Adsorption Kinetics of Manganese (II) in wastewater of Chemical laboratory with Column Method using Sugarcane Bagasse as Adsorbent

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Abstract. The purpose of this research is to separate manganese (II) metal in the wastewater using sugarcane bagasse as an adsorbent. Experimental design, the independent variables are contact time (0; 30; 60; 90; 120; 150; 180; 210; 240 minutes, respectively) and activation treatment (without activation, physical activation, activation by H2SO4 0.5 N and activation by NaOH 0.5 N. Fixed variables consist of adsorbent mass (50 g), adsorbent particle size (30 mesh), flow rate (7 L/min) and volume of adsorbent (10 L). The dependent variable is the concentration of manganese. The results showed that the separation process of manganese by adsorption method was influenced by contact time and activation type. The kinetic studies show that the adsorption mechanism satisfies the pseudo-second-order kinetics model. Maximum adsorption capacity (qm) for adsorbents without treatment is 0.971 mg/g, physical treatment is 0.889 mg/g, chemical treatment by H2SO4 is 0.858 mg/g and chemical treatment by NaOH is 1.016 mg/g.

1. Introduction

The existence of metals in the environment comes from two sources. The first comes from natural processes such as chemical weathering, geochemical activities, decaying plants, and animals. Other sources are derived from the activities of chemical and other industries. The Manganese metal in water can form into manganese bicarbonate, Mn(HCO3)2, manganese chloride, MnCl2, and manganese sulfate MnSO4. Iron and manganese are dissolved in water in the form of Fe (II), Mn (II), in an insoluble state which has the form of Fe (OH) 3, Mn(OH)4 and also can be in colloidal form, which bonded to humid acid.[1].

There are five basic methods for separation of metals in water containing iron and manganese i.e.; by phosphate, ion exchange or adsorption, oxidation filter, aeration followed by filtration, and chemical oxidation followed by filtration.[2]. The Removal of Fe and Mn form groundwater and surface water can be done by several methods such as oxidation, alkalization, contact filtration, ion exchange, membrane processes, biological filtration and in situ method. [3,4].

In this research the separation of Mn using column system as adsorption method. Adsorption is the withdrawal of a substance by another substance so that it attaches to the surface of the adsorbent material. The use of this method applies to the purification of water and fecal matter or organisms. The
adsorbate as used since it is wastewater with Mn > 0.5 ppm metal content and as adsorbent from the waste of cane juice sale business in form of bagasse.

Heavy metal handling processes can be carried out in various ways such as adsorption, ion exchange, with membrane and precipitation. The adsorption process is more widely used because it has many advantages including non-toxic side effects, very effective to absorb heavy metals and as well as more economically. [5].

The sugarcane bagasse (SCB) can be used as an adsorbent to adsorb dye [6,7], heavy metal ions such as arsenic ion [8], manganese ion [9], iron ions [10] and another adsorbent [11] to adsorb manganese (II). Preparation of adsorptions using SCB with acid and alkali based on parameters pH, temperature, contact time, adsorbent dosage and particle size of the adsorbent. [8].

Adsorption is the process of ion absorption by absorbent particles onto solid surfaces. [12]. Sorption process is divided into two, namely adsorption and absorption. The adsorption process occurs if the ion is retained on the surface of the absorbent particles, whereas the absorption occurs if the binding process takes place inside the absorbent particles.

Adsorption generally occurs based on the interaction between the metal and functional groups present on the surface of the adsorbent through ion exchange interaction or complex formation, usually occurs on solid surfaces containing functional groups such as -OH, -NH, -SH and COOH.

The components that contribute to the adsorption process between heavy metals and adsorbents of agricultural waste are the presence of active hydroxyl (-OH), carbonyl (C = O), carboxyl (-COOH), amine (-NH2), amide (-CONH2) and thiols -SH).[13]. There are several factors which influence metal adsorption process there is contact time, the particle size of adsorbent, flow rate, activation, and metal type. Adsorption of chromium in aqueous solutions by column method using a peanut skin as adsorbent which activated by HNO3 0.1 M is influenced by adsorbate flow rate factor, column height of adsorbent and concentration of adsorbate which varies from 0 ppm, 30 ppm, 50 ppm, and 100 ppm. Variation of flow rate is 0 litre min up to 10 litre / minute, while column height 2.5 cm to 10 cm with adsorption capacity equal to 0.4937 mg/g. [14].

