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Modification of Pineapple Leaf Cellulose with Citric Acid for Fe^{2+} Adsorption

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Abstract : Pineapple leaves have a high cellulose content, and it can be used as adsorbent for ion Fe^{2+} adsorption. Cellulose of pineapple leaf have low ability to adsorb, and modification by citric acid can increase ion Fe^{2+} adsorption. The purpose of this reseach were : (1) to determine the effect of citric acid concentration and temperature for cellulose modification forward the adsorption capacity (2) determine the effect of Fe^{2+} initial concentration forward in adsorption (3) determine the adsorption mechanism of the modified cellulose. Citric acid concentration were applied for reseach ; 0.1; 0.3; 0.6; and 0.9 mol/L respectively. Meanwhile for temperature modification used were 25, 50, 80, and 120°C. The characterization of modified cellulose was evaluated by BET (*Brunnear Emmet Teller*) analysis. The concentration of Fe^{2+} used were 20, 40, 60, 80, 100, and 120 mg/L. The isotherm mechanism adsorption was determined following Langmuir and Freundlich model. The result showed that modified cellulose with citric acid at 0.6 mol/L give Fe^{2+} adsorption by 2.45 mg/g. Modification cellulose at 80°C was able to adsorp Fe^{2+} in 2.26 mg/g. Moreover, this adsorbent has 733.725 m^2/g of surface area and 162.17 Å of pore size. Meanwhile, the initial Fe^{2+} concentration for adsorption was reached at this best adsorption (2.74 mg/g) using 80 mg of modified cellulose adsorbent. And it was predicted the adsorption mechanism following Freundlich isotherm model.
Keywords : Fe^{2+} ion, adsorption, modification, pineapple leaves cellulose.

Introduction

Fe^{2+} is one of an inorganic pollutant that needs to be constricted in water resources. In certain concentration, Fe^{2+} could endanger the human life such as skin irritation and itching. The most effective way to decline heavy metal is through adsorption [1], compared the previous method of coagulation and flocculation, ultrafiltration are costly in implementation [2]. Adsorption is usually utilizing plant waste as the adsorbent [3]–[6].

Pineapple leaves are known to have a high cellulose content (70-80%) [7], therefore it could be used as an adsorbent for Fe^{2+} ion . Cellulose as the adsorbent is considered to be less effective for Cu^{2+}, Cd^{2+}, dan Zn^{2+} adsorption [8], hence it needs to be modified in order to add carboxyl groups on the cellulose of pineapple leaves. Cellulose modified by citric acid is known to be more effective compared to another solvent, because it has a number of carboxl groups [9]–[11]. Carboxyl group on citric acid would react with the cellulose, therefore it could increase the capacity of Fe^{2+} adsorption.

Modification of cellulose adsorbent is strongly affected by the concentration of citric acid and temperature on the modification procedure [12]. A high concentration of citric acid could add more carboxyl groups on the cellulose of pineapple leaves. Hence, the main purpose of this study is to identify the effect of modified cellulose on the Fe^{2+} adsorption capacity.

Methods

Materials and Equipment

Materials used in this study were pineapple leaves, iron sulfate hydroxide 99% (*Merk*), citric acid 95% (AR), sodium hydroxide (*Smart lab*), aqua dest, and filter paper. While equipment needed in this study were set of glassware, 80 mesh sieve, analytical balance, oven, *Shimadzu* FTIR 8400S, SEM, AAS *Shimadzu* AA-6200, SAA Quantachrome *Nova Station A*.

Procedure

Adsorben preparation

Pineapple leaves are washed and heated in oven at 50 °C for 24 hours. The dried pineapple leaf smoothed using blander and sieved 80 and 120 *mesh*. The product of pineaple leaf powder further applied for study.

Activation by NaOH

A 13.913 g of Pineapple leaf powder was added by 280 mL NaOH of 0.1 mol/L. The mixture was stirred for 2 hours then filtered. The residue was heated in oven at 50 °C for 24 hours. The powder particles were analyzed its cluster function and morphology using FTIR spectrophotometer and SEM.

