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Biosorption of Pb(II), Cu(II) and Cd(II) from Aqueous Solution Using Cassava Peel Waste Biomass

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The research of biomass modification from cassava peel waste (*Manihot esculenta crans*) with nitric acid and mercaptoacetic acid has been carried out. The result of biomass modification was used as adsorbent of single and multiple metal ions Pb(II), Cu(II) and Cd(II). Adsorption capacities of metal ions adsorbed (mg g^{-1} adsorbent) were optimum at pH around 4 and 5. From thermodynamic data the adsorption capacities for metal ions Pb(II), Cu(II) and Cd(II) on biomass modified by 1.0 M mercaptoacetic acid are higher than on biomass modified by 0.5 M mercaptoacetic acid and on biomass activated by HNO_3, with the order of the adsorption capacities for each metal ion as follow; Pb(II) > Cu(II) > Cd(II). Adsorption energies of the metal ions Pb(II), Cu(II) and Cd(II) on cassava peel biomass modified by mercaptoacetic acid and activated by HNO_3 are at a range of 13.239-22.972 kJ mol^{-1}, forming physical adsorption. On the multiple metal adsorption, Pb(II) ion competitions toward adsorbent are higher than Cu(II) and Cd(II) ions on biomass modified by mercaptoacetic acid and activated by HNO_3.

Key Words: Cassava, Biomass, Adsorption, Modification.

INTRODUCTION

The contamination of heavy metals in our environment as a major problem has been increasing gradually as a result of industrial activities and technological development, posing a significant threat to the environment and public health because of their toxicity, accumulation in the food chain and persistence nature[1-3]. Some of heavy metals from industrial waste water such as Cd, Pb and Cu may not be degraded biologically and chemically[4-6]. Several techniques have been developed to minimize the heavy metal ion concentration from waste water such as chemical precipitation, ion exchange, evaporation, electroplating and membrane processes, but these are very expensive[7-9]. One of the alternative techniques is an adsorption method using biological materials as adsorbent (such as agricultural by-products, fungi, algae biomass and others biological materials), mainly because of its low cost, high metal binding capacity, high efficiency in dilute effluent and environmental friendly[9-11].

The use of agricultural by-products for the removal of heavy metal from wastewater has continued in recent years because they are simple, cheap and low cost[12-14]. One of biomass material from agriculture product which is not still used, but it has good potential as heavy metal adsorbent, is cassava peel waste, because it contains non reduction cellulose which is effective to bind metal ions. Cassava waste biomass reduced Cd(II), Cu(II) and Zn(II) single ion concentration from aqueous solution[15]. Activation of cassava waste biomass using nitric acid showed uptake capacities of two metal ions around 85 mg g^{-1} adsorbent for Cu(II) ion and 60 mg g^{-1} for Zn(II) ion. Binding of these metal ions can occur because there are hydroxyl and sulphydryl group on cassava peel biomass[16]. Cassava peel biomass is agriculture product waste and it is abundance in all provinces of Indonesia.

Modification of biomass from cassava waste biomass was also reported by Abia *et al.*[17] using thioglycollic acid solution and showed that there was adsorption capability increasing upon metal ions Cd(II), Cu(II) and Zn(II) by using 0.5 M thioglycollic acid and 0.1 M thioglycollic acid if compared by inactivated biomass[17]. Furthermore, Horsfall and his team studied effect of mercaptoacetic acid to activate cassava waste biomass[18]. The result showed that adsorption capabilities of cassava waste biomass to bind metal ions Cu(II) and Cd(II) increase after modified by mercaptoacetic acid at 0.5 M concentration.

In this paper, investigation of cassava peel waste adsorption modified by mercaptoacetic acid and HNO_3 in single and multiple metal ion solution as an adsorbent for the sorption of Pb(II), Cd(II) and Cu(II) ions from aqueous solution is reported.

