

Porous Carbon Adsorbent from Humin Derived from Thai Leonardite for Methylene Blue Dye Adsorption

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Abstract

Leonardite is by-product from lignite mine found in northern Thailand. Leonardite is generally known as natural source of humic substances. Humic substances can be divided into three major fractions, i.e. humin, humic acids and fulvic acids. These fractions can be extracted by using solution adjusted to different acid alkaline (pH levels). Humin is a major product that can be extracted from Thai leonardite and it is over 80% yield of product. The morphology of humin is non-conductive bulk material with few porous structures. It can be used as adsorbent for dye adsorption or heavy metal and used as catalyst supporter. The synthesis of porous carbon from humin via carbonization process was investigated in this research. Humin was carbonized at different temperatures and characterized by SEM, FTIR, UV-Vis and BET. Porous carbon from humin was used in methylene blue dye adsorption. The result indicates that the particle size of humin was decreased with well-dispersed and non-agglomerate humin was observed in higher carbonization temperature. The adsorption capacity of humin was increased with increasing of temperature up to 700°C and decreased at 900°C according to surface area and porosity results. Although the carbon content of humin was increased at higher temperature, the function group used as adsorbent was decomposed.

Keywords: leonardite, humic substance, humin and carbon absorbent
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1. Introduction

Dyes dissolved in industrial wastewater are the main problem which cause varied side effects to surrounding environment [1]. Dyes at approx 10-15% was released into water resources exhibiting organic compounds highly resistant to degradation [2]. A large quantity of dyes from various

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industries such as apparel, textile and so on have been used which is the cause of health problems and environmental pollution. Recently, several researchers have reported that the carcinogenic toxicity of dyes is harmful to humans and animals [3]. Hence, promising technologies have been investigated to solve this problem. One of these is adsorption, the process is a well-known method for water decontamination applications because it is simple to design, convenient to use, low-cost for reusability and also, the formation of toxic substances [5]. Various factors related to the adsorption efficiency of dye are based on nature of dyes, pH of adsorbate solution, pH at point zero charge (pzc), porosity and surface functional of adsorbent. There are many types of sorbents that are often studied, such as zeolite, silica and activated carbon [6]. Activated carbon was widely selected for the removal from wastewater since it is a simple process, but the price is still high. Therefore, there is a need for simple and inexpensive materials. From such issues, most researches have focused on natural materials which are easy to find, or may be a by-product or waste material from industries which needs additional cost reduction [7].

Thailand is a significant producer of lignite, which is used almost exclusively for power generation or as source of energy for cement and steam engine industries. Total national lignite production is around 21 million tons per year [8]. In Southeast Asia, Thailand is one of the biggest lignite mines [9] and leonardite is a by-product of lignite mine. In general, leonardite is a rather complex material predominately made of carbon (55% by weight) [10]. Leonardite in nature has about 20-70% organic composition and when passing carbonization process, organic matter can be converted to activated carbon [11]. Leonardite is known as natural source of humic substances. Humic substances have organic complex structures, high molecular weight, and are durable to decay. The decomposition of plant and animal residues results in carbon molecules as components of humic substances. Humic substances are main components of soil, coal, dystrophic lakes and sea water [12]. The properties and detailed structure are based on the condition of soil, water resources and the extraction method [13]. Humic substances can be divided into three major fractions: humin, humic acids and fulvic acids and can be extracted using solution adjusted to different acid alkaline (pH levels). Humin is an organic matter insoluble in water at all pHs forming as dark brown solids which are in homogenous and their structures are often vaguely described. Humic acid and fulvic acid can be extracted from soil and other solid phase using a strong base at high pH. Our previous study found that humin was a major product which was over 80% yield of product whereas humic acid and fulvic acid were only 10-20% of product (unpresented data) and it is possible to improve its properties and used as adsorbent for heavy metal or dye adsorption.

