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Synthesis of Hydrochar Cassava peels with hydrothermal carbonization method and applications as hard water softener

Dzikria Sari Pratiwi[1*], Wirda Udaibah[1], Kustomo[1]
[1]Department of Chemistry, Faculty of Science and Technology, Universitas Islam Negeri Walisongo Semarang, Indonesia

Corresponding author:
dzikriatiwi@gmail.com

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Abstracts

Groundwater before being used is very important to pay attention to the quality of the water. Water has good quality if it is in accordance with several parameters, including chemical, physical, and biological parameters. Mineral salt content is one of the chemical parameters that can be used to determine the quality of water. In this study, the synthesis of cassava peel hydrochar was successfully carried out using the hydrothermal carbonization (HTC) method. This material was developed to reduce waste of cassava peel biomass and overcome the problem of water hardness. HTC cassava peel was developed as an alternative hard water softener adsorbent. The results of FTIR characterization on hydro-activation (activating hydrochar) and hydro-non (non-activating hydrochar) contain functional groups of O-H stretch, C-H stretch, $C\equiv C$ stretch and C=C stretch. Observation of surface morphology by SEM method on hydro-non in the form of large sheets, while the surface on hydro-activities in the form of small sheets. The adsorption capacity of hydro-active against Ca^{2+} ions and Mg^{2+} ions were 85.240 mg/g and 87.210 mg/g, respectively. Meanwhile, the hydro-non adsorption capacity of Ca^{2+} and Mg^{2+} ions were 84,736 mg/g and 85,713 mg/g. The kinetics of hydro-active adsorption on Mg^{2+} ion took place on order 3 (0.000003 min^{-1}) while when adsorption of Ca^{2+} ion took place on order 0 (0.0324 min^{-1}).

Keywords: Hydrochar; water softener; adsorption; NaOH; Cassava peels

1. Introduction

Groundwater before being used is very important to pay attention to the quality of the water. Water has good quality if it is in accordance with several parameters, including chemical, physical, and biological parameters. Mineral salt content is one of the chemical parameters that can be used to determine the quality of water [1]. According to Ramya et al., (2015) the salt content of $Mg(HCO_3)_2$ and the mineral $Ca(HCO_3)_2$ can make water hardness. Hard water is very important to contribute to the intake of magnesium and calcium, especially for humans. Based on PERMENKES RI No. 32 of 2017 concerning the requirements for drinking water quality and the maximum permissible level of hardness ($CaCO_3$), which is 500 mg/L [3].

According to research conducted by Cayono et al, several residents of Sidokumpul Village in Kec. Bungah, Kab. Gresik, has kidney disease. The causes of people's kidney disease are: diabetes, taking excessive drugs, hypertension, and damaged glomerulus, namely kidney stones which can be caused by consuming too much calcium. Calcium minerals that come out with the urine and in high amounts or called hypercalciuria indicate if there is a potential for kidney disease [4].

Considering the negative impact of consuming excessive hard water on health, it is necessary to special treatment on water so that the level of hardness, especially in drinking water can be reduced to comply with water quality standards. Processes that can be carried out include adsorption, ion exchange, filtration. The adsorption method was chosen because it has several advantages compared to other methods, namely, the required cost is relatively low, high efficiency and effectiveness, the adsorbent can be used repeatedly, and the process is relatively simple (regeneration) [5].

Cassava peel has many benefits, namely it can be used as organic fertilizer, animal feed, bio energy and processed food. According to [6], cassava peel can be used as hydrochar, because cassava peel which has a white color has a carbon content of 59.31%. Hydrochar from cassava peel can absorb chemical compounds in water and liquid waste. So far, the utilization of cassava peel waste has not been maximized, waste from cassava peel can be used as raw material for hydrochar [7].

Hydrothermal carbonization (HTC) is a thermochemical method that usually involves hydrolysis, decarboxylation, condensation and aromatization reactions in the liquid phase and is usually carried out using water. Hydrolysis of water acts as a glycosidic group in cellulose and hemicellulose biomass, this can help produce a higher amount of porous hydrochar as a carbon product [8]. The three main products of the HTC process are gaseous products, liquid bio-yl, and solid hydrochar. This process can be carried out at high temperatures (300-800 °C) and low temperatures (200-250 °C) [9].

