



Aubergine-based Biosorbent for Heavy Metal Extraction

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Abstract

In this study, an alternative inexpensive and eco-friendly Aubergine (Eggplant)-based biosorbents were synthesized for removing Cu²⁺, Ni²⁺, and Co²⁺ heavy metal ions from the aquatic region. Moreover, how the physical properties and water treatment performance were affected by their corn starch and oil contents were investigated. Their extraction capacity was evaluated by performing Flame atomic absorption spectroscopy (FAAS). ASTM D 792 standard was complied with to calculate biosorbent density. Indeed, the untreated eggplant stalk-based biosorbent adsorbed 5.36 mg of Co²⁺ ions and 4.99 mg of Ni²⁺ ions, and 4.84 mg of Cu²⁺ ions from 25 mL of initial solution that contained 7.00 ppm of each ion for 30 minutes, at room temperature with 175 rpm agitation speed by Eggplant-based biosorbents.

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1 INTRODUCTION

Heavy metals have been used since ancient times. Humans still have been affected by their toxicity even today. The burning of coals that abounded with heavy metals in the industry triggers an increase in their exposure time and dosage by people. Especially, these toxic ions can reach the food chain via water easily. For that reason, water treatment studies are extremely important for a healthy ecosystem [1,2]. The organic and inorganic treatment methods were suggested for water purification as electrochemical treatment, chemical sediments, ion exchange, and reverse osmosis. But, these traditional methods have nominal efficiency, are costly, and are not fit for huge-scale production [3-8]. Hence, an alternative way is extremely important to provide.

Nowadays, biosorbents have appeared as an alternative, an easy-reachable, and eco-friendly method among conventional methods for removing heavy metal ions from water sources. Biomass has the natural potential to remove heavy metal ions from the aquatic regions both metabolically and physiochemically [9,10]. Non-living biomass like shrimp, bark, crab shell, etc., had been used as a fundamental biosorbent source [10-17]. For example, we often consume eggplant as a stuffed, grilled, roasted, stir-fried, or baked in many ways during daily life. The stem and skin part of eggplant generally remain organic wastes in Figure 1a. Some eggplant usually has purple due to the anthocyanin pigment in Figures 1b, c. The skin of the eggplant has abounded with hydroxyl (-OH) and carboxyl (C=O) groups ready to attach to heavy metal ions, and the stem part occurs from lignocellulosic structures that abounded in the same groups. So, these parts of eggplant had the potential to be used for the adsorption of heavy metal ions [18-21].

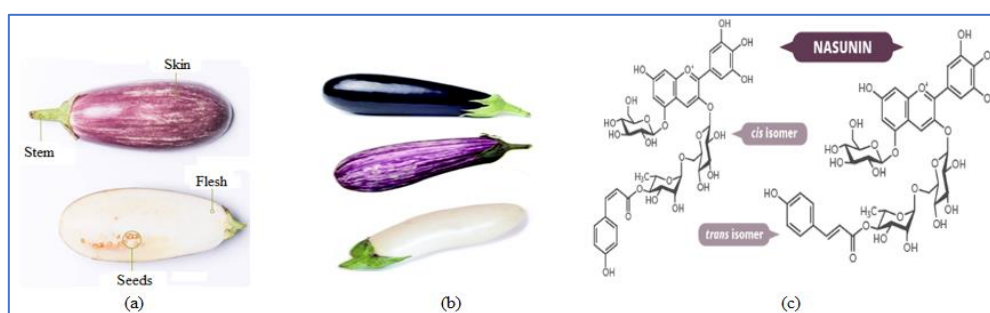


Figure 1. Parts of eggplant (a), the variety of color (b), and cis and Trans isomers of Anthocyanins [18-21]

In this research, six different biosorbents were synthesized from Eggplant to remove Co^{2+} , Ni^{2+} , and Cu^{2+} ions from the water. Terminally, how contents strike their extraction achievement during 30 min at 24 °C was determined.

2 MATERIAL AND METHOD

2.1 Material

The starch (Corn), oil (sunflower), the vinegar of apple (4-5% acetic acid), and Eggplant were received from a local grocery store in Zakho. Nickel (II) Nitrate Hexahydrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Copper (II) chloride dihydrate $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, and Cobalt (II) Acetate $\text{C}_4\text{H}_6\text{CoO}_4$ were purchased from Merck.

2.2 Methods

Surface images of biosorbents were taken with Am Scope brand microscope that exists in the biology lab at Zakho University. The concentration of solutions was measured with PerkinElmer brand Flame atomic absorption spectroscopy (FAAS) at the research center of Zakho University. Eggplant (*Solanum melongena*) stalk had dried in the oven for 48 h at $103 \pm 2^\circ\text{C}$. Then, all biosorbents were ground by an Arshia brand coffee grinding machine.

