INVESTIGATION ON THE ABILITY OF A NATURAL ADSORBENT CORN STALK IN REMOVING HEAVY METAL IONS FROM AQUEOUS SOLUTION

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ABSTRACT

The prospect in using a bio-adsorbent corn stalk to remove metal ions from solution in batch operation was investigated. Corn stalk with shapes variation has ability to remove single metal ion in aqueous solution over than 80%. In binary metal ions solution, the competition of Cd^{2+} and Cu^{2+} to adsorb on adsorbent surface at pH 4.5 was then studied. With concentration variation ratios such as: 20:40; 30:30 and 40:20 were found: Cd<Cu; Cd>Cu and Cd>Cu respectively. The total removal ability was almost the same at 62.5% for each concentration variation. The adsorption kinetic results are appropriate with the second order of kinetics equation model and diffusion equation model. It is indicated that the interaction of metal ions on corn stalk occurs chemically. The adsorption tends to take place on porous area of the adsorbent. The adsorbed diffuse to internal site of adsorbent. The ability of corn stalk to adsorb the metal ion shows its potential as a natural adsorbent.

Keywords: natural adsorbent, corn-stalk, adsorption, binary, metal ion.

INTRODUCTION

The most heavy metal ions pollutant is coming from chemical industrial wastewaters; the effluent is a source of contaminant into natural water resources (Sangiumsak and Punrattanasin, 2014).Consequently, these metals accumulate in the environment, especially to form complex compounds with organic and inorganic materials in aquatic ecosystems (Kampalanonwat and Supaphol, 2014).Heavy metals are non-biodegradable pollutant material and high potential toxicity. It has been known as a threat to the environment and public health. Heavy metals have potential to damage the physiology and human biological system, if it exceeds the tolerance level; it causes various diseases (Liu H., *et al.,* 2013; Akpomie and Dawodu, 2015).

Water purification is one of the best methods to overcome this problem (Singhal, S., *et al.* 2014). There are several purification processes for water contaminated by heavy metals. Adsorption process is more efficient and less expensive than other technology entrapment of heavy metals (Liu, W., *et al.,* 2013). Other processes are coagulation and precipitation chemistry, electro-flotation (Da Mota, *et al.,* 2014; Liu, W., *et al.,* 2013), ion exchange and membrane separation (Mahmoudkhani, R., *et al.,* 2014).

The adsorbent is a solid substance that can absorb fluid particles in an adsorption process (Fonseca, B., *et al.* 2011).The adsorbent can be divided into two inorganic materials such as sand (Fonseca, B., *et al.* 2011; Haryanto, B. and Chang, CH., 2014; 15), zeolite (Montoya, H., *et al.,* 2013) and the organic carbon (Liu, H., *et al.,* 2013), the polymer (Kampalanonwat and Supaphol, 2014; Liu, W., *et al.*, 2013),the biomass (Miao and Zhang, 2012; Song, Wen, *et al.,* 2015). Cornstalk has good potential to be used as an adsorbent. As an agricultural byproducts, this material existence is abundant, neglected and untapped (Liuchun, Z., *et al.,* 2010A and B; Chen, S., *et al*., 2011;

Naushad, M., 2014). Scanning Electron Microscope (SEM) indicates the nature of the surface of the corn stalks as a shaft structure which is useful in adsorbing metals (Vafakhah, S., *et al.,* 2014). With regard to pore diameter, the pore diameter corn stalks is ± 50 μm, 10 times greater than activated carbon and zeolite which is only about 3-6 μm (Montoya, H., *et al.,* 2013). Corn stalk is composed of cellulose as major constituents with huge numbers of hydroxyl groups (Liuchun, Z, *et al.,* 2010A). These functional hydroxyl groups have an affinity for metal ions to bind by donation of an electron pair from hydroxyl groups to form complexes with the metal ions in solution (Demirbas, A., 2008). Raw corn stalks with hydrogen bonds between molecules, lead to lower adsorption capacity. Several modifications to break the hydrogen bonds to increase the adsorption capacity have been reported (O'Connell, D., *et al.,* 2008).

