Modified Starch of *Amorphophallus Campanulatus* as a Novel Adsorbent for Water Adsorption

Ajeng Yulianti Dwi Lestari\(^1\), Mohamad Djaeni\(^2\)*, dan Ahmad Muhammad Fuadi\(^3\)

\(^1\)Department of Chemical Engineering, Faculty of Industrial Technology, Islamic University of Indonesia, Jl. Kaliurang KM 14.5, Besi, Sleman 55584 Special Region of Yogyakarta, Indonesia
\(^2\)Department of Chemical Engineering, Faculty of Engineering, Diponegoro University, Jl. Prof. Soedarto, SH, Tembalang, Semarang 50275, Central Java, Indonesia
\(^3\)Department of Chemical Engineering, Faculty of Engineering, Muhammadiyah University of Surakarta, Ahmad Yani Pos Tromol 1, Pabelan, Kartasura, Sukoharjo, Central Java

*Corresponding author: m.djaeni@undip.ac.id*

**Abstract**

A novel adsorbent manufactured from *Amorphophallus campanulatus* (Porang or Suweg or Elephant Foot Yam or Foot Yam) starch and employed to adsorb water from wet air. The experiment focused on the adding of sodium hydroxide in various concentration of sodium hydroxide (10:1, 10:2.5, 10:5, 10:10, 10:20, 10:30, 10:40 mmol/mmol) and its effect to form the new adsorbents shape and chemical bonds. Experimental data were also fitted with several models of isotherm adsorption and adsorption kinetics. Analysis with FTIR and SEM showed that sample C7 (modified starch with NaOH 40:10 mol) is the adsorbent that could adsorb more water from air and also proved that foot yam starch can be feasible to be synthesized as an adsorbent for water adsorption. The results also showed that this novel adsorbent fitted with pseudo second order kinetic model and Freundlich isotherm model with maximum adsorption capacity calculated 2.006 g water/g adsorbent.

**Keywords**: elephant foot yam; starch; sodium hydroxide; water adsorption

**Abstrak**

*PATI UMBI AMORPHOPHALLUS CAMPANULATUS TERMODIFIKASI SEBAGAI ADSORBEN BARU UNTUK ADSORPSI AIR.* Adsorbent baru berhasil dibentuk dari pati umbi Amorphophallus campanulatus (Porang atau Suweg) yang kemudian digunakan untuk mengadsorpsi air dari udara lembab. Penelitian berfokus kepada pengaruh penambahan variasi konsentrasi natrium hidroksida (NaOH) (10:1, 10:2.5, 10:5, 10:10, 10:20, 10:30, 10:40 mmol pati/mmol NaOH) atas pembentukan morfologi serta ikatan kimia dari adsorbent baru. Data eksperimen kemudian dicocokkan dengan beberapa model isotherm serta kinetika adsorpsi. Analisis dengan menggunakan FTIR dan SEM menunjukkan bahwa sampel C7 (perbandingan pati modifikasi dengan NaOH 40:10 mol) adalah adsorbent yang dapat menjerab air lebih banyak dibandingkan dengan adsorbent yang lainnya. Hal ini menunjukkan bahwa adsorbent dapat menjerab air dari udara lembab dan membuktikan bahwa umbi porang ini layak untuk dijadikan sebuah sumber adsorbens alami yang baru. Hasil juga menunjukkan bahwa data eksperimen menunjukkan kesesuaian dengan model kinetika semi orde dua dan model isotherm Freundlich dengan kapasitas adsorpsi maksimal 2,006 g air/g adsorben.

**Kata kunci**: umbi Suweg; pati; NaOH; adsorpsi air
INTRODUCTION
Separation process is the one of substantial process in all major industries as influences the quality of the product. Adsorption is applied to separate hydrocarbon in liquid phase, air separation and air purification. Adsorption is the process that can separate objects which neither impossible to apply nor impracticed by conventional techniques (Kneabel, 2009). Zeolite, activated carbon, activated alumina are used as adsorbent. But recently there are researches that concern on making of the novel adsorbent. This novel adsorbent is made not only from unusual sources as paper waste (Khalili et al., 2001) but also made from the polysaccarides.

