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Feasibility Study of Agriculture By-Product in Removing Heavy Metals in Wastewater through Adsorption

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Abstract: The widespread water pollution issues are becoming the major water threat in Malaysia. The ability of agricultural by-products to remove contaminants from water was investigated and reviewed in this study. Coffee waste, rice husk and mango leaves were utilized in the uptake of Cu(II) in batch experiments. The effect of pH, contact time and initial copper concentration were studied. Equilibrium data were fitted into Langmuir and Freundlich isotherm models. The data was fitted better in Langmuir isotherm with correlation coefficient of 0.8991, 0.9949 and 0.9918. The maximum adsorption capacity was 15.24, 12.30 and 15.77 mg/g on coffee waste, rice husk and mango leaves respectively which indicated the adsorption was in monolayer pattern. The results revealed that coffee waste, rice husk and mango leaves are capable to remove Cu(II) when compares with other adsorbent. The study also revealed the use of different agriculture by-products in the remediation of heavy metal and pollutants contamination in wastewater.

Keywords: Adsorption, Rice Husk, Coffee Waste, Mango Leaves, Cu(II)

1. Introduction

Since 98% of Malaysia's fresh water supply comes from rivers, the changes and conditions of the river system have attracted much attention. Severe water pollution and deterioration of quality of water happens in the past few years because of the hasty impromptu urbanization and industrialization and also population growth [1]. Illegal discharge of chemicals comprising heavy metals from different sources either point sources or non-point sources into water becomes a crisis to humans and the aquatic living species. According to the details reported by Department of Environment (DOE), there were only 477 rivers left in Malaysia in 2017 when compared to 579 rivers in 2008 [2].

Water treatment methods are essential in treating polluted water and wastewater. Adsorption is recognized as an effective water treatment method in term of cost. Agriculture by-products may be used

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as the adsorbents in adsorption treatment method in water and wastewater because of low cost. In adsorption water treatment method, there are two types of adsorbents which are conventional adsorbents and non-conventional adsorbents [3]. Activated carbons, zeolites, silica gel and activated aluminas are the examples of commonly used adsorbents while agriculture wastes and natural materials are the examples of non-conventional adsorbents.

Agriculture by-products are the unwanted residues resulted from agricultural activities and food processing industries. Agriculture wastes are considered as low cost adsorbent when compared to the activated carbon used in the elimination of heavy metals contained in water [4]. Agriculture by-products can be the effective adsorbent with the characteristics including high capacity of adsorption, can be found obtained easily in vast amount, cheap and has the ability to recover the metal ions adsorbed.

Wasted coffee grounds have a composition of polyhydroxy polyphenol functional groups which exist as a tannin-embedding substance in coffee waste, which functions to adsorb the heavy metals effectively by complexation. Rice husk is the main by-product from the industry of rice mill, accounting for 20% of the total weight of rice plant and contains 74.5% organic matter which consists of cellulose, hemicellulose, lignin, and crude protein with about 20% silica which exists in the cellular membrane. Mango is a fruit native to the Indian subcontinent that belongs to the genus *Mangifera* and the Anacardiaceae family. The major significant sorption in mango leaves are cellulose, hemicellulose, pectins, and lignin, which can be found in the cell wall of leaves.

In this study, adsorption was run by using coffee waste, rice husk and mango leaves to remove the copper (II) ions (Cu(II)). The goal of the research was to study the possibility of coffee waste, rice husk and mango leaves as the alternative adsorbents on the uptake of Cu(II). The parameters such as the effect of pH, contact time and initial metal concentration were studied to achieve the objective. The equilibrium data were presented by Langmuir and Freundlich isotherm models.

2. Materials and Methods

2.1 Preparation of adsorbents and stock solution from [5], [6] and [7].

The wasted coffee grounds samples were graciously supplied by a local cafe after roasting a unique kinds of coffee beverages (known as “Greek coffee”). Samples of rice husks were obtained from a local rice mill. Mature mango leaves were collected from a local fruit yard. The prepared adsorbents were washed and then dried in the oven at 80 ºC, grinded into powder using mixer and sieved with the sieve size of 475-525 µm. By dissolving copper (II) nitrate trihydrate ($Cu(NO_3)_2.3H_2O$) in deionised water, a 100 mg/L Cu(II) stock solution was made. To acquire the necessary concentration of Cu(II) solution utilised in the experiment, required dilution of the stock solution was carried out.

2.2 Batch adsorption experiments

The experiments were conducted under different parameters (pH, contact time and initial metal concentration) to test the performance of coffee waste, rice husk and mango leaves in removing Cu(II) from aqueous solution. All samples were conducted twice in the identical conditions and the mean results were obtained.

