

# Adsorption of Natural Organic Matter (NOM) In Peat Water by Local Indonesia Tropical Clay Soils, Tahun Terbit 2017 (penulis kedua dari tiga penulis)

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## 1 ADSORPTION OF NATURAL ORGANIC MATTER (NOM) IN PEAT WATER BY LOCAL INDONESIA TROPICAL CLAY SOILS

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1 **ABSTRACT:** A series of experiment on the adsorption of natural organic matter (NOM) originated from peat water in Central Kalimantan, Indonesia by local peat clay soils had been carried out. A selected local peat clay soil (LPC) and activated local peat clay soil (ALPC) had been used as adsorbents. The activation of the local peat clay soil was carried out by immersing it in 1 M HCl solution at 900 °C. The effects of pH on the adsorption capacities were investigated. It has been found that at lower pHs (3-5) the adsorption capacities increased significantly. A rotary shaker was set at 180 rpm as an agitator in performing the kinetically behaviour and adsorption isotherm of NOM onto the LPC and the ALPC. It was found that the equilibration time for the LPC and the ALPC were 180 and 150 minutes, respectively. The kinetics equation model that most fitted to the adsorption experimental data for the both adsorbents was pseudo-second order kinetics model ( $r^2 > 0.99$ ). The Dubinin-Radushkevich depicted the data more accurately to describe the NOM-LPC and NOM-LAPC adsorption isotherms ( $r^2 > 0.99$ ). Further analysis on the peat water NOM characteristics and local clay (LPC and ALPC) suggested that physical adsorption, mainly electrostatic interactions enhanced adsorption process and hydrophobic or solute driven adsorption dominated in the early stage of the process, followed by a chemical adsorption process.

*Keywords: Adsorption, NOM, Local clay soils, Dubinin-Radushkevich isotherm*

### 1. INTRODUCTION

The presence of natural organic matter (NOM) in water may create problems in drinking water treatments [1]. NOM causes the presence of color, taste, odor, low pH, and smell problems in water [2]. NOM is also responsible for the formation of hazardous by-product substances after a disinfection process [3], microbiological regrowth in water distribution system, and enhance a formation of biofouling on a membrane surface [4]. In Indonesia, people who live in a peat land area have a problem with their water due to the presence of NOM. Almost all surface water and shallow groundwater in eastern coastal area of Sumatera, low land area of Kalimantan, and coastal area of Papua contains a high concentration of NOM.

Technology commonly used to remove NOM in water may vary e.g. ion-exchange resin filtration, disinfection, and advanced oxidation process (AOP) by ozone [5]. However, these technologies require an advanced modification to be operated efficiently, which cost a substantial amount of money [6]. Generally, NOM can be removed by applying a low-cost method such as a coagulation-flocculation method [7] and at specific condition by adsorption [6]. However, the removal efficiencies of NOM by those processes depend on the molecular weight and the characteristics of NOM itself [8]. Referring to Sharp et al. [9], coagulation-flocculation processes

are only effective to remove NOM with a strong hydrophobicity characteristic and a large molecular weight. Coagulation-flocculation processes could be expensive due to a high dosage of coagulants required, consequently the sludge production may significantly increase which needs additional treatments [6]. On the other hand, adsorption process can become a viable option that offers an environmentally friendly approach and a low-cost technology to remove NOM, only if the adsorbent is relatively cheap and widely available. Unlike coagulation-flocculation processes, adsorption has been well-known effective in removing NOM with a low and a high molecular weight [10].

Adsorption is a process that can remove many types of soluble contaminants in water [11]. Activated carbon is one of adsorbents that generally used to remove organic contaminant in water. Excellence performances of this carbonaceous material in adsorbing NOM have been reported to some extent [12], [13]. Activated carbon somehow needs modification that requires additional treatments [12], therefore an effort to find adsorbent that is cheap, easily found, and has a high uptake capacity become one of a current interest. The use of a local peat clay (LPC) as an adsorbent to remove soluble heavy metals in water has become a main subject of some research [14], [15], as well as in removing soluble organic contaminants [16]. Clay possesses adsorption capabilities of organic

contaminants due to the negative charge on the clay materials [17]. However, no further study on NOM adsorption specifically NOM from tropical peat water by a local clay from Indonesia has been found yet. The characteristic of NOM and a local clay soil may differ from one to other locations which may suggest a different adsorption behavior. Based on that, a specific study on this matter is important.

The aim of this study is to investigate the adsorption behavior of NOM onto a local peat clay soil (LPC) and an activated local peat clay soil (ALPC) from Indonesia. The LPC as an adsorbent that does not need any additional treatment was the main subject in this research.

