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Development of solid waste of tofu industry immobilized on silica surface as adsorbent for the adsorption of Cd (II) using method of continuous flow column

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Abstract. The aim of this research is to determine the removal efficiency of Cd (II) based on the pH variation and the optimum pH on the batch method, the adsorbent height variation and flow rate in continuous flow column which using tofu solid waste industry which was immobilized silica as adsorbent, also to characterize and to identify functional groups of the absorbent using the FTIR analysis. The pH variation used was 2,3,4,5, and 6. Adsorbent height variation used was 2 cm and 4 cm. Then, variation of flow rate used was 5 ml/min and 10 ml/min. Determination of pH optimum was done using One-Way Anova analysis and continued with Duncan test and descriptive analysis based on the table and graphic. The analysis data of the removal efficiency of Cd (II) in continuous flow column was explained by the descriptive analysis. The pHPCZ was 8.4. The pH optimum was 6 with the removal efficiency 48.14%. The removal efficiency of Cd (II) in continuous flow column for the adsorbent height variation 2 cm and 4 cm which were 38,22% and 43,42% respectively. The removal efficiency of Cd (II) in continuous flow column for the flow rate 5ml/min and 10ml/min each by 38.22% and 39.01%. The result of FTIR analysis of the adsorbent conducted before the adsorption shown that there were functional groups of C=O (vibrate at 1651.07 cm-1), Si-O-Si (462.92 cm-1 and 1095.6 cm-1), O-H (3425.58 cm-1), and N-H (3749.62 cm-1). While, the result of the FTIR analysis after the adsorption shown that there were Si-O-Cd (956.72 cm-1) and Cd-N (412.78 cm-1).

1. Introduction

The industrial process could cause pollution because of its heavy metals. Water pollution caused by heavy metal can be a salt which derived from heavy metal and the toxic compound from heavy metal in water. Heavy metals from industrial activities or natural process which are able to pollute water are Hg, Pb, Cd, Cr, Cu, Cd, and Zn [1].

A method occurred to be used in driving down those metal is adsorption method. Adsorption is the additional concentration component of certain on the surface between the two of the phase [2]. Adsorption has simpler concept and this method is also economical in order to solve the problem of water pollution by heavy metal [3].

Solid waste derived from the tofu industry is carried by liquid waste and can be utilized as an adsorbent because it was still having the same properties with tofu although had been destroyed. Tofu contains the protein that is able to absorb amino acids and this condition can be utillized as an adsorbent or as the metal ions in the water. Nohong [4], reported that waste of tofu has the capacity to optimally adsorb chromium species in sewage leachate is up to 100% while for iron is up to 95.53% in batch method.

The increasing of the adsorption by industrial waste shows that this immobilization method can be conducted. According to Amaria et al. [5], immobilization using silica can be stored for a long time, can be used in columns and this adsorbent is durable on changes done by chemicals.

Industrial activities always produce routine emission continuously so as they are required to do continuous sewage treatment. The use of continuous reactor adsorption has been used in a number of studies.

Previous research using continuous reactor produced an efficiency of Cr6+ allowance to 39.35% with the flow rate of 120 l/min and height of adsorbent was 15 cm [6]. Adsorption with the continuous reactor influenced by several factors of them which are the rate flow, initial concentration solution and the number of adsorbent [7].

2. Methods

2.1. Materials

Material used were solid waste industrial tofu, HCl 1 M, NaOH 1 M, $3CdSO_4.8H_2O$ as source of Cd (II), Na_2SiO_3 to immobilize the adsorbent, HNO_3 0,1 M, HCl pitch, wool glass, and paper strain.

The continuous flow column used is consisted of column adsorption with its internal diameter of 2.54 cm and with 20 cm in its length. Glass wool with the thickness of 0.5 cm laid on the basis of the adsorbent and glass beads with the thickness of 0.5 cm used on the surface of adsorbent to produce a uniform inlet flow [8].

