Chemical Modification of Unwanted Flora (*Hanguana Malayana*) as Activated Carbon to Remove Methylene Blue and Congo Red

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Abstract

Wastewater is well-known hot issue of environmental pollutions that require a solution hurriedly. Organic dye is a severe toxic contaminant in water. In this work, *Hanguana Malayana* used as carbon source was chemically activated as activated carbon. The biochar was carried out by the pyrolysis through the heat treatment at 200 °C under low O_2 atmosphere. The resulting powder was activated by using $ZnCl_2$ under hydrothermal conditions at 120 °C for 24 h, and further heat-treated at 300 °C for 1 h. The as-prepared product was verified by XRD, FT-IR, SEM, and BET. There were large surface area and many functional groups on the surface of the as-prepared product. All amounts of methylene blue (20 ppm, 50 mL) were removed by 50 mg of activated carbon, meanwhile very few amounts of Congo red (20 ppm, 50 mL) were eliminated. This work showed the benefits on increasing an add-value of *Hanguana Malayana* by the chemical process together with eliminating unwanted flora and toxic dye chemicals in water.

Keywords: methylene blue, Congo red, activated carbon, adsorption, *Hanguana malayana*

Introduction

Up to now, the contamination of toxic chemicals in natural water has still occurred continually that can observe apparently from the colored and fetid water, and the death of aquatic animals and plants (Lellis, Fá varo-Polonio, Pamphile, & Polonio, 2019). Synthetic dyes are introduced in dyeing processes of many activities such as texture, car, furniture, etc., and the rest is leaved into natural water resource that counted as a main cause of wastewater. Because it shows severe impact widely on ecosystem, health and so on, especially dyes including of anionic and cationic structures (Tkaczyk, Mitrowska, & Posyniak, 2020). Among of wastewater treatments such as photocatalysis, bioremediation, electrical and advanced oxidation processes (Rajasulochana & Preethy, 2016), an adsorption applied by smart material is better in case of practical and low-cost procedures (Yagub, Sen, Afroze, & Ang, 2014). Due to dyes categorized as seriously dangerous chemical in spite of very low amount on health and environmental issues, the dyes contaminated in water resource must be removed urgently. Considering the ionic structure, anionic and cationic dyes are mostly applied, resulting contamination in water resource. A variety of adsorbents have been evaluated and optimized the removal performance of dyes in water such as layered double oxide (Intachai, Pimchan, & Sumanatrakul, 2019), layered double hydroxide and the modified adsorbent (Intachai, Boaulan, & kongsune, 2020), clay mineral (Minisy, Salahuddin, & Ayad, 2021), activated carbon (Salem, Teimouri, & Salem, 2020), etc. Various types of the adsorbents provide the different benefits based on high removal efficiency of dyes such as selectivity, sensitivity and stability. The preparation of new adsorbent material and the increase of adding value of unwanted raw material are an interesting challenge.

Activated carbon (AC) is intensively used as pristine adsorbent, modified material and so on because of simple preparation and modification, and large surface area (Moosavi et al., 2020). Besides, bio-carbon sources are availably abundant such as unwanted flora, coconut and palm oil shell, coffee ground, and so on that can be modified as the activated carbon for optimizing the removal efficiency of toxic dyes contaminated in water (Gautam et al., 2015). The usage of activated carbon based on various carbon sources has been investigated so far because of the resulting properties, for example; large surface area, and high stabilities on light and chemical exposure for long-time period, as well as many times of reusability (Gautam et al., 2015; Sanmuga Priya & Senthamil Selvan, 2017; Tian et al., 2019). As we known, *Hanguana malayana* has not modified as activated carbon.

Hanguana malayana is an unwanted flora, which mostly formed in water resources of south area of Thailand. The invasion of *Hanguana malayana* in natural water resources causes the evident issue of deteriorated water together with interfering the growth or blooming of wanted plant, concealing the beautiful scenery, and obstructing boat traffic and sunlight-irradiation and O_2-diffusion into underwater ecosystems. In this work, the elimination of *Hanguana malayana* synergizing with increasing an added value was carried out by chemical activation as activated carbon, and used as the adsorbent for removing methylene blue and Congo red dyes in water. The efficiency of dye removal by the as-prepared activated carbon (using *Hanguana malayana* as carbon based-precursor) was comparatively evaluated to commercial activated carbon. It is firstly reported on the success in the modification of *Hanguana malayana* as activated carbon and its application as the adsorbent on removing cationic methylene blue and anionic Congo red.