## 2. METHODOLOGY

### 2.1 Adsorbents Preparation and Characterization

NOM and the LPC were derived from a Gambut area, District of Banjar, South Kalimantan-Indonesia. The LPC was taken from 2 m underneath the peat soils. The LPC was cleaned by washing it with clean water to remove impurities. The wet soil then was dried and crushed using a porcelain mortar to obtain a fine granulated clay. The fine granulated clay was then sieved. All granules larger than sieved mesh number 70 ( $>212\mu\text{m}$ ) were rejected and smaller than that were used as the LPC adsorbent. The ALPC was prepared by immersing the LPC in 1 M HCl solution at 90 °C for 3 hours. The immersed LPC was weighed at 8 g, taken out and then mixed with 25 ml of 1 M HCl. This mixture of soil-acid was washed with distilled water, and dried at least for 24 hours at room temperature ( $\pm 25\text{ }^\circ\text{C}$ ).

The LPC and the ALPC characterization included identifying its mineral compositions and loss on ignition (LOI) were carried out using XRF Instrument (X-Ray Fluorescence) Spectrometer (ADVANT XP+ ThermoARL XRF) and X-Ray Diffraction (XRD) PANalytical X'Pert PRO PW3040/x0. The FTIR method (Jasco FTIR 4200) was used to analyze functional groups consisted on the surface of the adsorbents. In addition, specific surface area of the LPC and the ALPC was determined using BET surface area analyzer (NOVA 3000). The cation exchange capacity (CEC) was determined by employing volumetric method. Zeta potential analyzer (Delsa Nano C) was used to measure the zeta potential of the adsorbent at different pHs.

### 2.2 Batch Experiment of NOM Adsorption

A series of batch experiments were carried out to perform the adsorption of NOM by the LPC and the ALPC. A series of 250 ml erlenmeyer flasks filled with 200 ml peat water with concentrations range of 0.5 to 3.5 mg L<sup>-1</sup> were contacted with 0.5 g L<sup>-1</sup>. The

erlenmeyer flasks containing mixture of adsorbent and adsorbate were agitated using rotary shaker set at 180 rpm for a pre-determined time. After adsorption process, the solution was flowed through a 0.45  $\mu\text{m}$  membrane using a vacuum pump. The amount dissolved organic carbon (DOC) which represents NOM was determined by a TOC Analyzer. To determine the UV<sub>254</sub>, UV<sub>456</sub>, and UV<sub>656</sub>, a UV Spectrometer (Beckman DU-600) was used referred to standard methods for water and wastewater [18]. The value of UV<sub>254</sub> represents the presence of aromatic compounds in the solution, while the ratio of UV<sub>456</sub>/UV<sub>656</sub> or E<sub>4</sub>/E<sub>6</sub> is related to the presence of a larger molecular weight or a smaller molecular weight of NOM. SUVA (specific UV absorbance) as a parameter related to the presence of aromatic compounds and hydrophobicity characteristic of NOM [19], was determined by multiplying the value of UV<sub>254</sub> by 100 and then divided by its DOC value.

### 2.3 Effect of pH on NOM Adsorption

A mixture of peat water solution and the LPC or the ALPC dosage of 0.5 g L<sup>-1</sup> was used, agitated at 180 rpm for 300 minutes. Peat water with 32.98 mg L<sup>-1</sup> of DOC concentration was used in the experiments. The variations of pH applied were 3, 4, 5, 6, 7, 8 and 9. The pH of the solution was adjusted by adding 0.05 M HCl or 0.05 M NaOH.

### 2.4 Kinetic of NOM Adsorption

Contact times applied were 2, 5, 10, 20, 40, 60, 90, 120, 180, 240, 300 and 360 minutes. The LPC or the ALPC dosage was 0.5 g L<sup>-1</sup>, with initial DOC concentration of peat water was 32.98 mg L<sup>-1</sup>. The pH value was adjusted to 5, which is the best condition indicated by previous experiment on the effects of pH on the adsorption process.

#### 2.4.1 Pseudo-first order kinetic model

The Lagergren's equation (Eq. 1), describes the liquid-solid adsorption phenomena based on the adsorption capacity of the solid [20]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (1)$$

Where  $q_e$  and  $q_t$  represent the adsorption capacity at equilibrium (e) and at time (t), respectively (mg g<sup>-1</sup>), t is the contact time (minute) and  $k_1$  is the pseudo-first order constant (min<sup>-1</sup>).