Furthermore, the adsorption kinetics is the rate of absorption of fluid by the adsorbent within a certain period. An investigation of heavy metal adsorption process with different kinetic models can be used to describe the level of absorption of adsorbate on the adsorbent (Chen, S., *et al.,* 2011). Various studies have reported that the adsorption kinetics data is empirically derived by using a model equation of pseudo first order and pseudo second order equation (Chen, S., *et al.,* 2011, Liu, H., *et al.,* 2013, Arshadi, *et al.,* 2014).Both pseudo equations were used to plot the experimental data to examine the kinetics of adsorption and find a suitable model based on the coefficient correlation (r^2) obtained. The model can also be used to identify the chemical reactions, occur or not on the adsorbent during the adsorption process [Ozacar, M., *et al.,* 2008; Liu, H., *et al.,* 2013].

Adsorption occurs on the outer surface and the inner surface of the pores inside the adsorbent (Fonseca, B., *et al.,* 2011).On an adsorbent, ion diffusion can be divided into two such as: the external and internal

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diffusion. The external diffusion is if the ions absorption only covering the outer surface of the adsorbent (Fonseca, B., *et al.* 2011). If the ion diffusion occurs on the inner surface and pores, then this process is called internal diffusion (Al-Degs, Y.S., *et al.,* 2006). To a solution containing multicomponent, if evaluated based on physical-chemical properties, every dissolved ions each have different properties such as particle size, electron configuration and electronegativity (Perry, R.H., *et al.,* 1999). These differences can affect the mechanism of adsorption. As a result there is substance which is preferred (dominant) by adsorbent and there substance which is less preferred. This is known as preferential adsorption (Liu, H., *et al.,* 2013).

This research is to evaluate the potential of corn stalk to absorb metal ions Cd^{2+} and Cu^{2+} in binary aqueous solution on batch adsorption system. The competitive kinetic adsorption capacity was investigated on variations of concentration ratio Cd^{2+} and Cu^{2+} and in variation of pH. Pseudo first order and second order equations were used to confirm the chemical reactions occured or not on the adsorbent. By equation models, the adsorption process occurs on the outer site surface and the pores inside the adsorbent were confirmed. Furthermore, were then investigated that the metal ions diffusion occurs on external of the corn stalks surface or in the intra pores, and the preferential adsorption towards one of the two ions type in binary solution Cd^{2+} and Cu^{2+}.

MATERIAL AND METHODS

Cadmium acetate (Cd $(CH_3COO)_2.2H_2O$) as a source of cadmium (Cd^{2+}), copper (II) sulphate ($CuSO_4$) as the source of copper (Cu^{2+}), purchased from Merck KgaA, Darmstadt, Germany and then used as the model binary contaminant. Hydrochloric acid (HCl) purchased from Mallinckrodt Baker, Inc, Paris and sodium hydroxide (NaOH) purchased from Merck KgaA, Darmstadt, Germany, both were used to control the pH variation of the deionized water. they were used to dissolve copper and cadmium as a binary solution.

The natural adsorbent was collected from corn plantation in the Medan city, Indonesia.Raw corn stalk was cutted smoothly and sieved to have shape size variation such as:half, fourth circle, 50 and 70 mesh size.Each type was cleansed by deionized water several times (aquadestilator, W4l Water Still Favorit, Indonesia). To confirm the corn stalk already clean, the pH meter was used to measure each washing water until constant point. The wet corn stalk was dried by putting in an oven at 55^0C (Memmert UN 55, Indonesia) until the weight of the corn stalk was constant (Haryanto and Chang, 2014).

Measurement of the adsorption capacity of corn stalk on single and binary solutions were then performed. Batch adsorption operation was running in an erlenmeyer (0.5 L) which was shaken for 120 minutes with variation of rotations per minute (rpm). The erlenmeyer containers were shaken on an orbital shaker (d72379, Hechingen Edmund Buhler GmbH, KS 15A, Germany). The sample was taken in range of time 10 to 20 minute until 120

minutes. The concentration of metal ion in the solution was analized by atomic absorption spectrometry (AAS) AA-7000 Series, Shimadzu Corporation, Japan. The measurements of the adsorption capacity of corn stalk on single metal solution were performed with variations of adsorbent's shape, pH solutions and shaking times/stirring speed. For all experiment, 100 ml solution within 50 ppm metal ion was mixed with 1 gram adsorbent and kept at constant room temperature. For adsorption kinetic measurement of single metal ion, the adsorbent was chosen with fourth circle shape. The sample taken was 2 ml every teen minute contact time from 10 to 120 minute and analized by AAS.