Methods

Materials

Hanguana malayana was collected at Phatthalung in Thailand. Zinc chloride ($ZnCl_2$) was purchased from Asia Pacific Specialty Chemicals LTD. Commercial activated carbon (abbreviated as CAC) was obtained by Sigma-Aldrich. Methylene blue ($C_{16}H_{18}ClN_3S$) and Congo red ($C_{32}H_{22}N_6Na_2O_6S_2$) from Acros were used as the representative cationic and anionic dye, respectively, where the chemical structures are showed in Figure 1. All chemicals are reagent grade and were used directly without any further purification.

Preparation of activated carbon

Hanguana malayana was used as the carbon based-precursor for preparing activated carbon by the chemical activation. Firstly, the stalk of *Hanguana malayana* was chosen and cleaned, cut into small pieces ($\sim 1\ cm^2$), dried in air oven at 110 °C, respectively. Secondly, the selected pieces were heat-treated about 200 °C in low O_2 atmosphere until whole part of each piece was completely changed into black, ground to obtain powder, sized via 60 mesh of sieve, respectively. Thirdly, the resulting biochar was activated by reacting with an aqueous solution of $ZnCl_2$ through hydrothermal treatment at 120 °C for 24 h. The adding amount of the activating agent ($ZnCl_2$) was twice of the weight of the biochar used. The solid sample was separated by centrifugation, washed several times with deionized water till a negative $AgNO_3$ test was obtained, then heated at 80 °C for 24 h. Finally, the obtained product was further heated at 300 °C for 1 h. The as-prepared activated carbon was abbreviated as AC.

Elimination of dyes from aqueous solution

The capacity of the as-prepared activated carbon (AC) and commercial activated carbon (CAC) was evaluated by capturing cationic methylene blue and anionic Congo red in water on the surface at room temperature under the dark region. The batch adsorption was tested with 50 mL of each 20 ppm dye solution (methylene blue and Congo red), using 25 and 50 mg of the adsorbent under magnetic stirring for 60 min. At the different reaction time (0, 10, 20, 30, 40, 50 and 60 min), the concentration of the remaining dye amount was analyzed using the absorbance of the dye in the aqueous solution (carried out using UV-VIS spectrophotometer) compared to the calibration curve. The dye adsorption capacity of adsorbent at any contact time was calculate, in addition, the adsorption kinetics and isotherms were also explored as the equations in Table 1.

Characterization

Powder X-ray diffraction (XRD) pattern was conducted in the 2θ range of 2-70° on a Bruker D8 ADVANCE diffractometer using monochromatic CuKα radiation (λ = 1.5418 Å). Fourier transformed infrared (FT-IR) spectrum was carried out in the wavenumber range of 4000-400 cm^{-1} on a Perkin Elmer Spectrum One FT-IR spectrophotometer by KBr disk method. Scanning electron microscopic (SEM) image was obtained on a FEI Helios Nanolab G3 CX DualBeam FIB-SEM operated at 10 kV. Nitrogen adsorption/desorption isotherm was measured on a Micromeritics ASAP 2010 equipment after the product was degassed at 150 °C under vacuum for 3 h, and the specific surface area was calculated using the Brunauer-Emmett-Teller (BET) equation. UV-visible absorption spectra of the remaining dye solution were recorded in the wavelength range of 200-800 nm using a Shimadzu UV-1700 Pharmaspec UV-VIS spectrophotometer.

Table 1 Equations used to explore the efficiency of dye adsorption and corresponding parameter

Parameter	Equation
adsorption efficiency (%)	$(C_0 - C_t)/C_0 \times 100$
adsorption capacity at equilibrium, q_e (mg/g)	$(C_0 - C_e)/m \times V$
adsorption capacity at any time, q_t (mg/g)	$(C_0 - C_t)/m \times V$
pseudo-first order	$\log(q_e - C_t) = \log q_e - k_1 t/2.303$
Pseudo-second order	$t/q_t = 1/k_2(q_e)^2 + t/q_e$
Langmuir	$C_e/q_e = C_e/q_m + 1/K_L q_m$
Freundlich	$\log q_e = \log k_F + (1/n)\log C_e$

Where "C_0, C_t and C_e" are the concentration (mg/L) of dye at initial time (C_0), different "t" time (min) (C_t) and equilibrium (C_e), q_e (mg/g) is adsorption capacity at equilibrium, m (g) is the mass of adsorbent, V (L) is the volume of dye solution, k_1 (min^{-1}) and k_2 ($g \cdot mg^{-1} \cdot min^{-1}$) are the pseudo-first order and pseudo-second order rate constants, respectively, q_m (mg/g) is the theoretical maximum adsorption capacity, K_L (L/mg) is Langmuir adsorption equilibrium constant, 1/n is the heterogeneity factor, K_F ($(mg/g)(L/mg)^{1/n}$) is Freundlich constant.

