Color Removal of Pulp and Paper Mill Wastewater Using Residual Eucalyptus Wood

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ABSTRACT

This study investigated the color removal efficiency of pulp and paper mill wastewater using residual eucalyptus wood as a method to minimize the solid wastes generated from pulp and paper processes. The activated carbon used in this study as the color adsorbent was produced from residual eucalyptus wood. The carbon was activated with phosphoric acid and carbonized in a furnace at 500°C for 60 min. Effects of types and amounts of activated carbon on color removal efficiency were evaluated. Three types of solid wastes, consisting of wood chip, bark, and mixed wood (wood chip:bark, 1:1), were investigated at a loading of 1, 3, 5, and 7 g/100 mL under contact times of 30, 60, 90, and 120 min. The results showed that 7 g of wood chip activated carbon/100 mL under all contact times gave color removal efficiency of 94-97%. However, the highest adsorption capacity of 216 ADMI/g occurred at 1 g of adsorbent used. Freundlich isotherms were satisfactorily fitted to experimental data for the best condition with high correlation coefficients. The color removal efficiency depended on surface area, pore volume, structure, and characteristics of the activated carbon.

1. INTRODUCTION

At present, Thailand has a high rate of paper use leading to increasing waste in the paper industry. The paper industry requires large volumes of processed water of high purity and generates large amounts of wastewater from digestion, lignin extraction, and bleaching processes, which are highly colored. Approximately 20 m^3 of fresh water are required to process 1 ton of eucalyptus wood for producing pulp and paper. Moreover, one ton of eucalyptus wood can produce about 0.534 ton of paper and generate solid waste such as bask, wood chip and dust of about 0.074 ton, 0.43 ton, and 0.018 ton, respectively. The pulp and paper production generates a significantly large amount of pollutants characterized by high concentrations of suspended solids (SS), COD, toxicity, and biochemical oxygen demand (BOD) (Pokhrel and Viraraghavan, 2004). Pulp and paper mill wastewater is a dark brown colored liquid known as 'black liquor' (Kumar et al., 2021). The pulp and paper mill effluent color is largely due to lignin derivatives and polymerized tannins removed during pulping and bleaching processes, which are resistant to degradation due to the presence of carbon-to-carbon biphenyl linkages (El-Bestawy et al., 2008). The color of paper mill wastewater is one of the major environmental problems because of the difficulty of treating by conventional methods. Production of various types of paper has been defined as a business that is harmful to health because it produces color and toxic substances from the production process (Armstrong et al., 1998). Color not only causes bad aesthetical effects but also reduces the self-purification capacity of rivers by inhibiting photosynthetic production of oxygen and direct destruction of aquatic communities (Chooaksorn, 2012). Due to these risks, the Department of Industrial Works of Thailand provides water quality standard values for controlling the color of effluent from the industry. The effluent standard of color is 600 ADMI

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for pulp production and 350 ADMI for paper production (MNRE, 2018). Meeting the regulatory discharge standards for pulp and paper mill wastewater has become more difficult because of its recalcitrant and colored dissolved organic matter (DOM) (Shi et al., 2016). The effluent is normally treated by biological process such as aerated lagoon and activated sludge processes. The biological processes are very effective for removing the nonsettleable colloidal solids and to stabilize the organic matter, but are unsuitable for removing the color (Yadav et al., 2012).

Many processes are available to remove color from pulp and paper wastewater. Activated carbon has a well known high adsorption capacity and can absorb both color and odor. The activated carbon prepared from prickly pear seed cake by phosphoric acid activation is effective for removing cationic and anionic dyes such as methylene blue and methyl orange from aqueous solution (El maguana et al., 2020). Moreover, a maximum reduction of dying effluent in color and COD of 91.84% and 75.21% was observed using bamboo-based activated carbon (Ahmad and Hameed, 2009). Additionally, the performance of oat hull activated carbon was studied and the results showed that COD and color removal from landfill leachate were up to 90% (Ferraz and Yuan, 2020). Therefore, the color removal efficiency of pulp and paper effluent using residual eucalyptus wood as activated carbon absorbent was investigated in this study.