EXPERIMENTAL

Biomass preparation: Cassava was cleaned and washed by deionized water, air-dried, cut into 5 cm pieces and peeled to get the cassava peeling wastes. The cassava peel wastes were ground using food processor (Philips 2000), dried in an oven at 105 °C (Heraeus) for 24 h and then screened through a 100-mesh Tyler screen to obtain a good quality of biomass.

Activation and modification of biomass: The biomass obtained was activated by soaking 500 g biomass in excess 0.3 M HNO_3 for 24 h to remove any debris or soluble biomolecules that might interact with metal ions, followed by washing thoroughly with deionized water up to obtained pH of 7.1 and then dried in the air. The biomass activated was grouped into two parts. The first part was left untreated and the second part (1 g) was added 250 mL of 0.5 M mercapto-acetic acid and 1.0 M mercaptoacetic acid, followed by stirring for 24 h at temperature of 30 °C while maintaining a pH of 7.1.

Effect of pH: In all the sets of experiments, 25 mL of metal ion solutions was mixed with 20 mg biomass in bottle at optimum conditions and then system pH was adjusted at various pHs of 3, 4, 5, 6, 7 and 8. The mixture was shaken using shaker for 1 h. The supernatant solution obtained was analyzed by AAS.

Adsorption process of biomass with metal ions: Adsorption process was carried out using 3 kinds of adsorbents namely; cassava peel biomass before and after activated by mercaptoacetic acid (Adsorbent: SK_1 = activated by HNO_3, SK_2 = activated by mercaptoacetic acid 0.5 M, SK_3 = activated by mercaptoacetic acid 1.0 M). The batch technique absorption is applied in present studies. Reaction tube was filled by adsorbent and then it was added metal ion solution with various variables as parameters investigated. Then, it was shaken and centrifuged to separate filtrate and deposit. Filtrate was taken and analyzed by an atomic absorption spectrophotometer (AAS) model Perkin-Elmer 3110.

Effect of single metal ion concentration: For determining adsorption capacity, 25 mL of metal ion Pb(II) was used with different concentrations; 0, 20, 40, 80, 100 mg L^{-1} and they was interacted in bottle obtained 20 mg of biomass and then adjusted up to pH of 5. After that, mixture between the metal ion and the biomass was shaken by 1 h and left over night. This experiment was also conducted for metal ion Cu(II) and Zn(II).

Multiple metal ion adsorptions: For determining capacities and adsorption energies of multiple metal ion, it was used 25 mL of multiple metal ions Pb(II), Cu(II) and Cd(II) with various concentrations; 0, 20, 40, 80, 100 mg L^{-1}. They were interacted in bottle obtained 20 mg of biomass at the interaction time of 60 min, the system pH of 5 and the temperature of 30 °C and they were left a nigh. Finally, a supernatant solution obtained was measured by AAS.

RESULTS AND DISCUSSION

Effect of pH: The effect of pH on the adsorption of metal ions on cassava peel waste adsorbent SK_1, SK_2 and SK_3 can be seen in Figs. 1-3. Adsorption capacities (metal ion adsorbed (mg g^{-1} adsorbent)) were analyzed over a range pH 3.0-8.0. They were apparent from the results that the metal adsorption depends on pH. As the pH increased from 3.0-5.0, adsorption capacity increased. Adsorbent material of this experiment primarily contains weak basic from functional group -SH. This can be explained by the theory of acid-base equilibria, in the pH range 3.0-5.0 and in this range the binding of heavy metal cations is determined primarily by the state of dissociation of weak basic groups. At low pH conditions allow hydrogen and hydronium ions to compete with Pb(II), Cu(II) and Cd(II) for metal-binding sites on the cassava peel biomass adsorbent, causing low adsorption of Pb(II) for pH 3-4, Cu(II) for pH 3 and Cd(II) pH 3-4. At pH values of 4-5, there are lower numbers of competing hydrogen ions and more ligands are exposed