#### 2.4.2 Langmuir isotherm model

Ho (2006) [20] explained that if the kinetic experimental data is well suited to the pseudo-

second order kinetic model (Eq. 2), chemical processes dominate the adsorption process.

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2)$$

Where  $k_2$  represents the second order kinetic constant ( $g \text{ (mg} \cdot \text{min)}^{-1}$ ).

### 2.5 NOM Adsorption Isotherm

In this experiment, the pH of the peat water was adjusted to 5 (as an optimum pH based on the result of the experiment on the effect of pH on the adsorption of DOC), and the contact time was set to 300 minutes as there was no further adsorbate uptake occurred after this time. The DOC concentrations were varied from 32.98, 29.82, 20.76, 16.22, 11.04 and 8.02  $\text{mg L}^{-1}$ . Isotherm models used to examine the data in this experiment were: Langmuir, Freundlich and Dubinin-Radushkevich (D-R) models.

#### 2.5.1 Langmuir isotherm model

The Langmuir isotherm model (Eq. 3) assumes that adsorption process occurring at homogeneously specific adsorption sites of the adsorbent without any interaction involved with adsorbed molecules [10].

$$\frac{C_e}{q_e} = \frac{1}{k_L q_m} + \frac{1}{q_m} C_e \quad (3)$$

The term  $k_L$  is the Langmuir isotherm constant ( $\text{L g}^{-1}$ ) which expresses the sorbent affinity. The term  $q_e$  and  $q_m$  represent adsorption capacity ( $\text{mg g}^{-1}$ ) and maximum adsorption capacity ( $\text{mg g}^{-1}$ ), respectively.  $C_e$  is the equilibrium concentration of the sorbate ( $\text{mg L}^{-1}$ ).

#### 2.5.2 Freundlich isotherm model

Freundlich isotherm model (Eq. 4) describes the adsorption process onto heterogeneous surfaces which not limited only to monolayer, but also applicable to multilayer surfaces [21].

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \quad (4)$$

The constant  $k_F$  referred as the Freundlich constant related to an adsorption capacity and  $n$  is a constant indicates the adsorption intensity.

#### 2.5.3 Dubinin-Radushkevich isotherm model

Dubinin-Radushkevich isotherm model (Eq. 5) is an isotherm model that can be used to distinguish the type of adsorption process (physical adsorption or chemical adsorption).

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (5)$$

Where  $\beta$  is a constant related to the adsorption energy per mol of adsorbate ( $\text{mol}^2 \text{ kJ}$ ),  $q_m$  is a theoretical maximum adsorption capacity ( $\text{mg g}^{-1}$ ), and  $\varepsilon$  represents the Polanyi potential. The average adsorption energy  $E$  ( $\text{kJ mol}^{-1}$ ) can be calculated using Eq. 6. When the value of  $E$  is  $< 8 \text{ kJ mol}^{-1}$ , the adsorption process is dominated by physical process. If a value of  $E$  lies between  $8\text{-}16.8 \text{ kJ mol}^{-1}$ , the adsorption process involves a chemical sorption or means of ion-exchange [22].

$$E = \frac{1}{\sqrt{-2\beta}} \quad (6)$$

## 3. RESULT AND DISCUSSION

### 3.1 Peat Water Characteristics

The peat water characteristics were investigated on a previous research [2]. By knowing the characteristics of adsorbate, the adsorption process can be further studied. The Gambut peat water has a pH of 5.43 and a DOC concentration of 32.98  $\text{mg L}^{-1}$ . The peat water was consisted of 69.7% of NOM with a strong hydrophobicity characteristic. In term of molecular weight, NOM from the tropical peat water in Kalimantan contains 62.7% NOM with molecular weights of  $< 1 \text{ kDa}$ , 14.1% NOM with molecular weights in between  $1\text{-}3 \text{ kDa}$ , while the remains (23.2%) is NOM with molecular weights more than  $3 \text{ kDa}$ . The measurement on zeta potential of the peat water at pH between 2 to 11 depicted that the zeta potentials at all those pH conditions were negatives which similar with previous report [3], and the zero point of charge could not be detected. This condition is probably due to the ionization of carboxylic groups at lower pHs and ionization of phenol groups at higher pHs, therefore at higher pHs, the amount of negative charged species on NOM surface are increased.

The SUVA value of the peat water was found to be  $4.99 \text{ L mg}^{-1} \text{ m}^{-1}$  [2]. This result indicated that most of the NOM component consisted of humic materials with a high degree of hydrophobicity and aromaticity. NOM with a higher value of SUVA was reported to be easily removed by an adsorption process [23].

