STUDY OF FEASIBILITY OF MEANDG'S (Litsea sp) SAWDUST FOR THE REMOVAL OF CADMIUM FROM SIMULATED AQUEOUS SOLUTION

[1*]Muhammad Nazar, [1]Ibnu Khaldun, [1]Kana Puspita and [1]Habibati

[1]Department of Chemistry Education, Faculty of Education and Teacher Training, Syiah Kuala University, Darussalam, Banda Aceh 23111, Indonesia
*Coorresponding Author: mnazar@unsyiah.ac.id

Abstract

In this research, a series of batch laboratory experiments were conducted to examine the feasibility of Meandg's (Litsea sp) saw dust for the removal of cadmium from simulated aqueous solution by using adsorption method. The research was carried out by studying the influence of pH of initial solution, contact time, adsorbent dosage, stirring speed, and the initial concentration of cadmium. The sawdust particle size used was < 150 mesh and the experiments were conducted at room temperature of 27ºC (±2ºC). The residual concentration of cadmium from all batch experiments were analyzed using Atomic Adsorption Spectrophotometer (AAS) and each component equilibrium data was analyzed using Langmuir and Freundlich adsorption isotherms. The research findings shown that the optimum conditions are found to be at the pH of 6, the initial concentration of cadmium of 500 ppm with contact time of one hour, 3 gram of sawdust, and the optimum stirring at the speed of 350 rpm. The adsorption capacity of medang sawdust according to Langmuir and Freundlich isotherms are found respectively to be of 2.29 mg/g and 0.55 mg/g.

Key words: Litsea sp, sawdust, cadmium, adsorption

Introduction

Modern industries such as paper mill, textile, plastics, cosmetics and ceramics give significant bad impact to the environment by exposing hazardous chemical waste like heavy metal. (Andarto, 2007). The contamination of heavy metal have been a crucial worldwide issue that rise the concern among environmentalist and scientist due to the environmental damage caused by metal exposure. Among the heavy metals those usually contaminating the surronding are cadmium (Cd), chromium (Cr), silver (Ag), lead (Pb), Zinc (Zn), mercury (Hg), Copper (Cu), Iron (Fe), nickel (Ni), and Cobalt (Co). All of mentioned metals are very toxic to both environment and human being. (Purwaningsih, 2009).

One of dangerous heavy metals is Cadmium (II) which is not only canot be docomposed by microorganism but also accumulates in environment especially in wáter. The contaminating wáter then being used by human, animals and plants for long period leads to some chronic deseases (Suhud, 2012). Cadmium is very toxic even in a very small amount with tolarable limit in wáter about $2x10^{-4}$ ppm. The Ministry of Health of Indonesia set the savety limit for cadmium in fish to 1 ppm. However, According to FAO and WHO the tolarable limit is 500 µg per person or 7 µg/kg bodyweight.

Chronic toxicity caused by cadmium exposure leads to fisiological system damage including respiratory disorder, blood circulation disorder, heart attack and osteoporosis. Furthermore, longtime accumulation of cadmium causes the damage of kidney and and anemia. (Maulana, 2012). There are alot of industries such as alloy production, ceramics pigmenting process, thermoplastics and batery associated with cadmium (Volesky, 1993; Al-Hashimi, 2013). Since above mentioned industries release cadmium as waste, removing and lowering the concentration of cadmium become very urgent to implement. The romoval of heavy metals usually conducted by using several methods including ion Exchange, filtration, electrochemical process, evaporation and adsorption (Ossman and Mansour, 2013). However, the most simple to do is adsorption method.

In the adsorption method, the common adsorbent used is activated carbón, but it is relatively expensive, thus an alternative cheap adsorbent obtained from sawdust is intoduced. The sawdust which is come from biomass can be directly used as adsorbent without any longtime-treatment and preparation. In addition, the sawdust contains polypolar functional groups and polysacaride which has cationic properties enable the sawdust to be an efective adsorbent (Safarik, et al, 2007; Noonpui et al, 2010; Begum and Al-Haji, 2013; Shukla, 2002).