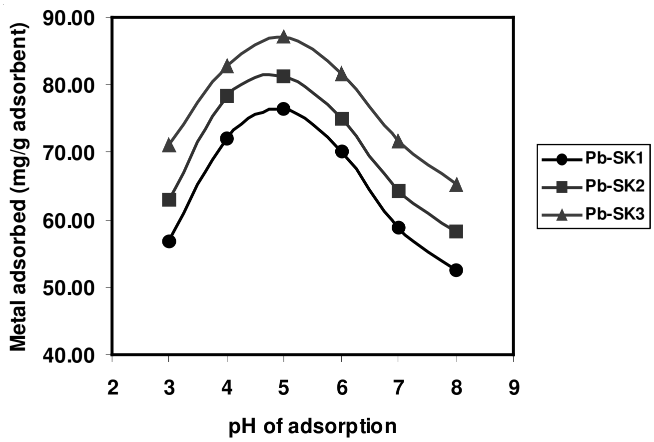

Fig. 1. Effect of pH upon Pb(II) adsorption

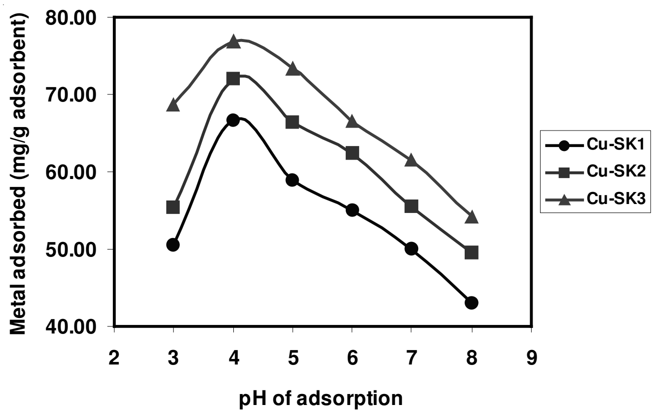

Fig. 2. Effect of pH upon Cu(II) adsorptiont

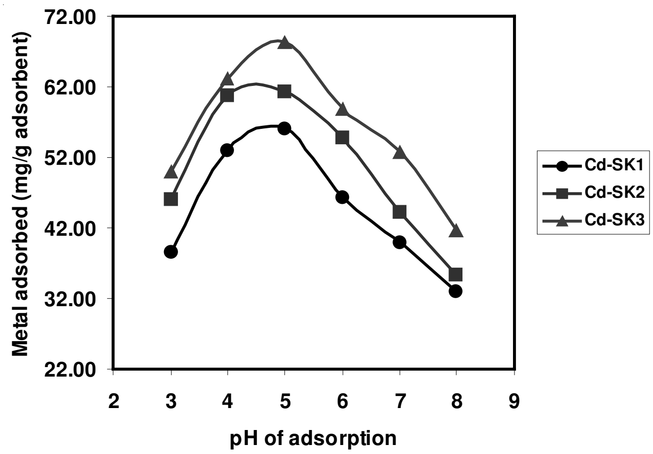

Fig. 3. Effect of pH upon Cd(II) adsorption

with negative charges, resulting in the higher Pb(II), Cu(II) and Cd(II) ion sorption. It can be explained that at pH below 4 or 5, the overall surface charge on the cells of biomass became positive charge, which inhibited the approach of positively charge Pb(II), Cu(II) and Cd(II) cations[19-21]. At the pH above 5, the hydroxyl complexes were formed which may cause decrease in adsorption capacity[22,23]. This result is consistence with the result of Riaz *et al.* using cotton waste biomass[1].