Results on aromatic substances measurements on the peat water were:  $\text{UV}_{254} 1.65 \text{ cm}^{-1}$ ,  $\text{UV}_{465} 0.098 \text{ cm}^{-1}$  and  $\text{UV}_{656} 0.015 \text{ cm}^{-1}$ . The  $\text{UV}_{465}/\text{UV}_{656}$  or  $E_4/E_6$  is 6.41. A smaller ratio value of  $E_4/E_6$



indicates that the presence of NOM with a smaller molecular weight is more abundant compared to a larger molecular weight organic substances [24]. The value of  $E_4/E_6$  at 6.41 is considered as a relatively large value; the NOM of the peat water from South Kalimantan used in this study was dominated by organic substances with a higher molecular weight.

### 3.2 Characteristics of the LPC and the ALPC

The LPC and the ALPC characteristics are summarized in Table 1. The highest percentage of minerals found in the LPC and the ALPC was  $SiO_2$  based minerals. The cation exchange capacities (CEC) of the adsorbents were considerably high which could exhibit a higher adsorption capacity. Based on the XRD analysis, the main minerals of the LPC were kaolinite, montmorillonite, chloritoid, and quartz. The LOI values of both soils were higher than the LOI of clay soil from other regions such as Turkey, 8.73% [22] or Tunis, 5.3% [25]. The specific surface area (SSA) of the LPC ( $47.2 \text{ m}^2 \text{ g}^{-1}$ ) was found to be relatively smaller for a general clay soil, while the specific surface area for the ALPC was  $107.4 \text{ m}^2 \text{ g}^{-1}$ . The ALPC had almost doubled specific surface area compared to a natural clay such as the LPC.

Table 1 Characteristics of the LPC and the ALPC

Parameter		LPC	ALPC
Chemical composition	$SiO_2$ (%)	56.8	82.3
	$Al_2O_3$ (%)	15.9	5.48
	$Fe_2O_3$ (%)	3.7	0.54
CEC (meq 100 $g^{-1}$ )		16.6	12.8
LOI (%)		24.6	15.6
SSA ( $m^2 \text{ g}^{-1}$ )		47.2	107.4

The FTIR test on the LPC before and after adsorption of NOM is illustrated in Fig. 1. The FTIR test conducted described a wide band was existed between wavelengths 3401.8, 3621.7 and 3694.9  $cm^{-1}$  which was possibly due to the stretching vibration of silanol group (Si-OH) and HO-H vibration from water molecule adsorbed by the silica surface. A vibration at 1712.5  $cm^{-1}$  indicated the presence of carboxylic functional group [25]. Generally, clay minerals consist of functional group such as -OH, -S(Al,Si,Fe)-OH or -COOH at its surface and specifically at the broken edge of the mineral particles. Moreover, the presence of oxide or hydroxide such as aluminium hydroxide, silicon hydroxide and iron hydroxide were abundant. Those elements created hydroxyl groups at the clay surface. A surface hydroxyl group such as S(Al,Si,Fe)-OH is an important adsorption site for any surface reactions that this reaction further could be classified as a sorbent motivated adsorption [10]. There were

no new peaks found before and after the adsorption process.

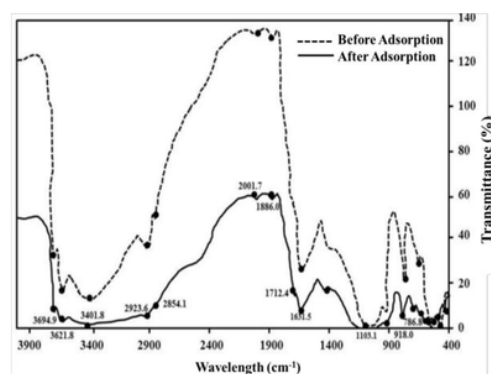


Fig. 1 FTIR results on the LPC before and after the adsorption processes

### 3.3 Effects of pH on the NOM Adsorption by LPC

The effects of pH on the adsorption capacity of the LPC for DOC,  $UV_{254}$ , SUVA and  $E_4/E_6$  parameters were examined.