The purpose of this experiment was to determine the characterization of cassava peel hydrochar using the hydrothermal carbonization method. The results of this synthesis will be used as a water softener so that its performance and adsorption kinetics will be determined.

2. Experiments Procedure

Tools and materials

The tools used in this research are hydrothermal autoclave, furnace, oven, analytical balance, glassware, Fourier Transform Infra-Red (FTIR) Perkin Elmer Frontier, Scanning Electron Microscope (SEM) Phenon Pro X, and UV-Vis Spectrophotometer Shimadzu D2600i.

The ingredients in this study were cassava peel from the Grobogan area, Central Java, deionized water, buffer solution pH 10, $CaCl_2.2H_2O$, $MgSO_4.7H_2O$, Na_2EDTA, 1 N NaOH, 0.3 N NaOH, 0.1 N HCl, murexide indicator, and EBT indicators. All chemicals are obtained from Merck with pa. specifications.

Hydrochar Synthesis with Carbonization (HTC) Cassava Peel

Hydrocar with carbonization (HTC) was synthesized according to the research [10]. The cassava peel is cut into small pieces and then dried in the sun to dry and then blended until smooth. Furthermore, as much as 25 grams of dry cassava peel and 250 mL of deionized water were put into a hydrothermal autoclave. HTC was carried out at 2000C for 1 hour. The sample was filtered and the residue was oven-dried at 800C for 24 hours [10], [9].

HTC samples were chemically activated. 10 grams of cassava charcoal was soaked in 0.3 N NaOH solution for 24 hours. The resulting hydrochar was washed using 0.1 N HCl and distilled water until the pH was neutral. The samples obtained were dried in an oven for 3 hours at a temperature of 100 C [11]. Furthermore, for activated hydrochar it is abbreviated as "hydro-aktv" and for non-activating hydrochar it is abbreviated as "hydro-non".

HTC Material Characterization

The synthesized HTC was then characterized using FTIR to identify the functional groups present on the surface of the hydrochar sample [10], [11]. In addition, the material was also characterized by SEM which was used to determine the surface morphology of the hydrochar [11].

Adsorption Process

At this stage the adsorbed hard water is artificial hard water, namely by mixing 2.4 grams of $CaCl_2.H_2O$ and 1.6 grams of $MgSO_4.7H_2O$ then dissolved using distilled water in a 1000 mL volumetric flask to obtain 450 ppm Ca^{2+} ions and 450 ppm Mg^{2+} ions.

As much as 0.5 g of HTC cassava peel adsorbent was mixed with 100 mL of hard water. Adsorption for 50 minutes while stirred at a speed of 150 rpm. Next, the mixture was filtered and the filtrate was analyzed titrimetrically to determine the levels of Ca^{2+} and Mg^{2+} ions remaining after adsorption.

Determination of Hardness

Total hardness (Ca^{2+} and Mg^{2+}) was analyzed by complexometric titration using 0.01 M Na_2EDTA solution and EBT indicator. The titration is carried out slowly until the color changes from a wine red to blue [12]. The determination of the Ca^{2+} ion level was carried out by complexometric titration using a 0.01 M Na_2EDTA solution and a murexide indicator (30-50 mg). The mixture has been titrated until the color changes from pink to purple [12].

Determination of Adsorption Capacity

This adsorption capacity was determined by interacting 0.5 gram of cassava peel hydrochar adsorbent to 100 mL of hard water. This was done by varying the adsorption concentrations of Ca^{2+} and Mg^{2+}, namely 150 ppm, 300 ppm, and 450 ppm. The mixture was stirred at 150 rpm for 50 minutes. After being filtered, the filtrate was analyzed titrimetrically.