Effect of Citric Acid Concentration on the Adsorben Modified

A 2 g of pineapple leaf powder activated was added 50 mL of citric acid for each concentration: 0.1; 0.3; 0.6; and 0.9 mol/L. Then it was stirred for 200 minutes and filtered. The residue was dried at 50°C for 24 hours. A 0.3 g of modified adsorbent added 50 mL of Fe^{2+} 100 mg/L. The mixture was ajusted pH 4 and stirred for 60 minutes then filtered. The filtrate was analyzed using AAS.

Effect of Temperature on the Modification of Fe^{2+} Adsorption

A 2 g of pineapple leaf powder activated added 50 mL of citric acid 0.6 mg/L, then stirred for 200 minutes at a different temperature: 25; 50; 80; 120°C and filtered. The residue was dried at 50°C for 24 hours. Adsorption test was conducted with the same procedure as explained above. Cellulose absorbent powder modified citric acid was analyzed using FTIR and SEM.

Effect of Fe^{2+} concentration on the adsorption

A 0.3 g of modified adsorbent added in 50 mL Fe^{2+} 20, 40, 60, 80, 100, 120 mg/L., and adjusted to pH 4. The mixture was stirred for 60 minutes then filtered. The Fe^{2+} concentration in filtrate was analyzed using AAS.

Result and Discussion

Effect of Citric Acid Concentration on the Adsorben Modified

The effect of citric acid concentration on Fe^{2+} absorption was presented on the curve of Figure 1. Cellulose absorbent from pineapple leaves shows that modification by using 0.6 mol/L citric acid resulted in the highest Fe^{2+} absorption, approximately 2.45 mg/g.

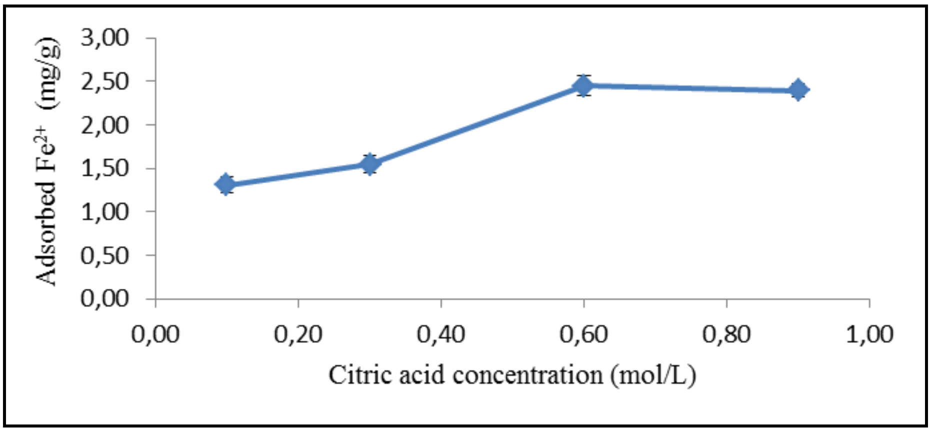


Figure 1. The effect of citric acid concentration on Fe^{2+} adsorption

Basically, it could increase the C=O group on the cellulose of pineapple leaves and consequently, increase the Fe^{2+} adsorption. Meanwhile, modified adsorben with citric acid at 0.9 mg/L give less fortunate Fe^{2+} adsorption by 2.40 mg/g.

Effect of Temperature on the Modification of Fe^{2+} Adsorption

The modified temperature on the 0.6 mol/L citric acid was conducted at a various temperature of 25, 50, 80, and 120°C. The effect of temperature modification on Fe^{2+} absorption is presented in Figure 2. The result shows that esterification was started to work at 20°C and 60°C, where some part of a carboxyl group (-COOH) on citric acid was reacted with pineapple leaves cellulose. Esterification reaction of citric acid is demonstrated in Figure 2.

