

REMEDIATION OF HEAVY METALS FROM PHARMACEUTICAL EFFLUENT STREAMS BY PROMISING BIO REMOVAL TECHNIQUE THROUGH CUMIN RESIDUE

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Abstract. Considering high concentrations of numerous hazardous and toxic contaminations, particularly heavy metals, industrial waste water has become a major problem. Among the various methods for treatment of pollutions, adsorption proceeding is really promising method for the ministration of the industrial effluent. This study examined the possibility of using *adsorbents* derived from the solid biomass *residues of cumin varieties* as the available biomass in Pharmacy faculty to *decontamination of heavy metals from Pharmaceutical effluents*. The initial concentration of heavy metals/metalloid such as Nickel, Zinc, Copper, Cobalt and Lead in the untreated effluents and treated by *Cuminum Cyminum* and *Bunium Persicum* residues were analyzed by ICP-OES. The findings from current study revealed the studied herbal extraction residues can decrease the concentration of heavy metals: Lead, Cobalt, Nickel, Zinc and Copper of the pharmaceutical effluents and waste water significantly ($P \leq 0.05$) and the scientific evidences have yielded impressive outcomes for removing total Lead by more than 88% efficacy.

Keywords: Contaminations, heavy metals, pharmaceutical effluent, biosorbent, cumin seed residue, adsorption.

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1. Introduction

The scarcity of water is a significant issue for majority of countries around the world. The contamination of natural water sources by chemical and microbial pollutants causes a crucial problem and threat to the ecosystem and particularly endangers public health (Tavakoli-Hosseiniabady *et al.*, 2018; Mahmoud *et al.*, 2020; Al-Baldawi *et al.*, 2021; Giwa *et al.*, 2021; Šolcová *et al.*, 2022; Mishra *et al.*, 2023; Afzal & Mahreen, 2024; Lotfi *et al.*, 2025). Pharmaceuticals are prevalent contaminants in water sources, as approximately 30-90% of these substances persist in our bodies without breaking down and latterly penetrate into the environment terminated by humans or animals (Mishra *et*

al., 2023). Heavy metals refer to metallic substances that possess a high density and relatively low toxicity levels. This group encompasses elements such as lead (Pb), mercury (Hg), copper (Cu), cadmium (Cd), zinc (Zn), arsenic (As), chromium (Cr) and iron (Fe) (Schmitz, 2018). The harmful effects of heavy metals on both humans and animals stem from prolonged exposure to low levels of contamination present in our surroundings, such as the air we inhale, the water we consume and the food we eat (Mokhtarzadeh *et al.*, 2021). Heavy metals pose significant health risks, making the precise measurement of their residues a matter of considerable concern. The presence of heavy metals in the human body can lead to various adverse effects, including disorders of the nervous system, kidney failure, genetic mutations and different forms of cancer, neurological issues, respiratory problems, cardiovascular complications, immune system suppression and infertility (Obayomi *et al.*, 2024). Lead exposure is a significant factor that contributes to disorders of the central nervous system, anemia and damage to multiple organs including the kidneys, liver, heart and blood vessels. It adversely affects the immune and reproductive systems as well as the digestive tract and it is also linked to the onset of cancer and various types of malignancies (Mokhtarzadeh *et al.*, 2021). Nickel is linked to several types of cancers affecting the blood, brain and bone, as well as causing local infections. Nickel poisoning results in disruptions to cellular biological activities, stunted growth, reduced hematuria and interference with iron absorption can occur (Wu *et al.*, 2025). Acute Nickel toxicity can lead to skin inflammation and negatively impact the heart (Wu *et al.*, 2025). The level of toxicity is influenced by several factors, including the pathway of exposure, quantity used, solubility, oxidation state of the metal, maintenance percentage, duration of application, as well as individual characteristics such as age and sex. Additionally, frequency of use, absorption rate and effectiveness of excretion mechanisms also play significant roles in determining overall toxicity (Lu *et al.*, 2022).

Agricultural residue has the potential to serve as a significant asset in enhancing food security (however, if not managed, treated or disposed of appropriately, these residues may lead to environmental pollution and pose risks to human health (Aazami *et al.*, 2017; Shirkhan *et al.*, 2022). Food and agricultural losses and residue can be examined from two distinct viewpoints: one focuses on the environmental issues related to residue, while the other emphasizes food security standards associated with food. Food residue occurs at every stage of the food life cycle, including agricultural production, industrial manufacturing, processing and distribution. This residue is rich in valuable elements such as phytochemicals, proteins, flavor compounds, polysaccharides and fibers that can be utilized as nutraceuticals and functional ingredients. The utility model proposed relates to technologies designed for water treatment and sewage management, particularly emphasizing the adsorption method to remove metal ions from polluted natural and industrial waste water. This technique can contribute to generating potable water as well as water that is appropriate for agricultural use, chemical processes, petroleum industries and food processing (Qasem *et al.*, 2021). Additionally, it improves the biological and physicochemical properties of drinking water while promoting a closed-loop system. Current methods for treating waste water with metal ions generally employ sorbents derived from either inorganic or organic materials. Among these various treatment approaches, adsorption is recognized as the most commonly used technique for extracting heavy metals from waste water (Mokhtarzadeh *et al.*, 2021; Shirkhan *et al.*, 2022). The application of organic sorbents or biosorbents offers a more efficient means of cleansing natural and waste water from heavy metal ions. However, this approach necessitates

further technological advancements for the production or enhancement of these sorbents, as well as methods for their integration and extraction from water, along with strategies for their regeneration or disposal. Utilizing organic residue materials from the food or processing sectors as sorbents presents an opportunity to address both the challenge of residue management and the issue of treating waste water polluted with heavy metals (Martin Cervantes *et al.*, 2023; Ziarati *et al.*, 2023).

