Adsorption and kinetics study of manganese (II) in waste water using vertical column method by sugar cane bagasse

H Zaini1, S. Abubakar2, T Rihayat1 and S Suryani1

1 Chemical Engineering, Politeknik Negeri Lhokseumawe
2 Electrical Engineering, Politeknik Negeri Lhokseumawe

Email: halimzaini60@gmail.com

Abstract. Removal of heavy metal content in wastewater has been largely done by various methods. One effective and efficient method is the adsorption method. This study aims to reduce manganese (II) content in wastewater based on column adsorption method using absorbent material from bagasse. The fixed variable consisted of 50 g adsorbent, 10 liter adsorbate volume, flow rate of 7 liters / min. Independent variable of particle size with variation 10 – 30 mesh and contact time with variation 0 - 240 min and respon variable concentration of adsorbate (ppm), pH and conductivity. The results showed that the adsorption process of manganese metal is influenced by particle size and contact time. The adsorption kinetics takes place according to pseudo-second order kinetics with an equilibrium adsorption capacity (qe: mg / g) for 10 mesh adsorbent particles: 0.8947; 20 mesh adsorbent particles: 0.4332 and 30 mesh adsorbent particles: 1.0161, respectively. Highest removal efficiency for 10 mesh adsorbent particles: 49.22% on contact time 60 min; 20 mesh adsorbent particles: 35.25% on contact time 180 min and particle 30 mesh adsorbent particles: 51.95% on contact time 150 min.

1. Introduction
The existence of metals in the environment comes from two sources. First of all natural processes such as chemical weathering, geochemical activities, decaying plants and animals. Other sources are derived from the activities of chemical and other industries. One of the most important metals for humans is manganese needed as nutrient and the body needs 10 mg of the manganese that can be obtained from food. If the levels are excessive this element is toxic to the respirator. In the water for public consumption problems that often occur also concerns the color of water. Manganese concentrations greater than 0.5 mg / liter can cause a strange taste in the drink and leave a brown color on the laundry and can also cause damage to the liver.

According to [1] the composition of the chemical elements of ground water depends on the layers of land passed. If through lime soil, then the water will become a container because it contains Ca (HCO₃)₂ and Mg (HCO₃)₂. If through granite rocks then the water is soft and aggressive because it contains gas CO₂ and Mn (HCO₃)₂. Sludge Mn will give stains on the material / objects are white. The existence of this element can cause smell and taste in the drink. Besides, the concentration of 0.5 mg / liters of this element is the result of an air barrier that can be achieved [2]. Furthermore, Iron and manganese are dissolved in water in the form of Fe²⁺, Mn²⁺, in an insoluble state in the form of Fe(OH)₃, Mn(OH)₃ and can also be in colloidal form bonded to humic acid [3].

3 To whom any correspondence should be addressed.
Adsorption generally occurs based on the interaction between metal and functional groups present on the surface of the adsorbent through ion exchange interaction or complex formation, usually occurring on solid surfaces containing functional groups such as -OH, -NH, -SH and COOH. According to [4] the components involved in the adsorption process between heavy metals and adsorbents of agricultural waste are the presence of active hydroxyl groups (-OH), carbonyl (C = O), carboxyl (-COOH), amines (-NH2), amides (-CONH2) and thiols (-SH). There are several factors that influence metal adsorption process that is contact time, particle size of adsorbent, flow rate, activation, metal type.

Many methods have been developed to reduce the heavy metal content present in water, such as sedimentation, vaporization, coagulation, electrochemical, electrophoresis and ion exchange, filtration. However, all of these methods are considered inefficient because they require substantial funds and are less effective in their operations [5].

One reasonably good method is that the adsorption method can be adsorption by batching and batch system adsorption with a column system that operates continuously using single, multiple columns. In parallel or in series column system. When compared to these last two methods, the column system is much better than the stirring system. The column system does not require a large space, the surface of the tool used is relatively small, while the stirring system spans the place and the wider space. The stirring system still requires further separation steps such as filtration, without going through the filtration stage of the separation system has not occurred despite adsorption already occurring. In the column system of separation of solids in liquids occurs at once with the process of separation.