2.3 Preparation of biosorbents

The ingredient of the biosorbents was corn starch, eggplant stalks, and skins powder weighted shown in Table 1. The substances were mixed with 25 mL of pure water into the beaker. Afterward, 3 mL of acetic acid (AA) was added and stirred for a while to break the long-chain molecules of the starch. Lastly, 1-2 mL of sunflower oil were

dropped on the solution as a plasticizer to re-crystallize broken polymer chains. It was stirred on the heater at 75 °C until gelation occurred. Then, they were left to dry at 105±2 °C for 45 minutes as seen in figure 2.

Table 1. Content of biosorbent

ABSORBENT	1	2	3	4	5	6
EGGPLANT	1g.E/	1.5g E/	2g E/	1g E/	1.5g E/	2g E/
	2g S	1.5gS	1g S	2g S	1.5g S	1g S
	0.5 mL Oil	0.5 mL Oil	0.5 mL Oil	1 mL Oil	1 mL Oil	1 mL Oil

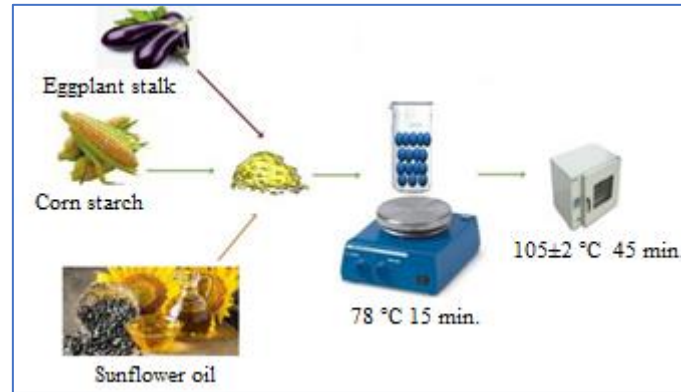


Figure 2. Preparation of biosorbents

2.4 Solubility test (%)

The solubility method was described by equation (1) [22]. Firstly, the samples were dried in the oven at 103±2 °C for 24 hours. Secondly, they were weighted (W_i) and rinsed with 50 mL of distilled water at 175 rpm. Then, they were dried and weighed. Finally, the solubilities of the biosorbent were calculated by the equation given.

$$S = \left(\frac{W_i - W_f}{W_i} \right) \times 100 \quad (1)$$

W_i : Initial mass; W_f : Final mass.

2.5 Water intake (%)

The water intake (%) values of biosorbents, weighed measurements after being kept in water for 24 hours, were calculated according to the formula in (2).

$$SW = \left[\frac{M_w - M_d}{M_d} \right] \times 100 \quad (2)$$

M_d = Sample initial weight (g); M_w = the weight of the sample after immersion in water (g); SW = water uptake rate (%).

2.6 Density test (g/cm³)

Air-dry weights of the samples having measured under laboratory conditions according to [23]. Then, those samples were immersed in water and weighed. Hence, the density of those samples calculated belongs to the given equation in (3)

$$D = \left(\frac{M_a}{M_w} \right) \quad (3)$$

Here, M_a = weight of the sample in the air (g). M_w = the weight (g) in water.

The essential parameter of Uv-vis spectrophotometry is an arrangement of wavelength. If the empirical measurements applied at that wavelength do not correct one, the result will be wrong.

2.7 Batch experiment

25 mL Cu^{2+} , Co^{2+} , and Ni^{2+} heavy metal ions solutions (7 ppm) were prepared freshly from stock (50 ppm) solutions of Nickel (II) Nitrate Hexahydrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Copper (II) chloride dihydrate $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, and Cobalt (II) acetate $\text{C}_4\text{H}_6\text{CoO}_4$. The 25 mg biosorbent was for each section. Adsorption occurred at 24°C , 175 rpm, and for 30 minutes. The adsorption performance of biosorbents had evaluated by the given equation in (4).

$$Q = \frac{[(\text{Co}-\text{Ce}) \cdot V]}{m} \quad (4)$$

The initial concentration of heavy metal ion solution is Co (mg/L), and the final concentration is Ce (mg/L). The volume (V) of the solution in a liter (L), and (m) is the mass of biosorption in gram units.

2.8 Morphology of biosorbents

The surface photograph of biosorbents was taken by microscope (Fig. 3). The biosorbents obtained from different biomass explain why their surface appeared different.

