

# Activated carbon from Nypa (Nypa fruticans) leaves applied for the Fe and Mn removal

*by Ahmad Saiful Haqqi*

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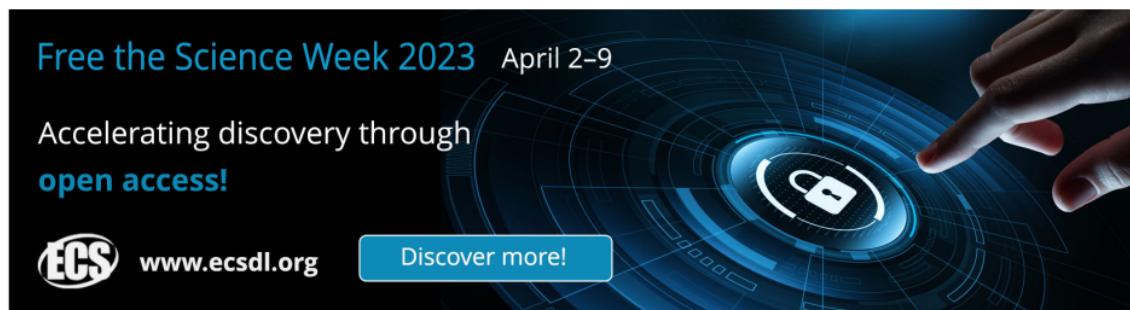
## Activated carbon from *Nypa (Nypa fruticans)* leaves applied for the Fe and Mn removal

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## Activated carbon from *Nypa (Nypa fruticans)* leaves applied for the Fe and Mn removal

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**Abstract.** *Nypa palm (Nypa fruticans)* is a type of palm-shaped mangrove. A nypa leaf contains 28.9% cellulose so that it is possible to produce an activated carbon applied for heavy metal removal in the solution. Thus, this study aimed to remove Fe and Mn in the FeCl<sub>3</sub> and MnCl<sub>2</sub> solution using the activated carbon produced from nypa leaves. In the experimental procedure, 5 grams activated carbon from nypa leaves (the particles that could pass through 40, 80, and 120 mesh size and retained on the sizes of 50, 100, and 150 mesh) were added and undergone in a batch system (for 60 and 120 minutes). The concentrations of Fe and Mn in the solution were investigated using the Atomic Absorption Spectrophotometer (AAS). The results showed that there were significant decreases in the Fe and Mn concentrations at the 60-minutes contact time with 150 mesh particle size (the absorption capacity values of Fe and Mn were 59.96 and 96.94 wt.%, respectively). This was due to the bigger surface area of the adsorbent and the longer contact time resulting in better interaction between the activated carbon from nypa leaves to remove Fe and Mn concentrations in the solution.

### 1. Introduction

*Nypa palm (Nypa fruticans)* is a palm species with special characteristics, and it grows throughout pond estuaries in brackish water. *Nypa* leaves as a part of the *nypa palm (Nypa fruticans)* contain 28.9% cellulose[1]. Pore structure in the cellulose is able to absorb heavy metals[2]. Some factors that may affect adsorption capacity are contact time, surface area, solubility of adsorbate, molecular size, temperature and degree of acidity (pH)[3]. Ali et al.[4] found that *nypa* leave adsorbent successfully adsorbed the metal chromium (Cr VI) up to 94.41 wt.% removal.

Indonesia is one of the countries which has very large land areas. Based on the results of an updated compilation of land map evaluation, inherited land data (legacy soil data), and soil survey until 2011, peatland area in Indonesia is around 14.9 million ha[5]. Additionally, the regulation of the Minister of Health of the Republic of Indonesia Number 492/MENKES/ PER/IV/2010 states that the maximum permitted levels of Fe and Mn concentrations in the raw water are 0.3 and 0.1 mg.L<sup>-1</sup>, respectively. Water sources in peat or swamp areas are generally shallow with special characteristics,