For binary system, a solution is provided in pH 4.5 with shaking speed 60 rpm and corn stalk shape 70 mesh. Adsorption process of the Cd^{2+} and Cu^{2+} ions were done by mixing the adsorbent with the binary metal ions with variation of ratio concentration such as: 20:40, 30:30 and 40:20. The adsorption operation with the effect of contact time were done, with the certain concentration, pH for single solution to measure the adsorption capacity. Further for binary solution, the variation of ratio concentration 30:30 were used to evaluat the metal ions adsorption competition.

The amount of adsorbed metal per unit mass of adsorbent at equilibrium (Equation 1), the amount of adsorbed metal per unit mass of adsorbent at time t (Equation 2) and the percentage removal at time t (Equation 3) can be calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m_{ads}} \tag{1}$$

$$q_t = \frac{(C_0 - C_t)V}{m_{ads}} \tag{2}$$

$$R\% = \frac{(C_0 - C_e)}{C_0} \cdot 100\% \tag{3}$$

Description of the equation, qe is the mass of metal adsorbed at equilibrium (mg / g) and qt is the mass of metal adsorbed at time t (mg / g). R% is the percentage of metal removed (%). C_0 is the initial metal concentration (mg / L), Ct is the metal concentration at time t (mg / L) and Ce is the metal concentration at equilibrium (mg / L). V is the volume of solution (L) and m_{ads} is the mass of adsorbent (g), (Liuchun, Z., *et al.,* 2010; Liu, W., *et al.,* 2013; Liu H., *et al.,* 2013; Vafakhah, S., *et al.,* 2014; Arshadi, *et al.,* 2014; Qinghai, H., *et al.,* 2014).

For kinetic adsorption model, the equations of first order (4) and second order (5) respectively expressed as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2,303}t \tag{4}$$

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$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (5)$$

These models have been widely used to describe the kinetics of absorption of both metals and organic compounds in various types of adsorbent (Chen S., *et al.,* 2011; Liu H., *et al.,* 2013; Arshadi, *et al.,* 2014). In many cases, the first order kinetic model equation is less compatible with the entire range of contact time, and mostly applies to the early stages of the adsorption process (Liu H., *et al.* 2013). Second order equation seems to be a better model than the equation. This can be evidenced by the correlation coefficient (r^2).

Diffusion is a process of the migration of a substance in solvent from the high concentration to low concentration. The adsorption process is understood as a process of migration of a substance from the solvent to penetrate the surface of the adsorbent. If the diffusion of an ion only covers the outer surface of the adsorbent or has limitations, it is referred to as an external diffusion and can be described using the following equation (Liu H., *et al.,* 2013):

$$ln \frac{C_t}{C_0} = -z.t + C \qquad (6)$$

C_0, C_t, and A/V respectively the initial concentration of the solution, the concentration at time t, and the ratio between the total particle surface area to volume of solution. A/V can be calculated in accordance with what has been done by Liu H., *et al.,* (2013). Where m is the mass of adsorbent (g), d is the particle diameter (m), and ρ is the density of adsorbent (g/cm3). External diffusion coefficient, k_f (cm/s), can be determined from the slope of the line from the plot of ln (C_t/C_0) versus t.

If the metal ion diffusion occurs in the inner surface and pores, then this process is called internal diffusion. Internal diffusion can be described by experimental data using the following equation:

$$q_t = k_{id}\sqrt{t} + C \qquad (7)$$

Where qt is the adsorption capacity at time t (mg/g), the kid is a diffusion coefficient (mg/g.min^{0,5}) and t is the time of adsorption (Chen S., *et al.,* 2011).

RESULTS AND DISCUSSIONS

The shapes variation of adsorbent corn stalks such as: half, fourth spherical, 50 mesh and 70 mesh size the adsorption capacity were evaluated. The adsorption process was conducted at contact time 24 hours with rotation 220 rpm. Figure-1 demonstrated the determination of removal percentage (%R) using equation (3). The results showed that the percentage of adsorbed metal ions tend to be constant at fourth spherical shape, 50 and 70 mesh. Adsorbent with 70 mesh shape has the largest percentage removal 88.5%. Cornstalk 70 mesh shape has larger surface area possible to increase the adsorption