The effect of pH values (2, 3, 4, 5, 6, 7, 8, 9 and 10) on removing Cu(II) (10 mg/L, 20mL) were determined using 0.1 g of coffee waste, rice husk and mango leaves powder with the agitation speed of 150 rpm for 2 hours. pH value was adjusted by the adding of sodium hydroxide (NaOH) or hydrochloric acid (HCl).

The influence of contact time was demonstrated by stirring 0.1 g of coffee waste powder in 20 mL of Cu(II) solution with concentration of 10 mg/L, stirring speed of 150 rpm and optimum pH value of 5 which was obtained in the study over the contact time of 5, 10, 15, 30, 60 and 120 minutes. The steps were repeated with rice husk and mango leaves powder.

The effect of initial metal concentration on coffee waste was realized by mixing 0.1 g of coffee waste powder with 20 mL of Cu(II) solution with the concentrations of 10, 20, 30, 40, 50, 60 and 70 mg/L at the agitation speed of 150 rpm and optimum pH value of 5 at the period of 2 hours. The steps were repeated with rice husk and mango leaves powder.

The uptake capacity of the adsorption of Cu(II) and the removal efficiency was calculated by using Eq.(1) and (2):

$$q_e = (C_o - C_e)\ (V / m) \quad (1)$$

$$Removal\ efficiency\ (\%) = [(C_o - C_e) / C_o\ ] \times 100 \quad (2)$$

where q_e is the amount of metal adsorbed (mg/g), C_o is the initial concentration of Cu(II) (mg/L), C_e is the concentration of Cu(II) when the adsorption is in equilibrium (mg/L), V is the volume of solution (L) and m is the mass of adsorbent (g).

3. Results and Discussions

3.1 Effect of pH

Within the pH value of 2 to 10, the influence of pH on the extraction of Cu(II) present in solution by coffee waste, rice husk and mango leaves were accessed and the results were shown in Figure 1. The rate of the adsorption of Cu(II) using three respective adsorbents were the lowest at pH 2, which was the highest acidity in the experiment. The removal efficiency of Cu(II) at pH 2 was 15.34% for coffee waste, 8.22% for rice husk and 15.19% for mango leaves. Low pH value of solution indicated the increased in the presence of hydronium which competed the active binding sites in adsorbent with copper. The adsorption of copper using coffee waste increased sharply from 60% at pH 3 up to 76.43% at pH 5 which was the maximum adsorption percentage for coffee waste. Afterwards, the percentage of removal of Cu(II) remained almost constant. Cu(II) adsorption for rice husk raised drastically from 35.37% at pH 3 to 90.06% at pH 6 where the maximum adsorption efficiency was recorded. The pH value was opted at pH 5 in the elimination of Cu(II) as the precipitation of copper occurred from pH 5 onwards.

