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Comparative Biosorption of Cu(II) and Pb(II) Ions from Aqueous Solutions using Soursop (Annona muricata L) Leaf Powder: Characterisation, Isotherm and Kinetic Studies

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ABSTRACT. Heavy metals are a major contaminant as they originate from natural and anthropogenic activities. Extremely high levels of Cu(II) and Pb(II) ions in drinking water are harmful to the aquatic environment and human health. This work assessed the biosorption potential of *Annona muricata* L. leaf (AML) powder for Cu(II) and Pb(II) ions in the batch method. The Fourier-transform infrared (FTIR) spectrophotometer, pH_{slurry}, and pH of point-zero-charge (pH_{PZC}) analyses were carried out to characterise the functional groups in AML. The biosorption of the investigated heavy metal ions was examined as a function of biosorption time, AML dose, pH, and initial Cu(II) ion concentrations. AML showed good selectivity and biosorption capacity towards Pb(II) ions relative to Cu(II) ions. Biosorption kinetics and isotherms could be described by the pseudo-second-order and Langmuir models, respectively. The determined monolayer biosorption capabilities for Cu(II) and Pb(II) ions were 0.460 mmol/g (29.23 mg/g) and 0.911 mmol/g (188.76 mg/g), respectively. Based on these results, AML shows potential as a unique biosorbent for reducing Cu(II) and Pb(II) ions from aqueous solutions.

Keywords: Annona muricata, Biosorption, Heavy metals, Kinetic, Isotherm

INTRODUCTION

Contaminated water with heavy metal ions has been recognised as a significant environmental problem, particularly in developing nations (Liu et al., 2022). Most heavy metals in the environment come from human activities, specifically foundries, burning fossil fuels, waste incinerators, mining, gasoline and smelters. Significant heavy metal ions that must be removed from wastewater comprise mercury (Hg), lead (Pb), zinc (Zn), copper (Cu), cadmium (Cd), and chromium (Cr) (Ilia et al., 2003; Mamta & Dhriti, 2021). Although Cu(II) ion is crucial to human survival and health, it can be harmful in high doses, just like other heavy metal ions. Ingestion of toxic levels of Cu(II) ion can cause severe, systemic damage to capillaries, mucosal irritation and corrosion, kidney and liver failure, and central nervous system irritation and depression. According to the Environmental Quality Act (1974), 0.20 mg/L is the maximum safe level for water used for human consumption (Hanafiah et al., 2022). Another heavy metal, Pb(II) ion, has been discharged into water supplies from a variety of human activities. It is a highly toxic and harmful element that can accumulate in the human body, causing anaemia, encephalopathy, and hepatitis. This is because it destroys

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the hematopoietic system and damages the central brain, kidneys, and liver. Toxic levels of Pb(II) ions in drinking water are capped at 0.10 mg/L under the Environmental Quality Act of 1974 (Ahmad et al., 2009; Chuanbin et al., 2022). To protect human life and health, eliminating Cu(II) and Pb(II) ions from wastewater is a crucial task.

Several advanced technologies have been adopted to eradicate heavy metals from wastewater, namely ion exchange, chemical precipitation, electrochemical deposition, ultra-filtration and flotation (Zafar et al., 2020; Chuanbin et al., 2022). Nevertheless, the high cost of these technologies makes them unfeasible for widespread use, especially in developing nations. The biosorption technique is another alternative method to solve such problems because of its portability, low cost, and potent efficacy in eradicating heavy metals at low concentrations, especially those between 1 and 100 mg/L (Haidong & Ke, 2020). Conventional biosorbents such as activated carbons (ACs) might not be favourable because they are costly to produce and regenerate (Amanda et al., 2021). Thus, biosorbents made from bioresources need to be developed because of their low cost and potential application in developing countries.

The biosorption of heavy metals using agricultural materials has received great attention as these materials are easily available and renewable resources. Furthermore, they have a double benefit: (i) it lessens the waste products whose disposal can become a major and expensive issue, and (ii) it recycles the waste into biosorbents that can be used to clean water (Ahmad et al., 2009). Thus, various agricultural waste materials have been applied to eradicate heavy metal ions from wastewater. They include tangerine peel (Abdić et al., 2018), soya beans (Gaur et al., 2018), modified jackfruit wood sawdust (Mutiara et al., 2018), modified date pits (Krishnamoorthy et al., 2019), corn cob (Kumar et al., 2018), lemon peels (Meseldzija et al., 2019), persimmon leaf (Lee and Choi, 2018), roasted date pits (Mohammed et al., 2015), tobacco leaves (Yogeshwaran & Priya, 2021), aquatic plants such hyacinth roots (Jahangiri et al., 2021), Ludwigia stolonifera root and shoot (El-Amier et al., 2021), moringa seeds (Tokay & Akpınar, 2021), and mixed banana and potato peels (Ashfaq et al., 2021). The biosorption of heavy metals utilising these classes of materials may be ascribed to their various functional groups, such as lignin, cellulose, extractives, hemicellulose, simple sugars, lipids, starch and proteins, that facilitate the complexation of heavy metals (Jahangiri et al., 2021).