Adsorption of metal ions: Thermodynamic study was applied using isotherm adsorption of cassava peel biomass SK_1, SK_2 and SK_3 upon metal ions Pb(II), Cu(II) and Cd(II) determining some parameters, *i.e.*, adsorption capacity (n_m), adsorption equilibrium constants (K) and adsorption energy (E). Calculation was based on adsorption data of metal ion at various concentrations (Figs. 4-6) with using an equation proposed by Langmuir below:

$$C/n = 1/n_mK + C/n_m$$

where, C is the equilibrium concentration (mg L^{-1}) and n is the adsorbed amount of metal ion per gram of biomass at equilibrium (mg g^{-1} biomass). n_m is the maximum amount of metal ion per unit weight of biomass to form a complete mono layer on the surface bound at high C (mg g^{-1} biomass). K is constant related to the affinity of the binding sites (L mg^{-1}).

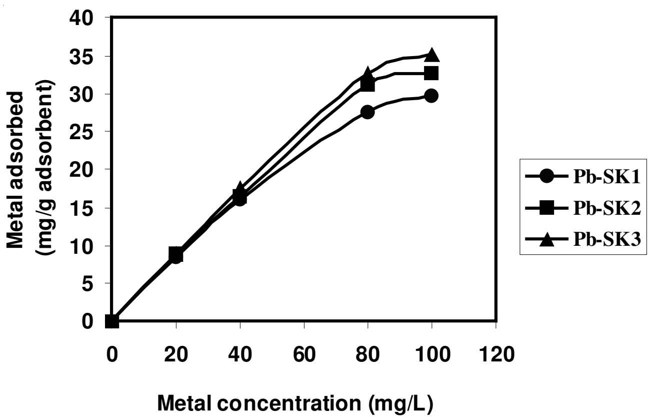

Fig. 4. Effect of Pb(II) ion concentration *versus* amount of ion adsorbed (mg g^{-1} adsorbent)

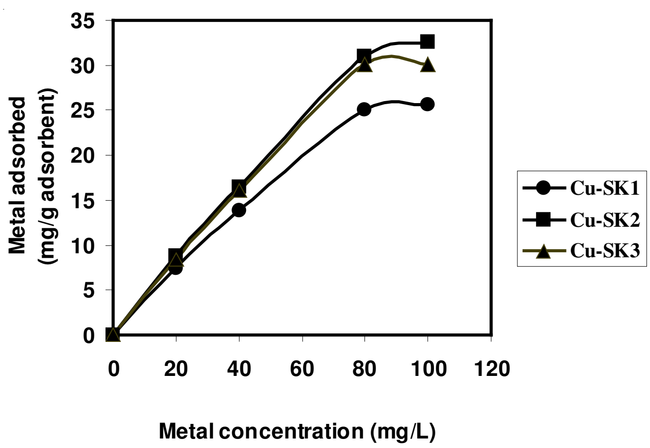

Fig. 5. Effect of Cu(II) ion concentration *versus* amount of ion adsorbed (mg g^{-1} adsorbent).

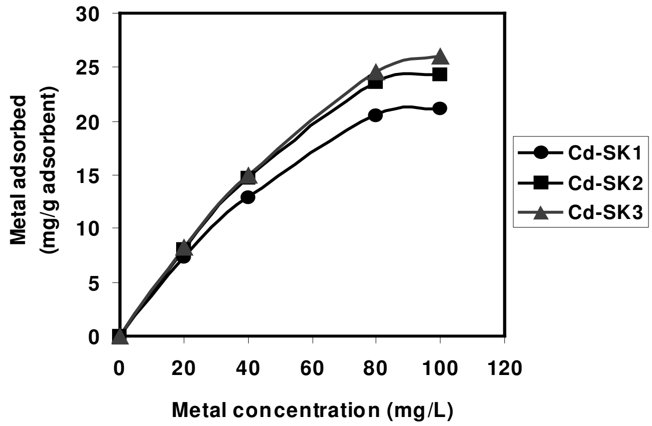

Fig. 6. Effect of Cd(II) ion concentration *versus* amount of ion adsorbed (mg g^{-1} adsorbent)

A plot of C/n *versus* C indicates a straight line of slope $1/n_m$ and an intercept of $1/n_mK$, therefore the Langmuir constant (K) and the maximum adsorption capacity (n_m) are determined by intercept and slope[24]. While, the values of adsorption energies are identified based on Gibbs free energy change equation, below:

$$\text{Adsorption energy} = \Delta G^o \text{ ads} = -R\,T \ln K$$

where, R is gas constant (8.314 JK^{-1} mol^{-1}) and T is temperature in Kelvin (K).

