REMOVAL OF NICKEL, COPPER, AND ZINC IONS FROM AQUEOUS SOLUTION USING COFFEE BEAN HUSK (CFH)

Tran Dac Chi, Duong Thi Thuy Linh, Tran Le Minh*

School of Environmental Science and Technology, Hanoi University of Science and Technology, 1 Dai Co Viet, Hai Ba Trung, Ha Noi, Viet Nam

*Email: minh.tranle@hust.edu.vn

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Abstract. Agricultural waste has received much attention for its potential of being efficient and low-cost adsorbents to remove heavy metals from water. This paper presents a batch investigation of the potential of an adsorbent produced from coffee bean husk for removing copper, nickel and zinc ions from aqueous solution. At the initial pH of 5.0, a dose of 10 g/L, initial concentration of 50 mg/L, shaking speed of 100 rpm, particle size of 0.6 -1 mm and at 25 °C, the removal of nickel, copper, and zinc ions reached 95 % and the highest adsorption capacity of coffee bean husk approached 23, 32, and 22 mg/g, respectively. The adsorption isotherm of these ions preferred to the Freundlich isotherm with the relative coefficient $R^2$ equal and or greater than 0.98. Thus, an initial conclusion drawn from the study was that coffee bean husk could potentially be as an effective and economical adsorbent for removing nickel, copper, and zinc ions from the aqueous solution.

Keywords: heavy metals removal, coffee bean husk, adsorption.

Classification numbers: 3.3.2, 3.4.2.

1. INTRODUCTION

Heavy metals like nickel, copper, and zinc are major pollutants in wastewater from electro-plate, mining, smelting, etc. because of their toxic, non-biodegradable, and persistent nature. A low-cost method for removing heavy metals treatment using bio-sorbents that can be produced from agricultural waste available in abundance received an increased attention from researchers.

Viet Nam is one of the largest coffee bean producers and exporters in the world. In 2018, its coffee bean export reaches 1.64 million tons [1]. It is estimated that the process of every ton of fresh coffee berry yields 0.3 to 0.4 ton of coffee bean and generates 0.18 ton of coffee husk. The coffee bean husk resulted from the dry processing method generally contains the dried outer skin (berry pulp) and parchment (thin inner skin) of the coffee bean. At present, a small amount of this waste is composted, other usages have been explored however limited. One direction for using this waste is to make adsorbents for water treatment in general, heavy metal removal in
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particular. This study was carried out to investigate the possibility of removing some heavy metals by adsorbent produced from wasted coffee bean husk in Viet Nam.

2. MATERIALS AND METHODS

2.1. Adsorbate

All chemicals used in the experiment are of analytical grade. Stock solution of each metal at concentration of 1 g/L were prepared by dissolving the desired quantity of its nitrate in distilled water and were diluted with distilled water to produce 50 mg/L working solution.

A sample of wastewater was collected from a copper-plating workshop at the Dongyun Making Plate Ltd., Northern Division. The concentrations of Ni^{2+}, Cu^{2+}, and Zn^{2+} in the sample were 12.5, 54.0, and 5.4 mg/L, respectively.

2.2. Adsorbent

A sample of dried coffee bean husk was collected from a coffee bean separation mill in Nghe An province of Viet Nam. The husk was washed, sun dried, crushed, and screened with a sieve of 0.6 - 1.0 mm mesh size. The crushed coffee bean husk was then activated with deionized over-heated steam at 50 g/L, 121 °C in an hour. The treated sample was later washed with distilled water until the washing are colorless and then dried at 100 °C to produce the bio-sorbent, hereinafter referred to as CFH in this article.

The use of untreated coffee husk minimizing the energy or chemical reagents for carbonation or activation processes. Thereby reducing the amount of secondary waste as well as more environmentally friendly.

2.3. Adsorption study

The adsorption experiments were conducted separately in the batch model in identical conditions of pH, contact time, and adsorbent doses. For each batch, the specified volume of each metal’s working solution and the CFH were placed in a 100 mL conical flask and agitated at a constant speed of 100 rpm in a water bath at 25 °C. A blank sample was conducted without adsorbent and under controlled conditions similar to the experiments with adsorbates. The absorbed solution was filtered using Waterman 0.45 µm filter paper. The residual concentration of nickel, copper, and zinc ions in the absorbed solution was analyzed by atomic absorption spectroscopy (AAS) 800 Perkin Elmer. The initial pH and equilibrium pH of adsorbed solution was measured by Toledo pH meter.

The removal of metal ions was calculated using Eq. (1).

\[ E = \frac{C_0 - C_e}{C_0} \times 100\% \]  

where: \( C_0 \): the initial concentration of metal ions in mg/L; \( C_e \): concentration of metal ions at equilibrium in mg/L; \( E \): removal efficiency, %.