Iran ranks among the wealthiest nations globally with regard to genetic resources, particularly concerning medicinal and unidentified wild plants, several of which are exported (Shariatzadeh *et al.*, 2025). Bioactive compounds from medicinal herbs have possible health benefits with antioxidative, anticarcinogenic, antihypertensive, antimutagenic and antimicrobial activities (Krochmal-Marczak *et al.*, 2025). Persian traditional medicine know as diverse prosperous towards *evolving an integrated approach of full lifecycle of a sustainable product or process of medicinal and aromatic plants* in various herbs regarding not only to strengthen the body but also treat various diseases and disorders since ancient times. Cumin, the dehydrated seed of the *Cuminum cyminum* L plant, belongs to the parsley family (Taqui *et al.*, 2024). *Cuminum cyminum* L. (Apiaceae), referred to as Cumin is a strong aromatic of dried ripe fruit of *Cuminum cyminum* L. and has been used in Iranian folk medicine since more than 200 years ago (Allaq *et al.*, 2020). The fruits have been extensively utilized as an Iranian traditional medicine for the medicaments of toothache, diarrhea and epilepsy (Sahana *et al.*, 2011; Khosravi *et al.*, 2015; Mohseni *et al.*, 2021). Cumin is the most widely used medicinal plants in some countries and especially in Iran, which is cultivated to a large extent due to use its essence. Cumin cultivation area in Iran is 542841 ha that it is 25.7% of the total Iran cultivated area of medicinal plants (Piri *et al.*, 2018). In laboratory of Pharmacognosy and chemistry of Natural Products in pharmacy Faculty, the cumin residues after extraction were available *in abundant quantity*. This study examines the possibility of using *adsorbents* derived from the solid biomass *residues of cumin varieties: Cuminum Cyminum L. and Bunium Persicum L., to decontaminating of heavy metals from Pharmaceutical effluents*.

2. Materials & methods

2.1. Material preparation

Adsorbent: Green and Black Cumin residues

In current study, a screw press was operated under mechanical pressure, which enables the solid-liquid phase separation. Mechanically extracted oil was obtained using an oil extractor (ZY 22A, CJHZYG, China) after extraction of green and black cumin seeds separately, the oil was filtered and the residues were separated and gathered for adsorption of heavy metals from pharmaceutical effluent samples. After mechanical extraction, the green and black cumin seeds residues samples were stored in different separate plastic bags at refrigerated temperature (4 C) for further analyses.

Adsorbent particle size

The crusher sieve was used for the reduction of particle size of the dried Cumin residues samples and for particle size distribution, respectively. The sieves were mechanically vibrated for 15 minutes which was sufficient for separation to take place. The crusher sieve was used for the reduction of particle size of the dried. The screens were subjected to weighing balance before and after the vibration to get the mass and size

of the cumin residue particles retained on each sieve. The particle size range used in this study was 0.15 mm to 1.5 mm.

Pharmaceutical Effluents samples

Effluents from 8 Educational and research laboratories in pharmaceutical sciences Faculty, Azad university in Tehran, including, Pharmaceutical Sciences Research Center (Effluent 1&2), Toxicology (Effluent 3&4), Analytical chemistry (Effluent 5& 6), General Chemistry Labs (7&8) were used in current study. Effluent 1&2 samples were from the same laboratory but were collected on separate occasions with a 2 week time interval. Although Effluent 1 and Effluent 2 come from the same waste water treatment project, they were examined and considered as 2 different effluents due to the variability of their characteristics. The characteristic is attributed to the significant experiments which occurred following the first sampling event.

After collection, the waste water effluent samples were collected in new polypropylene bottles (2 L) capped with double stoppers and immediately transferred to the main research laboratory for investigation and analysis. Physico-chemical parameters such as Total Solids, Total hardness, pH, Electrical Conductivity, Total Dissolved Solids, Chloride, Sulphate, Dissolved oxygen, Calcium, Sodium, Cadmium, Lead, Zinc, Copper, Chrome, Manganese, Iron and Potassium were analyzed as per the standard methods (Ziarati *et al.*, 2017; 2023).

The initial concentration of heavy metals/metalloid such as Nickel, Zinc, Copper, Cobalt and Lead in the untreated effluents and treated by *Cuminum Cyminum* and *Bunium Persicum* residues were analyzed. After especial times: 48, 72 hours and 1 and 2 weeks (by/without stirring) final concentration of heavy metals in effluent samples were analyzed using ICP-OES, with the Optima 7300 V, Perkin Elmer and By combining an SCD detector and an echelle optical system, the *Optima 7300 DV* measured all studied heavy metals simultaneously regarding that ICP Software offers the ideal solution for economical elemental analysis.