Determination of Adsorption Kinetics

The adsorption kinetics was also carried out by interacting 0.5 gram of cassava peel hydrochar adsorbent to 100 mL of hard water. Adsorption using a stirrer using a speed of 150 rpm with time variations of 50, 40, 30, 20, 10 minutes. The concentration of Mg^{2+} and Ca^{2+} is 450 ppm. Then the mixture was filtered and the filtrate was analyzed titrimetrically.

3. Results And Discussion

Synthesis of Cassava Peel Hydrochar

Cassava peel powder was carbonized by hydrothermal method using an autoclave reactor for 1 hour at 200 °C. the ratio of cassava peel biomass and deionized water is 1:10 (g:mL) [10]. The hydrothermal method was chosen because it can convert biomass into hydrochar and increase the carbon content of the biomass [13]. Another advantage of the hydrothermal process is that the synthesis temperature is not too high due to the presence of water which can function as a pressure transmitting medium so that the temperature and pressure during the synthesis can be lower [14].

HTC was then activated with 100 mL of 0.3N NaOH by immersion for 24 hours. This process is done to clean mineral impurities and activate the HTC surface. The mineral elements in the activator enter between the hexagon plates of the hydrochar crystallites and separate the previously closed surfaces. Thus, during the heating process, the contaminant compounds in the pores are easier to release. This increases the active surface area and increases the absorption capacity of hydrochar [7], [15]. The HTC washing process was carried out until a neutral pH was carried out in order to remove the impurity material present in the hydrochar, to remove any remaining activator residue, and to reduce the ash content.

HTC Characterization

Fourier Transform Infra Red (FT-IR) Analysis

The results of the hydrochar synthesis were characterized using FTIR in order to see the functional groups of the cassava peel hydrochar sample. The FTIR spectra of hydrochar hydro-non, hydro-aktv and hydro-aktv that have been applied to hard water are presented in Figure 1.

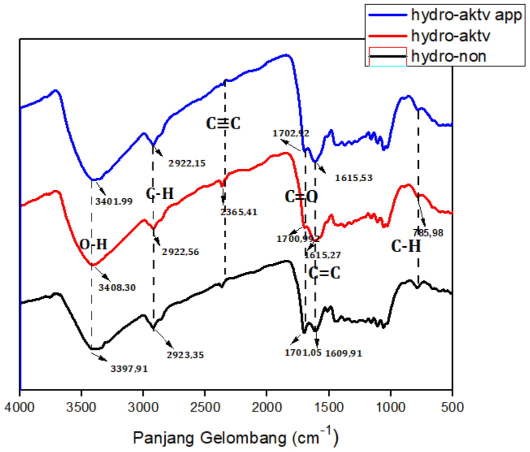


Figure 1. FTIR spectrum of hydrochar

Based on the spectrum of the FTIR results in Figure 1, it shows that on hydro-non and hydro-active, an absorption band appears at the wave 2365.41 cm-1. This indicates the presence of the C≡C group. The C≡C group confirmed the presence of alkynes [7]. However, after the application of hydrochar as an adsorbent the C≡C group became reduced and experienced a shift in its wavelength.

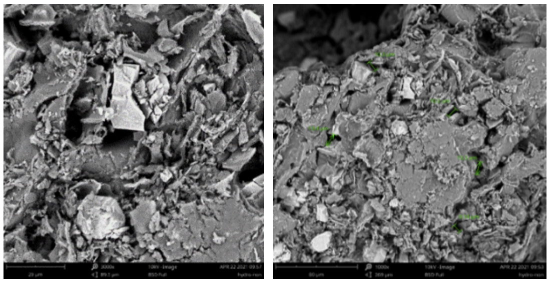
At the 1701.05 cm^{-1} wave, an absorption band appears which contains the C=O functional group which is only found in hydro-non, this C=O functional group is a carbonyl group. While in hydro-aktv and hydro-aktv app there is a weakening and stretching of the C=O functional group, this is due to the breaking of the ether bond in hemicellulose [10].

The peak associated with the carboxyl group experienced a change in intensity towards a lower wavelength after the sample underwent chemical activation with NaOH. This indicates that a new O-H group can be formed during the activation reaction [7].