In addition there is a difference in the size of the adsorbent particles used. The stirring system of particle size can be the same or smaller than the column system whereas the particle size system is larger. If a larger or smaller particle size is used the absorption process becomes ineffective.

2. Experimental procedure and methodology

2.1. Materials

This research used adsorbate from waste water (industrial waste water) containing Pb, Ca, Mn and Fe metals. The adsorbents are from bagasse with particle size of 10 mesh, 20 mesh and 30 mesh. This type of adsorbent consists of non-activated adsorbents.

Sugarcane bagasse were collected and used as sorbent for the biosorption of Mn(II) ions. The sugarcane bagasse sample was collected from traditional market around Lhokseumawe city. Samples were washed several times using reverse osmosis water to remove impurities, extraneous and dust. The samples then dried in sun dried for five days and in an oven at 105°C for 2 h. Finally, the dried bagasse was sieved to get the average adsorbent size of 10 mesh, 20 mesh and 30 mesh. The sieve sugarcane bagasse was then stored in a clean airtight plastic container and keep in desiccator, until the time of use.

2.2. Methods

The adsorption process in the vertical columns with a diameter of 6.35 cm and the height of the blank condition column of 38 cm. Each of the columns was inserted with absorbent 10 mesh, 20 mesh, 30 mesh (50 g).

The study was conducted with fixed variable particle size of 10 mesh, 20 mesh and 30 mesh. Flow rate 7 liter / min, 10 liter adsorbate volume, operating temperature of room temperature 30 °C. Variable free contact time 0; 30; 60s; 90; 120; 150; 180; 210 and 240 minutes. Response variables of remaining adsorbate concentration in solution (ppm), absorbed adsorbate concentration (ppm), adsorption capacity (mg / g), % removal.

In the adsorption process the amount of metal adsorbed in the adsorbent for contact time t is expressed by the equation:
Where:
\[ q_t = \frac{(C_0 - C_t)V}{m} \]  

Where:
\[ C_0: \text{Initial concentration of adsorbate (mg / l)} \]
\[ C_t: \text{concentration at } t \text{ (min)} \]
\[ V: \text{the volume of adsorbate (liter)} \]
\[ q_t: \text{adsorption capacity (mg / g)} \]

Percent Removal (%) of metal into adsorbent is expressed by the following equation:
\[ \% R = \left( \frac{C_0 - C_t}{C_0} \right) \times 100\% \]

Sample of analysis of data collected was analyzed using instrumentation method with Atomic Absorption Spectrophotometer (AAS).

3. Result and Discussion

3.1. The concentration of Mn in equilibrium (Ct)
Changes in the concentration of ions \( \text{Mn}^{2+} \) (Figure 1) over the contact time show the existence of differences with each other. This difference is influenced by the size of the adsorbent particle size may affect the absorption of Mn. The highest absorption occurs in adsorbents whose particle size is 30 mesh, then 10 mesh and last 20 mesh. Small particle sizes such as the 30 mesh adsorbent size in Mn absorption give better results compared to the 10 mesh and 20 mesh sizes. With a column system on 30 mesh particle size provides the best removal ability. Mn content in well water and drilling wells ranged from 0 to 5.26 ppm and drinking water quality standard of 0.5 ppm. Manganese (Mn), whose maximum requirement is 0.015 mg / l for drinking water and 0.5 mg / l for clean water [6].