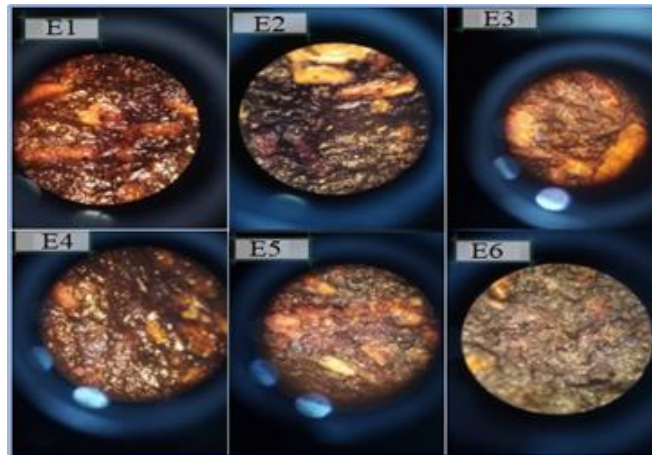


Figure 3. The surface of eggplant-based biosorbents. Eggplants, starch, and oil content ratio of biosorbent (1/2/0.5) for E1, (1.5/1.5/0.5) for E2, (2/1/0.5) for E3, (1/2/1) for E4, (1.5/1.5/1) for E5, (2/1/1) for E6 respectively

3 RESULTS

3.1 Water intake analysis of biosorbents

Water intake percentages of eggplant stalk-based biosorbent were given in (Fig 4). It was observed that when the amount of starch was decreased, the water intake amounts were increasing surprisingly [18, 22]. The biosorbent E3 was found as the highest water intake capacity with 147%. The E4 was determined, as the lowest water intake value with 101%.

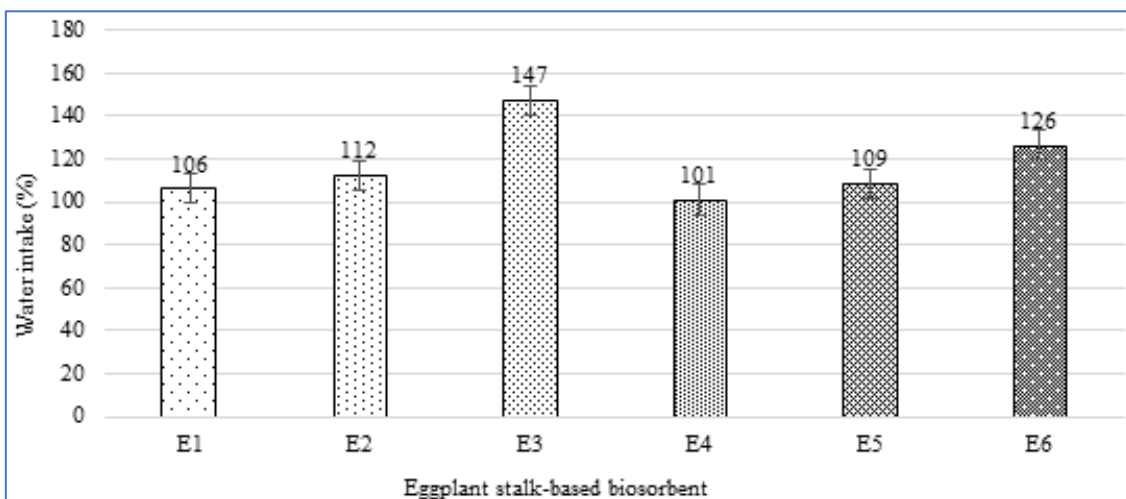


Figure 4. Water intake of eggplant-based biosorbents. Eggplants, starch, and oil content ratio of biosorbent (1/2/0.5) for E1, (1.5/1.5/0.5) for E2, (2/1/0.5) for E3, (1/2/1) for E4, (1.5/1.5/1) for E5, (2/1/1) for E6 respectively

3.2 Water solubility analysis of biosorbents

The solubility of Eggplant-based biosorbents were shown in Figure 5. The oil content was doubled like in the second group; E4, E5, and E5. The solubility fell surprisingly. The increasing amount of starch content also decreases the solubility. On the bar chart, E3 was the most soluble biosorbent with 48.1%, and E4 was found as the least soluble biosorbent.