This research was conducted to investigate the feasibility of low-cost adsorbent for methylene blue adsorption. Humin adsorbent was obtained from lignite mines in Lampang province, Thailand. Methylene blue (MB) was chosen as the model dye in this study because of its difficulty to degrade in nature and its strong adsorption onto solids. The effects of temperature in carbonization process and adsorption capacity of humin were studied in this research. The adsorbent capacity was characterized by Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectroscopy (FTIR), Brunauer–Emmett–Teller (BET) surface area and UV-vis spectroscopy, respectively.

2. Materials and Methods

Leonardite was collected from lignite mine at Mae Moh, Lamphang province, Northern Thailand. The sample was dried at 80°C for 24 h. Afterwards, the soil sample was milled into powder by mortar and sieved for selection of particle size between 180 to 500 μm . The extraction of humic substance from leonardite was carried out following the method suggested by Gracia [14], using

base-acid treatment. Soil extraction was performed by mixing 40 g of dry leonardite powder with 400 ml of KOH solutions at concentration of 0.1M solution for 3 h at room temperature. The extracted soluble containing humic acids (HA) + fulvic acids (FA) was further separated from insoluble fraction containing humin by centrifugation at 5000 rpm for 15 min. The humin fraction was dried at 90°C for 24 h. Dried humin fraction was milled into powder and carbonization at 300, 500, 700 and 900°C for 2 h. in horizontal furnace under nitrogen (N₂) atmosphere. The humin sample was characterized for morphology, chemical structure, pore volume and BET, surface area by Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectroscopy (FT-IR) and Brunauer–Emmett–Teller (BET), respectively. For the adsorption experiment, 1g of humin adsorbents and 25 ppm of methylene blue (25 mg/l) were added to centrifuge tubes. The tubes were centrifuged at 3,000 rpm for 5 min, and the humin adsorbents were filtered through filter paper. The color removal of MB dye solutions was analyzed by measuring the absorbance with a UV-Vis spectroscopy.

3. Results and Discussion

The SEM image in Figure 1 (a, b) of humin (1000x, 2000x magnification) at room temperature indicates that its morphology composed of particles with various shapes and sizes distribution. As a result of the mechanical force, the structure was broken down leading to the agglomeration of small particles in some areas. The humin is non-conductive bulk material with few porous structures and nonuniform. In Figure 1 (c, d, e and f), the morphology and particle size distribution of humin carbonized at different temperatures varying from 300, 500, 700 and 900 °C for 2 h in N₂ atmosphere are presented. The result indicates that the particle size of humin was decreased when carbonization temperature was increased. In addition, well-dispersed and non-agglomerate humin particle was observed at higher carbonization temperature because of the evaporation of water and the decomposition of organic matter in humin structure according to FT-IR result.

Figure 2 indicates that solid yield of humin was decreased when carbonization temperature was increased. As a result of thermal degradation, it causes water to evaporate and the organic matter to decompose (as shown in FT-IR result, Figure 3).

