Characteristics of *Amorphophallus campanulatus* Modified Starch as Novel Adsorbent for Nickel and Cadmium Removal from Aqueous Solution

A Y D Lestari¹ and L K Dewi²
¹Department of Chemical Engineering, Islamic University of Indonesia, Indonesia
²Department of Chemical Engineering, Brawijaya University, Indonesia
aydlestari@ui.ac.id

Abstract. Novel adsorbents are succesfully manufactured from *Amorphophallus campanulatus* (Porang or Suweg or Elephant Foot Yam or Foot Yam) starch. The experiment focused on modifying the starch with citric acid and detailing those morphologies and chemical bonds. Analysis with FTIR and SEM showed that PTM (modified porous porang starch) sample is the best adsorbent which has most stable of chemical bonding and also has the most pores that influence an adsorption phenomena. Isotherm adsorption analysis showed that the adsorption mechanism of Cd and Ni ions onto the surface of PB, PT and PTM followed the Temkin and Langmuir isotherm adsorption. Adsorption ability of PTM is the best than the other PB and PT which can adsorps 256,23 mg Cd/g PTM and 87,45 mg Ni/g PTM in 500 ppm synthetic aqueous solution.

1. Introduction

Adsorption is the process that can separate objects which neither impossible to be apply nor impractical by conventional techniques [1]. 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 [2] but also made from the polisaccarides. Polisaccarides which is choosen as adsorbents due to their easily to synthesize, have large adsorption capacity due to its large number of the –OH bond and cheap [3]. Elephant foot yam contains polisaccarides that not explore before. In the other hand, exposure of heavy metal ions on our environment especially cadmium and nickel caused some diseases, such as: liver, renal tubular disease, emphysema, dizziness, embolism, etc. So this project focused on evaluation of the characteristics of the citric acid modified the elephant foot yam starch adsorbents and their ability to adsorp both ion Cd²⁺ and Ni²⁺ in aqueous solution.

2. Materials and Methods

The main materials of this subject are foot yam tubers, pure distilled water, Merck’s citric acid and Merck’s ethanol. The selected fresh foot yam tubers is obtain from the farmers at Ngawi, East Java, Indonesia which has the itchy yellowish tuber.

a. Isolation and modification of starch from Foot Yam

Elephant foot yam starch (PB) is isolated from its fresh tuber by conventional process. Then, PB was porous followed by Chang’s method [4]. PB powder was mixed with pure distilled water at the same time heated at 90 °C for about 30 minutes. The mixture was then cooled in the 5 °C freezer for 3 day to
obtain the starch gel. The gel was cut into cubes and frozen at -10°C for another 48 hours. The frozen cubes were immersed in 90% ethanol at room temperature. The cubes were dried at 50°C for 6 hours and then heated at 110°C for 2 hours to remove the ethanol and water and to obtain white solid PT cubes. PT cubes then modified with citric acid which followed Ma’s method [5]. Synthetic PTM was begun with mixing ethanol and citric acid (10:3 v/v). The PT cubes then was added with the solution of ethanol citric acid. The mixture was stirred with 500 rpm overnight at room temperature. The slurry then heated at 110°C for 4 hours. The dried slurry then soaked with 90% ethanol to remove the excess citric acid. The mixture then dried at room temperature and resulted the PTM powder.

b. Characterization of the adsorbent
There are two characterization of this project. They are surface morphology characterization and chemical bonding characterization. The adsorbents surface morphology was visualized by FEI Inspect S50 Scanning Electron Microscope (SEM). The chemical bonding was determined with Thermo Nicolet Avatar 360 Fourier Transform Infrared Spectroscopy (FTIR).

c. Determination adsorption properties of adsorbent
Isotherm adsorption was determined by mixing 1.5 g of sample adsorbents (PB, PT, PTM) with 25 mL differential concentration of Ni and Cd synthetic waste water (100, 200, 300, 400, 500 ppm). Mixture then mixed well for about 30 minutes. After the mixing the adsorbent separated from the filtrate by the Whatmann 40 ashless filter paper, the final concentration of the mixture then analyzed using Perkin Elmer PinAAcle 900T Atomic Adsorption Spectrofotometry (AAS). Experimental data then fitted with Langmuir, Freundlich, Temkin and DubininRadushkevich isotherm model and studied which the appropriate model(s).

3. Result and Discussion

a. Effect of Citric Acid Modification

Figure 1. FTIR Spectrum of PB, PT and PTM.