Surface area of the absorbent was analyzed by Gemini VII 2390 V1.02 and surface image of the absorbent was analyzed by Field Emission Scanning Electron Microscopic JEOL JSM-
7600F at the Advanced Institute for Science and Technology (AIST), Hanoi University of Science and Technology (HUST).

3. RESULTS AND DISCUSSION

3.1. Adsorbent

The FTIR spectroscopic analysis indicated broad bands at 3441 cm\(^{-1}\) may be representing bonded –OH groups rather than -NH groups. This is because of the peak of O-H stretching is broad with rounded tip but the peak for bonded-NH group is a broad peak with two sharp spikes (primary amines). The bands observed at about 2955–2852 cm\(^{-1}\) may show the presence of C–H stretching but not aldehydic C-H because the aldehydic C-H stretching vibration occurs in the region of 2830 - 2700 cm\(^{-1}\) with the appearance of two intense bands. The peaks around 1722 cm\(^{-1}\) correspond to the C=O group and at 1652–1616 cm\(^{-1}\) C=C. The C–O band absorption peak is also observed at 1035 cm\(^{-1}\). The presence of these functional groups are important sorption sites of coffee husk to participate in Ni\(^{2+}\), Cu\(^{2+}\), Zn\(^{2+}\) binding from aqueous solution or industrial effluents.

With the particle size of CFH in the range of 0.6 -1.0 mm, the surface area was measured at about 0.39 m\(^2\)/g. The SEM image in Fig. 2 showed that CFH has a rough and heterogeneous surface.

![Figure 1. FT-IR analysis results of CFH.](image1)

![Figure 2. SEM image of CFH.](image2)

3.2. Effect of contact time

The adsorption increased with increasing contact time. Rapid uptake of metal ions occurred during the first 5 minutes of agitation. The rate of adsorption became slower afterward, and reached the equilibrium in 30 minutes for Cu\(^{2+}\) and 90 minutes for Ni\(^{2+}\) and Zn\(^{2+}\), resulting in the removal of these ions at 95 %. The fast-initial uptake in the early stage of adsorption was due to the fact that most of the binding sites on CFH that were free allowed quick binding of metal ions on the adsorbent. As the number of the binding sites became exhausted, the uptake rate slowed down due to competition of metal ions for decreasing availability of active sites [2]. According to the results, the contact time was fixed at 90 minutes for the further experiment to ensure equilibrium was achieved.

3.3. Effect of initial pH
Figure 3 compares the effect of initial pH on Ni\(^{2+}\), Cu\(^{2+}\), and Zn\(^{2+}\) ions adsorption. It is easy to explain low adsorption efficiency at the pH lower than 3 due to the competition of H\(^+\) ion against Ni\(^{2+}\), Cu\(^{2+}\), or Zn\(^{2+}\) ions for adsorptive sites on the surface of adsorbent. At the low pH, H\(^+\) ion has high concentration and high mobility and, therefore, are preferentially adsorbed rather than metal ions [3]. This competition is disappeared at initial pH higher than 5.0; 3.0; and 4.0 (at equilibrium pH 5.7, 4.9, and 6.4) for Ni\(^{2+}\), Cu\(^{2+}\), and Zn\(^{2+}\) ion, respectively. As pH increased, more adsorbent’s surface was exposed and carried negative charges, which results in less repulsion of metal ions. The adsorption efficiency yielded up to 88 %, 95 %, and 91 %, respectively for the metallic ions. The effect of pH higher than 6.0, 7.0 and 9.0 on adsorption of Cu\(^+\), Zn\(^+\), and Ni\(^-\) was not investigated due to partial hydrolysis of metal ions leading to the formation of MOH and M(OH)\(^-\) [4].

Figure 3. Effect of initial pH on nickel, copper, and zinc ions removal using CFH (Co 50 mg/L, contact time 90 minutes, shaking speed 100 rpm, dosage 10 g/L, and 25 °C).

Figure 4. Effect of adsorbent dose on Ni\(^{2+}\), Cu\(^{2+}\), and Zn\(^{2+}\) removal using CFH (Co 50 mg/L, initial pH 5, contact time 90 minutes, shaking speed 100 rpm and 25 °C).