Polisaccarides is choosen as adsorbents due to their easily to synthesize, has large adsorption capacity due to its large number of the –OH bond and cheap (O’ Connell et al., 2008). Corn starch (Wu et al., 2012), sweet potato starch (Wu et al., 2012), sugarcane (Niu et al., 2014), palm stone, oak and corn corb (Al Asheh et al., 2004) are polisaccaride sources that has been investigated. This project focused on modification the elephant foot yam starch with sodium hydroxide due to its ability to enlarge the water vapor adsorption strength in the raw foot yam starch. As the indicator the adsorbent morphology, chemical bonds also evaluated. This seected indicators refered to possibility as a performance of water adsorption.

MATERIALS AND METHODS
Materials
The main material of this subject is foot yam flour. Merck’s high grade methanol, hexane, sodium hydroxide, chloroform, sodium chloride and toluene were also used. All solutions are prepared by deionized water.

Isolation of Starch from Foot Yam
Starch isolation followed Ogungbenle’s (2007) method that started with extraction Foot Yam flour using the mixture of hexane-metanol-chloroform (with comparison 1:1:2, v/v/v) to remove fat that include on the flour using set of Soxhlet extraction. The crude starch was recovered when the defatted flour was steeped in the water for 16 h at room temperature then separated using centrifuged at 2,500 rpm for 10 min. The crude starch granules were purified by treating dilute 0.1 M NaOH and 0.1M NaCl-toluene. Then it is sedimented by centrifugation washed using diluted water. Final sediment was washed with methanol twice and air dried.

Modification of Starch Samples
Both Foot Yam flour and starch were weighed and mixed with addition of NaOH. The mixture stirred for 10 min then the spread out on an aluminium pan and was dried in the hot air oven 120°C for 12 h. The dried samples were the grounded that used as the sample adsorbents (A, B, C1, C2, C3, C4, C5, C6, C7) in this study which A was a native Foot Yam flour, B was a native Foot Yam starch, C1-C7 were modified Foot Yam starch with NaOH with comparison of NaOH:starch were 1:10, 2.5:10, 5:10, 10:10, 20:10, 30:10 and 40:10 (mol:mol).

Characterization of the Adsorbent
There are two characterizations of this project. They are surface morphology characterization and chemical bonding characterization. The adsorbents surface morphology was visualized with scanning electron microscope (SEM). Adsorbent pellets were fixed on the metal stubs then coated with gold. Images of the samples were scanned and photographed using a FEI Inspect S50.

The chemical bonding was determined with Shimadzu IR Prestige 21 Fourier Transform Infrared Spectroscopy (FTIR). First of all, the samples were powdered then mixed with KBr. The mixture also has been pelleted which fixed on the metal rings and then beamed with infrared. Result of this characterization was a spectrum which chemical bonds can be determined.

Determination Adsorption Properties of Adsorbent
a. Isotherm adsorption of adsorbent
Isotherm adsorption was determined by put 1 g of samples at differential temperatures (48, 43, 38, 33, 28, 23, 18°C) then calculated by gravimetry method in 5 days. Experimental data then fitted with Langmuir, Freundlich, Temkin and DubininRadushkevich isotherm model and studied which the appropriate model(s).

The adsorption isotherms showed the relations between the concentration of adsorbate and its degree of accumulation of water onto surface of adsorbent at room temperature. Several models of adsorption isotherm have been used to fit to the experimental data. Fitting model used to evaluate isotherm performances for water adsorption. These isotherm models are the Freundlich model, Langmuir model, Temkin model and DubininRadushkevich model.