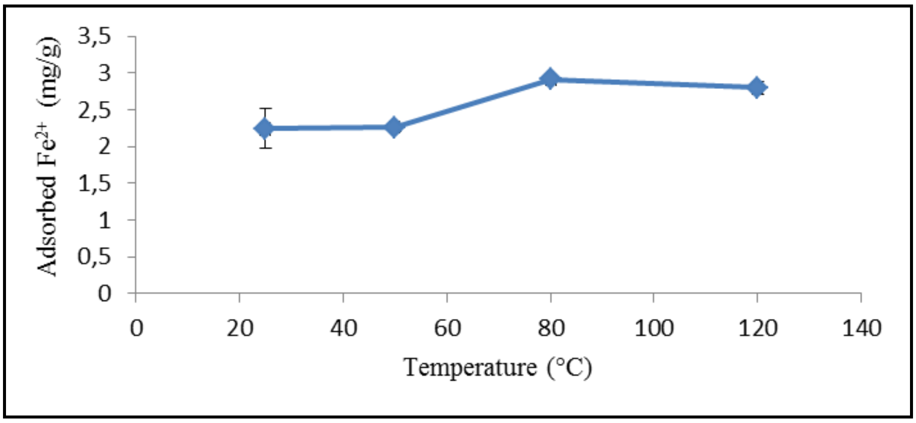


Figure 2. The effect of temperature modification toward Fe^{2+} adsorption

The highest amount of Fe^{2+} that adsorbed by 0.6 mol/L citric acid (80°C) was 2.26 mg/g. It means that the majority of a carboxyl group (-COOH) on citric acid has reacted with the cellulose. The amount of Fe^{2+} adsorbed can increase with higher temperature [13]. At 120°C, the adsorption capacity was decreasing as a result of cross-linking reaction on the modified cellulose, hence the amount of free carboxyl group (-COOH) become lower and reduce the adsorption.

Characterization of Modified Cellulose Adsorbent

BET analysis on cellulose adsorbent after the addition 0.1 mol/L NaOH and 0.6 mol/L citric acid is demonstrated in Table 1.

Table 1. Data characteristic of pineapple leaf fiber cellulose adsorbent

No	Cellulose Adsorbent pineapple leaf fibers	Surface area (m^2/g)	Pore size (Å)
1	The addition of NaOH 0.1 mol/L	695.419	157.04
2	Modifications using citric acid 0.6 mol/L at 80°C	733.725	162.17

The surface area of cellulose adsorbent activated was less compared to modified adsorbent. The bond of carboxyl and cellulose are stronger in midified cellulose adsorben by citric acid at 0.6 mol/L. The particles are difficult to remove and improving surface area. The increasing pore size of cellulose adsorbent occurred along with the improving surface area of modified adsorbent. The success rate of modification process with citric acid at 0.6 mol/L on the cellulose adsorben compared using FTIR spectrum.

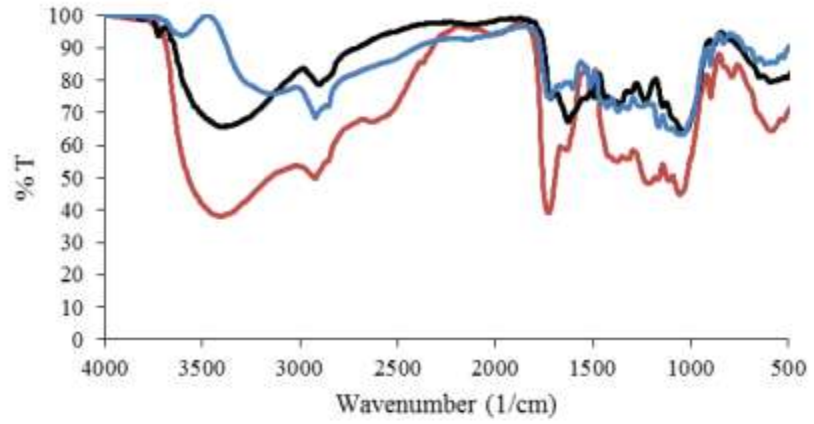


Figure 3. Infrared spectra of activated cellulose adsorben (black), modified cellulose adsorben (red), after adsorption (blue).