The transmission peak also appears at a wavelength of 1609.91 cm^{-1} indicating the presence of the C=C functional group in the hydro-non, hydro-active, and hydro-active apps due to the aromatization reaction during HTC. This is reinforced by the appearance of an absorption band at a wavelength of 785.98 cm^{-1} which indicates the presence of the C-H functional group so that an aromatization reaction occurs including aldol condensation and dehydration [7], [16].

Scanning Electron Microscope (SEM) Analysis

The results of the hydrochar synthesis were further characterized using a Scanning Electron Microscope (SEM) with a magnification of 3000x and 1000x. The results of SEM observations with cassava peel hydrochar samples can be seen in Figures 2 and 3.



(a) (b)

Figure 2. Hydro-non SEM (a) magnification 3000x (b) magnification 1000x

Table 1. Hard water adsorption results

	content Ca^{2+} (mg/L)	**content Mg^{2+} (mg/L)**	**Adsorption capacity of Ca^{2+} ions (mg/g)**	**Adsorption capacity of Mg^{2+} ions (mg/g)**
Before Application	32,480	22,283	83,504	85,543
Hydro-non	26,320	21,343	84,736	85,713
Hydro-aktv	23,800	13,948	85,240	87,210

The results of morphological observations on the hydrochar surface of cassava peels showed that hydro-aktv had more pores than hydro-non. The number of pores in hydrochar causes a large specific surface area. The pores that are formed in the hydro-aktv are formed after the activation process. Hydro-activation and hydro-non have almost similar morphology, this confirms that chemical activation with NaOH did not cause a significant change in the morphology of hydrochar. This is because the activation of NaOH only modifies the hydrochar surface, without affecting the morphology and the carbon core [17].

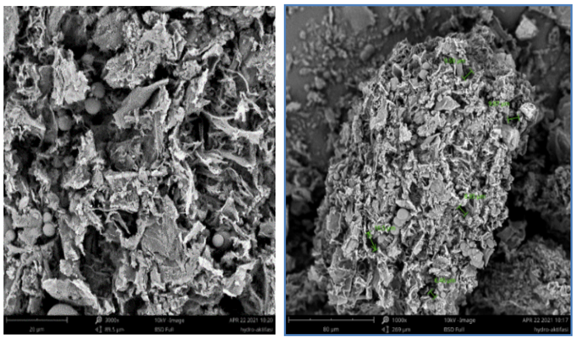

(a) (b)

Figure 3. SEM hydro-aktv (a) Magnification 3000x (b) Magnification 1000x

Hard Water Adsorption

The results of the analysis of hard water adsorption data can be seen in table 1. The data in table 1 shows that the concentration of hard water before being adsorbed has decreased. The samples of Ca^{2+} and Mg^{2+} ions before being applied with hydrochar had levels of Ca^{2+} and Mg^{2+} ions of 32.480 mg/L and 22.283 mg/L.

After being applied with hydro-non, it decreased by 26.320 mg/L and 21.343 mg/L with the adsorption capacity of 84,736 mg/g and 85,713 mg/g. Then after being adsorbed using hydro-activation, the concentration of Ca^{2+} and Mg^{2+} ions decreased again to 23,800 mg/L and 13.948 mg/L with their adsorption capacities of 85,240 mg/g and 87,210 mg/g, respectively.

Table 2. Adsorption capacity of Ca^{2+} ions

initial con.* (mg/L)	***Hydro-non***		***Hydro-aktv***	
	Ce (ppm)	**Qe (mg/g)**	**Ce (ppm)**	**Qe (mg/g)**
100	8,1648	18,3670	6,1236	18,7753
150	12,5874	27,4825	11,5668	27,6866
200	14,2884	37,4123	12,7575	37,4485
300	21,9429	55,6114	21,2625	55,7475
450	31,9788	83,6042	31,2984	83,7403

Note: *concentration

Determination of Adsorption Capacity

The adsorption capacity of hydro-activating against Ca^{2+} ions and Mg^{2+} ions is greater than after being adopted using hydro-non. Activated hydrochar has a greater ability to adsorb metals than unactivated hydrochar, because during the heating process, contaminants in the pores are easily released [13], [18].