2. METHODOLOGY

The pulp and paper wastewater was collected from the effluent of wastewater treatment plants at the mixed tank after being treated with the secondary clarifier process by grab sampling. The parameters of pH, color, COD, TSS, TDS, and TKN were investigated. The residual eucalyptus wood generated from pulp and paper processes was used as activated carbon for the color adsorbent. The characteristics of pulp and paper wastewater used in the study are described in Table 1. The BOD and COD ratio was low at about 0.15 because the effluent was already treated with biological processes. Therefore, adsorption proved an attractive alternative process to treat the color of the effluent after biological treatment. The carbon was activated with 85% phosphoric acid (wt:vol, 1:1) and soaked for 60 min. Activated carbon was then washed with deionized water several times until pH returned to neutral and dried at 105°C for 4 h (Patnukao and Pavasant, 2008; Kongsuwan et al., 2009), then carbonized in a furnace at 500°C for 60 min. (Kongsuwan et al., 2009). The activated carbon was crushed and filtered using a sieve to a particle size of 0.71 mm. (Chuyingsakuntip and Tangsathitkulchi, 2013). The physical characteristics of the residual eucalyptus wood and activated carbon are shown in Figures 1, 2, and 3.

Table 1. Characteristics of pulp and paper effluent used in this study

Parameter	Unit	Value
pH	-	7.8-8.2
BOD	(mg/L)	13-17
COD	(mg/L)	96-102
TSS	(mg/L)	10-13
TDS	(mg/L)	1,362-1,370
Color	ADMI (pH-Original)	379-384
	ADMI (pH-Adjust)	338-345
Conductivity	(µs/cm)	2,560-2,620
TKN	(mg/L)	3.24-3.86

Experiments were carried out to investigate the color removal efficiency in batch experiments. The experimental design comprised a 3×4×4 factorial design with 4 replications. The studied factors included the type of eucalyptus wood (wood chip, bark, and mixed wood), amount of activated carbon (1, 3, 5, and 7 g) and contact times (30, 60, 90, and 120 min) to determine the optimum condition of color removal efficiency. A 250 mL Erlenmeyer flask was used as an adsorption reactor with 100 mL working volume. The amount of each type of activated carbon was added according to the experimental design, and the sample was shaken at 120 rpm for 30, 60, 90, and 120 min. The color concentration was analyzed using a spectrophotometer following the ADMI method (Kumar et al., 2021; Azha and Ismail, 2021). The isotherms of Langmuir and Freundlich adsorption were also studied to evaluate the adsorption pattern.

3. RESULTS AND DISCUSSION

3.1 Effect of type and amount of activated carbon

Regarding the three types of activated carbon investigated, the maximum color removal efficiency was obtained from wood chips due to their physical properties such as porosity and surface area. Bark differs from wood chips in terms of its anatomical structure, properties and chemical composition as

Figure 1. Physical structure: eucalyptus wood chips (a); eucalyptus bark (b); eucalyptus wood chips after carbonization (c); and eucalyptus bark after carbonization (d)