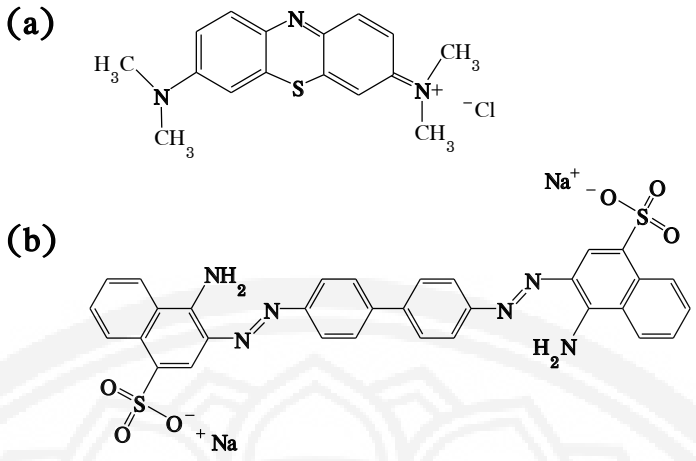

Figure 1 Chemical structures of methylene blue (a) and Congo red (b)

Results

The product (AC) prepared by the chemical activation with $ZnCl_2$ using *Hanguana malayana* as carbon based-precursor was characterized by X-ray diffraction (XRD) as shown in Figure 2. The XRD pattern of AC showed the diffraction peak at 2θ = 24.8° and 44.2°, corresponding to the reflection planes of (*002*) and (*100*), respectively, due to the amorphous carbon-like structure (JCPDS No 41-1487) (Gautam et al., 2015; Moosavi et al., 2020). The basal distance (d) was determined by the Bragg's equation ($2d\sin\theta = n\lambda$) where n (the first diffraction order) is assumed = 1 and λ (wavelength of CuKα) = 1.5414 Å. The d_{002} was 0.36 Å and d_{100} was 0.20 Å that accorded to the structural crystalline planes of activated carbon (Tian et al., 2019). It can be seen in the XRD pattern of AC, any diffraction peak was not observed, indicating the formation of pure activated carbon.

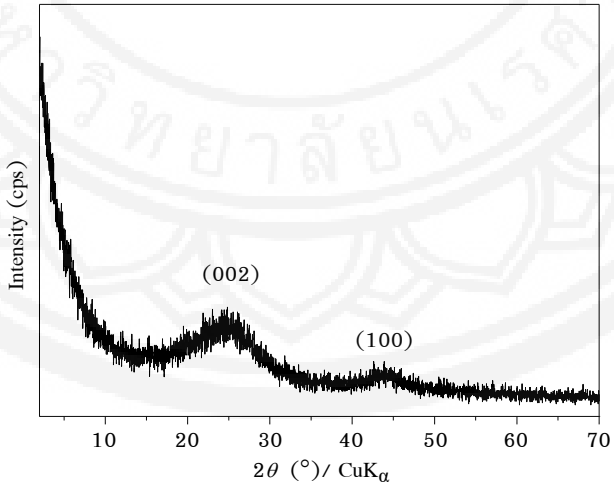

Figure 2 XRD pattern of the as-prepared activated carbon

To further confirm the formation of AC and identify the presence of functional groups on the surface, the infrared spectrum was interpreted as displayed in Figure 3. The infrared spectrum of the product demonstrated the vibration bands at 3430, 1610, 1577, 1013 and 573 cm^{-1}, which corresponded to −OH, aromatic C=C, −COOH, C−O and aromatic C−H, respectively. The infrared absorption data based on the functional groups could further verify the formation of activated carbon (Xu et al., 2014), according to the XRD result. The observed FT-IR band due to −COOH showed the acidic characteristic that might indicate the change in the surface charge in the presence of the aqueous dye solution.

