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Research Article

Investigation Usability of Biosorbents Obtained from Orange peels in Heavy Metal Adsorption

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ABSTRACT

In this study, six different orange peel-based biosorbents were produced to effectively remove Cu^{2+}, Ni^{2+}, and Co^{2+} heavy metal ions from the solution. The impact of oil and corn starch content on the physical properties and adsorption capacity of the biosorbent was investigated. Flame atomic absorption spectroscopy (FAAS) was used to determine the termal stability of the biosorbents. The density of the biosorbents was determined according to ASTM D 792 standards. The results of the analysis revealed that the best biosorbent was found to be untreated orange peels, with values of 4.87 mg of Co^{2+}, 5.83 mg of Ni^{2+}, and 4.29 mg of Cu^{2+} ions at a temperature of 24 °C, agitation speed of 175 rpm, and for a duration of 30 minutes.

Keywords: Biosorbents; Heavy metal ions; Orange peel-based

Portakal Kabuklarından Elde Edilen Biyosorbentlerin Ağır Metal Adsorpsiyonunda Kullanılabilirliğinin Araştırılması

ÖZET

Bu çalışmada, Cu^{2+}, Ni^{2+} ve Co^{2+} ağır metal iyonlarını çözeltiden etkili bir şekilde uzaklaştırmak için altı farklı portakal kabuğu bazlı biyosorbent üretilmiştir. Yağ ve mısır nişastası içeriğinin biyosorbentin fiziksel özellikleri ve adsorpsiyon kapasitesi üzerindeki etkisi araştırılmıştır. Biyosorbentlerin termal kararlılığını belirlemek için alevli atomik absorpsiyon spektroskopisi (FAAS) kullanılmıştır. Biyosorbentlerin yoğunluğu ASTM D 792 standartlarına göre belirlenmiştir. Analiz sonuçları, 24 °C sıcaklıkta, 175 rpm çalkalama hızında ve 30 dakika süreyle 4,87 mg Co^{2+}, 5,83 mg Ni^{2+} ve 4,29 mg Cu^{2+} iyonu değerleriyle en iyi biyosorbentin işlenmemiş portakal kabukları olduğunu ortaya koymuştur.

Anahtar Kelimeler: Biyosorbentler; Ağır metal iyonları; Portakal kabuğu bazlı

1. INTRODUCTION

Humans have utilized heavy metals in the form of jewelry and various other applications since ancient times without fully understanding the potential dangers they pose. Furthermore, the burning of coal, which contains heavy metals, for heating has contributed to the release of these toxins into the environment. Despite this, alternative energy sources are not being fully explored and methods that harm the environment and contribute to heavy metal contamination in the food chain are still being used. As a result, serious diseases caused by heavy metal contamination have emerged due to this neglect (Chaplin, 2019; Swanckaert et al., 2022; Ojovan et al., 2019; Yu and Kaewsarn 1999; Zhao et al., 1999; Minello et al., 2009).

Many studies have been conducted in recent years on wastewater treatment methods, such as electrochemical treatment, ion exchange, reverse osmosis, and chemical precipitation. However, these traditional methods often have poor performance, are expensive, and are not suitable for large-scale processing (Yu and Kaewsarn 1999; Zhao et al., 1999). Biosorbents have gained attention as a potential alternative to these traditional methods, as biomaterials have the natural ability to bind to heavy metals from aquatic environments (Karimi et al., 2022; Qi and Aldrich, 2008; Volesky, 2007; Ramazanoğlu et al., 2022a;b).

Methods of extracting heavy metals are now known to be categorized into three main categories: physical, chemical, and biological. Among these three categories, the biological method, known as biosorption, has gained popularity (Karimi et al., 2022; Qi and Aldrich, 2008). Biosorption is the ability of biomolecules or various biomass to bind to target ions or other charged molecules in aquatic environments. Biomass has been proposed as an alternative heavy metal treatment adsorption medium due to its low cost, availability, and efficiency (Volesky, 2007; Ramazanoğlu et al., 2022a;b).

As an alternative to conventional biomaterials, biosorbents have been shown to have the ability to remove heavy metals from aquatic environments through a process known as biosorption, which can be driven by physico-chemical or metabolic means (Ramazanolu et al., 2022). Examples of conventional non-living biomass that have been used as biosorbents include crab shells and shrimp (Apiratikul and Pavasant, 2008). In this study, six different orange peel-derived biosorbents were used to extract Co^{2+}, Ni^{2+}, and Cu^{2+} ions from aquatic environments, and their extraction performance was evaluated at 24°C for 30 minutes. The goal of this study is to investigate the potential of orange peel-derived biosorbents as an alternative to conventional biomaterials for the removal of heavy metals from aquatic environments.