![Figure 1. Effect of Contact Time on Mn (ppm) in adsorbate.](image)

Based on the data in table 2 and figure 2 the amount of \( \text{Mn}^{2+} \) metal ions absorbed into the adsorbent shows that the adsorption equilibrium occurs at 150 minutes, the magnitude of the time of the adsorption capacity is relatively the same. The best adsorption capacity occurs in adsorbents with 30 mesh particle sizes, then for the particle size of 10 mesh and last the particle size of 20 mesh. The difference in absorption occurs between each of the adsorbents aside from the particle size, also due to the porosity of each particle. The adsorbent porosity of a particle size of 30 mesh is better than that of the adsorbent whose particle size is 10 mesh and 20 mesh. Adsorption capacity of highest adsorbent bagasse 1.00 mg / g for 10 mesh adsorbents, 0.7 mg / g for 20 mesh and 1.10 mg / g adsorbents for 30 mesh adsorbents respectively at contact time of 60 minutes
Comparison of bio-adsorbent chemically activated camphor dyers of HCl resulted in the largest adsorption capacity of 1.698 mg/g [7]. The adsorption capacity of maize adsorbent to Mn metal in groundwater is 0.043 mg/g.

3.2. Capacity adsorption Mn on to SCB

The adsorption capacity of bagasse is higher than the capacity of corncob adsorption without activation (Figure 2). The adsorption capacity of the bagasse adsorbent is not activated under the capacity of chemically activated camphor adsorbents with HCl. Biosorption processes tend to occur rapidly, taking form few minutes to a couple of hours and it takes account transfer mass processes and adsorption processes. The biosorption kinetics is controlled mainly by convective and diffusive processes. In a first stage occurs the metal transference from solution to adsorbent surface neighborhood; then in the next step, the metal transference from adsorbent to intraparticle active sites; and finally, the metallic ion removal by the active sites via complexation, adsorption, or intraparticle precipitation. The first and second steps represent the resistance to convective and diffusive mass transferences and the last one is quick and non-limiting for the overall biosorption velocity.

![Figure 2. Effect of Contact Time on Capacity Adsorption Mn Onto Sugarcane Bagasse.](image)

Analogously to the biosorption isotherms, the biosorption kinetics in general present hyperbolic shape and they are described by various models. The models more used in biosorption studies are present on Table 3.

| Table 3. Kinetics Adsorption Model |
|-----------------------------------|
| **Pseudo-first-order**             |
| Differential equation              |
| $\frac{dq_t}{dt} = k_1 (q_e - q_t)$ |
| Integral equation                  |
| $\ln (q_e - q_t) = \ln q_e - k_1 t$ |
| Initial adsorption velocity        |
| $v_1 = k_1 q_e$                    |

| **Pseudo-second-order**            |
| Differential equation              |
| $\frac{dq_t}{dt} = k_2 (q_e - q_t)^2$ |
| Integral equation                  |
| $t/q_t = 1/k_2 q_e^2 - t/q_e$       |
| Initial adsorption velocity        |
| $v_2 = k_2 q_e^2$                  |
Based on the Figure 3 the Lagergren kinetic pseudo-first order equation for each of the adsorbents yields an equation which does not lead to the form of linear equations. This condition is proved by parameter $R^2$. The equality of the equation is shown if the value of $R^2$ equals 1, the closer to the value of 1. The value of $R^2$ is shown in Figure 3, where the value of $R^2$ is very far from the value of 1, ie for 10 mesh: 0.0242; For 20 mesh: 0.0270 and for adsorbents of 30 mesh: 0.0745. In addition the value of the adsorption capacity ($q_e$) of the calculation with the adsorption capacity value of the extrapolation results is different as shown in Figure 3.

### 3.3. Pseudo-First Order Kinetic

Based on Figure 3 the pseudo-second order Lagergren kinetics equation for each adsorbent yields the equation which leads to the form of the linear equation. This condition is proved by parameter $R^2$. The equality of the equation is shown if the value of $R^2$ equals 1, the closer to the value of 1. The value of $R^2$ is shown in table 6, where the value of $R^2$ is very far from the value of 1, ie for 10 mesh adsorbents: 0.9935; For 20 mesh adsorbents: 0.6664 and for adsorbents of 30 mesh: 0.9915. In addition, the adsorption capacity value ($q_e$) of the calculation with the adsorption capacity value of the extrapolation results is relatively different.