Langmuir adsorption isotherm describes the performance of a monolayer adsorbate on the outer surface of the adsorbent quantitatively. The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites (Dada et al., 2012). Langmuir model assumes that there is a uniform adsorption energy on the surface and there is no adsorbate transmigration in the plane of the surface. Based upon these assumptions, Langmuir represented the following equation:

$$q_e = \frac{q_0K_LC_0}{1+K_LC_0}$$

(1)
Langmuir parameters could be determined by transforming the equation into linear form:
\[
\frac{1}{q_e} = \frac{1}{q_0} + \frac{1}{Q_0K_tC_e}
\]  
where \( C_e \) is the equilibrium concentration of the adsorbate (g/L), \( q_e \) is the amount of water per gram of the adsorbent in equilibrium (g/g), \( Q_0 \) represents maximum monolayer coverage capacity (g/g) dan \( K_T \) for Langmuir isotherm constant (L/mg). The values of \( q_{max} \) and \( K_T \) were computed from the slope and intercept of the Langmuir plot.

Freundlich adsorption isotherm is used to describe characteristics for the heterogeneous surface (Dada et al., 2012). Freundlich resprented the following equation:
\[
Q_e = K_f C_e^\frac{1}{n}
\]
where \( K_f \) is Freundlich isotherm constant (g/L), \( n \) is adsorption intensity, \( C_e \) represents the equilibrium concentration of adsorbate (g/L) and \( Q_e \) is the amount of water adsorbed per gram of adsorbent at equilibrium (g/g). Linerizing of the Freundlich equation above we have:
\[
\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e
\]

The constant \( K_f \) is an approximate indicator of adsorption capacity, while it is a function of the strength of adsorption in the adsorption process (Voudrias et al., 2002). If \( n=1 \) then the partition between the two phase are independent of the concentration. If value \( > 1 \) it indicates not only a normal adsorption but also indicates cooperative adsorption (Mohan and Karthikeyan, 1997). Goldberg (2005) reported that the linear least squares method and the linearly transformed equations have been widely applied to correlate sorption data where is a heterogeneity parameter, the smaller, the greater the expected heterogeneity. This expression reduces to linear sorption process when \( n=1 \). If \( 1 < n < 10 \), this indicates a favorable sorption process.

Temkin contains a factor that explicitly taking into the account of adsorbent-adsorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption of all molecules in the layer would decrease linearly rather that logarithmic with coverage (Temkin and Pyzhev, 1940). As implied in the equation, its derivation is characterized by a uniform distribution of binding energies (up to some maximum binding energy) was carried out by plotting the quantity sorbed \( q_e \) against \( \ln C_e \) and the constants were determined from the slope and intercept. The model is given in following equation:
\[
q_e = \frac{RT}{b} \ln (A_T C_e)
\]
\[
q_e = \frac{RT}{b_T} \ln A_T + \left( \frac{RT}{b_T} \right) \ln C_e
\]
\[
B = \frac{RT}{b_T}
\]
\[
q_e = B \ln A_T + B \ln C_e
\]
where \( A_T \) is Temkin isotherm equilibrium binding constant (L/g), \( b_T \) is Temkin isotherm constant, \( R \) represents universal gas constant (8.314 J/molK), \( T \) is temperature at 298 K and \( B \) is constant related to heat of sorption (J/mol).

DubininRadushkevich isotherm is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface (Gunay et al., 2007). The model has often successfully fitted high solute activities and the intermediate range of concentrations data well.
\[
q_e = (q_0) \exp (-K_{ad} \varepsilon^2)
\]
\[
\ln q_e = (q_0) - (K_{ad} \varepsilon^2)
\]
where \( q_e \) is amount of adsorbate in the adsorbent at equilibrium (g/g), \( q_0 \) is theoretical isotherm saturation capacity (g/g), \( K_{ad} \) is DubininRadushkevich isotherm constant (mol²/kJ²) and \( \varepsilon \) is DubininRadushkevich isotherm constant. This model applied to determine the physical and chemical adsorption of metal ions with its mean free energy (E) per molecule of adsorbate.
\[
E = \left[ \frac{1}{2K_{ad}} \right]^{\frac{1}{2}}
\]
\[
\varepsilon = RT \ln \left[ 1 + \frac{1}{C_e} \right]
\]
where \( R, T, C_e \) represent the ideal gas constant (8,314 J/molK), absolute temperature (K) and adsorbate equilibrium concentration (g/L). Foo and Hamed (2010) said that one of the unique of this isotherm model lies on the fact that it is temperature dependent which when adsorption data at different temperatures are plotted as a function of logarithm of amount adsorbed (ln \( q_e \)) versus the square of potential energy (\( \varepsilon^2 \)), all suitable data will lie on the same curve named as the characteristic curve.