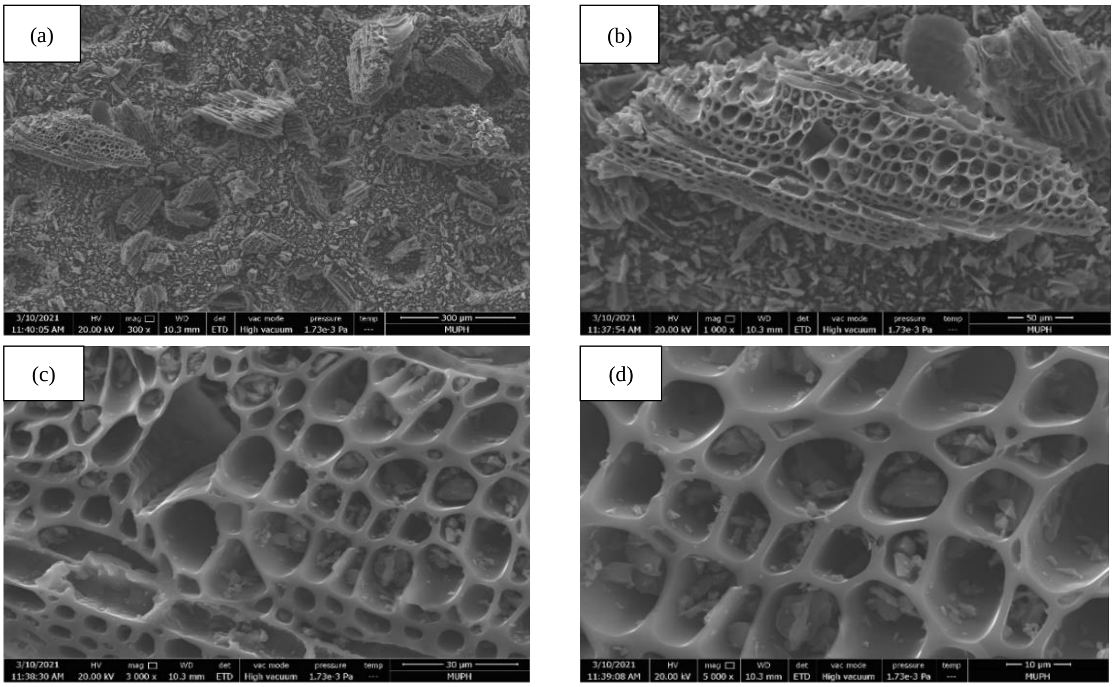

Figure 2. Physical characterization of wood chip activated carbon with SEM photographs of wood chip activated carbon: wood chips 500X (a); wood chips 1000X (b); wood chips 3000X (c); and wood chips 5000X (d)

shown in Figure 1. The physical structure of wood and bark AC are illustrated in Figures 2 and 3, respectively. The eucalyptus wood chip AC is mainly composed of tube structures, which should promote the velocity of liquid diffusion for the adsorption process. However, bark AC consists of xylem and phloem and is a narrow layer of tissue. The pore size of wood chip AC was larger than bark AC and exhibited nonuniform pore size from 3.597 μm to 23.89 μm, while bark AC had similar pore size from 8.467 μm to 14.75 μm as shown in Figure 4. The fixed carbon in bark was higher than in wood chips, namely,

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13.10% in bark and 16.42% in wood chips. The volatile matter content of wood chips and bark was 83.23% and 75.05%, respectively. The ash in bark was approximately four times higher than that of others, namely, 0.5% in wood and 1.35% in bark. (Kiatgrajai et al., 1994; Kongsuwan et al., 2009; Borgesa et al., 2019). Moreover, the results showed that when using wood chips of 7 g/100 mL, the highest color removal efficiency of 97% was obtained, as shown in Figure 5(a). Moreover, TDS decreased from 1,370 mg/L to 713 mg/L and conductivity also decreased from 2,620 µs/cm to 1,220 µs/cm as illustrated in Table 2. However, the highest adsorption capacity of 216 ADMI/g occurred at 1 g of adsorbent used. When using bark and mixed wood of 7 g/100 mL, the highest color removal efficiencies of 84 and 89% were obtained, as shown in Figures 5(b) and 5(c), respectively.

