Pseudo Order Kinetics Model to Predict the Adsorption Interaction of Corn-Stalk Adsorbent Surface with Metal Ion Adsorbate Cu (II) and Fe (II)

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Abstract. The adsorption process using cornstalk as adsorbent was used to remove the single metal ion such as copper ion and cadmium ion. The adsorption kinetics of each contaminant then used to predict the interaction type of metal ion on surface of corn stalk by calculating pseudo order 1st and 2nd. The identification type as chemically or physically interaction was predicted from the quality of r² by plotting the adsorption capacity (q) and time (t). The r² were 0.01 and 0.99 for pseudo order 1st and 2nd respectively for Fe (II). The r² were 0.26 and 0.999 for pseudo order 1st and 2nd respectively for Cu (II). The result of adsorption interaction of metal ion and surface function of corn stalk is chemical type. SEM/EDX confirmed the Cu²⁺ presence on cornstalk surface.

1. Introduction
The corn crop is one of Indonesian main plant. Corn is a primary food in some parts of the region in Indonesia. It is grown in all regions of Indonesia (AR Nabilla et al., 2014). The side product of corn plantation such as corncob and cornstalk is available abundantly and usually ignored or burned. The characteristic of the cornstalk with porous structure has potential to use as natural adsorbent (Wang et al., 2016).

Heavy metals cause problems to the environment because it can induce high toxicity to ecosystems and human (PB Tchounwou et al., 2012). Adsorption is a process that occurs when a fluid has an existing substance dissolved in solution, bound to a solid (adsorbent) caused by chemical-physical force between the substances and the absorbent. Heavy metal as adsorbate substances adsorbs by adsorbents generally studied using a batch system. Several factors affect the adsorption process are such as pH, temperature, concentration and contact time (S Vafakhah, et al., 2014; M Karnib, et al., 2014; B Haryanto and CH Chang, 2014).

Equation 1 is to calculate the amount of adsorbed metal per unit mass of adsorbent at equilibrium. Equation 2 is used to calculate the amount of adsorbed metal per unit mass of adsorbent at time t. Equation 3 is used to calculate the percentage of metal ions removed at time t. The equations are as follows:
\[ q_e = \frac{(C_0 - C_e)V}{m_{ads}} \]  

(1)

\[ q_t = \frac{(C_0 - C_t)V}{m_{ads}} \]  

(2)

\[ R\% = \left(\frac{C_0 - C_e}{C_0}\right) \times 100\% \]  

(3)

In which \( q_e \) and \( q_t \) is the adsorption ability at equilibrium and at time \( t \) (respectively (mg g\(^{-1}\)); \( R\% \) is the removal percentage of metal ions (%). \( C_0 \) is the initial metal concentration (mg L\(^{-1}\)), \( C_t \) is the metal concentration at time \( t \) (mg L\(^{-1}\)) and \( C_e \) is the metal concentration at equilibrium (mg L\(^{-1}\)). \( V \) is the volume of solution (L) and \( m_{ads} \) is the mass of adsorbent (g) (L Wen, et al., 2013; L Haibin, et al., 2013; B Haryanto, et al., 2014).

Measurement of the adsorption ability \( q_t \) is by increasing contact time \( t \) during adsorption process which produces the adsorption kinetic data. Haibin, et al., 2013 have used the adsorption kinetic data empirically to describe and evaluate adsorption type using pseudo first order (equation 4) and second order (equation 5) models. The models were used to identify the interaction of adsorbate on absorbent during the adsorption process. Correlation coefficient \( r^2 \) qualities have been widely used to identify the adsorption interaction either chemically or physically. Pseudo 1\(^{st} \) order is related to physical interaction and pseudo order 2\(^{nd} \) is related to chemical interaction (Chen Suhong, et al., 2011; Liu Haibin, et al., 2013; M Arshadi, et al., 2014). The pseudo first order and second order shown as following equations:

\[ \frac{1}{q_t} = \frac{k_t}{(q_e)t} + \frac{1}{q_e} \]  

(4)

\[ \frac{t}{q_t} = \frac{t}{q_e} + \left(\frac{1}{k_2q_e^2}\right) \]  

(5)

The idea of this study to apply the pseudo order 1\(^{st} \) and order 2\(^{nd} \) equations to identify the type of adsorption interaction of metal ion \( Fe^{2+} \) and \( Cu^{2+} \) on cornstalk surface base on correlation coefficient \( r^2 \). The empirical data of adsorption process on single substance of \( Fe^{2+} \) and \( Cu^{2+} \) as adsorbates and cornstalk as adsorbent with batch system were used.

2. Method
For this study, the method applied has three steps. The first step was the adsorption experiment with the batch system. The adsorption kinetic used equation (2) and (3) to get the ability of corn stalk \( q_t \) and percentage of removal metal ion (\( R\% \)) by adding the adsorption time until reach equilibrium condition. The calculation base on initial concentration of metal ions (Co =50 ppm) dissolved in liquid phase and the concentration at certain time \( C_t \) of metal ion adsorbed on adsorbent surface; with the liquid phase pH 4.5 and shacked in Erlenmeyer with 200 rpm.

Figure 1. The steps of experimental design: adsorption process, pseudo model and identification the interaction
The second step was applying equation (4) to plot the $1/qt$ versus $1/t$ to get information of the relationship ($r^2$) for pseudo order 1st. The equation (5) was used to plot the $t/qt$ versus $t$ to get information of the relationship ($r^2$) for pseudo order 2nd. The correlation coefficient ($r^2$) was then used to identify the interaction type.

