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# A green approach for the treatment of industrial effluent for hazardous metals of chromium and lead

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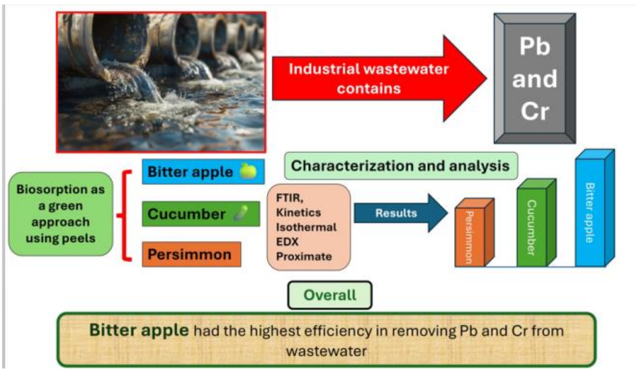
## Graphical abstract




## Abstract

This study explores the efficacy of plant-derived biosorbents - bitter apple, persimmon, and cucumber peels – as a green chemistry solution for the removal of toxic heavy metals, specifically lead (Pb) and chromium (Cr), from sewage water collected from Harnoli and Piplan, Pakistan. Batch biosorption experiments were conducted using biosorbent doses of 1, 2, and 3 g $L^{-1}$ at contact times of 24 and 48 hours. Heavy metal concentrations were measured using Atomic Absorption Spectroscopy (AAS), and results were statistically validated through one-way ANOVA (Pb: $F(5,30) = 18.42$, $p < 0.001$; Cr: $F(5,30) = 16.89$, $p < 0.001$), followed by Duncan's multiple range test. Biosorption efficiency increased proportionally with biosorbent dose and contact time. Bitter apple peels at 3 g for 48 h achieved the highest removal in Piplan samples, reducing Pb from 0.64 to 0.14 ppm and Cr from 0.41 to 0.10 ppm. The reduction in the concentration of Pb and Cr using bitter apple peels was 78.1 and 75.6%, respectively, in comparison to the control. Persimmon showed similarly high performance (Pb: 0.24 ppm; Cr: 0.16 ppm), while cucumber peels, although less efficient, still achieved meaningful Pb removal. FTIR analysis confirmed the presence of hydroxyl, carboxyl, and carbonyl groups responsible for metal binding via ion exchange and complexation. Notably, a selective adsorption trend was observed, with higher affinity for Pb than Cr across all biosorbents, which highlights the practical applicability of agro-waste biosorbents in low-cost wastewater treatment technologies.

**Keywords:** biosorbents; heavy metal removal; plant peels; sewage water treatment; wastewater treatment

## Highlights

- Evaluated bitter apple, persimmon, and cucumber peels as low-cost biosorbents for Pb and Cr removal from sewage water.
- Batch biosorption with varying biosorbent doses (1–3 g/L) and contact times (24–48 h) was carried out.
- Bitter apple peels showed the highest removal: Pb reduced from 0.64 to 0.14 ppm; Cr from 0.41 to 0.10 ppm.
- Selective adsorption with higher affinity for Pb than Cr across all biosorbents was observed.

## 1. Introduction

One of the most pressing issues facing the globe today is the contamination of ecosystems, which has a major impact on several illnesses and higher death rates globally (Zeng *et al.*, 2016; Dai *et al.*, 2021). Industrial wastewater frequently contains heavy metals, including lead (Pb) and chromium (Cr), because of different mining, metal processing, and manufacturing activities (Kanwal *et al.*, 2023; Gang *et al.*, 2024). To maintain a healthy ecological environment, heavy metal pollutants in wastewater must be removed. Their redox behavior results in oxidative stress, DNA injury, and long-term health issues (Ullah *et al.*, 2023). Technologies for wastewater treatment - including physical, biological, and chemical processes - are frequently utilized in primary, secondary, and tertiary phases (Patel *et al.*, 2021). However, the worldwide scientific agreement predicts that water pollution will emerge as a primary environmental stressor, overtaking climate change in the next few decades (Shahzad *et al.*, 2021).

Different techniques, such as chemical precipitation, ion exchange, membrane filtration, and adsorption, are employed to eliminate heavy metals. Nevertheless, numerous options are expensive and harmful to the environment. Green chemistry presents a viable option, focusing on the creation of environmentally friendly processes and materials (Sayed *et al.*, 2021a, b, 2022; Syeda *et al.*, 2022). Among these, utilizing plant-derived biomass for biosorption has demonstrated significant potential (Al-Shannag *et al.*, 2017; Sayed *et al.*, 2024a, b). Agro-waste materials, particularly peels from fruits and vegetables, contain active functional groups (such as -COOH, -OH, $-NH_2$) that engage with metal ions, rendering them effective, affordable, and sustainable biosorbents (de Paiva *et al.*, 2021; Wang *et al.*, 2021; Selvanarayanan *et al.*, 2024; Venkatraman *et al.*, 2024; Maruthai et al, 2025).

Even with positive findings from earlier research, the biosorption capacity of specific plant-based materials is still insufficiently investigated. This study is the first to evaluate the biosorption capacity of bitter apple (*Citrullus colocynthis*), cucumber (*Cucumis sativus*), and persimmon (*Diospyros kaki*) peels for Cr and Pb removal from real sewage effluents in Pakistan. Therefore, the current study was aimed at 1) assessing the effectiveness of chromium and lead removal using peels from persimmon, cucumber, and bitter apple as biosorbents and 2) examining the biosorption efficiency at different biosorbent amounts and varying contact durations utilizing actual sewage water samples collected from industrial areas in Pakistan.

