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ADSORPTION KINETICS ON BASIC RED 46 REMOVAL USING *Cerbera odollam* ACTIVATED CARBON

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Abstract

This paper presents the adsorption study of Basic Red 46 onto a non-edible sea mango or scientifically known as *Cerbera odollam*. The *Cerbera odollam* activated carbon was produced using chemical activation method using potassium hydroxide (KOH) as activating agent. The *Cerbera odollam* activated carbon produced was then characterized using Scanning Electron Microscope (SEM) for the analysis of surface morphology and Brunauer-Emmett-Teller (BET) for surface area. It was shown that this activated carbon has developed new pores on its surface and the BET surface area measured was 451.87m^2/g. The *Cerbera odollam* activated carbon was further used for adsorption of Basic Red 46 in batch process. The experimental parameters studied are adsorbent dosage and pH of the solution. It was found that the best pH of solution is at pH 11 and increasing the adsorbent dosage will increase the removal of Basic Red 46 where the highest is by 1.0 g/L. Conducting the kinetic analysis, the experimental data has fitted well on pseudo-second-order kinetic model compared to pseudo-first-order kinetic model.

Keywords: Adsorption, Basic dye, Activated carbon, Adsorption kinetics, *BR46*.

1. Introduction

Effluents from dyeing and finishing processes are mostly high colored with huge volume of suspended organic solid [1]. Around 10^6 tones and more than 10,000 different synthetic dyes have been created annually worldwide from industrial

Nomenclatures

C_0	Initial concentration, mg/L
C_e	Equilibrium concentration, mg/L
C_t	Concentration at interval times, mg/L
k_1	Lagergren's first-order rate constant, 1/h
k_2	Second-order rate constant, g/mg.h
q_e	Equilibrium adsorption uptake, mg/g
q_t	Adsorption uptake at interval times, mg/g

Greek Symbols

λ	Wavelength

Abbreviations

BR46	Basic Red 46
COAC	*Cerbera odollam* activated carbon
KOH	Potassium hydroxide

activities and from all of that, about 10% are discharged in industrial effluent freely without any treatment [2]. Dyes consists a wide range of chemical organic compound with complex chemical structure which accounts physiochemical, thermal and optical stability commonly manufactured from synthetic origin that maybe carcinogenic and mutagenic to human [3, 4]. The released of dyes into the river can be easily noticed since dyes are highly visible and bring dramatic source of pollution in the aquatic life [5].

Due to the toxicity of dyes used, researches on their elimination using conventional treatment approaches were heavily conducted [6]. However, this method was insufficient to purify wastewater containing dyes due to their boundaries such as less effectiveness, creation of secondary sludge, sensitive operating conditions and the additional cost incurred for further disposal [7]. Therefore, it is required to treat textile wastes before discharged into river using other effective method [1].

Adsorption with activated carbon is a well-studied technique to remove trace amount of adsorbate from aqueous solution [8]. The method was selected as the source of activated carbon is easily available, low cost, showing great efficiency, biodegradability and able to treat dyes at high concentration [9]. Moreover, it is shown to be an effective and attractive method for elimination of non-biodegradable contaminants including dyes in wastewater [10]. However, commercial activated carbon was expensive and not so economical for wastewater treatment [11]. Hence, producing activated carbon from agricultural or natural products becomes necessary. Some examples of agricultural waste that has been used as activated carbon to treat dyes were summarized in Table 1.

In this study, a new potentially low cost activated carbon source was derived from *Cerbera odollam*. The non-edible sea mango is also locally called in Malaysia as pong-pong, buta-buta, nyan or yellow-eyed cerbera [19]. *Cerbera odollam* belongs to *Apocynaceae* family where it can be found in many Asian countries such as Malaysia, Cambodia, Sri Lanka, Myanmar and Vietnam [20]. In Malaysia, it is abundantly obtainable as it is grown on roadside land.

Cerbera odollam while still green look likes small mangoes, with green fibrous shell enclosing almond-shaped kernels that contained two cross-matching white fleshy halves rich with carbonaceous and lignocellulose materials [21]. Exposing it to air, made the white kernel turns to violet, then turn to dark grey, and finally turn to dark brown or black [22]. The objectives of this paper are to synthesis and characterize activated carbon from *Cerbera odollam* as well as to study the adsorption isotherms of Basic Red 46 in batch process by varying two operating conditions which are adsorbent dosage and pH of the solution.