According to Figure 3, after the addition of NaOH, adsorption band of pineapple leaf cellulose was marked at wavelength 3361.70 cm^2 as the extent vibration of O-H group. After the addition of citric acid 0.6 mol/L, cellulose shows a significant increase in the intensity of adsorption band at wavelength 3406.03 cm^{-1} as O-H group of citric acid, while the emersion of C=O group was marked at wavelength 1728.08 cm^{-1}.

After the adsorption process, adsorption band was moved from 3406.03 cm^{-1} to 3165.73 cm^{-1}, thus shows an interaction between O-H group from adsorbent with the Fe^{2+} ion. The decreasing the intensity of adsorption band was also found on C=O group at wavelength 1728.86 cm^{-1}. Fe-O group was marked at 718.23 cm^{-1}, thus shows an interaction between ion with the hydroxyl group on cellulose adsorbent modified by citric acid.

Fe^{2+} Adsorption on adsorbent affected by concentration of Fe^{2+}

The result of Fe^{2+} adsorption on adsorbent affected by the various concentration of Fe^{2+} is demonstrated in Figure 4.

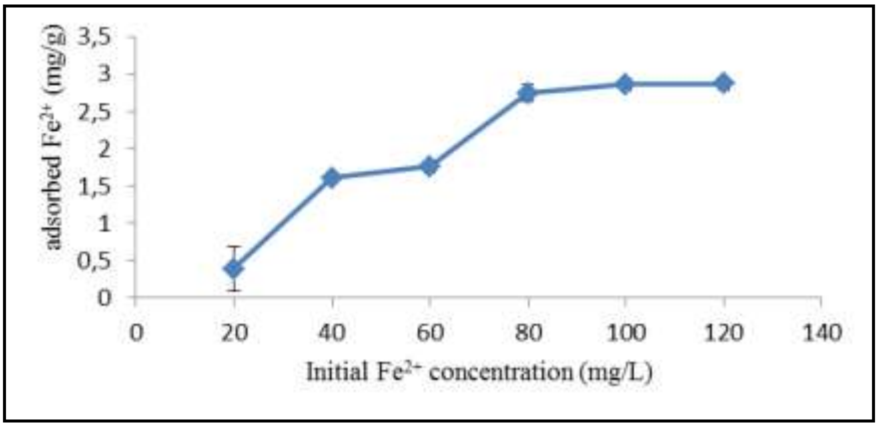


Figure 4. The effect of initial Fe^{2+} on its adsorption

Adsorption process at concentration 20, 40, 60, and 80 mg/L was progressed rapidly with amount of adsorbed Fe^{2+} ranged from 1.61; 1.76; and 2.74 mg/g. At concentration 100 mg/L and 120 mg/L, adsorption was stable with only a few increment. It is proven that pineapple leaf cellulose adsorbent modified by 0.6 mol/L citric acid was reached the balance at 80 mg/L concentration. While above 80 mg/L, Fe^{2+} at the adsorbent surface would experience desorption.

Adsorption Mechanism

Understanding the mechanism of Fe^{2+} adsorption on modified adsorbent is using Langmuir and Freundlich isotherm model. Langmuir and Freundlich isotherm adsorption was shown in Figure 5 and Figure 6. The parameter of Langmuir and Freundlich isotherm adsorption was shown in Table 2.