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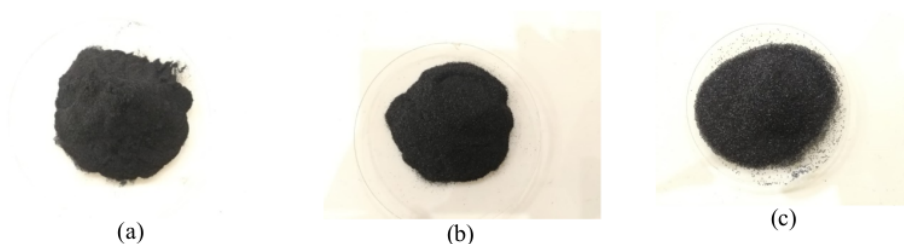
such as having dark brown to black (145 - 850 PtCo) color and high organic content (138 - 1560 mg.L<sup>-1</sup> KMnO<sub>4</sub>) as well as containing iron (Fe) ≤ 25 mg.L<sup>-1</sup>, manganese (Mn) with levels ≤ 1 mg.L<sup>-1</sup> and sour acids (pH 3.7-5.3)[6, 7]. Fe and Mn concentrations that exceed the permitted levels may cause some health problems. Meanwhile, based on quality standard parameters, peat water that exceeds the maximum permitted level is for clean water.

One method that can be used to reduce Fe and Mn contents in the water is through an adsorption method. Adsorbents with natural ingredients have several advantages for overcoming dangerous and toxic metals in the environment, including relatively low cost, easy to obtain, renewable and environmentally friendly[8]. Therefore, this study aims is to investigate the activated carbon fabricated from nypa leaves as the Fe and Mn removal in the solution.

## 2. Materials and methods

### 2.1 Adsorbent preparation

Nypa leaves used in this study were collected from the coastal area in Kotabaru, South Kalimantan-Indonesia. Nypa leaves were washed with water for several times to remove impurities then dried under the sun. The leaves were cut into small pieces to dry easily. Next, the leaves were calcined in the furnace in the air (300°C for 1 hour). The carbon formed was crushed using a grinder and sieved with different sizes (the particles that passed through 40, 80 and 120 mesh and retained in 50, 100 and 150 mesh size). The appearance of carbon formed with various sizes can be seen in figure 1.



**Figure 1.** Carbon Powder Based on Different Size  
(a) 50 mesh; (b) 100 mesh; (c) 150 mesh

### 2.2 Proximate analysis

A proximate test equipment was employed to measure the water content, ash content and crude fibre[9].

### 2.3 Activation process

The adsorbent was activated by dissolving the powder in 0.1 M citric acid solution (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>) and stirred for 2 hours. The adsorbent was then filtered and dried in an oven at 100°C for 4 hours. The dried adsorbent was washed using distilled water to neutralize the pH then dried again in an oven at 80°C for 2 hours. Finally, the nypa leaf activated carbon was ready to be contacted with the artificial metal solution[9].

### 2.4 Adsorption process (the effect of particle size and contact time)

100 ml of each FeCl<sub>3</sub> and MnCl<sub>2</sub> solution of 0.5 mg.L<sup>-1</sup> were put into different Erlenmeyer flasks. Then 5 grams of nypa leaf activated carbon with different sizes (the particles that retained in 50, 100, and 150 mesh) were poured into the Erlenmeyer flasks which had been filled up with the artificial metal solution. Afterward, the mixed solution was stirred using a shaker with a speed of 100 rpm. The

stirring process was carried out for 30 and 60 minutes. Last, the solution was filtered, and the filtrate was analyzed using Atomic Absorption Spectrophotometer (AAS) to determine the Fe and Mn contents in the artificial solution[9].

### 3. Results and discussion

#### 3.1 Characterization

##### 3.1.1 Proximate analysis

The proximate analysis was performed to determine the moisture content, ash content and crude fiber content in the carbonized samples of nypa leaf powder. The results of the proximate analysis are presented in table 1.

**Table 1.** Characteristics of nypa leaves after carbonization.

Characteristics	Contents (%)
Moisture	3.66
Ash	10.08
Rough fibre	18.26

Based on table 1, it is recorded that the water content of nypa leaf carbon powder is 3.66%. Indeed, before the carbonization, the samples were dried, so that the water content in the samples was quite low. The low water content in the samples caused the pores of the adsorbent to become bigger and made the surface area wider[10]. Because the samples were made of natural ingredients, it did not only contain carbon but also some other minerals. Mostly the mineral disappeared during the carbonization and activation process, while the rest remained in the samples. The remaining mineral was assumed to be ash[11]. As seen in Table 1, the value of ash content in nypa leaf carbon powder in this study is 10.08 wt.%. The values of water content and ash content in nypa leaf carbon powder qualify the Active Charcoal Quality Standards based on the 1995 SNI (Indonesian Standard), where the maximum water content and ash content in the active carbon powder are 15 and 10 wt.%, respectively. Furthermore, fiber is a constituent component of the cell walls in plants, which usually includes cellulose, hemicellulose and lignin. The crude fiber content in the nypa leaf carbon powder in this study was 18.26 wt.%. As a comparison, the results of previous research on agar solid waste revealed that the crude fiber content of agar solid waste was 38.05 wt%. This value was higher than that of the nypa leaf carbon powder in this present research. The high content of crude fiber was caused by the fact that most of the waste was fiber concentrate which no longer could be extracted. Besides, the crude fiber level also indicated the carbon in the samples. In other words, the higher the level of crude fiber, the higher was the carbon contained in the samples[12]. The higher carbon content also caused the surface area to widen [13-23]. The presence of nitrogen functional groups in amine functional groups on the carbon surface will increase the adsorption capacity.