possibility which then increased the adsorption capacity to remove the metal ion compared with a fourth and a half circle and 50 mesh shape. The amount of adsorption is proportional to the surface area. The adsorptive capacity of adsorption is determined by the surface area of the adsorbent (Da Motta, *et al.,* 2014).
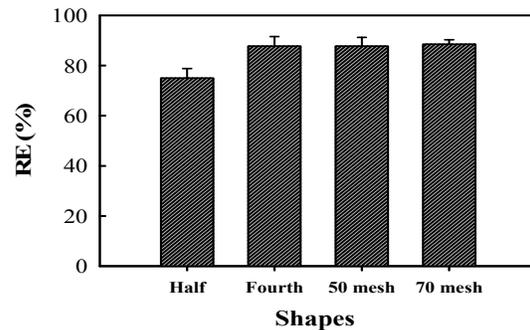
Figure-1. Removal efficiency of Cd^{2+} ion on shapes variation of adsorbent at 220 rpm and contact time 120 min.
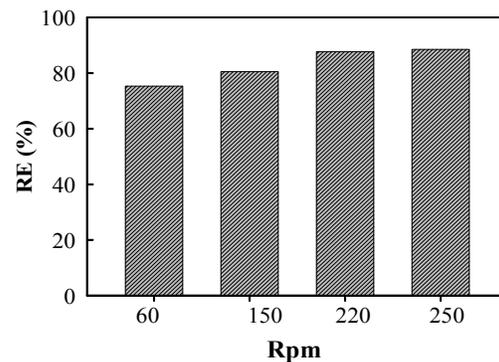
Figure-2. Removal efficiency of Cd^{2+} ion on rotation speed variation for fourth spherical shape with contact time 120 min.

The adsorption ability of Cd^{2+} by the corn stalks with fourth-spherical shapes with stirring speed variation was then investigated. Variations in the speed used were 60, 150, 220 and 250 rpm. Effect of rotation speed of adsorption operation to removal ability is shown in Figure 2. With rotation speed 250 rpm was it possible to remove 88.51% Cd ion with contact time 24 hours. It was slightly higher compared to 220 and 150 rpm but spend more rotation energy compared to using 60 rpm.

The rotation speed of stirring has been reported to greatly affect the adsorption process. The lower stirring speed will be lowering the adsorption capacity. However if the speed is too fast, it can lead the adsorbate that have been adsorbed on surface will be released. In addition, it can result in the damaged of the adsorbent structure (Da Motta, *et al.,* 2014).

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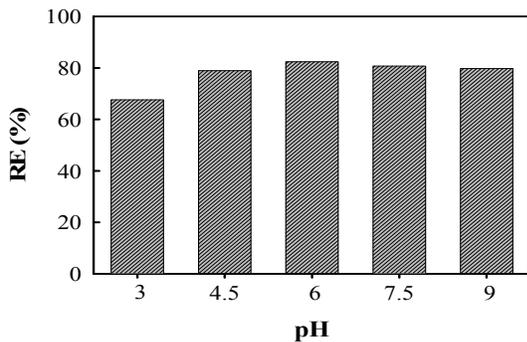
Figure-3. Removal efficiency the Cd ions at contact time 120 min with variation of pH solution at 220 rpm.

Selection of the pH is to avoid precipitation of metal based on constant solubility of each metal (Liu H., *et al.*, 2013). To evaluate the effect of pH, various pH have been used: 3; 4.5; 6; 7,5 and 9 to Cd^{2+} concentration of 50 ppm with fourth circle shape cornstalk. The results of the analysis on the influence of pH to the solution as carried out can be seen in Figure 3. The maximum adsorption capacity (qmax) is highest at pH 6 is 83.38% of the total metals are adsorbed. Whereas at lower pH, the maximum adsorption capacity is tends to be smaller, where at pH 3 and 4.5 are 68.00% and 77.8% respectively. This condition is affected by the concentration of H^+ in the solution, which will increase if is lower pH (pH 3 to 4.5). The presence of H^+ ions in the solution will affect the absorption of Cd^{2+} ions to the active functional groups on the surface of the adsorbent. H^+ will interact with the active site on the surface of the adsorbent thereby blocking Cd_2^+ ions adsorbed on the surface or at intra pores area. At higher pH 6 to 7.5, the activity of H^+ will decrease; the tendency of Cd^{2+} ions adsorbed becomes larger. This opinion is according to research conducted by Liu W., *et al.*, (2013) which states that the pH of the solution may inhibit or accelerate the process of adsorption in accordance with the functional groups on the adsorbent used and the kind of metal to be adsorbed.

