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Evaluation of Removal Efficiency of Four Heavy Metals [Lead (Pb^{+2}), Cadmium (Cd^{+2}), Zinc (Zn^{+2}) and Nickel (Ni^{+2})] Using *Mentha piperita* and Investigation of Its Bioactive Constituents

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Abstract: Metals in the environment raise questions about food safety and, by extension, about human existence. Rocks, ores, volcanoes, and the weather-induced metal leaching the natural sources of heavy metals in ecosystems are the products of processes that result in soil. When the quantity of heavy metals in some ecosystems rises dramatically as a result of human activity, it becomes a serious problem. This work aims to utilise Mentha piperita and other affordable materials to extract heavy metal ions from wastewater. A new, eco-friendly technique called biosorption has recently come to light. The presence of heavy metals in a country's water supply is one of the most pressing environmental concerns. Heavy metal poisoning of water supplies has been rampant, endangering aquatic and terrestrial species alike. We investigated the extent to which Mentha piperita was able to adsorb several metal ions, including Lead (Pb^{+2}ions), Cadmium (Cd^{+2}ions), Zinc (Zn^{+2}ions) and Nickel (Ni^{+2}ions). The removal percentage of Cadmium Cd^{+2}, Lead Pb^{+2}, Zinc Zn^{+2}, Nickel Ni^{+2} were 44%, 28%, 39% and 20% respectively. While recorded (40%, 26%) for Cd^{+2} and Pb^{+2}, (38%, 38%) for Cd^{+2} and Zn^{+2}, (34%, 18%) for $Cd^{+2}$and Ni^{+2}, (24%, 36%) for Pb^{+2} and Zn^{+2}, (21%, 17%) for Pb^{+2} and Ni^{+2}, (33%, 16%) for Zn^{+2} and Ni^{+2}, (31%, 19%, 29%) for Cd^{+2}, Pb^{+2}, Zn^{+2} , (29%, 15%, 14%) for Cd^{+2}, Pb^{+2}, Ni^{+2}, (26%, 27%, 13%) for Cd^{+2}, Zn^{+2}, Ni^{+2}, (14%, 24%, 12%) for Pb^{+2}ions, Zn^{+2}ions, Ni^{+2}ions (22%, 12%, 19%, 10%) for Cd^{+2} ions, Pb^{+2}ions, Zn^{+2}ions , Ni^{+2}ions respectively. The expensive cost of activated adsorbents limits their widespread application. Therefore, we need to find long-term solutions that address the root cause of the problem.

Keywords: Cadmium (Cd^{+2}), Lead (Pb

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Introduction

Because of their strong interactions with the soil matrix, heavy metals can become mobile when weather patterns change [1]. Considering that plants are an integral part of the soil's ecosystem, It is possible for a rise in pollutants to have a detrimental effect on the health and growth of plants, and eventually, on the safety of foods that are derived from plants. Peppermint, also known as *Mentha piperita,* is a member of the Lamiaceae family and is a hybrid plant that developed from water-mint, also known as-Mentha aquatica, and spearmint, also known as-Mentha spicata. Dyeable rhizomes grow from 30-90 cm of this perennial herbaceous plant [2]. Sandy soils with good drainage, half shade and full sun are ideal. Phenols, terpenes, and tannin are all present in peppermint. Peppermint is a plant that has multiple uses, including as a spice, a leafy green that can be eaten, and a therapeutic oil that can be extracted. Research has shown that mint volatile oil has several uses in the beverage, food, gum, cosmetic[3, 4]. Many different kinds of disease-causing microbes and pathogens are present in the contaminated waterways around the towns. Because of their tolerance for potentially harmful ions in the environment, plants—which rely on photosynthetic processes to produce food—are able to absorb trace elements, particularly heavy metals [5]. Due to the fact that human and animal-diets, rely on medicinal herbs and a variety of vegetable meals, the biomagnification of certain accumulative pollutants in the final trophic chain is produced by this. For a long time and even now, people have turned to medicinal plants as a mainstay for illness prevention, symptom relief, and treatment [6]. Unwashed food can transmit parasites and other diseases that are in the water supply from animals and humans through urine and faeces. Because of this, there are significant hazards to human health associated with releasing untreated wastewater from homes and businesses into the environment [7]. Among the many approaches used to disinfect domestic waste is the introduction of metal ions like copper and silver. Although metal ions are effective disinfectants, they also persist in the water and pose a pollution risk when used in large quantities [8, 9]. An extended exposure to plants containing heavy metals (e.g., lead(Pb^{+2}ions), cadmium(Cd^{+2}ions), zinc(Zn^{+2}ions), and nickel (Ni^{+2}ions) in excess of the maximum allowable limit) may result in severe health complications [10–13], dermatitis, poisoning, mental retardation, harm to the neurological system, and anaemia are some of the conditions that can be caused by this substance. Furthermore, heavy metals can be easily introduced into plants during growing and processing [14]. About 80% of people residing in remote locations rely only on herbs for the treatment of various illnesses, according to the (WHO) [15]. Herbs have pharmacological effects, but they can also be harmful if they contain heavy metals or pesticides, which should be considered while treating specific disorders.