2. MATERIALS AND METHODS

2.1 Materials

Corn starch, apple cider vinegar (4-5% acetic acid), sunflower oil, and oranges were obtained from a local grocery store in Zakho. Nickel (II) Nitrate Hexahydrate $Ni(NO_3)_2.6H_2O$, Copper (II) chloride dihydrate $CuCI_2.2H_2O$, and Cobalt (II)Acetate $C_4H_6CoO_4$ were procured from Merck.

2.2 Methods

The surface images of biosorbents were captured using a microscope Am Scope brand in the biology lab at Zakho University. The concentration of solutions was determined using a Perkin Elmer brand Flame atomic absorption spectroscopy (FAAS) at the research center of Zakho University. Orange (Citrus sinensis) peels were dried in an oven for 48 hours at a temperature of 103±2°C. Subsequently, all biosorbents were ground by operating an Arshia brand coffee grinding machine to obtain fine powder for further analysis. These steps were taken to ensure accurate and reliable results in the study.

2.2.1 Preparation of biosorbents

The ingredients of the biosorbents like cornstarch, oil, and orange peels were weighed as given in Table 1 and placed in a 500 ml beaker. Then, 25 ml of distilled water has added to the solution. Following this, 3 ml of acetic acid was added and stirred for a while to break the long-chain molecules of the starch. After, 1-2 ml of sunflower oil had appended as a plasticizer to re-crystallize broken polymer chains, and the solution was stirred on the heater at 75 °C continuous gelation occurred. Finally, left to dry at 105±2 °C for 45 minutes (Figure 1).

Table 1: Content of biosorbents

ABSORBENT	1	2	3	4	5	6
ORANGE	1g.O/2g.S 0,5 ml Oil	1, 5g.O/1, 5g.S 0,5 ml Oil	2g.O/1g.S 0,5 ml Oil	1g.O/2g.S 1 ml Oil	1, 5g.O/1, 5g.S 1 ml Oil	2g.O/1g.S 1 ml Oil

Figure 1. Preparation of biosorbents

2.2.2 Solubility test (%)

The solubility test was applied by according to equation (1) (Da Rosa Zavareze, et al 2012; Galus, et al. 2012; Jayasubramanian and Balachander, 2016). Samples were taken and incubated in a drying and sterilization oven for 24 hours at 103±2°C. They were then weighed (W_i) and rinsed with 50 ml of distilled water at 175 rpm. The samples were taken out of the water, dried, and weighed again. Finally, the solubility of the biosorbents was calculated using the values obtained in this process.

$$S = \left(\frac{Wi - Wf}{Wi}\right) * 100 \quad (1)$$

Wi: Initial mass; Wf: Final mass.

2.2.3 Water intake (%)

The solubility test was determined by Gontard et al. in 1992 according to equation (1) (Gontard et al. 1992; Mysiukiewicz and Sterzyński, 2017). The water intake (%) values of biosorbents whose weighing measurements after being kept in water for 24 hours, were calculated according to the formula given in (2).

$$SW = \left(\frac{Mw - Md}{Md}\right) * 100 \quad (2)$$

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

2.2.4 Density test (g/cm³)

The air-dry weights of the samples were measured under laboratory conditions by immersing them in water and weighing them. The density of the samples was then calculated using the equation given in (3)(ASTM D 792 (2004).

$$Density = (\frac{Ma}{Mw}) \quad (3)$$

Here, Ma = weight of the sample in the air (g). Mw = The weight of the sample in water (g) is given.

2.2.4 Batch experiment

25 ml of 7 ppm solutions of Cu^{2+}, Co^{2+}, and Ni^{2+} heavy metal ions were freshly prepared from 50 ppm of Nickel (II) Nitrate Hexahydrate (Ni $(NO_3)_2.6H_2O$), Copper (II) chloride dihydrate ($CuCI_2.2H_2O$), and Cobalt (II) Acetate ($C_4H_6CoO_4$). 25 mg of biosorbents were used for each heavy metal ion solution. The adsorption conditions were set at 24°C for 30 minutes and at 175 rpm of agitation speed. The sorption performance of the biosorbents was evaluated using the equation given in (4) (Abbar et al., 2017).

$$Q = \big((Co - Ce) * V\big)m \quad (4)$$

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

2.2.5 Morphology of biosorbents

The surface photographs of the biosorbents, which were synthesized from orange peels with various ingredients, resulting in a variety of surface features, were taken using a microscope and are shown in Figure 2.