#### 3.2 Batch adsorption

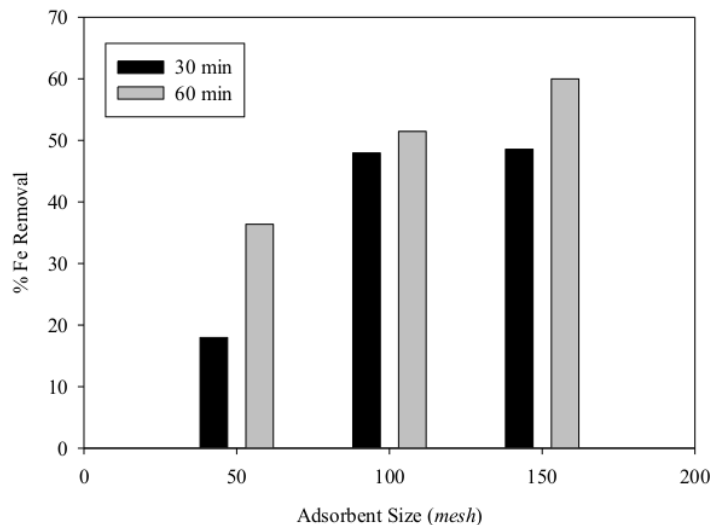
##### 3.2.1 Fe adsorption using Nypa leaf activated citric acid ( $C_6H_8O_7$ ) 0.1 M

The Fe adsorption process using nypa leaves (*Nypa fruticans*) activated citric acid ( $C_6H_8O_7$ ) 0.1 M was carried out in the artificial  $FeCl_3$  solution (with an initial concentration of  $0.5 \text{ mg}\cdot\text{L}^{-1}$ ). This solution would be contacted against the adsorbent with different contact time (30 and 60 minutes) and different sizes of adsorbent (the particles that retained on 50, 100, and 150 mesh). The effect of contact time and adsorbent size on Fe concentration are presented in table 2.

**Table 2.** Effect of contact time and adsorbent size on Fe concentration (mg/L).

Time (minute)	Adsorbent Size (mesh)		
	50	100	150
30	0.410	0.260	0.257
60	0.318	0.243	0.200

The result above indicated that the concentration of Fe decreased when the contact time was longer. The smallest value of Fe concentration was at 60 minutes with 150 mesh adsorbent size, which was equal to  $0.2 \text{ mg.L}^{-1}$ . The longer contact time created the diffusion process and the attachment of  $\text{Fe}^{3+}$  ions to the surface of the adsorbent was better that subsequently caused the Fe concentration to decrease [24]. Moreover, the smaller the particle size of the adsorbent, the bigger was the surface area of the adsorbent that caused a smaller Fe concentration. The correlation between the contact time and particle size of the adsorbent on Fe adsorption can be seen in figure 2.

**Figure 2.** Adsorption curve of fe at different contact time and adsorbent particle size.

The trend of the adsorption showed that the removal percentage increased along with the increase of contact time. This was due to the longer contact time that resulted in better interaction between nypa leaf adsorbent with  $\text{Fe}^{3+}$  ions, thus more  $\text{Fe}^{3+}$  ions were adsorbed by the nypa leaf adsorbent through the  $\text{Fe}^{3+}$  ion exchange reaction with  $\text{H}^+$  ions in the activated nypa leaf adsorbent. The maximum removal percentage reduction of Fe at the 60-minutes contact time with a particle size of 150 mesh was 59.96 wt.%. This is in accordance with a theory which states the longer contact time used, the greater decrease in Fe level because the process of the adsorbate absorption is more optimal [25]. Furthermore, the higher the size of the carbon mesh, the greater was the capacity of adsorption because the particle size became smaller so that the surface area of the activated carbon was greater, which made more active parts to absorb [26]. As a comparison with the Granular Activated Carbon (GAC) adsorbent, the maximum removal percentage of Fe with the same dose and contact time in Fe solution was 99.5% [27].