Materials and Methods

Solutions of various metal ions and adsorbents prepared

Chemically pure solutions of various metal ions (lead, cadmium, nickel, and copper nitrates) were utilised. To make stock solutions (1000 mg/L), we dissolved the necessary amount of metal ions in double distilled water. The adsorbent Mentha piperita came from a local community in Hillah city, India. All filth and debris wiped away from the mentha by washing it with double distilled water and then drying it at 80 °C before use. For subsequent examination, the samples were further crushed into a fine powder and passed through a 0.5 mm sieve before being sealed in an airtight container.

Gas chromatography-mass spectrometry of an ethanolic *Mentha piperita* leaf extract

An ethanolic leaves extract of Mentha piperita was subjected to a GC-MS analysis for the purpose of this study. A TG-5 column was set up in accordance with references [16, 17]. The film had a thickness of 0.25 micrometres, and its internal diameter was 30 metres by 0.25 millimetres. The temperature of the oven rose from sixty degrees Celsius to two hundred degrees Celsius, which is a three-degree Celsius per minute increase, when 1.0 mL/min of helium-a carrier gas was added. In this experiment, we used an injector that was heated to 230 degrees Celsius and had a volume of 0.1 microliters for the injection. One half of the injection was done in n-hexane and half in other solvent. The mass spectroscopy process employed a power setting of 70 eV and a 40-450 amu range. We also searched the Microsoft library (which includes WILEY and NIST) and matched the findings with data from Microsoft publications.

Manufacturing of Artificial Wastewater

By employing the analytical quality chemical method, distilled water was used to create solutions of metal ions. In order to get the desired concentration, the solutions were diluted. The experiment's results were analysed by plotting the concentration of each ion (Lead (Pb^{+2}ions), Cadmium (Cd^{+2}ions), Zinc (Zn^{+2}ions) and Nickel (Ni^{+2}ions)) against the volume of EDTA used to attain the endpoint, using a calibration curve.

Experimental setup for batch adsorption

The metal ion solutions were made by dissolving the salt in 1L of distilled water with 1g of the chosen ion for each solution. Afterwards, the solution was shaken for a period of one hour after being treated with the adsorbent at the concentration that was required. The samples that were obtained were then filtered and examined to see whether or not they contained any metal ions. Before beginning the second phase of the experiment, the balanced mixture had to be stored for an additional hour. This was necessary in order to facilitate the continuation of the experiment. In practice, the removal percentage was calculated by dividing the change in the concentration of the tested metal ions by the concentration at the beginning of the laboratory experiment. This helped determine the measured removal percentage.