Table 1. Agricultural Waste-based Activated Carbon.

Dye	Activated carbon	References
Methlylene Blue	Oil palm fibre	[12]
Methlylene Blue	Pea Shells	[13]
Malachite Green	Corncobs agro waste	[14]
Rhodhamine B	Industrial solid waste	[15]
Astrazon Blue FRGL	Apricot stone	[16]
Astrazon Yellow	Apricot stone	[17]
Methlylene Blue	Durian shell	[18]

2. Materials and methodology

2.1. Basic Red 46

Basic red 46 (BR46) or known as Astrazon Red, a type of basic dye was used as an adsorbate while distilled water was used to prepare all the solution and reagents.

2.2. Preparation and characterization of activated carbon

Cerbera odollam was collected along road side of Jejawi, Perlis. The kernel was removed from brown fibrous shell and washed several time under running tap water to remove impurities. The sample was then rinsed with distilled water and dried in oven of 105ºC overnight. Following that, the sample was grinded and sieved to specific range of 1 to 2 mm. An accurate weight of sample was impregnated with equivalent weight of potassium hydroxide (KOH) at impregnation ratio of 1:1. The mixture was dehydrated in drying oven at 105 ºC overnight.

The dried solid mixture was pyrolysed in a horizontal tube furnace under high purity nitrogen (99.95%) with flow rate of 100 cm^3 per min till it reached the desired temperature of 600 ºC. The activated carbon was cooled under nitrogen influence and washed few times with hot distilled water. 1 M hydrochloric acid (HCl) was added to the solution in order to make the pH of 7 to 7.5. The activated carbon was dried and kept in air tight closed container. The sample was denoted as COAC for *Cerbera odollam* activated carbon.

The surface characteristic and morphological studies of *Cerbera odollam* activated carbon was carried out using Analytical Scanning Electron Microscope (SEM) JEOL JSM-640LAwhile the pore surface area was analyzed using ASAP2020 Micromeritics Brunauer-Emmett-Teller (BET).

2.3. Batch study

Stock solution of 1000ppm was prepared by dissolving 1 g of BR46 in 1 L of distilled water. To prevent decolorization by direct sunlight, the stock solution was covered using aluminium foil and kept in dark place before being used. Adsorption studies were conducted by preparing 100mL of 50ppm BR46 concentration in 250 mL conical flask. 100ppm of BR46 was prepared by diluting the stock solution using distilled water and adjusted the pH to be 3. 0.02g of *Cerbera odollam* activated carbon was added to the flask.

The sample was carried in Wisebath thermal water bath shaker at temperature of 25ºC with agitation speed of 150 rpm for 180 minutes. During the experiment, 5 ml samples of solution were taken from the flask at fixed time intervals.All samples were centrifuged for 10 minutes at 4000 rpm prior to analysis using a double beam Shimadzu UV-1800 UV-VIS Spectrophotometer using wavelength, λ of 532 nm. The steps were repeated for 0.04g, 0.06g, 0.08g and 0.1g for adsorbent dosage at pH5, 7, 9, and 11.

2.4. Adsorption kinetics

The kinetic studies were identical to the batch studies. The samples were taken at different time intervals and the concentration of BR46 was measured. The adsorption at time t, q_t (mg/g) was calculated using equation as shown in Eq. (1). Equation (1) shows the formula used to calculated q_t, where C_o and C_t are the initial concentration and concentration at time intervals, respectively. V is the volume and W is mass of adsorbent used.

$$q_t = \frac{C_0 - C_t}{w} V \tag{1}$$

Adsorption kinetic model is used to express the mechanism of solute sorption onto adsorbent. The sorption kinetics may be described by a pseudo first order and second order which are shown in Eq. (2) and Eq. (3). Equations (2) and (3) show the formula used respectively:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{2}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

where q_e is the equilibrium adsorption capacity, k_1 is the Lagergren's first-order rate constant and k_2 is second-order rate constant. The pseudo first-order model is assumed that the change of adsorbate uptake rate with time is directly proportional to the difference in saturation concentration and the amount of adsorbent uptake with time [23]. While, pseudo second-order rate equation can be used to predict the behaviour of adsorption for the entire adsorption which is to predict the kinetic behaviour of adsorption with chemical sorption being the rate controlling step.