A. muricata fruit or soursop contains numerous functional groups, including -NH₂ (amine), -COOH (carboxylic acid), C-O-C (ether), aromatic rings, and-OH (hydroxyl). However, few research articles have investigated the biosorption of heavy metal ions using A. muricata leaf (AML) powder. For instance, dried mature AML were made using a variety of techniques, including oven drying (OD), air drying (AD), furnace drying (FD), and low heat drying (LHD) (Paragas et al., 2018). The prepared leaves were used as a biosorbent to eradicate Ni(II), Zn(II), and Pb(II) ions from aqueous solutions. However, the biosorbent size and the pH solution of Pb(II) ions were not reported. The percentage of biosorption of Pb(II) ions was in the order of AD>FD>LHD>OD. AML was more selective in the biosorption of Pb(II) than Ni(II) and Zn(II). Samin et al. (2015) examined the Cu(II) ions biosorption using (0.01M) HNO₃-treated A. muricata leaves. The acid-treated AML had a porous surface with a biosorption capacity of 6.14 mg/g at pH 7, using 500 mg/L Cu(II) initial concentration, biosorbent dose of 0.25 g and contact time of 90 min (Samin et al., 2015). However, no research article reported the biosorption of Cu(II) ions in acidic solutions by untreated AML.

This study investigated the applicability of untreated fresh AML to biosorb Cu(II) and Pb(II) ions from aqueous

solutions. The AML surface was characterised by a Fourier-transform infrared (FTIR) spectrophotometer, pH of point-zero-charge (pH_{PZC}), and pH_{slurry}. In addition, physiochemical factors, including contact time, pH, biosorbent dose, and initial Cu(II) and Pb(II) concentrations, were investigated. Kinetic and isotherm models were applied to compute the biosorption rate and equilibrium biosorption capacity of AML, respectively.

METHODOLOGY

Biosorbent Preparation

A. muricata leaves were collected in Jengka, Pahang, Malaysia. Before being dried in an oven at 70 °C for an entire night, the fresh green leaves were cleaned multiple times with deionised water to remove soluble solutes and dust. It was sieved and ground to a particle size of 53–212 μm and was labelled AML.

Biosorbates Preparation

Cu(NO₃) and Pb(NO₃)₂ (Merck, Germany) were separately dissolved in deionised water with a few drops of 0.10 M HNO₃ added to avoid the precipitation of Cu(II) and Pb(II) ions to create stock solutions of 1000 mg/L. Appropriate dilution of the stock solutions by deionised water was carried out to obtain the required concentration of each heavy metal ion solution used later in the experiment. The chemicals used were all analytical reagent (AR) grade.

Characterisation

A Fourier-transform infrared (FTIR) spectrophotometer (PerkinElmer, Spectrum100, USA) was applied to inspect the functional groups of both untreated AML and AML loaded with Cu(II) and Pb(II) ions. After combining 0.10 g of AML with 50 mL of distilled water and letting the mixture sit for 24 h at 302 K, the pH_{slurry} was measured using a pH meter. A series of 50 mL (0.01 M) NaCl solutions were prepared with initial pH (pH_i) values ranging from 2 to 10 for the pH_{PZC} determination of AML. The NaCl solutions were then combined with 0.10 g of AML and stirred with a magnetic stirrer for 24 h. The solution's final pH (pH_f) was determined after the mixture was filtered through Whatman filter paper (No. 42). The pH_{PZC} value of AML was calculated by plotting Δ pH (pH_i-pH_f) against pH_i, and the point where the curve intersected the pH_i axis was taken as the value.

Batch Biosorption Experiments

Stoppered Erlenmeyer conical flasks were used for the single component biosorption experiments, and the working volume of the investigated heavy metal ions was maintained at 50 mL throughout the 120 min stirring period at 302 K and 360 rpm on a magnetic stirrer. The pH was varied from 2 to 5 to evade precipitation at upper pH, and the AML dose varied from 0.02 to 0.10 g to test the impacts of pH and AML dose to biosorb 0.1 mmol/L of Cu(II) and Pb(II) ions, respectively. The pH of the solutions was attuned with a pH meter (EUTECH Instruments, Singapore) through addition drops of 0.10 M NaOH and 0.10 M HCl solutions. The kinetics study used two heavy metal ion concentrations of 0.10 and 0.20 mmol/L, 0.02 g of AML, and pH 5. The Cu(II) and Pb(II) concentrations were diverse from 0.1 to 0.6 mmol/L in the isotherm study using 0.02 g of AML and pH 5. After filtering the mixture, the

concentration of the investigated heavy metal ions that remained was measured using an atomic absorption spectrophotometer (AAS, Perkin Elmer, PinAAcle 900T model, USA). All biosorption tests were run in duplicate, and the average of the two sets of results is shown here. The following equation was used to determine the biosorption capacity of AML for heavy metal ions per unit weight:

$$q_e = \frac{(C_i - C_e) \times V}{W} \tag{1}$$

where q_e (mg/g) is the quantity of heavy metal ions biosorbed, C_i (mmol/L) is the initial concentration of heavy metal ions, C_e (mmol/L) is the equilibrium concentration of heavy metal ions, W (g) is the quantity of AML, V (L) is the working volume of heavy metal ions solution.