Results and Discussion

Here, heavy metals are very stable in nature. This is due to their natural tendency to form complexes, their intense interaction with them, and their enhanced metabolic activity. It can actually settle in water and soil after being physically carried by a laboratory aqueous medium. This already makes it a major threat to natural ecosystems and all forms of life. To avoid additional harmful effects, it is very necessary to filter these heavy and harmful metals from wastewater before releasing them to nature. A variety of well-known techniques, including membrane filtration, ion exchange, and others, have been used in the process of removing harmful heavy metals from wastewater [18, 19]. a lack of efficiency, a high demand for energy, the precipitation of toxic substances, an inadequate use of resources, and so on. are some of the downsides of these technologies [20]. Adsorption is one such process that is being studied as a potential solution to these drawbacks; it has a significant effect on the bioavailability and transport of harmful metals. Heavy metals from wastewater can be effectively remedied with this low-cost method. Another benefit of adsorption is that it is usually reversible, meaning the adsorbent may be regenerated back [24, 25]. pH, starting concentration, contact time, and rotation speed are among the several variables that impact the effectiveness of adsorbents [21, 22]. In this case, the heavy metals were successfully eliminated by *Mentha piperita*. The removal percentage of Cadmium Cd^{+2}, Lead Pb^{+2}, Zinc Zn^{+2}, Nickel Ni^{+2} were 44%, 28%, 39% and 20% respectively. While recorded (40%, 26%) for Cd^{+2} and Pb^{+2}, (38%, 38%) for Cd^{+2} and Zn^{+2}, (34%, 18%) for $Cd^{+2}$and Ni^{+2}, (24%, 36%) for Pb^{+2} and Zn^{+2}, (21%, 17%) for Pb^{+2} and Ni^{+2}, (33%, 16%) for Zn^{+2} and Ni^{+2}, (31%, 19%, 29%) for Cd^{+2}, Pb^{+2}, Zn^{+2} , (29%, 15%, 14%) for Cd^{+2}, Pb^{+2}, Ni^{+2}, (26%, 27%, 13%) for Cd^{+2}, Zn^{+2}, Ni^{+2}, (14%, 24%, 12%) for Pb^{+2}, Zn^{+2}, Ni^{+2} (22%, 12%, 19%, 10%) for Cd^{+2}, Pb^{+2}, Zn^{+2} , Ni^{+2} respectively.

The low clearance % of mixed ions was caused by competition and interaction among the ions. An efficient adsorbent for metal ions, the Silybum marianum is abundant, inexpensive, and readily available. The classification of heavy metals as essential or non-essential is based on their function in the body of the organism. The proper operation of all biological and biochemical processes, including those involving humans, depends on micronutrients or essential metals or including Cr;Cu;Mn;Mo;Ni;Fe;Se, and Zn. Biological functions of non-essential metals like lead, mercury, cadmium, and arsenate are unknown. Given their non-biodegradable nature and potential toxicity, heavy metals present a substantial hazard to both ecosystems and human health, even at low concentrations. [23].

Cadmium is primarily produced as a consequence of human activity, such as mining and metallurgy, the combustion of waste, and the improper application of pesticides and fertilisers in agricultural settings. Cadmium is a significant contributor to the global pollution problem. Extensive research has demonstrated that it is lethally toxic to terrestrial and aquatic organisms [25, 26]. Greater levels of Cd exposure may result in diminished rates of photosynthesis, water absorption, and nutrient assimilation in plants. Plants cultivated in soils rich with Cd have stunted development, root dryness, and ultimately plant mortality. In order for enzymes like urea and glyoxalase to activate, nickel is a crucial component for plant development and growth. Additionally, photosynthesis, nitrogen metabolism, and seed germination all rely on nickel.