Biochemical oxygen demand (BOD)

For Biological Oxygen Demand, 24 pharmaceutical effluent samples were processed after collection immediately for the determination of initial oxygen and incubated at 20°C for 5 days for the determination of BOD5 (FDA, 2013; Mokhtarzadeh, *et al.*, 2021).

Statistical methods

Statistical analysis was performed with SPSS Version 11.0 statistic software package. Data were expressed as the mean $\pm$ SE (standard error) of triplicate measurements. Duncan's multiple range tests was used to assess differences in heavy metals contents in Pharmaceutical effluents samples, different dose of bio-adsorbent of green and black cumin residues, different time and pH of the samples. Each sample data was the mean of 5 subsamples. A p value of 0.05 or less was considered as statistically significant.

3. Results and Discussion

Effluents from eight distinct pharmaceutical educational and research laboratories within the Pharmacy Faculty at Tehran Medical Sciences, Azad University were studied. The variability is linked to significant experiments conducted after the initial sampling. Upon collection, the pharmaceutical effluents and waste water samples were promptly

transported to the main research laboratory for further analysis. The physico-chemical parameters assessed included Total Solids, Total Hardness, pH, Electrical Conductivity, Total Dissolved Solids, Chloride, Sulphate, Dissolved Oxygen, Calcium, Sodium, Cadmium, Lead, Zinc, Copper, Chromium Manganese, Iron and Potassium were analyzed as per the standard methods. The initial concentration of heavy metals/metalloid such as Lead, Cobalt, Zinc, Nickel and Copper in the untreated effluents and treated by of *Bunium Persicum* and *Cuminum Cyminum* were analyzed at the same time and same protocol. The findings of the current study reveal the presence of several heavy metals in effluents from the laboratories, specifically Nickel, lead and Cobalt. Contaminated effluents interacts with the bio-adsorbent within a flow reactor or a stirred reactor, where it is combined with a mixture of spent residue materials of *Bunium Persicum* L. and *Cuminum Cyminum* L. in a certain proportions. The duration of contact was established according to the starting concentration of metal ions and the target final concentrations. Once the adsorption process is complete, the adsorbent is filtered out and disposed of accordingly (Mokhtarzadeh *et al.*, 2021).

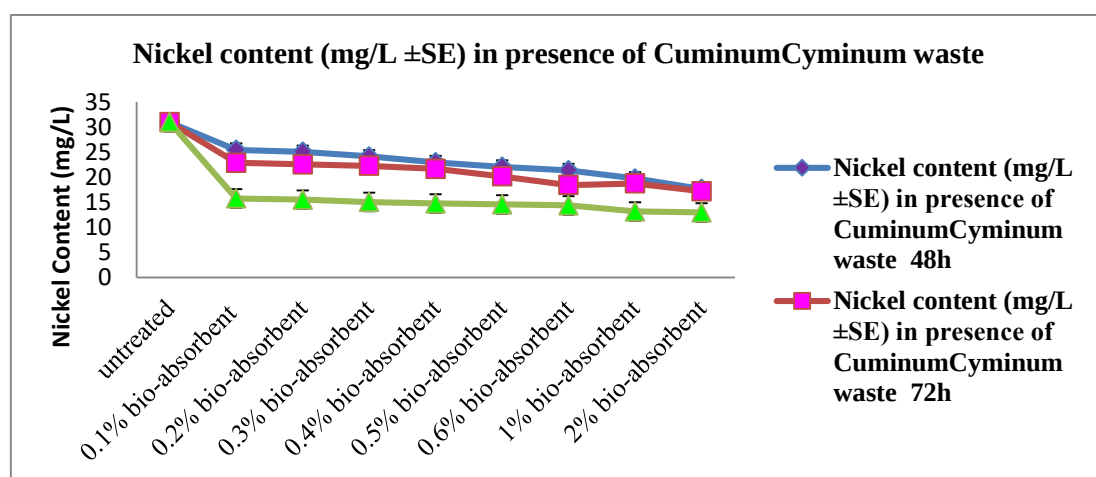


Figure 1. Effect of contact time on the removal of Nickel content in the effluent samples, in presence of *Cuminum Cyminum* L. residue, initial Nickel concentration 28.731 (mg/L), bio-adsorbent doses=0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 1, 2 mg

Figure 1 illustrates the results related to Nickel concentrations in the presence of *Cuminum Cyminum* as the bio-adsorbent. This figure comprises three diagrams representing different time intervals during which treatment with cumin residue occurred. All diagrams demonstrate a significant reduction in nickel levels in the effluents following exposure to cumin residue, but it also shows Nickel content in the effluents after treating with 1 and 2% bio-absorbents for 48 hours shows a significant reduction ($P \leq 0.003$).

Figure 2 presents the results for Nickel concentrations in pharmaceutical effluents which treated with *Bunium Persicum* L. residue. Like Figure 1, it includes three diagrams depicting various time frames with different bio-absorbents doses. The results indicate a decrease in Nickel concentration from 28.73 (mg/L) after treatment with 2% *Bunium Persicum* residue to 18.743 (mg/L±SE) 0.004 after 48 and 19.006±0.002 (mg/L±SE) after 72 hours and further down to 15.321±0.003 and 15.623±0.002 (mg/L±SE) after one week with 2% bio absorbent of green and black cumin respectively. Therefore, Nickel content

in waste water after 48, 72 hours and one week of treatment with *Bunium Persicum* and *Cuminum Cyminum* residue shows a significant reduction ($P \leq 0.005$).