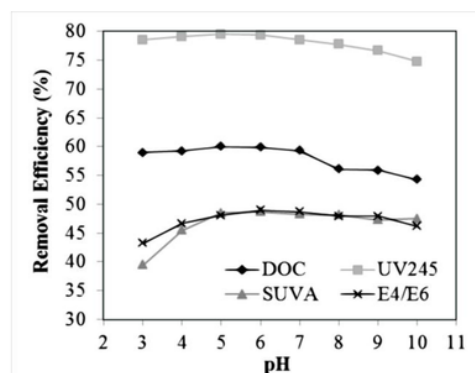


Fig. 2. Effects of the pH of the peat water on DOC,  $UV_{254}$ , SUVA and  $E_4/E_6$  adsorption onto the LPC

The removal of DOC and  $UV_{254}$  from the peat water was found to be effective at acidic conditions (pH 3-5). The removal efficiencies of DOC by adsorption for pH 3 and 5 were 57.96% and 60.01%, respectively, while for  $UV_{254}$ , were 77.72% and 79.28%, respectively. The NOM removal efficiency could be higher if the adsorbent has a positive charged on its surface because NOM of peat water in this study was a negatively charged compound at pHs ranged of 2-11. The favor condition for its adsorption was at low pHs due to the presence of  $H^+$  ions [26]. The electrostatic charge of the peat water as well as pH at point of zero charge of the LPC was 5.2 which may explain the phenomenon. It has been mentioned that during the experiment, NOM of the

peat water was negatively charged, and at  $\text{pH} < 5.2$ , the LPC will be positively charged. The opposite electrostatic charges between NOM and the LPC surfaces yield electrostatic attractive force. This force apparently increased the efficiency of the NOM adsorption. When the  $\text{pH}$  of the solution  $> 5.2$ , the surface of the LPC tended to be negatively charged. When the electrostatic charge of the NOM and the surface of the adsorbent were same (negative), repulsive force appeared and reduced the adsorption of the NOM onto clay (the LPC).

As illustrated in Fig. 2, the removal of SUVA and  $E_4/E_6$  was also increased at  $\text{pH}$  3-6 and tended to decrease at  $\text{pH} > 7$ . The adsorbed SUVA at  $\text{pH}$  5 and 6 were 48.56% and 48.65%, respectively, while for  $E_4/E_6$ , the NOM removal efficiencies were 49% and 49.2%, respectively. The SUVA adsorbed is related to the adsorption degree of DOC and  $\text{UV}_{254}$ . The effect of  $\text{pH}$  on the adsorption of humic substances is due to the diffusion characteristic of humic substances caused by the differences of molecular size of humic acid. At lower  $\text{pH}$  values, humic acid tends to diffuse faster [27].

### 3.4 Effects of Contact Time and NOM Adsorption Kinetics

This study on the effect of contact time on NOM adsorption showed that the ALPC reached the equilibrium state faster rather than the LPC. The equilibrium time for DOC adsorption by the LPC and the ALPC were 150 and 180 minutes, respectively. The adsorption efficiency of DOC was only 58.2% for the LPC and 65.4% for the ALPC. Better results were showed for  $\text{UV}_{254}$  adsorption. At 40 minutes of contact time, percentage removal of  $\text{UV}_{254}$  by the LPC and the ALPC were 78.1% and 83.9%, respectively. Overall, the ALPC gave a higher removal efficiency of NOM compared to the LPC which was caused by the higher value (more than 2 times) of its specific surface area.

The adsorption of NOM onto the LPC and the ALPC intensively occurred at the initial 40 minutes of the contact time. The existence of a fast adsorption at the early stage is related to the physical adsorption process [10]. In this case, the physical adsorption is mainly due to the electrostatic force and van der Waals. The van der Waals force affects large molecules to be adsorbed onto an adsorbent.

The change of SUVA and  $E_4/E_6$  values during adsorption process is presented in Fig. 3. At the early stage, that is 0 to 10 minutes, the SUVA value decreased significantly, and then slowly increased before it was relatively steady after 180 minutes. This trend can be interpreted that at the early stage of adsorption, NOM with a higher SUVA values (hydrophobic, aromatic, and large molecular weight of NOM) were in favor for the adsorption process. The following process, increasing of SUVA value,

indicated that adsorption of NOM with a smaller SUVA value increased (hydrophilic and smaller molecular weight of NOM). After 180 minutes, there was no other significant changes of its removal efficiencies which indicated that there were no further reactions existed.

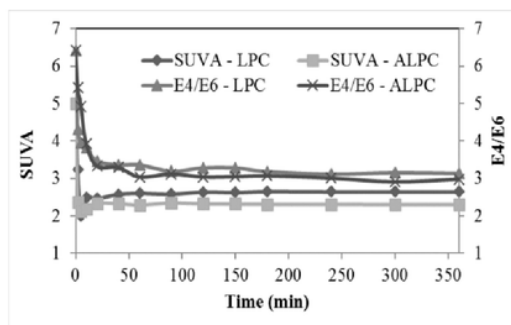


Fig. 3 The change of SUVA and  $E_4/E_6$  against contact time

The change of  $E_4/E_6$  ratio of peat water shows a similar trend to the decreasing value of SUVA. The  $E_4/E_6$  ratio decreased at the initial 5 minutes of adsorption process and not significantly changed after 90 minutes. The decrease value of  $E_4/E_6$  corresponded to the specimen of NOM contained in peat water during adsorption process. A lower value of  $E_4/E_6$  indicated that NOM with a large molecular weight more dominant in the peat water [24].