Table 1. GC-MS analysis of the ethanolic leaves extract of *Mentha piperita*

No.	RT (min)	Area%	Name	Quality	CAS Number
1	7.688	0.15	2-Ethylhexanol	52	000104-76-7
2	9.008	0.09	2-Ethylhexyl glucuronide	32	00051-11-0
3	12.435	0.37	Carvol	94	000099-49-0
4	14.007	0.04	1-Cyano-3,4-epithiobutane	85	000003-08-1
5	17.484	3.24	1,2-Epithio-3-hexanol	27	000000-00-0
6	22.444	0.09	Myotonine chloride	53	000590-63-6
7	23.006	0.12	2-Ethylhexyl beta-D glucopyran	61	000011-72-0
8	26.04	0.11	Methyl palmitate	99	000112-39-0
9	28.593	0.48	Methyl linoleate	99	056599-58-7
10	28.733	0.16	Methyl oleate	99	000112-62-9
11	30.814	0.18	N-DIMETYLPALMITAMIDE	94	000000-00-0
12	33.636	0.72	Palustric acid	90	002769-94-0
13	34.046	0.47	Diisooctyl phthalate	90	027554-26-3
14	34.767	92.37	VestinolAH	94	000117-81-7
15	38.296	0.34	Squalene	98	007683-64-9
16	39.925	0.36	Cannabinol, trifluoroacetate	74	118190-34-4
17	43.609	0.96	Germanicol	41	000000-00-0

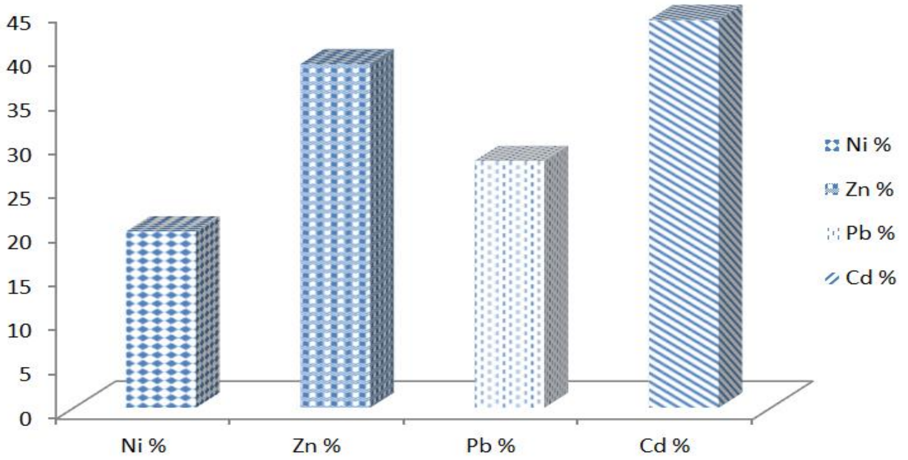

Figure 1. Ion Solution percentage (Cd), (Pb), (Zn) and (Ni) in Single Ions removal absorbent at same conditions using *Mentha piperita* natural adsorbent.

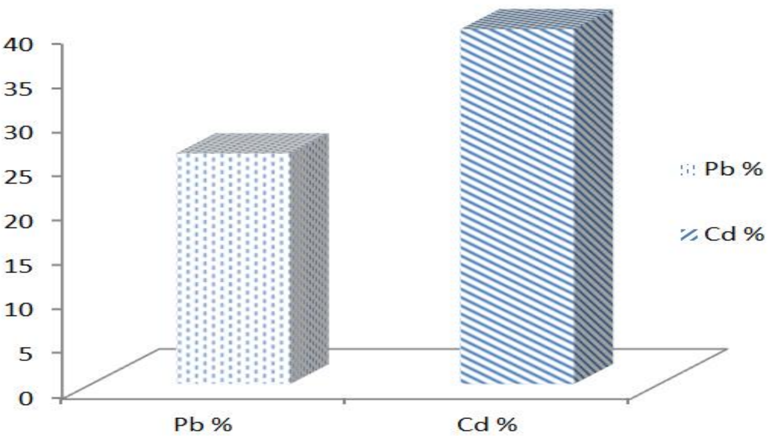

Figure 2. Ion Solution percentage (Cd), and (Pb) in binary Ions removal absorbent at same conditions using *Mentha piperita* natural adsorbent.