## 2. Materials and Methods

### *2.1. Sample Collection*

Sewage water samples were collected from two industrial regions in Punjab, Pakistan: Harnoli and Piplan. Samples were collected in clean 5-liter polyethylene bottles and transported immediately to the laboratory. The samples were filtered to remove large particulates and stored at 4°C until further use.

### *2.2. Preparation of Biosorbents*

Plant peels of persimmon (*Diospyros kaki*), cucumber (*Cucumis sativus*), and bitter apple (*Citrullus colocynthis*) were collected from local markets. The peels were washed thoroughly with deionized water to remove adhering dust and soluble impurities, sun-dried for 5–7 days, and then oven-dried at 60°C for 24 hours. The dried material was ground into a fine powder and sieved to obtain uniform particle sizes (0.5 mm).

### *2.3. Collection of wastewater samples*

Sewage water samples from Harnoli and Piplan were randomly gathered and analyzed for HM concentration using atomic absorption spectroscopy. The pH and physical characteristics of the water were also documented (**Table 1**).

**Table 1:** The pH and physical appearance of sewage water

| Water samples | pH | Physical appearance |
|---|---|---|
| Harnoli (H) | 8 | Turbid |
| Piplan (P) | 7.5 | Turbid |

### *2.4. Experimental Setup*

Batch biosorption experiments in triplicate were conducted in 250 mL Erlenmeyer flasks, each containing 100 mL of untreated sewage water and biosorbent at three concentrations: 1, 2, and 3 g $L^{-1}$. The flasks were placed on an orbital shaker and agitated at 150 rpm at room temperature (25 ± 2 °C), and the natural pH of the wastewater samples was monitored throughout the experiments. Two contact times were investigated: 24 and 48 hours. Additionally, control samples (0 g/L biosorbent) were maintained for both sites and contact times. All treatments, including controls, were performed in triplicate (n = 3). In total, the study comprised 36 biosorbent-treated conditions (3 biosorbents × 2 sites × 3 doses × 2 times) and 4 control conditions (2 sites × 2 times), yielding 40 distinct experimental setups (**Table 2**).

**Table 2:** Parameters of experimental setup

| Parameters | Variables | | |
|---|---|---|---|
| Biosorbents | bitter apple | cucumber | persimmon |
| Biosorbent doses | 1g $L^{-1}$ | 2 g $L^{-1}$ | 3 g $L^{-1}$ |
| Sewage water sources | Piplan | Harnoli | |
| Contact time | 24 h | 48 h | |

After the contact period, solutions were filtered through Whatman No. 42 filter paper. Residual concentrations of Pb and Cr were determined using an Atomic Absorption Spectrophotometer (PerkinElmer AAnalyst 400). Calibration curves were generated using certified standards. Quality control included running blanks and spiked samples.

### *2.5. Analytical procedures*

After the contact period, solutions were filtered through Whatman No. 42 filter paper. Residual concentrations of Pb and Cr were determined using an Atomic Absorption Spectrophotometer (PerkinElmer AAnalyst 400). Calibration curves were generated using certified standards. Quality control included running blanks and spiked samples.

The adsorption capacity of each biosorbent for Pb and Cr was calculated using the following equation:

$$q_e = \frac{(C_o - C_e).\ V}{m} \quad (3)$$

Where $q_e$ = adsorption capacity in mg/g; $C_0$ = initial concentration (mg/L); $C_e$ = equilibrium concentration (mg/L); V = volume of solution (L); m = mass of biosorbent used (g).

The removal efficiency (R%) was calculated using the following equation:

$$R(\%) = \frac{(C_o - C_e)}{C_o} \times 100 \quad (3)$$

Where $C_0$ = initial and $C_e$ = equilibrium metal concentrations. Data were expressed as mean ± SD.

*2.6. FTIR Characterization*

FTIR analysis was conducted on biosorbent samples before and after metal adsorption to identify functional groups involved in biosorption. Spectra were recorded in the 4000–500 $cm^{-1}$ range using a Bruker Alpha II FTIR spectrophotometer. Shifts and intensity changes in peaks were analyzed to identify biosorption-related interactions.

*2.7. Statistical Analysis*

All experiments were carried out in triplicate, with results presented as mean ± standard deviation (SD) to account for variability in the experiments. Statistical analyses were conducted using IBM SPSS Statistics (version 20.0) to assess the impact of biosorbent type, dosage, contact duration, and sampling location on the removal of heavy metals. A one-way analysis of variance (ANOVA) was conducted individually for Pb and Cr to assess if there were statistically significant differences between the treatment groups (biosorbent type × dosage × contact time). The assumptions of normality and variance homogeneity were checked before analysis. Duncan's Multiple Range Test (DMRT) was utilized for post hoc comparisons to determine which specific treatment combinations exhibited significant differences in metal removal efficiency. A significance level of $p < 0.05$ was applied for every test conducted.

## 3. RESULTS AND DISCUSSION

*3.1. FTIR analysis*

FTIR spectroscopy was used to identify functional groups in bitter apple, cucumber, and persimmon peels, which contribute to their potential as biosorbents for heavy metal ions (**Figure 1**). The FTIR spectrum of bitter apple peel revealed a broad band at 3346 $cm^{-1}$, indicating hydroxyl (–OH) groups, along with sharp peaks at 2917 and 2850 $cm^{-1}$ corresponding to aliphatic C–H stretches. Carbonyl (C=O) stretching was evident at 1700 and 1690 $cm^{-1}$, and carboxylate ($COO^-$) groups were confirmed by bands at 1559 and 1420 $cm^{-1}$. The presence of C–O and C–O–C stretching at 1012 and 1143 $cm^{-1}$ suggested polysaccharide and glycosidic linkages, important for metal ion binding via ion exchange and complexation (Kanwal *et al.*, 2024) as observed in the present study.