Result of calculation was obtained value of some thermodynamic parameters as listed in Table-1.

TABLE-1
LANGMUIR PARAMETERS ON ADSORPTION PROCESSES OF Pb(II), Cu(II) and Cd(II) ON CASSAVA PEEL BIOMASS ACTIVATED BY 0.3 M HNO_3 (SK_1), MERCAPTOACETIC ACID 0.5 M (SK_2) AND MERCAPTOACETIC ACID 1.0 M (SK_3) AT 30 ºC

Metal-Adsorbent	R^2	n_m (μmol g^{-1})	K (10^3) (L mg^{-1})	E (kJ mol^{-1})
Pb-SK_1	0.942	294.118	1.984	18.938
Pb-SK_2	0.951	322.581	2.460	19.475
Pb-SK_3	0.944	357.143	2.566	13.837
Cu-SK_1	0.920	270.270	1.248	17.783
Cu-SK_2	0.960	285.714	2.212	19.210
Cu-SK_3	0.940	303.030	10.000	22.972
Cd-SK_1	0.964	208.333	1.627	18.444
Cd-SK_2	0.973	238.095	2.060	19.033
Cd-SK_3	0.967	256.410	0.201	13.239

From the Table-1, it can be observed that adsorbent capabilities of SK_2 and SK_3 to adsorb metal ions are higher than adsorbent of SK_1. These show that SK_2 and SK_3 after modified by mercaptoacetic acid have functional groups which are more relatively active in binding metal ions. Modification of cassava peel biomass (B) with mercaptoacetic acid produces –SH (sulphuhydril) group with reaction as follow:

$$\text{Biomass-OH} + HSCH_2CO_2H \rightarrow \text{Biomass-SH} + H_3CO_2^- + H^+$$

$$B\text{-}CH_2OH + HSCH_2CO_2H \xrightarrow[\text{HO}\ddot{N}H_2]{H^+} B\text{-}CH_2\text{-}S\text{-}CH_2CO_2H + H_2O$$

$$B\text{-}CH_2\text{-}S\text{-}CH_2CO_2H \rightarrow B\text{-}CH_2\text{-}SH + HONH\text{-}CH_2CO_2H$$

Existence of -SH group causes metal ions which have characteristic as borderline acid and soft acid can be adsorbed well, because -SH group is soft acid. At the adsorbent of SK_1, the available of functional group is only -OH group characterized as a hard base. Base on hard and soft acid base concept, the hard acid will interact strongly with the hard base and the soft acid will interact strongly with the soft base[13]. After cassava peel biomass modified by mercaptoacetic acid, Pb(II), Cu(II) and Cd(II) occur an increasing of adsorption capacity because there is -SH group which enables the metal ions (Mn^+) characterized as borderline acid [Pb(II) and Cu(II)] and as soft acid [Cd(II)], they will interact strongly with adsorbent through the group as reaction below:

$$M^{n+} + B\text{-}CH_2\text{-}SH \rightarrow (B\text{-}CH_2\text{-}S)_n - M + H^+$$

Adsorption energies of Pb(II), Cu(II) and Cd(II) on the adsorbent of SK_1, SK_2 and SK_3 are around 13.239-22.972 kJ mol^{-1}. These adsorption energies are too small to be identified as chemical bond energy and they are bigger if observed as physical induction. Chemical bond energy is usually higher than 40 kJ mol^{-1} as a covalent bond and an electrostatic interaction, while induction energy[25] is smaller than 10 kJ mol^{-1}. Therefore, it can be concluded that generally, the occurred adsorption on the metal ions is physical adsorption. These are in accordance with a research result obtained by Horsfall *et al.*[18], stating that adsorption process of metal ion Cu (II) and Cd (II) on cassava biomass is physical adsorption with an energy range of 8-16 kJ mol^{-1}.