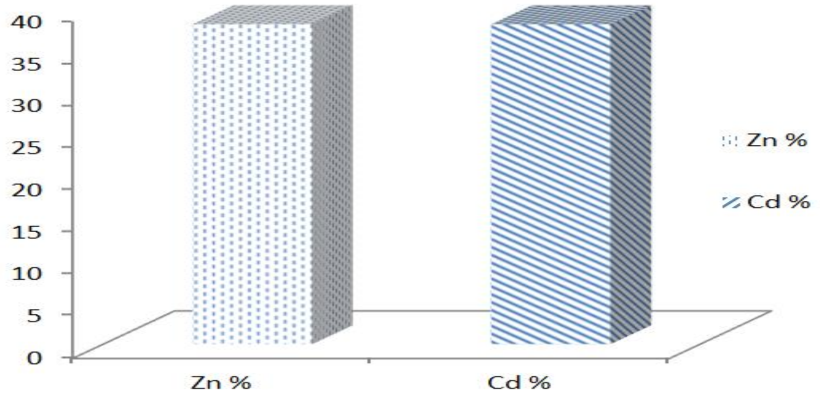

Figure 3. Ion Solution percentage (Cd), and (Zn) in binary Ions removal absorbent at same conditions using *Mentha piperita* natural adsorbent.

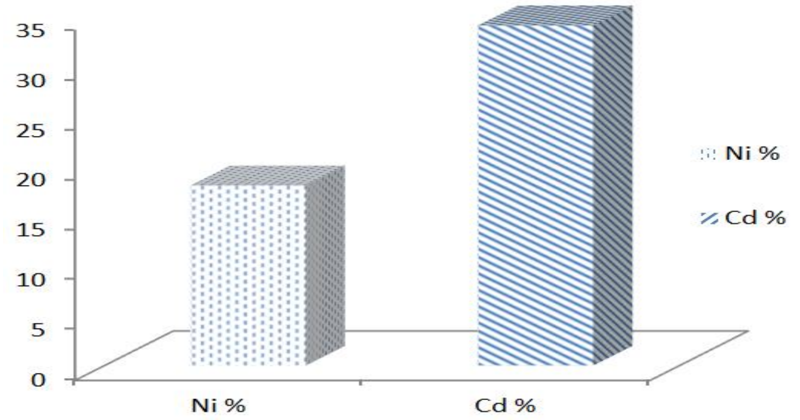

Figure 4. Ion Solution percentage (Cd), and (Ni) in binary Ions removal absorbent at same conditions using *Mentha piperita* natural adsorbent.

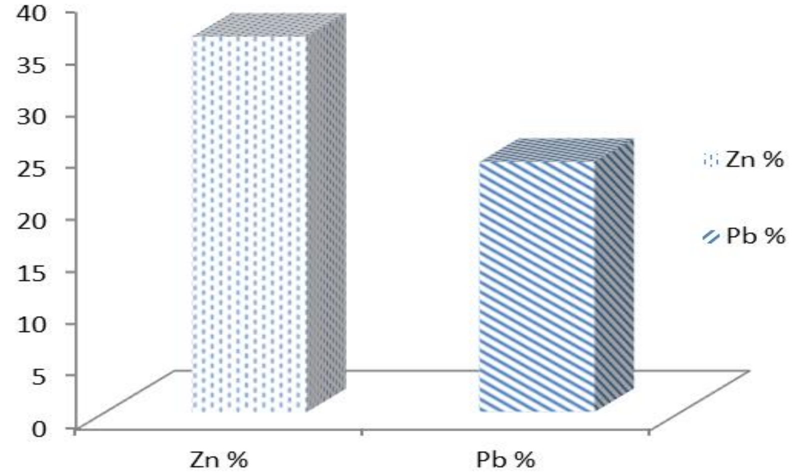

Figure 5. Ion Solution percentage (Pb), and (Zn) in binary Ions removal absorbent at same conditions using *Mentha piperita* natural adsorbent.

