorption of heavy metals by citrus peels. Journal of Hazardous Materials, 2008, 157(1), pp. 8–17. DOI: https://doi.org/10.1016/j.jhazmat.2007.12.076