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Study on preparation of water hyacinth-based activated carbon for pulp and paper mill wastewater treatment

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Abstract

Mulberry pulp and paper mills produce high chemical- and organic matter containing waste water in Thailand. Many of the mills are not equipped with wastewater treatment unit; their untreated effluent is directly discharged into recipient water resources. The effluent constituents are well recognized as acute and chronic pollutants that are hazardous to the environment. The present study aimed to investigate the utilization of an activated carbon from a low-cost material and to examine its adsorption performance using batch and fixed-bed adsorption. Water hyacinth was used as a raw material for activated carbon production *via* a chemical activation method. The results showed that water hyacinth-based activated carbon (WHAC) provided a high surface area of 912-1,066 m^2g^{-1} and exhibited micropore structure. Based on the Freundlich fit, the maximum adsorption capacity of COD and color was 4.52 mgg^{-1} and 13.57 $Pt\text{-}Cog^{-1}$, respectively. The fixed bed adsorption provided maximum removal efficiency of 91.70 and 92.62% for COD and color, respectively. A continuous adsorption data agreed well with the Thomas kinetic model. In summary, water hyacinth can be used as a low-cost material for activated carbon production with high removal efficiency of COD and color for pulp and paper mill wastewater treatment.

Keywords

Activated carbon, Adsorption, Pulp and paper mill wastewater, Water hyacinth

Introduction

One of the most successful and widespread businesses is pulp and paper production in northern Thailand. Although most of the pulp and paper mills are operated on small scale, they generate a significant amount of wastewater: as much as 60 m^3ton^{-1} of produced paper (Thompson *et al.,* 2001). Normally, the mills are operated without wastewater treatment units; therefore, raw wastewater is directly discharged into natural recipient water bodies. In addition, pulp and paper wastewater has brown color due to presence of lignocellulosic materials, which are poorly degraded by microorganisms and can be accumulated in living tissues of aquatic species. Consequently, traces of those materials can be transported and dispersed through food chains (Sreekrishnan 2001). To treat the colored effluent from these pulp and paper mills is required a costly advanced treatment technology (Tantemsapya *et al.,* 2004). Currently, several advanced technologies such as coagulation and precipitation (Stephenson and Duff 1996), flocculation and coagulation (Wang *et al.,* 2011), electro-coagulation (Kalyani *et al.,* 2009), ozonation (Kreetachat *et al.,* 2007) and wet oxidation are applied to treat paper and pulp mill wastewater (Laari *et al.,* 1999).

Meanwhile, the biological treatment method cannot completely remove organic matter and color from wastewater because the lignocellulosic constituents are poorly biodegradable (Tantemsapya *et al.,* 2004). However, white- and brown-rot fungi have been found capable of removing lignin (Wu *et al.,* 2005). Meanwhile, adsorption technology is widely used to remove COD and color from pulp and paper wastewater because of its advantages, such as requirement of less land area (compared to the conventional biological method), low sensitivity to diurnal variation, resistance to toxic substances in wastewater, flexibility in design and operation and high treatment performance. Shawwa *et al.* (2001) reported that activated coke showed 90% removal of color, dissolved organic carbon, chemical oxygen demand, and adsorbable organic halides from the pulp bleaching process. Activated carbon is used as tertiary for treatment of

paper and board industry wastewater. Activated carbon provides an excellent adsorption efficiency for removal of cationic demand and color (Temmink and Grolle 2005). Activated carbon is an adsorbent most commonly used to treat wastewater (Alatalo *et al.,* 2013, Hameed and Rahman 2008) and is able to adsorb most of the organic materials from wastewater (Zhang and Chuang 2001). Fast kinetic and high adsorption capacity with high internal surface area and pore volume are the advantages that make activated carbon more attractive than other adsorbents (Gautam *et al.,* 2014, Mehdi Jahangiri *et al.,* 2013, Soto *et al.,* 2011).

From a sustainable point of view, reducing the cost of advanced treatment technology by using a costless and natural abundant carbonaceous material for activated carbon production has been studied more comprehensively (Mohan *et al.,* 2008, Okman *et al.,* 2014, Shawwa *et al.,* 2001). Agricultural residuals, such as coconut shell, nut shell, rice husk and bagasse, have been extensively used as a precursor for activated carbon production. Water hyacinth is one of the most abundant biomasses and has high carbon content that can be found in local natural water resources all the year round. In addition, water hyacinth bloom has been considered a serious threat to aquatic ecological systems due to blockage of sun light and death of water hyacinth increases the amount of organic substances in the basin. Thus, producing activated carbon from water hyacinth for pulp and paper mill wastewater treatment is beneficial not only in terms of waste minimization but also for reduction of environmental problem. Therefore, the present study aimed at investigating preparation of activated carbon from water hyacinth at different conditions and testing its adsorption performance mulberry pulp and paper wastewater treatment.