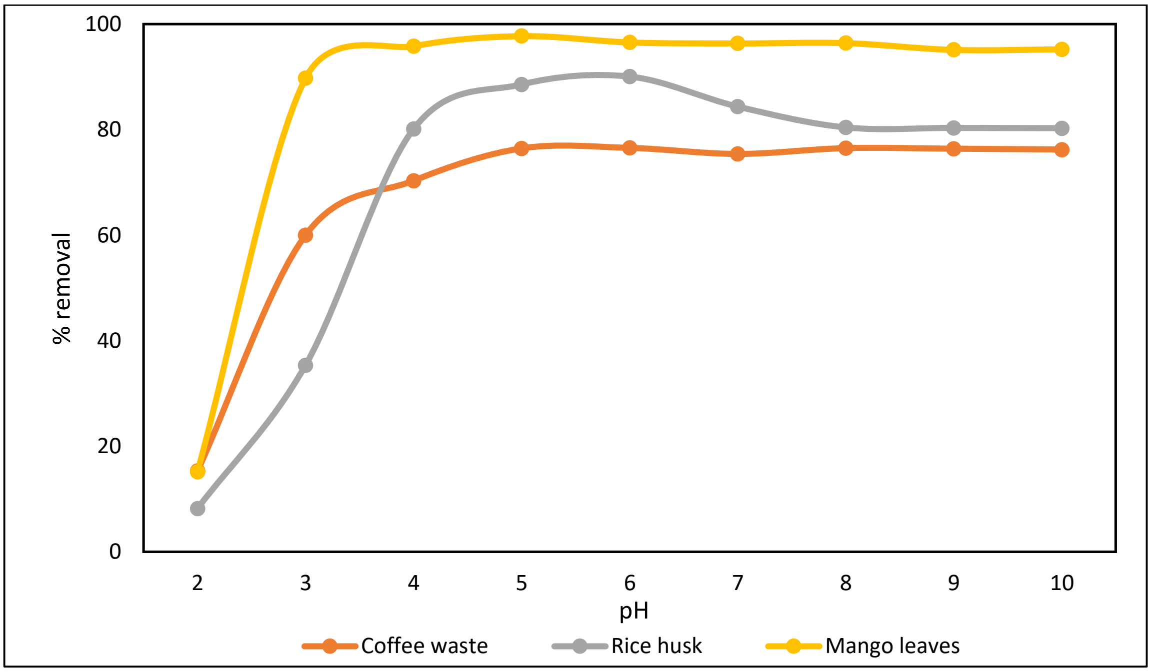

Figure 1: Effect of pH on the percentage of adsorption of Cu(II)

3.2 Effect of contact time

Figure 2 shows the consequence of contact time on the efficiency of the extraction of copper. The graph revealed the adsorption of Cu(II) using coffee waste, rice husk and mango leaves increased with contact time before the point of equilibrium was attained.

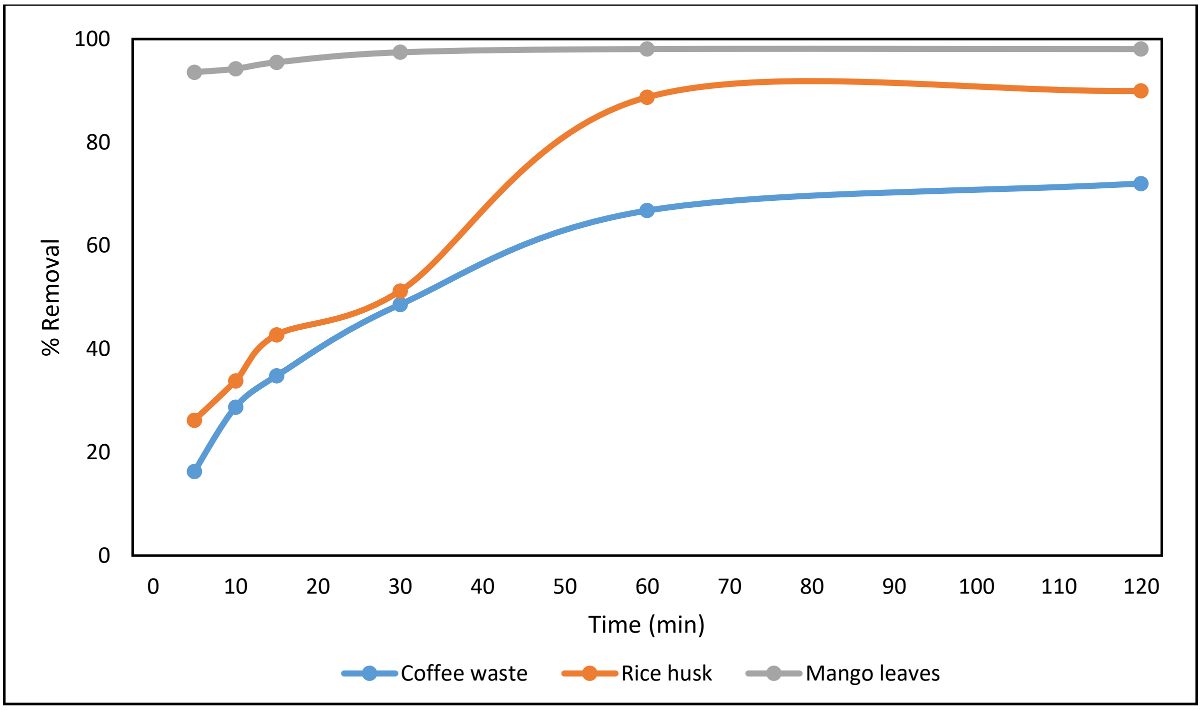

Figure 2: Effect of contact time on the percentage of adsorption of Cu(II)

The uptake of copper ions on coffee waste increased rapidly from 16.28% in the first 5 minutes to 66.79% in one hour and 72.04% in two hours until equilibrium was reached. The percentage of Cu(II) adsorbed on rice husk was 26.22% in the first 5 minutes, which then continued to increase and remain the same value, that was 89.97% after 2 hours once the reaction between binding sites and copper ions were balanced. Removal of copper ions on mango leaves were different with another two adsorbents in which the uptake reached 93.59% just in the first 5 minutes, then the rate of adsorption became slower until equilibrium was achieved in one hour at 98.08% of removal efficiency.