Kinetic parameters obtained from the experiments are presented in Table 2.

Table 2 Parameters of adsorption kinetic

Kinetic Parameter	LCP	ALCP
qe exp. ( $\text{mg g}^{-1}$ )	39.8	43.68
Pseudo-first order		
$k_1$ ( $\text{min}^{-1}$ )	0.0193	0.0173
qe ( $\text{mg g}^{-1}$ )	14.24	19.98
$r^2$	0.7269	0.7483
S%	29.86	29.18
Pseudo-second order		
$k_2$ ( $\text{g mg}^{-1}\text{min}^{-1}$ )	0.0212	0.0273
qe ( $\text{mg g}^{-1}$ )	39.68	43.67
$r^2$	0.9981	0.9987
S%	7.24	2.07

The correlation coefficient ( $r^2$ ) and the deviation standard of experimental data (S) were used to choose which the kinetic model can best describe the experimental data of NOM adsorption onto the LPC and the ALPC. The pseudo-second order kinetic model depicted data more accurately. Furthermore, the higher value of  $k_2$  compared to  $k_1$  also indicates that pseudo-second order which describes a fast process followed by a slower process fitted the data more accurately. The high value of  $k_2$  from the pseudo-second order kinetic model of the ALPC

indicated that the NOM adsorption driving force was stronger compared to the LPC. This corresponded to the specific surface area of the ALPC was wider than that in the LPC.

Several studies suggested that pseudo-second order kinetic model is the most suitable model to describe organic adsorption phenomenon [27]. In this case, the adsorption process was consisted of two stages [20]. The first stage of the adsorption process was a relatively quick process and could be dominated by a physical sorption such as an electrostatic force driven sorption, van der Waals attraction force or ion exchange process. The second stage was a slower process and in some cases, could be regarded as a diffusion controlled reaction. Based on the experimental data and the characteristics of the peat water, at the initial stage of the process, physical adsorption process was more dominant. The slower process at the second stage may be a reaction between hydrophilic and NOM with a small molecular weight with the adsorbent. The hydrophilic sites and those small molecules of NOM may intrude into the micropores of the adsorbent. The transport of NOM molecules to this micropores was driven by a diffusion process (a relatively slow process). Any chemical reaction was probably also occurring between surface functional groups of the adsorbent with the moieties of NOM [28]. Another possibility of the chemical reaction to occur was ion exchange, since the CEC of both the LPC and the ALPC were considerably high.

### 3.5 NOM Adsorption Isotherms

Calculated isotherm parameters obtained from the experimental data are presented in Table 3. In this experiment, DOC was used as a representation of NOM. The use of DOC to represent NOM has an advantage, because DOC can represent the existence of humic and non-humic substances in the peat water.

Table 3 Adsorption isotherm parameter

Isotherm Parameter	LCP	ALCP	
Langmuir	$k_L$ (L mg <sup>-1</sup> )	0.249	0.313
	$R_L$	0.11-0.33	0.09-0.28
	$q_m$ (mg g <sup>-1</sup> )	51.8	54.3
	$r^2$	0.9773	0.9742
Freundlich	$k_F$	12.6	14.91
	$n$	0.4654	0.4472
	$r^2$	0.9734	0.9791
Dubinin-Radushkevich	$B$ (mol <sup>2</sup> kJ <sup>-2</sup> )	0.0049	0.0046
	$q_m$ (mg g <sup>-1</sup> )	159.8	164.4
	$E$ (kJ mol <sup>-1</sup> )	10.1	10.43
	$r^2$	0.99	0.99

Based on the value of  $r^2$  of the experimental data, the most suitable isotherm model to describe the

NOM adsorption process was Dubinin-Radushkevich (D-R) isotherm model ( $r^2 > 0.99$ ). In general, D-R isotherm can predict adsorption process mechanism based on the adsorption energy (E). The E value obtained from the model for the LPC was 10.1 kJ mol<sup>-1</sup> and for the ALPC was 10.43 kJ mol<sup>-1</sup>, thus the adsorption process of NOM for both adsorbents was probably controlled by the chemical processes. The ion exchange process may occur between the surface functional groups of an adsorbent with the moieties of the NOM [29].