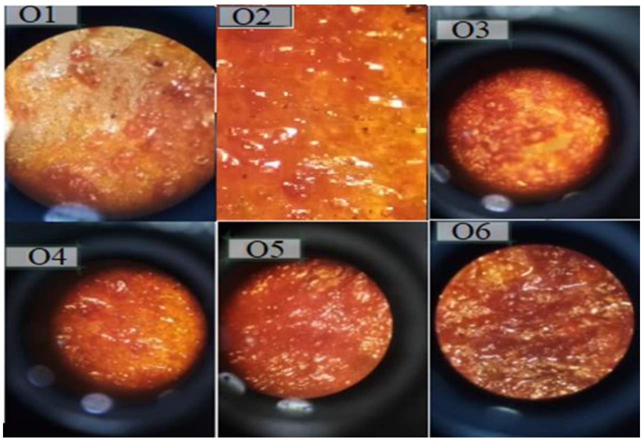


Figure 2. Depicts the orange peels-based biosorbents with varying ratios of orange peels, starch, and oil content. Specifically, the ratio used for O1 is (1/2/0.5), for O2 is (1.5/1.5/0.5), for O3 is (2/1/0.5), for O4 is (1/2/1), for O5 is (1.5/1.5/1), and for O6 is (2/1/1) respectively.

3. RESULTS AND DISCUSSION

3.1. Water intake analysis of biosorbents

The bar chart in Figure 3 provides a visual representation of the water intake capacity of orange peel-based biosorbents with varying ratios of orange peels, starch, and oil content. The research of has shown that the percentage of water intake decreases as the amount of orange peel content increases, specifically from O1 to O3. This can be seen in the chart as the bars for O1, O2 and O3 decrease in height as the orange peel content increases (Whistler ve BeMiller, 1996; Guntekin et al., 2008; Bilgin et al., 2014; Özdemir and Ramazanoğlu, 2019a; 2019b).

Furthermore, it is also observed that when the starch content remains constant, the water adsorption capacity decreases. This highlights the importance of the starch content in determining the water intake capacity of the biosorbents. In addition, the chart is divided into two groups based on the oil content, the first group (O1, O2, and O3) contains 0.50 ml of oil, while the second group (O4, O5, and O6) contains 1.00 ml of oil. Due to the hydrophobic nature of the oil, it is expected that the second group has a lower water intake compared to the first group, and this can be observed in the chart as well.

In summary, the bar chart in Figure 3 illustrates the relationship between the water intake capacity of orange peel-based biosorbents and the ratio of orange peels, starch, and oil content used in their synthesis. The research has shown that increasing the orange peel content and decreasing the starch content in the biosorbents can decrease the water intake capacity, while increasing the oil content can further decrease the water intake capacity due to its hydrophobic nature (Whistler ve BeMiller, 1996; Guntekin et al., 2008; Bilgin et al., 2014; Özdemir and Ramazanoğlu, 2019’a; 2019b). The solubility of the biosorbents was calculated according to the equation in (1). Additionally, Figure 3 illustrates the water intake values.