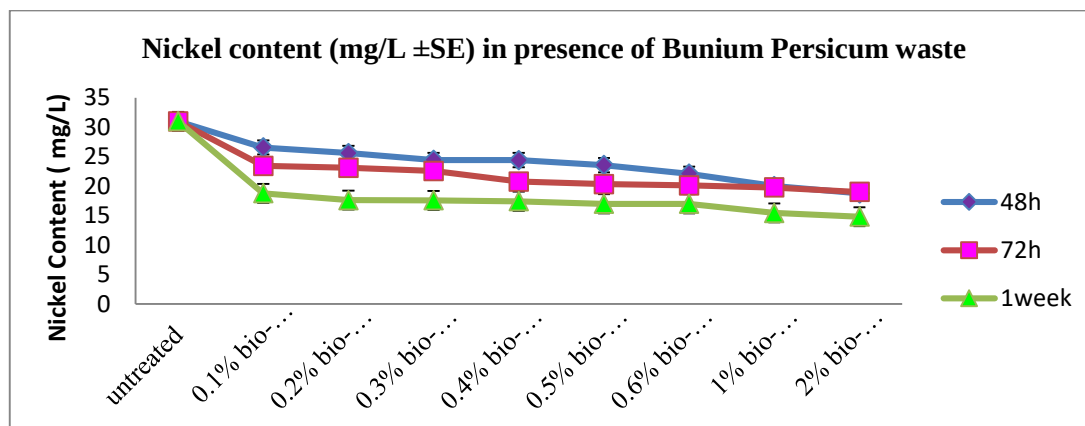


Figure 2. Effect of contact time on the removal of Nickel (Ni) content in presence of *Bunium Persicum* residue, initial Nickel concentration 28.731 (mg/L), bio-adsorbent doses=0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 1,2 mg

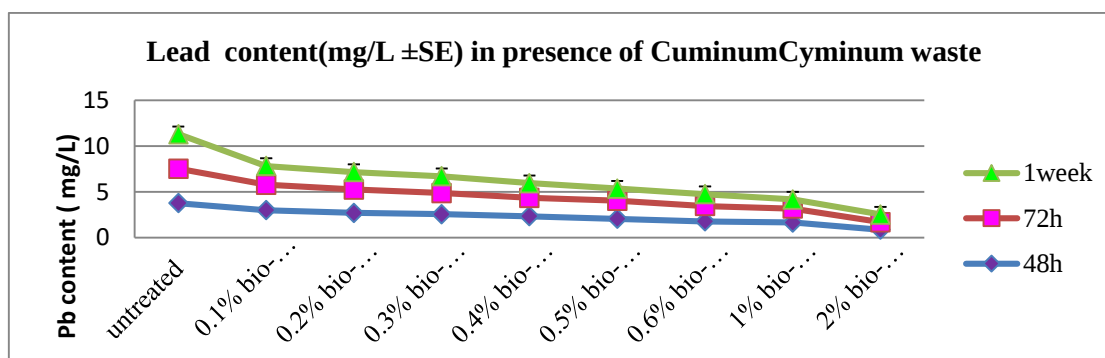


Figure 3. Effect of contact time on the removal of Lead content in the presence of *Cuminum Cyminum* residue (initial Lead concentration 3.768 (mg/L), bio-adsorbent doses: 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 1,2 mg

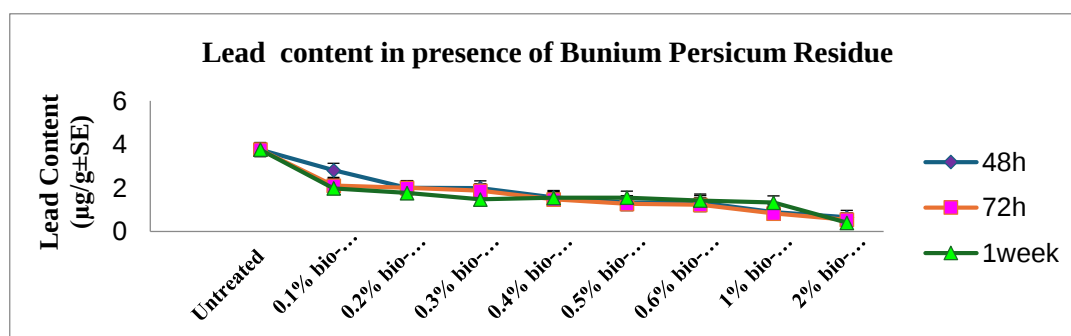
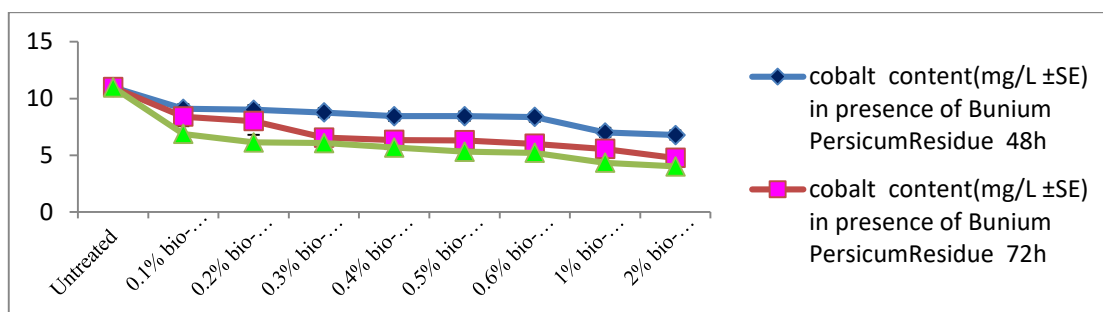