RESULTS AND DISCUSSION

Characterisation of AML

FTIR analysis was conducted to detect the existence of a surface-bound functional group in AML, serving as the active group for Cu(II and Pb(II) ions biosorption. AML and AML loaded with Cu(II) and Pb(II) ions, as well as their respective FTIR spectra, are shown in Figure 1 (a-c). Figure 1 (a) shows some characteristic bands in the range of 3600 to 3100 cm⁻¹ indicating the presence of stretching -OH and -NH₂ groups.

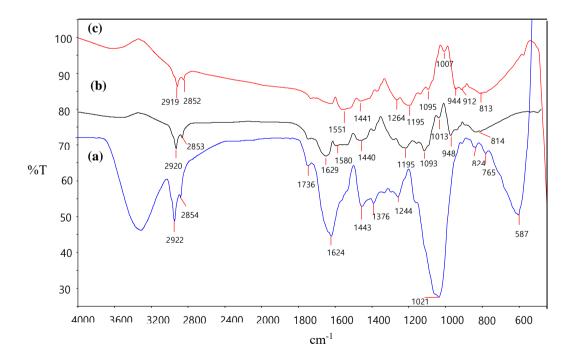


Figure 1. FTIR spectra of (a) AML, (b) Cu(II) loaded AML, and (c) Pb(II) loaded AML

Table 1. FTIR analysis of AML before and after biosorption of the	investigated heavy metal ions
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		Cu(II) ions	Pb(
Wavenumber	Before	After	Differences in	After	Differences in	Assignment	
range (cm ⁻¹)	biosorption	biosorption	shift	biosorption	shift		
3600-3000	3529	3545	+16	3562	+33	-OH and -NH ₂	
1740-1680	1736	1744	+8	1744	+8	-C=O	
1670-1600	1624	1629	+5	1600	-24	-NH and C=C	
1150-1000	1021	1013	-8	1007	-14	-C-O-C	

The broad peak from 3500 to 2500 cm⁻¹ represents the -COOH group. The bands in the range of 2917 to 2851 cm⁻¹ represent vibration stretching of aliphatic C-H groups in alkanes. The band at 1731 cm⁻¹ signifies the –C=O stretching vibration of the carboxylic acid. The bands around 1600 cm⁻¹ correspond to -NH₂ and -C=C- bending vibrations. The strong band at 1020 cm⁻¹ indicates the -C-O-C- group, while the band at 587 cm⁻¹ is assigned to the aromatic ring of =C-H bending (out of the plane). Figure 1 (b and c) displays that the intensity of the peaks decreased or shifted after loading AML with the investigated heavy metal ions, and important functional groups in biosorption are summarised in Table 1. These observations highlighted that carboxyl, amino, hydroxyl and aromatic groups were all involved in heavy metal ions biosorption, and that could occur via electrostatic attraction in addition to complexation interactions (Paragas et al., 2018; Ezeonuegbu et al., 2021).

The pH_{slurry} of AML was 6.34. Carboxylic acid groups were responsible for making AML acidic, as confirmed by the FTIR spectrum. The pH_{PZC} plot is shown in Figure 2, with a value of 5.98. At pH > pH_{PZC}, the AML surface would be more negatively charged, encouraging the biosorption of the investigated heavy metal ions.

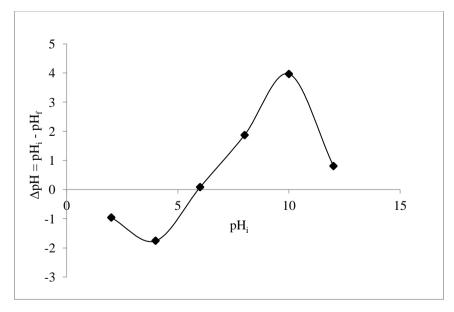


Figure 2. The pH_{PZC} plot of AML

Batch Biosorption Tests

Effects of pH and AML Dose

Figure 3 displays the influence of pH on the biosorption of Cu(II) and Pb(II) ions onto AML. As the pH of the solution was raised from 2 to 5, more heavy metal ions were biosorbed on AML due to the increase of the negatively charged sites on AML (Fig. 2). At pH 2, the q_e value was very low for Pb(II) ions, while it reached zero for Cu(II) ions because the electrostatic repulsion being so great between the protonated functional groups in AML and the investigated heavy metal ions. On the other hand, at pH > 2, AML's deprotonated functional groups, like its carboxyl groups, increased over time and exhibited a stronger propensity to biosorb the investigated heavy ions (Alcaraz et al., 2020). Consequently, the succeeding biosorption tests were directed at pH 5.