In the cucumber peel, characteristic O–H stretches appeared at 3506 and 3323 $cm^{-1}$, with C–H bands at 2918 and 2830 $cm^{-1}$. Carbonyl and carboxylate groups were indicated by peaks at 1700, 1593, and 1500 $cm^{-1}$. Additional peaks at 1030 and 1049 $cm^{-1}$ indicated anhydride and alcoholic groups, and a C=C stretch at 1617 $cm^{-1}$ suggested unsaturation. These groups support diverse interactions, including hydrogen bonding and chelation (Gang *et al.*, 2024), and ultimately improve the adsorption potential of the biosorbent as observed in the present study.

Persimmon peel showed similar O–H and C–H stretches at 3302 and ~2900 $cm^{-1}$, respectively. C=O stretching appeared at 1700 $cm^{-1}$, and a CO–O–CO anhydride peak was detected at 1013 $cm^{-1}$. C=C stretching (1610–1650 $cm^{-1}$) indicated unsaturation. The presence of hydroxyl, carbonyl, and anhydride groups suggests capacity for ion exchange and metal-ligand coordination.

All three biosorbents shared common functional groups essential for metal uptake - namely, hydroxyl, carbonyl, and carboxylate moieties. These groups facilitate biosorption through mechanisms such as ion exchange, complexation, and hydrogen bonding (Murtaza *et al.*, 2021; Batool *et al.*, 2023). While bitter apples showed a strong profile of carboxyl and polysaccharide groups, cucumber exhibited greater diversity, and persimmon presented a simpler but effective set of polar functionalities. These differences may influence their biosorption performance and selectivity toward heavy metals.

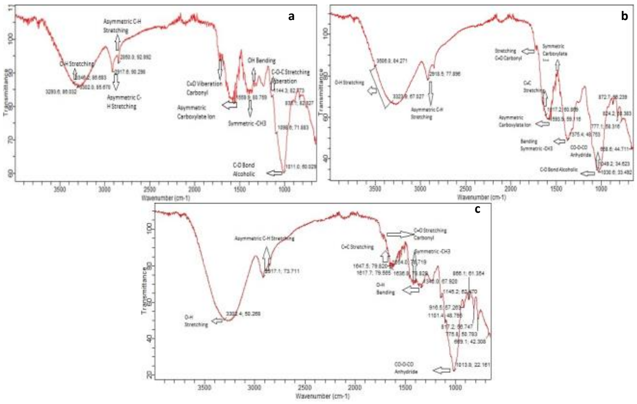
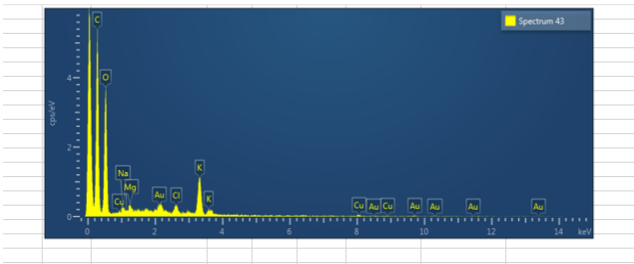


**Figure 1.** FTIR spectra of a) bitter apple peels, b) cucumber peels, and c) persimmon peels.




| Element | Line Type | Apparent Concentration | k Ratio | Wt% | Wt% Sigma | Standard Label | Factory Standard | Standard Calibration Date |
|---|---|---|---|---|---|---|---|---|
| C | K series | 41.2 | 0.412 | 54.74 | 0.96 | C Vit | Yes | |
| O | K series | 32.97 | 0.111 | 37.02 | 0.87 | SiO2 | Yes | |
| Na | K series | 0.77 | 0.003 | 0.54 | 0.14 | Albite | Yes | |
| Mg | K series | 0.48 | 0.003 | 0.41 | 0.09 | MgO | Yes | |
| Cl | K series | 0.95 | 0.008 | 0.79 | 0.1 | NaCl | Yes | |
| K | K series | 6.1 | 0.052 | 4.89 | 0.2 | KBr | Yes | |
| Cu | L series | 0.04 | 4E-04 | 0.06 | 0.34 | Cu | Yes | |
| Au | M series | 1.42 | 0.014 | 1.55 | 0.33 | Au | Yes | |
| Total: | | | | 100 | | | | |

**Figure 2.** EDX Pattern of peels of Bitter Apple

*3.2. Energy Dispersive X-ray Spectroscopy (EDX) of peels of Bitter Apple*

EDX analysis was conducted on bitter apple peels, revealing the presence of carbon (54.74%) and oxygen (37.02%), as well as metallic ions including Sodium

(0.77%), Magnesium (0.48%), Chlorine (0.95%), Potassium (6.1%), Copper (0.04%), and Gold (1.42%) (**Figure 2**). The high weight percentage of carbon and oxygen (91.76%) reflects the abundance of organic compounds in the plant.