Adsorption of Cd (II) using a variety of adsorbents have been widely conducted. For example Saccharomyces cerevisiae (Volesky, 1993), old newspapers (Ossman, 2013), agricultural wastes (Al-Hashimi, 2013), and polyaniline coated with sawdust (Ossman 2011). Sawdust contains cellulose, hemicellulose and lignin, the -OH group on the cellulose makes wood sawdust potential to be used as an adsorbent of metal ions in the environment (Crini in Mohadi et al., 2013). Several studies on sawdust as an adsorbent of heavy metals have also been published including chromium adsorption using Havea brasiliensis sawdust (Ahmad et al., 2009), meranti and Mansonia sawdust as adsorbent of Cu (II) and Pb (II) (Ahmad et al., 2009; Ofomaja et al, 2010) and adsorption of cobalt using pine sawdust (Musapatika et al., 2012).

Other species of Wood which can be used as a heavy metal adsorbent is medang. Medang (Litsea sp) is one of common Wood used for furniture production in Aceh. Vast majority of furniture small industries in Aceh used medang as raw materials thus produce lot of medang's sawdust. Therefore, in this research, medang sawdust which is collected from some local furniture industries was used as adsorbent to remove Cd (II) from aqueous solution.

Materials and Method

Sawdust preparation and chemicals

The sawdust of medang was obtained from local furniture industry and used for the preparation of adsorbent. It was washed with distilled water to remove surface impurities and dried at 110 °C for 24 h, ground and sewed with Blender to increase the surface area. All chemicals used were of analytical grade. Stock solutions of heavy metal ion (Cd^{2+}) (1000 ppm) was prepared from $CdSO_4$ $8H_2O$ (Merck). A hot plate magnetic stirrer was used for all the adsorption experiments. Filtering process was performed by using a 150 mesh filter. Atomic absorption spectrometer (AAS) (Model AA 6300 SHIMADZU) was used to analyze the concentrations of Cd ion.

Batch adsorption experiments

The batch technique was employed to obtain equilibrium data due to its simplicity. Batch adsorption were performed at room temperature and different pH of Cd solution, contact time, mass of adsorbent, stirring speed and initial Cd concentrations to obtain equilibrium isotherms. For isotherm studies, adsorption experiments were carried out by shaking 3 g of sawdust samples with 100 ml flasks filled with 25 ml of Cd solution at a concentration range 50–500 mg/L at speed of 350 rpm for 60 minutes. After equilibrium the suspension was filtered with syring and the metal solution was then analyzed using AAS. In order to obtain the adsorption capacity, the amount of ions adsorbed per mass unit of sawdust (mg/g) was computed using Langmuir and Freundlich isotherm expressions:

$$\frac{C}{qe} = \frac{1}{bK} + \frac{1}{b}C \quad \text{.................................} \quad (1)$$

Where C is metal ion concentration at equilibrium (mg/L), q_e is the amount of metal ion adsorbed at equilibrium (mg/g), b is adsorption capacity and K is the equilibrium constant.

$$q_e = \frac{(Co-Ce)V}{W} \quad \text{...................................} \quad (2)$$

Where, q_e is the amount of metal adsorbed at equilibrium (mg/g), Co is the initial metal concentration (mg/L), Ce is the equilibrium metal ion concentration (mg/L), V is the volume of aqueous phase (L) and W is sawdust weight (g)

Results and Discussion

Effect of pH on the adsorption of Cd (II)

The pH of solution is an important factor for adsorption to be successfully conducted since the solubility of such a metal is pH dependent. To obtain the optimum pH of metal ion solution, the adsorption at the pH range 2 to 7 as depicted by figure 1 was conducted.

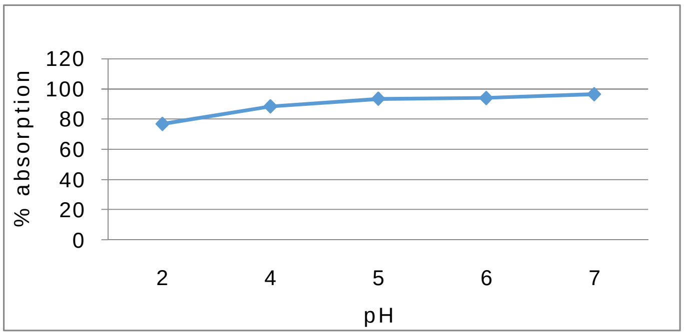

Figure 1. Adsorption of Cd at different pH

The graph illustrates that the adsorption of Cd (II) increase as pH increase but relatively constant at the pH 5, 6 and 7. However, the lower adsorption occurred at acidic solution due to competition between Cd^{2+} and hydrogen ion to be bound to the adsorbent. H^+ inhibits Cd^{2+} to approach the adsorbent resulted in less effective adsorption. Therefore the solution pH were set at 6 for other experiments.