In the adsorption process which separates amount of manganese metal adsorbed in the adsorbent is expressed by the equation as follows;

$$ q_t = \frac{(C_0 - C_t) V}{m} $$

$q_t$: adsorption capacity at the time, $C_0$: initial Mn concentration in adsorbate at contact time = 0 min, $C_t$: Mn concentration in adsorbate at contact time = t min, $m$: mass adsorbent and $V$: adsorbate volume.

The Removal efficiency (R) of metal from adsorbate into adsorbent is expressed by the following equation:

$$ R = \frac{(C_0 - C_t)}{C_0} \times 100\% $$

Kinetics model equation of pseudo-first order expressed as follows [15];

$$ \frac{d q_t}{d t} = k_1(q_e - q_t) $$

Integration equation (3) for boundary conditions $q_t = 0$ up to $q_t = q_e$ and $t = 0$ up to $t = t$, obtained the following form of linear equation:

$$ ln (q_e - q_t) = ln q_e - k_1t $$

Parameter $q_e$: adsorption capacity at equilibrium (mg/g), $k_1$: constant ana rate pseudo orde 1 (.min$^{-1}$) can be calculated from plot ln $(q_e - q_t)$ versus t (min).

Kinetics model of pseudo-first order can be modification [16] equation pseudo-second order is expressed by the following equation:

$$ \frac{d q_t}{d t} = k_2(q_e - q_t)^2 $$

Integration equation (5) for boundary conditions $q_t = 0$ up to $q_t = q_e$ and $t = 0$ up to $t = t$, obtained the following form of linear equation:

$$ \frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e} $$
Parameter \( q_e \) (mg/g) dan \( k_2 \): constanata rate pseudo orde 2 (g.mg\(^{-1}\)min\(^{-1}\)) can be calculated from plot \( t/q_t \) versus \( t \). Simbol \( t \): contact time (min), \( v_1 \): initial rate first order, \( v_2 \): initial rate second order.

2. Material and methods

2.1. Materials

This research uses adsorbate from wastewater of Chemical laboratory of Lhokseumawe State of Polytechnic-Indonesia which contains ions Fe, Mn, Ca and Pb. The Adsorbent from sugarcane bagasse (SCB), which used it is 50 grams for adsorbent without treatment (untreated), physical treatment, chemical treatment by \( H_2SO_4 \) 0.5N and NaOH 0.5 N, respectively.

2.1.1. Adsorbent

The adsorbent is made from sugarcane bagasse which can be imported from SGB business area around of Lhokseumawe –Aceh-Indonesia. SGB is cleaned, dried by sunrise, reduction of particle size by using a scissor, crusher. The particle size of adsorbent which is used is 30 mesh sieve. The adsorbents which 30 mesh are dried by the oven at 80 °C until they are constantly weighed and also physically and chemically activated.

The SCB for without treatment were collected from sugar mill and washed with deionized water several times to remove impurities and other dissolved components such as coloring agents before it could be used in the experiment. After washing, SCB was heated in an oven at 80 °C for 24 h.

The SCB for physical treatment was boiled for 2 h and washed with deionized water several times to remove impurities and other dissolved components such as coloring agents before it could be used in the experiment. After washing, SCB was heated in an oven at 80 °C for 24 h.

The SCB for chemical treatment was treated with \( H_2SO_4 \) 0.5N and NaOH 0.5N solutions in order to investigate and compare the capacity of metal adsorption by treated SCB and untreated SCB. For this reason, 150 g of dried SCB was treated in 1000 mL \( H_2SO_4 \) 0.5N and NaOH 0.5N solutions for 24 h. After filtration, the treated SCB was washed with deionized water until the solution reached a pH value of 7. Then it was dried at 70 °C in an oven for 24 h.

2.1.2. Adsorbate

This research used adsorbate contains ions such as Fe, Mn, Ca and Pb ions to be taken from wastewater of Chemical laboratory of Lhokseumawe State of Polytechnic.

