

# Effect of Temperature on Adsorption of Humic Acid from Peat Water onto Pyrophyllite

Muhammad Ali. Zulfikar

**Abstract**—The sorption of humic acid from peat water onto pyrophyllite under the influence of temperature has been investigated. Batch adsorption experiments were carried out using peat water as an adsorbate from Bukit Timah, Dumai City, Riau. It was observed that the amount of humic acid removed increase with increasing temperature. Thermodynamic parameters data indicated that the humic acid removal was non-spontaneous and endothermic under the experimental conditions, with the enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) of  $+29,44 \text{ kJ mol}^{-1}$  and  $+74.96 \text{ J mol}^{-1}$ , respectively.

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

## I. INTRODUCTION

**H**UMIC substance, which are present in peat water, adversely affect water quality in several ways: causing undesirable color and taste, binding with heavy metals and biocides and reacting with chlorine during water treatment to produce trihalomethanes [1]-[5], which affect human health very seriously and can even cause cancer [5]. Therefore, the presence of humic acid in peat water has been a great concern and measures have to be taken to minimize the presence of humic acid in peat water and in other water resources.

Among the many existing methods, adsorption has shown to be a promising technique to remove these organic matters from aqueous solution, which has great importance due to the ease of operation and comparable low cost of application in the adsorption process. 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 [6], [7].

Pyrophyllite is a non-swelling hydrous aluminum silicate with the chemical formula  $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$ . 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 [8]. 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 [7]-[11]. However, the adsorption properties of pyrophyllite towards humic acid from peat water are scarcely known.

In this paper, it was aimed to study the effect of temperature on adsorption of humic acid from peat water. In addition, thermodynamic parameters were also studied.

## 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 [12]. 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.

### 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  $110 \text{ }^\circ\text{C}$  for 2 h and kept in a desiccator.

Adsorption experiments were carried out in 50 mL flasks immersed in a thermostatic shaker bath at  $25 \text{ }^\circ\text{C}$ ,  $45 \text{ }^\circ\text{C}$ ,  $65 \text{ }^\circ\text{C}$  and  $85 \text{ }^\circ\text{C}$  in thermostatic shaker bath for 2, 5, 10, 15, 20, 25, 30, 45, 60, 75, 90, 120 and 180 minutes. Pyrophyllite samples of 5 g were mixed with 50 mL of peat water. At the end of the predetermined time interval, the suspension was taken out and the supernatant was centrifuged. 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.

### III. RESULTS AND DISCUSSION

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

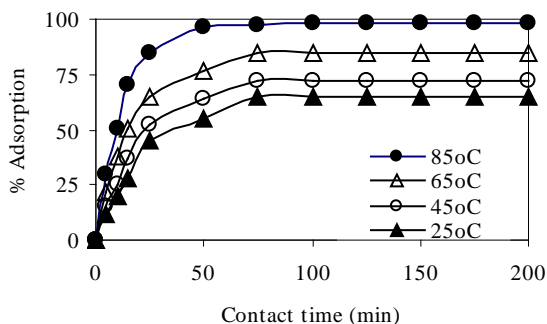


Fig. 1 Effect of temperature on humic acid adsorption from peat water

From Fig. 1, it also shows that the amount of humic acid adsorbed on pyrophyllite is enhanced with increasing temperature. Increasing of temperature is known to increase the diffusion rate of the humic acid molecule across the external boundary layer and the internal pores of the adsorbent particles. Furthermore, increasing temperature may produce a swelling effect within the internal structure of the adsorbent enabling large humic acid to penetrate further [13]-[15]. The increasing adsorption of humic acid with increasing temperature, it was due to more interaction between adsorbate and adsorbent [16].

The thermodynamic parameters such as Gibbs free energy, enthalpy and entropy changes for humic acid sorption on pyrophyllite are calculated from the temperature dependent sorption isotherms. The Gibbs free energy change ( $\Delta G^\circ$ ) of the sorption reaction is given by:

$$\Delta G^\circ = -RT \ln K_L \quad (3)$$

where  $R$  (8.314 J/mol K) is the gas constant,  $T$  (K) absolute temperature and  $K_L$  (L/mg) is the Langmuir isotherm constant.

The Gibbs free energy change indicates the degree of spontaneity of the adsorption process and the higher value reflects a more energetically favourable adsorption [17]. The Gibbs free energy change ( $\Delta G^\circ$ ) is also calculated as:

$$\Delta G^\circ = \Delta H^\circ - T \cdot \Delta S^\circ \quad (4)$$

Combining equation (3) and (4) and rearranging:

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R.T} \quad (5)$$

The value enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) can be evaluated from the slope and intercept of the linear plot of  $\ln K_L$  vs  $1/T$  (Fig. 2).

