



Original Articles

Removal of [Pb⁺², Cu⁺², Cd⁺², Zn⁺²] Heavy Metals from Wastewater Using *Hordeum vulgare* and Screening of Its Metabolite Profiling Using FTIR Technique

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Abstract:

Background: Adsorption is a powerful tool for the efficient removal of heavy metals from wastewater. In general, heavy metals are considered to be significant hazardous contaminants. The process of adsorption is one of the most effective methods for cleaning water that has been contaminated. There are many benefits associated with the adsorption process, including its availability, low cost, and environmentally beneficial nature.

Objective: : An investigation was carried out to determine whether or not *Hordeum vulgare* is capable of eliminating heavy metal cations from wastewater, specifically Pb⁺², Cu⁺², Cd⁺², Zn⁺². Within the scope of this investigation, a batch adsorption method was utilized to simulate artificial water.

Materials and Methods: In order to remove dust and grime from the *Hordeum vulgare*, they were given a thorough cleaning before being dried. Following that, it is immediately utilized in a variety of adsorbent/metal ion ratios. The metal ion concentration starts at one thousand parts per million. Under the same conditions of heavy metal removal, an investigation was conducted to determine the percentage of removal for single, binary, and tertiary ions, as well as the percentage of removal for mixed ion solution (3% gm/ml) adsorbent. The pH value was kept at a range of 5 to 6 during the experiment, and the temperature was kept at 25 Co throughout the experiment.

Results: The major constituents were FT-IR Peak values (Wave number cm⁻¹): 669.30 (Strong), 684.73 (Strong), 827.46 (Strong), 873.75 (Strong), 927.7 (Strong), 1010.70 (Strong), 1236.37 (Strong), 1313.52 (Strong), 1417.68 (Medium), 1604.77 (Bending), 2358.94 (Unknown), and 3269.34 (Bending) with Functional group assignment alkyl halides, Alkenes, Alkenes, alkyl halides, alkyl halides, alkyl halides, Amide, and Amide respectively. *Hordeum vulgare* was found to be effective in removing heavy metals, as determined by the findings of the observation and analytical procedure. The removal percentage of Pb⁺², Cu⁺², Cd⁺², Zn⁺² were 37%, 70%, 48% and 32% respectively. While recorded (28%, 65%) for Pb⁺² and Cu⁺², (32%, 41%) for Pb⁺² and Cd⁺², (29%, 22%) for Pb⁺² and Zn⁺², (68%, 39%) for Cu⁺² and Cd⁺², (65%, 20%) for Cu⁺² and Zn⁺², (42%, 23%) for Cd⁺² and Zn⁺², (21%, 59%, 37%) for Pb⁺², Cu⁺², Cd⁺², (19%, 54%, 18%) for Pb⁺², Cu⁺², Zn⁺², (19%, 35%, 17%) for Pb⁺², Cd⁺², Zn⁺², (15%, 49%, 29%, 14%) for Pb⁺², Cu⁺², Cd⁺², Zn⁺². The elimination percentage was accomplished in less than an hour after coming into contact with an adsorbent loading ratio of 25 grams per liter. The clearance percentage of mixed ions, on the other hand, was rather low. This was due to the fact that the ions competed with one another and interacted with one another. In addition to being readily available in large quantities at a reasonable cost, the *Hordeum vulgare* has the potential to be utilized as an effective metal ion adsorbent.

Conclusion: *Hordeum vulgare* is an effective method for the elimination of heavy metals. additional Nevertheless, research is necessary in order to identify the chemicals that serve as inhibitors.

Keywords: *Heavy metals, Adsorbent, Synthetic wastewater, Hordeum vulgare.*



Introduction:

An important crop that is grown all throughout the world is barley, also known as *Hordeum vulgare* L. In the same way that it is significant in other crops, nitrogen remobilization efficiency is necessary since it is the primary factor that determines grain production and seed quality [1,2]. The senescence of leaves is a lengthy developmental process that is of critical importance to the physiology and metabolism of plants. There are a great number of genes that are either up- or down-regulated throughout the process of leaf senescence. These genes are specifically involved in the shift from anabolism to catabolism [3]. They have strong ties to both the main and secondary metabolisms. Adsorption is a powerful tool for the efficient removal of heavy metals from wastewater. As a rule, heavy metals are thought of as very dangerous pollutants. Adsorption often makes use of activated carbon as an adsorbent due to its high adsorption capacity. Adsorption has been classified as an adequate alternative to conventional methods of heavy metal removal from industrial wastewater, including precipitation [4], ion exchange, solvent extraction, and membrane. The rise in industrial and agricultural output, along with population growth and urbanisation, has led to an increase in the creation of wastewater containing heavy metals and other toxic compounds. The incorrect handling of these wastewater flows has contaminated land and water resources in diverse ways, posing a multitude of health risks to humans and other creatures. A variety of factors affect the rate of heavy metal buildup in barley. Species of barley, heavy metal type, bioavailability, redox, pH, temperature, cation exchange capacity, and root secretion are all aspects to consider [5, 6]. Water is a necessary ingredient in all human activity, including farming. There is a severe lack of freshwater resources globally, and these resources account for just 0.6% of the world's total water resources. They might not have enough resources to satisfy all of humanity's needs in the years to come [7]. As a result of rising population and increased

demand for fresh water, freshwater resources have been rapidly depleting. Humans can't survive without access to freshwater supplies, so this is a major worry. As a result of the growing need for freshwater, the quantity of wastewater has also increased. There has been a shift in perspective on treated wastewater from a disposal problem to a potential new resource for water usage in agriculture, industry, and cities [8, 9]. The majority of the cities in Palestine have wastewater collection systems

accessible for utilization. Because they are located within the boundaries of the municipality, a great number of small industries discharge their effluent into the municipal infrastructure. There are significant levels of heavy metals present in these wastewaters, in addition to other types of contaminants. The removal of heavy metals from wastewater has been accomplished by the utilization of a variety of techniques, including membrane filtration, adsorption, and ion exchange and others. One of the most effective methods for sterilizing water that has been contaminated is called adsorption [10-15]. There are many benefits associated with the adsorption process, including its availability, low cost, and environmentally beneficial nature. In order to facilitate the removal of heavy metals from wastewater, the purpose of this research is to generate a proposal for an adsorbent that is both inexpensive and abundantly available in natural resources. A study was conducted to explore the effects of various operational parameters, including adsorbent dose and contact time, on the removal of lead, copper, cadmium, and zinc.

Materials and Methods Plant preparation Preparation of ethanolic seeds Extract of *Hordeum vulgare*

The gathering of the *Hordeum vulgare* took place at the hilla city, which is located in Iraq. Following the process of macerating the powdered form of *Hordeum vulgare* in methanol at a concentration of 90%, the powdered form was filtered. A crude extract was obtained by first filtering the extract and then concentrating it with a Boeco Rotary Evaporator RVO 400 SD, which was built by Boeco in Germany [16, 17].

This process was repeated until the mixture was completely concentrated. Following the dissolution of the crude extract in the smallest quantity of deionized distilled water in a separating funnel, the mixture was then mixed with hexane. At the conclusion of a thorough shaking of the combination, it was placed aside for a day in order to give it the opportunity to settle.

Examination of *Hordeum vulgare* using Fourier Transform Infrared Spectroscopy (FTIR)

In order to collect the FTIR spectra of both native and defatted GLVs, we used an FTIR instrument (Model/Make: IFS 25, Bruker, Germany) that was controlled by a PC-based programme [18–20]. Using KBr, a small quantity of powdered leaf samples was first transformed into pellets, and then a thin film was created by exerting pressure, all in preparation for FTIR analysis. A range of wave numbers from 4000 cm⁻¹ to 500 cm⁻¹ was used to gather data regarding the transmittance of infrared light. Three separate analyses were performed on each sample, with untreated KBr pellets serving as a control. Spectral data was compared to a reference in order to determine the functional groups present in the sample.

Adsorbent Preparation and Wastewater Preparation using Synthetic Materials

The *Hordeum vulgare* were powdered and crushed until they were smaller than one millimetre. It was then immediately used as a natural adsorbent after the pulverised powder had been sieved. The metal ion solutions were prepared using distilled water and the analytic grade chemical method. In the laboratory, we worked on diluting the solutions to the correct practical concentrations to obtain the desired results. At the same time, the concentration of each of the ions already studied in these experiments – Pb⁺², Cu⁺², Cd⁺², and Zn⁺² – was measured against the volume of EDTA (ethylenediaminetetraacetic acid, or H₄C₁₀H₁₂N₂O₄). A calibration curve was drawn for each of them [21]. This was done in order to interpret the results of these experiments.

