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Adsorption performance of fixed-bed column for the removal of Fe (II) in groundwater using activated carbon made from palm kernel shells N Sylvia1,4, L Hakim1, N Fardian2 and Yunardi3 1Department of Chemichal Engineering, Malikussaleh University, Lhokseumawe, 24351, Indonesia 2Department of Nutrion, Medical School, Malikussaleh University, Lhokseumawe, 24351, Indonesia 3Department of Chemical Engineering, Syiah Kuala University, Banda Aceh 23111 Indonesia. E-mail: nxsylvia@gmail.com Abstract.

When the manganese is beneath the worthy constrain, at that point the evacuation of Fe (II) particle, the common metallic compound contained in groundwater, is one of the foremost vital stages within the preparing of groundwater to gotten to be consumable water. This ponder was pointed at exploring the execution of a fixed-bed adsorption column filled, with activated carbon arranged from palm part shells, within the expulsion of Fe (II) particle from groundwater. The impact of critical parameters such as bed profundity and the stream rate was examined. The bed depth.adsorbent.(varied.from.7.5, 10 and 12 cm) and flow rate.(varied from 6, 10 and 14 L/minute). The Fe (II) particle concentration was confirmed by Atomic Absorb Spectrophotometer.

From that point the comes about were affirmed employing a breakthrough curve appearing that stream rate and bed profundity influenced the curve. The mathematical model that used to predict the result was the Thomas and Adams-Bohart model. This model is used to process design, in which predicting time and bed depth needed to meet the breakthrough.

This study reveals that the Thomas model was the most appropriate one, including the use of Palm Kernel Shell for processing groundwater. Agreeing to the Thomas Show, the most elevated capacity of adsorption (66.189 mg/g) of 0.169-mg/L of groundwater was

accomplished with a stream rate of 6 L/minute, with the bed profundity at 14 cm. 1.

Introduction The need of clean water is increasing along with the development of people and technology. This requires various facilities including clean water, whereas most people use groundwater. Groundwater contains relatively high Fe. In the body, A small amount of Fe is needed to develop red blood cell, but higher amounts can cause dangerous ailments to human health and the environment.

Thus, a further processing step is required in groundwater to be safe to use[1]. One method to eliminate Fe in groundwater is adsorption. This is performed by activated carbon as the adsorbent. The most important part of the process was using effective and cheap adsorbent, one of it is palm kernel shells [2, 3, 4].

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In crude palm kernel oil, only a small portion palm kernel shell of which is used as fuel, the rest is thrown away and ultimately impacts the environment such as odor and pollution on the ground if it accumulates in large quantities. Okoroigwe et al [5] mentioned that palm kernel shell was effective to be used as active carbon for water treatment.

Types of adsorption is two, the batch and the continuous (column) systems. The continuous (column) system is considered more efficient compared to a batch system, and more appropriate to be used in larger scales. Two methods used in a column system down flowed and up flow [6, 7, 8, 9]. In this research, down flow was used due to its easier operation on flow rate.

The success of adsorption by column system was determined by several factors such as flow rate, effluent fluid concentration and the height of bed adsorbent. Mathematical methods have been developed to describe pollution mass in the column-shaped adsorbent. As mentioned by Messaoudi et al [10] performed research on Congo Red bio-sorption (CR) in fixed bed column of fluid using shell jujube.

The highest bio-sorption capacity was 80.49 mg/g) out of 100 mg/L CR fluid, reached in the flow rate of 2.8 mL/min, bed depth 4 cm and JS particle sizes of 50-100 μm. Data gained was coherent to Thomas Model. Mohamed [11] conducted research using spent Tea Leaves (STL) in adsorption Crystal Violet (CV) from textile plant waste by fixed bed column.

Fourier transform infrared (FT-IR) spectroscopy and thermal analysis (TGA) were used for analysis. Based on the breakthrough curve, the optimal result was reached in 30 mg/l of concentration, 20 cm of bed height and 5 ml/min of flow rate. Nassar et al [1] conducted research on Fe and Mn adsorption on palm fruit bunch and maize cob on fixed bed column.

He analysed the effect of the process variable of bed height, low rate, and percentage breakthrough. The results showed that that the adsorbent used was effective in adsorbing metal ion. Most studies of metal ion wells in ground water are conducted using a batch system that is generally very easy to apply in laboratory studies and is limited to the processing of waste water in small quantities. Data obtained under batch conditions are generally not appropriate for most treatment systems.

