Optimization of Preparation Conditions and Characterization for *Dialium cochinchinensis* Seed Activated Carbon

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Abstract

Dialium cochinchinensis seed activated carbon (DCS-AC) was prepared for adsorption process. Under characterization, it was found that the iodine number is highest when using H_3PO_4 was chemical activation reagent in the ratio Char and H_3PO_4 was 1:1.5, giving the highest iodine adsorption value of 892.91 mg g^{-1}. The SEM image shows that Char has less porosity than DCS-AC/H_3PO_4 and has an average pore size in mesopore. The DCS-AC/H_3PO_4 has a specific surface area of 230.96 m^2 g^{-1} which is greater than Char. The highest percentage reactive red 120 sorption on DCS-AC/H_3PO_4 at equilibrium was 60 %. These results indicated that DCS-AC/H_3PO_4 could provide an alternative granular adsorbent for the removal dye in wastewater.

Keywords: *Activated Carbon, Adsorption, Iodine number; Dialium cochinchinensis seed*

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1. Introduction

Currently, it is found that various industries such as textiles, cosmetics, paper and dyes are using many synthetic dyes which affect the environment. A dye is one of the major constituents of the wastewater discharge. The high of BOD value reflects that the source of water highly lacks oxygen. Moreover, the dye contaminated with heavy metals and also carcinogenic, causing a great impact on aquatic organisms to reduce water pollution; thus, it is required to treat wastewater. There are many methods of wastewater treatment, such as photocatalysis (Puma et al., 2008; Ibrahim et al., 2013) and separation membrane (Yilin et al., 2019). However, the adsorption process with activated carbon is widely used for removal of pollutants from wastewater treatment (Liou, 2010). The many agricultural wastes materials for preparation activated carbon such as rice husk (Sagnik et al., 2011), potato peels (Lairini et al., 2013), the pericarp of rubber fruit (Hayeeye et al., 2014) and almond shell (Saeed et al., 2016). This research is to prepare the new adsorbents from *Dialium cochinchinensis* seed for the dye adsorption. *Dialium cochinchinensis* seed is one of an economic crop of Pattani province in Thailand. Seedy *Dialium cochinchinensis*, which are OTOP products, was released and needed in the market, resulting in many seed wastes. Therefore, *Dialium cochinchinensis* seed wastes were selected for preparing the new natural adsorbent (DSC-AC) to be used instead of expensive commercial activated carbon. The new adsorbents were characterized by BET surface area, Iodine number, SEM image and the point of zero charges (pH_{pzc}).

2. Objectives

The objectives of the study were prepared adsorbent from *Dialium cochinchinensis* seed waste which expected advantages, convenience and high adsorption capacity for dye adsorption. Moreover, it may be an eco-friendly and alternative adsorbent for wastewater treatment.

3. Materials and Methods

3.1 Materials

Dialium cochinchinensis seed was kept from Yarung, Pattani province. Zinc Chloride; $ZnCl_2$, Phosphoric acid; H_3PO_4 and Potassium hydroxide; KOH were purchased from Sigma-Aldrich. Sodium hydroxide; NaOH and hydrochloric acid; HCl used for pH adjustment were purchased from Labscan Ireland

and Merck, respectively, are performed over the range between (400 – 4000) cm^{-1} for a prepared sample. The adsorbate (reactive dye 120) was purchased from Sigma-Aldrich.

3.2 Preparation of DCS-AC

Dialium cochinchinensis seed (DCS) wastes were wash and dried in the oven at 120 °C. In the carbonization process, it was conducted in a muffle furnace at 400°C for three hours. Then, the mixing the Char (DCS) with various chemical reagents activation (H_3PO_4, KOH and $ZnCl_2$) at vary the ratio between Char: chemical reagents of 1:0.5, 1:1.0, 1:1.5, 1:2.0, 1:2.5, and 1:3.0 conducted at 450 °C for 1.0 h in the muffle furnace. It was then the obtained activated carbon was washed with distilled water until to neutral pH value. Finally, it was dried in the oven at 110°C for 24 h. and was kept in a desiccator

3.3 Characterization

Characterizations were investigated by iodine number, scanning electron microscopy (SEM– Quanta 400), BET surface area and pore size distribution (Model Autosorb 1 MP Quantachrome Instruments, FL, USA), elemental composition (C, H, N, O) analysis (FLASH EA 112 elemental analyzer), and point of zero charges (pH_{pzc}).