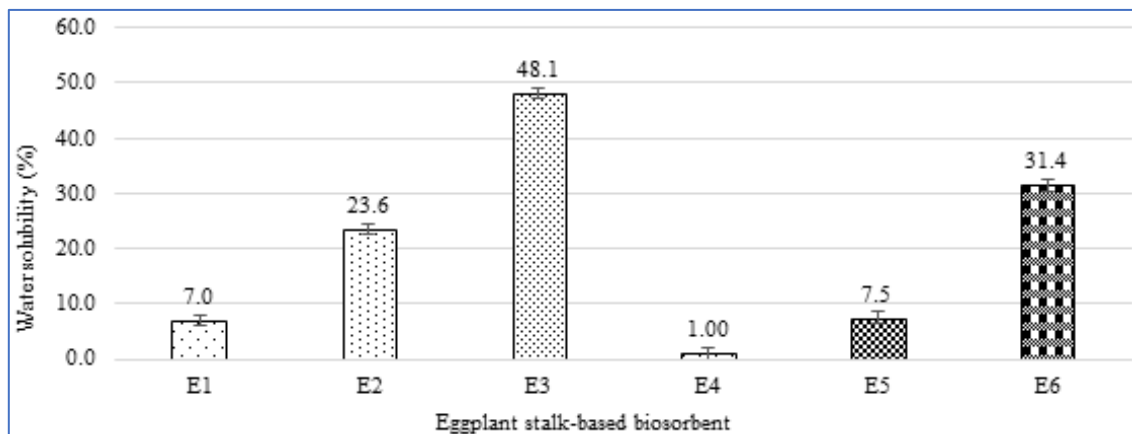


Figure 5. Water solubility of eggplant -based biosorbents. Eggplants, starch, and oil content ratio of biosorbent (1/2/0.5) for E1, (1.5/1.5/0.5) for E2, (2/1/0.5) for E3, (1/2/1) for E4, (1.5/1.5/1) for E5, (2/1/1) for E6 respectively

3.3 Density of biosorbents

The density of eggplant-based biosorbents was represented in Figure 6. The intensity of biosorbents increased with the raised amount of starch and oil contents [18,23]. The amount of eggplant powder was diversely proportional to intensity too. Also, the increased sunflower oil content slightly heightens the density due to the adsorption of eggplant powder.

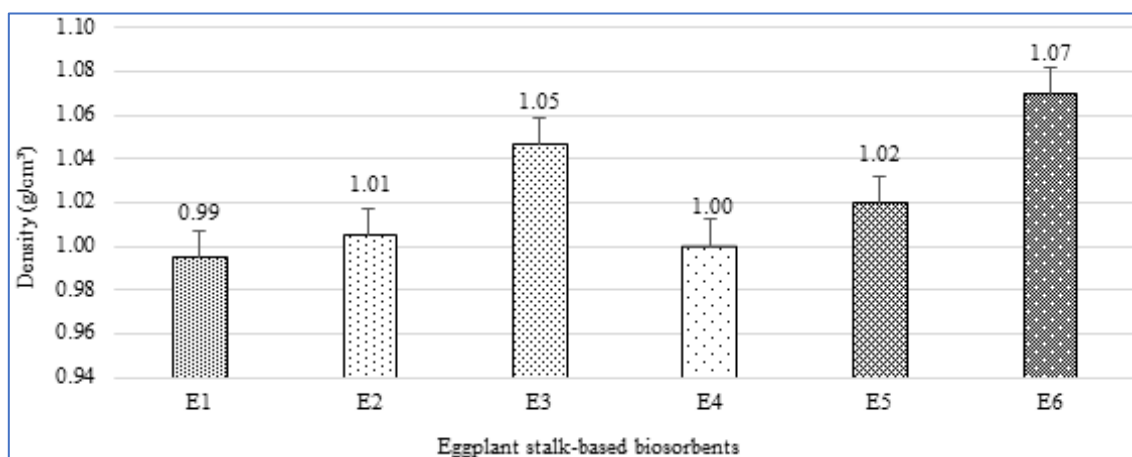


Figure 6. Density of eggplant-based biosorbents. Eggplants, starch, and oil content ratio of biosorbent (1/2/0.5) for E1, (1.5/1.5/0.5) for E2, (2/1/0.5) for E3, (1/2/1) for E4, (1.5/1.5/1) for E5, (2/1/1) for E6 respectively

3.4 Adsorption studies of biosorbents

Eggplant stalk-based biosorbent adsorption values of Co^{2+} , Ni^{2+} , and Cu^{2+} heavy metal ions have been given in Figure 7.