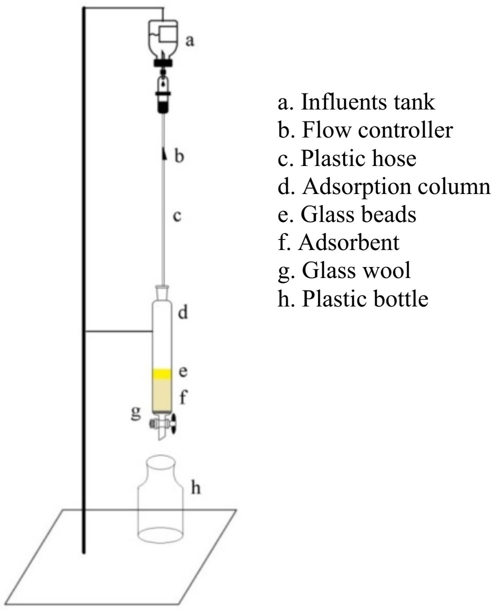

Figure 1. Continuous flow column

2.2. Preparation and Characterization of Adsorbent
Solid waste tofu from filtered industrial liquid waste was dried with an oven at 40°C for 8 hour. The tofu was mashed and sifted with 100 mesh. The adsorbent as much as 6 g was put into a 100 mL beaker glass and then was added with 50 mL of Na_2SiO_3 [9]. Concentrated HCl was added until a gel-like solution was formed. Afterward, the acidity of the mixture was neutralized. The gel formed was dried then mashed and sifted with 60 mesh [10].

The characterization of adsorbent was conducted using a Fourier Transform Infrared (FTIR) spectrophotometer, both before and after adsorption of Cd (II).

2.3. Reagents
50 mg/L Cd (II) solution were from $3Cd(NO_3)_2.8H_2O$. Other reagents were HCl 1 M and NaOH 1 M used to set up the acidity. Then, Na_2SiO_3 and concentrated HCl used to immobilize the adsorbent.

2.4. Determination of the pH_{PCZ}
pH of zero charge potential (pH_{PCZ}) indicates the surface adsorbent is neutral. The determination of pH_{PCZ} was conducted using NaCl solution (100 ml, 1 M) added 1 g adsorbent, then in a shaker 100 rpm, and within 24 hours at room temperature. pH that is used is pH 2 to 12.

2.5. Determination of Optimum pH
Variations of pH used in this research were 2, 3, 4, 5 and 6 [3]. The setting was carried out using 1 M HCl and 1 M NaOH. Cd (II) that had been prepared was later transfered into a beaker glass as many as 100 ml and then mixed with 0.5 g of adsorbent. Then, the solution was stirred with the speed of 100 rpm at room temperature for 120 minutes. Finally, sample solutions were analyzed with Atomic Absorption Spectrophotometry (AAS).

2.6. Experiments in Continuous Flow Column
For continuous reactor, adsorbent height variation used was 2 cm and 4 cm, variation of flow rate used was 5 ml/min and 10 ml/min.

2.7. Data Analysis
Data analysis was conducted to calculate the adsorption efficiency of Cd (II), statistical and descriptive analysis based on the data was conducted to obtain the result.

Cd (II) efficiency calculation was based on initial of Cd (II) and the concentration after contacted with adsorbent with the equation as follows:

$$\text{Efficiency (\%)} = \frac{Co - C}{Co} \text{ x } 100\% \quad (1)$$

where *Co* expresses initial concentration of Cd (II) (mg/L) and *C* expresses concentration of Cd (II) (mg/L) after adsorption (concentration which is not absorbed).

Removal percentage of Cd (II) in continuous flow column calculation was based on total value of metal ions adsorbed to the column and total value of metal ion distributed to the column. Total amount of metal ions adsorbed to the column (q_t) can be calculated with the following equation [11]:

$$q_t = \frac{Q}{1.000} \int_{t:0}^{t:t_t} C_{ad} \, dt \quad (2)$$

where Q expresses flow rate (mL/min), *t* expresses time of adsorption (min) and C_{ad} expresses concentration of removed Cd (II) (mg/L).