Contact time

The contact time range 15 to 80 minutes, this equilibrium time has to be determined in order to let the optimum interaction between sawdust and the metal. Since the contact time is one of important factors of adsorption, five different experiments were carried out to investigate the optimum adsorption of Cd^{2+}.

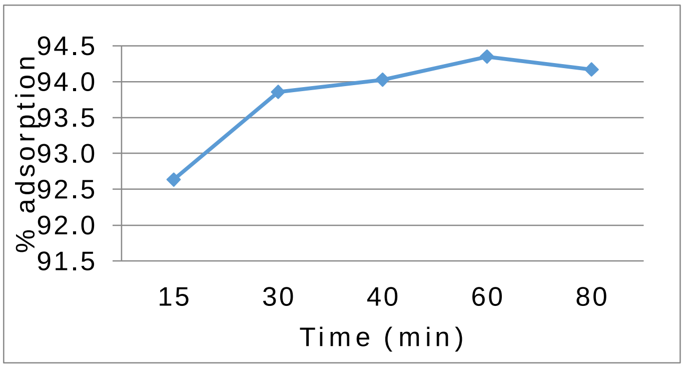

Figure 2. Adsorption of Cd at various contact time

The optimum adsorption occurs at 60 minutes of contact time and the gradual increase of adsorption happened from 15 minutes to 60 minutes as depicted in figure 2. On the other hand, adsorption decrease slightly when the contact time of 80 minutes. This lower adsorption could be due to adsorbent saturation lead to fully occupied surface of adsorbent and all functional groups responsible to adsorb the metal has been blocked by the metal layers.

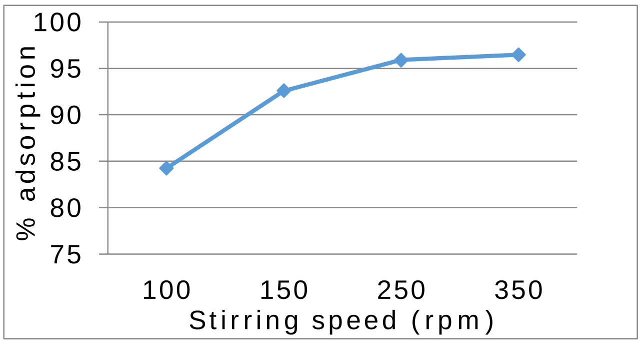

Figure 3. Effect of stirring speed on adsorption of Cd^{2+}

Effect of stirring speed

The graphic shows the significant increase of adsorbed Cd as stirring speed up until 350 rpm. There was only 84 % of Cd adsorbed when stirred at 100 ppm, whereas at the speed of 350 rpm, the amount of Cd ion adsorbed increase by 12%. When the solution was stirred faster, the probability of two components (adsorbent and sawdust) to collide was greater lead to the effective adsorption of Cd by the functional groups on the surface of sawdust. (Mosavian et al., 2012).

Study of Isotherm

In order to investigate the adsorption capacity of medang sawdust the batch experiment was set to be at all other optimum conditions (pH=6, stirring speed=350 rpm, contact time=60 min, 3 g of sawdust) and the serial concentration of Cd was prepared at 50, 100, 150, 250, 400 and 500 ppm. As depicted in figure 4, the more concentrated the initial concentration of Cd^{2+}, the greater the adsorption.

