Adsorption of Lead and Copper Using Water Hyacinth Compost (*Eichornia Crassipes*)

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ABSTRACT

Adsorption of heavy metals, Pb and Cu, has been carried out using compost from plant water hyacinth *(Eichornia crassipes).* First step of the composting was fermentation of fresh hyacinth plants with molasses and water. Once formed, the compost was used as an adsorbent for the adsorption of Pb and Cu. The water hyacinth compost was then characterized to determine the humic acid content, as well as the functional groups Determination of optimum conditions on the adsorption of Pb and Cu was performed with adsorbent mass variations, variations in pH, and the concentration variation. Adsorption isotherm was also determined. The results showed that the adsorption of Pb optimally occurs using 1.2 g of adsorbent mass of 1.2 g at solution pH of 5. As for the adsorption of Cu, the optimum adsorption conditions occur in the adsorbent mass of 0.8 g at pH 6. At the optimum conditions, the compost could adsorb 95.13% Pb and up to 91.42% Cu. Pb and Cu adsorption using adsorbents of water hyacinth compost followed Langmuir model.

Key words: compost, water hyacinth (*Eichornia crassipes*), adsorption, isoterm adsorption

INTRODUCTION

Indonesian waters are now polluted by heavy metals, mostly due to industrial activities. If the waste from industrial activity is not treated and discharged directly into the water bodies such materials will contaminate the surrounding environment. Heavy metals into the water system will undergo by three processes namely precipitation, dilution and dispersion, then absorbed by organisms that live in these waters [1]. Mature leaf compost has the ability to reduce the dissolved heavy metals through cation exchange process [2]. Compost from garden waste mainly foliage has been shown to have a high ability to adsorb heavy metals, oils, fats, nutrients, and harmful organic substances from the water because of its high content of compost and the large of absorption surface area [3]. The compost consisting of humic acid, fulvic acid and humin has ability for forming metal complexes through cation exchange, chelate formation and the formation of electrostatic bonds [2]. Because of the carboxyl group (-COOH) on humic which can bind to the cation, the compost can be categorized as a weak acid cation exchanger [2].

Adsorption is a process which a component moves from one phase to the surface of another phase, the second phase is the substance primarily solid. In adsorption process, the adsorbent is a substance that has the character of binding molecules on its surface in the porous solids. Several requirements that must be met by the adsorbent are to have a large surface area, porous, active and pure, and does not react with the adsorbate [4].

In general, the adsorption can be divided into two types: physical adsorption and chemical adsorption. Physical adsorption is adsorption caused by the interaction between the adsorbent and the adsorbate on the surface because of the van der Walls attractive forces or hydrogen bonds [5].The adsorption is characterized by low adsorption heat of 10,000 calories per mole of adsorbate and reversible adsorption equilibrium and equilibrium can be achieved quickly [5]. Chemical adsorption involving strong interaction between adsorbate with adsorbent, thus not free to move from one part to another part of the surface. This adsorption is not reversible, adsorbents should be heated at high temperatures to separate the adsorbate, requires thermal activation and adsorption energies ranging from 20,000 to 100,000 calories per mole of adsorbate [6].

Adsorption capacity is affected by several factors such as contact time, pH, concentration of adsorbate and adsorbente mass. This research was focused on studying the adsorption factors include, adsorbent mass, pH, and adsorbate concentration on the adsorption of Pb (II) and Cu (II) by water hyacinth compost adsorbent. Mass of adsorbent and contact time will affect the adsorption process, in which the mass of adsorbent required depends on the concentration of the adsorbate. The higher the concentration of the adsorbate, the greater the mass of adsorbent required for the adsorption process. Sufficient contact time allows diffusion process and attachment of adsorbate molecules will be able to run well [7].