Mango leaves owned the largest surface area and the highest number of binding sites among the three adsorbents which allowed the highest percentage of copper ions to bind rapidly onto the sites in the first 5 minutes. When the time increased, the binding sites became limited as most of the binding-free sites had been occupied and the Cu(II) in the aqueous solution had to compete with each other on the remaining binding sites which were available.

3.3 Effect of initial metal concentration

The results of the relationship between initial copper concentration and the performance of removal using three adsorbents were depicted in Figure 3. The percentage of elimination of Cu(II) reduced when the initial concentration of copper present in aqueous solution increased. The amount of Cu(II) declined from 80.50% to 70.36% on coffee waste, 97.48% to 81.33% on rice husk and 98.20% to 87.69% on mango leaves when the concentration of 10 mg/L to 70 mg/L of Cu(II) solution was used.

When the preliminary concentration of copper ions in aqueous solution was low, the copper ions were free to react with the abundant binding sites available, which resulted in the high removal of copper. When the initial concentration of Cu(II) used was high, lacking of binding sites for complexation became the problem as the large number of copper ions strived to bond on the binding sites which were limited as the dosage of adsorbent was constant and thus gave a low uptake of Cu(II).

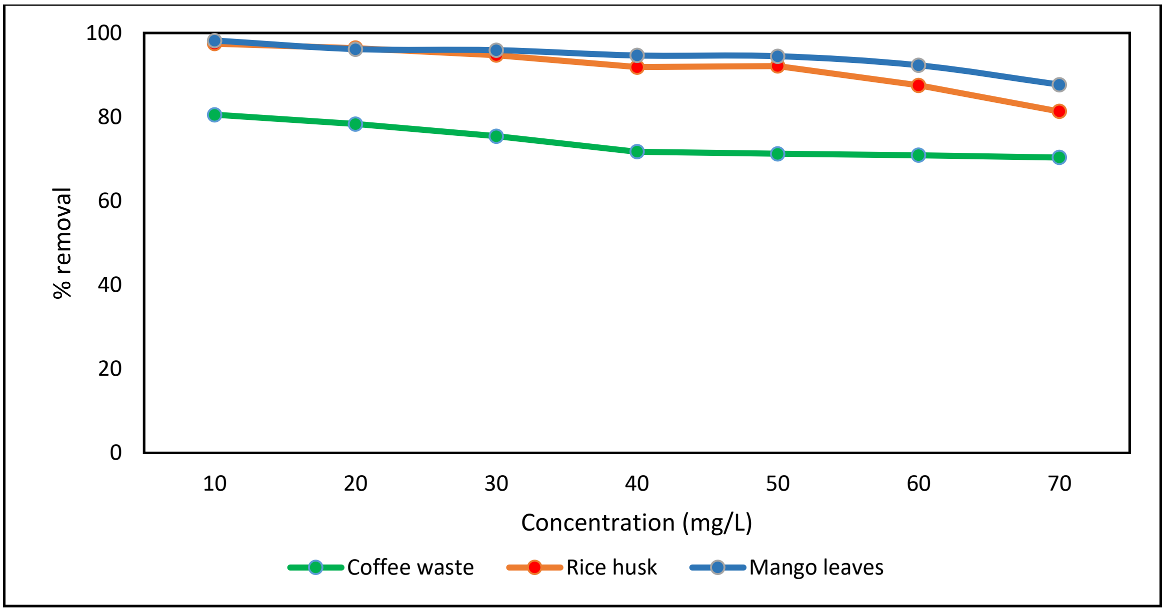

Figure 3: Effect of initial metal concentration on the percentage of adsorption of Cu(II)

3.4 Adsorption isotherm

Langmuir and Freundlich isotherms were utilized to examine the equilibrium data collected methodically and in details. Langmuir isotherm was fitted to equilibrium adsorption which assumed a monolayer pattern adsorption taking place on the exterior of the adsorbent with a restricted number of similar binding sites. Langmuir isotherm is outlined in Eq.(3):

$$C_e / q_e = [1 / (q_m k_e)] + [C_e / q_m] \quad (3)$$

where q_m is the maximum adsorption capacity (mg/g) and k_e is the Langmuir isotherm constant (L/mg) which can be ascertained from the graph of C_e/q_e versus C_e.