![Figure 3. Pseudo-Second Order Kinetic](image)

The rate limiting step of the adsorption was studied by using different kinetic models based on research [8], such as pseudo-first-order, pseudo-second-order adsorption equation, elovich equation and the intraparticle diffusion model. Kinetics data was best fitted with the pseudo-second-order type. This method has been successfully applied for reduce the risk of Mn(II) from ground water samples by using SCB adsorbent. Based on Figure 4, the extrapolation results showed significant differences between each adsorbent. This difference is due to differences in particle size. For 10 mesh adsorbents: 0.8947 mg/g; 20 mesh: 0.4332 mg/g and 30 mesh: 1.0161 mg/g.

![Figure 4. Effect of contact time to efficience removal Mn(II) on to SCB](image)
According to Figure 4, the size of the adsorbant particles on the metal removal of Mn (II) is very influential. The particle size of 30 mesh is the highest separation, then the particle size is 10 mesh and the last is 20 mesh. The highest removal efficiency for each adsorbent was 49.22% for 10 mesh adsorbents at 60 minutes, 35.25% for 20 mesh adsorbents at 180 minutes and 51.95% for 30 mesh adsorbents at 150 minutes.

**Esfandiar et al (2014)**, has studied about sugarcane bagasse (SCB) as biosorbent were used to remove Mn(II). The maximum experimental Mn (II) removal efficiencies is 63%, respectively, were obtained. Additionally, a chemical treatment of SCB had a significant effect on the adsorption, as maximum removal increased up to 99%. The ability to eliminate each of the adsorbents is influenced by the contact time, internal and external properties of the adsorbent.

The use of sugarcane bagasse as adsorbent is considered effective enough to decrease the fatty acid free fat content of frozen vegetable, the biggest decrease 57.3% with particles size 200 mesh particle size 50 g, 2 hours contact time [10, 11, 12]. Adsorption of bagasse which was activated with NaOH for 3 hours to Pb (II) was batched with 76.7% removal ability at 60 minutes. Physicochemical characteristics of waste water.The physicochemical characteristics such as turbidity, alkalinity, hardness, TDS, Chorine and other ions concentration will be measure for waste water.

### 3.4. Effect of Contact Time to PH Value

The pH of the aqueous solution is an important operational parameter in the adsorption process because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups.

According [13], the potential to remove Zn(II), Cd(II) and Mn(II) form aqueous solution biosorption using maze stalks as an agriculture waste, was investigated in batch experiments. Different factors influencing metal adsorption such as contact time, initial metal ion concentration, pH, ionic strength and temperature were investigated. The adsorption process was relatively fast and equilibrium was established after about 90 min. The optimum initial pH for manganese by maize stalks was 5.6.

The potential to reduce the risk of Mn(II) from ground water through adsorption using Sugar Cane Bagasse (SCB) as a low cost natural waste was investigated. The adsorption was taken in batch experiments under different parameters such as pH (2.0-10.0), weight of phase (0.25-2.5 g), contact times (10-180 min), initial concentration (2.0-10.0 ppm). The removal efficiency may be maximum at pH 5 on adsorption by using sugarcane bagasse [14].

![Figure 5. Effect of contact time to pH Value](image)

### 3.5. Effect of Particle Size to PH Value

Based on Figure 5, the particle size of the adsorbent affects the pH value of the wastewater solution. However, the pH value that gives a big change is the adsorbent whose particle size is 30 mesh, while
for the 10 mesh and 20 mesh particles the pH is relatively stable. In general, the pH value of the solution ranges from 4 to 5.5. This pH value is relatively equal to the pH obtained from manganese adsorption using a corncob adsorbent of 5.6 magnitude.

4. Conclusion
Based on the data of research, data processing, discussion and comparison to previous research can be summarized the following conclusion: The adsorption of manganese (II) metal in wastewater using adsorbent of sugarcane bagasse is affected by contact time and particle size of the adsorbent. Adsorption kinetics of manganese (II) is adsorption kinetics of the pseudo-second order. Adsorption capacity at equilibrium (qe) manganese (II) for particles size 10 mesh adsorbents: 0.8947 mg/g; 20 mesh: 0.4332 mg/g and 30 mesh: 1.0161 mg/g. The highest removal efficiency of manganese (II) metal waste for 10 mesh adsorbents: 49.22% at contact time of 60 minutes; 20 mesh: 35.25% at contact time 180 min and 30 mesh: 51.95% at contact time 150 min.

