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Toxic Element Sorption Rates by Waste Biomass of Vegetable Tubers *in vitro*

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Abstract

The main purpose of this study was to determine the absorption rates and amounts of toxic elements in heavy metal solutions prepared *in vitro* by different vegetable peels. The As and Mo contents of the obtained filtrate were determined between 0.062 (Black radish) and 2.290 (Sweet potatoes) to 0.153 (Onion) and 1.949 mg/kg (Sweet potatoes), respectively. The percentages of Cd and Co removed by plant adsorbents were calculated as 99.06% (Brown onion) and 99.37% (Celery) and 99.03% (Onion) and 99.26% (Celery), respectively. In addition, the percentages of Cr removed by plant adsorbents were determined as 99.04%(Onion) and 99.37% (Celery), while the percentages of Ni removed by plant adsorbents were determined as 99.03% (Onion) and 99.28% (Celery). The toxic element detected in the highest amounts in the solutions filtered from plant adsorbent filters was As, followed by Mo, Al, Se and Cd in decreasing order. Radish adsorbent removed the most Al.As a result, plant materials can be a good source for heavy metal removal and their heavy metal removal capacity can be increased by their modification.

***Keywords*:** Adsorbens, filtrate, toxic elements, ICP-OES.

1. Introduction

Heavy metal pollution, which can negatively affect all living things, can be eliminated or reduced using a range of more expensive standard or traditional techniques. Since heavy metals pose a significant environmental risk, their discharge into running waters or rivers is a major concern [1]. Rapid and continuous growth of industries has increased the demand for fresh water and as a result has increased the amount of wastewater discharged which contains many organic and inorganic substances in the form of heavy metals, aromatic compounds, dyes, pigments etc. Many of these are known as hazardous pollutants due to their potential toxicity to human health and physical and chemical processes such as chemical precipitation, ion exchange, membrane separation, biodegradation, chemical oxidation, solvent extraction and adsorption are applied to remove these pollutants from aqueous solution [2, 3]. Waste materials from agriculture and industry, fruit waste, plant waste, natural inorganic substances and bioadsorbents are used as non-traditional adsorbents [4]. Large amounts of toxic elements can reach the human body through plant crops grown in soil contaminated with wastewater and other industrial wastes [5]. Toxic metals, which can enter the body in smaller amounts through ingestion of polluted water, skin contact or inhalation, can accumulate

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in vital organs of the human body, disrupting their normal functions and preventing their vital activities, and can cause internal imbalances because they can be used instead of the body's basic elements when constantly exposed to toxic elements [6].

Banana peel, cotton-based adsorbents and orange peel are the most commonly used agricultural waste adsorbents in the treatment of toxic elements in wastewater [7-10]. Agricultural waste filtration has also been used extensively, and filters sensitive to the size of metal ions to be removed from the solution have been developed [11]. Many studies have focused on the research and development of materials such as wheat hulls, orange peels, wood waste, sunflower leaves, etc., that have the capacity to adsorb heavy metal ions from solutions into their pores and adsorption active sites [12, 13]. In recent decades, with the increase in the flow of toxins into the atmosphere, it is noteworthy that waters are polluted by toxic metallic species that do not decompose and have persistent properties in the environment [14, 15]. However, these pollutants show significant bioaccumulation levels in plants and fish [16, 17].

Agricultural wastes for the production of activated carbon as adsorbent mostly come from fruit peels and seeds, and wastes generated in the production of cereals such as rice, coffee, corn and maize are attracting increasing attention [18]. Since the selective removal of metal ions from water has been attributed to the chelation of metals in agricultural waste materials, it has been stated that the adsorption of toxic heavy metals by natural adsorbents may be related to the presence of metal chelate-forming functional groups, carboxylic and hydroxylic groups [19, 20]. Plant wastes such as peanut shells, sunflower shells, corn shells, coffee shells, walnut shells, and rice hulls, which are widely used to remove toxic metals from wastewater sources, are used as a low-cost adsorbent material due to their easy availability and lack of economic use, leading to zero waste discharge into the environment [21-24]. Fruit peel, which is rich in carbon-rich organic compounds such as cellulose, hemicellulose, pectin, chlorophyll and other low molecular weight compounds, is a waste material obtained from fruits with a high potential to reduce toxic metals. It has been reported that orange peel is one of the most frequently used adsorbent materials for this purpose [25]. Biosorption process is considered as a green technology for wastewater treatment and is a suitable technology for the treatment of low concentration and high volume wastewater due to its high efficiency in removing dissolved metals from solutions with dilute concentrations and its procedure over a wide temperature and pH range without releasing secondary pollutants [26, 27]. The main purpose of this study was to determine the absorption rates and amounts of toxic elements in heavy metal solutions prepared in vitro by different vegetable peels.