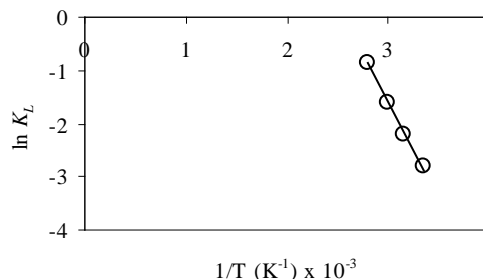


Fig. 2 Plot of  $\ln K_L$  for the adsorption of humic acid from peat water on pyrophyllite as function of inverse of temperature ( $K^{-1}$ )

The values obtained from Fig. 2 are tabulated in Table 1. A positive value of the standard enthalpy change indicates that the sorption process is endothermic and thus the adsorption of humic acid on pyrophyllite is entropy driven [18].

One possible explanation to this positive entropy is that adsorbent and humic acid compound are dissolved well in water, and the hydration sheath of adsorbent and humic acid have to be destroyed before sorption process.

This dehydration process needs energy, and it is favored at high temperature [19]. The enthalpy change ( $\Delta H^\circ$ ) for chemisorption is in the range 40-120 kJ/mol [20]. Since the value of  $\Delta H^\circ$  observed in the system is lower than 40 kJ/mol, the adsorption of humic acid from peat water onto pyrophyllite by physisorption.

The positive values of Gibbs free energy ( $\Delta G^\circ$ ) obtained indicate the non-spontaneous nature of adsorption process at the range of temperatures being studied. It can also noted that the value of  $\Delta G^\circ$  become more negative with the increase of temperature, which indicates that the reaction is more favorable at high temperatures. The positive value of entropy

Temp. (°C)	$K_L$ (L/mg)	$\Delta G^\circ$ (kJ/mol)	$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/mol)
25	0.06	6.97		
45	0.11	5.84	29.44	74.96
65	0.20	4.52		
85	0.43	2.51		

change ( $\Delta S^\circ$ ) implies some structural changes during the sorption process, which leads to an increase in the randomness at the solid-solution system [19], [21], [22].

### IV. CONCLUSION

The main aim of this study was to investigate the effect of temperature on humic acid adsorption from peat water using pyrophyllite as an adsorbent. The result from this work

showed that the temperature has an important role in the adsorption of humic acid compounds onto pyrophyllite. Thermodynamic parameters data indicated that the humic acid sorption process was non-spontaneous and endothermic under the experimental conditions, with the Gibbs free energy ( $\Delta G^\circ$ ) in the range of 6.97-2.51 kJ mol<sup>-1</sup>, enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) of 29.44 kJ mol<sup>-1</sup> and 74.96 J mol<sup>-1</sup>, respectively.

#### ACKNOWLEDGMENT

The author is very grateful to Bandung Institute of Technology for the financial support this research study.