Total value of metal ion sent to the column (m_t) can be calculated with the following equation [12]:

$$m_t = \frac{C_0 Q \, t}{1.000} \quad (3)$$

Finally, removal percentage can be calculated by equation [11]:

$$\text{\% Removal} = \frac{q_t}{m_t} \text{x } 100\% \quad (4)$$

2.8. Statistical analysis
The determination of the optimum pH was tested with *Anova One-Way*. Before data tested by *Anova One-Way*, it would be tested of normality and homogeneous by *One Sample Kolmogorov-Smirnov*. After data tested by *Anova One-Way*, it would result significant difference that would be followed with Duncan test.

2.9. Descriptive analysis
Descriptive analysis was based on data in table form and charts based on the data obtained from research that was done. Analysis was described that all experiment data and calculation have been done succesfully.

3. Results and discussion

3.1. Characteristic of adsorbent
Characteristic of adsorbent physically before and after immobilized shown at Fig 2.

(a) **(b)**

Figure 2. Adsorbent (a) before and (b) after immobilized by silica

Fig 2. shows that tofu solid waste industry before immobilized by sodium a silicate had the color of white bone and tofu solid waste industry after immobilized by sodium a silicate had the color of white. Before and after immobilization, tofu solid waste industry had a powder form and smooth texture. Adsorbent before immobilization sifted with mesh 100, while adsorbent after immobilization sifted with mesh 60.

3.2. Determination of pH_{PCZ} of adsorbent
Based on experiment, pH_{PCZ} of adsorbent was 8,4. It is indicated that an adsorbent set at pH under 8,4 had a positive charge, while an adsorbent set at pH above 8,4 had a negative charge. Adsorption Cd (II) theoretically would be better implemented at pH above pH_{PCZ} of adsorbent, but were constrained with a Ksp value of $3Cd(NO_3)_2.8H_2O$ was a relatively low namely $2.5x10^{-14}$ so that when adsorption doing at pH above pH_{PCZ} of adsorbent, hydroxide of a solution of the Cd^{2+} was to be formed and Cd^{2+} ion will be precipated as $Cd(OH)_2$. This indicate that adsorption has to be carried on at below pH_{PCZ} of adsorbent.

3.3. The effect of pH
Based on the conducted research, the removal efficiency of Cd (II) in pH of 2, 3, 4, 5 and 6 were 2.35%, 27.03%, 41.85%, 42.44% and 48.14%. The lowest removal efficiency of Cd (II) as much as 2.35% at pH of 2 and the highest efficiency removal of Cd (II) as much as 48.14% at pH of 6.

Based on normality test, the number of significance was 0.200. It means that the data was normal distribution. Then, homogeneous test shows that number of significance was 0.133, it means that data was homogeneous. After the data ware normal distribution and homogeneous, it would be tested by *Anova One-Way*. Based on *Anova One-Way*, the significant difference value calculated was 0.000. This means every variation of pH will result differences significantly. Afterward, the Duncan test was carried out and it can be seen that optimum pH was 6 with removal efficiency of Cd (II) was as much as 48.14%.

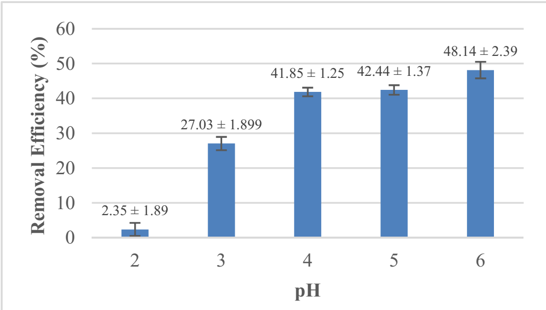

Figure 3. Removal Efficiency of Cd (II) in various pH

Based on the graph shown, there was an increase in removal efficiency from pH of 2 to pH of 6. The pH itself was one factor that affected the adsorption. Metal ion that had the lowest pH had more H^+ concentration so that it can be compete with ion Cd (II) of interacting with the site active of an adsorbent. The more acidic the solution, the more affected the metal ions in solution. This situation led the surface of the adsorbent covered by H^+ ions so that it caused a repulsive force against Cd (II) [13]. This can be seen from the lowest removal efficiency of Cd (II) at pH 2 as much as 2.35%.