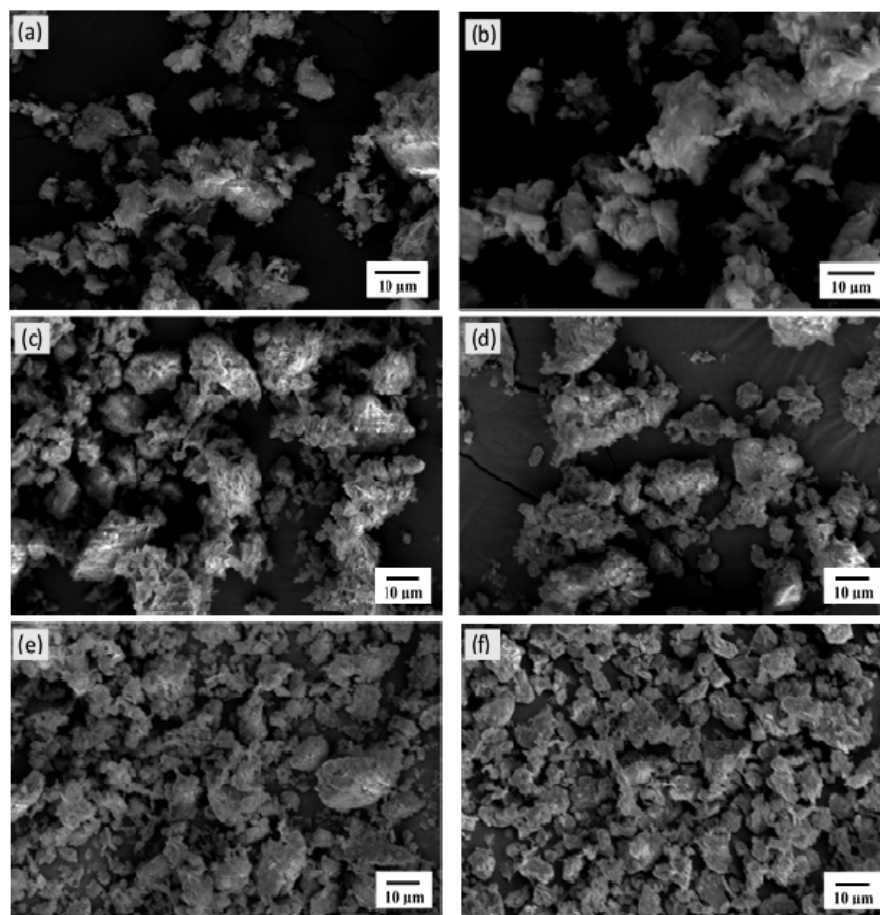


Figure 1. SEM image of (a) Humin at 1000x magnification and (b) at 2000x magnification at room temperature (c) Humin extracted from leonardite soil via carbonization process for 2 h in N₂ atmosphere at 300 °C, (d) 500 °C , (e) 700 °C and (f) 900 °C.

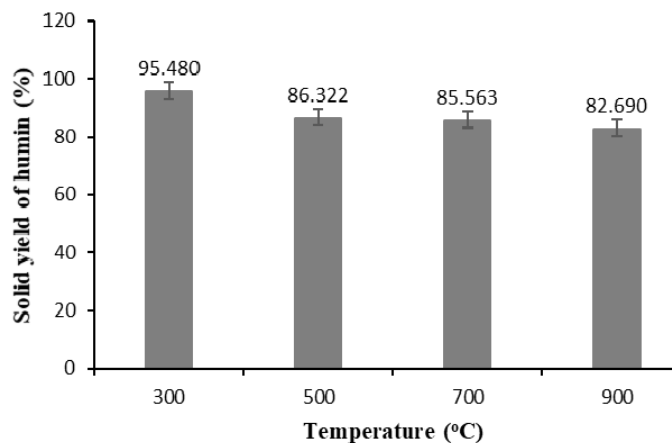


Figure 2. Solid yield of humin extracted from leonardite soil via carbonization process at different temperatures for 2 h in N_2 atmosphere.

The FT-IR spectra of humin via carbonization process at different temperatures for 2 h in N_2 atmosphere recorded in the range of $4000\text{--}400\text{ cm}^{-1}$ are presented in Figure 3. The spectra bands were similar in various conditions. The spectra bands were around $3700\text{--}3500\text{ cm}^{-1}$ (O-H stretching), 1005 cm^{-1} (C-OH stretch of aliphatic alcohol), 910 cm^{-1} (=C-H stretching) and $700\text{--}400\text{ cm}^{-1}$ (aromatic band). The humin at spectra bands around $700\text{--}400\text{ cm}^{-1}$ (aromatic band) and carbonized at $300\text{ }^{\circ}\text{C}$ was slightly increased compared to the humin at room temperature. In addition, the spectra bands around $3700\text{--}3500\text{ cm}^{-1}$ (O-H stretching) were decomposed at $500\text{ }^{\circ}\text{C}$ due to the evaporation of water. However, the spectra bands around $700\text{--}400\text{ cm}^{-1}$ (aromatic band), 1005 cm^{-1} (C-OH stretch of aliphatic alcohol) and 910 cm^{-1} (=C-H stretching) were decreased when carbonization temperature was increased due to the decomposition of organic matter and moisture.