### *3.3. Proximate analysis of peels of bitter apples, cucumber, and persimmon*

Gravimetric analysis was conducted to determine the structural composition of the biosorbents - bitter apple, cucumber, and persimmon peels—using the loss on ignition (LOI) method. 10 g of each dried peel powder was analyzed for moisture content, total carbon, volatile matter, ash, and organic matter. The results (**Table 3**) confirmed that all three biosorbents contained substantial amounts of organic constituents, essential for biosorption activity. Persimmon and cucumber peels exhibited particularly high organic matter content, indicative of rich biopolymeric matrices suitable for metal ion interaction, whereas bitter apple showed comparatively higher ash content, suggesting a greater proportion of mineral residues.

**Table 3.** Proximate analysis of the peels of the cucumber

| Test | Bitter apples | Cucumber | Persimmon | Methods |
|---|---|---|---|---|
| Physical Form | Powder | Powder | Powder | Visual |
| Color | Light Green | Brown | Orange | Visual |
| Moisture | 10.9% | 6.3% | 7.56% | Karl Fisher Titrator |
| Carbon | 46% | 54% | 55.40% | Loss on Ignition |
| Volatile Compounds | 33% | 39% | 39.9% | Loss on Ignition |
| Ash | 20.11% | 6% | 4.5% | Loss on Ignition |
| OM | 79.89% | 93.7% | 95.5% | Loss on Ignition |

### *3.4. Untreated sewage water analysis (Control group)*

Untreated sewage water samples from Piplan and Harnoli were analyzed using Atomic Absorption Spectroscopy (AAS) to determine the concentrations of toxic heavy metals, specifically lead (Pb) and chromium (Cr) (**Figure 3**). Subsequent treatment trials were conducted using biosorbents derived from cucumber, persimmon, and bitter apple peels, applied over 24 and 48-hour contact times. The effectiveness of each biosorbent in removing Pb and Cr was assessed through AAS. Statistical analyses were performed on both treated (experimental) and untreated (control) groups to validate the significance of the observed reductions in metal concentrations.

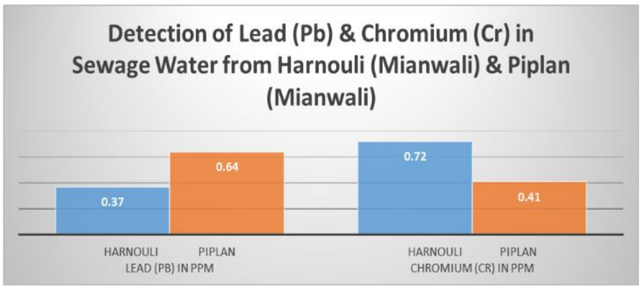



**Figure 3.** Detection of Pb and Cr in sewage water from Harnouil and Piplan

### *3.5. Treated sewage water classification (Experimental group)*

The treated sewage water samples, constituting the experimental group, were categorized according to biosorbent dosage levels (1, 2, and 3 g $L^{-1}$) and contact times (24 and 48 hours). Batch biosorption experiments demonstrated a positive correlation between the amount of biosorbent used and the efficiency of heavy metal (HM) removal. Similarly, extended contact time was associated with enhanced metal uptake, indicating that both biosorbent dosage and exposure duration are critical parameters influencing the biosorption process.

### *3.6. Biosorption Efficiency of Persimmon, Bitter Apple, and Cucumber Peels*

The removal efficiencies of Pb and Cr from sewage water using persimmon, bitter apple, and cucumber peel powders were evaluated under varying dosages (1, 2, and 3 g $L^{-1}$) and contact times (24 and 48 h). Atomic Absorption Spectroscopy was used to quantify residual metal concentrations. Across all biosorbents and both water sources (Harnoli and Piplan), increased biosorbent dosage and longer contact time generally resulted in improved heavy metal removal.

### *3.7. Persimmon peel as biosorbent*

In Harnoli, sewage water, persimmon peels showed a substantial Pb reduction from 0.37 ppm (control) to 0.12 ppm at 3 g $L^{-1}$ after 48 h, removing 67.6% of Pb compared to the control. Cr levels dropped from 0.72 ppm to 0.29 ppm under the same conditions, removing 59.7% of Cr compared to the control. Similar results were observed in Piplan samples, where Pb decreased from 0.64 ppm to 0.24 ppm, removing 62.5% of Pb compared to the control, and Cr from 0.41 ppm to 0.16 ppm, removing 61% of Cr compared to the control, confirming the efficacy of persimmon peels in removing both metals (Figures 4a-d).

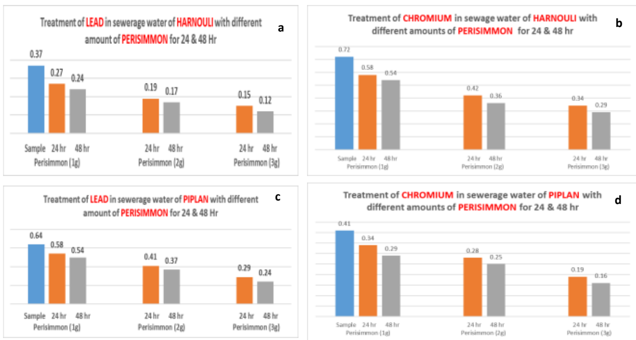


**Figure 4.** Effect of treatment of a) Pb in sewage water of Harnoli by different amounts of persimmon, b) Cr in sewage water of Harnoli by different amounts of persimmon, c) Pb in sewage water of Piplan by different amounts of persimmon, d) Cr in sewage water of Piplan by different amounts of persimmon

### *3.8. Bitter apple peel as biosorbent*

Bitter apple peels demonstrated the highest Pb removal efficiency among the three biosorbents. In Piplan samples, Pb dropped from 0.64 ppm to 0.14 ppm using 3 g $L^{-1}$ for 48 h, removing 78.1% of Pb compared to the control, while Cr reduced from 0.41 ppm to 0.10 ppm, removing 75.6% of Cr compared to the control. In Harnoli, Cr decreased from 0.72 ppm to 0.11 ppm, removing 84.7% of Cr compared to the control, and Pb from 0.37 ppm to 0.05 ppm, removing 86.5% of Pb compared to the control (**Figures 5a-d**). These results suggest that bitter apple possesses strong binding capabilities for both Pb and Cr.