#### REFERENCES

- [1] J.C. Rojas, J. Pérez, G. Garralón, F. Plaza, B. Moreno, M.A. Gómez, "Humic acids removal by aerated spiral-wound ultrafiltration membrane combined with coagulation-hydraulic flocculation", *Desalination*, vol. 266, pp. 128-133, 2011.
- [2] C.S. Uygurera, S.A. Suphandaga, A. Kercb, and M. Bekbolet, "Evaluation of adsorption and coagulation characteristics of humic acids preceded by alternative advanced oxidation techniques", *Desalination*, vol. 210, pp. 183-193, 2007.
- [3] D. Sonea, R. Pode, F. Manea, C. Ratiu, C. Lazau, I. Grozescu, and G. Burtica, "The comparative assessment of photolysis, sorption and photocatalysis processes to humic acids removal from water", *Chemical Bulletin of "POLITEHNICA" Univ. (Timisoara)*, vol. 55, no. 69, pp. 148-151, 2010.
- [4] C. Sun, Q. Yue, B. Gao, R. Mu, J. Liu, Y. Zhao, Z. Yang, and W. Xu, "Effect of pH and shear force on flocs characteristics for humic acid removal using polyferric aluminum chloride organic polymer dual-coagulants", *Desalination*, vol. 281, pp. 243-247, 2011.
- [5] W.S. Ngah, S. Fatinathan, N.A. Yosop, "Isotherm and kinetic studies on the adsorption of humic acid onto chitosan-H<sub>2</sub>SO<sub>4</sub> beads", *Desalination*, vol. 272, pp. 293-300, 2011.
- [6] M. Dogan, Y. Ozdemir, and M. Alkan, "Adsorption kinetics and mechanism of cationic methyl violet and methyl blue dyes onto sepiolite", *Dyes Pigm.*, vol. 75, pp. 701-713, 2007.
- [7] J. Sheng, Y. Xie, and Y. Zhou, "Adsorption of metyhlene blue from aqueous solution on pyrophyllite", *App. Clay. Sci.*, vol. 46, pp. 422-424, 2009.
- [8] A. Gucek, S. Sener, S. Bilgen, and M.A. Mazmanci, "Adsorption and kinetic studies of cationic and anionic dyes on pyrophyllite from aqueous solutions", *J. Colloid Interface Sci.*, vol. 286, pp. 53-60, 2005.
- [9] M. Erdemoglu, S. Erdemoglu, F. Sayilkan, M. Akarsu, S. Sener, and H. Sayilkan, "Organo-functional modified pyrophyllite: preparation, characterisation and Pb(II) ion adsorption property", *App. Clay. Sci.*, vol. 27, pp. 41-52, 2004.
- [10] S. Saxena, M. Prasad, S.S. Amritphale, and N. Chandra, "Adsorption of cyanide from aqueous solutions at pyrophyllite surface", *Sep. Purif. Technol.*, vol. 24, pp. 263-270, 2001.
- [11] H. Sayilkan, S. Erdemoglu, S. Sener, F. Sayilkan, M. Akarsu, and M. Erdemoglu, "Surface modification of pyrophyllite with amino silane coupling agent for the removal of 4-nitrophenol from aqueous solutions", *J. Colloid Interface Sci.*, vol. 275, pp. 530-538, 2004.
- [12] M.B. Amran, and M.A. Zulfikar, "Color removal of congo red dyestuff by adsorption onto phyrophyllite", *Int. J. Environ. Sci.*, vol. 67, no. 6, pp. 911-920, 2010.
- [13] G. Mckay, "Adsorption of dyestuffs from aqueous solution with activated carbon : I : Equilibrium and batch contact time studies", *J. Chem. Technol. Biotechnol.*, vol. 32, pp. 759-772, 1982.
- [14] H. Hiroyuki, M. Fukudas, A. Okamoto, and T. Kataoka, "Adsorption of acid dye cross linked chitosan fibers equilibria", *Chem. Eng. Sci.*, vol. 48, no. 12, pp. 2267-2272, 1994.
- [15] M. Saker, and S. Podar, "Study of adsorption of methyl violet onto flyash", *Proc. Ind. Annual Communication*, vol. 31, pp. 213-215, 1994.
- [16] K.K. Pandey, G. Prasad, and V.N. Singh, "Use of wallstronite for the treatment of Cu(II) rich effluent", *Water Res.*, vol. 19, pp. 869-872 1989.
- [17] N. Yeddou, and A. Bensmaili, "Equilibrium and kinetic modelling of iron adsorption by eggshells in a batch system: Effect of temperature.", *Desalination*, vol. 206, pp. 127-134, 2007.
- [18] M. Salman, B. El-Eswad, and F. Khalili, "Adsorption of humic acid on bentonite", *App. Clay. Sci.*, vol. 38, pp. 51-56, 2007.
- [19] H. Xie, D. Wu, Z. Jiao, X. Li, S. Zhang, Y. Lan, and C. Cheng, "Kinetic and thermodynamic sorption study of radiocobalt by magnetic hydroxyapatite nanoparticles", *J. Radioanal. Nucl. Chem.* DOI 10.1007/s10967-011-1458-3, 2011.
- [20] M. Alkan, O. Demirbas, S. Celikcapa, and M. Dogan, "Sorption of acid red 57 from aqueous solution onto sepiolite", *J. Hazard. Mater.*, vol. B116, pp. 135-145, 2004.
- [21] J. Rahchamani, H.Z. Moausavi, and M. Behzad, "Adsorption of methyl violet from aqueous solution by polyacrylamide as an adsorbent: Isotherm and kinetic studies", *Desalination*, vol. 267, pp. 256-260, 2011.
- [22] C. Namasivayam, and D. Sangeetha, "Removal and recovery of vanadium (V) by adsorption onto ZnCl<sub>2</sub> activated carbon: Kinetics and isotherms", *Adsorption*, vol. 12, pp. 103-117, 2006.