b. Adsorption kinetic of adsorbent
Adsorption kinetic also studied in this case by gravimetry method of the 1 g samples at room temperature for 7 days. The kinetic datas then fitted with the pseudo second order and second order kinetic models.

The constant rate of adsorption was determined from first order, pseudo first order, second order and pseudo second order equations. The pseudo second order given by (Ho and Mckay, 1999):
\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left( \frac{1}{q_e} \right) t
\]
\( K_2 \) (ml/min) is the rate constant for pseudo second order kinetic and \( t \) is time. A plot of against \( t \) gives as the slope and intercept.

The typical second order rate equation in solution systems is as follows (Okewale et al., 2013):
\[
\frac{dc_t}{dt} = -k_2 C_t^2
\]
Integrating equation above with boundary conditions of \( C_t=0 \) and \( C_t=C_0 \) at \( t=0 \) to yield:
\[
\frac{1}{c_t} = K_2 t + \frac{1}{C_0}
\]
where \( C_0 \) and \( C_t \) (mg/L) is the concentration of solute at equilibrium and at time \( t \) (min), \( k_2 \) (L/mg.min) is the rate constant of second order.
RESULTS AND DISCUSSION

Starch Isolation and Modification

Starch isolation is from Foot Yam flour according to Ogungbenle (2007) which used some organic solvents. Solvents used methanol, chloroform and hexane to remove the flour impurities. Flour impurities are proteins, fats, oils, ash, lipids, fosfor and fiber (Zhu, 2014). In this experiment, the raw material contained 70.61% starch then it increased became 85.66% starch contained after the defatting process with those three solvents. This Foot Yam flour value is larger than reported by Hoover (2001). This defatting method is preferable because of its simplicity. The other method as reported by Yuliana et al. (2012), Chua et al. (2012) and Pacheco et al. (2012) which need advance maintenance. Accordingly, it is said that the starch defatting may effective using methanol, chloroform and hexane.

There are four ways to modify a starch. They are chemical, physical, enzymatical and genetical modification (Kaur et al., 2012). Adding sodium hydroxide is the one of chemical modification. Sodium hydroxide modification caused color and appearance changing of adsorbents (Zhou et al., 2012). Sample C1, C2, C3, C4, C5, C6 and C7 changed to brown from its nature color (ivory) and rougher than sampel A and B. As reported before by Kumar and Bandyopadhyay (2006), Memon et al. (2007), Rehman et al. (2006), Sciban et al. (2006) and Hanafiah et al. (2006) that NaOH is selected because either its easily to handling, cheap or it included in the one of modifying agent that could optimize the adsorption capacities (Wan Ngah and Hanafiah, 2007).

Modified starch using sodium hydroxide that occurred chemical reaction (Lawal et al., 2008):

\[ St - OH + NaOH \leftrightarrow St - ONa + H_2O \]  

This reaction caused starch gelatination then didn’t made the starch retrograded and pulled out amylose. It resulted the adsorbent solidified and rough. Futhermore, the alkali addition could cut the strong hydrogen bonding on the starch polymerization chain (Duanmu et al., 2007).