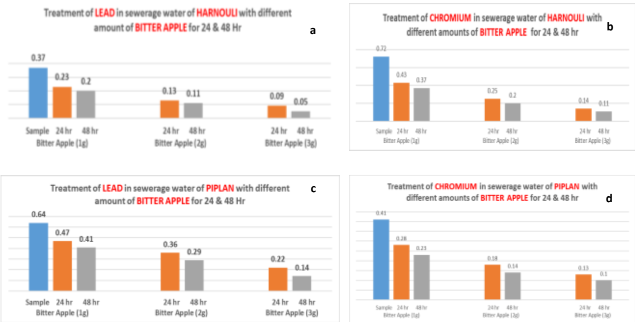



**Figure 5.** Effect of treatment of a) Pb in sewage water of Harnoli by different amounts of bitter apple, b) Cr in sewage water of Harnoli by different amounts of bitter apple, c) Pb in sewage water of Piplan by different amounts of bitter apple, d) Cr in sewage water of Piplan by different amounts of bitter apple

### *3.9. Cucumber peel as biosorbent*

Cucumber peel powder exhibited moderate but consistent biosorption activity. In Harnoli sewage, Pb concentration dropped from 0.37 ppm to 0.23 ppm (3 g $L^{-1}$, 48 h), removing 37.8% of Pb compared to the control, while Cr decreased from 0.72 ppm to 0.47 ppm, removing 34.7% of Cr compared to the control. In Piplan samples, Pb removal was highest at 24 h, with a decline from 0.64 ppm to 0.43 ppm, removing 32.8% of Pb compared to the control. However, Cr biosorption showed inconsistent trends, with slightly lower efficacy at 48 h than 24 h in some cases, suggesting potential re-release or saturation effects (**Figures 6a-d**).

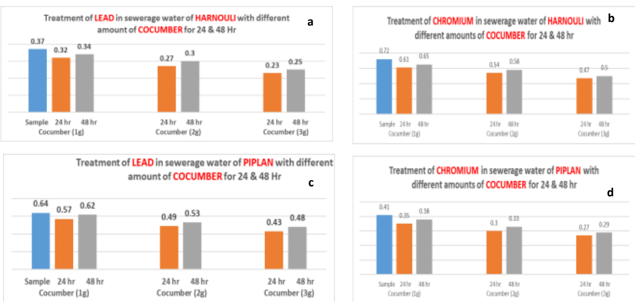



**Figure 6.** Effect of treatment of a) Pb in sewage water of Harnoli by different amounts of cucumber, b) Cr in sewage water of Harnoli by different amounts of cucumber, c) Pb in sewage water of Piplan by different amounts of cucumber, d) Cr in sewage water of Piplan by different amounts of cucumber

### *3.10. Effect of biosorbent dose and contact time on heavy metal removal*

The biosorption efficiency for both Pb and Cr increased with increasing biosorbent dose and contact time across all tested fruit peels. Among the tested biosorbents, bitter apple peels exhibited the highest removal efficiency at the maximum tested dose of 3 g $L^{-1}$ and 48-hour contact time. In sewage water from Piplan, Pb concentration was reduced from 0.64 ppm to 0.14 ppm, corresponding to a removal efficiency of 78.1%, and Cr was reduced from 0.41 ppm to 0.10 ppm, yielding a removal efficiency of 75.6%. The calculated adsorption capacities were 0.167 mg $g^{-1}$ for Pb and 0.103 mg $g^{-1}$ for Cr, confirming the high sorption potential of bitter apple peels under these conditions. Similarly, persimmon peels at the same dose and contact time showed substantial removal: Pb was reduced to 0.24 ppm (62.5%) and Cr to 0.16 ppm (60.9%), though with slightly lower adsorption capacities than bitter apple. Cucumber peels, while less effective overall, still demonstrated meaningful Pb removal, with reductions up to 52.2%.

### *3.11. Statistical Analysis*

To determine the significance of biosorbent type, dosage, and contact time on the removal efficiency of Pb and Cr, a one-way ANOVA was performed, followed by Duncan's Multiple Range Test (DMRT) at a significance level of $p \leq 0.05$. The analysis revealed statistically significant differences among treatments for both metals in the Piplan and Harnoli sewage water samples. In the Piplan wastewater treatments, the ANOVA results for Pb showed $F(11, 24) = 28.67$, $p < 0.001$, and for Cr, $F(11, 24) = 25.43$, $p < 0.001$. For Harnoli samples, Pb removal had an $F(11, 24) = 31.02$, $p < 0.001$, while Cr removal was significant with $F(11, 24) = 27.89$, $p < 0.001$. **Table 4** summarizes the treatment effects in Piplan sewage water. The highest reduction in Pb (0.14 ppm) and Cr (0.10 ppm) was achieved using 3 g $L^{-1}$ of bitter apple for 48 h. The reduction in the concentration of Pb and Cr was 78.1 and 75.6%, respectively, in comparison to the control. Persimmon also demonstrated significant performance, with Pb and Cr dropping to 0.24 and 0.16 ppm, respectively, under the same treatment conditions. The statistical groupings (denoted by superscript letters) confirmed the significance of differences across treatments. Treatments with the same letters were not significantly different, supporting the robustness of the experimental design.