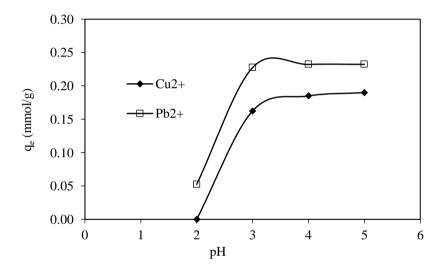


Figure 3. Impact of different pH solutions on biosorption of the investigated heavy metal ions (AML dose: 0.02g; initial heavy metal ions concentration solution: 0.1 mmol/L; working volume: 50 mL; stirring speed: 360 rpm; temperature: 302 K, and contact time: 120 min.).

Figure 4 displays the impact of AML dose on the biosorption of the investigated heavy metal ions. With increasing AML dose, fewer ions were biosorbed onto AML. At higher AML doses, biosorption sites may overlap or aggregate, reducing the available surface area for adsorbates (Kamarudzaman et al., 2022). Thus, for the ensuing kinetics and isotherm experiments, 0.02 g of AML was chosen.

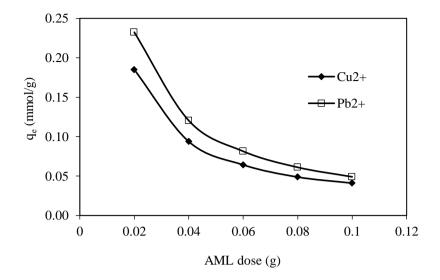


Figure 4. The effect of AML dose on biosorption of the investigated heavy metal ions (initial heavy metal ion concentrations: 0.1 mmol/L; pH 5; working volume: 50 mL; stirring speed: 360 rpm; temperature: 302K, and contact time: 120 min.).

Biosorption Isotherm Studies

Figure 5 compares the biosorption capacity of AML (q_e , mmol/g) to the equilibrium concentrations of the investigated heavy metal ions (C_e , mmol/L). Both heavy metal ions' equilibrium biosorption capacities increased as their initial concentrations increased. This was likely due to an increased mass transfer rate of adsorbates on the biosorbent (Hanafiah et al., 2022). Furthermore, the quantity of Pb(II) ions biosorbed onto AML was higher and more speedily than that for Cu(II) ions may be due to the difference in their hydration energy and electronegativity (Fan et al., 2021). Due to their lower hydration energy (1502 kJ/mol) compared to Cu(II) ions (2121 kJ/mol), Pb(II) ions may start losing all of their hydration water as they diffuse through the AML. Moreover, the Pauling electronegativity of Pb (2.33) is greater than that of Cu (1.90), exhibiting a greater affinity for Pb(II) ions towards the active sites of biosorbents (Fan et al., 2021). Other researchers observed similar findings for the analogous biosorption process using different biosorbents (Kurniawan et al., 2014; Lee & Choi, 2018; Castanho et al., 2021).

Analyses of the biosorption isotherm data shown in Figure 5 were performed using Langmuir (Eq. 2) (Langmuir, 1918) and Freundlich (Eq. 3) (Freundlich, 1926) isotherm models.

$$\frac{c_e}{q_e} = \frac{c_e}{q_{max}} + \frac{1}{K_L q_{max}}$$

$$log q_e = log K_F + \frac{1}{n} log C_e$$
(2)

where q_{max} (mmol/g) is the theoretical biosorption capacity, C_e (mmol/L) is the equilibrium concentration of heavy metal ions, q_e (mmol/g) is the experimental equilibrium biosorption capacity, K_L (L/mmol) is Langmuir isotherm

constant related to the strength of biosorbate-biosorbent collaboration, K_F and n are Freundlich isotherm constant correlated to the biosorption capability and strength, respectively. Linear plots of C_e/q_e and $\ln q_e$ versus C_e , individually, were constructed (Figures not shown).

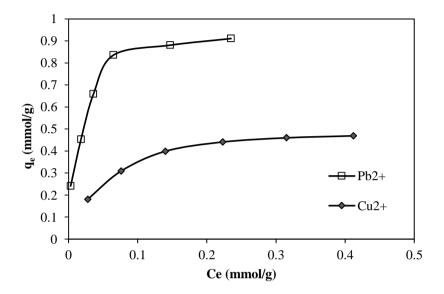


Figure 5. Biosorption isotherm plots of the investigated heavy metal ions using AML (AML dose: 0.02 g; pH 5; working volume: 50 mL; stirring speed: 360 rpm; temperature: 302K, and contact time: 120 min.).

Straight line slopes and intercepts were used to determine the Langmuir (q_{max} and K_L) and Freundlich (K_F and n) constants, as reported in Table 2. It can be seen that the Langmuir isotherm model was well appropriate to the experimental data ($R^2 > 0.95$), confirming the homogeneity of the active sites on AML. The maximum monolayer biosorption capacities of AML to the investigated heavy metal ions were 0.460 mmol/g and 0.911 mmol/g, respectively, which showed greater capacity than other biosorbents found in the literature (Table 3).