At pH 9, the solution is alkaline conditions and dominated by OH⁻, so competition Cd^{2+} to H^+ is reduced. However, these conditions also cause other interactions, where there will be new interactions between Cd^{2+} to OH⁻ to reduce interaction with the surface of the adsorbent. For higher levels of OH⁻ which will result in precipitation which decreases the metal concentrations in solution but is not caused by adsorption process. This is in accordance with the opinion of Liu W., *et al.,* (2013) and Liu H., *et al.,* (2013) .They found adsorption process is going badly at high pH because it will have precipitation. The results of this analysis support the idea Liu H., *et al.,* (2013), which declared that the concentration of H^+ and OH⁻ in the solution affect the adsorption capacity. Influences obtained are depending on the type of active site owned by the adsorbent.

Furthur results were on the effect of contacts time and adsorption kinetics. The adsorption contact time is

one of the parameters of the adsorption process because time is a factor that can reflect the kinetics of an adsorbent in interacting with the adsorbate. Time can also be used as an indicator to determine the level of efficiency of the use of the adsorbent.

In this study the variation of contact time is 10, 20, 30, 40, 50, 60, 70, 80 and 120 minutes. The adsorption process has been calculated by the Equations (2) and (3). The results of the measurement of contact time on the adsorption capacity of a single solution Cd^{2+} and Cu^{2+} is demonstrated in Figure-4 A and B.

(a)

(b)
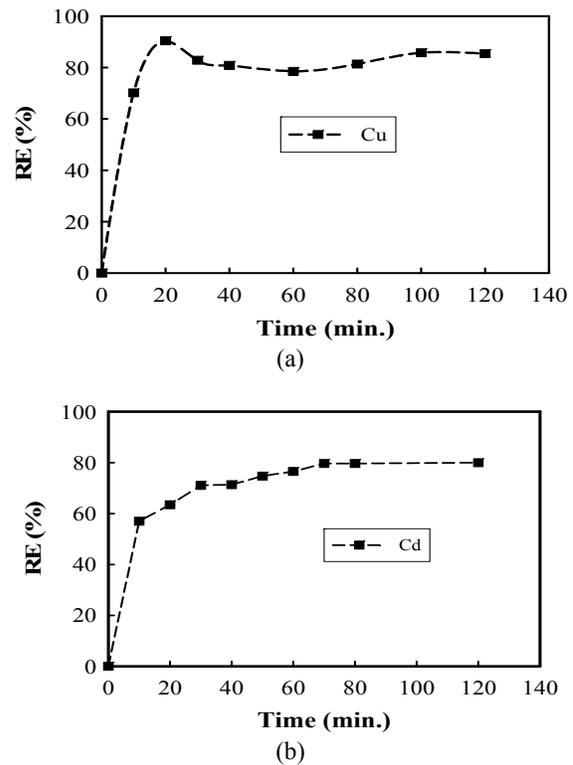
Figure-4. Adsorption kinetics of (A) Cd^{2+} and (B) Cu^{2+} ions at pH 4.5 and 220 rpm.

The process of adsorption of each metal ion adsorbed become greater with increasing contact time. This is due to the longer time interaction with adsorbate and adsorbent, resulting in increased adsorbate adsorbed on the surface until it reaches equilibrium. To achieve adsorption equilibrium will require sufficient contact time between the adsorbate with an adsorbent (Arshadi M., *et al.,* 2014). From the adsorption kinetics can be seen that the concentration of Cd^{2+} and Cu^{2+} are adsorbed continuously to increase and reached constant at 70 minutes and 100 minutes with the adsorption capacity of 80% and 82% respectively for Cd^{2+} and Cu^{2+}.