The weakness of the batch system between the contact times in the batch system is too short to reach the equilibrium state in the column system. While the continuous system is inexpensive in operating costs and is able to adapt to the ongoing process [10]. Based on previous research to analyze the performance of adsorbent, this research focused on the effectiveness of adsorption column using palm kernel shell as active carbon, in this matter was down flow fixed-bed column [2,3,4,5]. 2.

Mathematical description Various simple mathematical models have been developed to describe and possibly predict the dynamic behaviour of the bed in column performance [12]. The mathematical models such Thomas and Bohart-Adams are the most used to describe the dynamic behaviour of pollutants removal in fixed-bed column [10]. Thomas model is most one the most general and widely used in the column performance theory.

This model has been applied for biosorption progress where the external and internal diffusion limitations are absent [13, 14], the maximum adsorption capacity, where qo of an adsorbent is necessary in the design of an adsorbent column. The Thomas model is commonly applied to determine qo, where the model is given in equation 1. (1) where kT is the Thomas rate constant (L/mg.min), C0 is the initial lead concentration (mg/L), Ct is the equilibrium concentration (mg/L) at time t (min), qo is the maximum column adsorption capacity (mg/g), Q is the volumetric flow rate through column (L/min), m is the mass of adsorbent in the column (g).

The Bohart-Adams model assumes that the adsorption rate is proportional to both the residual capacity of the adsorbent and the concentration of the adsorbing species [15]. The Adams–Bohar

Model is used for the description of the initial part of the breakthrough cure, this model is limited to range of the condition used. Where the model is given in equation 2: (2) From this equation, values describing the characteristic of the operational parameters of the column Z is the bed depth (cm), No is the column adsorption capacity in BDST model (g/L), u (cm/min) is the linear velocity calculated by dividing the flow rate by the column sectional area, kAB is the adsorption rate constant (L/mg·min). 3. Experimental procedure and methodology 3.1.

Preparation of palm kernel shell activated carbon Palm kernel shell was obtained from a palm oil company, PT. Syaukat Sejahtera, Grugok, Bireuen, Aceh, Indonesia. The raw palm kernel shell was washed with deionized water several times to remove all traces, such as oil and dirt. The material was dried in an oven having a temperature of 100? until its weight is constant.

Carbonization of the material was achieved by heating at 400oC in a furnace for 3 hours under air. The carbonized material was ground into fine particles and sieved to a particle size of 50 mesh. Activation of the carbonized particles was performed by physical heat treatment in a furnace at a temperature of 800oC for one hour under air.

The activated carbon was then cooled to a room temperature before it was used as an adsorbent. 3.2. Activated carbon analysis The results of the activated carbon quality test prior to activation and after activation are listed in Table 1. The characteristic of kernel shell palm before activated and after activation is done by using scanning electron microscopy SEM (JSM-6510LA).

The functional groups of palm kernel shell before and after activated were identified by Fourier transform infrared FTIR (Jasco 4100). 3.3. Fixed Bed column studies The groundwater sample was taken the local groundwater well in the Faculty of Chemichal Engineering, Malikussaleh University, Lhokseumawe, Indonesia, consisting of Fe (II), Ca (II) and Mg (II). Ca (II) and Mg (II) content are relatively small at 0.01 mg/L.

But the content of Fe (II) is quite large at 0.169 mg/L. The concentration of Fe (II) is made influent (C0) 0,169 mg/l, pH 7.09, the flow rate was varied among 6; 10; and 14 L/min. the model of flow was down flowing fixed-bed column continuously as shown in Figure 1. Palm kernel shell adsorbent used was placed in a column of 30 cm and 6.4 cm in diameter, whereas the height of adsorbent in a column was varied to 7.5; 10 and 12.5

cm. For several minutes, samples were collacted as much as 5 ml to be analysed using AAS (AA-6300 Shimadzu) as effluent Fe (II) in concentration (Ct). The flow was stopped once the column was fully marked by Ct = C0. In this model, fluid was absorbed on to

the superficial layer of palm kernel shell. The top layer of adsorbent was a place of direct contact to fluid at its highest concentration (C0), while the lower layer of adsorbent will absorb the liquid in lower concentration. After a certain period, the top layer will be full and be less efficient in absorbing than the lower layer will replace it.