High specific areas and S_{BET} values ($1200\text{--}1807\text{ m}^2/\text{g}$) were obtained for all AC materials. The results of BET surface area of humin prepared at different temperatures ($300, 500, 700$ and $900\text{ }^{\circ}\text{C}$) are shown in Table 1, indicated that BET surface areas are quite lower than commercial activated carbons. BET surface area values were higher in cases of increasing carbonization temperature from $300\text{ }^{\circ}\text{C}$ to $700\text{ }^{\circ}\text{C}$ but lower at carbonization temperature of $900\text{ }^{\circ}\text{C}$. The pore size of humin was almost unchanged and remained at about $3.6\text{--}3.9\text{ nm}$. In addition, pore volume was estimated from nitrogen adsorption at a relative pressure of 0.95 which was similar to that from $300\text{ }^{\circ}\text{C}$ to $700\text{ }^{\circ}\text{C}$ and decreased at $900\text{ }^{\circ}\text{C}$. This finding can be explained in terms of contraction of some pore wall that blocked and/or reduced the pore size.

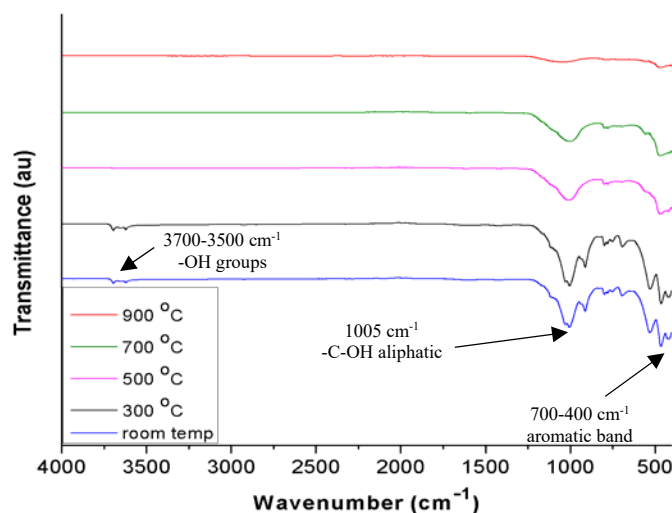


Figure 3. FT-IR spectra of humin via carbonization process with different temperatures for 2 h in N_2 atmosphere.

Table 1. Physical and adsorption properties of humin with different temperatures for 2 h in N_2 atmosphere.

Temperature (°C)	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)
300	29.88	0.10	3.97
500	31.56	0.11	3.69
700	37.45	0.12	3.69
900	16.25	0.07	3.95

Humin carbonization was performed at different temperatures (300, 500, 700 and 900 °C) for 2 h. From Figure 4, it can be observed that the adsorption capacity of the methylene blue (MB) on carbonized humin was increased with increasing of carbonization temperature but decreased at 900 °C. Approximately 90% of MB was removed from the solutions with contacting time of 5 min. The result can be explained from BET surface area, pore volume (Table 1) or perhaps there are functional group that are changed with carbonization process which can make MB adsorption capacity of humin better. It might be that the carbonization may increase the adsorption efficiency and it is assumed that increasing of carbonization temperatures can lead to the increase of surface area, pore volume of the adsorbent and the formation of activated carbon. In addition, adsorption capacity is approximately 5 times higher than 80%.

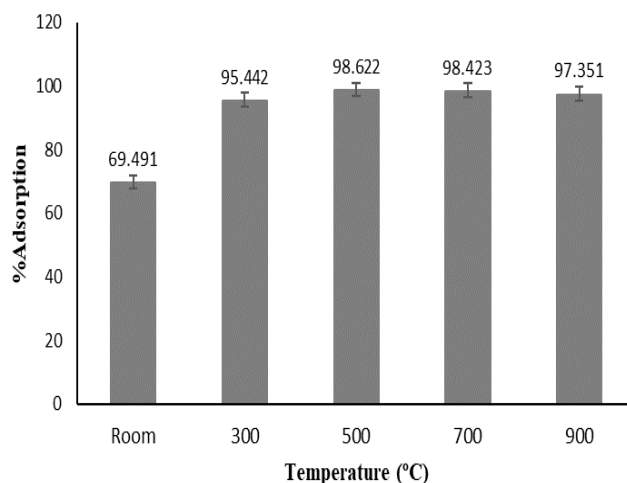


Figure 4. Methylene blue adsorption capacity of humin via carbonization process at different temperatures for 2 h in N_2 atmosphere.