Adsorbents Characterization

Synthetic adsorbent then analyzed with SEMand FTIR. SEM photograph showed in Figure 1 above with 5,000x magnification of A, B, C1 and C7. This sphere with few pores. There was some staple surrounding the granules, it may the impurities of the flour as reported by Zhu (2014) that flour impurities could be ash, protein, lipid, fosfor and fibres. Because the flour defattiting shape of B was also spheres but it smoother and tinier then A. C1 and C7 represented modified Foot Yam starch with sodium hydroxide. C1 was modified by 10:1 mol/molNaOH:water and C7 was modified by 40:10 mol/molNaOH:water. The photograph of C1 and C7 showed that adsorbent from spheres became amorphous. It was caused by starch gelatinization process with sodium hydroxide. Gelatinization could increase the adsorption capacity of starch because it causes crystalline structure to become amorphous which is desirable for water adsorption which also published by Boonfung and Ratanaphanee (2010).

Figure 2 represented FTIR spectra of the chemical bonding that occurred in the adsorbent B, C1 and C7. Spectra of B showed the \(-OH\) bonds on wavelength 3,420.90/cm, 3,445.01/cm for C1 and C7 bonds on 3,389.08/cm. It said that the C7 contained the largest of \(-OH\) concentration in this adsorbent due to its lowest %transmittance. This might effected the ability to adsorp water as Boonfung and Ratanaphanee (2010) reported that hydroxyl bond could adsorp hydrogen bond in water molecule.

![Figure 1. SEM photograph of sample A, B, C1 and C7](image-url)
Figure 2. FTIR spectra of B, C1 and C7

Figure 3. Gravimetry chart during adsorption process

Water Adsorption

Figure 3 showed the gravimetry chart during adsorption process. Every single line had different pattern which indicated that every single adsorbent has its adsorption capacity. Line A showed that sample A has the slowest mass increasing and line C7 showed the best increasing. It said that C7 is the more promising adsorbent because of its largest adsorbing capacity. Accordingly, it evidenced that starch gelatinization made the structure of adsorbent became amorf which the rich hydroxyl amylose pulled out and adsorb more water.

Adsorption Isotherm of Adsorbent

Figure 4 and Table 1 showed the fitting of adsorbent C7 with models of isotherm adsorption. It showed that C7 fitted more suitably with Freundlich isotherm adsorption model that could be said there is an indication of surface heterogeneityofheadsorbent (Wang et al., 2010). The calculated data was showed that the maximum adsorption capacity of adsorbent C7 was 2.006 g water/g adsorbent. This value is larger than as reported by Wei Rong and Hui Yan (2002) who found the monolayer adsorption capacities of native rice strach is 1.17 g water/g adsorbent and modified rice starch is 1.67 g water/g adsorbent. Besides, this monolayer adsorption capacity of C7 is fewer than cassava (native and modified) which published by Okewale et al. (2013) that calculated that monolayer adsorption capacity of native cassava starch is 5.75 g/g and modified cassava starch is 7.09 g/g. This result has been compared with various other conventional adsorbents and showed in Table 1. Table 1 showed that C7 is more promising to adsorb water among the conventional adsorbents due to its larger water adsorption capacities.
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Table 1. Adsorption parameters of C7 in different adsorption models

<table>
<thead>
<tr>
<th>Adsorption Model</th>
<th>Langmuir</th>
<th>Freundlich</th>
<th>Temkin</th>
</tr>
</thead>
<tbody>
<tr>
<td>q_0</td>
<td>2.096</td>
<td>2.006</td>
<td>1.162</td>
</tr>
<tr>
<td>K_L</td>
<td>23.850</td>
<td>27.027</td>
<td>0.075</td>
</tr>
<tr>
<td>R^2</td>
<td>0.953</td>
<td>0.957</td>
<td>0.957</td>
</tr>
</tbody>
</table>