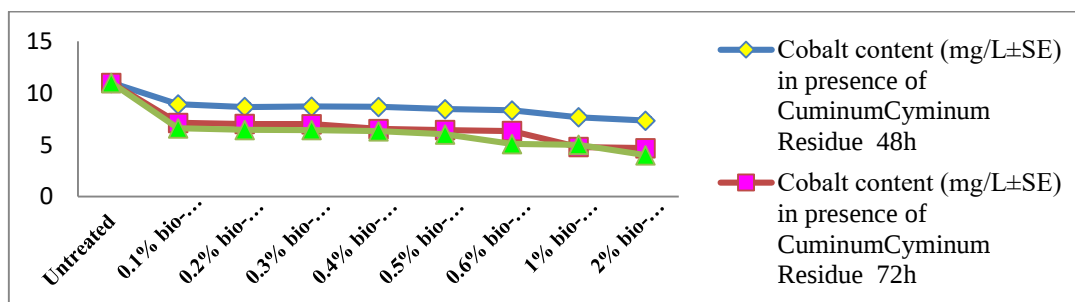
Figure 4. Effect of contact time on the removal of Lead (Pb) content in the presence of *Bunium Persicum* residue (initial Lead concentration 3.768 (mg/L), bio-adsorbent doses: 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 1,2 mg

Figures 3 and 4 displays the lead concentrations in the effluents treated with *Cuminum Cyminum* and *Bunium Persicum* residue respectively. Results in Figure 3 in presence of 2% *Cuminum Cyminum* residue revealed the significant potential removal of Lead from contaminated effluents and after 48 hours the remained toxic heavy metal

decreased to 0.832 mg/L, while the decrease trend in lead concentrations following treatment with 2% bio-absorbent in more time did not exhibit any notable and significant variations at the 48-hour, 72-hour and one-week marks.



Figures 5. Effect of contact time on the removal of Cobalt content in the presence of *Bunium Persicum* residue (initial Cobalt concentration 10.989 (mg/L), room temperature (25 ± 2 °C), bio-adsorbent doses=0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 1,2 mg



Figures 6. Effect of contact time on the removal of Cobalt content in the presence of *Cuminum Cyminum* residue (initial Cobalt concentration 10.989 (mg/L), room temperature (25 ± 2 °C), bio-adsorbent doses=0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 1,2 mg

Figures 5 and 6 illustrate the Cobalt concentrations in the contaminated effluents and waste water treated with *Bunium Persicum* and *Cuminum Cyminum* residues respectively, also indicating a significant decrease ($p \leq 0.05$) in Cobalt concentrations even with low dose of bio-adsorbent: 0.1 % after 48, 72 hours and 1 week of treatment.

The mean concentration of Copper (Cu) in the pharmaceutical effluents and waste water treated with bio-adsorbents was measured using ICP-OES and the findings were reported as the average level in mg/L in Table 1 and Table 2, after 48 hours, 72 hours, 1 week and 2 weeks (with the action of stirring and without stirring) respectively. All concentrations were expressed as (mg/L $\pm$ SE). The contents obtained for each sample is the average of 3 repetitions of the measurement. Decreasing of Cu by 0.5 % of bio-adsorbent was significant even after 48 hours ($P \leq 0.05$). The most efficacy of adsorbing Cu by 2% bio-mass of *Cuminum Cyminum* residue after 2 weeks through stirring the samples and bio-adsorbent.

Table 1. Treating Copper in waste water/pharmaceutical effluent samples in presence of *Cuminum Cyminum* residue