Materials and Methods

Preparation of activated carbon : Water hyacinth was collected from Phayao Lake, located in the northern part of Thailand. It was washed and subsequently dried before use. The material was ground and sieved to 2 mm size. Then, it was mixed with zinc chloride ($ZnCl_2$) 1:1 ratio at 80 ºC for 60 min and subsequently oven dried for 24 hr. Later, the mixture was carbonized using a furnace from room temperature upto the desired temperatures (400, 600 and 800 ºC) with heating rate of 10 ºC min^{-1} and held for 60 min under N_2 (99.99%) atmosphere with a flow rate of 100 ml min^{-1}. The sample was then cooled to room temperature under N_2 atmosphere and cleaned with hot distilled water till pH of the washing solution became neutral and chloride residues were not detected when using 1 mole of a silver chloride solution was used. Finally, the synthesized activated carbon was dried at 105 ºC for 24 hr.

The surface area, pore volume and pore size distribution of hyacinth-based activated carbon (WHAC) was measured by an automatic adsorption-desorption system (BELSORP-mini II, BEL Japan Inc.), based on N_2 adsorption data at -196 ºC. The surface area was calculated using the Brunauer-Emmett-Teller equation over the relative pressure (P/P_0) of 0.05-0.35. The surface physical morphology of WHAC was observed with scanning electron microscope and adsorbent was thinly scattered onto adhesive tape placed on a brass bar. Excess sample was removed by an air sprayer. Finally, the sample was coated with gold in JEOL (JFC-1100E Ion) sputter device and transferred into the JEOL (JSM-6400) sample chamber at accelerating voltage of 15 kV.

Batch adsorption experiment : Only the highest surface area of synthesized activated carbon was employed to investigate the adsorption performance in the present study. Wastewater sample used in the experiment was collected from the Mulberry Pulp and Paper Factory located in Chiang Mai province, Thailand. The initial COD and color concentration of wastewater used in the experiment was approximately 674 mg l^{-1} and 831 Pt-Co. Initially, the optimum contact time was carried out in a batch experiment. Ten grams of WHAC was mixed with 250 ml of raw wastewater sample under a constant agitation rate of 200 rpm at 25 ºC, and then 5 ml of wastewater sample was taken at every 10 min interval over the range of 60 min. The equilibrium time from the previous batch experiment was also used to investigate the effect of the adsorbent dosage. The experiment was conducted similar to the optimum contact time experiment, except for the amount of activated carbon, which varied from 1 to 5 g. Each experiment was repeated twice and averaged. The experimental data were eventually plotted and compared with two basic adsorption isotherms: Langmuir and Freundlich.The removal percentage of WHAC for COD and color were calculated.

Fixed-bed adsorption experiment : The continuous adsorption performance of WHAC was tested using a glass column with 1.0 cm inner diameter and 60 cm height. WHAC (20.15 g) was packed into the column, followed by layers of cotton and courage sand with 30 cm of final bed height. The mulberry pulp and paper mill wastewater was continuously introduced to the column with a down flow rate of 0.8 $mlmin^{-1}$. Treated effluent was collected and analyzed effluent to influent concentration(C_e/C_0) ratio reached 0.9.The wastewater characteristics, COD and color were analyzed according to the Standard Methods for the Examination of Water and Wastewater (AWWA *et al.,* 2012). COD concentration was analyzed by closed-reflux titrimetric method, while color concentration was estimated with UV-Visible spectrophotometer (PG Instruments, T60U Scanning Spectrophotometer) at 455 nm wavelength, which was expressed as unit of platinum-cobalt (Pt-Co).

Results and Discussion

Brunauer–Emmett–Teller (BET) surface area, pore size and pore volume of the produced WHAC is shown in Table 1. All WHAC samples showed high surface area of 912, 1,066 and 1,054 m^2g^{-1} for carbonization at 400, 600 and 800 ºC, respectively.