The increasing of pH in Cd (II) solution caused H^+ concentration to be decreased that caused the surface of the adsorbent to be less positive so that the adsorbent became easier to adsorb Cd (II) ions compare with at the lower pH [13]. It can be seen from the highest removal efficiency of Cd (II) at pH 6 as much as 48.14%. But, at higher pH, adsorption of Cd (II) was lower because of the formed precipitation. Hence, the most optimum pH based on our research is pH was 6 that had the highest removal efficiency.

Immobilized adsorbent by Na_2SiO_3 also affected the adsorption of Cd (II). Immobilization was done in order to enrich the surface of adsorbent because silica has a broad surface and active sites that can be chemically bonded. The active sites itself are silanol (-SiOH) and siloxane (-Si-O-Si-) that can interact with metal ions.

3.4. *The effect of height in the continuous flow column*

Removal of Cd (II) with the tofu solid waste industry immobilized silica on continuous flow column with variation height of adsorbent using optimum pH Cd (II) solution were obtained by batch method at pH 6. Flow rate used 5 ml/min and solution concentration used 50 mg/l. The experiment was conducted over 120 minutes with the collection of sample every 10 minutes.

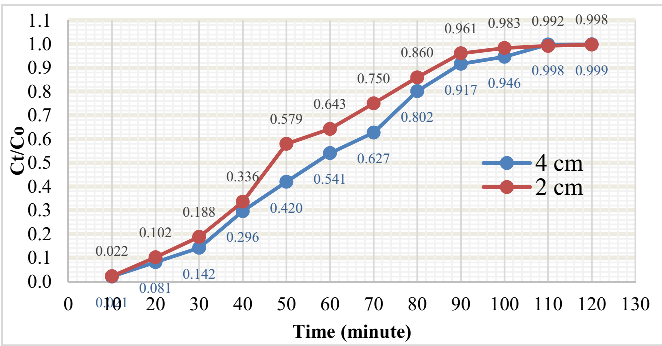

Figure 4. Removal of Cd (II) based on the variation height of adsorbent

Fig 4. shows that the longer time contact adsorbent to adsorbate reactor continuous, the higher concentration value of adsorbate that comes out.

The saturation of the adsorbent took place in the inlet region of the adsorbent [14]. The increasing concentration occurs in the sample collection at 100th minute. Experiment with 2 cm of column height showed that the total amount adsorbate approaching the value of influent concentration at 49.01 mg/l and 110th minute on experiment 4 cm of column height showed that the total amount of concentration adsorbat 49.70 mg/l.

Based on experiment that has been carried out, the percentage removal of variations of an adsorbent height were 2 cm and 4 cm each were 38,22% and 43,42% respectively. The result of persentage removal with height 4 cm was higher than 2 cm because the total ions are adsorbed on 4 cm is higher than 2 cm. Adsorption Cd (II) using 4 cm is better than 2 cm based on percent removal. Furthermore, it was due to the fact that the column height of 4 cm contains a greater number of a mass of an adsorbent if compared with 2 cm so that 4 cm had more active site on the surface adsorbent that could interact with Cd (II).

3.5. The effect of flow rate in the continuous flow column

Removal of Cd (II) with the tofu solid waste industry immobilized silica on continuous flow column with variation height of adsorbent using optimum pH Cd (II) solution were obtained by batch method at pH 6. Height of adsorbent used was2 cm and solution concentration used 50 mg/l. The experiment was conducted over 120 minutes with the sample every 10 minutes.

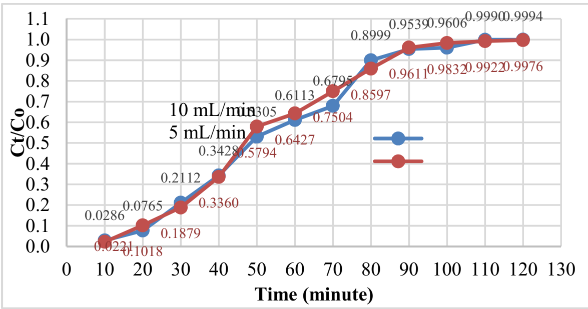

Figure 5. Removal of Cd (II) variation based on the flow rate of adsorbent

The high of flow rate of used provides a considerable transfer of adsorbate. If the more adsorbate transferred in the reactor continuous, the concentration on effluent become higher. The flow rate had an impact on the contact time of adsorbate in the continuous flow column. The lower flow rate used, the longer adsorbate contact on an adsorbent in continuous flow column so that the process will provide better adsorption.