Copper content (mg/L $\pm$ SE) in presence of <i>Cuminum Cyminum</i> residue	48h	72h	1week	1week	2week	2week
				(Stirred solution)		(Stirred solution)
0.1% bio-adsorbent	101.33 $\pm$ 0.003	100.06 $\pm$ 0.004	95.43 $\pm$ 0.004	81.52 $\pm$ 0.002	84.33 $\pm$ 0.005	77.62 $\pm$ 0.003
0.2% bio-adsorbent	98.76 $\pm$ 0.002	92.45 $\pm$ 0.003	90.01 $\pm$ 0.004	74.21 $\pm$ 0.002	78.91 $\pm$ 0.004	73.29 $\pm$ 0.003
0.3% bio-adsorbent	92.11 $\pm$ 0.002	89.01 $\pm$ 0.006	82.17 $\pm$ 0.004	70.18 $\pm$ 0.003	74.21 $\pm$ 0.003	70.14 $\pm$ 0.005
0.4% bio-adsorbent	92.09 $\pm$ 0.002	88.02 $\pm$ 0.004	88.44 $\pm$ 0.002	68.21 $\pm$ 0.003	74.08 $\pm$ 0.003	68.52 $\pm$ 0.003
0.5% bio-adsorbent	90.18 $\pm$ 0.003	86.98 $\pm$ 0.002	86.04 $\pm$ 0.002	62.33 $\pm$ 0.003	76.59 $\pm$ 0.003	63.19 $\pm$ 0.003
0.6% bio-adsorbent	85.81 $\pm$ 0.003	85.43 $\pm$ 0.003	81.22 $\pm$ 0.003	60.44 $\pm$ 0.002	74.22 $\pm$ 0.002	59.81 $\pm$ 0.002
1% bio-adsorbent	82.23 $\pm$ 0.003	80.41 $\pm$ 0.003	74.81 $\pm$ 0.003	58.76 $\pm$ 0.003	69.08 $\pm$ 0.002	54.33 $\pm$ 0.002
2% bio-adsorbent	75.44 $\pm$ 0.001	71.54 $\pm$ 0.002	68.05 $\pm$ 0.002	53.23 $\pm$ 0.003	56.89 $\pm$ 0.003	50.76 $\pm$ 0.002
Untreated	126.87 $\pm$ 0.002	126.87 $\pm$ 0.002	126.87 $\pm$ 0.002	126.87 $\pm$ 0.002	126.87 $\pm$ 0.002	126.87 $\pm$ 0.002

*SE= Standard Error

Table 2. Treating Copper in waste water/pharmaceutical effluent samples in presence of *Bunium Persicum* residue

Copper content (mg/L $\pm$ SE) in presence of <i>Bunium Persicum</i> residue	48h	72h	1week	1week	2 week	2week
				(Stirred solution)		(Stirred solution)
0.1% bio-adsorbent	105.66 $\pm$ 0.005	100.52 $\pm$ 0.004	98.71 $\pm$ 0.004	85.42 $\pm$ 0.003	90.17 $\pm$ 0.004	82.17 $\pm$ 0.005
0.2% bio-adsorbent	100.07 $\pm$ 0.003	96.52 $\pm$ 0.004	92.88 $\pm$ 0.005	78.93 $\pm$ 0.003	84.62 $\pm$ 0.003	78.19 $\pm$ 0.003
0.3% bio-adsorbent	96.54 $\pm$ 0.002	91.52 $\pm$ 0.002	89.31 $\pm$ 0.003	73.82 $\pm$ 0.003	80.03 $\pm$ 0.004	73.81 $\pm$ 0.003
0.4% bio-adsorbent	94.18 $\pm$ 0.003	90.02 $\pm$ 0.003	86.51 $\pm$ 0.004	70.24 $\pm$ 0.003	78.64 $\pm$ 0.002	70.09 $\pm$ 0.002
0.5% bio-adsorbent	90.76 $\pm$ 0.003	87.53 $\pm$ 0.003	84.39 $\pm$ 0.003	68.71 $\pm$ 0.005	76.89 $\pm$ 0.006	68.23 $\pm$ 0.004
0.6% bio-adsorbent	90.43 $\pm$ 0.003	86.11 $\pm$ 0.004	82.06 $\pm$ 0.003	61.25 $\pm$ 0.004	74.39 $\pm$ 0.003	62.18 $\pm$ 0.003
1% bio-adsorbent	87.91 $\pm$ 0.003	82.81 $\pm$ 0.003	76.51 $\pm$ 0.004	59.03 $\pm$ 0.002	72.07 $\pm$ 0.002	58.89 $\pm$ 0.001
2% bio-adsorbent	82.17 $\pm$ 0.001	79.67 $\pm$ 0.003	73.49 $\pm$ 0.003	57.32 $\pm$ 0.002	70.71 $\pm$ 0.003	54.38 $\pm$ 0.003
Untreated	126.87 $\pm$ 0.002	126.87 $\pm$ 0.002	126.87 $\pm$ 0.002	126.87 $\pm$ 0.002	126.87 $\pm$ 0.002	126.87 $\pm$ 0.002

*SE= Standard Error

Decreasing of Cu by 0.5 % of bio-adsorbent was significant even after 48 hours ($P \leq 0.05$) and the results of removal of Cu by both of cumin residues followed the same process and procedure. In comparison of both cumin residues, although the results of *Cuminum Cyminum* bio-adsorbent seems more efficient, but no significant differences was statistically observed.