Experiments the laboratory process called batch adsorption

At the beginning of the laboratory work, all solutions of the metal ions studied were prepared by dissolving only one gram of the corresponding ion in only one liter of distilled water. This was done for each solution. After adding adsorbent to the solution at a specific concentration, the mixture was agitated for one hour [22-25]. After that, we collected the samples, filtered them, and checked them for metal ions. The second step of the experiment required the mixture to rest for an additional hour after it had been balanced. Finding the elimination percentage was as simple as dividing the decrease in metal ion concentration by the initial concentration of metal ions (C_i):

$$\frac{C_i - C_f}{C_i} \times 100$$

The initial concentration of metal ions is denoted by C_i. The terminal concentration of metal ions is denoted as C_f.

Results and Discussion

The major constituents were FT-IR Peak values (Wave number cm⁻¹): 669.30 (Strong), 684.73 (Strong), 827.46 (Strong), 873.75 (Strong), 927.7 (Strong), 1010.70 (Strong), 1236.37 (Strong), 1313.52 (Strong), 1417.68 (Medium), 1604.77 (Bending), 2358.94 (Unknown), and 3269.34 (Bending) with Functional group assignment alkyl halides, Alkenes, Alkenes, alkyl halides, alkyl halides, alkyl halides, Amide, and Amide respectively. *Hordeum vulgare* was found to be effective in removing heavy metals, as determined by the findings of the observation and analytical procedure. The removal percentage of Pb⁺², Cu⁺², Cd⁺², Zn⁺² were 37%, 70%, 48% and 32% respectively. While recorded (28%, 65%) for Pb⁺² and Cu⁺², (32%, 41%) for Pb⁺² and Cd⁺², (29%, 22%) for Pb⁺² and Zn⁺², (68%, 39%) for Cu⁺² and Cd⁺², (65%, 20%) for Cu⁺² and Zn⁺², (42%, 23%) for Cd⁺² and Zn⁺², (21%, 59%, 37%) for Pb⁺², Cu⁺², Cd⁺², (19%, 54%, 18%)

for Pb²⁺, Cu²⁺, Zn²⁺, (19%, 35%, 17%) for Pb²⁺, Cd²⁺, Zn²⁺, (15%, 49%, 29%, 14%) for Pb²⁺, Cu²⁺, Cd²⁺, Zn²⁺ With an adsorbent loading ratio of 25 g/L, the removal percentage was accomplished in less than an hour after the substance was used. However, the percentage of mixed ions that were removed was rather low. This was due to the fact that the ions came into competition with one another and interacted with one another. It is possible to employ the *Hordeum vulgare* as an effective metal ion adsorbent not only because it is readily available in large quantities but also because it is inexpensive. The outcomes of this study are displayed in Table 1. The results showed a decline in the trend of metal ion removal when compared to solutions containing only one metal. Table 2 shows that the percentage of Pb²⁺, Cu²⁺, Cd²⁺, and Zn²⁺ removed was 61, 80, and 50.5 for the single ions, respectively. A reduction to 51.75, 70, 41.5, and 30 was seen for tertiary ions, but the values for binary ions became 49.5-45, 75-77.5, 45-48.5, and 30-30.5, respectively. As the amount of ions combined decreases, the removal percentage of metal ions also drops. It is the result of ion competition and interaction in the solution that these results have dropped [20]. *Hordeum vulgare* is an efficient adsorbent; at 25 g/L, it effectively removes Pb²⁺, Cu²⁺, Cd²⁺, and Zn²⁺ ions from artificial wastewaters with concentrations of up to 1000 ppm, all at ambient temperature (25 °C) and pH values between 5 and 6. However, when the adsorbent dose was changed, the removal percentage for both Cd²⁺ ions (50.5% and 32.5%, respectively) was low. Furthermore, researchers discovered that increasing the amount of adsorbent used resulted in an increase in the removal efficiency. One possible explanation for this growth is that there are more adsorption sites available for ion interactions, and another is the larger surface area that becomes available at higher adsorbent dosages. The ideal condition could only be achieved after one hour of contact between solo and mixed ions. During the course of the experiment, there was no discernible reduction in the concentration of the solution. The ideal duration of contact, as found in this study, differs from the