Iodine number is the mass of iodine adsorbed on the surface of adsorbents. The procedure for the determination of iodine number defined by ASTM D4607-94 (Philadelphia, 2006) as follows; 0.1 g of adsorbents was added with 10 ml of 5% HCl swirled in a conical flask until the entire adsorbent was wetted. The wetted solution was then boiled for exactly 30 s and the solution was cooled to room temperature. Then 100 ml of standard 0.1 N (0.05 M) iodine solutions were added to the contents of the conical flask. This solution was filtered using a Whatman 2V filter paper, and 50 ml of this filtrate was then titrated with 0.10 N sodium thiosulphate until the yellow colour had almost disappeared. 1 ml of the starch indicator was added, and the titration was continued until the blue colour just disappears. The equilibrium concentration is determined by calculation using the amount of sodium thiosulphate used in the titration. The procedure was repeated with each adsorbent.

The point of zero charges was determined using the pH drift method (Jia, Xiao, & Thomas, 2002) as follows: 50 ml of the pH of 0.1 M NaCl solution was adjusted between 2 and 12 by using 0.1 M HCl or 0.1 M NaOH; DCS-AC was added into each of the pH-adjusted solutions and equilibrated for 24 h; final pH was measured and plotted between initial pH and the final pH at which the curve crossed the line $pH_f = pH_0$ was taken as the pH_{pzc} of the DCS-AC (Hayeeye et al., 2017).

3.4 Adsorption studies

100 mg L^{-1} of reactive red 120 was prepared by dissolving in distilled water. 0.10 - 0.60 g of DCS-AC/H_3PO_4 was added into 50 ml of 100 mg L^{-1} reactive dye solution at pH 4. The before and after adsorption of reactive red 120 concentration was determined by UV-Vis spectrophotometer at a wavelength of 512 nm. The percentage removal of reactive red 120 was calculated from the equation (Puma et al., 2008) as follows:

$$\%RE = \frac{C_0 - C_e}{C_0} \times 100$$

where C_0 is the initial concentration of reactive red 120 (mg L^{-1}), C_e is the equilibrium liquid-phase concentration of reactive red 120 (mg L^{-1}). The residual dye concentration was calculated based on the previously determined calibration curve.

4. Results and Discussion

The results of the study of the influence of DCS-AC stimulants showed that in Table 1. The DCS-AC activation using H_3PO_4 in the ratio between DCS-AC and H_3PO_4 was 1:1.5, giving the highest iodine adsorption value of 892.91 mg g^{-1}. Because the phosphate group helps increase the pore structure of activated carbon. The ratio of phosphoric acid is higher than 1.5 with decreasing the iodine number of the DCS-AC because the activated carbon to reduce the Iodine adsorption efficiency. Thus, phosphoric acid causes the pore size to be larger, but the surface area is lower (El-Sayed et al., 2014) and the iodine adsorption of activated carbon prepared with activation temperature of 450 °C and 1:1.5 impregnation ratio is highest iodine number. This may be attributed to more extensive reaction of H_3PO_4 and surface carbon. Moreover, it may be excessive carbon burn-off at a 1:1.5 impregnation ratio (Deng et al., 2010; Saka, 2012).

Table 1 Influence of impregnation ratio and activation reagents of DCS-AC at 450°C for 1 hour

Impregnation ratio	Iodine Number		
	H_3PO_4	KOH	$ZnCl_2$
1:0.5	621.24	703.05	740.31
1:1.0	686.26	621.24	672.74
1:1.5	892.91	538.76	839.24
1:2.0	793.28	490.62	639.22
1:2.5	292.62	411.62	588.94
1:3.0	120.80	156.06	201.27

The results of the study of the influence of time and methods (Table 2) used to stimulate DCS-AC showed that DCS-AC activation by burning method for 1 hour gave the maximum iodine adsorption value of 889.57 mg g^{-1}, which may be attributed to the more extensive reaction of H_3PO_4 and surface carbon. The iodine adsorption value is high cause to high adsorption efficiency also.