4. Conclusions

The adsorbent has been successfully prepared from humin. Carbonization temperature has a significant effect on particle size, surface area values, pore volume and carbon content leading to adsorption efficiency of humin. Decreasing adsorption capacity may be related to decreasing surface area. The porosity and adsorbent properties could be predicted from this result. It also indicates that these materials used in this work could be effective adsorbents for practical use in the future.

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References

- [1] Metivier-Pignon, H., Faur-Brasquet, C. and Cloirec, P.L., 2003. Adsorption of dyes onto activated carbon cloths: approach of adsorption mechanisms and coupling of ACC with ultra filtration to treat coloured wastewaters. *Journal of Separation and Purification Technology*, 31, 3–11.
- [2] Ghodbane, H., Hamdaoui, O., 2009. Intensification of sonochemical decolorization of anthraquinonic dye acid blue 25 using carbon tetrachloride. *Journal of Ultrasonics Sonochemistry*, 16(4), 455-461.

- [3] Rafatullah, M., Sulaiman, O., Hashim, R. and Ahmad, A., 2010. Adsorption of methylene blue on low-cost adsorbents: a review. *Journal of Hazardous Materials*, 177, 70–80.
- [4] Dabrowski, A., 2001. Adsorption from theory to practice. *Journal of Advances in Colloid and Interface Science*, 93, 135–224.
- [5] Gayatri, S. L. and Ahmaruzzaman, Md., 2010. Adsorption technique for the removal of phenolic compounds from wastewater using low-cost natural adsorbents. *Journal of Science & Technology*, 5(2), 157-166.
- [6] Mohammed, M.A., Shitu, A. and Ibrahim, A., 2014. Removal of methylene blue using low cost adsorbent: a review. *Research Journal of Chemical Sciences*, 4, 91-102.
- [7] Bailey, S.E., Olin, T.J., Bricka, M. and Adrian, D.D., 1999. A review of potentially low-cost sorbents for heavy metals. *Journal of Water Research*, 33, 2469–2479.
- [8] World Energy, 2016. World energy resource 2016, [online] Available at: <https://www.worldenergy.org/data/resources>
- [9] Teparut, C. and Sthiannopkao, S., 2011. Mae Moh Lignite Mine and Environmental Management. *Journal of Geosystem Engineering*, 14(2), 85-94.
- [10] Schwarzenbach, R.P., Gschwend, P.M. and Imboden, D.M., 1993. *Environmental Organic Chemistry*. New York : John Wiley & Sons Inc.
- [11] Janoš, P., Michalek, P. and Turek, L., 2007. Sorption of ionic dyes onto untreated low-rank coal oxihumolite: a kinetic study. *Journal of Dyes and Pigments*, 74, 363-370.
- [12] Aiken, G.R., McKnight, G.R., Wershaw, R.L. and MacCarthy, P., 1985. *Humic Substances in Soil, Sediment and Water : Geochemistry, Isolation and Characterization*. New York: Wiley.
- [13] Berbara, R.L.L. and García, A.C., 2014. Humic substances and plant defense metabolism. In: P. Ahmed and M.D. Wani, eds. *Physiological Mechanisms and Adaptation Strategies in Plants under Changing Environment*. New York : Springer, pp. 297-319.
- [14] Garcia, D. and Cegarra, J., 1996. A comparison between alkaline and decomplexing reagents to extract humic acids. *Journal of Fuel Processing Technology*, 48, 51-60.