Figure 1 represented FTIR spectra of the chemical bonding that occurred in the adsorbent PB, PT and PTM. The black line represented PTM spectrum, the dark blue line represented PT spectrum and the light blue line represented PB spectrum. Spectra of PB, PT, PTM showed the –OH bonds on wavelength around 3.400/cm, the C=O bonds on wavelength around 1.800/cm, the C-O bonds on wavelength 1.000/cm. Main focus on this research was the –OH bond. Initial PB –OH bond had the appearance of a little bit wide to the right. After the modification, both PT and PTM’s –OH bonds was tend to be more symmetrical. It can be said that the process of modification with citric acid may alter- OH bond.

b. Characterization of Adsorbents
SEM photograph showed in Figure 2 below with 1.000x magnification of PB, PT and PTM. Figure PB that represent the pure foot yam starch showed that sphere with few pores. There was some staple surrounding the granules, it may the impurities of the starch as reported by Zhu [6] that starch
impurities could be ash, protein, lipid, fosfor and fibres. Figure PT represent the porous foot yam starch showed that the spheres are smoother and have more pores than figure PB. Figure PTM represents the modified porous foot yam starch that has more amor ph, porous and clean structure. Modification process influences the morphology and chemical bonding of adsorbents. Based on those characteristic, the PTM sample has more compromising adsorbent for adsorption process.

![Figure 2. SEM Photograph of PB, PT and PTM.](image)

c. **Effect of the initial Cd and Ni concentration**

The relationship between the initial Cd and Ni ion concentration and the adsorption capacities of PB, PT, PTM for them was studied. As shown in Figure 3 and Figure 4, the adsorption capacities of PB, PT and also PTM for Cd and Ni were correlated with the initial Cd and Ni ion concentration because the process was depent on the concentration. When the concentration rose from 100 ppm to 500 ppm, the adsorption capacities of PB, PT and PTM increased from 13.8 to 68 mg/g, 24.7 to 199 mg/g, 49.7 to 256 mg/g for Cd ion adsorption and 9.2 to 25.3 mg/g, 29.66 to 61.88 mg/g, 45.51 to 87.45 mg/g for Ni ion adsorption.

![Figure 3. Effect of the initial Cd concentration onto PB, PT and PTM.](image)
**Figure 4.** Effect of the initial Ni concentration onto PB, PT, PTM

d. *Isoterm Adsorption of Ni and Cd onto Adsorbents*

The adsorption isotherms showed the relations between the concentration of adsorbate and its degree of accumulation of Ni and Cd 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 [7]. Langmuir model assumes that there is 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:

$$q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e}$$  \hspace{1cm} (1)

Langmuir parameters could be determined by transforming the equation into linear form:

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{Q_0 K_L C_e}$$  \hspace{1cm} (2)

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 $K_L$ for Langmuir isotherm constant (L/mg). The values of $q_{max}$ and $K_L$ were computed from the slope and intercept of the Langmuir plot of vs Freundlich adsorption isotherm is used to describe characteristics for the heterogeneous surface [7]. Freundlich represented the following equation:

$$Q_e = K_f C_e^{\frac{1}{n}}$$  \hspace{1cm} (3)

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). Linearizing of the Freundlich equation above we have:

$$\ln Q_0 = \ln K_f + \frac{1}{n} \ln C_e$$  \hspace{1cm} (4)
The constant $K_f$ is an approximate indicator of adsorption capacity, while is a function of the strength of adsorption in the adsorption process [8]. 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 coorperative adsorption [9]. Goldberg [10] reported that the linier least squares method and the linierly 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 linier adsorption isotherm 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 [11]. 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 [12]. The model has often successfully fitted high solute activities and the intermediate range of concentrations data well.

\[ q_e = (q_s) \exp(-K_{ad} \varepsilon^2) \]  
\[ \ln q_e = (q_s) - (K_{ad} \varepsilon^2) \]

where $q_e$ is amount of adsorbate in the adsorbent at equilibrium (g/g), $q_s$ is theoretical isotherm saturation capacity (g/g), $K_{ad}$ is DubininRadushkevich isotherm constant (mol$^2$/kJ$^2$) and $\varepsilon$ is Dubinin Radushkevich 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.

\[ E = \left[ \frac{1}{\sqrt{2b_{DR}}} \right] \]  
\[ \varepsilon = RT \ln \left[ 1 + \frac{1}{C_e} \right] \]

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 Hameed [13] 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 ($e^2$), all suitable data will lie on the same curve named as the characteristic curve.

e. **Cadmium sorption isotherm**

Figure 3, Figure 4 and Figure 5 showed the plot of data isotherm of Cd adsorption onto the PB, PT and PTM adsorbents. They showed that the Cd adsorption onto PB and PTM are suitable with Temkin isotherm while Cd adsorption onto PTM is suitable with Langmuir isotherm. It said that Cd adsorption onto PB and PTM are heterogenous whereas Cd adsorption onto PTM is occured in monolayer adsorption.