Table 1 : Values of BET surface area, pore diameter and volume of synthesized water hyacinth-derived activated carbon (WHAC)

Temperature (ºC)	BET surface area ($m^2 g^{-1}$)	Average pore diameter (Å)	Pore volume ($cm^3 g^{-1}$)
400	912	7.14	0.27
600	1,066	7.72	0.27
800	1,504	8.78	0.19

The production yield of the sample carbonized at 400, 600 and 800 ºC was 35, 32.5 and 16.3%, respectively. Highest BET surface area was obtained from the sample carbonized at 600 ºC. The surface area of activated carbon gradually decreased with increasing temperature higher than 600 ºC. This result agrees with the studies of activated carbon production from shell (Katesa. *et al.,* 2013), reedy grass leaves (Xu *et al.,* 2014), residue from biomass gasification (Runtti *et al.,* 2014) and bamboo (González *et al.,* 2014).

The biomass consisted of various mixtures of organic compounds and polymer, with lignin cellulose and hemicellulose as major compounds. The composition and properties of biomass are dependent on plant species, soil nutrients and growing climate of the plantation (Ioannidou and Zabaniotou 2007, Prakash and Karunanithi 2008). During carbonization, the volatile fraction of biomass is thermally degraded, resulting in the development of pores. After further increasing the temperature higher than 600 ºC, the cell wall of biomass becomes more degraded, causing larger pore size and less surface area.The SEM morphology of WHAC sample carbonized at 600 ºC was also observed, as shown in Fig. 1. It was viewed at a magnification of X1,000. It can be seen that WHAC is mainly composed of well-developed micropore structure, and the average pore diameters rely on the micro porous category.

As mentioned earlier, only WHAC with highest surface area (carbonized at 600 ºC for 1 hr) was selected to examine the adsorption performance in both batch and continuous adsorption tests. The results of contact time experiment indicated that adsorption equilibrium time reached in approximately 40 min. As illustrated in Fig. 2, COD and color were rapidly adsorbed during the first 40 min, resulting in a large reduction in their concentrations over that time period; after that, the adsorption rate slowed down and became almost stable. Therefore, the 40 min mixing time was used as adsorption equilibrium time. At equilibrium, the concentration of COD and color was 130.67 mg l^{-1} and 24.67 Pt-Co, respectively. The removal percentage of COD and color was 80.61 and 97.03%, respectively. The faster adsorption rate occurred at the beginning, possibly due to the availability of uncovered surface area of the adsorbents. However, the adsorption capacity depends not only on total surface area but also the functional groups of the internal pore surface of activated carbon (Ahmedna *et al.,* 2000). The adsorption equilibrium time obtained from earlier test was also

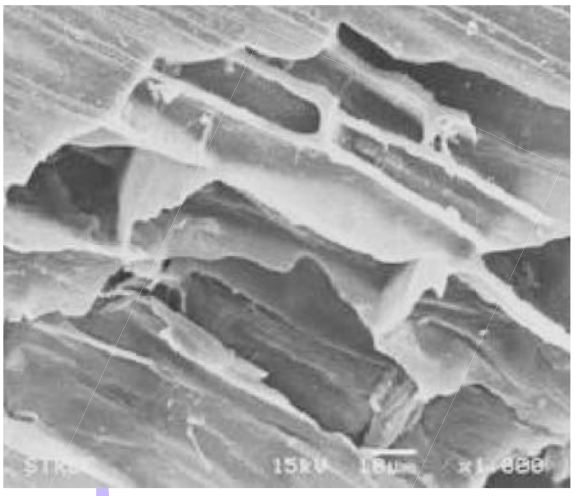

Fig. 1 : Micrograph showing micropore structures of WHAC activated by $ZnCl_2$ and carbonized at 600 ºC for 60 min

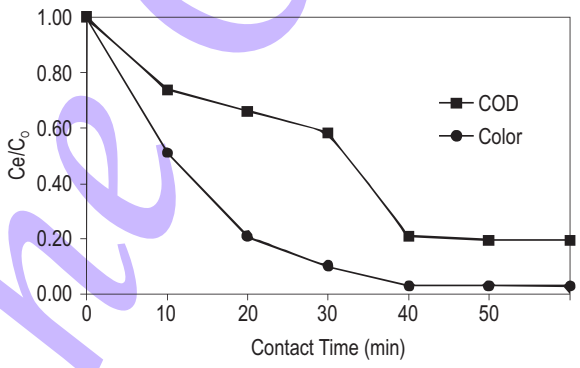

Fig. 2 : Effect of contact time on COD (■) and color (●) adsorption

applied to observe the adsorption characteristic of WHAC for both COD and color removal. The experimental data were curve-fitted to Langmuir and Freundlich adsorption isotherms.