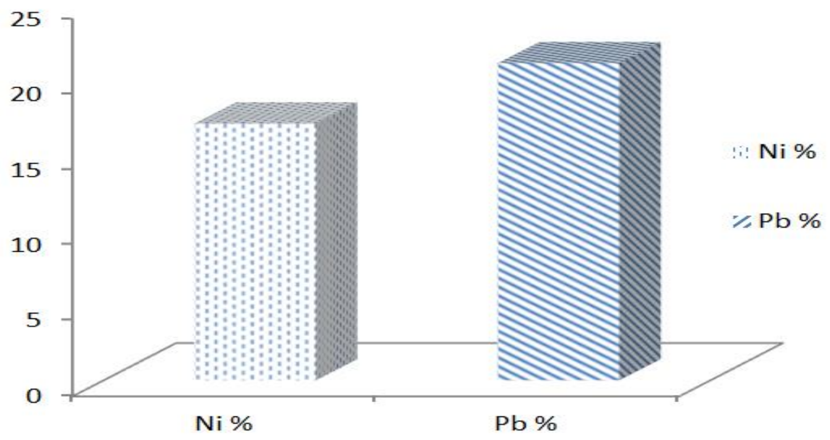

Figure 6. Ion Solution percentage (Pb), and (Ni) in binary Ions removal absorbent at same conditions using *Mentha piperita* natural adsorbent.

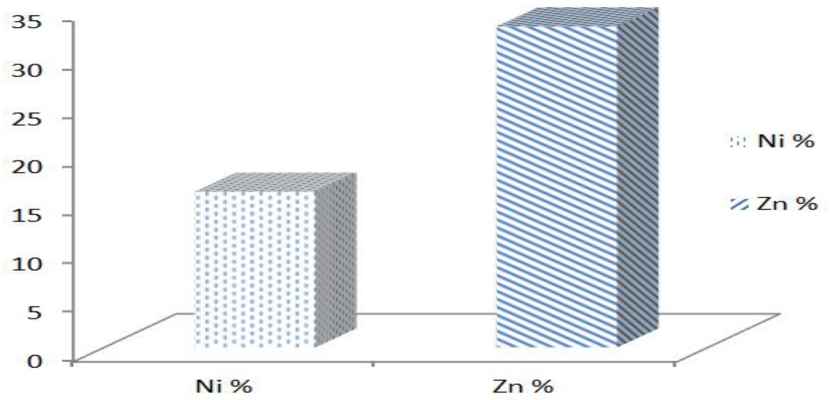

Figure 7. Ion Solution percentage (Zn), and (Ni) in binary Ions removal absorbent at same conditions using *Mentha piperita* natural adsorbent.

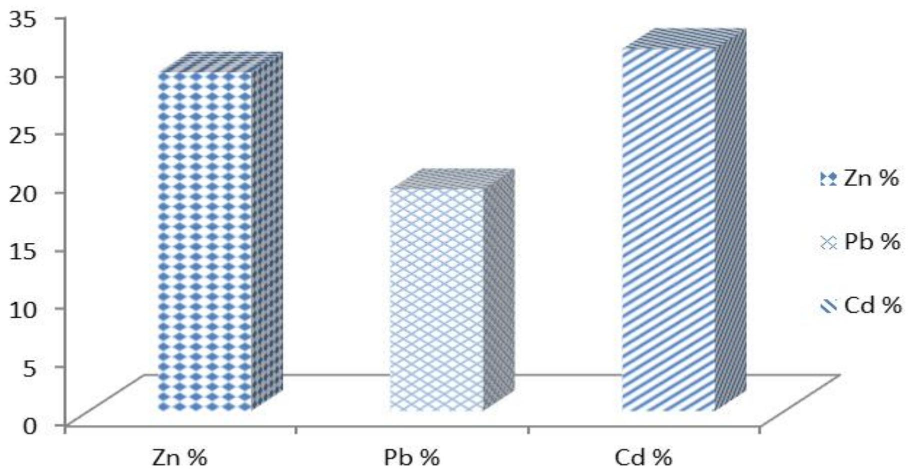

Figure 8. Ion Solution percentage (Cd), (Pb) and (Zn) in tertiary Ions removal absorbent at same conditions using *Mentha piperita* natural adsorbent.