Dimensionless equilibrium parameter, RL, as expressed in Eq.(4) is employed to forecast the affinity of the adsorbents towards the copper ions. RL value stipulates the nature shape of isotherm. Adsorption is unpropitious when RL is greater than 1, linear when RL is equivalent to 1, favorable when RL is in between 0 and 1, and irreversible when RL is equal to 0.

$$R_L = 1 / [1 + K_e C_o] \quad (4)$$

The coefficient of determination, R^2 of the elimination of Cu(II) by coffee waste, rice husk and mango leaves were 0.8991, 0.9949 and 0.9918 respectively as shown in Figure 4, which indicating the equilibrium data apt well to the Langmuir isotherm. Maximum uptake capacity was 15.24 mg/g, 12.30 mg/g and 15.77 mg/g respectively. Adsorption process which utilized three different adsorbents were favourable as the range of values of RL were in between 0 and 1 as sorted out in Table 1.

Table 1: Values of R_L for the concentration of copper ions on the adsorbents

Co (mg/L)	Coffee waste (K_e = 0.0626)	Rice husk (K_e = 0.5811)	Mango leaves (K_e = 0.5036)
	R_L	R_L	R_L
10	0.615006	0.146821	0.165673
20	0.44405	0.079227	0.090318
30	0.347464	0.054251	0.062081
40	0.285388	0.041247	0.047295
50	0.242131	0.033272	0.038197
60	0.210261	0.027882	0.032035
70	0.185805	0.023994	0.027585

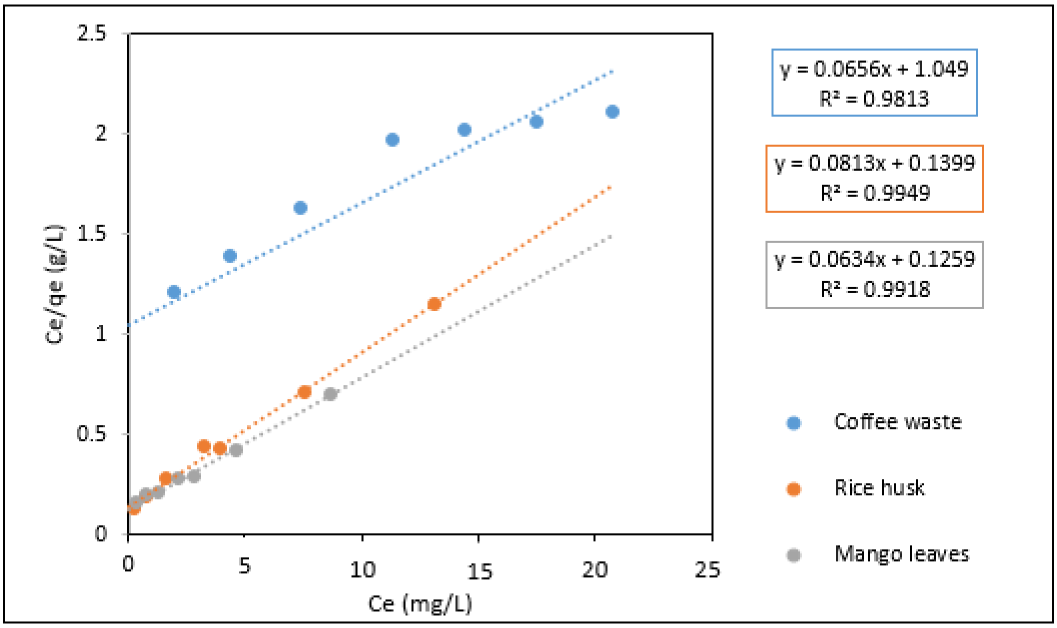

Figure 4: Langmuir isotherm plot for the adsorption of Cu(II) onto three adsorbents

Freundlich isotherm assumes the adsorption is in multilayer pattern and a dissimilar surface with an irregular dissemination of adsorption heat throughout the surface (binding sites are not equal). Freundlich isotherm is expressed in Eq.(5):

$$log\ Q_e = log\ K_F + (1/n)(log\ C_e) \tag{5}$$

where K_F is the capacity of adsorption (L/mg) and n is the intensity of adsorption.

Values of n and K_F were determined from the gradient and the intercept of the straight lines of in the graph as shown in Figure 5. Straight lines with the gradient of 1/n and the intercept of log K_F of coffee waste, rice husk and mango leaves were determined from the graph.