Table 3. Treating Zinc (Zn) in waste water/pharmaceutical effluent samples in presence of *Cuminum Cyminum* residue

Zinc content (mg/L $\pm$ SE) in presence of <i>Cuminum Cyminum</i> residue	48h	72h	1week	1week	2week	2week
				(stirred solution)		(stirred solution)
0.1% bio-absorbent	207.66 $\pm$ 0.006	198.89 $\pm$ 0.007	180.54 $\pm$ 0.005	151.17 $\pm$ 0.005	171.29 $\pm$ 0.004	131.88 $\pm$ 0.004
0.2% bio-absorbent	198.74 $\pm$ 0.004	195.29 $\pm$ 0.004	175.44 $\pm$ 0.003	150.11 $\pm$ 0.004	166.54 $\pm$ 0.002	130.18 $\pm$ 0.005
0.3% bio-absorbent	194.38 $\pm$ 0.003	190.66 $\pm$ 0.005	170.01 $\pm$ 0.006	140.16 $\pm$ 0.007	137.82 $\pm$ 0.005	128.76 $\pm$ 0.003
0.4% bio-absorbent	190.18 $\pm$ 0.004	186.52 $\pm$ 0.003	167.83 $\pm$ 0.003	137.61 $\pm$ 0.006	135.48 $\pm$ 0.007	125.82 $\pm$ 0.005
0.5% bio-absorbent	186.52 $\pm$ 0.004	182.77 $\pm$ 0.005	164.22 $\pm$ 0.004	129.19 $\pm$ 0.005	119.86 $\pm$ 0.006	123.11 $\pm$ 0.007
0.6% bio-absorbent	184.71 $\pm$ 0.003	180.27 $\pm$ 0.004	160.09 $\pm$ 0.005	124.16 $\pm$ 0.004	115.29 $\pm$ 0.005	120.06 $\pm$ 0.004
1% bio-absorbent	180.06 $\pm$ 0.004	178.91 $\pm$ 0.005	158.32 $\pm$ 0.004	105.27 $\pm$ 0.004	110.93 $\pm$ 0.008	100.04 $\pm$ 0.006
2% bio-absorbent	160.34 $\pm$ 0.004	158.33 $\pm$ 0.004	146.25 $\pm$ 0.005	98.78 $\pm$ 0.005	100.18 $\pm$ 0.005	93.28 $\pm$ 0.005
Untreated	209.45 $\pm$ 0.002	209.45 $\pm$ 0.002	209.45 $\pm$ 0.002	209.45 $\pm$ 0.002	209.45 $\pm$ 0.002	209.45 $\pm$ 0.002

*SE= Standard Error

The mean concentration of Zinc (Zn) in the pharmaceutical effluents and waste water treated with both cumin bio-adsorbents was measured by ICP-OES and the findings were reported as the average level in mg/L in Table 3 and Table 4, after 48 hours, 72 hours, 1 week and 2 weeks (with the action of stirring and without stirring) respectively. Decreasing of Zn by 2 % of bio-adsorbent was significant even after 48 hours ($P \leq 0.05$). The most efficacy of adsorbing Cu by 2% bio-mass of *Bunium Persicum* residue after 2 weeks through stirring the samples and bio-adsorbent.

In this study, we revealed an important data about by using Agro/food residues such as *Bunium Persicum* residue and *Cuminum Cyminum* residues in cleaning up the pharmaceutical effluents. They can decrease the concentration of heavy metals of the waste water magnificently and significantly ($P \leq 0.05$) such as Lead, Cobalt, Nickel, Zinc and Copper. Current study also showed that Lead content as one of the most important heavy metals that is very dangers for human lives and can have a bad impact on human organs of the body, can be removed significantly after treating by *Cuminum Cyminum* and *Bunium Persicum* residues. Following each sorption experiment, Lead content in the contaminated waste water samples after treating with *Bunium Persicum* residue after one week of treatment with 2% of bio-absorbent showed more decreasing than treating with *Cuminum Cyminum* residue, although no significant differences statistically observed ($P \geq 0.005$).

In comparison of the findings from current study with similar works, recent study by Mokhtarzadeh and the team revealed that tomato residue had a great impact on adsorbing Nickel content in waste water after two weeks of treatment. The reduction of Ni was significant and mean content of 183.54 ± 1.00 decreased to 130.78 ± 0.11 mg/L $\pm$ SE. That last studied also revealed that in the presence of 0.1% and 2% Tomato Pomace, the effectiveness in removing Cobalt was nearly identical; however, it exhibited a lower trend. This indicates that the bio-adsorbent has a greater capacity to selectively accumulate Cobalt ions compared to nickel ions when the quantity of bio-adsorbent

remains constant. In current investigation, the initial Nickel content 28.731 ± 0.002 decreased to 15.321 ± 0.003 and 15.623 ± 0.002 (mg/L $\pm$ SE) after one week with 2% bio absorbent of *Cuminum Cyminum* and *Bunium Persicum* residues respectively.

Table 4. Treating Zinc (Zn) in waste water/pharmaceutical effluent samples in presence of *Bunium Persicum* residue