Table 2. Biosorption isotherm parameters for the investigated heavy metal ions biosorption using AML

Heavy	q e, exp	q max cal	Langmuir isoth	Freu	Freundlich isotherm model		
Metals	(mmol/g)	(mmol/g)	K_L R ²		K_F	n	R ²
			(L/mmol)		(mmol/g)		
Cu(II)	0.460	0.545	1.180	0.998	0.716	2.811	0.934
Pb(II)	0.911	0.974	0.878	0.951	1.720	3.015	0.900

Table 3. Evaluation of biosorption capacities of the investigated heavy metal ions by various agricultural materials as biosorbents

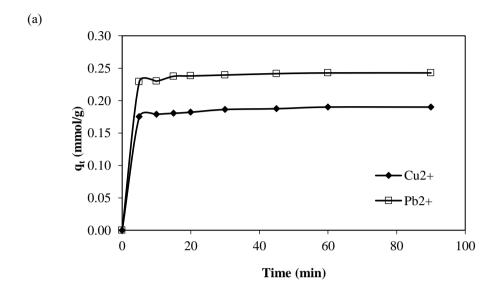
Biosorbent			Cu(II) i	on	Biosorbent	Pb(II) ion				
	Temp. pH q _{max} , Reference			Reference		Temp.	pН	q _{max} ,	Reference	
	(K)		(mg/g)			(K)		(mg/g)		
A. muricata	298	4	4.16	Kurniawan et al.	an et al. Tangerine		5	1.55*	Abdić et al. (2018)	
seeds powder				(2014)	peel					
A. muricata	298	7	6.14	Samin et al.	Soya bean	310	7	0.55	Gaur et al. (2018)	
leaf powder				(2015)						
Roasted date	298	7	$4.88^{\text{@}}$	Mohammed et	Persimmon	298	6	22.59	Lee & Choi (2018)	
pits				al. (2015)	leaves					
Lemon peel	298	3	13.2	Meseldzija et al.	Modified	NM	NM	1.44	Mutiara et al. (2018)	
				(2019)	Jackfruit					
					Wood					
					Sawdust					
Tangerine	298	5	1.63*	Abdić et al.	Modified	303	6	101.35	Krishnamoorthy et	
peel		_		(2018)	date pits				al. (2019)	
Corn cob	313 5 6.24		Kumar et	Mature A.	303 NM		166.67	Paragas et al. (2018)		
				al.(2018)	muricata leaf					
ъ.	200		10.42	T 0 C1 '	powder	200	_	20.06	1.16 . 1.(2021)	
Persimmon			Mixed	308	5	20.96	Ashfaq et al. (2021)			
leaves				(2018)	banana and					
Win and alain a	298	_	16.95	A 1 1	potato peels	298	_	80.80	E1 Amin of al	
Winemaking	298	5	16.93	Alcaraz et al. (2020)	Ludwigia	298	6	80.80	El-Amier et al., (2021)	
wastes				(2020)	stolonifera roots				(2021)	
Shiitake	298	NM	22.7	Castanho et al.	Ludwigia		7	65.52		
stalks			stolonifera		,	03.32				
starks				(2021)	shoots					
Moringa	294	6	23.3	Tokay &	Water	298	5	50.00	Jahangiri et al.	
seeds	271	O	23.3	Akpınar, (2021)	hyacinth	270	3	50.00	(2021)	
seeds				7 inpinui, (2021)	roots				(2021)	
Spent	333	5	0.34	Kamarudzaman	Tobacco	303	1	179.4	Yogeshwaran &	
mushroom			0.0.	et al. (2022)	leaves	202	•	1,,,,	Priya, (2021)	
compost				(= -,					,, (-=-/	
Fresh A.	302	5	29.23	This study	Fresh A.	302	5	188.76	This study	
muricata leaf		-			muricata leaf		-			
powder					powder					

^(*) means that the unit converts from mmol/g to mg/g, NM: Not mentioned, and (®) means that value was provided from the kinetics study.

Biosorption Kinetic Studies

The changes in the quantity of the investigated heavy metal ions biosorbed on AML as time-dependent at two different concentrations of 0.1 and 0.2 mmol/L are shown in Figure 6. The plots showed a very rapid initial biosorption process within the first 5 min where up to 95% of both heavy metal ions were biosorbed onto AML, possibly owing to (i) the abundance of usable biosorption sites and (ii) the high strength of biosorbate-biosorbent interaction (K_L) as shown in Table 2. Afterwards, a dynamic equilibrium biosorption process where only a minor alteration in the quantity of the

investigated heavy metal ions biosorbed was detected by way all available biosorption sites were filled. In addition, the biosorbed of the investigated heavy metal ions increased proportion to their initial concentration. This may be because higher concentrations of the heavy metal ions exert a superior dynamic strength, permitting them to overwhelm the mass transfer resistance between the biosorbent and liquid phase (Hanafiah et al., 2022).