The correlation coefficient ($r^2$) quality of first order kinetic is used to indicate the physical interaction of adsorbate and adsorbent. The correlation coefficient ($r^2$) quality of second order kinetic is used to indicate the chemical interaction. The quality of correlation coefficient ($r^2$) is near to one indicate the interaction type on each model. The Figure 1 is the steps flow that has been used in this study. Confirmation in the presence of metal ion was applied by Scanning Electron Microscope-Energy Dispersive Spectroscopy (SEM/EDS) Bruker. Metal ion concentration was measured by Atomic absorption spectroscopy (AAS), AA-700 Series, Shimadzu Corporation, Japan.

3. Result

The Table 1 shows the result of adsorption capacity ($qt$) and removal percentage ($R\%$) of Fe and Cu by series of time. With the same result then used to get the $R\%$ and then the data were plot in Figure 2 for Fe and 3 for Cu. The concentration of metal ion was analyzed by using AAS. From the data at Table 1 and Figure 2 then searched the adsorption capacity which tends to reach equilibrium for Fe (II) at 80 to 120 min. It was similar to Cu (II) which was about 100 to 120 minutes with higher capacity. The adsorption capacity of Fe (II) was about 60% and Cu (II) was about 85%.

| Chemical | Fe (II) | Cu (II) |
|----------|---------|---------|
| t (time) | $qt$ | $R\%$ | $qt$ | $R\%$ |
| 0        | 0.000  | 0.000  | 0.000 | 0.000 |
| 10       | 2.881  | 57.615 | 4.606 | 90.788 |
| 20       | 3.750  | 75.065 | 4.521 | 90.958 |
| 30       | 3.319  | 66.375 | 4.541 | 90.918 |
| 40       | 3.766  | 75.315 | 4.539 | 90.922 |
| 50       | 3.384  | 67.685 | 4.557 | 90.887 |
| 60       | 3.003  | 60.055 | 4.574 | 90.852 |
| 70       | 2.915  | 58.305 | 4.571 | 90.859 |
| 80       | 2.828  | 56.555 | 4.567 | 90.866 |
| 90       | 2.992  | 59.838 | 4.551 | 90.897 |
| 100      | 3.156  | 63.120 | 4.536 | 90.928 |
| 110      | 3.028  | 60.555 | 4.512 | 90.979 |
| 120      | 2.900  | 57.990 | 4.519 | 90.962 |

Figure C shows the same drift kinetic base on the adsorption capacity ($qt$). The both results then used to measure the information of relationship ($r^2$) for pseudo order 2nd. The correlation coefficient ($r^2$) was then used to identify the interaction type by using equation 4 and 5. First and second orders of pseudo equation were used to plot the data of adsorption kinetic. Adsorptions kinetic of Fe (II) are as shown in Figure 3 (A) for pseudo order 1st and 3 (B) for order 2nd. The quality of correlation coefficient ($r^2$) was significantly different. The 1st order is 0.0089 and the 2nd order is 0.9909. The correlation for Fe (II) which interacts with functional group on cornstalk is chemically (Chen Suhong, et al., 2011; Liu Haibin, et al., 2013; M Arshadi, et al., 2014).
Figure 2. Adsorption kinetic of (A) Ion Fe$^{2+}$; (B) Cu$^{2+}$ base on R% and (C) base on adsorption capacity

Figure 3. Pseudo order kinetic for Fe (II)
For Cu (II) shows similar trend of the quality of correlation coefficient ($r^2$). First and second order of pseudo equation were found that 0.2609 and 0.9999 respectively. As shown in Figure 4 (A) for pseudo order 1st and 4 (B) for order 2nd, the quality of correlation coefficient ($r^2$) was also significantly different. For both of chemical compound, Fe (II) and Cu (II) have chemically interaction on cornstalk (Chen Suhong, et al., 2011; Liu Haibin, et al., 2013; M Arshadi, et al., 2014).

![Figure 4](image_url)

**Figure 4.** Pseudo order kinetic for Cu (II)

![Figure 5](image_url)

**Figure 5.** SEM fresh cornstalk 50 mesh

The physical structure of cornstalk adsorbent was taken by SEM/EDX. Figure 5 shows the profile of the 70 mesh cornstalk. It is the SEM result with 500 x magnitude. The porous characteristic of cornstalk is an advantage to use as adsorbent. The higher the surface area an adsorbent will increase the potential to adsorb the metal ions. The EDX confirmed the presence of metal ion contaminant represent by analyzing Cu (II) on cornstalk adsorbent. Table 2 is the confirmation of the chemical compound on cornstalk surface. It was compared to Table 3 as the result of chemical compound after contaminated by metal ion Cu (II). The result is indicating the possible interaction of copper ion chemically on sand surface as predicted by calculating the adsorption kinetic by using pseudo order 1st and 2nd.
4. Conclusions

The $r^2$ of data adsorption kinetics for Fe (II) were 0.01 and 0.99 for pseudo order 1st and 2nd respectively. For Cu (II), the $r^2$ were 0.26 and 0.999 for pseudo order 1st and 2nd respectively. The $r^2$ of both contaminants have quality for pseudo order 2nd. The interaction type of metal ion on surface on corn stalk with higher quality $r^2$ pseudo 2nd was identified. From the result was found that the interaction of metal ions Cu$^{2+}$ and Fe$^{2+}$ with the functional group on surface of corn stalk is chemically. SEM/EDX confirmed the Cu$^{2+}$ presence on cornstalk surface. The result of adsorption interaction of metal ion and surface function of corn stalk is chemically adsorption of interaction type.

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