This layer is named the adsorption zone. The relation of Ct/C0 and t, 3

Figure 1. Laboratory scale fixed bed adsorption Column. 4. Result and discussion The characterization of the adsorbent used in this study includes the quality functional group test and the active carbon texture analysis before and after the activation. 4.1.

Element analysis of activated carbon, FTIR and SEM analysis The determination of moisture content in Table 1 aims to determine the hygroscopic nature of activated carbon. The amount of water vapour in the air as well as the length of the cooling, grinding and sieving processes influence the water content contained in the activated charcoal. High water content in activated carbon can reduce the adsorption power.

Measurement of ash content on activated carbon aims to determine the percentage of mineral content. The higher the mineral content, the higher the ash content other than that, the ash can interfere with the adsorption process because of the excessive ash content can lead to blockage of the pores of activated carbon so as to decrease the ability of adsorption. The volatile substances are substances other than water, i.e.,

non-carbon compounds and ash contained in the activated carbon. The high volatile substances caused by imperfect decomposition of non-carbon compounds such as CO2, CO, and H2. High volatile substances in activated carbon can reduce the adsorption ability. Carbon content will be higher after physically activated.

This indicates that the palm kernel shell fits into the active carbon. 4

Table 1. Element analysis of activated carbon. _No _Testing type _Raw palm kernel shell_Palm kernel shell activated carbon_____(pysical _ _ _ _ Teratment) _ _ 1 _Water_7.64 _4.81 _ _ 2 _Ash _1.79 _2.53 _ _ 3 _Vaporized steam _30.39 _14.18 _ _ _ (950oC) _____4 _Carbon _60.18 _78.48 _ _ _ _ Figure 2.

FTIR spectra palm kernel shell and activated carbon. The activated carbon activation function of the palm kernel shell is analyzed using FTIR (IRPrestige-2, Shidmazu). The functional group analysis was performed to find out the functional group changes occurring on activated carbon, prior to activation and after physics activation. The FTIR spectrum of the activated carbon and palm kernel shell in Fig.

2 has an absorption band at the 4000-2500 cm-1 wave number which is a vibration of C-H, O-H, and 2500-2000 cm-1 indicating the presence of C = C vibration. The absorption is at the wave number 1550 – 650 cm-1 which are the C-O. The resulting activated carbon has an absorption pattern with the O-H (3686, 3363.9 cm-1), C-H (3049.5 cm-1), C-O (1249, 962.5 and 756.1 cm-1), and C = C (2565.3, 2370.5 and 2179.6 cm-1) bond types [10].

The presence of O-H and C-O bond indicates that the activated carbon produced tends to be more polar. Thus the resulting activated carbon can be used as an adsorbent. 5

3rd ICChESA 2017 _IOP Publishing _ _IOP Conf. Series: Materials Science and Engineering 334 (2018) 012030 _doi:10.1088/1757-899X/334/1/012030 _ _ Figure 3. FTIR spectra palm kernel shell and activated carbon.

The SEM observation in the palm kernel shell before activated shown in Figure 3 on the left has a non-uniform particle size and the poros are not yet formed. This is because the process of activation has not been done so that the shape of the surface is still tightly bound to each other causing the morphology and topography of carbon do not form pores.

SEM observation of palm kernel shell after physical activation Figure 3 right side of the surface of the pores seen more open pores spread over the surface and walls of active carbon cavity of palm kernel shell. If the activated carbon is cleaner than the impurities the pores is more and the surface area is greater. 4.2. Effect of folw rate on breakthrough curve Breakthrough curve for column was determined by plotting the ratio of Ct/C0 against time, as shown in Figure 4.

The column was found to perform effectively in the lowest rate of 6 L/min. Previously, breakthrough and exhaustion was reached at a flow rate of 6 to 14 L/min. The column breakthrough time (Ct/C0 = 0.05) was reduced from 1000 minutes to 500 minutes, by flow rate was increasing between 6 to 14 L/min. This was due to the decline of contact time, limiting the contact of Fe (II) against activated carbon.

