Adsorption interaction model of adsorbents white sand with heavy metals cadmium (Cd$^{2+}$) naturally

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Abstract. This study aimed to analyze the adsorption ability of white sand in the metal ions adsorb cadmium (Cd$^{2+}$) with a concentration of 70 ppm to a solution with a pH of 4.5. The white sand is used is 40 mesh. This research was conducted by batch adsorption operation naturally and adsorption kinetics modeling. Kinetics of adsorption reached equilibrium at time $t = 120$ minutes with the percentage concentration of adsorbed Cd$^{2+}$ 30.7%. In the adsorption kinetics modeling correlation coefficient is almost the same between the equations of first order and second order in the amount of 0.97 and 0.99. The result indicated that the type of interaction Cd$^{2+}$ ions on the surface of white sands occur in chemistry and physics. The adsorption kinetics of diffusion modeling of internal and external diffusion of the correlation coefficient has 0.95 and 0.85. From this data it can be seen that in this study is modeling kinetic internal diffusion trend that shows adsorbent particles are inter sand surface area that experienced internal inter-particle pore diffusion.

1. Introduction

The presence of heavy metals in the environment become a serious concern, because their numbers are increasing, the toxicological properties of heavy metals, as well as the entry of heavy metals into water bodies that affect water quality [1]. Heavy metals also contaminate soil is a major concern because of the high concentration of heavy metals that can endanger human life and the environment [2] Pollution caused by heavy metals in industrial waste water pose serious environmental problems because it is toxic and not biodegradable [3]. Most abundant waste containing heavy metals are generally derived from industrial waste [4].

The heavy metal pollution occurs in aquatic systems and soil. One of the best ways to help overcome this contamination is the water purification [5]. Compared with some of the water purification process of heavy metal adsorption process is more efficient and less expensive than technology entrapment of other heavy metals [6] such as: coagulation and precipitation chemistry, electroflotation [7][6] ion exchange and membrane separation [8].

Various researchers have conducted a study of heavy metals to reduce the negative impact on the lives [7][6]. Literature survey revealed that some types of natural materials have been used as an adsorption material in recent years which has many industrial applications and environments [9]. A number of techniques are available to purify water using natural materials has attracted attention.
because of its effectiveness and environmental friendliness. White sand has good potential to be used as an adsorbent, because it have different abilities to adsorb heavy metals and have an advantage in terms of abundance in nature [10].

To measure the adsorption capacity, can be done using the Equation 1, 2 and 3 [11][12][13][14].

\[
q_e = \frac{(C_0 - C_e)V}{m} \quad (1)
\]

\[
q_t = \frac{(C_0 - C_t)V}{m} \quad (2)
\]

\[
R% = \frac{C_0 - C_t}{C_0} \times 100\% \quad (3)
\]

Where, \(q_e\) = Mass of adsorbed metal at equilibrium (mg / g), \(q_t\) = Mass of adsorbed metal at time t (mg / g); \(R\%\) = Percentage of adsorbed metal (%), \(C_0\) = Initial metal concentration (mg / L), \(C_t\) = Concentration at time t (mg / L), \(C_e\) = The equilibrium concentrations (mg / L), \(V\) = Volume of solution(L), \(m\) = Mass of adsorbent (g).

The adsorption kinetics is the absorption rate of a fluid by adsorbent within a certain timeframe. To investigate the heavy metal adsorption process, the different kinetic models used to describe the rate of absorption of adsorbate on adsorbent [15]. In various studies, adsorbs kinetics of data empirically derived using a model equation of first order and second order equation [6][15][16] Equation pseudo first order (Eq. 4) and a pseudo second order (Eq. 5) [13][14][17].

\[
\frac{t}{q_t} = \frac{k_1}{q_e} \times \left(1 - \frac{q_t}{q_e}\right) \quad (4)
\]

\[
\frac{t}{q_t} = \frac{k_2}{q_e} \left(1 - \frac{q_t}{q_e}\right) \quad (5)
\]

Modeling internal diffusion and external diffusion can be used to evaluate the ability of adsorption of heavy metal cadmium (Cd\(^{2+}\)) on the type of adsorbent white sand. Equation 6 is the internal diffusion kinetics model and equation 7 is an external diffusion kinetics model [14][18].

\[
qt = kdt^{1/2} \quad (6)
\]

\[
Ln\frac{C_t}{C_0} = -k_f (A / V) t \quad (7)
\]

The use of this equation aims to study the kinetics of the adsorption / average velocity and determines the appropriate modeling of experimental data based on the correlation coefficient (R\(^2\)) obtained by plotting the data experiment with equations of first order and second order equation. In addition, this model can also be used to identify whether during the adsorption process chemical reaction occurs or not on the adsorbent [6][15][16].

This study aims to determine the effect of contact time on the adsorption capacity of white sand on Cd\(^{2+}\) solution. The adsorption capacity of the contact time is used to determine the adsorption kinetics model by white sand adsorption occurs to determine whether chemical or physical and determining diffusion model occurring in the adsorbent. This study will be useful in reducing the impact of heavy metal pollution in bodies of water and add to the economic value of white sand.