To determine metal ion competition on cassava peel biomass of SK_1, SK_2 and SK_3, it was tested with using multiple metal solutions consisting of Pb(II), Cu(II) and Cd(II) at the interaction time of 60 min, the temperature of 30 °C and the pH of 5. The result obtained is shown in Figs. 7-9.

The calculation based on adsorption data of multiple metal ions at various concentrations (Figs. 7-9) using equation proposed by Langmuir[24] followed by Davydov[26] and Jin *et al.*[27]. The obtained data is listed in Table-2. If compared with adsorption capacity value of single metal ion and multiple metal ions as listed in Table-3, it can be observed that the adsorption capacity value of the multiple metal ions on the same adsorbents is lower than the single metal ion. If compared at the same conditions on the single metal adsorption process, it will be observed that each metal ion occur decreasing of adsorption, as presented in Table-3. These occur because on multiple metal adsorption occurs competatively among metals causing a binding more than one metal ion on adsorbent active cites.

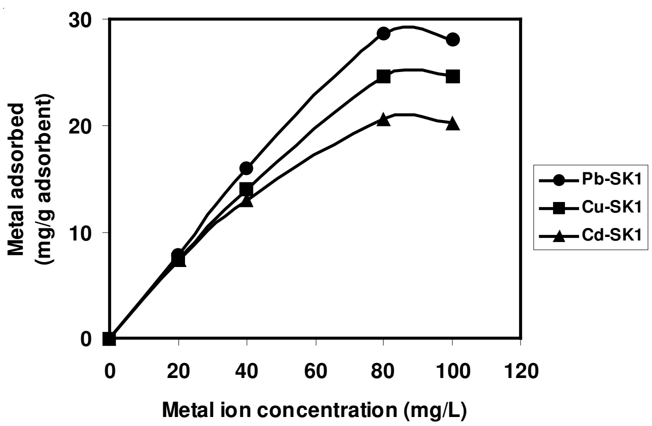

Fig. 7. Effect of multiple metal ion concentrations [Pb(II), Cu(II) and Cd(II)] *versus* amount of ions adsorbed (mg g^{-1} adsorbent SK_1)

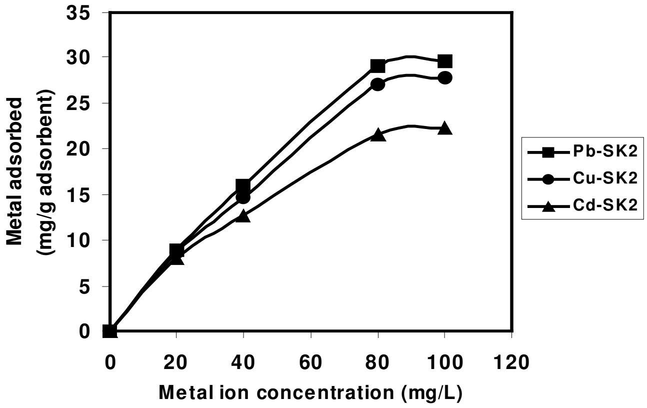

Fig. 8. Effect of multiple metal ion concentrations [Pb(II), Cu(II) and Cd(II)] *versus* amount of ions adsorbed (mg g^{-1} adsorbent SK_2)