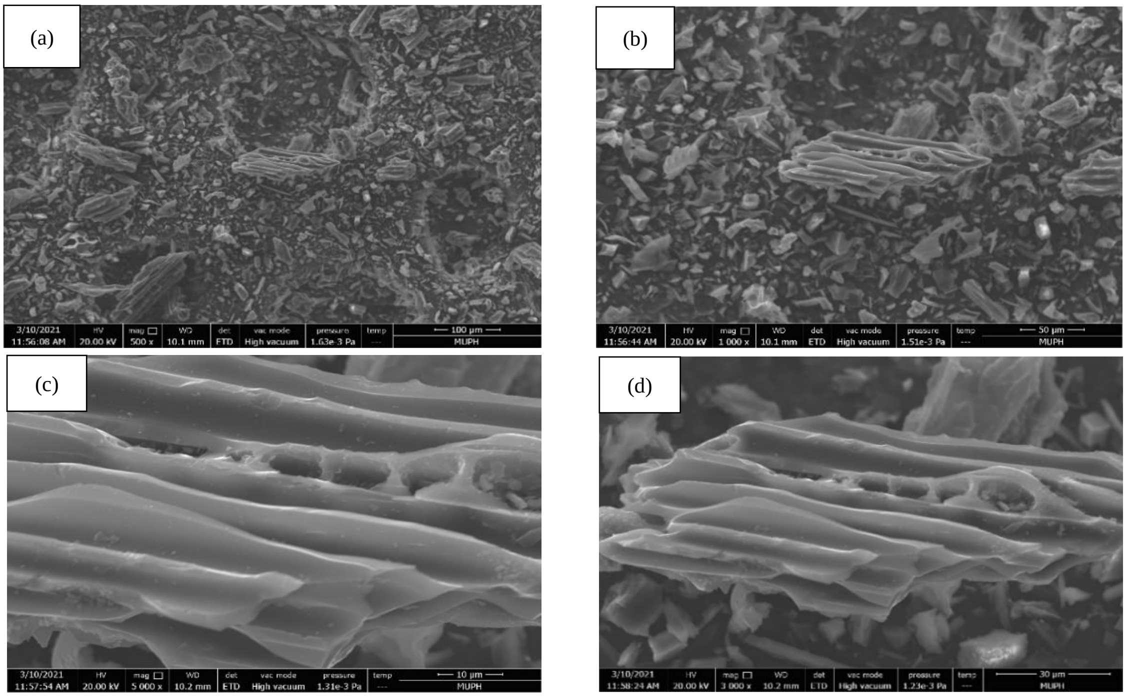

Figure 3. Physical characterization of bark activated carbon with SEM photographs of bark activated carbon: bark 500X (a); bark 1000X (b); bark 3000X (c) and bark 5000X (d)

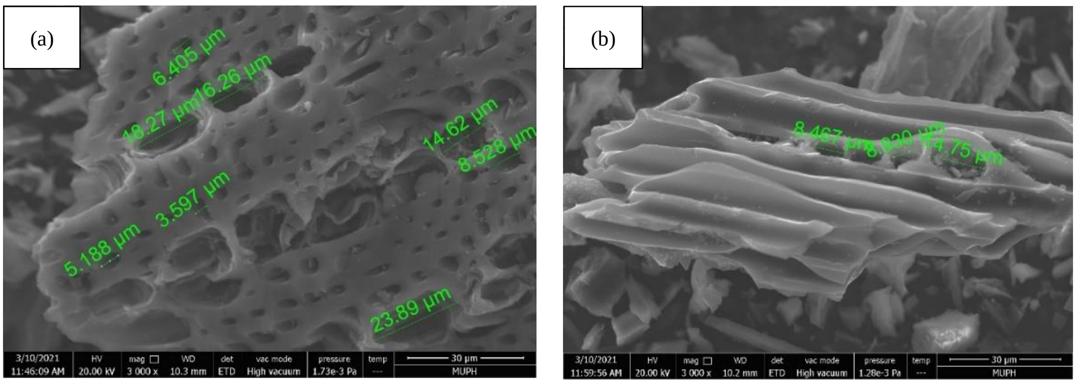

Figure 4. Surface characteristics and pore sizes of wood chip AC (a), and bark AC (b)

3.2 Effect of contact time

The effect of contact time was determined on color removal in batch experiments. Regarding the three types of activated carbon from loading at 1, 3, 5, and 7 g/100 mL for a contact time of 30, 60, 90, and 120 min, the efficiency of adsorption increased with increasing contact time. However, color adsorption rapidly increased in the first period. After that, the color adsorption gradually decreased.