The optimum contact time of Cu^{2+} ion adsorption occurs after 10 minutes by 89%. Adsorption of metal ions Cu^{2+} after 20, 30, 40, 60, 80, 100 and 120 minutes are likely to decline, but on a small scale. Adsorption capacity

is already constant after reaching 100 to 120 minutes. With stirring effect, a number of Cu^{2+} metal ions can enter the pores of adsorbent corn stalks down to the intra pores and difficult to escape. However, the existing of Cu^{2+} metal on outer surface pores corn stalks, can undergo desorption back, especially because of the effect of stirring speed. In the 10th minute, the adsorption capacity reached optimum conditions but however, there are metals that interact in outer sphere that have weak bonds with the adsorbent; making it easy to desorpt.Therefore, we must obtain optimum contact time in which the metal ion Cu^{2+} cannot be separated again, marked by constant adsorption capacity. The adsorption process can occur in two phases: the early going quickly then in the second stage adsorption capacity slowly drops due to the substances adsorbed into the adsorbent has been saturated, so the adsorbent no longer able to adsorb these substances (Arshadi M., *et al.,* 2014).

For binary systems, the effect of ion concentration ratio of Cd^{2+} and Cu^{2+} on adsorption competition, has been carried out with a ratio of the initial concentration (C_0) Cd^{2+}/Cu^{2+} are 20:40 ppm; 30:30 ppm; and 40:20 ppm, is presented in Figure 5. In comparison, the concentration of Cd^{2+}/Cu^{2+} ppm 20:40; 30:30 ppm; and 40:20 ppm, obtained a total capacity of 63.58%; 60.69%; and 63.85%, sequentially. From the analysis conducted, it can be seen that the maximum adsorption capacity (qmax) is proportional to the concentration of metal ions in solution. These indications show that the interaction between the metal ions on the adsorbent will increase with increasing concentration. It supports research conducted by Abid and Ayadi (2011) which states adsorption capacity will be even greater if the adsorbate concentration increases due to the increases interaction between adsorbent and adsorbate.
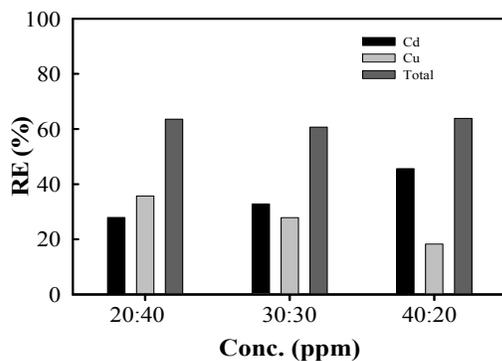
Figure-5. Removal efficiency of Cu^{2+} and Cd^{2+} ions binary with pH 4.5 and 60 rpm with contact time 120 min.

The data in Figure-6 states that the contact time affects both Cd^{2+} and Cu^{2+} which can be adsorbed by the cornstalks. Based on the analysis, in general it can be seen that the largest adsorption capacity changes occurred in the first 20 minutes. In increasing time, the adsorption capacity tends to be constant for the entire metals adsorbed in the solution. At pH 4.5, the total adsorption

capacity has increased significantly. At the time interval $t_0 = t_1 = 0$ minutes up to 20 minutes are of $q_0 = 0\%$ to $q_1 = 58.92\%$. In the next minute, ie $t_2 = 40$ minutes only a little change is obtained $q_2 = 59.50\%$. Later equilibrium is achieved at $t_6 = 120$ minutes with a value of $q_6 = 60.69\%$.From the results demonstrated in Figure-5 and 6 show that the Cd^{2+} ion adsorb greater than ionCu^{2+}, this can be influenced by the basic properties of an individual metal associated with the ion adsorption process. Liuchun, *et al*. (2010A) also found Cd^{2+} atom is more easily absorbed organic substances or living tissue, compared to Cu^{2+}.
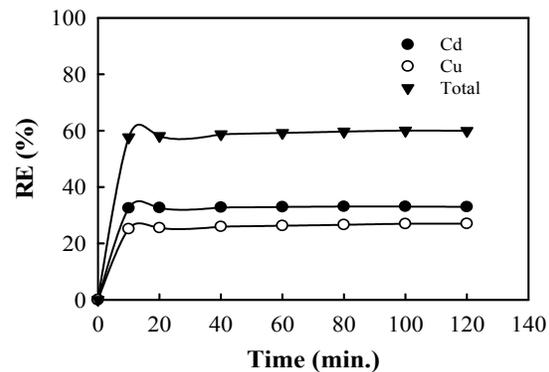
Figure-6. Adsorption kinetics of Cd^{2+}/Cu^{2+} ions at pH 4.5 and 60 rpm.