2. Materials and method

2.1. Preparation of biosorbents

Vegetables used as filter adsorbent were collected from the agricultural ecosystem of Konya, Turkey. The collected samples were firstly crushed, cleaned, rinsed with tap and deionized water, the tuber skins were peeled and finally dried in an oven at 70 °C for 48 h. To obtain homogeneous powders, the plant samples were finely crushed and ground with a stainless steel grinder (Mulino AR 151 ARZUM, TURKEY) and then sieved through a stainless steel sieve with a pore size (0.5 mesh) to obtain known particle sizes. The obtained powder was stored in glass bottles for later use.

2.2. Solutions

Initial metal ion concentrations (Table 1) in each solution containing toxic elements were determined by ICP-OES. A 10 ppm solution was prepared for each element and 50 ml was poured onto 3 g of sample in the setup and allowed to filter. The amount of adsorbed metal ions for each parameter was determined by the difference between the initial metal ion concentration and the concentration of metal ions in the upper solutions. Each determination was made three times and the average value was calculated for each experiment. The diameter of the burette used in the filter setup was 0.1348 mm and the amount of each adsorbent placed separately in the burette was 3 g. The height of the adsorbent placed in the burette was adjusted to be 1 cm. Each time, 50 ml of the solution containing toxic elements was passed through this adsorbent filter (Figure 1).

Table 1. Initial metal ion concentrations in each solution containing toxic elements

Solution	Al	As	Ba	Cd	Co	Cr	Mo	Ni	Pb	Se
Concentrations (ppm)	10.178	10.020	10.318	11.261	11.155	10.835	10.919	11.077	10.493	10.254

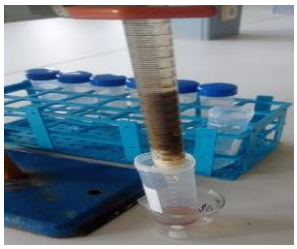

Figure 1. Bioadsorbent device in which toxic element solutions are filtered

The filtration process was carried out by passing through separate adsorbents for each element solution. The toxic element contents of the obtained filtrate were determined by ICP-OES.

2.3. Element analysis

Element contents of the samples were determined by ICP-OES (Agilent-5110) device. The raw results (reading values) obtained as a result of the reading were multiplied by the coefficient determined for each sample and thus the element amounts in the sample were determined in mg /kg unit [28].

2.4. Statistical analysis

The JMP statistical program was used for the statistical analysis of results. Statistically changes were determined by the analysis of variance (ANOVA) procedure in all data ($p<0.01$ and $p<0.05$) [29].

3. Results and discussion

The heavy metal concentrations in the filtrate after passing each toxic element solution (Al: 10.178; As: 10.020; Ba: 10.318; Cd: 11.261; Co: 11.155; Cr: 10.835; Mo: 10.919; Ni: 11.077; Pb: 10.493; Se: 10.254 mg/kg) at certain concentrations through the adsorbent filters prepared by grinding the tuber peels of different vegetables are presented in Table 2.

Table 2. The concentrations of heavy metals passing through some vegetable tuber peels (mg/kg) ***** $p<0.05$