Zinc content (mg/L $\pm$ SE) in presence of Bunium Persicum residue	48h	72h	1week	1week	2week	2week
				(stirred solution)		(stirred solution)
0.1% bio-absorbent	188.45 $\pm$ 0.008	183.27 $\pm$ 0.005	165.43 $\pm$ 0.004	148.21 $\pm$ 0.003	160.01 $\pm$ 0.005	140.15 $\pm$ 0.004
0.2% bio-absorbent	182.19 $\pm$ 0.006	180.02 $\pm$ 0.006	160.32 $\pm$ 0.008	143.21 $\pm$ 0.004	156.32 $\pm$ 0.005	138.22 $\pm$ 0.005
0.3% bio-absorbent	180.11 $\pm$ 0.004	176.54 $\pm$ 0.005	159.41 $\pm$ 0.005	141.28 $\pm$ 0.003	150.76 $\pm$ 0.006	132.66 $\pm$ 0.005
0.4% bio-absorbent	178.62 $\pm$ 0.005	171.29 $\pm$ 0.006	152.11 $\pm$ 0.004	138.79 $\pm$ 0.004	141.89 $\pm$ 0.004	130.06 $\pm$ 0.005
0.5% bio-absorbent	174.39 $\pm$ 0.004	170.11 $\pm$ 0.005	150.21 $\pm$ 0.004	136.44 $\pm$ 0.007	139.71 $\pm$ 0.004	126.72 $\pm$ 0.003
0.6% bio-absorbent	170.92 $\pm$ 0.007	167.83 $\pm$ 0.002	142.19 $\pm$ 0.004	119.05 $\pm$ 0.003	130.87 $\pm$ 0.005	115.87 $\pm$ 0.005
1% bio-absorbent	150.56 $\pm$ 0.009	148.54 $\pm$ 0.003	138.76 $\pm$ 0.006	108.45 $\pm$ 0.004	120.01	95.63 $\pm$ 0.003
2% bio-absorbent	130.32 $\pm$ 0.005	140.54 $\pm$ 0.005	130.27 $\pm$ 0.007	100.23 $\pm$ 0.004	112.08 $\pm$ 0.003	90.54 $\pm$ 0.005
Untreated	209.45 $\pm$ 0.002	209.45 $\pm$ 0.002	209.45 $\pm$ 0.002	209.45 $\pm$ 0.002	209.45 $\pm$ 0.002	209.45 $\pm$ 0.002

*SE= Standard Error

In comparison of the findings from current study with similar works, recent study by Mokhtarzadeh and the team revealed that tomato residue had a great impact on adsorbing Nickel content in waste water after two weeks of treatment. The reduction of Ni was significant and mean content of 183.54 ± 1.00 decreased to 130.78 ± 0.11 mg/L $\pm$ SE. That last studied also revealed that in the presence of 0.1% and 2% Tomato Pomace, the effectiveness in removing Cobalt was nearly identical; however, it exhibited a lower trend. This indicates that the bio-adsorbent has a greater capacity to selectively accumulate Cobalt ions compared to nickel ions when the quantity of bio-adsorbent remains constant. In current investigation, the initial Nickel content 28.731 ± 0.002 decreased to 15.321 ± 0.003 and 15.623 ± 0.002 (mg/L $\pm$ SE) after one week with 2% bio absorbent of *Cuminum Cyminum* and *Bunium Persicum* residues respectively.

4. Conclusion

The harmful effects of heavy metals on both humans and animals stem from prolonged exposure to low levels of contamination present in our surroundings, which encompasses the air we inhale, the water we consume and the food we eat, among other sources. Heavy metals may migrate from industrial locations to waterways such as canals and rivers due to direct discharges and the runoff from contaminated areas. Additionally, storm water runoff from urban streets can carry considerable quantities of heavy metals. This contamination eventually affects agricultural land used for cultivating animal feed. Heavy metals found in waste water, including lead, mercury, cadmium, arsenic and chromium, present considerable risks to both the environment and human health because

of their toxic properties and resilience in the ecosystem. A range of treatment techniques is utilized to efficiently eliminate these pollutants. Ultimately, these metals can enter the body through the ingestion of food or water that has been tainted by metals from dairy animals or through utensils utilized for transporting and cleaning water. Additionally, infants may be exposed through pipe connections to contaminated water sources, such as canal water. These are among the origins of heavy metal exposure. The process of adsorbing or bio-adsorbing heavy metals from industrial effluents has proven effective. Some heavy metals, including certain chemical acids, are relatively inexpensive byproducts of various industrial operations. The selection of an appropriate method is influenced by various factors, including the nature and concentration of metals, the volume of waste water, regulatory standards and cost factors. For large-scale operations, chemical precipitation is commonly utilized, whereas advanced techniques such as reverse osmosis or adsorption are favored when high removal efficiency or the treatment of trace concentrations is required. Additionally, sustainable methods like phytoremediation are increasingly attracting attention for their environmentally friendly applications. Results indicated that economically feasible and readily accessible bio-adsorbents can effectively facilitate the extraction of heavy metals, specifically lead (Pb) at high concentrations. Additionally, it was observed that the efficiency of heavy metal removal was influenced by both the dosage and particle size of the low-cost adsorbent. The optimal contact time required to achieve maximum adsorption was determined to be 48 hours. We recommend utilizing *Bunium Persicum* and *Cuminum Cyminum* residues after extraction process, to reduce heavy metal concentrations in contaminated pharmaceutical effluents and waste water by heavy metals and the findings have yielded impressive outcomes. The findings of the current study reveal the presence of several heavy metals in waste water which are released into local waterways and the canals, specifically Nickel, lead and copper. *Our study suggests* that due to mitigate the levels of these hazardous heavy metals in the waste water, employing the herbal extraction by-product of cumin by the efficacy of more than 88 % removal heavy metals on average *will* assist in lessening the global impact of metal contamination in our environment.

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