Adsorption Cd (II) using the flow rate 5 ml/min was better than 10 ml/min. This is proven by the percent removal adsorption Cd (II) using flow rate 5 ml/menit (43.798%), while the percent removal adsorption Cd (II) that using flow rate 10 ml/min (37.374%). The results of the percent removal using flow rate 5 ml/min higher than the flow rate 10 ml/min because more the total ion transferred.

3.6. Characterization of the adsorbent

FTIR performed on an adsorbent before and after contact with Cd (II) to know functional groups during an adsorbent played a role in the removal of Cd (II).

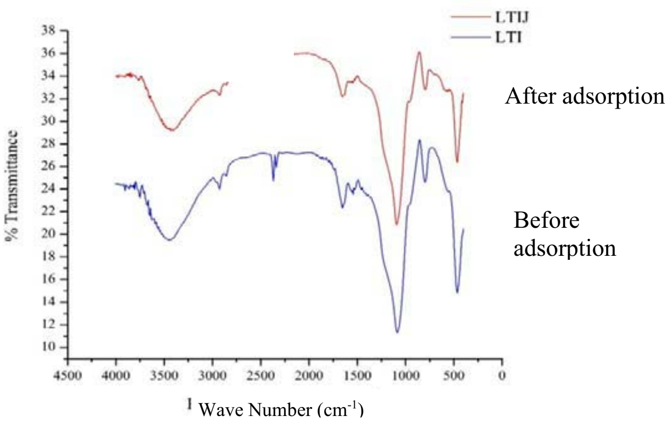

Figure 6. FTIR spectra of the adsorbent

Based on the results of adsorbent characterization before adsorption, it revealed that there was peak at 1651.07 cm^{-1} indicates C=O peptide, peak at 3425.58 cm^{-1} and 1087.85cm^{-1} indicates O-H carboxylate and peak at 3749.62 cm^{-1} indicates N-H [15]. Immobilized silica on the adsorbent shows by the peak at 462.92 cm^{-1} and 794.67 cm^{-1} indicates Si-O-Si. The strong peak at 1087.85cm^{-1} indicates Si-O from Si-O-Si [9].

Adsorption Cd (II) by an adsorbent can be shown by the change of peak. The change of peak occurs at 3425.58 cm^{-1} to 3410.25 cm^{-1} indicates that there was interaction between Cd (II) and –OH, although it was relatively low. The peak change Si-O-Si at the adsorbent after adsorption occurs at 1087.85 cm^{-1} to 1095.6 cm^{-1} indicates that adsorbent interact with Cd (II).

The peak at 956.72 cm^{-1} indicates Si-O-Cd stronger than the peak before adsorption. Peak at 410.85 cm^{-1} indicates Cd-N although rather weak. N at Cd-N is N from peptide bond at the adsorbent. All shift occurring on spectra infrared in adsorbent of tofu solid waste industry immobilized silica indicated that there was adsorption Cd (II) by adsorbent of tofu solid waste industry immobilized by silica.

4. Conclusions

Based on the results and discussion of the research, adsorbent had pH_{PCZ} was 8.4, Cd (II) adsorption with solid waste industrial tofu and immobilized silica using continuous flow column produced significant differences at variation pH and at pH of 6, the removal efficiency was 48,14%, while the height of adsorbate at 2 cm and 4 cm were each resulted efficiency of 38,22% and 43,42%, and also various flows rate at 5 mL/min and 10 mL/min were each resulted efficiency of 38,22% and 39,01%. Characterization of adsorbent using FTIR indicates that there were C=O (1651.07 cm^{-1}), Si-O-Si (462.92 cm^{-1} and 794.67 cm^{-1}), O-H (3425.58 cm^{-1}), and N-H (3749.62 cm^{-1}), and after the adsorption shown that there were Si-O-Cd (vibrate at 956.72 cm^{-1}) and Cd-N (410.85 cm^{-1}).

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