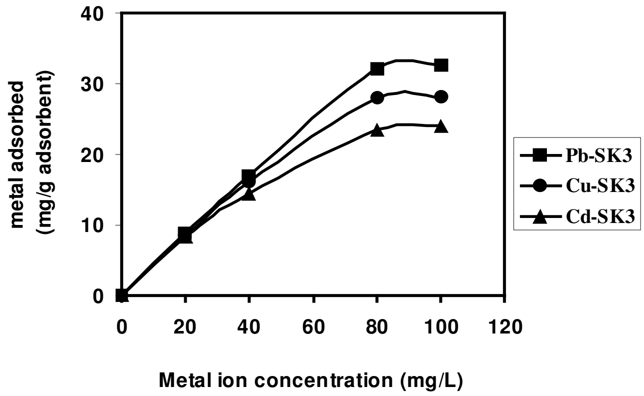

Fig. 9. Effect of multiple metal ion concentrations [Pb(II), Cu(II) and Cd(II)] *versus* amount of ions adsorbed (mg g^{-1} adsorbent SK_3)

TABLE-2
LANGMUIR PARAMETERS ON ADSORPTION PROCESSES OF MULTIPLE METAL IONS Pb(II), Cu(II) AND Cd(II) ON CASSAVA PEEL BIOMASS ACTIVATED BY 0.3 M HNO_3 (SK_1), 0.5 M MERCAPTOACETIC ACID (SK_2) AND 1.0 M MERCAPTOACETIC ACID (SK_3) AT 30 ºC

Metal-Adsorbent	R^2	n_m (μmol g^{-1})	K (10^3) (L mg^{-1})	E (kJ mol^{-1})
Adsorbent SK_1				
Pb	0.937	274.118	1.753	18.816
Cu	0.926	256.410	1.363	18.182
Cd	0.969	200.000	0.182	13.107
Adsorbent SK_2				
Pb	0.966	294.118	2.642	19.849
Cu	0.965	277.778	1.977	19.119
Cd	0.958	217.391	0.179	13.067
Adsorbent SK_3				
Pb	0.961	330.581	2.810	20.005
Cu	0.964	277.778	2.277	19.475
Cd	0.976	232.558	2.241	13.634

Conclusion

Adsorption capacities of metal ions adsorbed (mg/g adsorbent) were optimum at pH around 4 and 5. Adsorption capacities for Pb(II), Cu(II) and Cd(II) ions on cassava peel biomass modified by mercaptoacetic acid 1.0 M are highest than on cassava peel biomass modified by 0.5 M mercaptoacetic acid and on cassava peel biomass activated by nitric acid, with the order; Pb(II) > Cu(II) > Cd(II) on each adsorbent, respectively.

TABEL-3
LANGMUIR PARAMETERS ON ADSORPTION PROCESSES OF METAL IONS Pb(II), Cu(II) AND Cd(II) ON CASSAVA PEEL BIOMASS ACTIVATED BY 0.3 M HNO_3 (SK_1), 0.5 M MERCAPTOACETIC ACID (SK_2) AND 1.0 M MERCAPTOACETIC ACID (SK_3) AT 30 ºC

Metal-Adsorbent	Single metal ion n_m (μmol g^{-1})	Multiple metal ion n_m (μmol g^{-1})
Adsorbent SK_1		
Pb	294.118	274.118
Cu	270.270	256.410
Cd	208.333	200.000
Adsorbent SK_2		
Pb	322.581	289.118
Cu	285.714	277.778
Cd	238.095	217.391
Adsorbent SK_3		
Pb	357.143	330.581
Cu	303.030	277.778
Cd	256.410	232.558

Adsorption energies on Pb(II), Cu(II) and Cd(II) on cassava peel biomass modified by mercaptoacetic acid and on cassava peel biomass activated by nitric acid are around 13.239-22.927 kJ mol^{-1}, forming physical adsorption. On the adsorption of multiple metal ions, competition of metal ion Pb(II) toward adsorbent is higher than Cu(II) ion, as well as Cd(II) ion on cassava peel biomass modified by mercaptoacetic acid and on cassava peel biomass activated by nitric acid.

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