optimal duration, which is 90 minutes [19]. This study found that sixty minutes was the sweet spot for contact time to achieve a maximum cleaning and removal efficacy of 98.2%. This finding agrees with the findings of an earlier research in the same area. In separate research [17, 18], it has already been discovered that the leaves of some trees have the potential to act biologically as adsorbents. In order for this laboratory study to be successful, twelve different, unstudied types of tree leaves weighing only two grams were actually crushed. At the same time, the leaves were subjected to a set of practical tests to determine whether or not they were able to absorb and remove these metal ions from wastewater, especially zinc, lead, and nickel. During these tests, 200 milliliters of artificial wastewater was used, which in the laboratory contains approximately 50 milliliters per liter of metal ions that were selected in the experiment, which was conducted at a constant temperature, which is room temperature [20-24]. The results of further experiments showed that the process of removing cadmium, lead and nickel ions was indeed accomplished with a high degree of biological effectiveness. It was shown through these experimental tests that the calculated percentage of lead (Pb²⁺), cadmium (Cd²⁺), and nickel (Ni²⁺) that were experimentally removed in the laboratory is 94%, 77.2%, and 85.7%, respectively. An adsorbent material with a concentration of 5 mg/L was used during the experiment, and here each solution had a concentration of 0.5 g/L. On the other hand, in the laboratory, it was found that the removal percentage was lower for a solution mixture with mixed metals [25-29], as it reached 3.5% for lead and 13.2% for nickel.

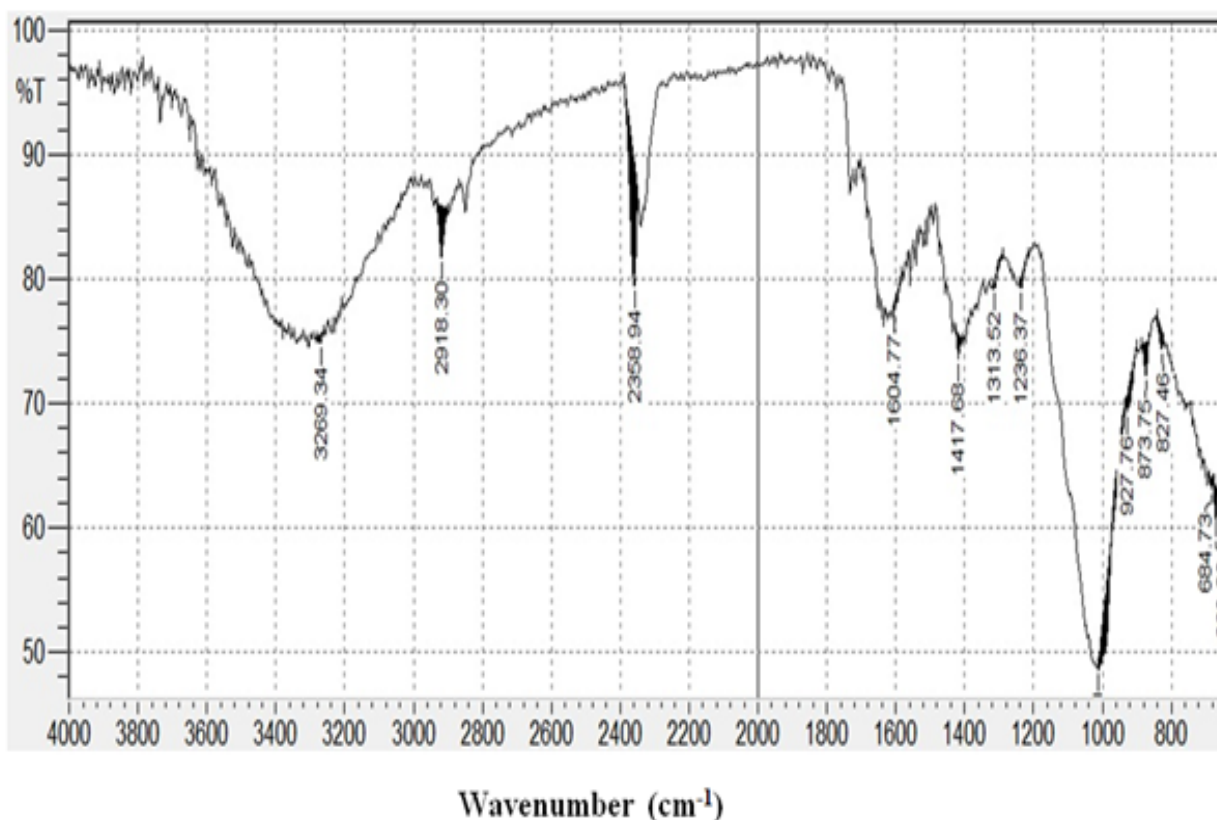


Figure 1. Fourier-transform infrared spectroscopic profile solid analysis of *Hordeum vulgare*.