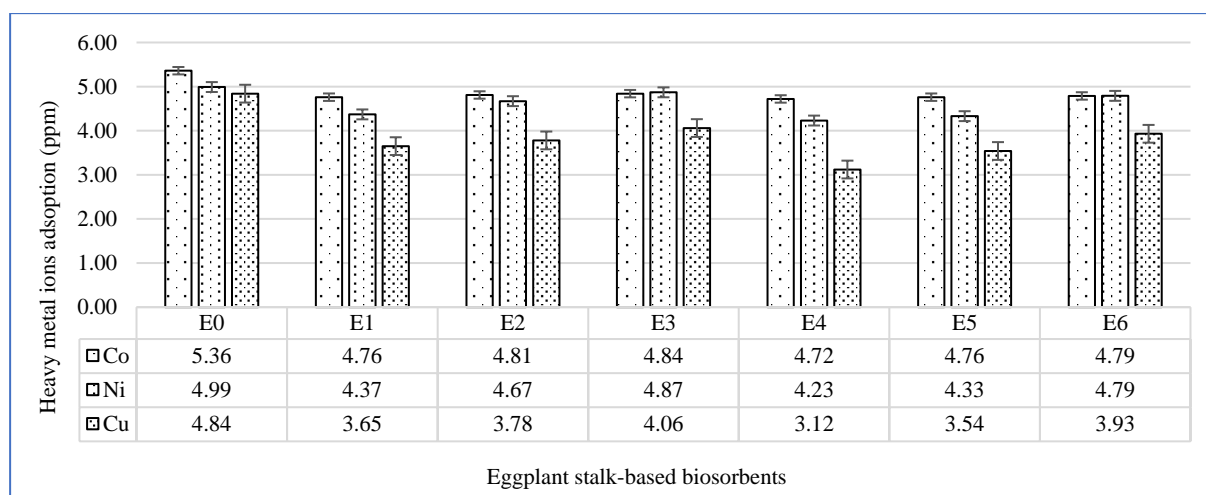


Figure 7. Heavy metal adsorption capacity of eggplant stalk-based biosorbents. Biomass, starch, and oil content ratio of biosorbent (1/2/0.5) for E1; (1.5/1.5/0.5) for E2; (2/1/0.5) for E3; (1/2/1) for E4; (1.5/1.5/1) for E5; (2/1/1) for E6 respectively

It monitors from the bar graph reference biosorbent has the best adsorption capacity. Also, an expanded volume of biomass content raised the sorption capacity. Generally, biosorbents that have more oil ingredients have poor sorption than others. In heavy metal ions adsorption studies, the biosorbent E4 has the minimum sorption performance with a value of 4.72 mg for Co^{2+} ions, 4.23 mg for Ni^{2+} ions, and 3.12 mg for Cu^{2+} ions. However, the biosorbent E0 has the highest extraction performance at 5.36 mg for Co^{2+} ions, 4.99 mg for Ni^{2+} ions, and 4.84 mg for Cu^{2+} ions.

4 CONCLUSION

The water intake analysis showed that the increased oil substance and eggplant stalk content decreased water intake capacity. The biosorbent E3 was obtained as the highest water absorbent with a value of 147 %. The biosorbent E1 was found as the weakest water sorbent one with a 101 % of weight increase. In the density analysis, biosorbent E6 was found to be the one that has the largest density at 1.07 g/cm^3 , and biosorbent E1 was determined the lowest one with a value of 0.99 g/cm^3 . In the water solubility, the sunflower oil content decreased the solubility of all biosorbents. The highest solubility was recorded as 48.1% belonging to biosorbent E3 among other groups. The biosorbent E4 was identified as the least soluble one with a value of 1.00%. The solubility of biosorbents increased with raising the number of ingredients. Moreover, the water adsorption capacity of biomass was inversely proportional to starch content and showed different performances depending on the biomatrix. That shows the diminished starch amount increased the solubility. In the adsorption step, the untreated Eggplant stalk provided the highest Co^{2+} , Ni^{2+} , and Cu^{2+} ions adsorption among its groups. Moreover, the increased oil amount reduced the heavy metal ion adsorption. Additionally, decreasing the amount of starch content also dismissed adsorption capacity. Oppositely, the raised amount of biomass increased the adsorption performance. The density of all biosorbents was directly proportional to adsorption capacities. According to the results, the Eggplant stalk and skin are fit for heavy metal extraction. Further studies can be about the determination of optimum conditions.

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Author Contributions

Doğu RAMAZANOĞLU: Conceptualization, Methodology, Software, Validation, Resources, Data Curation, Writing - Original Draft, Writing - Review & Editing, Visualization, Supervision, Project administration

Zaman Adnan MOHAMMED: Validation, Formal analysis, Investigation, Resources, Writing - Review & Editing

Khalid MAHER: Conceptualization, Methodology, Supervision, Funding acquisition

Idrees KHALO: Validation, Formal analysis, Investigation, Resources, Writing - Review & Editing

All authors read and approved the final manuscript.

Conflict of interest

No conflict of interest was declared by the authors.

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