On a higher flow rate, Fe (II) had no sufficient time to diffuse into the poros of activated carbon and Fe (II) was out of the column prior to equilibrium. Similar results were found in the adsorption of Fe and Mn of the fixed-bed system using Fruit Bunch and maize cob as adsorbing media in the column [1]. 4.3. Effect of different bed depths on breakthrough curve Breakthrough curve in various bed depths of 7.5 (50 g), 10 cm (150 g) and 12.5

cm (200 g) is shown in Figure 5, at a constant flow rate of 6 L/min, influent Fe (II) ion concentration of 0,169 mg/L and particles size of 50 μ m. The results indicate that by increasing the bed height from 7.5 to 12.5 cm the adsorption capacity of the column increased from 66.189 to 75.685 mg/g (Table 1). Observations show that the highest adsorption capacity happened in the higher bed.

This was caused by a wider surface of activated carbon, making more sites of adsorption [16]. Nevertheless, the conclusion is that the higher the bed depth, the better the qe. 6

Figure 4. Breakthrough curves: the effect of flow rate on Fe (II) adsorption (C0 = 0.169 mg/L, Z = 7.5 cm). _ Figure 5.

Breakthrough curves: the effect bed depth on Fe (II) adsorption (C0 = 0.169 mg /L, and flow rate 6 L/min).

4.4. Thomas Model The result in Table 2 was the capacity of adsorption in various flow rates, measured by the equation above (1). The Thomas model showed Constanta kT and q0 was measured by the plot In [C0/Ct-1] versus t on various flow rates.

Column data using Thomas Model was aimed to determine the Constanta Thomas (kT) and capacity adsorption (qe). Measurement coefficient (R2), Constant relative was measured by using linear regression and error less than 0.15 also shown in Figure 1, as the range of R2 were between 0.977-0.982. So the correlation Ct / C0 and t based on the equation was significant.

The higher the flow rate, the lower the qe but the kT number was increasing. As comparison, qe was formulated from calculation and research showed that the model was close to the experimental data. The Thomas model was appropriate for the adsorption process where internal and external diffusion are not limiting the process. [16]. 4.5.

Bohart-Adams Model The initial part of the breakthrough curve contained experimental data, which used the Bohart- Adams adsorption model for its description. This approach focused on the estimation of characteristic parameters such as maximum adsorption capacity (N0) and kinetic constant (kAB) from the Adams-Bohart model. For all breakthrough curves, respective value of N0, kAB was calculated and is presented in Table 3, together with the correlation coefficients (R2 > 0.906).

From Table 2, the value of N0 at all condition have no significant difference. The values of kAB increased with both initial Fe concentration and flow rate increase, but it decreased with bed depth increase. This shows that external mass transfer in the initial part of adsorption in the column has a large influence on the overall system kinetics [17]. Table 2.

The Thomas model parameters for the adsorption iron, C0 = 0.169 mg/ L Q, _Z, _kT _qe _R2 _ (L/ min) _(cm) _(L /mg.min) _(mg /g) _ _ _7.5 _0.095 _66.189 _0.981 _ _6 _10 _0.070 _70.875 _0.982 _ _12.5 _0.050 _75.685 _0.982 _ _10 _7.5 _0.124 _35.442 _0.979 _ _14 _7.5 _0.189 _5.577 _0.977 _ _ _ _7 _ _

Table 3. The Thomas model parameters for the adsorption iron, C0 = 0.169 mg/ L _Q, _Z, _kAB _N0 _R2 _ _ (L/ min) _(cm) _(L /mg.min) _(mg /L) _ _ _ _7.5 _0.005 _965.707 _0.906 _ _ _ _ _ _6 _10 _0.004 _967.871 _0.908 _ _ _ _ _ 12.5 _0.002 _970.658 _0.906 _ _ _ 10 _7.5 _0.030 _961.986 _0.910 _ _ _ _ 14 _7.5 _0.027 _736.021 _0.914 _ _ 5.

Conclusion On the basis of the experimental results of this investigation, activated carbon made of palm kernel shell is applicable for wastewater treatment to remove Fe (II) ion from groundwater. The adsorption of Fe was dependent on the flow rate and bed depth. The Thomas model adequately described the adsorption of Fe (II) ion on to activated carbon in column mode.

Acknowledgement The authors express their sincere gratitude to Malikussaleh University through the Ministry of Research, Technology and Higher Education for financial support of this research.

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