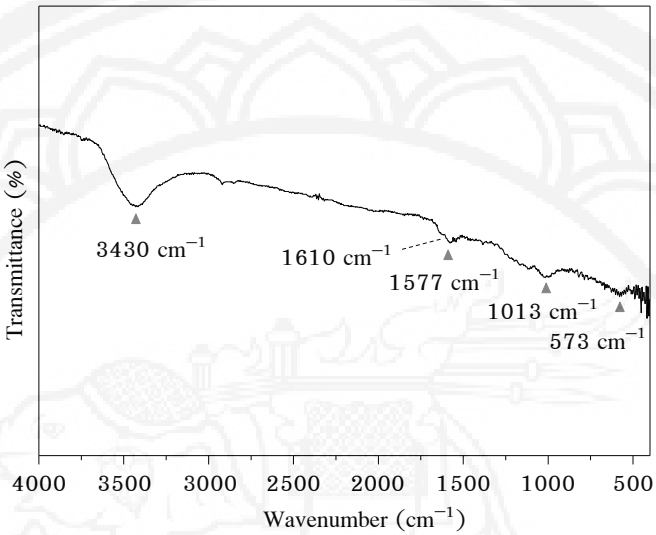

Figure 3 FT-IR spectrum of the as-prepared activated carbon

The surface properties and surface chemistry were also investigated by SEM image (Figure 4a) and N_2-adsorption/desorption isotherm (Figure 4b). The SEM image of the as-prepared AC revealed the dense packing particles with fissure, crack and flat surfaces. The result was indicative of the physical and chemical interactions on the surface (Palza, Delgado, & Govan, 2019).

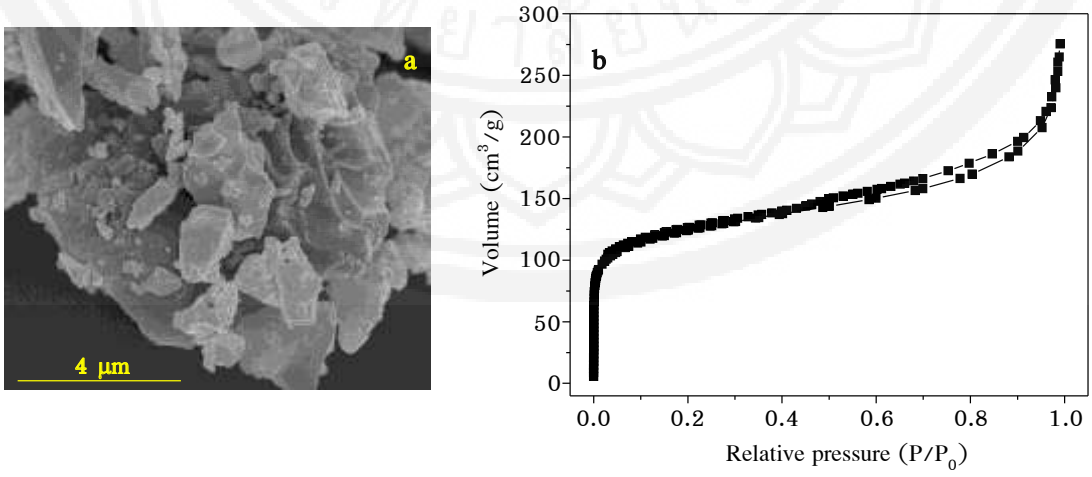

Figure 4 SEM microimage (a) and N_2-adsorption/desorption isotherm (b) of the as-prepared adsorbent

Evidently, the N_2 adsorption-desorption isotherm of AC was corresponding to type IV and H3 hysteresis loop that could indicate mesoporous material with the characteristic of the wedge-shaped pores (Palza et al., 2019). The BET specific surface area of AC was 403 m^2/g, whereas, the activated carbon prepared using Alligator weed showed the specific surface area about 303 m^2/g (Gautam et al., 2015). In compared with other activated carbon materials generated by using the carbon source with high ash content and low specific mass and density (Moosavi et al., 2020), the resulting specific surface area was quite large. On the experiments for preparing the activated carbon form *Hanguana malayana* excepting without activating with $ZnCl_2$, the specific surface area of the obtained sample was just 2.23 m^2/g. As a result, the increase of the specific surface area (from about 2 to 403 m^2/g) was due to the chemical activation with $ZnCl_2$ under the hydrothermal reaction, corresponding to the characteristic of the activated carbon (Sanmuga Priya & Senthamil Selvan, 2017).

