

# Adsorption of Humic Acid from Peat Water on Pyrophyllite

Muhammad Ali Zulfikar, and Henry Setiyanto

**Abstract**—The ability of raw pyrophyllite to adsorb humic acid from peat water has been investigated. The influences of contact time, dose of pyrophyllite and pH were the factors considered in the adsorption processes of humic acid from peat water. In addition, adsorption isotherms of humic acid onto the chitosan were also evaluated with the Langmuir, Freundlich and Sips approximations. Our results showed that the adsorption equilibrium occurred at contact time of 90 minutes. The maximum adsorption occurred at 10 gram adsorbent dosage and pH was 3.5. The data was well fitted to Langmuir isotherm.

**Keywords**—Adsorption, humic acid, peat water, pyrophyllite.

## I. INTRODUCTION

**H**UMIC substance is one of the main components of peat water that is consisted of large molecules with molecular weights ranging from thousands to hundreds of thousands [1] and have a backbone of aromatic and aliphatic residues with numerous substituents such as OH groups, ketones, carboxylic acid groups, amino acids/peptides, saccharides and amino saccarhrides [2]. Humic acid imparts a brown or yellow color in peat water and pose a serious environmental problem, particularly in drinking water treatment because of their taste and odor. They also tend to react with a variety of oxidants and disinfectants used for the purification of drinking water forming carcinogenic disinfection byproducts (DBPs) such as trihalomethanes and haloacetic acids [3]-[6].

Coagulation and flocculation [3], [4], [6], oxidation [4], photocatalysis [5], biofiltration [7] and membrane filtration [3], techniques have been developed to remove these substances. All of these alternative processes, however, have disadvantageous, e.g high operational cost and requires some chemicals. None of them therefore, is considered by industries to be commercially viable because economically unrealistic.

Adsorption is known to be a promising technique, which has great importance due to the ease of operation and comparable low cost of application in the adsorption process. Commercially activated carbon is the most widely studied and used as adsorbents for water and wastewater treatments.

However, activated carbon is n expensive adsorbent due to its high cost of manufacturing and regeneration [8]. For the purpose of removing unwanted hazardous compounds from contaminated water at a low cost, much attention has been focused on various naturally occurring adsorbents. Among these adsorbents, clay minerals have been shown to be the most promising alternatives due to their local availability, technical feasibility, easy engineering applications, highly specific surfaces area, and cost effectiveness [9], [10].

Pyrophyllite is a non-swelling hydrous aluminum silicate with the chemical formula  $Al_2Si_4O_{10}(OH)_2$ . It belongs to the family of silicate minerals that are composed of three infinite layers formed by the sharing of oxygen ions at three corners of the silica tetrahedra. A layer of octahedrally coordinated Al-OH ions holds the two layers of tetrahedrally coordinated Si-O ions together as a three-layer sheet [11]. Now, the application of pyrophyllite on waste water treatment has become of great interest because of its abundance in local reserves as well as its inexpensiveness. A considerable amount of work has also been reported regarding the potential use of pyrophyllite in the removal of heavy metal ions and dyes [10]-[14]. However, the adsorption properties of pyrophyllite towards humic acid from peat water are scarcely known.

In this paper, we report an investigation of pyrophyllite as an adsorbent material for the adsorption of humic acid from peat water. In this study, the effect of contact time, adsorbent dosage and pH on the adsorption were investigated. Adsorption isotherm models were also investigated.

## II. MATERIALS AND METHODS

### A. Materials

Pyrophyllite was obtained from PT. Kurnia Padalarang, West Java, Indonesia. The chemical composition of these one can be seen at [15]. Sodium hydroxide and hydrochloric acid used to adjust pH was purchased from Merck. Water used was generated from aqua demineralization system. All materials were used without further purification. The peat water sample was obtained from Bukit Timah, a sub district of Dumai city in Riau Province, Indonesia. Before mixing the peat water sample with adsorbent, its pH value was adjusted using sodium hydroxide and hydrochloric acid. The pH value was measured using 300 Hanna Instrument pH meter.

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### B. Methods

The pyrophyllite sample was milled in water in a Planet Style Ball Mill for 4 h. After filtration, the samples were dried at 110 °C for 2 h and kept in a desiccator.