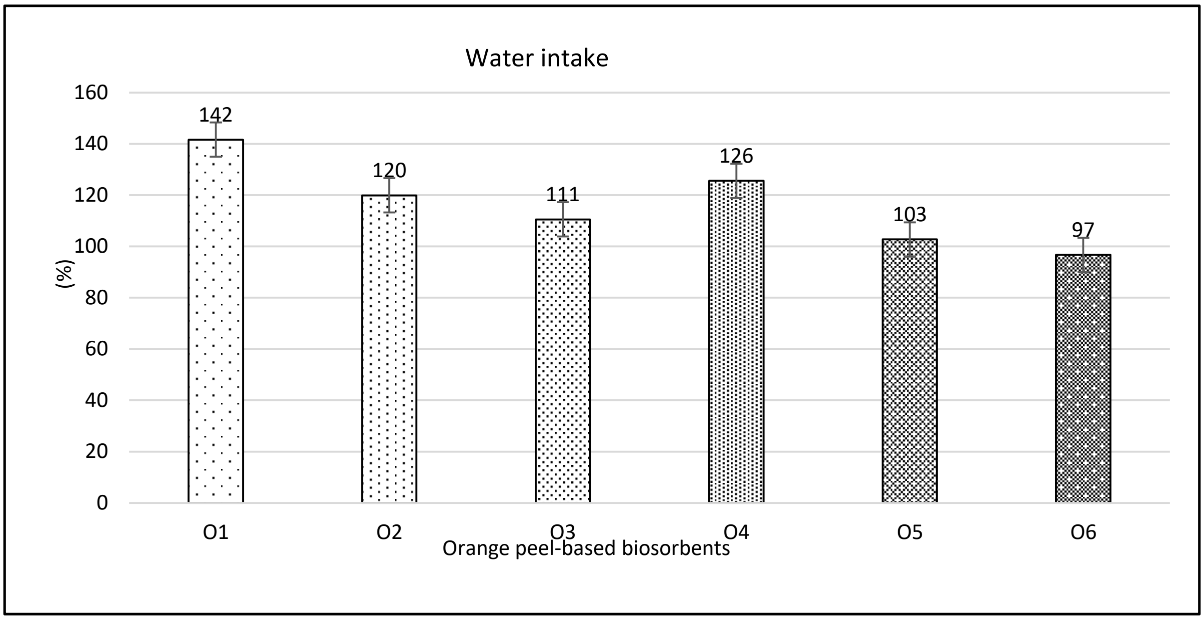


Figure 3 Illustrates the water intake of orange peels-based biosorbents with varying ratios of orange peels, starch, and oil content. Specifically, the ratio used for O1 is (1/2/0.5), for O2 is (1.5/1.5/0.5), for O3 is (2/1/0.5), for O4 is (1/2/1), for O5 is (1.5/1.5/1), and for O6 is (2/1/1) respectively.

3.2. Water solubility analysis of biosorbents

According to the research of (Whistler ve BeMiller, 1996; Guntekin et al., 2008; Bilgin et al., 2014; Özdemir and Ramazanoğlu, 2019a; 2019b), the solubility of biosorbents is affected by the ratio of ingredients used in their synthesis. Specifically, as the amount of starch in the biosorbent increases, the solubility of the biosorbent also increases. On the other hand, as the amount of sunflower oil in the biosorbent increases, the solubility of the biosorbent decreases. This is likely due to the hydrophobic nature of oil, which can reduce the biosorbent's ability to absorb water.

In the study, the biosorbent O4 was found to have the lowest solubility among the biosorbents tested. This is likely due to the high sunflower oil content in the biosorbent, which reduces its ability to absorb water. On the other hand, O3 was found to have the highest solubility among the biosorbents tested. This is likely due to the high starch content in the biosorbent, which increases its ability to absorb water. Overall, the research shows that the solubility of biosorbents can be fine-tuned by adjusting the ratio of ingredients used in their synthesis.

The water solubility of orange peel-based biosorbents is given in Figure 4.