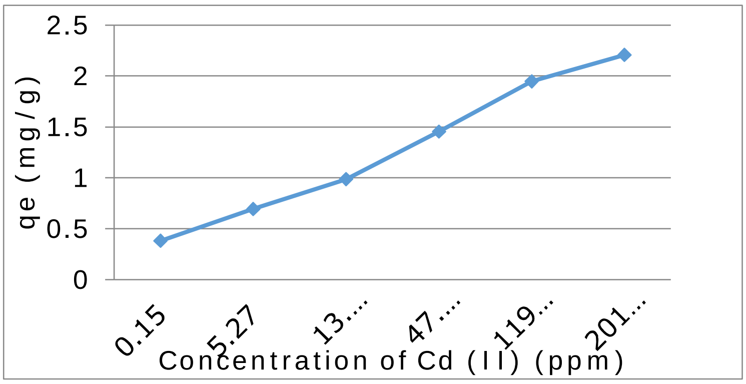

Figure 4. Effect of initial concentration of Cd (II) on the adsorption capacity

Isotherm of adsorption is a mathematical model devoted to illustrate the correlation between adsorbate and adsorbent and explaining how the adsorbent interact with the metal ions in this case is the interaction between sawdust and cadmium ion (Hashem Te al., 2013). There are abot 13 different models of isothermic expression those can be employed to analyse the adsorption data and among the popular and widely used are Langmuir's isotherm and Freundlich's isotherm. (Foo and Hameed, 2010).

Langmuir's Isotherm

Langmuir's isotherm expression is a quantitative model developed to explain the adsorption process by assuming that the adsorbent bear active sites capable of binding only one molecule. Thus only a monolayer adsorption occurs. The Langmuir isotherm expression is given by formula (1). By using the expression, plotting C/q_e versus C (as shown in figure 5) will result the straight line expression that enable us to determine the value of (b) i.e adsorption capacity and the equilibrium constant (K).

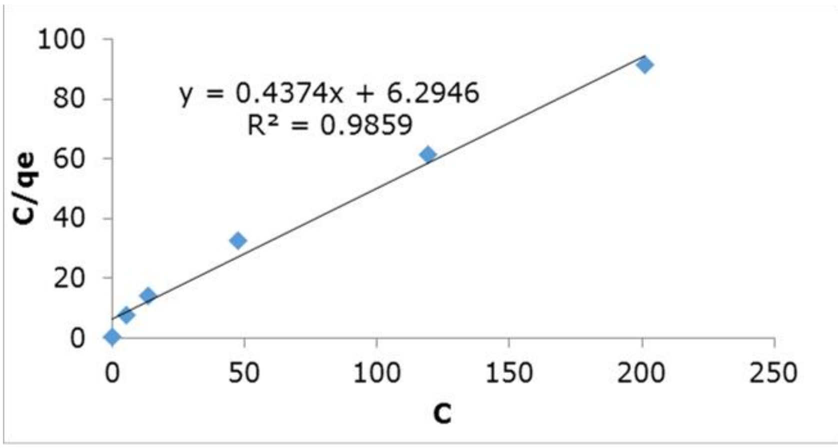

Figure 5. Langmuir isotherm

The adsorption capacity was found to be 2.3 mg/g and the equilibrium constant 0.07. Even though the adsorption capacity obtained from calculation through Langmuir isotherm was lower than what have been reported by Bulut and Tez (2009) which was 5.76 mg/g. The correlation value was sufficiently enough to conclude that the removal of Cd (II) ionic solution by using medang sawdust is appropriate to be modeled by Langmuir isotherm.

Freundlich Isotherm

The Freundlich isotherms has also been employed to model the removal of Cd (II) by medang sawdust. This model of isotherm assumes that the active sites appear in the adsorbent have different adsorption capacity and are capable of adsorbing more than one layer resulted in multilayer adsorption (Foo and Hameed, 2010). In Freundlich isotherm, Straight line expression is obtained by plotting log q_e against log C as The following formulas:

$$q_e = k.C^{1/n} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$
$$\text{Log } q_e = \log k + 1/n \cdot \log C \quad \ldots\ldots\ldots (4)$$

Where, q_e is the amount of metal ion adsorbed (mg/g), C is the initial concentration of metal ion (mg/L), k is the adsorption capacity (mg/g) and n is Freundlich constant.

The k value is obtained from the intercept and n value from the slope. Where k is a constant value expressing the quantity of adsorbed Cd (II) by medang sawdust or termed as (adsorption capacity) and n expressed the intensity of adsorption. The value of n is greater than 1 indicates that adsorption was favoured in the system (Hashem et al., 2013).