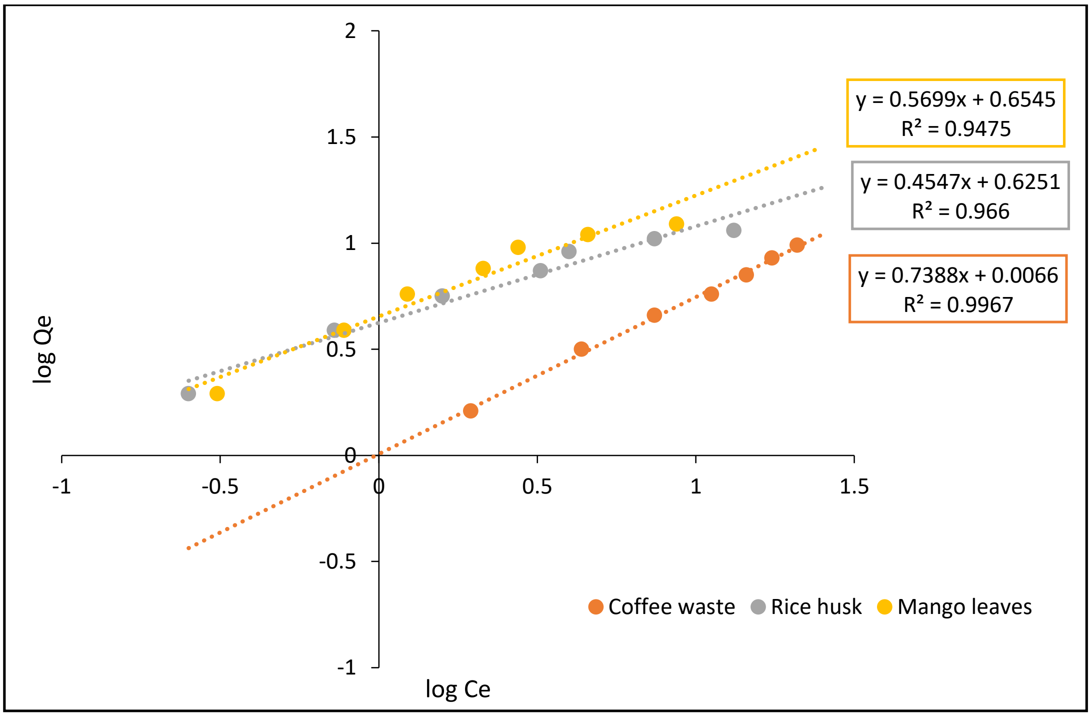

Figure 5: Freundlich isotherm plot for the adsorption of Cu(II) onto three adsorbents

The correlation of determination of coffee waste, rice husk and mango leaves were 0.9967, 0.9660 and 0.9475 respectively. From the graph, values of n and K_F were obtained, which was 1.3535 and 1.02 for coffee waste, 2.1993 and 4.22 for rice husk and 1.7547 and 4.51 for mango leaves. The value of n in the equation of Freundlich isotherm indicates the favourability of the adsorption process. Adsorption is favourable in the range of 2 to 10, slightly difficult in the value of 1 and 2 and weak adsorption process when the value of n is less than 1. According to the value of n acquired, the process of removal of Cu(II) on rice husk was beneficial. For coffee waste and mango leaves, the adsorption was moderately difficult as the n values were lying between 1 and 2.

The constants and correlation of determinations acquired from the plotted Langmuir and Freundlich isotherms were presented in Table 2. The results revealed that the Langmuir isotherm was the best fit model for the adsorption process on three adsorbents as the R^2 values were closest to 1 compared with Freundlich isotherm and the adsorption process of Cu(II) was mainly on monolayer pattern. According to the maximum adsorption capacity of three adsorbents, mango leaves gave the highest adsorption capacity which was 15.77 mg/g.

Table 2: Langmuir and Freundlich parameters for adsorption of Cu(II)

	Langmuir			Freundlich		
	R^2	q_m (mg/g)	K_e (L/mg)	R^2	K_F (mg/g)	n
Coffee waste	0.9813	15.24	0.0626	0.9967	1.02	1.3535
Rice husk	0.9949	12.30	0.5811	0.9660	4.22	2.1993
Mango leaves	0.9918	15.77	0.5036	0.9475	4.51	1.7547

3.5 Use of agriculture by-products in removing pollutants

A summary of work of the utilization of agriculture by-products in the adsorption of heavy metals and pollutants were tabulated in Table 3. The use of agriculture by-products had shown a great efficiency in the removal of hazard metals and pollutants.