According to [8], wastewater pH effect on the solubility of heavy metals. Solution that is too acidic will affect the adsorption capacity, the higher the acid pH adsorbate adsorbed increases. Initial concentration is crucial because it affects the rate of diffusion. Diffusion process tends to concentration. Adsorption capacity is affected by the nature of the adsorbent. Porous structure of the adsorbent related to the surface area, the smaller the pores of adsorbent will result in the greater surface area, the selective adsorption, and shall bind strongly to substances to be separated physically or chemically. Thus the adsorption rate will increase. Adsorption kinetics can be described by Langmuir, and Freundlich isotherm models. Freundlich theory assumes that the surface of porous adsorbent is heterogeneous with different heat distribution is not the same [9].

This study was aimed to determine the character of the water hyacinth compost (*Eichornia crassipes*) by FTIR and analysis of humic acid and metal content in water hyacinth compost, and studies the effect of adsorbent mass, pH and adsorbate concentration on the adsorption process of Pb and Cu using adsorbents of water hyacinth compost by batch method. Determination of interactions between the adsorbate adsorbent was determined by Langmuir and Freundlich adsorption isotherm.

EXPERIMENT

Equipment and Materials

The tools used were the bins enumerator tool, containers for composting could be a wooden box the size of 1m x 1m x 1m, scales, thermometer, strainer / sieve, analytical balance, plastic bottles, glass beaker, erlenmeyer, test tube, separating funnel, flask, porcelain cup, stop watch, oven, clamps, filter paper, shakers, centrifuges, pH meters, and AAS (AA-6200 Shimadzu), FTIR (Shimadzu).

Materials used in this study are the water hyacinth plant and all chemicals directly used as it bought from manufacture Sigma and Merck such as activator EM4, molasses, lead (II) nitrate, copper (II) sulfate, nitric acid, sodium hydroxide, and distilled water.

Composting of water hyacinth plant

A 5 sacks of hyacinth plants were inserted into the hyacinth plant thrasher, then hyacinth plants that have been enumerated are weighed. After weighing, the water hyacinth plants were fermented using EM4, molasses, and water with ratio 50 mL : 100 mL: 1 L. Next, it was inserted into the container and timber-sized 1m x 1m x 1m and closed. Every 3 days the compost was observed and stirred so that the heat could be controlled.

Characterization of water hyacinth compost

Composition of water hyacinth compost was determined by FTIR to determine the presence of functional groups (active sites) on the adsorbent water hyacinth compost. The content of humic acid with humic acid were determined by Schnitz method whilethe metal content of Pb and Cu was determined using AAS.

Dete Effect of adsorbent mass of water hyacinth compost on Pb and Cu adsorption

Lead (II) nitrat 10 ppm as much as 25 ml was soaked into an Erlenmeyer and was added 0.2 g of adsorbent hyacinth compost. Then it was shaken for 60 minutes at speed of 150 rpm. Once completed the solution was filtered. The supernatant was taken as much as 5 ml for determination of the final concentration of Pb using AAS method. The initial concentration of Pb in solution was also determined. The procedure was performed again with the same procedure for Cu (II) and the variation of the mass of adsorbent 0.4; 0.8, 1.2, 1.4, 1.6 g. The experiments were repeated 3 times.

Effect of pH on adsorption of Pb and Cu

A 1.2 gram of water hyacinth compost was placed into 100 mL Erlenmeyer as much as 1.2 gram, added with 25 mL of Pb (II) 10 ppm at pH 2. The mixturethen was shaken for 60 min with a shaker at a speed of 150 rpm. Subsequently the mixture was centrifuged at 3000 rpm for 15 minutes. 5 mL of the supernatant was diluted up to 25 mL.. The levels of Pb (II) in the solution then was measured by using atomic absorption spectrophotometer (AAS) at a wavelength of 283.3 nm. The above procedure was repeated for the solution of Pb (II) and Cu (II) at pH 2-7. For Cu (II) adsorption, the amount of adsorbent used was 0.8 grams and the wavelength for AAS measurement was 324.8 nm.