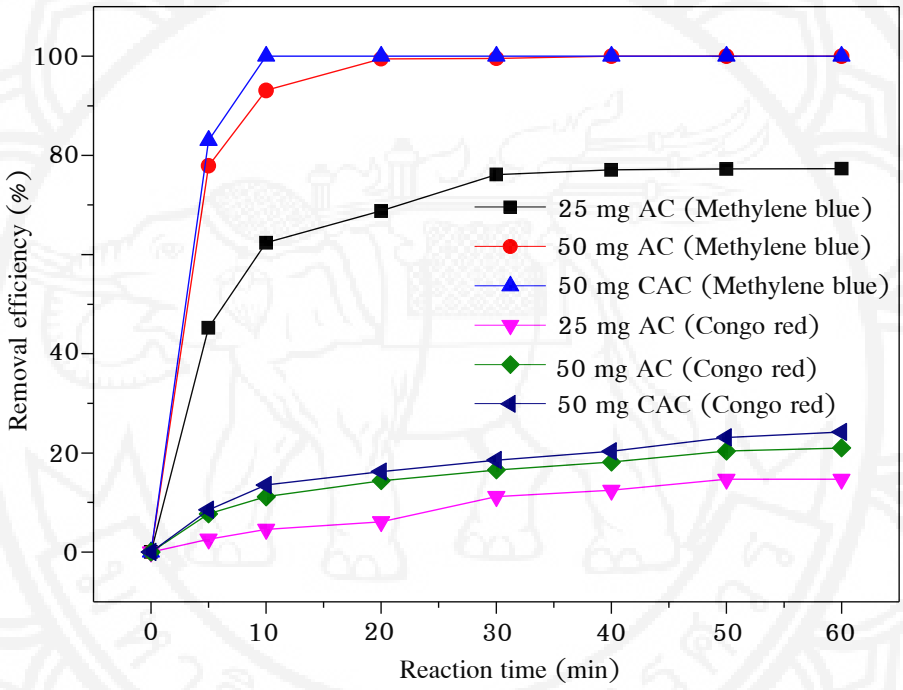

Figure 5 Removal efficiency (%) of methylene blue and Congo red using different amounts of the as-prepared activated carbon (AC) and commercial activated carbon (CAC)

The capacity of the as-prepared activated carbon (AC) was assessed by the removal performance of methylene blue and Congo red in comparison with that of commercial activated carbon (CAC) as displayed in Figure 5. On the longer contact time, the amounts of both methylene blue and Congo red were adsorbed on the surface until reaching the equilibrium time at 30 min. It can be seen in Figure 5, whole amount of cationic methylene blue in aqueous solution was eliminated by using 50 mg of AC, meanwhile, 25 mg of AC could capture the toxic cations just 77 % at 60 min of the contact time. At 10 min of the contact time, the removal of methylene blue was occurred fast because of the strong affinity between cationic methylene blue and negative-functional surface of AC. The reasons were supported by just 21 % of anionic Congo red adsorption (using 50 mg of AC), and the pH_{pzc} of the adsorbent = 5.8, obtained by the drift method (Lopez-

Ramon, Stoeckli, Moreno-Castilla, & Carrasco-Marin, 1999), where the pH of methylene blue solution was about 6.8 and Congo red solution was 6.2 in the presence of the adsorbent. Hereby, the repulsion between anionic dye and negatively charged surface of AC was the obstruction of the adsorption. To contrast, the adsorption capacity of CAC for removing of both methylene blue and Congo red was better than that on AC. However, their removal efficiency of methylene blue had not difference that varied by the contact time in the period gap just 5 min, implying the potential capacity of AC (from *Hanguana malayana*) on removing cationic methylene blue in aqueous solution. It might be due to lower surface area of AC than that of CAC, where *Hanguana malayana* is plant with low carbon content.