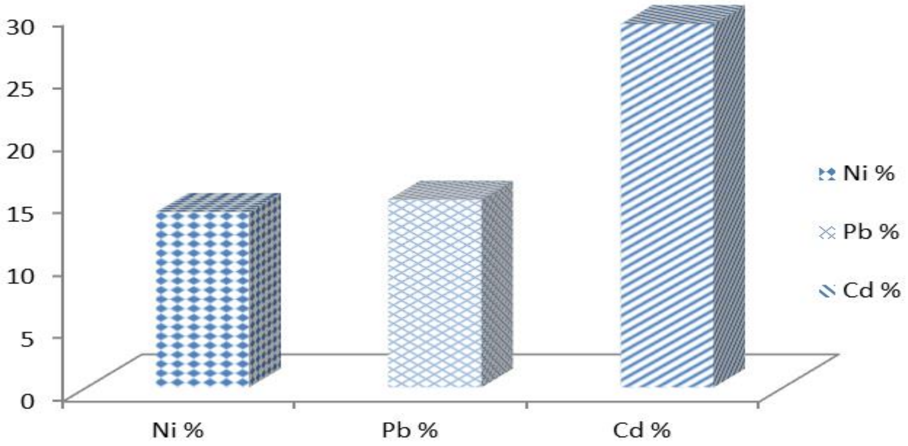

Figure 9. Ion Solution percentage (Cd), (Pb) and (Ni) in tertiary Ions removal absorbent at same conditions using *Mentha piperita* natural adsorbent.

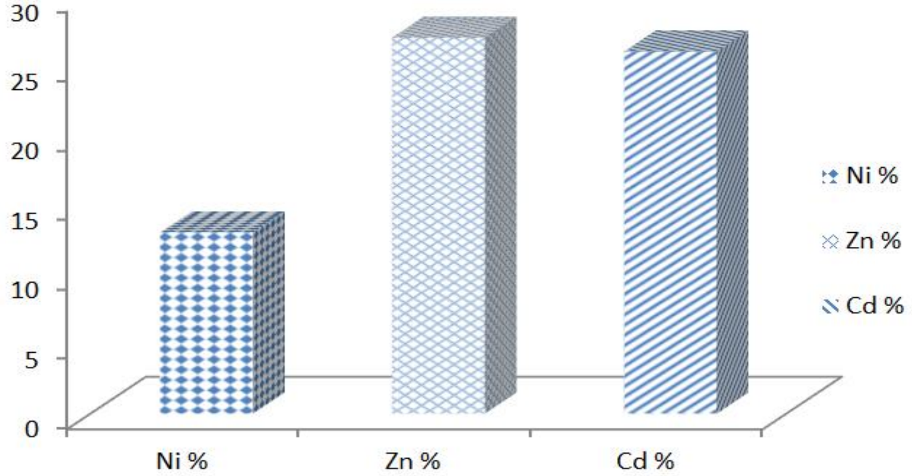

Figure 10. Ion Solution percentage (Cd), (Zn) and (Ni) in tertiary Ions removal absorbent at same conditions using *Mentha piperita* natural adsorbent.