Effect of adsorbate concentration on the adsorption of Pb and Cu

Solution of Pb (II) and Cu(II) were varied at 0.5 ppm, 1 ppm, 5 ppm, 10 ppm, 15 ppm, and 20 ppm at pH 5. As much as 25 mL of the solution was mixed with 1.2 g sample of water hyacinth compost in a 100 mL Erlenmeyer. Next, the mixture was shaken for 60 minutes with a shaker at a speed of 150 rpm. Supernatant of the mixture was taken 5 mL and diluted up to 25 mL.

RESULT AND DISCUSSION

Adsorption is the process by which a component or adsorbate moving from phase (solution) to the surface phase (solution) to the surface of another phase (adsorbent) which leads to changes in the concentration of adsorbate on the surface. This study examines the ability of water hyacinth compost is used as an adsorbent. This study includes several stages of composting of water hyacinth plants, compost characterization, determination of optimum adsorption conditions, and determination of the mechanism of adsorption.

Table 1. Characterization of water hyacinth compost

Code	EG	Compost EG
C organic (%)	32.11	20.46
C/N	20.0	18.0
Organik Substance	65.55	35.4
P (%)	0.19	0.22
K (%)	1.49	2.38
Na (%)	3.17	3.36
Ca (%)	1.72	3.24
Mg (%)	0.52	0.96
Pb (ppm)	0.80	-
Cu (ppm)	11.0	8.00
KTK (me/100 g)	80.13	83.4
Humic Acid (%)	-	2.82

Characterization by FTIR

Identification of the functional group of the compost was done at wave number of 4000-400 cm^{-1} using KBr pellets. There is a wide absorption band in the wave number 3382.91 cm-^{1} indicated the presence of O-H stretching vibration. The wave number 2923.89 cm^{-1} was an aliphatic CH stretching vibration. Strong absorption band at wave number 1660.60 cm^{-1} was the C=O stretching vibration of carboxylic acid salts. Moderate to weak absorption band at wave number 1548.74 cm^{-1} and 1514.02 cm^{-1} showed the C=C stretching vibration of aromatic compounds. Moderate absorption band at wave number 1415.66 cm^{-1} and 1386.73 cm^{-1} indicated the presence of CH_3 bending vibration. Absorption with strong intensity at wave number 1319.22 cm^{-1} indicated the presence of C-O stretching vibration of carboxylic acids. The presence of an amine was shown in wave numbers 1240.15 cm^{-1} for C-N absorptions. Moderate to weak absorption band at wave number 1095.49 cm^{-1} and 1035.71 cm^{-1} indicated the presence of aromatic C-H bending. At wave numbers 642.25 cm^{-1}, a weak absorptions indicate O-H bending.