These results also demonstrate the effect of stirring speed due to the stability and adsorption capacity to duringtime. If compared with the results of kinetics in Figure 4 for a single solution rotated 220 rpm, interaction adsorbate on the adsorbent surface is less stable than the binary solution rotates at 60 rpm. In addition, the adsorption capacity is also smaller than the adsorption capacity of a single solution in Figures-2 and 4.

(a)

(b)
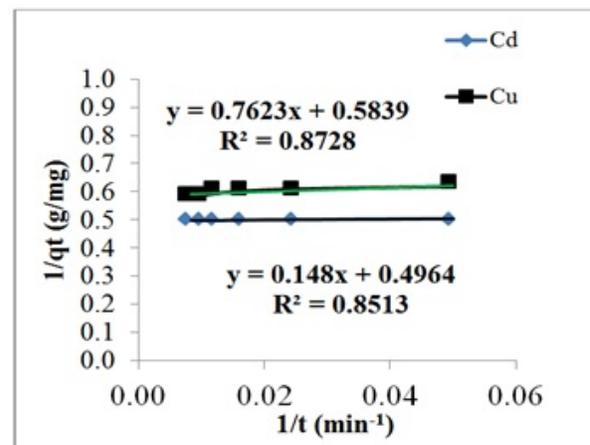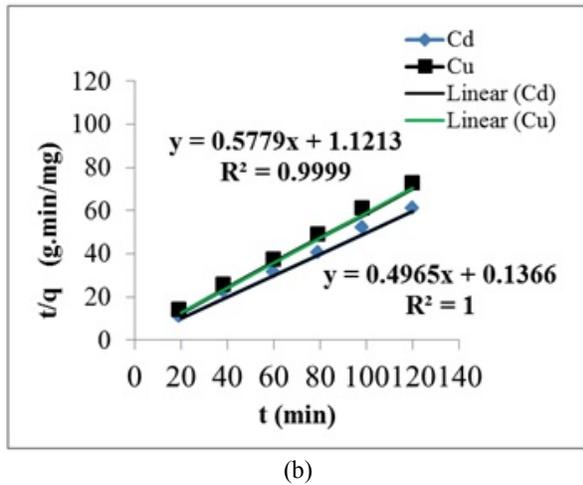
Figure-7. (A) Pseudo first order and (B) Pseudo second order at pH 4.5 and initial concentration Cd^{2+}/Cu^{2+} (30:30 ppm)

In this study, the adsorption kinetics data is empirically derived using models pseudo first order (Equation 4) and pseudo second order (Equation 5). This modeling is required to describe and evaluate adsorption mechanism and identify an average rate of adsorption on the adsorbent cornstalks for binary solution (Liu H., *et al.*, 2013). In addition, this model can also be used to identify whether during the adsorption process chemical reactions occur or not in the adsorbent based on the correlation coefficient (r^2). The correlation coefficient obtained by data plot of adsorption capacity (qt) versus time using the above equation. We get a graph like Figure 7A and 7B.

The data showed that the experimental results were better against the model pseudo second order compared to pseudo first order based on the value of the correlation coefficient (r^2). From the results of theoretical calculations, for example, the concentration of C_0Cd^{2+}/Cu^{2+} 30:30 ppm, the equation of first order has a value of $r^2 = 0.8728$ and equation second order has a value of $r^2 = 0.9999$. The correlation coefficient (r^2) of order two more close to one (1) compared to the first order. This shows that the pseudo second order model makes the data more representative adsorption system. If modeling is consistent with the experiment, the adsorption mechanism involves a chemical reaction (chemisorption) between the adsorbate and the adsorbent (Liu H., *et al.*, 2013).

According to Langmuir, adsorbed molecules are retained on the surface by the force of the valence of the same type to those that occur between atoms in the molecule. Because of their chemical bond to the surface of the adsorbent will then form a layer, in which the formation of the layer will further inhibit the absorption process, resulting in reduced effectiveness (Cheng W. *et al.*, 2008). Nonlinear properties shown by adsorption kinetics equation indicates that the adsorption competition is going on between Cd^{2+} and Cu^{2+} associated with the active side of the adsorbent.