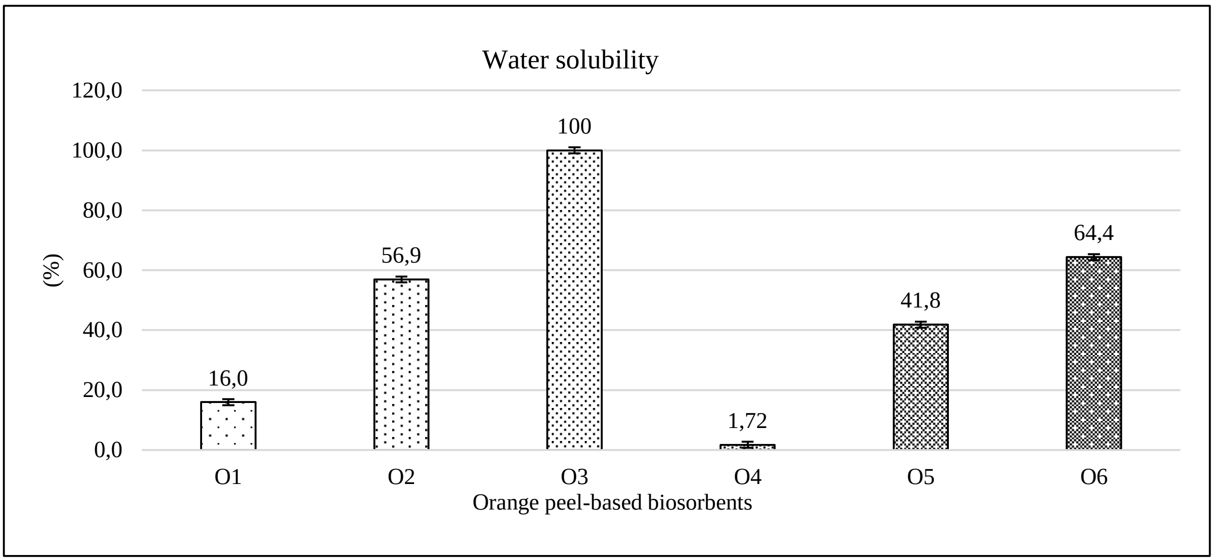
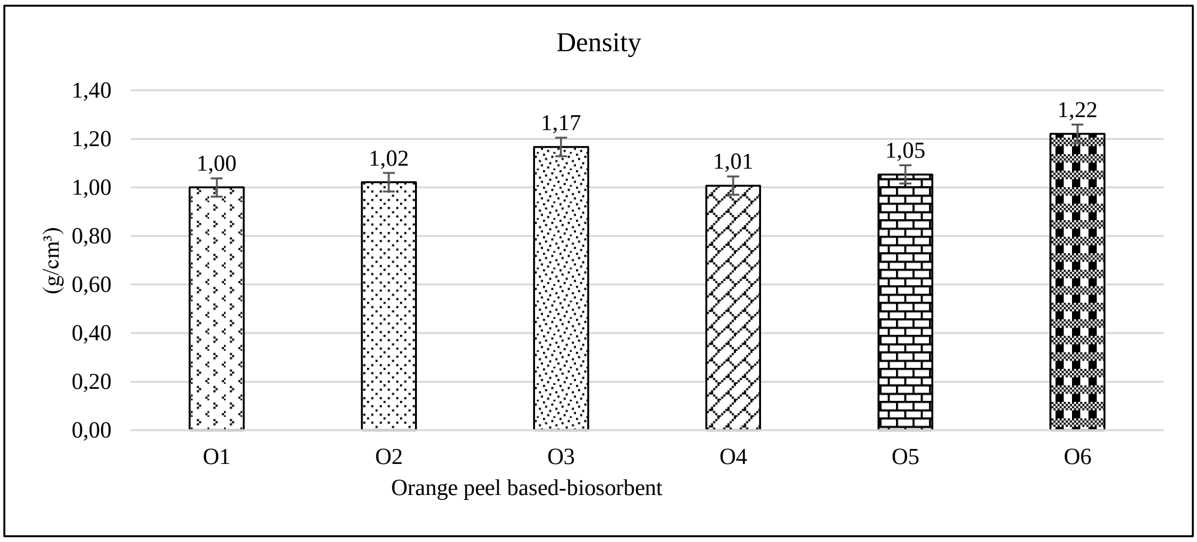


Figure 4 Illustrates the water solubility of orange peels-based biosorbents with varying ratios of orange peels, starch, and oil content. Specifically, the ratio used for O1 is (1/2/0.5), for O2 is (1.5/1.5/0.5), for O3 is (2/1/0.5), for O4 is (1/2/1), for O5 is (1.5/1.5/1), and for O6 is (2/1/1) respectively.

3.3. Density of biosorbents

The measurements were taken according to ASTM D 792 standards (ASTM D 792, 2004). When oil was used as a plasticizer during the preparation of the biosorbents, it was observed that the increased oil content led to an increase in the density of the biosorbents. However, an increased starch content resulted in a decrease in the volume of the biosorbents. Among the biosorbents, O4 had the highest density with 1.22 g/cm^3, whereas O3 had the least density with 1.00 g/cm^3. The bar chart in Figure 5 illustrates the density of orange peel-based