Adsorption experiments were carried out by mixing respectively of 5 g pyrophyllite with 50 mL peat water of unadjusted pH at 25°C in thermostatic shaker bath for 2, 5, 10, 15, 20, 25, 30, 45, 60, 75, 90, 120 and 180 minutes. At the end of the predetermined time interval, the suspension was taken out and the supernatant was centrifugated. The humic acid concentration of each peat water solutions was determined by spectrophotometer (Shimadzu UV-Vis 1601 model) at the  $\lambda$  300 nm. The percent of humic acid removal from peat water was calculated using the following equation:

$$\text{Removal (\%)} = [(C_i - C_e) / C_i] \times 100\% \quad (1)$$

where  $C_i$  and  $C_e$  are initial and final concentration of humic acid in solution, respectively. The adsorption capacity of an adsorbent at equilibrium with solution volume  $V$ , was calculated using the following equation:

$$q_e \text{ (mg/g)} = [(C_i - C_e) / m] \times V \quad (2)$$

where  $C_i$  and  $C_e$  are the initial and final concentration of humic acid in solution, respectively.  $V$  is the volume of solution (L) and  $m$  is mass of adsorbent (g) used.

The effect of pH on humic acid adsorption from peat water was studied in the suspension with pH range from 2.0 to 10.0 by adjusting the pH using dilute HCl and NaOH solution and using 5 g of pyrophyllite for 15, 30, 45, 60, 75, 90 and 120 minutes.

The effect of dosage of pyrophyllite on humic acid adsorption was investigated by mixing 50 mL peat water with different dosages (1, 3, 5, 7 and 10 g) for 60 minutes and at unadjusted pH.

To study of adsorption isotherm, the adsorption experiments were carried out by mixing 5 g pyrophyllite with 50 ml of peat water sample, which other conditions were held constant at pH unadjusted and temperature of 25 °C. The experimental data were calculated to determine the adsorption isotherm by using the Langmuir, Freundlich and Sips models.

### III. RESULTS AND DISCUSSION

Fig. 1 shows the effect of contact time on humic acid removal from peat water on pyrophyllite. Based on the plot, humic acid adsorption was relatively fast with more than 50% of peat water adsorbed in 30 minutes first. After 90 minute, it can be observed that the humic acid adsorption remained constant and this indicating the equilibrium has been established.

Fig. 2 illustrates the effect of pyrophyllite dosages on humic acid removal from peat water. The maximum humic acid removal of about 88.5% was observed at the dosage of 5 gram.

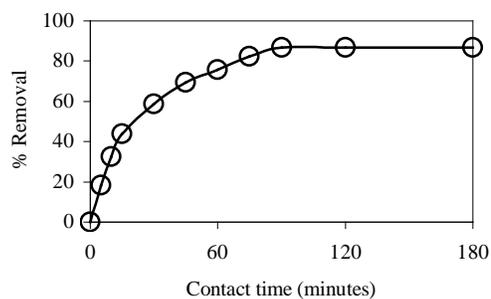


Fig. 1 Effect of contact time on humic acid adsorption from peat water

The percentage removal decreased slightly at higher dosage (up to 7 gram) of the adsorbent. It likely that a higher dosage causes particles to aggregate, overlapping and overcrowding, thereby reduce the availability of surface area for adsorption [16], [17].

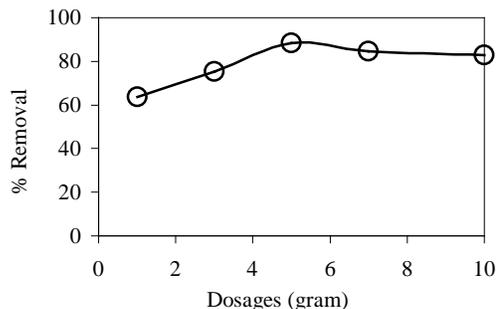


Fig. 2 Effect of adsorbent dosage on humic acid adsorption from peat water

The pH of the solution is an important variable that controls the adsorption of humic acid from peat water. As shown in Fig. 3, the adsorption of humic acid from peat water decreases as pH increases. The optimum humic acid removal from peat water was occurred at pH 3.5.

The decrease of humic acid removal may be related to the formation of negative surface charges of pyrophyllite at higher pH. Since the zero point of charge of pyrophyllite was at pH = 2.3 [18], the pyrophyllite surface in water had a negative surface charge. The surface charge became more negative as the pH increased non favoring the adsorption of humic acid.