Table 2 Influence of chemical activation method of DCS-AC/H_3PO_4

Adsorbent	Activation	Iodine Number (mg/g)
Char	-	302.90
DCS-AC/H_3PO_4	refluxed 2 h.	316.45
	refluxed 4 h.	542.80
	burned 0.5 h.	673.80
	burned 1 h.	889.57
	burned 1.5 h.	741.80
	burned 2 h.	519.84

The surface area can be found from the nitrogen adsorption isotherm at 77 K and the specific surface area, micropore volume and average pore size, as shown in Table 3. The results show that DCS-AC/H_3PO_4 has a specific surface area of 230.96 m^2 g^{-1} which is greater than Char because phosphate groups help increase the pore structure of activated carbon. The results showed that Char and DCS-AC/H_3PO_4 has an average pore size about 2 and 4 nm which is classified as a medium pore (mesopore) (Juang, Wu, & Tseng, 2002). Therefore, the pore size is an important factor affecting the adsorption efficiency.

Table 3 BET surface area, micropore volume and average pore size of Char and DCS-AC

Sample	BET Surface area (m^2 g^{-1})	Micropore volume (cm^3 g^{-1})	Average pore size (nm)
Char	39.57	0.019	1.92
DCS-AC	230.96	0.107	1.86

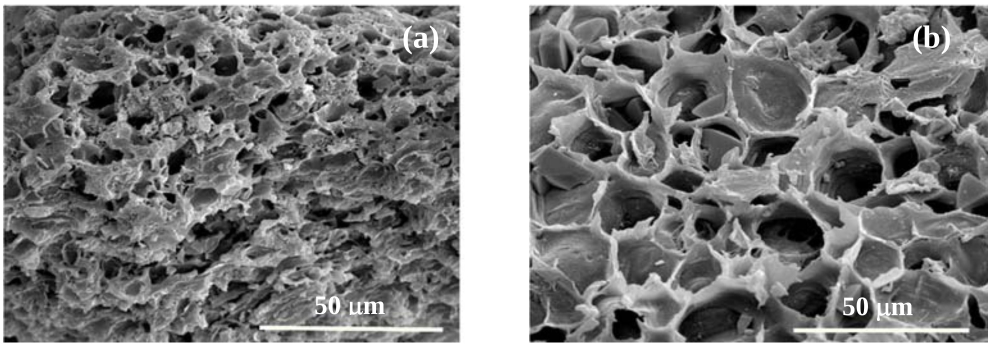

Figure 1 SEM micrographs of (a) char and (b) DCS-AC adsorbent at 450 °C for 1 h

Table 4 Elemental compositions of Char and DCS-AC /H_3PO_4

Sample	Elemental composition, wt%				
	C	H	N	O	Ash
Char	54.93	3.63	0.02	36.71	4.71
DCS-AC	56.16	4.10	0.03	35.91	3.80

Figure 1 shows SEM images from a scanning electron microscopic with a magnification of 5,000 to analyze the morphology of Char (a) and DCS-AC. (a) The surface of Char has less porosity than Figure (1)(b), which is the surface area of DCS-AC. It was confirmed that the appropriate amount of H_3PO_4 could increase the porosity of the DCS-AC. Moreover, the pore volume is also an important factor for adsorption efficiency.

The elemental composition of Char and DCS-AC was investigated. Table 4 presents that carbon of Char and DCS-AC found to be 54.93 % wt. and 56.16 % wt., respectively.