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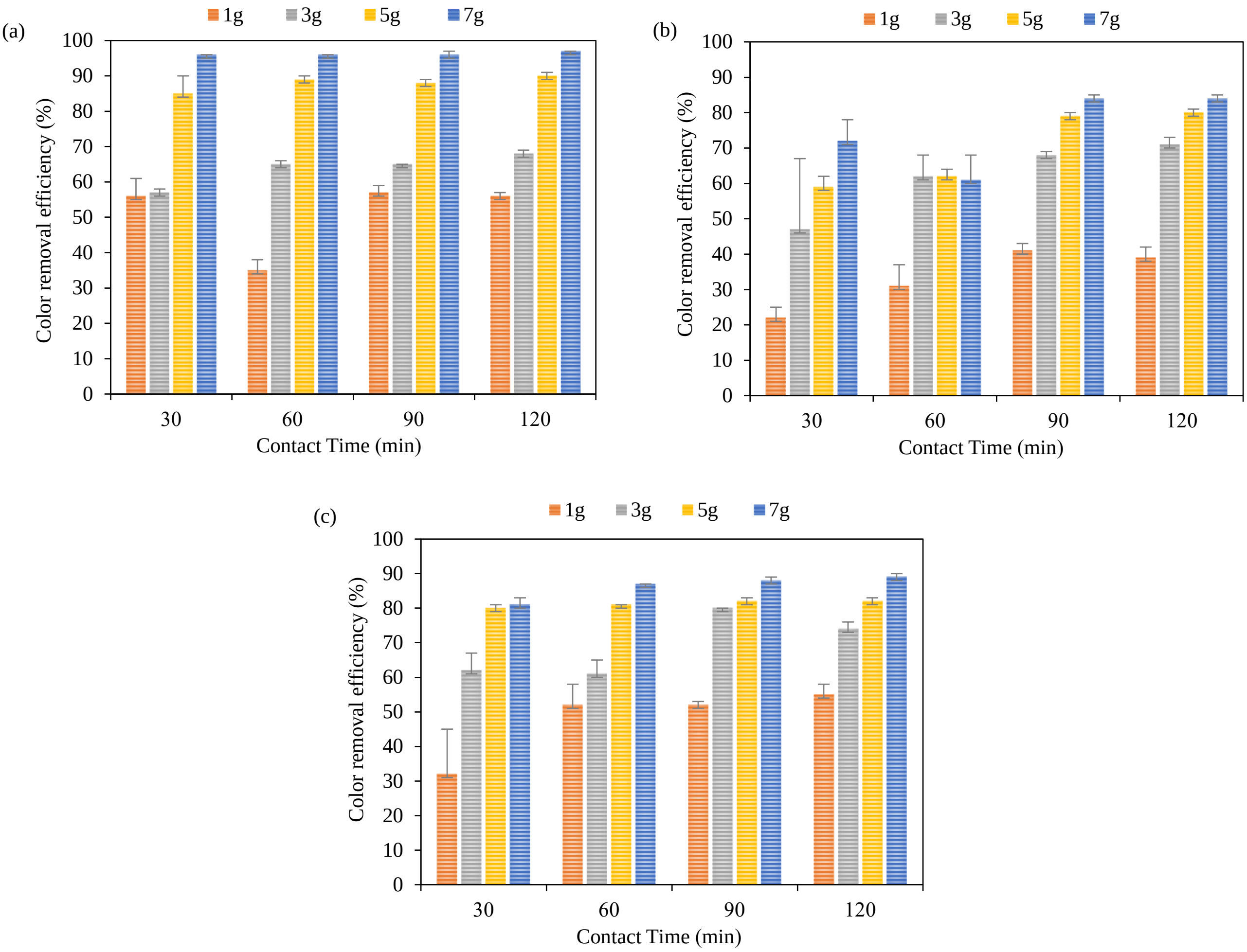