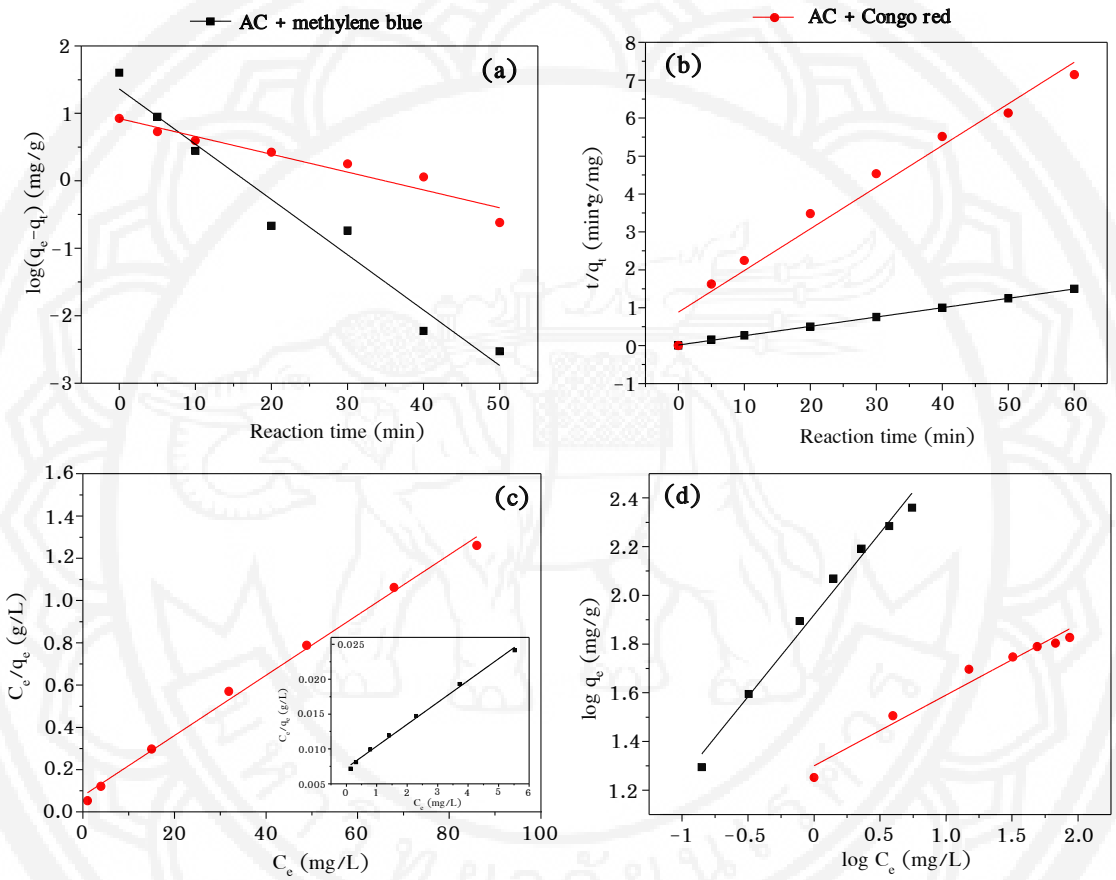

Figure 6 Adsorption kinetic models by pseudo-first order (a) and pseudo-second order (b) model, and adsorption mechanisms by Langmuir isotherm model (c) and Freundlich isotherm model (d) using 50 mg AC

The adsorption kinetic of AC on eliminating cationic methylene blue and anionic Congo red was investigated by fitting to the pseudo-first order and pseudo-second order models as shown in Figures 6a-6b. Considering the correlation coefficient (R^2), where the data are listed in Table 2, the best fit of the adsorption data of both dyes was followed to the pseudo-second order reaction. This could indicate that the adsorption of both methylene blue and Congo red in aqueous solution was based on the adsorbent and adsorbate with controlling the reaction rate. The parameters obtained by fitting as Langmuir and Freundlich isotherm models of the adsorption data (Figures 6c-6d) are listed in Table 2. The R^2 obtained by fitting as Langmuir isotherm model was more closed to 1 than that of Freundlich isotherm model. As a result, the adsorption mechanism of

the as-prepared adsorbent for removing both methylene blue and Congo red was occurred well by the monolayer adsorption on the surface. The maximum adsorption capacity (q_m) of AC was 323 and 70 mg/g for removing methylene blue and Congo red, respectively (Table 2).