![Figure 5. Cd onto PB.](image5)

![Figure 6. Cd onto PT.](image6)
Table 1 showed the details of Cd adsorption isotherm parameters onto PB, PT and PTM adsorbents.

**Table 1. Cadmium Isothem Parameters onto PB, PT and PTM**

|       | Langmuir | Freundlich |
|-------|----------|------------|
|       | $K_L$    | $q_0$      | $R^2$ |
| PB    | 0.017    | 0.568      | 0.99  |
| PT    | 0.003    | 3.788      | 0.975 |
| PTM   | 0.001    | 26.316     | 0.99  |
|       |           |            |       |
|       | $K_F$    | $n$        | $R^2$ |
| PB    | 0.215    | 1.727      | 0.271 |
| PT    | 0.112    | 0.829      | 0.975 |
| PTM   | 0.254    | 1.089      | 0.999 |
|       |           |            |       |
|       | $A_t$    | $B$        | $R^2$ |
| PB    | 0.559    | 0.158      | 0.078 |
| PT    | 0.031    | 1.982      | 0.985 |
| PTM   | 0.056    | 1.930      | 0.951 |
|       | $K_{ad}$ | $q_e$      | $R^2$ |
| PB    | 5.354    | 480,583    | 0.941 |
| PT    | 3.169    | 264,807    | 0.949 |
| PTM   | 2.050    | 184,380    | 0.94  |

**f. Nickel Sorption Isotherm**

Figure 6, Figure 7 and Figure 8 showed the plot of data isotherm of Ni adsorption onto the PB, PT and PTM adsorbents. They showed that the Ni adsorption onto PB and PTM are suitable with Langmuir isotherm while Ni adsorption onto PT is suitable with Temkin isotherm. It said that Ni adsorption onto PB and PTM are occured in monolayer whereas Ni adsorption onto PT is occured in heterogeneous layer.
Table 2 showed the details of Ni adsorption isotherm parameters onto PB, PT and PTM adsorbents.

|          | Langmuir | Freundlich | Temkin | Dubinin Radushkevich |
|----------|----------|------------|--------|-----------------------|
| PB       | 0.016    | 0.609      | 0.39   | 0.977                 | 1.036 | 0.089 |
| PT       | 0.003    | 1.658      | 0.942  | 0.968                 | 0.673 | 0.049 |
| PTM      | 0.001    | 25.000     | 0.987  | 0.985                 | 0.986 | 0.178 |

Comparison PB, PT and PTM with other Cd and Ni adsorbents

Table 3 showed the list of adsorption capacity of Cd and Ni by some synthetic adsorbents not only conventional adsorbent but also low cost natural based adsorbent. This study said that the PTM adsorbent had more compromising adsorbent among PB and PT for the Cd and Ni adsorption.
processes. Another advantage of PTM especially compared to adsorbent conventional is the availability of raw materials for the manufacture of adsorbent abundant sources of biomass, easily regenerated, adsorbent regeneration after use more environmentally.

| Adsorbents          | Adsorption Capacity (mg/g) | Initial Concentration (mg/L) | Reference     |
|---------------------|-----------------------------|------------------------------|---------------|
| PB                  | 68.23                       | 23.53                        | 500 200       | This study    |
| PT                  | 199.23                      | 61.88                        | 500 200       | This study    |
| PTM                 | 256.23                      | 87.45                        | 500 200       | This study    |
| Activated carbon    | 6.16                        | 9.15                         | 50 50         | [14]          |
| Coconut fiber       | 31.12                       | 10-140                       |               | [15]          |
| Crosslinked carboxymethyl KGM | 9.65                     |                              |               | [16]          |
| Amberlite IR 120 resin | 19.49                     |                              |               | [17]          |
| Amino modified cassava starch | 23.09                   |                              |               | [18]          |
| Crosslinked starch  | 397                         |                              |               | [19]          |
| Dialdehyde o phenylenediamine starch | 69.69                   |                              |               | [20]          |

4. Conclusion

Novel adsorbent was succesfully synthesized from *Amorphophallus campanulatus* starch modified by citric acid. The experiment focused on investigation of the effect of modification and the adsorption ability for Cd and Ni ions in aqueous solution. Modification caused starch more porous and the changed the infrared spectrum of –OH bonding. The adsorption behaviour is dependent on the initial concentration of Ni and Cd ion. Adsorption capacity Cd and Ni on PB, PT, PTM in 500 ppm aqueous are 68 mg/g and 25 mg/g, 199 mg/g and 61.88 mg/g, 256 mg/g and 87.45 mg/g. The adsorption follows the Langmuir and Temkin isotherm. The study also evaluates that the PTM is the more promising adsorbent among the PB and PT. So citric acid modification on the *Amorphophallus campanulatus* starch gave a potential application as another low cost natural based adsorbent.

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