This is evidenced by using the results of the FTIR characterization. The peak associated with the carboxyl group experienced a change in intensity towards a lower wavelength after the sample underwent chemical activation with NaOH. This indicates that a new O-H group can be formed during the activation reaction [7].

Table 3. Adsorption capacity of Mg^{2+} ions

initial con.* (mg/L)	*Hydro-non*		*Hydro-aktv*	
	Ce (mg/L)	Qe (mg/g)	Ce (mg/L)	Qe (mg/g)
100	8,680	18,264	6,440	18,712
150	11,760	27,648	9,520	28,096
200	65,600	26,480	65,320	26,936
300	21,000	55,800	21,000	55,800
450	32,760	83,448	31,080	83,784

Note: *concentration

The results of SEM characterization also prove that activated hydrochar is better at adsorption than inactivated hydrochar. The hydro-non surface morphology is in the form of large pieces, while the hydro-active surface morphology is in the form of small pieces so that the surface area is also large [17]. Therefore, hydro-activation is easier to adsorb Ca2+ and Mg2+ ions than hydro-non. The adsorption capacity data for Ca and Mg ions are presented in Tables 2 and 3.

Determination of the adsorption isotherm

The adsorption isotherm was determined by converting the Langmuir isotherm and Freundlich isotherm equations into a straight-line equilibrium curve. The equilibrium model in this study was determined by the value of the linear regression coefficient (R2) which was the highest or the value was close to 1. Determination of the adsorption isotherm pattern was obtained from research data

during the concentration optimization process. The concentration variations used in this study were 100, 150, 200, 300, and 450 ppm. Ca^{2+} Ion Adsorption Capacity. Table 4 shows the concentration of the adsorbate on the decrease in the level of Ca^{2+} ions. The adsorption of Ca^{2+} ions increased from a concentration of 100 ppm to 450 ppm. The maximum adsorption capacity was reached at a concentration of 450 ppm.

Based on Table 4, the hydro-active and hydro-non-ionic Ca^{2+} isotherm models are Freundlich isotherms because they have the strongest linear regression coefficient (R2). The Freundlich isotherm describes that the adsorbent surface is heterogeneous, ie each active group on the adsorbent surface has different adsorption capabilities [7], [18]. In the case of this Freundlich isotherm, there is an interaction between the molecules adsorbed on the adsorbent physically (physisorption), because the surface is heterogeneous. This is because the adsorbed Ca^{2+} ions are not strongly bound to the surface, thus causing the release of the adsorbed Ca^{2+} ions [19].

Table 3 shows the concentration of the adsorbate on the decrease in the level of Mg^{2+} ions. The adsorption of Mg^{2+} ions increased from a concentration of 100 ppm to 450 ppm. The maximum adsorption capacity was reached at a concentration of 450 ppm. Based on the data obtained, it shows that the hydro-active and hydro-non-ionic Mg^{2+} isotherm models are Freundlich isotherms because they have the strongest linear regression coefficient (R2). The Freundlich isotherm describes that the adsorbent surface is heterogeneous, ie each active group on the adsorbent surface has different adsorption capabilities [7], [18]. In the case of this Freundlich isotherm, there is an interaction between molecules that are physically adsorbed on the adsorbent (physisorption). This is because the adsorbed Mg^{2+} ions are not strongly bound to the surface, thus causing the release of the adsorbed Mg^{2+}

Table 4. Parameters and linear regression coefficients for the Ca^{2+} ions isotherm model

Hydro char	Isotherm Model Langmuir			Isotherm Model Freundich		
	Q_m (mg/g)	K_L (L/mg)	R^2	K_F (mg/g) $(L/mg)^{1/n}$	1/n	R^2
Hydro-non	555,55	0,00415	0,1147	18,958	11,025	0,96
Hydro-aktv	625	0,00491	0,6141	34,222	0,9299	0,9953