Table 1. Fourier Transform Infrared Spectrum peak values of solid analysis of *Hordeum vulgare*.

No.	Peak (Wave number cm ⁻²)	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area	Type of Intensity	Bond	Type of Vibration	Functional group assignment	Group frequency
1.	669.30	59.416	3.865	677.01	663.51	2.859	0.176	Strong	C-Cl	Stretch	alkyl halides	600-800
2.	684.73	63.115	0.860	690.52	678.94	2.285	0.038	Strong	C-Cl	Stretch	alkyl halides	600-800
3.	827.46	74.505	1.152	840.96	821.68	2.387	0.081	Strong	=C-H	Bending	Alkenes	650-1000
4.	873.75	72.300	2.593	885.33	866.04	2.555	0.131	Strong	=C-H	Bending	Alkenes	650-1000
5.	927.76	69.360	0.661	931.62	900.76	4.511	0.180	Strong	=C-H	Bending	Alkenes	650-1000
6.	1010.70	48.730	0.709	1012.63	933.55	18.575	0.677	Strong	C-F	Stretch	alkyl halides	1000-1400
7.	1236.37	79.328	0.352	1240.23	1217.08	2.182	0.052	Strong	C-F	Stretch	alkyl halides	1000-1400
8.	1313.52	79.285	1.798	1315.45	1290.38	2.296	0.008	Strong	C-F	Stretch	alkyl halides	1000-1400
9.	1417.68	73.681	0.430	1425.40	1408.04	2.204	0.073	Medium	C=C	Stretch	Aromatic	1400-1600
10.	1604.77	77.448	9.752	1608.63	1581.63	2.817	0.060	Bending	N-H	Stretch	Amide	1550-1640
11.	2358.94	79.466	3.998	2389.80	2349.30	2.488	0.880	Unknown	-	-	-	-
12.	2918.30	81.850	1.636	2931.80	2899.01	2.468	0.286	Strong	C-H	Stretch	Alkane	2850-3000
13.	3269.34	74.844	0.747	3280.92	3261.63	2.381	0.034	Bending	N-H	Stretch	Amide	3100-3500

Table 2. Mixed ion solution percentage removal adsorbent.

Mixed ion conc. (1000 ppm)	Conc. ppm after 1 hour	% Removal
Pb ²⁺	110	37%
Cu ²⁺	225	70%
Cd ²⁺	550	48%
Zn ²⁺	680	32%
Pb ²⁺	117	28%
Cu ²⁺	221	65%
Pb ²⁺	120	32%
Cd ²⁺	493	41%
Pb ²⁺	119	29%
Zn ²⁺	620	22%
Cu ²⁺	218	68%
Cd ²⁺	487	39%
Cu ²⁺	221	65%
Zn ²⁺	590	20%
Cd ²⁺	490	42%
Zn ²⁺	571	23%
Pb ²⁺	131	21%
Cu ²⁺	192	59%
Cd ²⁺	465	37%
Pb ²⁺	135	19%
Cu ²⁺	197	54%
Zn ²⁺	562	18%
Pb ²⁺	139	19%
Cd ²⁺	461	35%
Zn ²⁺	569	17%
Pb ²⁺	146	15%
Cu ²⁺	185	49%
Cd ²⁺	451	29%
Zn ²⁺	653	14%

Table 3. Percentage of removal for single, Binary and tertiary ions at same conditions.

Metal ions %	Single	Binary ions	Tertiary
Pb ²⁺	61	49.5-45	51.75
Cu ²⁺	80	75-77.5	70
Cd ²⁺	50.5	45-48.5	41.5
Zn ²⁺	32.5	30-30.5	30

Conclusions:

It has been demonstrated that *Hordeum vulgare* is an affordable adsorbent that may be utilized in the process of adsorbing heavy metal ions from artificial wastewater in the order of copper, lead, cadmium, and zinc by decreasing the concentration of the ions. However, the percentage of removal that was obtained was 80% for Cu²⁺, 61% for Pb²⁺, 50.5% for Cd²⁺ and 32.5% for Zn²⁺ when the adsorbent dose was 25

g/L and the solution concentration was 1000 ppm. The temperature at which this experiment was conducted was 25 degrees Celsius on the room temperature scale. While the optimal contact time for all single and mixed ion solutions was one hour, 1 hour was the optimal contact time. However, the fraction of ions that are removed diminishes as the quantity of mixed ions grows within the system.

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