A consistent trend of selective adsorption was observed across all biosorbents, with a higher affinity for Pb over Cr, likely due to $Pb^{2+}$'s lower hydration energy and greater polarizability. Statistical analysis confirmed these trends: ANOVA revealed significant effects of biosorbent type, dose, and contact time (Pb: $F(5,30) = 18.42$, $p < 0.001$; Cr: $F(5,30) = 16.89$, $p < 0.001$), with Duncan's post hoc test identifying significant pairwise differences among treatment levels. These findings demonstrate that plant-derived biosorbents, particularly bitter apple peel, are effective, low-cost, and sustainable options for the removal of toxic heavy metals from wastewater.

**Table 4.** Impact of varying quantities (1, 2, and 3 g) of bitter apple and persimmon as biosorbents for adsorbing HMs (Pb and Cr) in sewage water from Piplan over 24 and 48 h

| Bio-adsorbent | Treatments | Residual Conc after treatment | |
|---|---|---|---|
| | | Pb (ppm) | Cr (ppm) |
| Untreated | Control | 0.64j | 0.41i |
| Bitter apple | 1 g / 24 h | 0.47g | 0.28g |
| | 1 g/ 48 h | 0.41f | 0.23e |
| | 2 g / 24 h | 0.36e | 0.18d |
| | 2 g/ 48 h | 0.29d | 0.14b |
| | 3 g / 24 h | 0.22b | 0.13b |
| | 3 g/ 48 h | 0.14a | 0.10a |
| Persimmon | 1 g / 24 h | 0.54i | 0.34h |
| | 1 g/ 48 h | 0.50h | 0.29g |
| | 2 g / 24 h | 0.41f | 0.28g |
| | 2 g/ 48 h | 0.37e | 0.25f |
| | 3 g / 24 h | 0.29d | 0.19d |
| | 3 g/ 48 h | 0.24c | 0.16c |

Values in the column having the same letter are not significantly different ($p \leq 0.05$) according to Duncan's multiple-range test.

Similarly, **Table 5** presents results from Harnoli wastewater, where persimmon showed the most efficient Pb and Cr removal at 3 g $L^{-1}$ for 48 h, reducing Pb to 0.12 ppm and Cr to 0.29 ppm, compared to the respective controls, i.e., 0.37 and 0.72 ppm. Overall, there was a 67.6% reduction in Pb and 59.7% in Cr with the application of persimmon peels in comparison to the control. Cucumber biosorbent exhibited moderate removal efficiency, with some inconsistency in Cr adsorption, possibly due to secondary interactions or matrix effects. All biosorbent treatments were statistically different from the control ($p < 0.05$).

**Table 5:** Effect of different amounts (1, 2, and 3 g) of plants (persimmon and cucumber) on the adsorption of Pb and Cr in Harnoli wastewater after the interval of 24 and 48 h

| Plants | Treatments | Pb (ppm) | Cr (ppm) |
|---|---|---|---|
| Untreated | Control | 0.37k | 0.72k |
| Persimmon | 1 g / 24 h | 0.27g | 0.58h |
| | 1 g/ 48 h | 0.24ef | 0.54g |
| | 2 g / 24 h | 0.19d | 0.42d |
| | 2 g/ 48 h | 0.17c | 0.36c |
| | 3 g / 24 h | 0.15b | 0.34b |
| | 3 g/ 48 h | 0.12a | 0.29a |
| Cucumber | 1 g / 24 h | 0.32i | 0.61i |
| | 1 g/ 48 h | 0.34j | 0.65j |
| | 2 g / 24 h | 0.27g | 0.54g |
| | 2 g/ 48 h | 0.30h | 0.58h |
| | 3 g / 24 h | 0.23e | 0.47e |
| | 3 g/ 48 h | 0.25f | 0.50f |

Values in the column having the same letter are not significantly different ($p \leq 0.05$) according to Duncan's multiple range test.

*3.12. Isotherm Study*

In this study, isotherm models of adsorption were used to analyze the equilibrium behavior of Pb and Cr ions on the prepared adsorbents from Harnouli and Piplan sources. Equilibrium data were fitted with both the Langmuir and the Freundlich isotherms to understand the adsorption mechanism and the surface characteristics of the adsorbents (**Figures 7 and 10**). The Langmuir model was utilized to estimate the feasibility of monolayer adsorption onto a uniform surface of finite and energetically equivalent sites, while the Freundlich model was applied for adsorption onto heterogeneous surfaces with a non-uniform distribution of heat of adsorption. The comparison of fitting parameters and correlation coefficients of both isotherms facilitated the determination of the most appropriate isotherm for every adsorbent–metal system. This method yields an exhaustive picture of the adsorption capacity, surface heterogeneity, and possible application of the adsorbents for heavy metal removal from water.