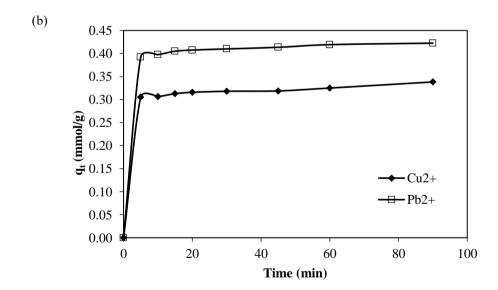


Figure 6. Impact of initial heavy metals concentration and biosorption time on biosorption process by AML at a concentration of **(a)** 0.1 mmol/L and **(b)** 0.2 mmol/L (AML dose: 0,02 g; pH 5; working volume: 50 mL; stirring speed 360 rpm, and temperature: 302K)

Figure 6 shows the results of an analysis of biosorption data using pseudo-first-order (PFO) (Lagergren, 1898) and pseudo-second-order (PSO) (Ho & McKay, 1999) models to inspect further the biosorption rate of the investigated heavy metal ions and their equations are presented as Eqs. (4) and (5), respectively.

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{4}$$

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \tag{5}$$

where q_e and q_t (mmol/g) refer to the amount of heavy metal ions biosorbed at equilibrium and at time t (min) and k_l (1/min) is the overall rate constant of PFO, h is the early biosorption rate and equal to K_2 q_e^2 (where K_2 is the total rate constant of the PSO of biosorption, g/mmol min). Table 4 lists the values for the PFO (q_e , k_l) and PSO (l/h, l/q_e) constants, which were determined by using the intercepts and slopes of straight-line plots of log ($q_e - q_l$) and t/q_l versus t (figures not shown). Noticeably, for the PFO model, the calculated and experimental q_e values were not consistent. Consequently, the PFO model cannot be relied upon to explain the kinetics behaviour of biosorption reactions. The R^2 values close to unity show that the PSO model applies to the biosorption process, and the calculated and experimental values of q_e agree satisfactorily.

Table 4. Parameters of PFO and PSO kinetic models of biosorption of the investigated heavy metal ions on AML at different initial concentrations

Heavy	Conc.	q _e , exp	Pseud	o-first-ord	ler		Pseudo-second-order			
Metals	(mmol/L)	(mmol/L)	q _{e, cal} (mmol/L)	k ₁ (min ⁻¹)	R ²	q_e , $_{cal}$ (mmol/g)	k ₂ (g/mmol min)	h (mmol/g min)	R²	
Cu(II)	0.10	0.190	0.048	0.095	0.743	0.193	0.127	0.175	0.999	
Pb(II)		0.243	0.185	0.079	0.732	0.248	0.097	0.229	1.000	
Cu(II)	0.20	0.338	0.072	0.053	0.647	0.342	0.036	0.305	0.999	
Pb(II)		0.423	0.067	0.033	0.466	0.428	0.028	0.393	0.999	

CONCLUSION

AML showed a rapid biosorption rate and excellent biosorption capabilities for Cu(II) and Pb(II) ions from water-based solutions. The hydroxyl (-OH), amine (-NH₂), carbonyl (-C=O), ether (C-O-C), and carboxyl (-COOH) groups onto AML represented as the functional sites for the investigated heavy metal ions. The results showed that biosorption of Cu(II) and Pb(II) ions by AML was pH dependent. The optimal experimental conditions were pH 5, 0.02 g AML dose, 20 min equilibrium biosorption time and 0.5 mmol/L initial heavy metal ions concentrations. Additionally, the pH_{PZC} value for the AML was 5.98. The amount of Pb(II) ions biosorbed on AML (0.911 mmol/g) was approximately two times that of Cu(II) ions at pH 5, indicating a greater selectivity of AML to Pb(II) than Cu(II) ions. AML has the potential to be a cheap and eco-friendly biosorbent for treating wastewater containing Cu(II) and Pb(II) ions.

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AUTHOR CONTRIBUTIONS

Waheeba A. Al-Amrani: conceptualisation, investigation, methodology, data analysis and writing; Nur Sabarina Syahirah Mohd Fathi: conceptualisation, investigation, methodology; Megat Ahmad Kamal Megat Hanafiah: data analysis, writing, reviewing and proofreading; and Haslizaidi: data analysis and investigation. All authors have read and agreed to the published version of the manuscript.

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COMPETING INTEREST

The authors declare no conflict of interest.

COMPLIANCE WITH ETHICAL STANDARDS

Not applicable.