Table 3: Application of agriculture by-products in removing heavy metals and pollutants

Agriculture by-product	Pollutants	Adsorption capacity	Removal efficiency (%)	Reference
Coffee waste	Copper	15.24 mg/g	80.50	[5]
Rice husk	Copper	12.30 mg/g	97.48	[6]
Mango leaves	Copper	15.77 mg/g	98.20	[7]
Mango peel	Copper	-	78.87	[8]
Papaya peel	Copper	-	79.00	[9]
Potato peel	Copper	-	77.00	[10]
	Nickel	-	51.00	
	Lead	-	77.00	
	Zinc	-	65.00	
Orange peel	Dye	312.50 mg/g	93.60	[11]
Pomelo peel	Dye	38.31 mg/g	94.20	
Passion fruit peel	Dye	51.81 mg/g	96.80	
Banana peel	Malachite green	-	96.00	[12]
	Methylene blue	-	98.00	
Coconut desiccated meat	Copper	18.19 mg/g	-	[13]
	Nickel	9.78 mg/g	-	
Sawdust	Copper	11.62 mg/g	88.46	[14]
	Lead	6.57 mg/g	91.68	
Eggshell	Silver	49.00 mg/g	-	[15]
	Copper	24.00 mg/g	-	
Eggshell	Cadmium	-	94.88	[16]

Eggshell	Nickel	2.6×10^{-8} mmol/g	62.00	[17]
	Copper	7.6×10^{-8} mmol/g	83.00	
	Cadmium	1.1×10^{-8} mmol/g	92.00	
Pineapple leaves	Lead	63.92 mg/g	-	[18]
	Cadmium	48.02 mg/g	-	
Neem leaves	Lead	174.70 mg/g	100.00	[19]
	Copper	154.50 mg/g	91.50	
	Chromium	144.20 mg/g	83.50	
	Zinc	133.40 mg/g	73.00	
	Nickel	122.50 mg/g	64.40	
	Cadmium	111.50 mg/g	50.90	
Green tea leaves	Chromium	34.59 mg/g	99.00	[20]

4. Conclusion

This study showed the removal of Cu(II) was influenced by pH, contact time and initial Cu(II) concentration. Optimum pH for the uptake of Cu(II) was pH 5. The removal of Cu(II) increased with the increased in contact time until the equilibrium was achieved. The uptake process of Cu(II) decreased with the increased in initial Cu(II) concentration. Langmuir isotherm was the best fit isotherm for coffee waste, rice husk and mango leaves with the correlation coefficient of 0.9813, 0.9949 and 0.9918 respectively. The adsorption of Cu(II) followed the monolayer pattern and the maximum adsorption capacity was 15.24, 12.30 and 15.77 mg/g for coffee waste, rice husk and mango leaves. The application of these adsorbents as the alternative way to remove Cu(II) is possible with the reasons of effectiveness, low cost and abundant. Agriculture by-products had shown their effectiveness in eliminating different heavy metal ions and pollutants present in water which are hazards to the human and other species. Application of coffee waste, rice husk and mango leaves to eliminate other heavy metal ions such as zinc, lead, nickel and cadmium in the wastewater to prove the effectiveness of these adsorbents are proposed to be implemented in the future work. Also, the effect of the temperature, amount of adsorbent and agitation rate on the uptake of Cu(II) are suggested to be investigated in the future.

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References

[1] S. De Gisi, G. Lofrano, M. Grassi and M. Notarnicola, “Characteristics and adsorption capacities of low-cost adsorbents for wastewater treatment: a review,” Sustainable Materials and Technologies, vol. 9, pp. 10–40, 2016, doi:10.1016/j.susmat.2016.06.002.

[2] New Strait Times, “NST Leader: what’s up, enforcers?,” New Strait Times, July 23, 2019. [Online]. Available: https://www.nst.com.my/opinion/leaders/2019/07/506380/nst-leader-whats-enforcers [Accessed July 23, 2019].

[3] G. Crini, E. Lichtfouse, L. D. Wilson and N. Morin-Crini, “onventional and non-conventional adsorbents for wastewater treatment,” Environmental Chemistry Letters, vol. 17, pp. 195-213, 2019, doi:10.1007/s10311-018-0786-8.

[4] A. Tripathi and M. R. Ranjan, “Heavy metal removal from wastewater using low cost adsorbents,” Journal of Bioremediation & Biodegradation, vol. 6, 2015, doi: 10.4172/2155-6199.1000315.

[5] G. Z. Kyzas, D. N. Bikiaris, M. Kostoglou and N. K. Lazridis, “Copper removal from aqueous systems with coffee wastes as low-cost Materials,” E3S Web of Conferences, vol. 1, pp. 1-5, 2013, doi: 10.1051/e3sconf/20130125004.