The curve-fit to the data with Langmuir and Freundlich adsorption isotherms is shown in Fig. 3. According to high R^2 values, both Langmuir and Freundlich adsorption isotherms can be used to describe the adsorption characteristic of COD and color. However, Freundlich adsorption isotherm provided higher linear regression (R^2) values than Langmuir for COD and color adsorption.

Langmuir adsorption isotherm exhibited high R^2 of 0.962 and 0.906 for COD and color, respectively. Based on Langmuir isotherm, maximum adsorption capacity of COD and color was 66.67 mgg^{-1} and 129.87 Pt-Cog^{-1}. The R_L of COD and color was 0.67 for COD and 0.08 for color, indicating that WHAC is favorable to adsorb COD and color from the mulberry pulp and paper mill wastewater. For Freundlich curve-fit, the plot provided a higher R^2

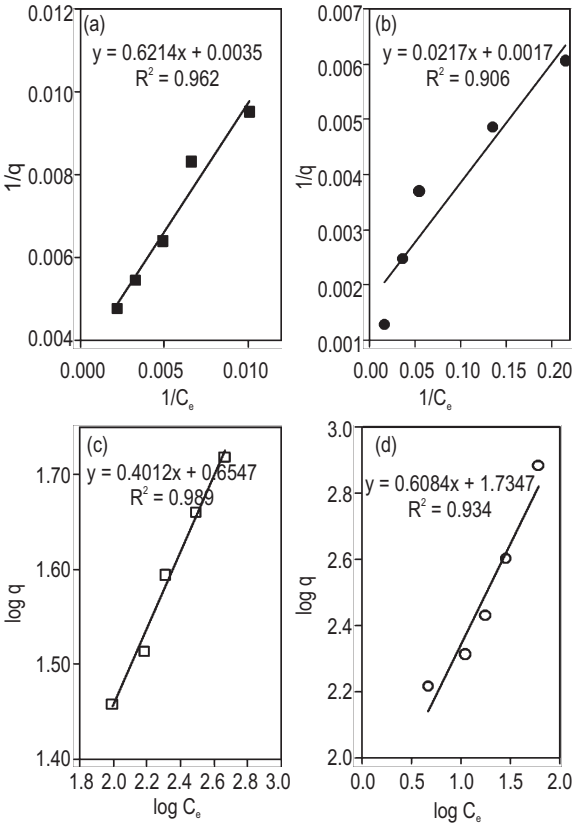

Fig. 3 : Adsorption isotherms; (a) ■ Langmuir: COD; b) ● Langmuir: color; (c) □ Freundlich: ○ COD and (d) Freundlich: color

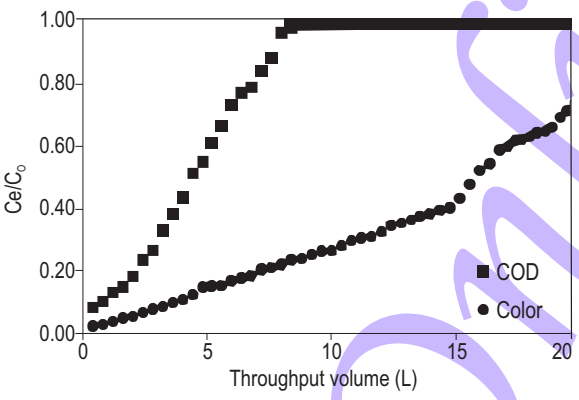

Fig. 4 : Breakthrough curves for COD (■) and color (●) removal

of 0.989 for COD and 0.934 for color. The K_F value for COD and color was 4.52 mgg^{-1} and 13.57 Pt-Cog^{-1}, whereas 1/*n* value was 0.40 and 0.61, respectively. The adsorption system was favorable, which is in agreement with the value of R_L obtained from Langmuir isotherm. The obtained adsorption capacity and 1/n values is in confirmation with the study of COD removal from paper mill and boardmill wastewater using activated carbon (Jain