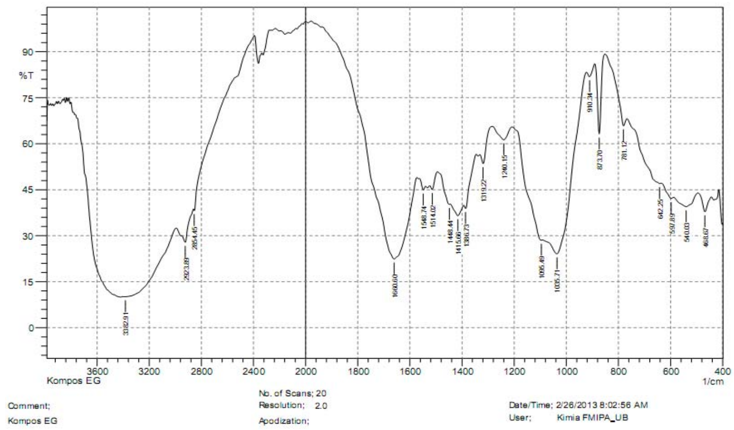

Figure 1. IR spectrum of water hyacinth compost adsorbent

Effect of adsorbent mass on the adsorption of Pb and Cu

Result of the treatment of adsorbent mass effect on percent adsorption was presented in figure 2. The adsorbent mass influenced on the adsorption process of Pb (II) and Cu (II) by water hyacinth compost adsorbent. For The percent of Pb(II) adsorption increased not significantly when used adsorbent at 0.2 to 1.2 gramsThis is caused by the greater mass of adsorbent used, the larger the number of functional groups that are responsible for adsorption. When the mass of adsorbent was increased, the amount of Pb (II) adsorbed was decreased. This is because by the time the mass of adsorbent 1.4 g occurred equilibrium between the amount of adsorbent to the concentration of Pb (II) occurs in the solution so that the rate of adsorption that takes place tends to slow and vice versa, which tends to increase the rate of desorption. Ions Pb (II) which has been bonded to an active group of adsorbents apart and back into the solution thus decreasing the amount of adsorption of Pb (II). As for the Cu (II) 0.2 to 0.8 gram, mass adsorption amount of Cu (II) increased. This is caused by, the increasing mass of adsorbent used, then the value of the ion adsorption also higher. Proportional to the mass of adsorbent increased with increasing particle number and surface area of the adsorbent thereby causing the amount of metal ion binding site increases and adsorption efficiency was increased.

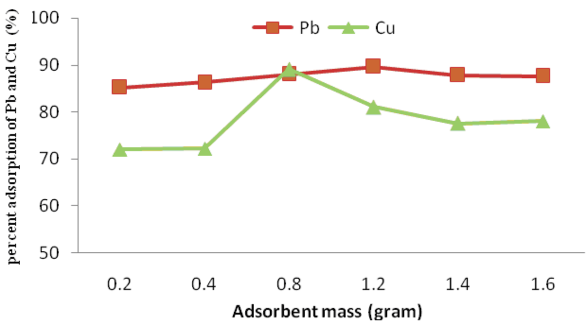

Figure 2. Determination of optimum mass to the adsorption of Pb (II) and Cu (II) by water hyacinth compost adsorbent.

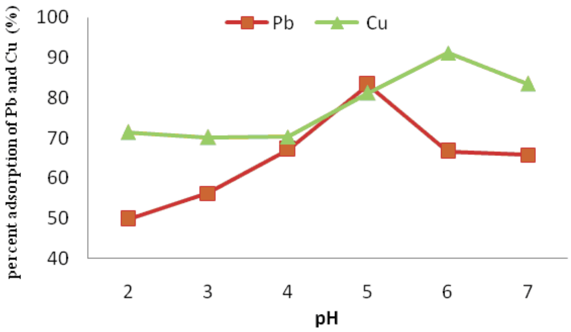

Figure 3. Determination of optimum pH for adsorption of Pb(II) and Cu(II) by water hyacinth compost adsorbent

Effect of pH on Adsorption of Pb and Cu

Determination performed using water hyacinth compost adsorbent with optimum mass for 1.2 g of Pb, Cu and 0.8 g and stirring speed of 150 rpm. Study the effect of pH performed with the batch system on pH variation of 2, 3, 4, 5, 6, and 7 was shown in Figure 3. It showed the adsorption of Pb (II) increased from pH 2 to pH 5, and declined from pH 6 to pH 7. Possibly due to the ability of the water hyacinth compost adsorbent to adsorb metal ions to be caused by the presence of functional groups present in the adsorbent. The functional groups are assumed cluster Lewis Bases -COOH,-CO,-NH. At this research the condition optimum from Pb (II) occurs on pH 5. This is due to the ionization constants of the carboxyl group adsorbents, where the ionization constants of the release free carboxyl group between pH 4-7. This means that the carboxyl group would be protonated at low pH (<pH 4) and will not bind with Pb (II). While at high pH (> PH4) will undergo deprotonation of the carboxyl group ($-COO^-$), where the negative charge of the carboxyl group will bind to the positive charge of Pb (II).