Figure 5. Color removal efficiency using eucalyptus wood chips (a); using eucalyptus bark (b); and using mixed wood (c) at activated carbon loading 1, 3, 5, and 7 grams for contact times of 30, 60, 90, and 120 min

Table 2. Characteristics of pulp and paper effluents after adsorption using wood chips AC for 120 min

Parameter	Unit	Amount of wood chips AC (g)			
		1 g	3 g	5 g	7 g
COD	(mg/L)	84-91	73-80	45-56	28-37
TSS	(mg/L)	7.6-8.2	5.8-6.6	5.6-6.4	4.6-5.4
TDS	(mg/L)	1,320-1,360	1,190-1,210	984-998	698-728
Color	ADMI (pH-Original)	158-171	117-128	35-43	10-11
	ADMI (pH-Adjust)	138-151	71-78	39-58	15-30
Conductivity	(μs/cm)	2,140-2,160	1,910-1,940	1,620-1,680	1,220-1,280

In addition, the highest color removal efficiency of 97% was obtained from wood chips loading at 7 g/100 mL for contact times of 120 min. This result was similar to that of El maguana et al. (2020) reporting that the adsorbed amount increased with contact time at the initial stage of adsorption and reached equilibrium in 120 min. Obviously, a specific period is desired for using a high amount of wood chip activated carbon. When the contact time increased to 120 min, the color removal efficiency significantly differed from that of 30 min. The highest color removal efficiency of 84% was observed when using 7 g/100 mL of bark-activated carbon as an adsorbent for 90 min. However, the highest color removal efficiency of about 89% was achieved using 7 g of mixed wood for 120 min as shown in Figures 5(a), 5(b), and 5(c). The effluent after adsorption had characteristics within the effluent standard of color according to the regulation of the Ministry of Industry. Freundlich isotherms were supposed to be satisfactorily fitted to these experimental data for the best condition of wood chip AC because of high correlation coefficients as shown in Table 3 and Figure 6. When comparing the R^2 values, the Freundlich equation represented a better fit of equilibrium experimental data than that of the Langmuir. Therefore, the color adsorption process of the wood chip activated carbon could be described more appropriately using the Freundlich isotherm, indicating the multilayer adsorption on the heterogeneous surface (Rajahmundry et al., 2021).

When contact time increased, the ability of adsorption also increased until equilibrium was achieved. In the first period, the fast initial adsorption occurred because the concentration gradient in the solution and the surface space of the adsorbent remained plentiful. After that, the ability of adsorption reduced until equilibrium was attained because the spaces had been fully absorbed with color and other substances (Srimoon, 2016). The fixed carbon contents and pore size of activated carbon were factors influencing the color removal efficiency (Okeola et al., 2012). Moreover, TDS concentration and conductivity decreased with increasing amount of adsorbent and contact time. To predict the mechanisms of the color adsorption process on different types of eucalyptus wood activated carbon, the Freundlich isotherm model described the adsorption process with a high coefficient of determination R^2 better than the Langmuir isotherm model.

Table 3. Langmuir and Freundlich's adsorption isotherm parameters

Activated carbon	pH	Langmuir adsorption isotherm			Freundlich's adsorption isotherm		
		Q_m (mg/g)	K_L=b (L/mg)	R^2	1/n	Kf (L/g)	R^2
Wood chips	pH original	11.86	0.070	0.4956	2.106	1.2990	0.6131
	pH adjust	14.22	0.024	0.7021	1.436	0.4976	0.8588
Bark	pH original	141.29	0.00057	0.9761	1.221	0.1801	0.9659
	pH adjust	-117.32	-0.00062	0.9721	1.009	0.0803	0.9751