Both the Langmuir and the Freundlich isotherms exhibited a correlation to the experimental data ( $r^2 > 0.97$ ). For Langmuir isotherm model, the calculated non-dimensional,  $R_L$  constant as  $1/(1+K_L C_0)$  expresses the basic characteristic of the isotherm model. If the value of  $R_L$  lies between 0-1, the adsorption process can be suitable for the model [30]. For the Freundlich isotherm, the coefficient of  $n$  describes the adsorption driving force and energy distribution at surface adsorbent that involved in the adsorption process [31]. Sahoo et al. (2014) [32] more specifically proposed that if the value of  $n < 1$ , the physical process is more dominant, and if  $n > 1$ , the chemical process or chemisorption is more dominant. The value of  $n$  of Freundlich isotherm for both adsorbents were smaller than one, thus it can be interpreted that the physisorption was more dominant for the whole adsorption process.

Table 3 shows that Freundlich isotherm was fit the data better for the NOM adsorption. The Freundlich isotherm model is proposed for both monolayer and multilayer adsorption on the heterogeneous adsorbent surface. Activation process of the ALPC by immersing it in a strong acid (HCl) might change the clay mineral's structure, and created more heterogeneous adsorption sites and increased its specific surface [33]. The  $k_F$  values obtained from NOM adsorption onto the LCP and the ALCP were 12.6 and 14.91, respectively, while if compared with other studies, which using nanomaterials and carbon materials as adsorbents, their  $k_F$  values obtained were in a range of 100-200 [34], [35]. This means that the adsorption capacity values yielded by the LCP and ALCP were smaller than other materials. This could be due to the surface area of the materials and the modifications done to the materials that could enhanced the adsorption process [36]. However, the ability of the LCP and the ALCP as low-cost adsorbents in removing NOM from peat water should be well-considered for its further possible development.

Results from the Langmuir's maximum adsorption capacity ( $q_m$ ), shows that the ALPC and the LPC maximum adsorption capacity only differs slightly. Therefore, the LPC is applicable to be used as an adsorbent instead of using the ALPC which require an additional activation process which may be costly.



### 3.6 Mechanisms of NOM Adsorption onto the LPC

As demonstrated by the FTIR spectra analysis results (Fig. 1), there were no new peaks showed in the transmittance after the adsorption process which corresponded that there was no additional chemical or functional groups formed during the adsorption process. If any new peaks in transmittance was found, reactions between adsorbate and adsorbent functional groups might exist [30]. It could be concluded that based on the FTIR spectra analysis results, the adsorption process between the LPC and NOM in the peat water was dominated by physical processes.

Results in adsorption kinetic model shows that pseudo-second order kinetic has an excellent fit to the experimental data. The fast reaction at the initial stage of process (40 minutes) followed by a slower reaction and tend to constant until 360 minutes of the contact time indicated that physical adsorption processes were more dominant to be occurred during the adsorption process compared to chemical processes which controlled the adsorption rate for the rest of the contact time. On the other hand, isotherm analysis showed that the Dubinin-Radushkevich isotherm model ( $r^2 > 0.99$ ) indicated that chemical reactions might be involved significantly in the adsorption process of NOM by the LPC. However, the other isotherms, the Langmuir and the Freundlich isotherm models suggested that physical processes were more suitable in describing the adsorption process.

The South Kalimantan peat water contained a high concentration of NOM due to its environment. This peat water is located and part of the peat land ecosystem that is rich in organic substances as products of biomass degradation. The main fractions of NOM in peat water are humic substances (60-90%) out of DOC, and fulvic substances [37]. Both fractions contain a high concentration of functional groups such as carboxylic group and phenolic group. An ionization of both functional groups increases the negativity of NOM in the peat water. Consider that adsorption process favors a low pH condition [23], [38] therefore, it suggests that for NOM with a negative charge, the physical process adsorption based on electrostatic interactions between NOM and positively charged of the surface of adsorbent might be dominant in this study.

To support in concluding of which mechanism that controlled the NOM adsorption process onto the LPC, measurement of zeta potential at pH range of 2-11 was conducted. The zeta potentials of the LPC before adsorption and after adsorption were measured. The zeta potential of peat water (NOM) was also measured. The measurement results are presented in the following Fig. 4.