The Freundlich model is the first known isotherm. Freundlich isotherm is widely used to be applied in adsorption evaluation on heterogeneous surfaces (Ho and McKay, 1999; Marandi, 2011), having two parameters, $K_F$ and n, of which n is generally considered as a parameter describing the heterogeneity of the surface. Linear Freundlich is:

$$q_e = K_F C_e^{1/n}$$

Langmuir isotherm models adsorption onto a solid surface with a monolayer coverage of adsorbate molecules, where all sites for adsorption are equal and one molecule occupies each site. It is found on the premise that once a site has been occupied, it is impossible to add more adsorption at the same site, and there is no interaction between adsorbed molecules. The model gives two important parameters: maximum capacity ($Q_m$) and the Langmuir constant ($K_L$), which relate to the affinity between adsorbent and adsorbate. From these, it predicts the amount of solute that will be adsorbed at any given equilibrium concentration, reflecting the effectiveness and surface characteristics of the adsorbent. Linear Langmuir is:

$$Qe = \frac{Q_m K_L C_e}{1 + K_L C_e}$$

Where $Q_e$ (mg/g) is adsorption capacity; $C_e$ is equilibrium metal concentration; $q_m$ is the maximum capacity of adsorption of metal; $K_F$ (mg/g (mg/L)1/n) and $K_L$ (L/mg) are the Freundlich and Langmuir isotherms constants, respectively, and n is the empirical constant depicting adsorption intensity, depending on the heterogeneity of the materials utilized as adsorbents and changes accordingly.

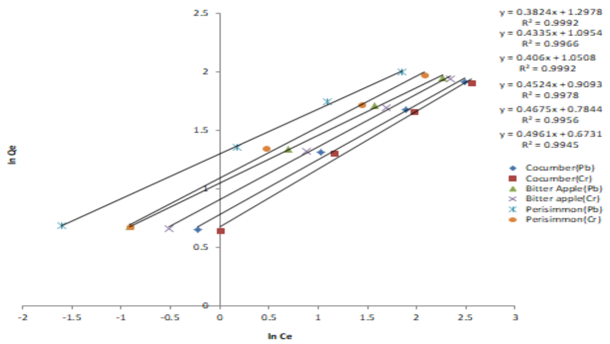



**Figure 7.** Freundlich isotherm at Harnouli

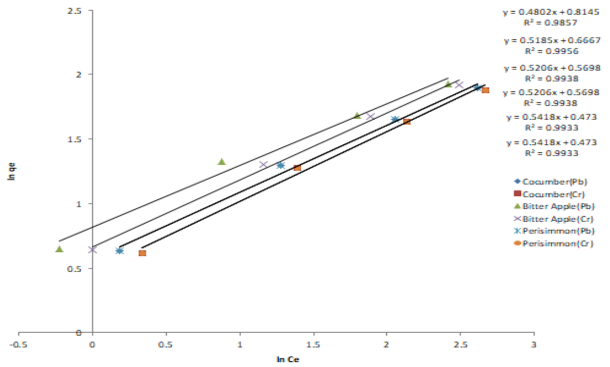



**Figure 8.** Freundlich Isotherm at Piplan

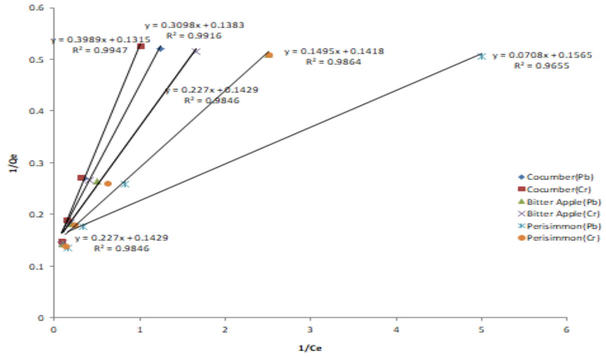



**Figure 9.** Langmuir Isotherm at Harnouli

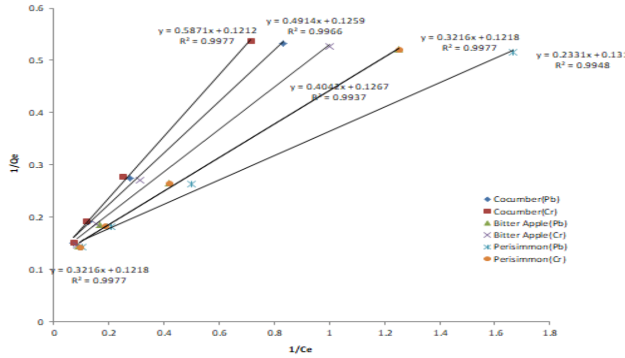



**Figure 10.** Langmuir Isotherm at Piplan

### *3.13. Kinetic Study*

Information on optimal conditions, sorption mechanism, and probable rate-limiting stages is encompassed within kinetic research for batch adsorption systems (Sahu *et al.*, 2020). To this end, pseudo-first-order and pseudo-second-order linear kinetics were used to fit the adsorption data, as displayed in Equations, respectively.

$$Q_T = Q_e\left(1 - \exp\left(-K_1 T\right)\right)$$

$$\frac{T}{Q_T} = \frac{1}{K_2 Q_e^2} \times \frac{T}{Q} + \frac{T}{Q_e}$$

Where $Q_T$ (mg/g) and $Q_e$ (mg/g) were the quantity of adsorbed metal at time T and equilibrium, respectively; $K_1$ and $K_2$ ($min^{-1}$ and g/mg) were the pseudo-first-order and pseudo-second-order constants, respectively (**Figures 11-14**).