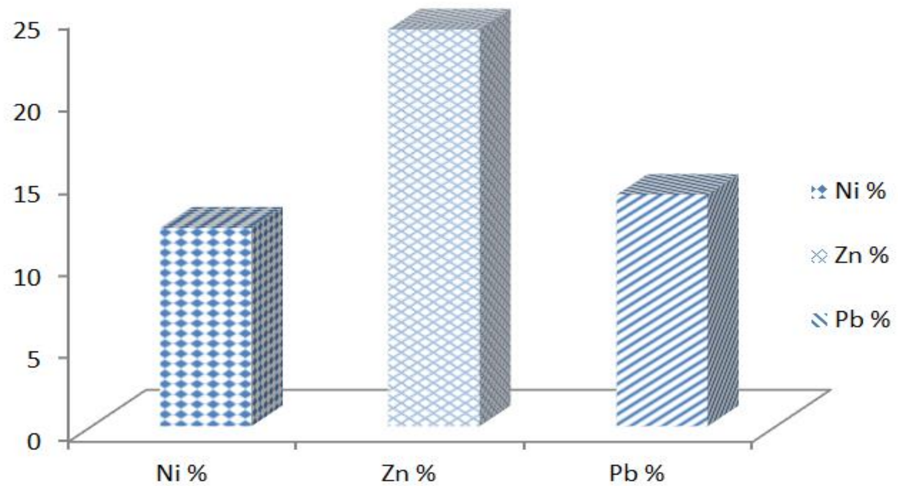

Figure 11. Ion Solution percentage (Pb), (Zn) and (Ni) in tertiary Ions removal absorbent at same conditions using *Mentha piperita* natural adsorbent.

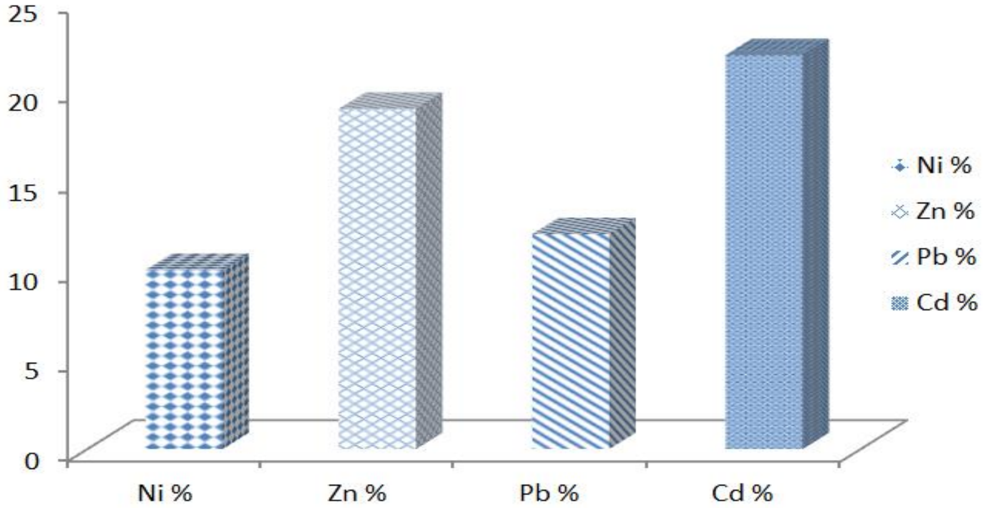

Figure 12. Ion Solution percentage (Cd), (Pb), (Zn) and (Ni) in Ions removal absorbent at same conditions using *Mentha piperita* natural adsorbent.

Conclusions

Heavy metal pollution stands as one of the most critical global challenges in the present era. Even in minute amounts, they can cause harm. Therefore, before discharging wastewater into open seas, it must be treated to remove these harmful elements. When it comes to removing heavy metals from wastewater, one method that is both effective and gentle on the environment is adsorption. The expensive cost of activated adsorbents limits their widespread application. Therefore, we need to find long-term solutions that address the root cause of the problem. This study demonstrated the ability of Mentha piperita, a medicinal plant, to transfer metals to its aerial portions when exposed to several metals (Cd^{+2}ions, Ni^{+2}ions, Pb^{+2}ions, and Zn^{+2}ions).

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