2.2. Methods

2.2.1. Adsorption column

Adsorption in a vertical column with 6.35 cm column diameter and 25 cm of empty state column height and adsorbent with a particle size of 30 mesh inserted into the column as much as 50 g (grams of mass adsorbent) without activation (untreated) inserted into the next column is collected and data is being collected. Similarly, 50 g physical activation adsorbent, 50 g of activation adsorbent by \( H_2SO_4 \) 0.5 N and 50 g activation adsorbent by NaOH 0.5N.

2.2.2. Experiment

The research was conducted system column methods with fixed variable of flow rate 7 L/min, the volume of adsorbate 10 L (liter), adsorbent mass 50 g, the particle size of adsorbent 30 mesh and operating temperature 30 °C. The independent variable of contact time (adsorption) 0; 10; 20; 30; 60; 90; 120; 150; 180; 210 and 240 minutes, respectively. The dependent or response variable is the Mn(II) concentration remaining in adsorbate (ppm), adsorption capacity (mg/g) and removal efficiency (%).

2.2.3. Analysis method

Quantitative analysis of manganese’s metals was analyzed using instrumentation method of Atomic Absorption Spectrophotometer (AAS) instrument based on SNI.6989.5.2009

3. Result and discussion

Many methods have been developed to reduce the heavy metal content, which presents in water, such as precipitation, membrane filtration, ion exchange, adsorption, and coprecipitation/adsorption.[17] However, all of these methods are considered inefficient because they required substantial funds and are less effective in their operations. One reasonably good method is that the
adsorption method can be adsorption by tank and the batch system with a column system that operates continuously. When compared to these last two methods, the column system is much more practical than the stirring system. The column system does not require a large space; the surface of the tool which is used is relatively small, while the stirring system spans the place and the wider space.

**Table 1. Analysis result of manganese (ppm)**

| t min | Untreated (U) | Physical (P) | H₂SO₄ (H) | NaOH (N) |
|-------|---------------|--------------|-----------|-----------|
| 0     | 9,935         | 9,935        | 9,847     | 9,847     |
| 30    | 5,607         | 6,720        | 5,558     | 4,571     |
| 60    | 5,079         | 5,871        | 5,470     | 6,007     |
| 90    | 5,490         | 6,974        | 6,574     | 6,164     |
| 120   | 6,017         | 4,728        | 5,929     | 4,835     |
| 150   | 5,577         | 5,275        | 5,597     | 4,852     |
| 180   | 5,275         | 5,997        | 6,700     | 4,767     |
| 210   | 5,704         | 5,490        | 6,896     | 6,359     |
| 240   | 5,470         | 5,734        | 6,339     | 6,115     |

Source: Analysis based on SNI.6989.5.2009

![Figure 1. Effect contact time (min) to adsorption capacity Mn (mg/g) ](image)

3.1. Adsorption capacity

In Figure 1, illustrates a difference in adsorption capacity for each type of adsorbent. The highest adsorption capacity occurs in the adsorbent which was activated by NaOH solution. For comparison at the contact time of 30 minutes, the highest adsorption capacity in the sequence was the adsorbent NaOH activated this, the also without activation, activation with H₂SO₄ and physical activation, respectively. The effect of caracterisctic adsorbent and effect contact time are an important factor affecting removal of metal ions in solution.[18]
The adsorption capacity of Mn (II) with corncob as adsorbent at equilibrium time is 0.00534 mg/g up to 0.03742 mg/g. [19]. The adsorption capacity of maize adsorbent to remove Fe and Mn in groundwater was 0.430 mg Fe/g and 0.043 mg Mn/g. The maximum adsorption capacity ($q_e$) in adsorbent without activation is 0.971 mg/g, adsorbent with physical activation is 1.041 mg/g, adsorbent activation by H$_2$SO$_4$ 0.5N solution: 0.858 mg/g and adsorbent which was activated by NaOH 0.5 N solution is 1.016 mg/g. The comparison of the above data resulted in adsorption of the adsorbent of sugarcane bagasse in this study is much more efficient and effective than corncobs.[20]

![Graph showing pseudo-first order kinetic model](image)