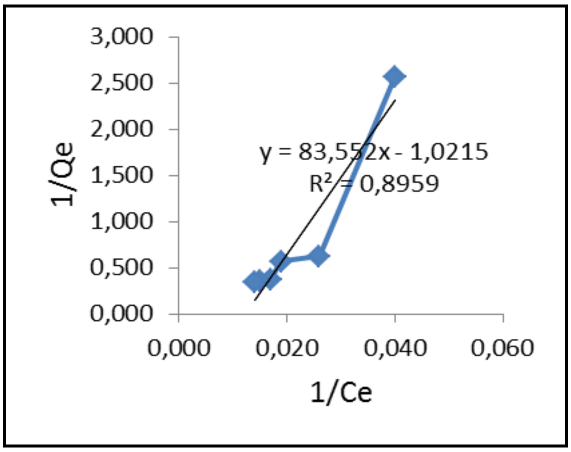


Figure 5. Langmuir isotherm adsorption

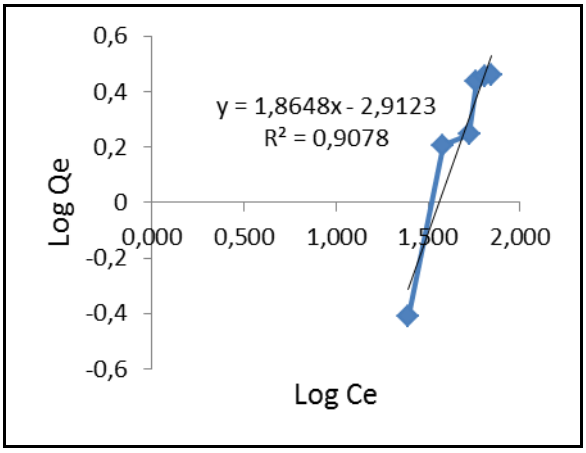
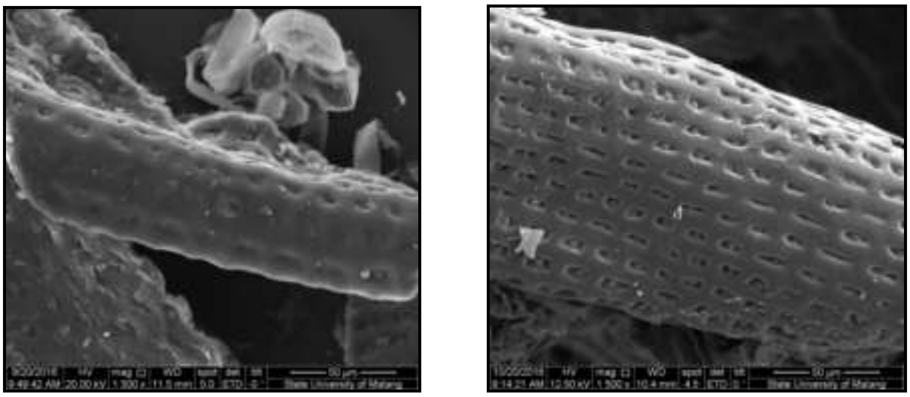


Figure 6. Freundlich isotherm adsorption

Table 2. Langmuir and Freundlich isotherm adsorption parameter

Langmuir Isotherm		Freundlich Isotherm	
R^2	0.8595	R^2	0.9078
b	-82. 264 L/mg	n	0.5362 mg/g
Qm	0.0119 mg/g	K_f	0.0012 L/mg

The Freundlich isotherm equilibirum models for Fe^{2+} adsorption using modified of pineapple leaf cellulose by citric acid giving linear regression with R^2 0.9078 so the Fe^{2+} adsorption by physical adsorption. The afinity and intaction power of modified adsorben to adsorb Fe^{2+} was 0.0012 mg/L and 0.5362 mg/g. The Fe^{2+} adsorption process through on pore modified cellulose adsorben surfaces.



(a) (b)

Figure 7. SEM image of activated cellulose adsorben (a), and modified adsorben (b)

The surface of activated and modified cellulose adsorben (figure 7) was monitored by scanning electron microscope (SEM). The activated cellulose adsorben with NaOH 0.1 mol/L (a) appears impurities on the pore surfaces. The activated adsorben has smaller pore size (157.04 Å) than modified cellulose adsorben (162.17 Å).

Conclusion

Modification of cellulose on pineapple leaves on Fe^{2+} adsorption influenced by citric acid concentration and temperature. The optimum adsorption on Fe^{2+} was 2.74 mg/g using 80 mg of modified cellulose adsorbent. And it was predicted the adsorption mechanism following Freundlich isotherm model.

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