3.4. Effect of adsorbent dose

The amount of adsorbent significantly influenced the outcome of metal adsorption. As the results presented in Figure 4, the Ni\(^{2+}\), Cu\(^{2+}\) and Zn\(^{2+}\) adsorption efficiencies were steadily increased from 40 %, 82 %, and 43 % to 85 %, 90 %, and 80 % when adsorbent dosage increased from 1.0 to 5.0 g/L, respectively. However, an increase in adsorbent dose from 5.0 g/L to 10.0 g/L only resulted in a marginal gain of 5 - 10 % in adsorption efficiency for all metal ions. Further addition of adsorbent up to 15 g/L did not result in any change in the efficiencies. In other words, at higher dosage, the equilibrium uptake of Ni\(^{2+}\), Cu\(^{2+}\), and Zn\(^{2+}\) ions did not increase significantly with increasing dosage of the adsorbent. Such behavior is expected due to the saturation level attained during the adsorption process. This finding agrees with Koumanova [5].

3.5. Adsorption isotherm

The linearized Langmuir adsorption isotherm equation which is valid for monolayer adsorption onto a surface with a finite number of identical sites is presented as follows:

\[ \frac{c_e}{q_m} = \frac{c_r}{q_m} + \frac{1}{b_q m} \]  

(2)
where: \( C_e \): concentration of Ni (II), Cu\(^{2+}\), and Zn\(^{2+}\) ions in solution at equilibrium (mg/L); \( q_e \): the amount of Ni\(^{2+}\), Cu\(^{2+}\), and Zn\(^{2+}\) ion adsorbed at equilibrium (mg/g); \( q_m \): the theoretical maximum adsorption capacity (mg/g); \( b \): the Langmuir constant (L/mg).

The linear plot of \((C_e/q_e)\) versus \((t/q_e)\) with correlation coefficient \( R^2 \) over Ni\(^{2+}\), Cu\(^{2+}\), and Zn\(^{2+}\) ions was 0.93; 0.92; and 0.91, respectively. These data indicate the applicability of Langmuir adsorption isotherm (Figure 5).

Freundlich adsorption isotherm adopts multilayer adsorption on heterogeneous surfaces. Linearized form of the Freundlich equation is given by the following equation.

\[
\ln q_e = \ln K_f + \frac{1}{n} \ln C_e
\]

where: \( q_e \): the amount of Ni\(^{2+}\), Cu\(^{2+}\), and Zn\(^{2+}\) ions adsorbed at equilibrium time (mg/g); \( C_e \): concentration of Ni\(^{2+}\), Cu\(^{2+}\), and Zn\(^{2+}\) ion in the solution at equilibrium (mg/L); \( K_f \): the equilibrium parameter (mg/g); \( n \): an empirical parameter.

Table 1. Adsorption isotherm parameters of Ni\(^{2+}\), Cu\(^{2+}\), and Zn\(^{2+}\) using CFH.

| Metal ions | Langmuir isotherm | Freundlich isotherm |
|------------|-------------------|---------------------|
|            | \( q_m \) (mg/g)  | \( b \) (L/mg)     | \( R^2 \) | \( K_F \) | \( n \) | \( R^2 \) |
| Ni\(^{2+}\) | 23.87             | 0.082               | 0.935     | 2.668    | 1.80    | 0.989    |
| Cu\(^{2+}\) | 31.95             | 0.327               | 0.923     | 0.604    | 3.48    | 0.984    |
| Zn\(^{2+}\) | 22.23             | 0.123               | 0.911     | 2.743    | 1.85    | 0.981    |

Table 1 compared isotherm parameters of the adsorption of Ni\(^{2+}\), Cu\(^{2+}\), and Zn\(^{2+}\) using CFH. It is not difficult to release the maximum adsorption capacity of CFH for Cu\(^{2+}\) is 31.95 mg/g, higher than that of Ni\(^{2+}\) and Zn\(^{2+}\) ions with 23.87 mg/g and 22.0 mg/g, respectively. It means coffee bean husk prefers to Cu\(^{2+}\) adsorption than Ni\(^{2+}\) and Zn\(^{2+}\) ions. Comparing correlation coefficient (\( R^2 \)) of Langmuir and Freundlich isotherms. The correlation coefficient of both adsorption isotherms is higher than 0.91. This may suggest that the Ni\(^{2+}\), Cu\(^{2+}\), and Zn\(^{2+}\) adsorption adhered to both Langmuir and Freundlich models. However, the correlation coefficient \( R^2 \) of Freundlich isotherm (0.98) was found higher than that of Langmuir isotherm 0.93, 0.92, and 0.91. The adsorption of Ni\(^{2+}\), Cu\(^{2+}\), and Zn\(^{2+}\) using CFH is preferred to Freundlich isotherm.
Coffee wastes include not only husk generated from fresh coffee processing, but also coffee grounds generated from cafeterias. Chung-Hsin Wu [6], Basma G. Alhogbi [7], Do Thuy Tien [8], George Z. Kyzas [9] showed that all types of coffee wastes as shown above could be used as an absorbent for removing heavy metals from wastewater. Table 2 compared the Ni$^{2+}$, Cu$^{2+}$, Zn$^{2+}$ adsorption capacity of CFH obtained in this study with those in the previous studies. Comparing the results of Basma G. Alhogbi [7], the Ni$^{2+}$ and Zn$^{2+}$ adsorption capacity of CFH treated at 121 °C in an hour was improved in comparison with coffee husk adsorbent that was only washed with water. The adsorption capacity was found to increase from 12.98 mg/g and 11.11 mg/g to 23.87 mg/g and 22.23 mg/g for Ni$^{2+}$ and Zn$^{2+}$, respectively. However, the Cu$^{2+}$ adsorption capacity of CFH was 31.95 mg/g, lower than that of untreated coffee grounds (UCG) of 49.34 mg/g in the study of George Z. Kyzas [9]. Especially, the Cu$^{2+}$ adsorption capacity of UCG was significantly improved (56.9 mg/g) after being activated with 2% formaldehyde solution.