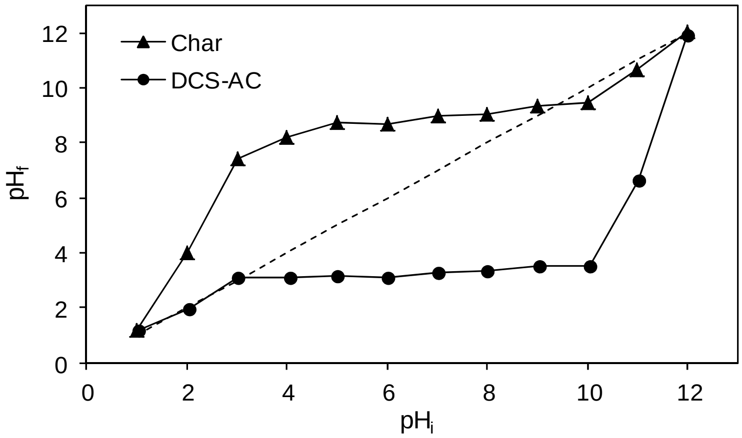

Figure 2 The point of zero charges (pH_{pzc}) of Char and DCS-AC

The point of zero point charge of Char and DCS-AC were 9 and 3, respectively. Thus, pH 5 of reactive red 120 dye solution < pH zpc of Char this indicates the surface was positively and pH 5 of reactive red 120 dye solution > pH zpc of Char this indicates the surface was negatively charged.

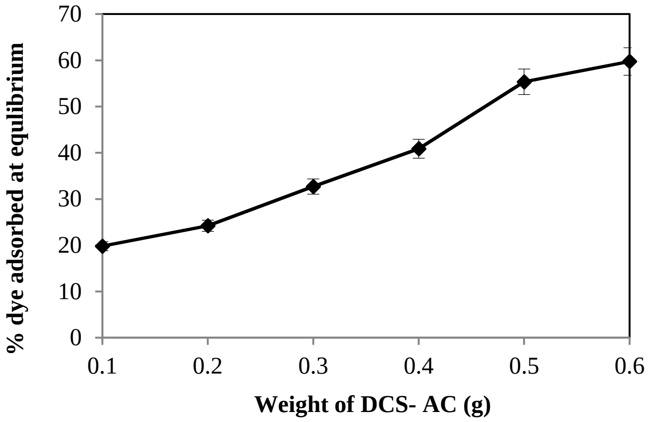

Figure 3 The effect of the weight of DCS-AC (0.1-0.6 g) for reactive red 120 sorption

In the adsorption process, the different dosages of DCS-AC (0.1 – 0.6 g) content in 100 mg L^{-1} reactive red 120 solutions at pH 5 were studied, as shown in Figure 13. The results indicated that the percentage of adsorbed dye increased with increasing DCS-AC dosage due to the availability of more adsorption sites (Thakur, & Kaur, 2017). The highest percentage of reactive red 120 dye sorption at equilibrium was 60 %.

5. Conclusion

Dialium cochinchinensis seed activated carbons (DCS-AC) were successfully prepared by a facile method from biomass materials and activation with H_3PO_4. The DCS-AC/H_3PO_4 has content, high carbon and low ash. From the characteristic results, it was found that the optimum preparation conditions were the burning at 450 °C for 1 hour and the Char: H_3PO_4 ratio was 1: 1.5, resulting in the highest iodine number was 892.91 mg g^{-1}. The BET surface area of DCS-AC/H_3PO_4 was 230.96 m^2 g^{-1}, and the average pore size was classified as mesopore. Besides, the morphology of the electron microscopy (SEM) has been studied. From the SEM image, DCS-AC/H_3PO_4 has porosity more than Char. It confirms that the activation with H_3PO_4 at optimum can increase the porosity. The point of zero point charge of DCS-AC/H_3PO_4 was 3.0 this indicates the surface of DCS-AC/$H_3PO_4$was negatively charged. The highest percentage adsorbed of reactive red 120 at equilibrium was 60 % on DCS-AC/H_3PO_4 0.6 g. It indicated that the DCS-AC/H_3PO_4 might be useful in the adsorption process of industrial wastewater treatment.

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