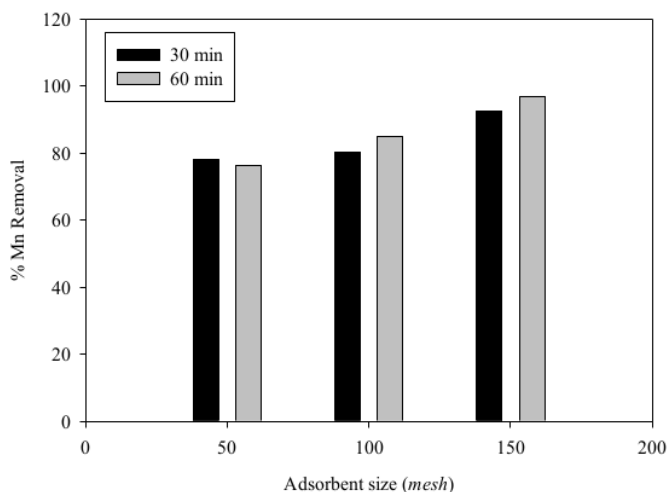
### 3.2.2 Mn adsorption using Nypa leaf activated citric acid ( $C_6H_8O_7$ ) 0.1 M

The Mn adsorption process using nypa (*Nypa fruticans*) leaf activated citric acid ( $C_6H_8O_7$ ) 0.1 M was carried out in  $MnCl_2$  solution with an initial concentration of  $0.5 \text{ mg.L}^{-1}$ . This solution would be contacted against the adsorbent with different contact time (30 and 60 minutes) and different size of the adsorbent (the particles that retained on 50, 100 and 150 mesh). The effect of contact time and adsorbent size on Mn concentration are presented in table 3.

**Table 3.** The effect of contact time and adsorbent size on Mn.

Time (minute)	Adsorbent Size (mesh)		
	50	100	150
30	0.110	0.098	0.037
60	0.119	0.076	0.015

Table 3 shows that the concentration of Mn decreases when the time was longer. The smallest Mn concentration was at 60 minutes with 150 mesh adsorbent size, which was  $0.15 \text{ mg.L}^{-1}$ . Similar to the Fe adsorption, the absorption of  $Mn^{2+}$  ions also occurred better along with the longer contact time and the smallest size of the adsorbent. The correlation between the contact time and particle size of the adsorbent on Mn adsorption can be seen in figure 3.



**Figure 3.** Adsorption curve of Mn at different contact time and adsorbent particle size

The longer contact time resulted in greater interaction between the nypa leaf adsorbent and the  $Mn^{2+}$  ions, thus more  $Mn^{2+}$  ions are absorbed by the nypa leaf adsorbent through the  $Mn^{2+}$  ion exchange reaction with the  $H^+$  ion in the nypa leaf adsorbent that had been activated. From figure 2, it can be seen that an increase in absorption of Mn metal over time. However, at 50 mesh particle size, higher adsorption occurred at 30 minutes and decreased at 60 minutes. This condition was caused by the small surface area of the adsorbent. It made the adsorbent was no longer able to absorb because the  $Mn^{2+}$  ions had accumulated or became very dense in a faster time. Thus,  $Mn^{2+}$  ions which had been bound to the adsorbent would return to the solution or so-called desorption[28]. In this study, the maximum removal of Mn at 60 minutes contact time with a particle size of 150 mesh was 96.94 wt.%.

However, in the range of 30 to 60 minutes, the difference in the reduction of Mn levels was relatively small. It means that 30 minutes is the optimum time for nypa leaf adsorbent to absorb Mn in the solution. As a comparison with the granular activated carbon (GAC) adsorbent, the maximum removal percentage of Mn with the same dose and contact time in Fe solution was 97.4% [27].

#### 4. Conclusion

In conclusion, based on the results of the proximate analysis test on the nypa leaf powder, the nypa leaves are sufficient to be used as an adsorbent referring to the characteristics of the Active Charcoal Standard based on SNI 1995 (Indonesian Standard). The longer contact time and the bigger surface area of the adsorbent resulted in more interactions between the active carbon of nypa leaves and  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$  ions. Therefore, more  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$  ions were absorbed by the nypa leaf adsorbent. It occurred through the interaction between  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$  ions and  $\text{H}^+$  ions on the activated nypa leaf adsorbent.

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