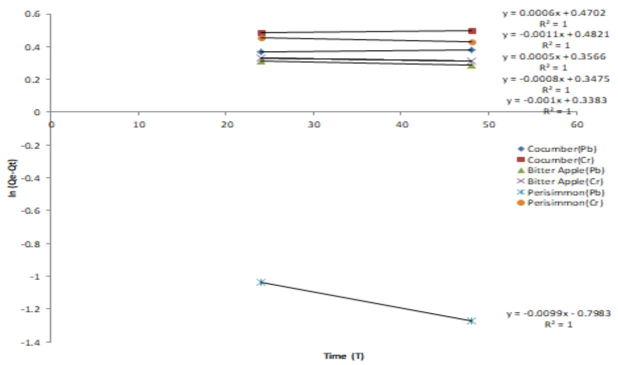



**Figure 11.** Pseudo-first-order kinetics at Harnouli

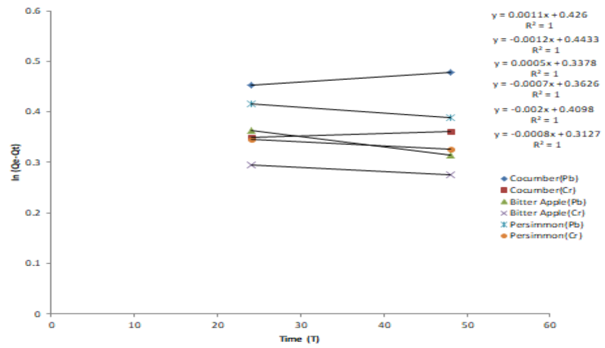



**Figure 12.** Pseudo-first-order kinetics at Piplan

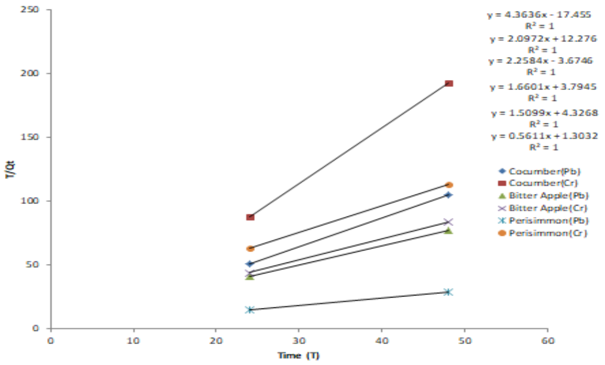



**Figure 13.** Pseudo-second-order kinetics at Harnouli

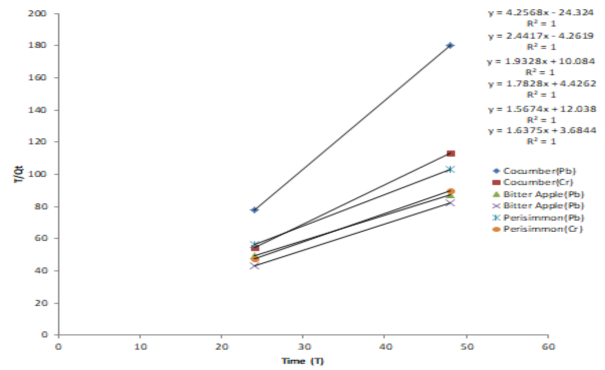



**Figure 14.** Pseudo-second-order kinetics at Piplan

## 4. Conclusions

This research showed the efficiency of biosorbents sourced from plants - bitter apples, persimmon, and cucumber peels - in eliminating lead (Pb) and chromium (Cr) from wastewater collected from Harnoli and Piplan. The findings indicated that both a higher biosorbent dosage and longer contact time greatly improved the efficiency of heavy metal removal of the biosorbents evaluated; bitter apple demonstrated the best performance, followed by persimmon and cucumber. Statistical analyses (ANOVA, $p < 0.001$) validated the importance of treatment effects in comparison to untreated controls. The reduction in the concentration of Pb and Cr using bitter apple peels was 78.1 and 75.6%, respectively, in comparison to the control. These biosorbents can be scaled in low-cost column-based systems for efficient use on industrial sites. These results endorse the viability of agricultural waste products as affordable, sustainable, and environmentally friendly substitutes for treating wastewater contaminated with heavy metals.

### *4.1. Recommendations for future work*

Future research should focus on the regeneration and reuse of these plant-based biosorbents to assess their economic and operational feasibility for long-term applications. Mechanistic and kinetic studies are recommended to elucidate the adsorption pathways, rate-limiting steps, and isothermal behavior of heavy metal uptake. Advanced surface characterization techniques such as SEM-EDX, FTIR mapping, and XPS can further clarify the interaction between metal ions and functional groups. Additionally, pilot-scale studies using continuous flow systems and the inclusion of mixed-metal or organic pollutant scenarios would support the scalability and real-world applicability of these biosorbents in wastewater treatment.

### Author contribution statement

**Bushra Nisar, Aeysha Sultan**: Writing – original draft, Writing – review and editing, Visualization, Validation, Supervision, Software, Resources, Project administration, Methodology, Funding acquisition, Formal analysis. **Muhammad Yasin, Fozia Batool, Hamid Mahmood, Syeda Laila Rubab, Aeysha Sultan, Muhammad Mustaqeem, Rashid Iqbal, Lala Gurbanova, and Jameel M. Al-Khayri**: Writing – review and major editing, Visualization, Validation, Software, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Allah Ditta**: Writing – review and major editing, Visualization, Investigation, Validation, Software, Resources, Project administration, Methodology, Formal analysis, Conceptualization. All the authors read and approved the final manuscript.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Data availability

Data will be made available on request from the corresponding author.

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