Table 2. Water adsorption capacity in various adsorbents

<table>
<thead>
<tr>
<th>Foot Yam modified starch</th>
<th>H_2O capacity (g/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica aerogel</td>
<td>1.35</td>
<td>Knez and Novak, 2001</td>
</tr>
<tr>
<td>Alumina aerogel</td>
<td>1.25</td>
<td>Knez and Novak, 2001</td>
</tr>
<tr>
<td>Mixed SiO2-Al2O3</td>
<td>1.15</td>
<td>Knez and Novak, 2001</td>
</tr>
<tr>
<td>MW A IPO 5</td>
<td>1.04</td>
<td>Ng et al, 2014</td>
</tr>
<tr>
<td>MCM-48</td>
<td>0.83</td>
<td>Ng and Mintova, 2008</td>
</tr>
<tr>
<td>KIT-1</td>
<td>0.81</td>
<td>Ng and Mintova, 2008</td>
</tr>
<tr>
<td>FSM-16</td>
<td>0.78</td>
<td>Ng and Mintova, 2008</td>
</tr>
<tr>
<td>HT A IPO 5</td>
<td>0.60</td>
<td>Ng et al, 2008</td>
</tr>
<tr>
<td>SAPO-37</td>
<td>0.55</td>
<td>Szostak, 2003</td>
</tr>
<tr>
<td>SAPO-17</td>
<td>0.54</td>
<td>Szostak, 2003</td>
</tr>
<tr>
<td>ZSM 20</td>
<td>0.46</td>
<td>Szostak, 2003</td>
</tr>
<tr>
<td>Mg-X</td>
<td>0.45</td>
<td>Stachet al., 2005</td>
</tr>
<tr>
<td>Na-X</td>
<td>0.34</td>
<td>Hunger et al., 1999</td>
</tr>
<tr>
<td>SAPO-20</td>
<td>0.34</td>
<td>Szostak, 2003</td>
</tr>
</tbody>
</table>

Table 3. Kinetic parameters of samples in different adsorption kinetic models

<table>
<thead>
<tr>
<th>Adsorption Model</th>
<th>A</th>
<th>B</th>
<th>C1</th>
<th>C7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo second order</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K_2</td>
<td>0.571</td>
<td>2.830</td>
<td>0.601</td>
<td>0.323</td>
</tr>
<tr>
<td>R^2</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>0.993</td>
</tr>
<tr>
<td>Q_e</td>
<td>2.004</td>
<td>2.004</td>
<td>2.004</td>
<td>2.004</td>
</tr>
</tbody>
</table>

| Second order |
| K_2              | 10^6 | 10^6 | 10^6 | 5.10^6 |
| R^2              | 0.916 | 0.937 | 0.872 | 0.974 |
| C_0              | 3.135 | 3.115 | 3.226 | 3.205 |

Kinetic Study of Adsorbent

Water adsorption on adsorbents was investigated as a function of a contact time with range 0-168 hours at room temperature. It was showed clearly that the water adsorption process was increased quite slowly until the end of experimental time. The fastest adsorption rate has been shown by C7. In order to determine the adsorption mechanisms and potential rate controlling step of water adsorption, the common kinetic models have been used such as pseudo first order model, pseudo second order model and second order.

The linier forms, the way of plots and each parameter were shown on Table 2. It could be seen that the experimental data were fitted by the pseudo second order model with R^2 of 0.993 than the other models. Result suggested that physical adsorption might be involved in the adsorption process (Liu and Zhang, 2015).

CONCLUSION

In conclusion, Foot Yam tuber were successfully prepared, modified and employed for water adsorption from air. Addition of NaOH has been investigated systematically. Foot Yam’s native and modified starches have been characterized by FTIR and SEM. The modified starch morphology was amorphous and had largest concentration of hydroxyl group on that chemical bonding. The experimental data were fitted to pseudo second order kinetic model which mean that this water adsorption belonged to physical adsorption. Adsorption process better fitted in Freundlich’s isotherm model with maximum adsorption capacity calculated 2.006 g water/g adsorbent.

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REFERENCES


Modified Starch of *Amorphophallus*... (Lestari et al.)