**Figure 2.** Pseudo – first order of linear kinetic model

| Kinetic Parameter | Untreated (U) | Physical (P) | H$_2$SO$_4$ (H) | NaOH (N) |
|-------------------|---------------|--------------|-----------------|----------|
| $R^2$             | 0.42          | 0.38         | 0.01            | 0.06     |
| $k_1$             | 0.01          | 0.01         | 0.00            | 0.00     |
| $q_e$ extrapolation | 0.99          | 0.99         | 1.00            | 1.00     |
| $v_1 \times 10^3$ | 7.0           | 6.0          | 1.0             | 5.0      |
| $q_e$ prediction  | 0.97          | 1.04         | 0.88            | 1.02     |
| % Error $q_e$     | 2.00          | 4.55         | 12.28           | 2.07     |

### 3.2. Kinetic Model of Pseudo-First Order

In table 2 above about the pseudo kinetics model parameter of order one, the result of linearity parameter ($R^2$) is a very small value compared to the value of the value of one. However, the value of
the adsorption capacity shows different values than the above, when compared to the adsorption capacity \((q_e)\), the experimental results with the extrapolation results from the less significant difference. The fastest initial adsorption rates are adsorbents without activation, physical activation, activation with \(H_2SO_4\) and activation with \(NaOH\). The parameters received or rejected by an equation depend on the linearity. If the linearity value is equal to one or nearly one, then the equation is acceptable. Conversely, if the value is very small compared to the price of one equation is rejected. Based on this fact the first order pseudo adsorption kinetics model on the manganese (II) adsorption process is not eligible. Therefore, knowing the adsorption kinetics model of manganese (II), it is necessary to continue the analysis using pseudo-second order adsorption kinetics model.

![Figure 4. Pseudo-second order of linear kinetic model](image)

**Table 3. Kinetic parameter of pseudo-second order**

| Kinetics Parameter | Untreated \(R^2\) | Physical \(R^2\) | \(H_2SO_4\) \(R^2\) | \(NaOH\) \(R^2\) |
|------------------|-----------------|-----------------|-----------------|-----------------|
| \(R^2\)          | 0,99            | 0,93            | 0,95            | 0,92            |
| \(k_2\)          | 2,07            | 0,08            | 326,36          | 237,48          |
| \(q_e\) extrapolation | 0,880          | 0,910           | -0,04           | -0,06           |
| \(v_2 \times 10^3\) | 2,00            | 3,00            | 0,07            | 1,00            |
| \(q_e\) prediction | 0,97            | 1,04            | 0,88            | 1,02            |
| % Error \(q_e\)  | 9,4             | 12,6            | 104,6           | 105,9           |

3.3. Kinetic Model of Pseudo-Second Order

Adsorption of Mn (II) using bagasse as adsorbent explains that the adsorption kinetics corresponds to a second order pseudo. That is the corresponding kinetic model for adsorption of metal ions using adsorbent from corn cobs such as Mn (II) and Cd (II) corresponds to second-order pseudo kinetic model,
Mn (II) adsorption capacity is 0.076 mg / g and Co (II): 0.302 mg / g. The kinetic and thermodynamic behavior of Fe (II) and Mn (II) adsorbents of activated carbon from bagasse shows the pseudo-second-order model and adsorption are endothermic and mainly physical. The kinetic study shows that the pseudo-second-order kinetic model best described the adsorption of metal ions. [21]

The adsorption kinetic data shows that Mn (II) adsorption process using corncob powder is well suited by the pseudo-order two – kinetic model. From the comparison, it can be concluded that the adsorption kinetics model of Mn (II) metal with bagasse produced the same thing.[22] As comparative with cationic dye removal by SGB The adsorption kinetics was found to follow the pseudo-second-order kinetic model with good correlation coefficient. [23]. Also, the adsorption of dye by SGB adsorbent was found to follow a pseudo-second-order rate equation. [24]. Modified SGB was found that the adsorption behavior was fit with pseudo-second-order model rather than a pseudo-first-order model. [25]

4. Conclusion
Based on literature review, the data of research result, which divide into the result of data processing and the result of the discussion, it can be concluded that an adsorption of manganese (II) metal in wastewater using adsorbent of bagasse is affected by contact time and activator types. Moreover, the maximum adsorption capacity of adsorbent without activation (untreated): 0.932 mg / g, physical activation: 1.041 mg/g, activation with H2SO4 0.5 N: 0.858 mg/g and activation with NaOH 0.5 N: 1.016 mg/g. Finally, the Manganese (II) adsorption kinetics model conforms to the pseudo-order two- kinetics model.

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