2. Method

The materials used in this study were white sand as adsorbent, obtained from Pantai Cermin located in the district of Pantai Cermin [11]. Cadmium from Merck KGaA, Darmstadt, Germany as a source of cadmium (Cd\(^{2+}\)), Hydrochloric Acid (HCl) from Mallinckrodt Baker, Inc., Paris and sodium hydroxide (NaOH) from Merck KGaA, Darmstadt, Germany as a pH regulator, water (H\(_2\)O) as a solvent of the tool aquadestilator (W4l Water Still Favorite), Indonesia. While the main equipment used in this study was Atomic Absorption Spectroscopy (AAS) (AA-7000 Series, Shimadzu Corporation, Japan), which
serves to measure metal ion concentration (Cd\(^{2+}\)), HCl 0.1 M and 0.1 M NaOH is provided to control the metal solvent solution Cd\(^{2+}\) with a concentration of 70 ppm on condition of acidity (pH) 4.5 solvent. White sand sifted with a 40 mesh sieve, and then the white sand washed with deionized water until the wash water pH constant, then the white sand is dried in oven (Memmert UN 55, Indonesia) at 60°C to constant weight.

In this study, Figure 1 shows the heavy metal adsorption process with a batch process without stirring (natural adsorption). Cd\(^{2+}\) solution with a concentration of 70 ppm were put in. Then, 10 g white sand added to beakerglass. To observe the adsorption capacity of the increase of time, samples were taken every 10 minutes as much as 2 mL for analysis. Sample concentration was measured by AAS analysis tools.

3. Results and discussion

3.1. Early treatment at the white sand adsorbent

Figure 1. Research stages.

Figure 2. White sand washing process adsorbent.
Pretreatment is done on Adsorbent namely washing and drying process. The washing process is shown in Figure 2. This process is carried out by washing the adsorbent material with distilled water repeatedly until the pH of distilled water after constant washing. The washing process is obtained that in order to eliminate the content of impurities existing on the white sand takes 8 washes. pH constant washing in the washing-6, 7 and 8 are at a pH of 6.8. According to Aji and Kurniawan (2012), the washing process is done on the white sand aimed to get the same conditions constant pH in each size white sand and also to remove impurities that are still attached to the sand like dust, dirt, and zat-other organic and inorganic substances [19]. Figure 3 shows the white sand on the conditions before and after washing. Condition white sand after washing looks cleaner without impurities.

After washing, then drying process is carried out in an oven at 60 ° C. Drying is done to obtain a constant weight of white sand in order to obtain uniformity of the mass of adsorbent. Data drying results can be seen in Figure 4. Adsorbent white sands require drying time for 130 minutes. Adsorbent mass is constant during the drying time of 110, 120 and 130 minutes. According Maulinact all (2013), the drying process is a process of reduction in the moisture content of materials to the level of a certain moisture content [20].

3.2 Effect of contact time and adsorption kinetics

Adsorption time is one of the parameters of the adsorption process because time is a factor that can reflect the kinetics of an adsorbent to interact with the adsorbate. Time can also be used as an indicator to determine the level of efficiency of use of the adsorbent. The adsorption process has been calculated by the equation (2) and (3). The results of the measurement of contact time on the adsorption capacity are given in Figure 5.

Figure 5 shows that Cd²⁺adsorbed greater with increasing contact time. It diesebabkan the longer
time interaction with adsorbate adsorbent causes increased adsorption capacity Cd$^{2+}$. According to Arshadi et all, that in order to achieve adsorption equilibrium will require sufficient contact time between the adsorbate with an adsorbent [16]. Viewable concentration Cd$^{2+}$ adsorbed continue to rise and reach the optimum point in the 120th minute with concentration Cd$^{2+}$ adsorbed 30.7%.

Figure 5. Effect of contact time on metal ion absorption Cd$^{2+}$ in solution by white sand adsorbent.

The adsorption kinetics is used to determine the rate of adsorption occurs on the adsorbent to adsorbat and affected by time. The contact time required to reach adsorption equilibrium adsorption rate is a metric. In this study, the adsorption rate testing has done by guessing the order of the reaction. Adsorption kinetics data empirically derived using a model pseudo pseudo first order and second order. Pseudo first order equations using equation (4) and the second order of the equation (5).

From the results of theoretical calculations, equation of first order (Figure 6A) and second order (Figure 6B) has a value of the correlation coefficient ($R^2$) are almost the similar. Comparison of the correlation coefficient ($R^2$) can be used to determine the appropriate modeling the adsorption process. The equation of order one has a $R^2$ value of 0.97 and the second order equations had $R^2$ value of 0.99. From the data obtained, it can be concluded that the adsorption process which takes place in the study involves the interaction of chemical (chemical adsorption) and physical interaction (physical absorption) between adsorbent and adsorbate on the surface occur simultaneously [11].
Modeling internal diffusion and external diffusion can be used to evaluate the ability of adsorption of heavy metal cadmium (Cd$^{2+}$) on the type of adsorbent white sand. In this study, diffusion modeling empirically derived using diffusion kinetics model of internal and external diffusion kinetics model. Internal diffusion kinetics model using equation (6) and external diffusion kinetics model using equation (7).

From Figure 7 (A) and (B) above shows the internal diffusion kinetics modeling has a value of $R^2 = 0.95$ and external diffusion has a value of $R^2 = 0.85$. The value of the correlation coefficient ($R^2$) internal diffusion is higher than the value of the correlation coefficient ($R^2$) external diffusion, from this data it can be seen that in this study is modeling kinetikanya internal diffusion trend. This shows that the adsorbent particles are inter sand surface area that experienced internal inter-particle pore diffusion.

4. Conclusion
Kinetics of adsorption reached equilibrium at time $t = 120$ minutes with the percentage concentration of adsorbed Cd$^{2+}$ 30.7%. In the adsorption kinetics modeling correlation coefficient is almost the same between the equations of first order and second order in the amount of 0.97 and 0.99. The result indicated that the type of interaction Cd$^{2+}$ ions on the surface of white sands occur in chemistry and physics. The adsorption kinetics modeling also shows a trend that shows the internal diffusion adsorbent particles are inter sand surface area that experienced internal inter-particle pore diffusion.

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