SUPPLEMENTARY MATERIALS

Not applicable

REFERENCES

Abdić, Š., Memić, M., Šabanović, E., Sulejmanović, J.& Begić, S. (2018). Adsorptive removal of eight heavy metals from aqueous solution by unmodified and modified agricultural waste: tangerine peel. International Journal of Environmental Science and Technology, 15(12), 2511-2518 http://doi.org.10.1007/s13762-018-1645-7

Ahmad, A., Rafatullah, M., Sulaiman, O., Ibrahim, M. H., Chii, Y. Y.& Siddique, B. M. (2009). Removal of Cu(II) and Pb(II) ions from aqueous solutions by adsorption on sawdust of Meranti wood. Desalination, 247(1), 636-646 https://doi.org/10.1016/j.desal.2009.01.007

Alcaraz, L., Garcia-Diaz, I., Alguacil, F. J.& Lòpez, F. A. (2020). Removal of copper ions grom wastewater by adsorption onto a green adsorbent from winemaking wastes. Bioresources, 15(1), 1112-1133

Amanda, L., Geoffrey D., F.& Nigel J.D., G. (2021). Insights into chemical regeneration of activated carbon for water treatment. Journal of Environmental Chemical Engineering, 9, 105555 https://doi.org/10.1016/j.jece.2021.105555

Ashfaq, A., Nadeem, R., Bibi, S., Rashid, U., Hanif, M. A., Jahan, N., Ashfaq, Z., Ahmed, Z., Adil, M.& Naz, M. (2021). Efficient Adsorption of Lead Ions from Synthetic Wastewater Using Agrowaste-Based Mixed Biomass (Potato Peels and Banana Peels). Water, 13(23), 3344

Castanho, N. R. C. M., de Oliveira, R. A., Batista, B. L., Freire, B. M., Lange, C., Lopes, A. M., Jozala, A. F.& Grotto, D. (2021). Comparative Study on Lead and Copper Biosorption Using Three Bioproducts from Edible Mushrooms Residues. Journal of Fungi, 7(6), 441

Chuanbin, W., Xutong, W., Ning, L., Junyu, T., Beibei, Y., Xiaoqiang, C.& Guanyi, C. (2022). Adsorption of Lead from Aqueous Solution by Biochar: A Review. Clean Technol., 4, 629-652 https://doi.org/10.3390/cleantechnol4030039

El-Amier, Y. A., Elsayed, A., El-Esawi, M. A., Noureldeen, A., Darwish, H.& Fakhry, H. (2021). Optimising the Biosorption Behavior of Ludwigia stolonifera in the Removal of Lead and Chromium Metal Ions from Synthetic Wastewater. Sustainability, 13(11), 6390

Ezeonuegbu, B. A., Machido, D. A., Whong, C. M. Z., Japhet, W. S., Alexiou, A., Elazab, S. T., Qusty, N., Yaro, C. A.& Batiha, G. E.-S. (2021). Agricultural waste of sugarcane bagasse as efficient adsorbent for lead and nickel removal from untreated wastewater: Biosorption, equilibrium isotherms, kinetics and desorption studies. Biotechnology Reports, 30, e00614 https://doi.org/10.1016/j.btre.2021.e00614

Fan, X., Liu, H., Anang, E.& Ren, D. (2021). Effects of electronegativity and hydration energy on the selective adsorption of heavy metal Ions by synthetic NaX zeolite. Materials, 14, 4066 https://doi.org/10.3390/ma14154066 Freundlich, H. (1926). Colloid and Capillary Chemistry. Methuen, London.

Gaur, N., Kukreja, A., Yadav, M.& Tiwari, A. (2018). Adsorptive removal of lead and arsenic from aqueous solution using soya bean as a novel biosorbent: equilibrium isotherm and thermal stability studies. Applied Water Science, 8(4), 98 http://doi.org/10.1007/s13201-018-0743-5

Haidong, H.& Ke, X. (2020). Chapter 8 - Physicochemical technologies for HRPs and risk control. In H. Ren & X. Zhang (Eds.), *High-Risk Pollutants in Wastewater* (pp. 169-207): Elsevier.

Hanafiah, M. A. K. M., Nurul Amira, A. B., Al-Amrani, W. A., Ibrahim, S., Nik Malek, N. A. N.& Jawad, A. H. (2022). Preparation, characterisation and application of sulphuric acid-treated soursop (*Annona muricata L.*) seeds powder in the adsorption of Cu(II) ions. Nature Environment and Pollution Technology, 21(1), 217-223 https://doi.org/10.46488/NEPT.2022.v21i01.024

Ho, Y. S.& McKay, G. (1999). Pseudo-second order model for sorption processes. Proc. Biochem, 34(5), 451-465 https://doi.org/10.1016/S0032-9592(98)00112-5.

Ilia, I., Torun, B., Sergey, D.& Jozef, P. (2003) EMEP Assessment Report - Part I, (Heavy metals): (Chapter 7).