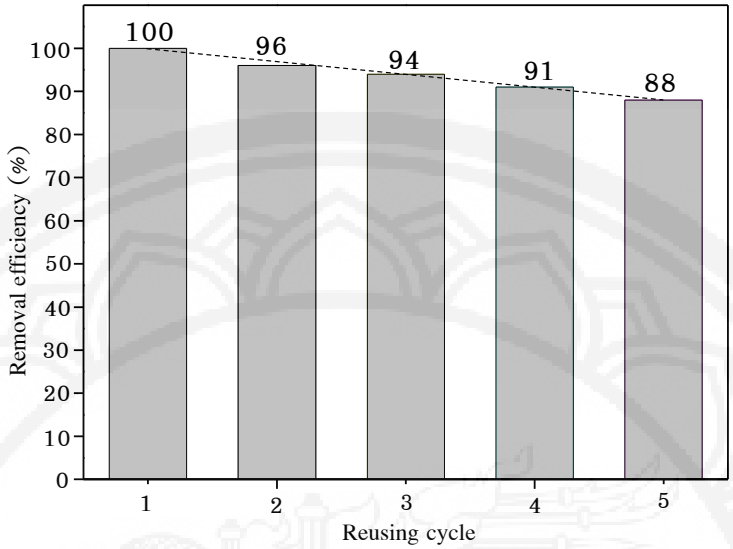

Figure 7 Reusing cycle of AC for removing methylene blue

To assess the adsorption performance, the reusability was tested by using 50 mg AC for removing methylene blue in aqueous solution (Figure 7). The adsorption capacity of AC showed the removal efficiency = 88 % on the fifth cycle. The slight reduction of the removal efficiency was occurred, it was might because of the change in the surface chemistry and the electronic structure, and the incomplete regeneration of the adsorbent (Moosavi et al., 2020).

Table 2 Parameters of various models on the adsorption of methylene blue and Congo red by the as-prepared activated carbon

Model	Methylene blue		Congo red	
	R^2	q_m (mg/g)	R^2	q_m (mg/g)
Pseudo-first order	0.9665	-	0.9310	-
Pseudo-second order	0.9996	-	0.9665	-
Langmuir isotherm	0.9961	323	0.9963	70
Freundlich isotherm	0.9863	-	0.9704	-

Discussion

The XRD pattern verified the formation of the activated carbon (AC) from *Hanguana malayana* by using $ZnCl_2$ as activating agent, supporting by the FT-IR band characteristics. The uptake of $ZnCl_2$ as the activating agent for generating AC was successful and additionally benefited on saving deionized water and without discharging toxic-chemicals in term of acidic (H^+) and basic (OH^-) activating agents. The as-prepared product showed the large surface area (403 m^2/g) that might promote the dye adsorption. The adsorption capacity of AC was selective to capturing of cationic methylene blue than that of anionic Congo red because of

the attractive force on the negative-charge AC surface, supporting by the pH at point of zero charge (pH_{pzc}). The adsorption of both methylene blue and Congo red by AC was followed by the pseudo-second order which controlled by the amounts of adsorbent and adsorbate, and monolayer coverage on the surface. The maximum adsorption capacity (q_m) of AC was 323 mg/g for removing methylene blue and 70 mg/g for removing Congo red. In comparison with CAC, the different contact time was just 5 min for removing whole amount of methylene blue by AC. The high adsorption performance of AC was evident with the 12% reduction of the removal efficiency after reused fifth cycle. Besides, AC adsorbent could eliminate methylene blue in water better than many adsorbents such as magnetic activated carbon from walnut shell (Salem et al., 2020), APT/C@NiFe-LDH composite (Tang, Mu, Zong, & Wang, 2018) and Fe_3O_4-kaolinite (Fei et al., 2020). The results could interpret the potential capacity of AC adsorbent that prepared from *Hanguana malayana*. The present work showed the advantages of (1) the chemical modification of the unwanted flora (*Hanguana malayana*) as activated carbon with the added value and (2) the removal of both *Hanguana malayana* in the natural water resource and organic dye (methylene blue and Congo red) in water.

Conclusions

Activated carbon was successfully prepared from *Hanguana malayana* as carbon based-precursor by activating with $ZnCl_2$ under the hydrothermal reaction at 120 °C for 24 h, and heat-treated at 300 °C for 1 h, and applied as the adsorbent for eliminating both cationic methylene blue and anionic Congo red dyes in water. The as-prepared activated carbon was an excellent adsorbent in term of low carbon content of the precursor on removing methylene blue with high adsorption performance throughout five times of the recycle. This study showed the potential method on both adding value of the unwanted flora (*Hanguana malayana*) by the modification as activated carbon and purifying wastewater contaminated with dye ions.

Acknowledgments

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