Adsorbens	**Al**	**Ba**	**Cd**	**Co**	**Mo**
	---------- **(mg kg^{-1})** ----------				
Potatoes	0.231±0.0006 CD*	0.096±0.0012 CD	0.093±0.0003 B	0.098±0.0003 BC	1.741±0.0262 B
Sweet potatoes	0.547±0.0044 B	0.092±0.0015 DE	0.102±0.0013 A	0.107±0.0021 A	1.949±0.0025 A
Jerusalem	1.299±0.0021 A	0.103±0.0012 AB	0.102±0.0015 A	0.104±0.0006 AB	0.588±0.0021 E
Red beat	0.638±0.0014 B	0.082±0.0009 F	0.083±0.0009 C	0.088±0.0019 DE	0.195±0.0015 H
Red radish	0.302±0.0016 C	0.088±0.0015 EF	0.085±0.0017 C	0.094±0.0012 CD	0.272±0.0014 G
Turnip	0.083±0.0012 D	0.098±0.0012 BC	0.102±0.0012 A	0.105±0.0026 A	1.049±0.0037 C
Black radish	0.217±0.0015 CD	0.105±0.0014 A	0.104±0.0014 A	0.107±0.0024 A	0.896±0.0032 D
Celery	0.556±0.0013 B	0.072±0.0014 G	0.071±0.0006 D	0.083±0.0008 E	0.242±0.0013 G
Brown Onion	0.345±0.1479 C	0.106±0.0020 A	0.106±0.0026 A	0.108±0.0012 A	0.153±0.0017 I
Garlic	0.249±0.0007 CD	0.087±0.0023 EF	0.092±0.0017 B	0.096±0.0019 C	0.334±0.0014 F

Bioadsorbens	**Cr**	**Ni**	**Pb**	**As**	**Se**
	---------- **(mg kg^{-1})** ----------				
Potatoes	0.091±7.876 E	0.094±0.0013 C	0.065±0.0007 C	1.535±0.0006 C	0.159±0.0006 F
Sweet potatoes	0.098±6.441 CD	0.104±0.0024 A	0.067±0.0007 C	2.290±0.0062 A	0.438±0.0005 AB
Jerusalem	0.100±1.493 ABC	0.104±0.0011 A	0.083±0.0012 A	0.168±0.0015 H	0.170±0.0012 E
Red beat	0.082±4.002 F	0.084±0.0024 D	0.064±0.0012 C	1.677±0.0015 B	0.043±0.0012 G
Red radish	0.085±2.821 F	0.097±0.0016 BC	0.056±0.0012 D	0.420±0.0011 G	0.433±0.0012 B
Turnip	0.099±9.012 BCD	0.105±0.0016 A	0.083±0.0015 A	0.512±0.0050 F	0.286±0.0021 D
Black radish	0.103±2.311 AB	0.104±0.0011 AB	0.082±0.0009 A	0.062±0.0020 J	0.442±0.0012 A
Celery	0.068±6.553 G	0.080±0.0007 D	0.030±0.0009 E	1.384±0.0082 E	0.023±0.0011 H
Brown Onion	0.104±4.010 A	0.107±0.0018 A	0.083±0.0005 A	1.481±0.0020 D	0.304±0.0017 C
Garlic	0.094±0.004 DE	0.094±0.0013 C	0.074±0.0012 B	0.134±0.0014 I	0.437±0.0017 AB

The toxic element detected in the highest amounts in the solutions filtered from plant adsorbent filters was As, followed by Mo, Al, Se and Cd in decreasing order. The As and Mo contents of the obtained filtrate were determined between 0.062 mg/kg (Black radish) and 2.290 mg/kg (Sweet potatoes) to 0.153 (Onion) and 1.949 mg/kg (Sweet potatoes), respectively. The Al contents of the filtrate were determined between 0.083 (Turnip) and 1.299 mg/kg (Jerusalem), while the Se contents of the filtrate are established between 0.023 (Celery) and 0.442 mg/kg (Black radish). The Cd contents of the filtrate were characterized between 0.071 (Celery) and 0.106 mg/kg (Onion). In addition, the Ni and Pb contents of the filtrate were characterized between 0.080 (Celery) and 0.107 mg/kg (Onion) to 0.030 mg/kg (celery) and 0.083 mg/kg (Jerusalem, turnip, onion), respectively. The lowest and highest Co (0.083 m/kg and 0.108 mg/kg) were determined in the filtrate samples passing through celery and onion peel filters. The Cr contents of the filtrate varied between 0.068 (Celery) and 0.104 mg/kg (Onion). The Al contents of the solution (filtrate) passing through bioadsorbents prepared from potato, red radish, black radish, onion and garlic peels were found to be statistically similar. In addition, the Cd, Co and Ni contents of the filtrate passing through sweet potato, Jerusalem, turnip, black radish and onion filters were also found to be statistically similar, but partial differences were observed in proportion. Also, the amounts of Pb in the heavy metal solution passing through jerusalem, turnip, black radish and onion bioadsorbents were found to be statistically similar. In general, the lowest and highest toxic element contents in the filtrate were determined in the filtrate passing through celery and onion peel filters, respectively. In addition, 90% of the toxic elements were determined in low amounts in the filtrate passing through the celery bioadsorbent filter.