| Adsorbent                                      | Ni$^{2+}$ | Cu$^{2+}$ | Zn$^{2+}$ | References                                      |
|-----------------------------------------------|-----------|-----------|-----------|------------------------------------------------|
| Coffee husk (CFH)                             | 23.87     | 31.95     | 22.23     |                                                  |
| Coffee grounds                                | 8.2       | 8.0       |           | Chung-Hsin Wu [6]                               |
| Coffee husk (CH)                              | 12.98     | 11.11     |           | Basma G. Alhogbi [7]                            |
| Coffee husk based activated carbon           | 1.97      |           |           | Do Thuy Tien [8]                                |
| Untreated Coffee grounds                      |           | 49.34     |           | George Z. Kyzas [9]                             |
| (UCG) - generated from cafeterias             |           |           |           |                                                 |
| Treated Coffee Grounds (TCG) with 2% formaldehyde solution |           |           | 56.9     |                                                 |

In a study by Do Thuy Tien [7], the Ni$^{2+}$ adsorption capacity of coffee husk after being treated at 400 °C for 30 minutes was found at 1.97 mg/g only. This suggests that CFH treated at 121 °C works more effectively than that carbonized at 400 °C.

3.6. Removal of Ni$^{2+}$, Cu$^{2+}$, Zn$^{2+}$ from wastewater

After precipitation, the wastewater sample has pH 4.5 and therefore it is not necessary to adjust pH. The adsorption experiment on the wastewater was undertaken under the conditions of 10 g/L CFH adsorbent dose, 90 minutes contact time, 100 rpm shaking speed and room temperature (25 - 27 °C).

These results showed that Cu$^{2+}$ adsorption efficiency of 96% was similar to the results obtained in the experiments with Cu$^{2+}$ without the presence of other metals. It means Cu$^{2+}$ adsorption was not affected by the presence of Ni$^{2+}$ and Zn$^{2+}$ ions at the experimental conditions. Meanwhile, adsorption efficiency was found to decline 76% and 51% for Ni$^{2+}$ and Zn$^{2+}$, respectively, even though the initial was 12.47, and 5.37 mg/L due to competition and occupation of Cu$^{2+}$ on activated site of CFH.
4. CONCLUSIONS

According to the results obtained in this study, some conclusions can be drawn as follows:

Under the experimental conditions, e.g. 25 °C and agitation speed of 100 rpm, the adsorption of Ni$^{2+}$, Cu$^{2+}$ and Zn$^{2+}$ ions is affected by initial pH, contact time, and CFH dosage. The maximum adsorption capacity of these ions was 23.87, 31.95, and 22.0 mg/g at the conditions of: i) initial pH in the range of 5.0 – 7.0, ii) Adsorbent dosage of 10 g/L, iii) contact time of 30 minutes for Cu$^{2+}$, and 90 minutes for both Ni$^{2+}$ and Zn$^{2+}$ adsorption.

CHF is not a selective absorbent material, it could be used to remove Ni$^{2+}$, Cu$^{2+}$, and Zn$^{2+}$ in aqueous solution.

The adsorption isotherm of Ni$^{2+}$, Cu$^{2+}$, and Zn$^{2+}$ was best described by both single and multi-layer models on the surface of the adsorbent produced from CFH. However, the Freundlich isotherm provides a better fitting to isotherm than Langmuir isotherm due to the higher $R^2$. Therefore, it can be suggested that some heterogeneity in the surface of the adsorbent plays a role in the Ni$^{2+}$, Cu$^{2+}$, and Zn$^{2+}$ adsorption.

CFH could be used to produce low-cost adsorbent for removing heavy metal Ni$^{2+}$, Cu$^{2+}$, and Zn$^{2+}$ from water and wastewater.

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