# Effect of Legume Seed Protein Isolates on Autolysis and Gel Properties of Surimi from Sardine (*Sardinella albella*)

Tanaji Kudre and Soottawat Benjakul

**Abstract**— Effects of protein isolate from mung bean (MBPI), black bean (BBPI) and bambara groundnut (BGPI) at different levels (0-1.5%, w/w) on autolysis and gel properties of sardine (*Sardinella albella*) surimi were evaluated. Breaking force and deformation of both kamaboko (40/90 °C) and modori (65/90 °C) gels increased with increasing MBPI, BBPI and BGPI levels ( $P<0.05$ ). When MBPI or BBPI or BGPI at a level of 1.5% was incorporated, breaking force of kamaboko and modori gels increased by 22.4-76.8, 24.9-95.3 and 90.0-135.3%, while deformation increased by 11.6-31.3, 13.1-42.7 and 26.4-61.39%, respectively. This was coincidental with lowered TCA-soluble peptide content. Myosin heavy chain (MHC) of modori gel was more retained as MBPI, BBPI and BGPI concentrations increased. The concomitant increase in water-holding capacity of resulting gel was obtained; however, the whiteness was slightly decreased ( $P<0.05$ ). The microstructure study reveal that modori gel added with MBPI or BBPI or BGPI at 1.5% were comparatively denser and more ordered than without protein isolate. Generally BGPI exhibited the superior gel enhancing effect than BBPI and MBPI, regardless of level added. Therefore, BGPI at an appropriate level could be an alternative food grade protein additive to improve gel properties of surimi.

**Keywords**—Autolysis, Legume seeds, Protein isolates, Sardine, Surimi gel, Texture analysis

## I. INTRODUCTION

**S**ARDINE (*Sardinella albella*) is a small coastal pelagic fish species, which can be used for surimi production in Thailand. Apart from the darken colour, surimi from sardine has the poorer gel properties than those produced from lean fish. This leads to the less demand of surimi from sardine. In general, dark fleshed fish have been reported to contain high level of proteases, which induce the protein degradation [1]. Proteolytic disintegration of myofibrillar proteins has an adverse effect on gel-forming properties of surimi. The breakdown of myofibrillar proteins inhibits the development of three-dimensional gel network [2]. When the gel is heated at 50-70 °C, an irreversible proteolytic degradation of myofibrillar proteins occurs, resulting in the disintegration of

the gel structure named ‘modori’ [3]. Modori gel is mainly due to the autolysis caused by heat-stable proteases such as cathepsins, alkaline proteases, and calpains [4]. (Although some proteases are leached out during washing process, some proteases, especially those bound with myofibrillar proteins are retained. Reference [5] found that both endogenous sarcoplasmic and myofibril-associated proteinases play an important role in degradation of myofibrillar proteins in lizardfish muscle, particularly at 60-65 °C, leading to gel weakening.

To alleviate the problems associated with protein degradation caused by the endogenous proteases, several protein additives have been used in surimi to improve the properties of surimi gels. Whey protein concentrate (WPC), chicken plasma protein (CPP) beef plasma protein (BPP), porcine plasma protein (PPP), egg white (EW), and rainbow trout plasma protein (RPP) can be used as food grade protease inhibitors in surimi [6], [7]. However, the use of BPP and CPP has been forbidden, because of bovine spongiform encephalopathy (BSE) and outbreak of avian influenza (AI), respectively. Egg white is expensive and has an undesirable egg-like odor, whilst blood plasma is associated with off-colour and off-flavour of resulting surimi gel. Plant protein isolate, particularly soy protein isolate, has been used in surimi industry owing to its safety and reasonable price [8].

Due to a variety of legume seeds in Thailand, those seeds can be used for production of protein isolates, which can be used as an alternative protein additive for surimi gel improvement. It has been reported that several legume seed extract contained trypsin inhibitors and was able to inhibit protease activity of fish muscle and surimi [8], [9]. Reference [10] stated that vicilin and legumin a major legume seed storage proteins were act as a co-gelling agent or binder in surimi gels. Protein isolates from selected legume seed can be a source of protease inhibitors which could lower modori phenomenon in surimi, and/or act as binder or filler, thereby improving gel property. The purpose of this study was to investigate the preventive effects of protein isolate from black bean and mungbean seeds on the hydrolysis of myofibrillar protein by endogenous proteases in surimi made from sardine (*Sardinella albella*) and to study the associated effects on surimi gel improvement.

Tanaji Kudre is with the Department of Food Technology, Faculty of Agro-Industry, Prince of Songkla University, Hat Yai, Songkhla, 90112, Thailand (corresponding author's phone:66-74286345 ; fax:66-7455-8866 ; e-mail: trustk9biotek@gmail.com).

Soottawat Benjakul is with Department of Food Technology, Faculty of Agro-Industry, Prince of Songkla University, Hat Yai, Songkhla, 90112, Thailand (e-mail: soottawat.b@psu.ac.th).