The ratios of heavy metals that could not be retained by plant adsorbents in toxic element solutions prepared at different concentrations passed through plant adsorbents are shown in Table 3. According to Table 3, the toxic elements that could not be removed much by the adsorbents were Al, As, Mo and Se.

Table 3. The rate of heavy metals passing through some vegetable tuber peels (%)

Bioadsorbens	Al	As	Ba	Cd	Co	Cr	Mo	Ni	Pb	Se
Potatoes	2.27	15.32	0.93	0.82	0.88	0.84	15.95	0.85	0.62	1.55
Sweet potatoes	5.37	22.85	0.89	0.91	0.96	0.91	17.85	0.94	0.64	4.27
Jerusalem	12.76	1.68	0.99	0.91	0.93	0.92	5.39	0.94	0.79	1.66
Red beat	6.26	16.74	0.80	0.74	0.79	0.76	1.78	0.76	0.61	0.42
Red radish	2.97	4.19	0.85	0.75	0.84	0.78	2.49	0.88	0.53	4.22
Turnip	0.82	5.11	0.95	0.91	0.95	0.91	9.61	0.95	0.79	2.79
Black radish	2.14	0.62	1.02	0.92	0.96	0.95	8.21	0.93	0.78	4.31
Celery	5.46	13.82	0.70	0.63	0.74	0.63	2.21	0.72	0.29	0.22
Brown Onion	3.39	14.78	1.03	0.94	0.97	0.96	1.40	0.96	0.79	2.96
Garlic	2.46	1.35	0.82	0.82	0.85	0.86	3.07	0.84	0.70	4.28

However, the adsorbent that removed the As element the most was Jerusalem and black radish. In addition, radish adsorbent removed the most Al. In addition, among the adsorbents, Red beat and Brown onion were the adsorbents that removed molybdenum the most. The adsorbents that captured the most selenium were red beat and celery. A significant portion of the other toxic elements were removed by the adsorbens. Therefore, these agricultural waste adsorbens showed a feature that can be used in the purification of water contaminated with heavy metals. The removal and/or retention rates (%) of heavy metals in toxic element solutions prepared at different concentrations passed through plant adsorbents by plant adsorbents are shown in Table 4. In general, the toxic elements removed at the highest rates by plant adsorbents were Cd, Co, Cr, Ni and Pb. The percentages of Cd and Co removed by plant adsorbents were calculated as 99.06% (Brown onion) and 99.37% (Celery) and 99.03% (Onion) and 99.26% (Celery), respectively.

Table 4. Heavy metal capture capacity's percent rates of some vegetable tuber peels

Bioadsorbens	Toxic elements (%)									
	Al	**As**	**Ba**	**Cd**	**Co**	**Cr**	**Mo**	**Ni**	**Pb**	**Se**
Potatoes	97.73	84.68	99.07	99.17	99.12	99.16	84.06	99.15	99.95	98.45
Sweet potatoes	94.63	77.15	99.11	99.09	99.04	99.10	82.15	99.06	99.36	95.73
Jerusalem	87.24	98.32	99.00	99.09	99.07	99.08	94.61	99.06	99.21	98.34
Red beat	93.73	83.26	99.21	99.26	99.21	99.24	98.21	99.24	99.39	99.58
Red radish	97.03	95.81	99.15	99.25	99.16	99.22	97.51	99.12	99.47	95.78
Turnip	99.18	94.89	99.01	99.09	99.06	99.09	90.39	99.05	99.21	97.21
Black radish	97.87	99.38	98.99	99.08	99.04	99.05	99.21	99.06	99.22	95.69
Celery	94.84	86.19	99.31	99.37	99.26	99.37	97.78	99.28	99.71	99.78
Brown Onion	96.61	85.22	98.97	99.06	99.03	99.04	98.60	99.03	99.21	97.04
Garlic	97.55	98.65	99.16	99.18	99.14	99.13	96.94	99.15	99.29	95.74