Where as for Cu (II) is shown by an increase in binding of Cu (II) at pH 2 to pH 6. While when the pH increased from pH 6 to pH 7 did not decrease significantly. Adsorption using water hyacinth compost is expected due to the active-COOH groups present in water hyacinth compost derived from humic. Because of the carboxyl group (-COOH) on humus which can bind to the cation, the compost can be categorized as a weak acid ion which can bind metal ions Cu (II) through the formation of ionic bonds and to not ignore the possibility of adsorption physical (van der Waals).

At pH 7, a decrease in the efficiency of adsorption of Cu (II) occured, this is due to the reactions that affect the adsorption process. Reactions that may occur are side reactions that can interfere with the main reaction in the adsorption process. Suspected reverse reactions that arise due to the formation of hydroxide compounds of Cu (II). Higher pH increase caused Cu (II) hydroxide precipitate will tend to form from Cu (II). This resulted in the number of ions Cu (II) present in the solution is decreased, so that the process of binding of Cu (II) which occurs also declined.

The influence of adsorbate Concentration against Adsorption of metals Pb and Cu

Determination performed using water hyacinth compost adsorbent with optimum mass for 1.2 g of Pb, Cu and 0.8 g and pH for Pb (II) by 5 and Cu (II) by 6, the stirring speed of 150 rpm. The performed varying concentration is at 0.5 ppm; 1 ppm, 5 ppm, 10 ppm, 15 ppm and 20 ppm. Relationship between the percentage concentration of Pb and Cu are absorbed by water hyacinth compost shown by Figure 4.

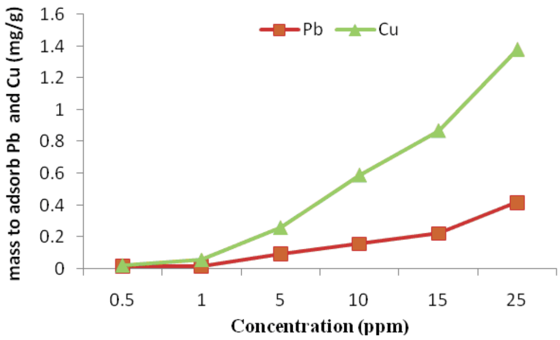

Figure 4. Determination of optimum concentration to the adsorption of Pb (II) and Cu (II) by water hyacinth compost adsorbent.

The uptake of metal ions Pb(II) and Cu(II) adsorbed was increase with increasing of Pb(II) and Cu(II) concentration from 0.5 to 25 ppm. Mass adsorbent of Pb(II) and Cu(II) can be adsorbed by adsorbent until concentration of 25 ppm. This indicated that the adsorbent of hyacinth compost was able to adsorb Pb(II) and Cu(II) maximum concentration 25 ppm. As a result of Pb (II) and Cu (II) adsorbed by the adsorbent hyacinth compost decreased the number of adsorbed. Based on the influence of the end concentration of Pb (II) and Cu (II) on the amount of Pb (II) and Cu (II) adsorbed, can be determined following Freundlich equation and Langmuir isotherm for Pb (II). It was shown on figure 5 and 6. Whereas isotherm equation of Langmuir and the Freundlich for Cu (II) was presented in figure 7 and 8.