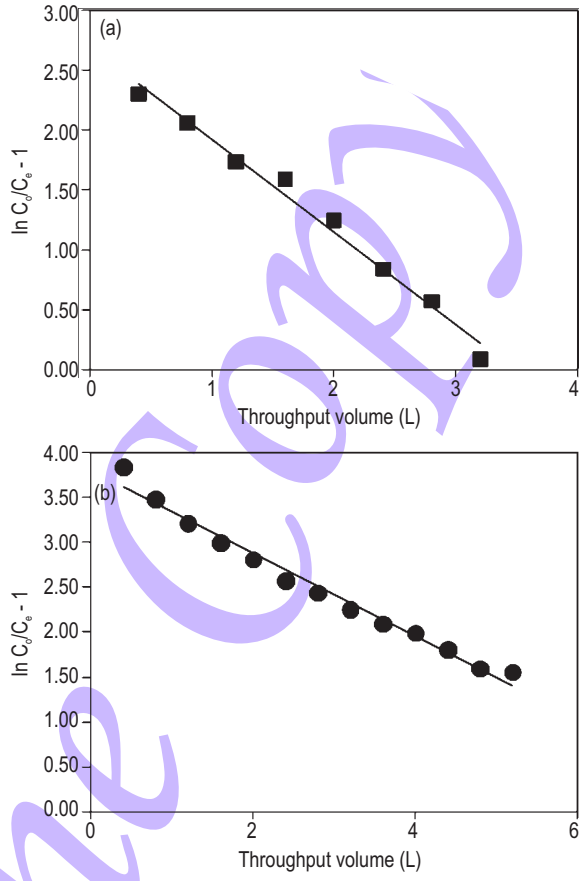

Fig. 5 : Kinetic approach results for water hyacinth-based activated carbon adsorption; a) COD (■) and b) color (●)

et al., 2009, Temmink and Grolle 2005, Zhang and Chuang 2001), which showed that activated carbon exhibited favourable adsorption.The study of COD and color removal from pulp mill wastewater using petroleum coke reported that the adsorption behavior can be described by Freundlich adsorption isotherm (Shawwa *et al.,* 2001). It can be implied that WHAC can be potentially used as an adsorbent for COD and color removal from mulberry pulp and paper mill wastewater.

The continuous adsorption performance of WHAC was observed using a vertical tubular adsorption reactor. The breakthrough curves obtained from the experiment are presented in Fig. 4. For COD, the curve was smooth and exhibited a sigmoid shape. The outlet COD concentration rapidly increased and reached the breakthrough point earlier than color. Meanwhile, the breakthrough curve for color adsorption gradually increased at a nearly constant rateover the entire test.

To determine maximum adsorption capacity and kinetic coefficient of WHAC, experimental data were fitted to equilibrium adsorption model. Thomas model is widely used for describing

Table 2 : Langmuir and Freundlich adsorption constantsof COD and color adsorption

Adsorbate	Langmuir				Freundlich		
	q_0	K_L	R_L	R^2	K_F	1/n	R^2
COD	66.67	0.007	0.67	0.962	4.52	0.40	0.989
Color	129.87	0.089	0.08	0.906	13.57	0.61	0.934

Table 3: Kinetic constants and maximum adsorption capacity of COD and color adsorption

Adsorbate	K_T	q_0	R^2
COD	0.00011	63.687	0.986
Color	0.00003	329.841	0.982

column adsorption characteristics (Salman *et al.,* 2011, Tamez Uddin 2009).

The effect of WHAC on COD and color adsorption is illustrated in Fig. 5. The initial part of the breakthrough curve was taken from C_e/C_oratio ranging from 0.08 to 0.32 for COD and from 0.02 to 0.15 for color. Thomas rate constant was obtained from the slope of plotting between $\ln(C_o/C_e\text{-}1)$ and volume while maximum adsorption capacity value was calculated from Y-interception point. The value of K_T, q_0 and $R^2$are presented in Table 3. The K_T value for COD and color was 0.00011 L $mg^{-1}h^{-1}$ and 0.00003 L Pt-$Co^{-1}h^{-1}$, respectively. Based on Thomas model, the maximum adsorption capacity (q_0) of COD and color was 63.687 mg g^{-1} and 329.841 Pt-Cog^{-1}, respectively. The removal efficiency of COD and color was higher than 91.70 and 92.62%. These results are in agreement with the adsorption test of cationic and anionic dyes (Auta and Hameed, 2013) and adsorption experiment of cationic and anionic dyes on activated carbon (Zaira Zaman Chowdhury *et al.,* 2012).These experimental data are well described by Thomas kinetic model, as indicated by the high R^2.

It was found that the produced water hyacinth-derived activated carbon (WHAC) exhibited high surface area and high adsorption capacity. The adsorption equilibrium of WHAC for chemical oxygen demand and color were fitted to Freundlich adsorption isotherm. Thomas kinetic model reasonably described the adsorption behavior of COD and color. The maximum adsorption capacity in fixed bed test was 63.687 mg g^{-1} and 329.841 Pt-Co g^{-1} for COD and color respectively.

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