In addition, the percentages of Cr removed by plant adsorbents were determined as 99.04% (Onion) and 99.37% (Celery), while the percentages of Ni removed by plant adsorbents were determined as 99.03% (Onion) and 99.28% (Celery). In addition, the percentages of Pb removed by plant adsorbents were found as 99.21% (Jerusalem, turnip, onion) and 99.95% (potatoes). It is seen that, among the plant adsorbents, the bioadsorbent that removed Pb the most was potato peel. On the other hand, the capacities of bioadsorbents to remove Al, As, Mo and Se were relatively low. However, despite their high potential to remove Ba, the Ba removal capacity of black radish and onion was low compared to other adsorbens. The percentages of Al and As removed by plant adsorbents were determined as 87.24% (Jerusalem) and 99.18% (Turnip) and 83.26% (red beet) and 99.38% (Black radish), respectively. The removal rate of Mo by plant adsorbents was calculated between 82.15% (Sweet potatoes) and 99.21% (Black radish), while the removal rate of Se by plant adsorbents was determined between 95.69% (black radish) and 99.78% (celery). The bioadsorbent with the highest removal capacity of heavy metals was celery shell (except for Al and As elements). As a result, plant materials can be a good source for heavy metal removal and their heavy metal removal capacity can be increased by their modification. The reason for the high removal of toxic elements by plant adsorbents may be due to the phenolic compounds they contain, their pH and their ion exchange capacity. In previous reports, it was explained that husks can be used to remove various toxic metals such as Cr^{6+} [30], Pb^{2+}, Cd^{2+}, Cu^{2+}, and Cr^{3+}) [22], Ni^{2+} [31], or Zn^{2+} [32]. Since the selective removal of metal ions from water has been attributed to the chelation of metals in agricultural waste materials, it has been stated that the adsorption of toxic heavy metals by natural adsorbents may be related to the presence of metal chelate-forming functional groups, carboxylic and hydroxylic groups [19, 20]. Generally, the chemical compos ition and physical structure of the precursor materials affect the physical properties of the adsorbent. More compact materials such as shells may lead to adsorbents with lower surface area, and thus the size and shape of the precursor materials may also affect the physical properties of the prepared adsorbents. In general, it is important to carefully consider the surface area, porosity and morphology of the precursor materials used when preparing adsorbents for specific applications [33]. It has been stated that pH has an effect on how heavy metals are trapped on the surface of the biosorbent [34]. The pH effects (pH between 2–8) on the biosorption behavior of both biosorbents for metal ions have been reported to be the optimum pH of the solution for the heavy metal ions studied as 6. It has been reported that this pH value is effective in removing heavy metals by the adsorbents since the metal ions can exist in their free form and hydroxide precipitation forms can be ignored [35]. The presence of additional H^+ ions competing with metal ions for biosorption sites reduced the sorption of metal ions in acidic media at low pHs ($pH < 4$), while at higher pH levels, metal ions were more likely to hydrolyze and form metal hydroxide accumulation [36, 37]. It has been stated that heavy metals form colloidal forms with OH- in aqueous media [38]. Ramavandi *et al.* (2014) provided a suitable approach for

optimization of the percentage removal of Cr by melon peel/melon peel by applying the Taguchi method. Omotosho and Sangodoyin (2013) [39] stated that as a result of using cassava peel in the adsorption and filtration treatment of wastewater from the same industry, the purified water (water removed from heavy metals) was suitable for irrigation.

4. Conclusion

This study confirms that plant peel–derived bioadsorbents are effective and sustainable materials for heavy metal removal, with particularly outstanding performance for Pb. Removal efficiencies reached 99.21% for Jerusalem artichoke, turnip, and onion, and 99.95% for potato peel, making potato peel the most efficient Pb adsorbent. Celery peel showed the lowest overall residual toxic element concentrations, indicating strong broad-spectrum adsorption capacity. Although removal efficiencies for Al, As, Mo, and Se were relatively lower, clear element-specific selectivity was observed among the bio-adsorbents. Overall, these findings highlight the strong potential of agro-waste–based bioadsorbents as low-cost and eco-friendly alternatives for sustainable water treatment, while emphasizing the need for further optimization to improve removal of less effectively adsorbed elements.

Conflicts of interest / Competing interests: The authors declare no competing.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Compliance with ethics requirements

Authors declare that they respect the journal's ethics requirements.

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