Jahangiri, F. M., Moutushi, H. T., Moniruzzaman, M., Hoque, S.& Hossain, M. E. (2021). Removal of lead from aqueous solutions and wastewaters using water hyacinth (Eichhornia crassipes) roots. Water Practice and Technology, 16(2), 404-419 http://doi.org/10.2166/wpt.2021.005

Kamarudzaman, A. N., Adan, S. N. A. C., Hassan, Z., Ab Wahab, M., Makhtar, S. M. Z., Abu Seman, N. A., Ab Jalil, M. F., Handayani, D.& Syafiuddin, A. (2022). Biosorption of copper(II) and iron(II) using spent mushroom compost as biosorbent. Biointerface research in applied chemistry, 12(6) https://doi.org/10.33263/BRIAC126.77757786

Krishnamoorthy, R., Govindan, B., Banat, F., Sagadevan, V., Purushothaman, M.& Show, P. L. (2019). Date pits activated carbon for divalent lead ions removal. Journal of Bioscience and Bioengineering, 128(1), 88-97 https://doi.org/10.1016/j.jbiosc.2018.12.011

Kumar, G. V. S. R. P., Rao, K. S., Yadav, A., Kumar, M. L.& Sarathi, T. V. N. P. (2018). Biosorption of copper(II) and manganese(II) from waste water using low cost bio adsorbents. Journal of Indian Chemical Society, 95, 1-8

Kurniawan, M. I., Abdullah, Z., Rahmadani, A., Zein, R.& Munaf, E. (2014). Isotherm and kinetic modeling of Pb(II) and Cu(II) uptake by *Annona muricata L.* seeds. Asian Journal of Chemistry, 26(12), 3588-3594 http://dx.doi.org/10.14233/ajchem.2014.16515

Lagergren, S., Svenska, B.K. (1898). Zurtheorie der sogenannten adsorption geloesterstoffe. Veternskapsakad Handlingar, 24, 1-9

Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. J. Am. Chem. Soc, 40(9), 1361e1403 https://doi.org/10.1021/ja02242a004

Lee, S.-Y.& Choi, H.-J. (2018). Persimmon leaf bio-waste for adsorptive removal of heavy metals from aqueous solution. Journal of Environmental Management, 209, 382-392 https://doi.org/10.1016/j.jenvman.2017.12.080

Liu, T., Lawluvy, Y., Shi, Y., Ighalo, J. O., He, Y., Zhang, Y.& Yap, P.-S. (2022). Adsorption of cadmium and lead from aqueous solution using modified biochar: A review. Journal of Environmental Chemical Engineering, 10, 106502 https://doi.org/10.1016/j.jece.2021.106502

Mamta, P.& Dhriti, K. (2021). Heavy Metals in the Environment. V. Kumar, A. Sharma & A. Cerdà (Eds.), Heavy metals in the ecosystem: Sources and their effects: Elsevier

Meseldzija, S., Petrovic, J., Onjia, A., Volkov-Husovic, T., Nesic, A.& Vukelic, N. (2019). Utilisation of agroindustrial waste for removal of copper ions from aqueous solutions and mining-wastewater. Journal of Industrial and Engineering Chemistry, 75, 246-252 https://doi.org/10.1016/j.jiec.2019.03.031

Mohammed, T. J., Azeez, R. A.& Lutffe, T. (2015). Biosorption of copper from synthesised wastewater using agriculture waste (Roasted date pits)india International Journal of Recent Scientific Research 6(3), 3063-3068

Mutiara, T., Rofiki, I.& Al Ghifari, M. A. D. (2018). Bio adsorbent from modified jackfruit wood sawdust for removal of lead ions. Materials Science Forum, 934 159-164 http://doi:10.4028/www.scientific.net/MSF.934.159

Paragas, D. S., Alejandro, G. S.& Pascual, M. S. (2018). Effect of different preparations of *Annona muricata L*. leaves on the biosorption of lead, nickel and zinc from aqueous solution. International Journal of Advanced Research, 6(4), 1175-1183 http://dx.doi.org/10.21474/IJAR01/6967

Samin, B., Fachrial, E., Almahdy, Munaf, E., Refilda, Chaidir, Z.& Zein, R. (2015). Adsorption profile of Cu (II) using soursop (Annona muricata L) leaves powder as biosorbent. Journal of Chemical and Pharmaceutical Research, 7(95), 22-27

Tokay, B.& Akpınar, I. (2021). A comparative study of heavy metals removal using agricultural waste biosorbents. Bioresource Technology Reports, 15, 100719 https://doi.org/10.1016/j.biteb.2021.100719

Yogeshwaran, V.& Priya, A. K. (2021). Adsorption of lead ion concentration from the aqueous solution using tobacco leaves. Materials Today: Proceedings, 37, 489-496 https://doi.org/10.1016/j.matpr.2020.05.467

Zafar, S., Khan, M. I., Lashari, M. H., Khraisheh, M., Almomani, F., Mirza, M. L.& Khalid, N. (2020). Removal of copper ions from aqueous solution using NaOH-treated rice husk. Emergent Materials, 3(6), 857-870 http://doi.org/10.1007/s42247-020-00126-w