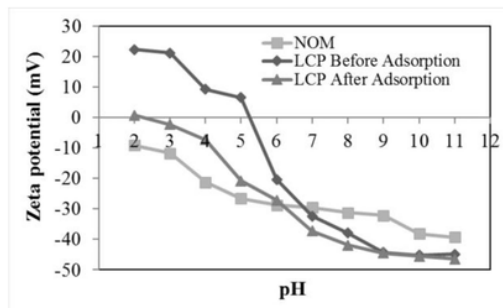


Fig. 4 Zeta potential of the LPC before and after adsorption and peat water

As shown in Fig. 4, the value of pH at the point of zero charge ( $\text{pH}_{\text{pzc}}$ ) of the LPC was 5.2, which means at  $\text{pH} > 5.2$  the zeta potential of the LPC will be negative, and positive at  $\text{pH} < 5.2$ . The values of  $\text{pH}_{\text{pzc}}$  after adsorption tended to decrease. The possible explanation for this case was that the attachment of negative charge of NOM onto the LPC. The interaction between NOM and the LPC was due to electrostatic interactions between the negative charge of NOM and the positive charge of the surface of the adsorbent (LPC). However, at  $\text{pH} > 5.2$ , the surface charge of the LPC was no longer positive, therefore another process or adsorption was existed. Furthermore, as demonstrated in Fig. 2, the removal efficiency and maximum adsorption capacity of the LPC was at  $\text{pH} = 5$ , and then decreased at  $\text{pH} 4$  and  $3$ , while zeta potential at  $\text{pH} 4$  and  $3$  was larger than at  $\text{pH} 5$ . These facts indicate that although electrostatic interaction contributed significantly in the NOM adsorption, there was still possibility that another process also involved. Adsorption of organic substances depends on the physical and chemical properties of the organic substances itself and the adsorbent. Some phenomena that possibly play an important role in the adsorption processes are ion-exchange, ligand exchange, van der Waals attractive force, hydrophobicity and competitive effects.

As explained in the NOM characterization section, the NOM of South Kalimantan peat water was more hydrophobic, has a high degree of aromaticity and was dominated by a large molecular weight organic substances. This characteristic was favorable for physical adsorption where electrostatic interaction between an adsorbate and an adsorbent occurred due to the negatively charged NOM substances and positively charged of the adsorbent surface. Another significant process that might be involved was van der Waals attractive force due to the abundant availability of large molecular weight of NOM in the peat water. With significant portion of hydrophobic substances, hydrophobic effect can create "solvent motivated sorption" of hydrophobic NOM onto the adsorbent surface.



#### 4. CONCLUSIONS

The experimental results show that the LPC and the ALPC from South Kalimantan were found to be effective to adsorb NOM of peat water. This peat water, which was derived from South Kalimantan, possessed characteristics of a high hydrophobicity, dominated by large molecules, contained a significant amount of aromatic substances and has a low pH. The local peat clay (LPC) could remove DOC and aromatic compounds of peat water. The ALPC performed better to adsorb NOM compared to the LPC. The favorable condition for adsorption was at a lower range of pH (3-5) which gave 81.75% removal of DOC and 91.96% for UV<sub>254</sub> parameter. The time required to reach the equilibrium state for the LPC and the ALPC in adsorbing NOM were 180 and 150 minutes, respectively. At the initial stage (40 minutes) of the contact time, the NOM was adsorbed vastly onto the surface of the adsorbents and was getting slower until the end of contact time. A fast process occurred indicated that physical process could be taken place. The FTIR transmittance analysis also indicated that the physical process was dominantly controlling the NOM adsorption process. Pseudo-second order kinetic model fitted to the experiment data ( $r^2 > 0.99$ ) which indicated that chemical process took a role in a small portion of the adsorption process (second stage). The maximum DOC adsorption capacities of the LPC and the ALPC were 51.8 mg g<sup>-1</sup> and 54.3 mg g<sup>-1</sup>, respectively. Isotherm model that best fitted to the experimental data was Dubinin-Raduskhevich isotherm ( $r^2 > 0.99$ ). It was suggested that the mechanisms involved in the NOM adsorption by the LPC were physical and chemical processes. Electrostatic interactions between positively charged surface of the LPC and NOM with negative charges distinguished the physical adsorption process. Another important interaction that might be involved in the adsorption process was van der Waals attractive force and hydrophobicity effects. For the chemical adsorption process, the process that possibly occurred was ion exchange between surface functional groups of adsorbent and NOM functional group as the moieties of NOM.

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# Adsorption of Natural Organic Matter (NOM) In Peat Water by Local Indonesia Tropical Clay Soils, Tahun Terbit 2017 (penulis kedua dari tiga penulis)

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