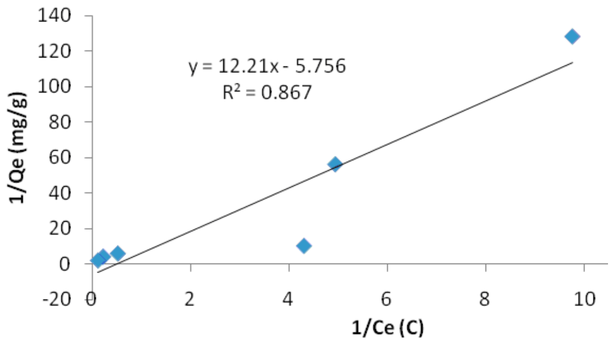

Figure 5. Graphic of Langmuir adsorption isotherms for Pb (II)

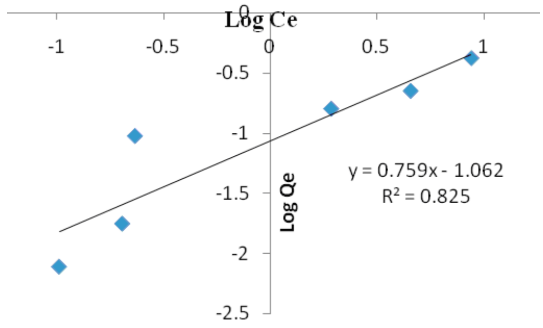

Figure 6. Graphic of Freundlich adsorption isotherms for Pb(II)

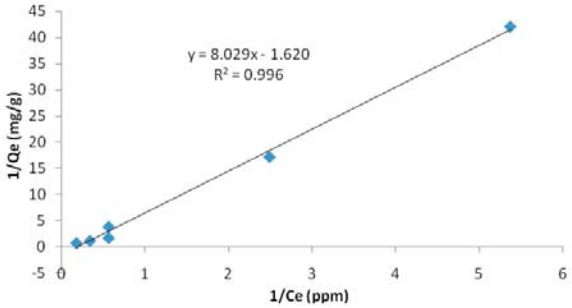

Figure 7. Graphic of Langmuir adsorption isotherms for Cu(II)

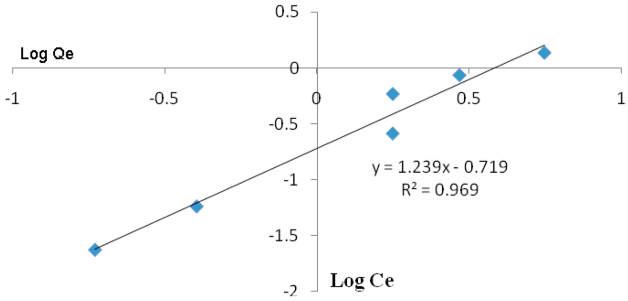

Figure 8. Graphic of Freundlich adsorption isotherms for Cu(II)

From the picture figure 5-8 above, it can be seen that the adsorption of metal ions Pb and Cu using water hyacinth compost followed Freundlich models. So these are more properly used to characterize the mechanism of adsorption of metal ions of Pb and Cu by water hyacinth compost. If the adsorption followed the Freundlich isotherm type then fisisorpsi multilayer adsorption takes place. Physic sorption mechanism allows the bonding between the metal ions contained in the solution and waste, in addition to bind to the adsorbent. Both of these bonds are only bound by van der Waals forces so that the bond between the adsorbate with the adsorbent is weak. This allows the adsorbate to move freely until the adsorption process takes place in many layers. Freundlich isotherm models also explained that the process of adsorption on the surface is heterogeneous in which not all have the power of the adsorbent surface adsorption.

CONCLUSION

Based on the results, it can be concluded that first the optimum adsorbent mass to adsorb metal ions of Pb (II) is 1.2 grams while the optimum adsorbent mass to adsorb metal ions of Cu (II) is 0.8 grams. Second, the optimum pH for adsorption of metal ions of Pb (II) is at pH 5, while the optimum pH for adsorption of metal ions of Cu (II) is at pH 6. Third, percent adsorption of Pb (II) was 95.13% Cu (II) was 91.42%, and Last, Langmuir isotherm model is more suitable to characterize the adsorption mechanisms occurring in the adsorption of water hyacinth compost on metal ions Pb and Cu in comparison with the Freundlich isotherm models. So it can be said that the occuring adsorption is kemisorpsi monolayer adsorption.

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