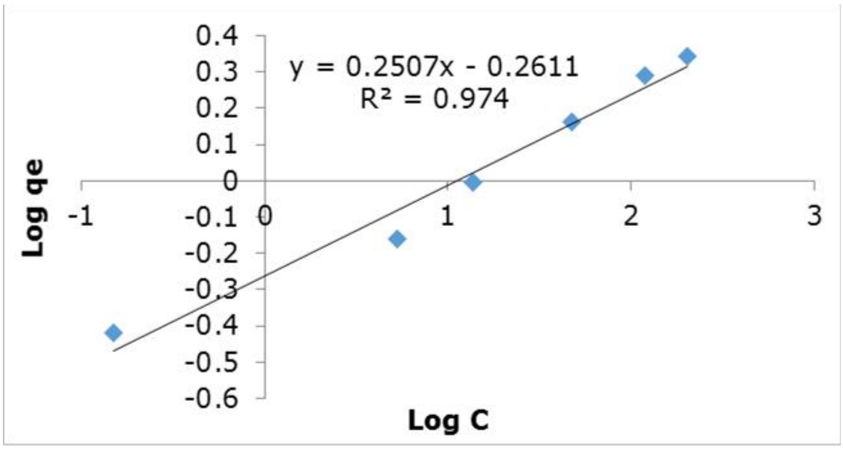

Figure 7. Freundlich Isotherm

In this experiments, the adsorption capacity of medang sawdust was found to be 0,548 mg/g which is greater then what have been reported by Bulut and Tez (2009) which was 0.24 mg/g. Furthermore, this batch experiment also gained a better n value with R^2= 0.974. This finding indicates that both Freundlich isotherms and Langmuir isotherm are firmly appropriate to be modeled to the adsorption of Cd (II) by medang's sawdust.

Conclusion

Based on the experiment conducted, the following conclusion can be drawn. Firstly, medang's sawdust can be effectively employed to adsorb Cd (II) from the solution and the optimum conditions is as follow: 3 gram of adsorbent at the stirring speed of 350 ppm for 60 minutes. Optimum pH was found to be 6 with 500 ppm of initial Cd concentration. According to Langmuir and Freundlich isothermal models, the adsorption capacity were respectively 2.29 mg/g and 0.55 mg/g. Secondly, the sawdust of medang seem to be more economical to be used as adsorbent in order to remove heavy metal from aqueous solutions rather than commercial adsorbents.

References

Ahmad, A., Chii, Y.Y., Ibrahim, M.H., Rafatullah, M., Siddique, B.M., and Sulaiman, O. (2009). Removal Of Cu(II) And Pb(II) Ions From Aqueous Solutions By Adsorption On Sawdust Of Meranti Wood. Desalination, 247:636-646.

Ahmad, W.A., Mohammed, N., Suratman, M., and Zakaria, Z.A. (2009). Chromium(VI) Removal From Aqueous Solution By Untreated Rubber Wood Sawdust. Deslination, 244:109-121.

Al-Hashimi, M.A.I. and Al-Safar, M.M. (2013). Removal Of Cadmium From Synthetic Water By Using Agricultural Wastes. Acta Technica Corviniensis, 6(2):131-138.

Bulut, Y. and Tez, Z. (2007). Removal of Heavy Metals From Aqueous Solution by Sawdust Adsorption. Journal of Environmental Sciences, 19:160-166.

Begum, K.M.T.M. and Alhaji, N.M.I. (2013). Adsorption Efficiency Of Sawdust In Activated And Surface-Modified Forms-A Comparative Study. Chem Sci Trans, 2(4):1364-1369.

Andarto, Y.C. (2007). Kinetika Adsorpsi Logam Berat Cr(VI) Dengan Adsorben Pasir Yang Dilapisi Besi Oksida. Ekuilibrium, 6(2):65-70.

Foo, K.Y. and Hameed, B.H. (2010). Insights Into The Modeling Of Adsorption Isotherm Systems. Chemical Engineering Journal, 156:2-10.

Hashem, A., Adam, E., Hussein, H.A., Sanousy, M.A., and Ayoub, A. (2013). Bioadsorption of Cd(II) From Contaminated Water on Treated Sawdust: Adsortion Mechanism and Optimazation. Journal of Water Resource and Protection, 5:82-90.