In a single solution, the dynamic adsorption behavior is usually evaluated using a diffusion model. Although the adsorption competition had a more complex process, this experiment attempted to apply the diffusion model to evaluate the competition adsorption in binary components. It could be the possibility that the adsorption process Cd^{2+}/Cu^{2+} occurs only on the outer surface/external adsorbent. Therefore, the adsorption process must be described using an external diffusion modeling. But if diffusion is likely to occur on the surface and pores of the adsorbent, the adsorption process can be described using internal diffusion modeling.
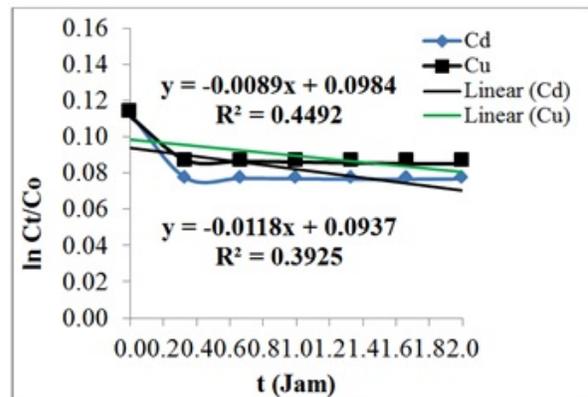
(a)
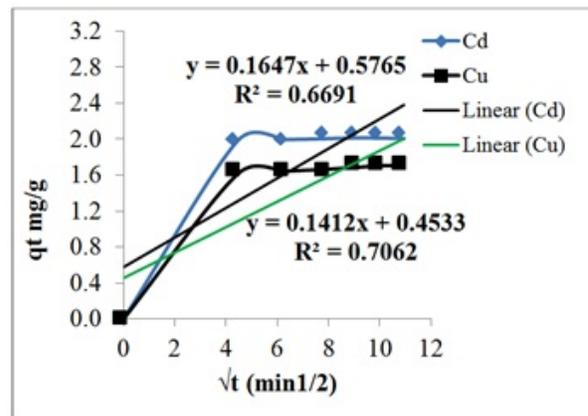
(b)

Figure-8. A External diffusion and B internal diffusion modeling at pH 4.5 and initial concentration Cd^{2+}/Cu^{2+} (30:30 ppm).

Diffusion modeling, external and internal theoretically can be applied and adapted to the experimental adsorption kinetics of data, so that the conclusion about the diffusion. The equations used to describe the diffusion modeling external and internal diffusion consecutively are Equation 6 and Equation 7. Both the above equation will be applied to the data of kinetic adsorption of Cd^{2+} and Cu^{2+}. The parameters of the external and internal diffusion model are plotted as in Figure 7 and 8.

The results of observations show that external and internal diffusion model can be used to evaluate the competition adsorption of heavy metals. Results diagram plots in Figures-7 and 8 are examples which show that the internal diffusion model has a correlation coefficient (r^2) higher than the external diffusion model. The low correlation coefficient of external diffusion model compared to internal diffusion model, due to the competition on the inner surface of ion diffusion in a binary solution is more real than the diffusion of ions on the outer surface only.

When plotted between qt (mg/g) and √t showed that the plot line does not correspond to the original line/line operations. This indicates that the diffusion film and intra-particle diffusion occur simultaneously (Sen and Gomez, 2011). This is also supported by the results of adsorption kinetics modeling analysis. Second order adsorption kinetics showed that the diffusion process that occurs is the internal diffusion. This means that when a mixture of metal ions adsorbed simultaneously/concurrently, the metal ion will compete on the surface of the adsorbent (site/pore). Thus, the process of this competition influences the diffusion of heavy metals and makes adsorption capacity will be smaller.

CONCLUSIONS

Cornstalk has adsorption rate which is significant in the first 10 to 20 minutes for both types of single and binary solutions. Forms of corn stalks affect the ability of adsorption, the larger surface area, the greater the ability to absorb metal ions. The highest adsorption capacity at pH 6, because the components of H^+ and OH^- not significantly interact with the functional groups on the surface of the adsorbent at acidic pH or with metal ions at alkaline pH. The higher the rotational stirring will increase the capacity of adsorption but destabilize interactions. Adsorption of the binary solution of Cd^{2+} and Cu^{2+} showed that the results of the competition Cd^{2+} ions can be absorbed more on organic compounds. In this study, the best adsorption kinetics modeling based on the correlation coefficient is the second-order model. This indicates that the interaction is chemisorption and internal diffusion occurs in the adsorbent cornstalks.

ACKNOWLEDGEMENTS

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