Table 5. Parameters and coefficients of linear regression of the Mg^{2+} ion isotherm model

Hidrochar	Isotherm Model Langmuir			Isotherm Model Freundich		
	Q_m (mg/g)	K_L (L/mg)	R^2	K_F (mg/g)(L/mg)$^{1/n}$	1/n	R^2
Hydro-non	-370,3703	-0,005871	0,4778	1,3341	1,1989	0,9982
Hydro-aktv	-100000	0,0002039	0,8758	3,2999	0,9285	0,9779

ions [19]. The isotherm parameters obtained have been summarized in table 5.

Determination of Adsorption Kinetics

1. *Hydro-Active Contact Time to Ca2+ ions 450 ppm*

Determination of the adsorption equilibrium time is to determine the minimum time required for the adsorbent to absorb the metal maximally until it reaches equilibrium. In this process, as long as equilibrium has not been reached, adsorption will continue [20]. Table 5 presents data on the contact time of hydro-active against Ca2+ ions.

Determination of reaction order in research

Based on the strongest linear regression coefficient (R2) or close to 1. The determination of the reaction order can be seen in table 6.

Table 6. Hydro-activation contact time to Ca^{2+} ion 450 ppm

Time (minute)	*Hydro-aktv*	
	Ce (ppm)	Qe (mg/g)
15	31,64	83,672
30	30,52	83,896
45	30,80	83,840
60	30,24	84,052
75	29,40	84,120

Reaction order

Based on the results of the kinetic equation for the reaction rate in table 7 hydrochar hydro-activation on Ca^{2+} ions is of order 0. This is because the linear regression coefficient (R2) is the strongest, which is 0.8834. Order 0 indicates that there is no reaction acceleration when reactants are added [21]. Figure 4 presents a 0-order reaction rate equation curve.

Table 7. Determination of the Ca^{2+} ion

Orde	Reaction Rate Equation	R^2
0	$y = -0{,}0324x + 31{,}998$	0,8834
½	$y = -0{,}0029x + 5{,}6579$	0,8833
1	$y = -0{,}0011x + 3{,}4666$	0,8831
1 ½	$y = 0{,}0004x + 0{,}1767$	0,8828
2	$y = 0{,}00003x + 0{,}0312$	0,8825
3	$y = 0{,}000002x + 0{,}001$	0,8815

From the reaction order 0 obtained the equation y=-0.0324x+31.998. The reaction order 0 has the following general equation:

$$[A]_t = -k_0 t + [A]_0 \tag{1}$$

Based on equation (1), y is the interpretation of the value of the residual concentration of Ca^{2+} ions $[A]_t$, 0.0324 is the slope value which states the reaction rate constant on the order of 0 (k0), x represents the reaction time that takes place (t), and the value of 31,998 is the intercept which states the value of the initial concentration of Ca^{2+} $[A]_0$ ions. From the data obtained, hydro-activation in adsorption of 450 ppm Ca^{2+} ion has a reaction rate constant of 0.0324 min^{-1}.

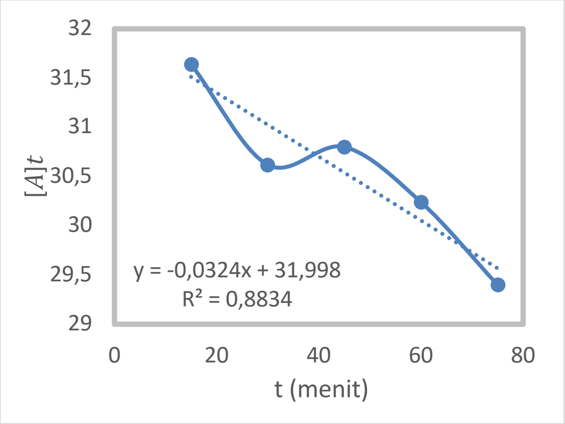


Figure 4. Reaction curve Order 0 in ion *Ca^{2+} hydro-aktv*

2. *Hydro-Active Contact Time to Mg^{2+} ion 450 ppm*

The determination of the reaction order in this study was based on the strongest linear regression coefficient (R2) or close to 1. The determination of the reaction order can be seen in table 8. Based on the results of the kinetic equation for the reaction rate in table 8, the hydrochar hydro-activation of the Mg2+ ion is of order 3. This is because the linear regression coefficient (R2) is the strongest, which is 0.8502. Order 3 indicates that the reaction rate is directly proportional to the cube of the concentration of a reactant [22]. Figure 5 shows the rate equation for an order 3 reaction.