Kapur, M. and Mondal, M.K. (2013). Mass Transfer and Related Phenomrns for Cr(VI) adsorption From Aqueous Solutions onto Mangifera indica Sawdust. Chemical Engeneering Journal, 218:138-146.

Kumar, M., Gupta, A. and Majumder, C.B. (2014). Adsorptive Removal Of Toxic Metal Chromium (VI) From Aqueous Solution By Using Sawdust. International Journal of Scientific Engineering and Technology, 3(5):500-506.

Lelifajri. (2010). Adsorpsi Ion Logam Cu(II) Menggunakan Lignin Dari Limbah Serbuk Kayu Gergaji. Jurnal Rekayasa Kimia and Lingkungan, 7(3):126-129.

Maulana, D.A. (2012). Kimia Lingkungan (Logam Berat Kadmium). (Online) https://ml.scribbd.com/doc/240274181/Penyakit-Itai-itai-Keracunan-Cadmium (diakses 2 Maret 2015).

Mohadi, R., Hidayati, N., Lesbani, A., and Saputra, A. (2013). Kajian Interaksi Ion Co^{2+} Dengan Selulosa Dari Serbuk Gergaji Kayu. Indonesian E-Journl of Applied Chemistry, 1(2):8-15.

Mosavian, M. T. H., Khazaei, I. and Aliabadi, M. (2012). Use of Sawdust of Aspen Tree for the Removal of Chromium (VI) from Aqueous Solution. Iranian Journal of Earth Sciences, 4: 25-30.

Musapatika, E.T., Moodley, K., Nzil, C., Ochieng,A., Onyango, M.S., and Singh, R. (2012). Cobalt Removal From Wastewater Using Pine Sawdust. African Journal of Biotechnology, 11(39):9407-9415.

Noonpui, S., Nakbanpote, W., Netpradit, S., and Thiravetyan, P. (2010). Color Removal From Water-Based Ink Watewater By Bagasse Fly Ash, Sawdust Fly Ash And Activated Carbon. Chemical Engineering Journal, 162(2):503-508.

Ofomaja, A.E., Oladoja, N.A., and Unuabonah, E.I. (2010). Competitive Modeling For The Biosorptive Removal Of Copper And Lead Ions From Aqueous Solution By Mansonia Wood Sawdust. Bioresource Technology, 101:3844-3852.

Ossman, M.E., Farag, H.A., and Mansour, M.S. (2011). Removal Of Cd (II) Ion From Waste Water By Adsorption Onto Polyaniline Coated On Sawdust. Desalination, 272(1-3):301-305.

Ossman, M.E. and Mansour, M.S. (2013). Removal Of Cd(II) Ion From Wastewater By Adsorption Onto Treated Old Newspaper. Internasioanl Journal of Industrial Chemistry, 4:13.

Purwaningsih, D. (2009). Adsorpsi Multi Logam Ag(I), Pb(II), Cr(III), Cu(II), And Ni(II) Pada Hibrida Etilendiamino-Silika Dari Abu Sekam Padi. Jurnal Penelitian Saintek, 14(1):59-76.

Safarik, I., Lunackova, P., Safarikova, M., Szablewska, E.M., and Weyda, F. (2007). Adsorption Of Water-Soluble Organic Dyes On Ferrofluidmodified Sawdust. Holzforschung, 61:247-253.

Shukla, A., Dubey, P., Margrave, J.L., Shukla, S.S. and Zhang, Y.H. (2002). The Role Of Sawdust In The Removal Of Unwanted Materials From Water. Journal of Hazardous Materials, 96(1):137-152.

Suhud, I., Hamzah, B., and Tiwow, V.M.A. (2012). Adsorpsi Ion Kadmium(II) Dari Larutannya Menggunakan Biomassa Akar and Batang Kangkung Air (Ipomoea aquatica Forks). Jurnal Akademika Kimia, 1(4):153-158.

Syauqiah I., Amalia, M., and Kartini, H.A. (2011). Analisi Variasi Waktu and Kecepatan Pengadukan Pada Proses Adsorpsi Limbah Logam Berat Dengan Arang Aktif. Info Teknik, 12(1):11-19.

Volesky, B., Holan, Z.R., and May, H. (1993). Cadmium Biosorption By Saccharomyces cerevisiae. Biotechnology and Bioengineering, 41:826-829.