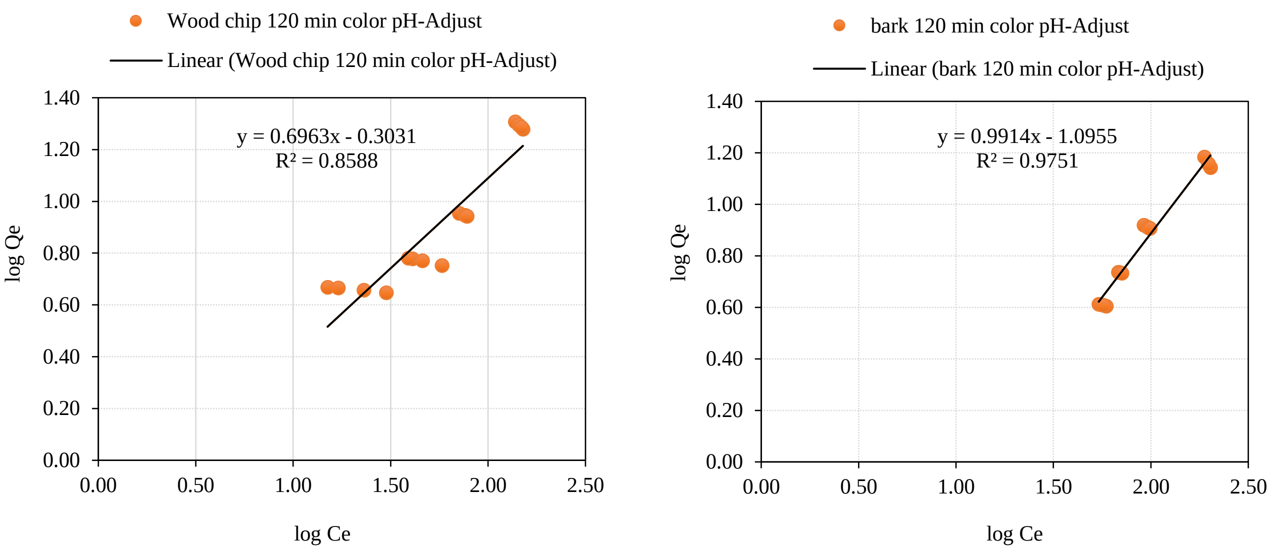

Figure 6. Freundlich isotherms of eucalyptus wood chip AC (a) and bark AC (b) for 120 min contact time

4. CONCLUSION

The use of activated carbon prepared from residual eucalyptus wood using phosphoric acid and carbonized in a furnace at 500°C for the removal of color of pulp and paper mill wastewater has been studied. The adsorption efficiency of wood chip AC was higher than bark and mixed wood due to its physical characteristics. The color removal efficiencies were slightly increased by increasing the amount of activated carbon from 1 to 7 g per 100 mL of wastewater. The adsorption process occurred rapidly on the surface of the adsorbent when using a large amount of the adsorbent because more surface area of the adsorbent was obtained. Moreover, the ability of absorbent increased with increasing contact time from 30 to 120 min. When contact time increased, the ability of adsorption also increased until equilibrium was achieved. Therefore, a shorter contact time was sufficient when using a higher amount of adsorbent. Regarding the experimental data, the eucalyptus wood chip activated carbon gave the highest color removal efficiency due to higher fixed carbon content and nonuniform pore sizes because of tube structure variation. The activated carbon can be regenerated with appropriate methods. If the activated carbon cannot be economically regenerated, it must be treated and disposed in an approved landfill. Therefore, the economical regeneration of activated carbon and other alternative biomass substances should be studied.

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REFERENCES

Ahmad AA, Hameed BH. Reduction of COD and color of dyeing effluent from a cotton textile mill by adsorption onto bamboo-based activated carbon. Journal of Hazardous Materials 2009;172:1538-43.