[6] K. M. El-Moselhy, M. A. Azzem, A. Amer and A. E. Al-Prol, “Adsorption of Cu(II) and Cd(II) from aqueous solution by using rice husk adsorbent,” Physical Chemistry: An Indian Journal, vol. 12, pp. 109, 2017.

[7] P. S. Onn, “Utilization of mango leaf as low-cost adsorbent for the removal of Cu(II) ion from aqueous solution,” Degree thesis, Dept. Chem. Sci., Universiti Tunku Abdul Rahman, Malaysia, 2011.

[8] S. V. A. R. Sastry, “Surface assimilation of copper (Cu^{2+}) from waste water using mango peel powder (MPP),” Acta Technica Corvininesis – Bulletin of Engineering, vol. 13, pp. 51-53, 2020.

[9] M. S. Shuhaimen, E. N. Abdulah, R. M. Salim, M. Armi, A. Samah, M. N. Omar and M. N. Ahmad, “Adsorption study on the removal of copper ions from aqueous solution using sodium hydroxide-modified carica papaya peels,” Malaysian Journal of Analytical Sciences, vol. 23, pp. 926-937, 2019, doi:10.17576/mjas-2019-2306-02.

[10] L. Massimi, A. Giuliano, M. L. Astolfi, R. Congedo, A. Masotti and S. Canepari, “Efficiency evaluation of food waste materials for the removal of metals and metalloids from complex multi-element solutions,” Materials, vol. 9, 2018, doi: 10.3390/ma11030334.

[11] N. T. H. Nhung, B. T. P. Quynh, P. T. T. Thao, H. N. Bich and B. L. Giang, “Pretreated fruit peels as adsorbents for removal of dyes from water,” in IOP Conference Series: Earth and Environmental Science, 2018, doi: 10.1088/1755-1315/159/1/012015.

[12] M. Dahiru, Z. Uba Zango and M. A. Haruna, “Cationic dyes removal using low-cost banana peel biosorbent,” American Journal of Materials Science, vol. 8, pp. 32-38, 2018, doi: 10.5923/j.materials.20180802.02.

[13] A. R. A. Rahim, Iswarya, K. Johari, N. Shehzad, N. Saman and H. Mat, “Conversion of coconut waste into cost effective adsorbent for Cu(II) and Ni(II) removal from aqueous solutions,” Environmental Engineering Research, vol. 26, 2020, doi:10.4491/eer.2020.250.

[14] F. A. El-Saied, S. A. Abo-Elenan and F. H. El-Shinawy, “Removal of lead and copper ions from polluted aqueous solutions using nano-sawdust particles,” International Journal of Waste Resources, vol. 7, 2017, doi:10.4172/2252-5211.1000305.

[15] Y. Xin, C. Li, J. Liu, J. Liu, Y. Liu, W. He and Y. Gao, “Adsorption of heavy metal with modified eggshell membrane and the in situ synthesis of Cu–Ag/modified eggshell membrane composites,” Royal Society Open Science, vol. 5, 2018, doi: 10.1098/rsos.180532.

[16] L. F. Muhaisen, F. Faisal Muhaisen and Z. M. Abdulkareem, “Egg shell as natural sorbent to remove cadmium ions from simulated wastewater,” Journal of Engineering and Sustainable Development, vol. 23, pp. 167-177, 2019, doi:10.31272/jeasd.23.6.12.

[17] J. Makuchowska-Fryc, “Use of the eggshells in removing heavy metals from waste water - the process kinetics and efficiency,” Ecological Chemistry and Engineering S., vol. 26, pp. 165-174, 2019, doi:10.1515/eces-2019-0012.

[18] A. Daochalermwong, N. Chanka, K. Songsrirote, P. Dittanet, C. Niamnuy and A. Seubsai, “Removal of heavy metal ions using modified celluloses prepared from pineapple leaf fiber,” ACS Omega, vol. 5, pp. 5285-5296, 2020, doi:10.1021/acsomega.9b04326.

[19] H. Patel, “Batch and continuous fixed bed adsorption of heavy metals removal using activated charcoal from neem (azadirachta indica) leaf powder,” Scientific Reports, vol. 10, 2020, doi:10.1038/s41598-020-72583-6.

[20] C. Jeyaseelan and A. Gupta, “Green tea leaves as a natural adsorbent for the removal of Cr(VI) from aqueous solutions,” Air, Soil and Water Research, vol. 9, 2020, doi:10.1177/ASWR.S35227.