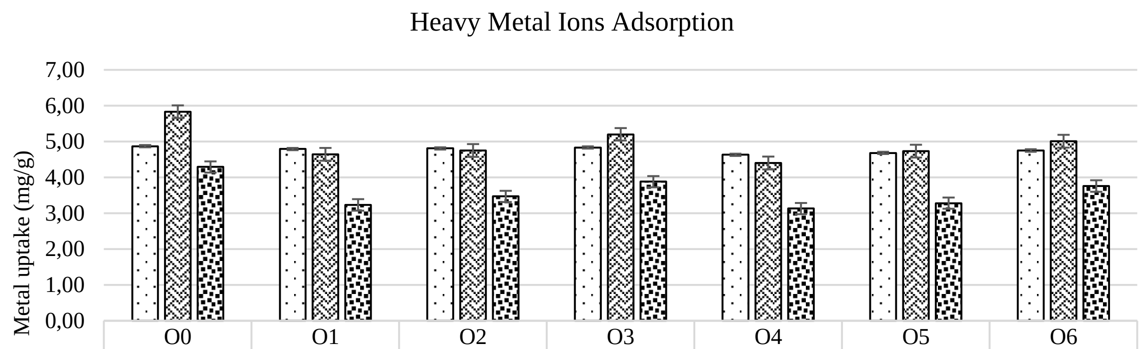


biosorbents.

Figure 5 Illustrates the density of orange peels-based biosorbents, which were synthesized with varying ratios of orange peels, starch, and oil content. Specifically, the ratio used for O1 is (1/2/0.5), for O2 is (1.5/1.5/0.5), for O3 is (2/1/0.5), for O4 is (1/2/1), for O5 is (1.5/1.5/1), and for O6 is (2/1/1) respectively.

3.4. Adsorption studies of biosorbents

It was determined that the untreated biosorbent O0 exhibited the highest biosorption with 4.87 mg of Co^{2+}, 5.83 mg of Ni^{2+}, and 4.29 mg of Cu^{2+} heavy metal ions during a half-hour period at 24 °C and 175 rpm agitation speed. The same conditions were used for the evaluation of the adsorption of Co^{2+}, Ni^{2+} and Cu^{2+} heavy metal ions by orange peel-based biosorbents, as depicted in Figure 6. It was found that the untreated biosorbent possessed better adsorption capacity. The adsorption capacity of heavy metal ions by orange peel-based biosorbents is illustrated in Figure 6.



	O0	O1	O2	O3	O4	O5	O6
Co	4,87	4,79	4,81	4,83	4,63	4,68	4,75
Ni	5,83	4,64	4,75	5,20	4,40	4,73	5,01
Cu	4,29	3,23	3,47	3,88	3,13	3,28	3,76

Figure 6 The ratio of orange peels, starch, and oil content for the biosorbent O1 was (1/2/0.5), for O2 was (1.5/1.5/0.5), for O3 was (2/1/0.5), for O4 was (1/2/1), for O5 was (1.5/1.5/1), and for O6 was (2/1/1) respectively.

4. CONCLUSION

In conclusion, it was observed that the enhancement of sorption capacity was caused by the increased volume of biomass content. The adsorption capacity was found to decrease with the increase in oil content, which may be due to the presence of lignocellulosic and extractive matter. The ratio between sizes was also found to be linearly proportional to the amount of mass lost during destruction. The chemical interactions exhibited by fillers from different biomasses were found to be characteristic, with dimensional and typical morphological properties resulting from differences in the intermolecular chemical bonding properties and recrystallization properties formed during the polymerization of the functional groups possessed by them.

In the water intake study, it was observed that the water intake amount decreased with increasing oil content, and that when the orange peel content increased, water sorption diminished. Additionally, the increased starch content was found to be inversely proportional to the water intake of the orange peel-based biosorbent.

In the water solubility study, it was found that the raised sunflower oil content decreased the solubility of all biosorbents, with biosorbent O3 being the most soluble with a value of 100% and biosorbent O4 being the least soluble with a value of 1.72%. The increasing amount of biomass was found to enhance the solubility of biosorbents, with an inverse proportion between biomass and starch content not being observed in a bioform.

In the density analysis, it was found that the increased oil content improves density for all biosorbents, with biosorbent O6 having the highest density of 1.22 g/cm^3 and biosorbent O1 having a density of 1.00 g/cm3.

In the adsorption step, untreated biosorbent O0 was found to have the highest adsorption of Co^{2+}, Ni^{2+}, and Cu^{2+} ions among its groups. Additionally, it was observed that the increased sunflower oil reduced the heavy metal ion adsorption and that decreasing the amount of starch content also lessened the adsorption capacity. Conversely, the raised amount of biomass was found to improve the adsorption performance, with the density of all biosorbents being directly proportional to adsorption capacities.

Overall, it was found that orange peels can be used as a biosorbent directly instead of other expensive water treatment methods. Further studies can be conducted to determine the optimum conditions of biosorbents and their carbonized form.

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