Ministry of Natural Resources and Environment (MNRE). Announcement of the Ministry of Natural Resources and Environment: Establishing Standards for Controlling the Drainage of Pulp and Paper Factories. Thailand: Ministry of Natural Resources and Environment; 2018. p. 13-6.

Armstrong AD, Bentley KM, Galeano SF, Olszewski RJ, Smith GA, Smith JR. The Pulp and Paper Industry. In: The Ecology of Industry. Washington, DC: National Academy Press; 1998. p. 101-41.

Azha SF, Ismail S. Feasible and economical treatment of real hand-drawn batik/textile effluent using zwitterionic adsorbent coating: Removal performance and industrial application approach. Journal of Water Process Engineering 2021; 41:Article No. 102093.

Borgesa ACP, Onwudilib JA, Andradec HMC, Alves CT, Ingram A, Vieira de Melo SAB, et al. Catalytic supercritical water gasification of eucalyptus wood chips in a batch reactor. Journal of Fuel 2019;255:Article No. 115804.

Chooaksorn W. Color removal technology in industrial wastewater. Burapha Science Journal 2012;17:181-91.

Chuyingsakuntip S, Tangsathitkulchi C. Adsorption of natural aluminium dye complex from silk-dyeing effluent using eucalyptus wood activated carbon. American Journal of Analytical Chemistry 2013;4:379-86.

El maguana Y, Elhadiri N, Benchanaa M, Chikri R. Activated carbon for dyes removal: Modeling and understanding the adsorption process. Journal of Chemistry 2020;2020:Article No. 2096834.

El-Bestawy E, El-Sokkary I, Hussein H, Keela AFA. Pollution control in pulp and paper industrial effluents using integrated chemical-biological treatment sequences. Journal of Industrial Microbiology and Biotechnology 2008;35:1517-29.

Ferraz FM, Yuan Q. Performance of oat hulls activated carbon for COD and color removal from landfill leachate. Journal of Water Process Engineering 2020;33:Article No. 101040.

Kiatgrajai P, Laohathai B, Sangkul S. Charcoal Briquette from river red gum. Thai Journal Forestry 1994;13:38-49.

Kongsuwan A, Patnukao P, Pavasant P. Binary component sorption of Cu (II) and Pb (II) with activated carbon from *Eucalyptus camaldulensis Dehn* bark. Journal of Industrial and Engineering Chemistry 2009;15:465-70.

Kumar A, Srivastava NK, Gera P. Removal of color from pulp and paper mill wastewater-methods and techniques: A review. Journal of Environmental Management 2021;298:Article No. 113527.

Okeola O, Odebunmi E, Ameen O. Comparison of sorption capacity and surface area of activated carbon prepared from prepared from *Jatropha curcas* fruit pericarp and seed coat. Chemical Society of Ethiopia 2012;26(2):171-80.

Patnukao P, Pavasant P. Activated carbon from *Eucalyptus camaldulensis Dehn* bark using phosphoric acid activation. Journal of Bioresource Technology 2008;99:8540-43.

Pokhrel D, Viraraghavan T. Treatment of pulp and paper mill wastewater: A review. Science of the Total Environment 2004;333:37-58.

Rajahmundry GK, Garlapati C, Ponnusamy, Kumar S, Alwi RS, Vo DN. Statistical analysis of adsorption isotherm models and its appropriate selection. Chemosphere 2021;276:Article No. 130176.

Shi X, Xu C, Hu H, Tang F, Sun L. Characterization of dissolved organic matter in the secondary effluent of pulp and paper mill wastewater before and after coagulation treatment. Water Science and Technology 2016;74(6):1346-53.

Srimoon R. Dyes treatment in wastewater using adsorption processes. Khon Kaen University Science Journal 2016; 44(3):419-34.

Yadav R, Upadhyay K, Maru S. Colour removal from paper mill effluent using activated carbon. Journal of Industrial Pollution Control 2012;28(1):45-50.