Acknowledgement
The authors express their gratitude and thanks to the Higher Education Ministry for Financial Support through the PPT (Penelitian Produk Terapan) Grant and Ditjen Penguatan Riset dan Pengembangan, Kemenristekdikti

References

[1] Sutrisno, T., and Suciastduti, E. 2010. Water supply technology. Rineka Cipta.
[2] Setiyono, A. 2014. Study of Manganese Content (Mn) In Well Water Dug in Karang Nunggal Village Kabupaten Tasik Malaya. Environmental Health Journal. Vol.10 No.1
[3] Sari, W.K., Karnaningrum, N. 2015. Study of Removal Iron and Manganese Using Cascade Aeroator and Rapid Sand Filter In Well Water Dug. Environmental Departemen- Institut of Technology Surabaya-Indonesia.
[4] Ahalya, N., Ramachandra, T.V., Kanamadi, R.D. 2003. Biosorption of Heavy Metals. Research Journal of Chemical and Environment. 7(4),71-79.
[5] Irmawati, A., Ulfin, I. 2013. Utilization of Peanut Skin Biomass For Adsorption of Chromium In Aqueous Solutions By Column Method. Chemistry Departement-Institute of Technology Surabaya.
[6] Munfiah, S., Nurjazuli., Setiani, O. 2013. Physical Quality and Chemical Well Water Drilling and Drilling at Working Area of Puskesmas Guntur II KabupatenDemak. Journal of Environmental Health-Indonesia. Vol 12 No 2, October 2013
[7] Mandasari, S., Purnomo, A. 2016. Removal of Fe Ion and Mn in water with camphor wood sawdust. Technic Journal Institutute of Technology Surabaya. Vol.5 No.1,(2016) ISSN:2337-3539 (2301-9271 Print)
[8] Ahmed, S., A., El-Roudi, A.M., Salem, A., A. 2015. Removal Mn(II) from Gound Water by Solid Wastes of Sugar Industry. http://scialert.net/fulltext/?doi=jest.2015.338.351&org=11
[9] Esfandiar, N., Nasemejad, B., Ebadi, T. 2014. Removal Mn(II) form goundwater by sugarcane bagasse and activated carbon (a comprative study): Application of response Surface Methodology (RSM). Journal of Industrial and Engineering Chemistry 20 (2014) 3726-3736
[10] Ratno, Mawarani, L.J., Zulkifli. 2013. The Effect of Sugar Cane As Adsorbent on Jelantah Oil Pretreatment Process on Biodiesel Characteristics. Technic Journal POMITS Vol 2 No 2 (2013) ISSN: 2337-3539 (2301-9271).
[11] Nurgayati, I., Sutrisno, J. 2011. Sugar Cane Waste as Heavy Metal Absorvent Ph. National Seminar: Development of Eco-Friendly Technology Toward Environmental Sustainability
[12] Rihayat, T., Saari, M., Suraya, A.R., Mahmood, M.H., Dahlan, K.Z.H.M., Yunus, W.M.Z.W. Sapuan, S.M. Synthesis and thermal characterization of polyurethane/clay nanocomposites
based on palm oil polyol. Polymer - Plastics Technology and Engineering, Vol. 45, Issue 12, (2006):1323-1326

[13] El-Sayed, G.O., Dessouki, H., A., Ibrahiem, S., S. 2011. Removal of Zn(II), Cd(II) and Mn(II) From Aqueous Solutions by Adsorption On Maize Stalks. The Malaysian Journal of Analytical Sciences, Vol 15 No 1 (2015): 8-21

[14] Khrisnakumari, B., Isyshawarya, P., Gayathri, R., G., R., Sangeetha, N. 2016. 2016. Removal of Iron Content From Drinking Water By Using Coconut Coir And Sugar Bagasse. International Conference on Breakthrough in Engineering, Science & Technology-2016 (INC- BEST’16).