Table 7. Hydro-activation contact time to Mg^{2+} ion 450 ppm

Time (minute)	*Hydro-aktv* Ce (ppm)	Qe (mg/g)
15	33,1024	83,3795
30	31,1283	83,7743
45	31,1489	83,7702
60	30,2778	83,9444
75	30,1077	83,9785

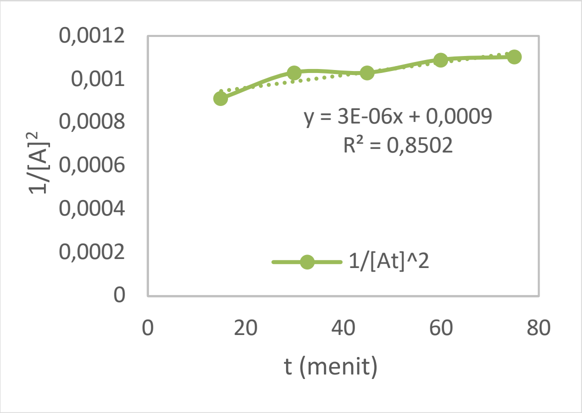


Figure 5. Reaction order curve of order 3 Mg^{2+} ions hydro-aktv

From the reaction order 3, the equation y=-0.000003x+0.0009 is obtained. The reaction order 0 has the following general equation:

$$\frac{1}{[A]_t^2} = 2k_3 t + \frac{1}{[A]_0^2} \qquad (2)$$

Table 8. Determination of the reaction order of the Mg^{2+} ions hydro-aktv

Orde	Persamaan Laju Reaksi	R²
0	$y = -0{,}0456x + 33{,}205$	0,8267
½	$y = -0{,}0041x + 5{,}7636$	0,8307
1	$y = -0{,}0014x + 3{,}5035$	0,8347
1 ½	$y = 0{,}0001x + 0{,}1734$	0,8386
2	$y = 0{,}00005x + 0{,}0301$	0,8425
3	$y = 0{,}000003x + 0{,}0009$	0,8502

Based on equation 2, y is the interpretation of the value of one per of the residual concentration of Mg^{2+} ions $[A]_t$, 0.000003 is the slope value which states the reaction rate constant of order 3 (k3), x represents the reaction time that takes place (t), and the value of 0.0009 is the intercept which states the value of one per of the initial concentration of Mg^{2+} $[A]_0$ ions. From the data obtained, hydro-activation in adsorption of 450 ppm Mg^{2+} ion has a reaction rate constant of 0.000003 min^{-1}.

4. Conclusion

Hydrochar from cassava peel was successfully synthesized using the HTC method and has alcohol, aldehyde, alkane, alkyne, and carboxylic acid functional groups. The morphology of the activated hydrochar is in the form of smaller pieces so that it has pores that tend to be larger. The adsorption capacity of hydro-active against Ca^{2+} ions and Mg^{2+} ions were 85.240 mg/g and 87.210 mg/g, respectively. Meanwhile, the hydro-non adsorption capacity of Ca^{2+} and Mg^{2+} ions were 84,736 mg/g and 85,713 mg/g. Hydro-aktv is better at adsorption of Mg^{2+} ions because the reaction rate kinetics is on the 3rd order and has a reaction rate constant of 0.000003 min^{-1}. Meanwhile, the kinetics of the reaction rate of the hydrochar activation in adsorption of Ca^{2+} ions took place on the order of 0 and had a reaction rate constant of 0.0324 min^{-1}.

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