Besides the factors addressed above, it has been suggested in previous study that the humic substances, especially humic acid may exist in a spherical structures at lower pH and change into rather linear or stretched structure at higher pH [19], [20]. This would result in less amount of humic acid adsorbed in the adsorbent pores. Therefore, the increase in the size of humic acid macromolecules with increasing pH solution can be another factor contributing to the reduction of removal of peat water at higher pH.

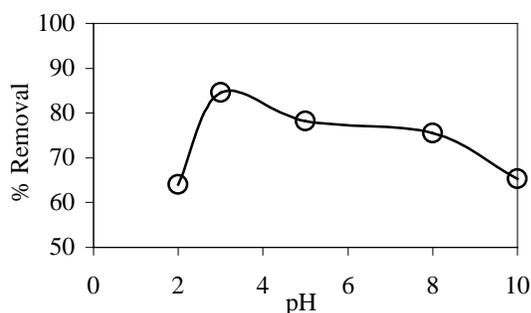


Fig. 3 Effect of pHs on humic acid adsorption from peat water

Adsorption isotherms describe how adsorbates interact with adsorbents at constant temperature. Sorption equilibrium data provide fundamental physicochemical information for evaluating the applicability of sorption process as a unit operation. In the present investigation the equilibrium data were analysed with Langmuir, Freundlich and Sips isotherms. The non-linear form of Langmuir isotherm is expressed as:

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

Where  $C_e$  is the equilibrium concentration (mg/L),  $q_e$  is amount of adsorbate adsorbed per unit weight of adsorbent (mg/g),  $q_m$  and  $K_L$  are Langmuir constants related to maximum adsorption capacity (mg/g) and energy of adsorption (L/mg), respectively. The results showed that the data can be fitted with the Langmuir equation (Fig. 4) and value of  $q_m$  in our experiment was found to be 205.15 mg/g.

Humic acid removal from peat water was also analyzed using Freundlich equation. In Freundlich adsorption isotherm, the model assumes a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface. The isotherm experimental data were fit to the Freundlich model by using equation below:

$$q_e = K_f C_e^{1/n} \quad (4)$$

Where  $C_e$  is the equilibrium concentration (mg/L),  $q_e$  is amount of adsorbate adsorbed per unit weight of adsorbent (mg/g) and  $K_f$  and  $n$  are Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

Sips isotherm is employed to analyze the equilibrium data obtained during batch adsorption studies. Sips model is a combination of Langmuir and Freundlich models, having features of both Langmuir and Freundlich equations. It is expressed as:

$$q_e = \frac{q_m \cdot K_{eq} \cdot C_e^n}{1 + K_{eq} \cdot C_e^n} \quad (5)$$

where  $K_{eq}$  (L/mg) represents the equilibrium constant of the Sips equation and  $q_m$  (mg/g) is the maximum adsorption capacity.

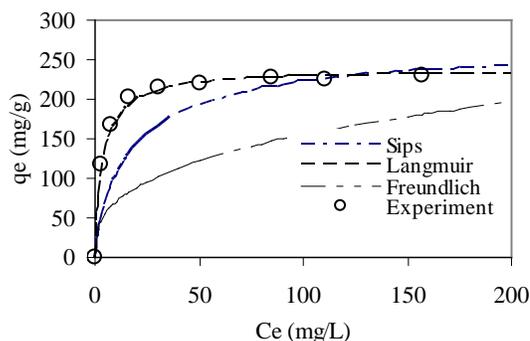


Fig. 4 Non-linear isotherm of humic acid adsorption from peat water

The Sips isotherm model is characterized by the heterogeneity factor,  $n$ , and specifically when  $n = 1$ , the Sips isotherm equation reduces to the Langmuir equation and it implies a homogenous adsorption process.

The maximum adsorption capacity of pyrophyllite obtained from the Sips isotherm was 237.2 mg/g. As shown in Fig. 4, the Langmuir isotherm model showed better fit to the experimental isotherm data than the Freundlich and Sips isotherm models.

#### IV. CONCLUSION

The main aim of this study was to investigate the possibility pyrophyllite used as an adsorbent material. In this study, the removal of humic acid from peat water under the influences of contact time, adsorbent dosage and pH was investigated. The optimum humic acid removal occurred at contact time of 90 minutes, adsorbent dosage was 5 gram and pH was 3.5. The adsorption of humic acid onto pyrophyllite beads follows the Langmuir model, with the maximum adsorption capacity was 205.15 mg/g.

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