3. Result and Discussion

3.1. Characterization of activated carbon

In order to illustrate the effect of chemical activation on the surface of *Cerbera odollam*, SEM analysis was conducted. Figure 1 shows the new pores were developed on the surface of COAC. This indicated that there is a chemical reaction between *Cerbera odollam* and potassium hydroxide (KOH) as well as implication of the operating temperature [22]. The surface area analysis of COAC using BET was found to be 451.87 m^2/g.

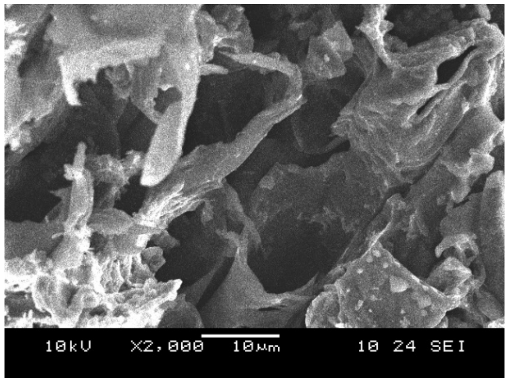

Fig. 1. SEM Image of COAC.

3.2. Batch studies

3.2.1. Effect of pH

The effect of pH solution on BR46 removal also varied by different pH which were 3, 5, 7, 9 and 11 as shown in Fig. 2. Figure 2 shows that the adsorption of BR46 increased with pH of solution increased. The highest uptake was found to be at pH 11 and the lowest is at pH 3. Hameed et al. [11] reported that lower adsorption uptake at acidic pH is due to the presence of excess H^+ ions/protons competing with the cationic groups on the dye for adsorption sites.

3.2.2. Effect of adsorbent dosage

The effect of adsorbent dosage on adsorption of BR46 was conducted. Initial BR46 concentration was set to be 100 mg/L and the varied adsorbent dosages were 0.2, 0.4, 0.6, 0.8 and 1.0 g/L as shown in Fig. 3. Figure 3 shows that the adsorption of BR46 increased with increasing of adsorbent dosage. Lowest adsorption uptake is by 0.2 g/L while highest adsorption is by 1.0 g/L. El Haddad et al. [24] reported that when the active sites on the adsorbent are fully occupied with adsorbate it is difficult for other adsorbate to bind to the active sites.

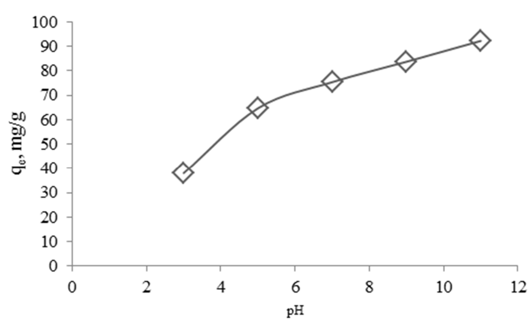

Fig. 2. Effect of pH on BR46 removal.

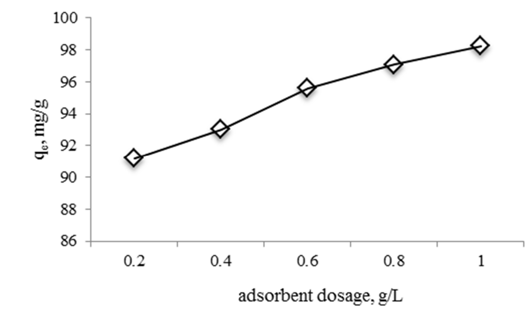

Fig. 3. Effect of adsorbent dosage on BR46 removal.

3.3. Adsorption kinetics

In this study, the pseudo-first order kinetic model was used to predict sorption kinetics as showns in Eq. (2). Figures (4) and (5) show that for pseudo-first order kinetic model, when *ln* $(q_e - q_t)$ was plotted against t for all different adsorbent dosage and pH, a straight line was obtained with slope of k_1 and intercept of *ln* q_e where k_1 is the first order adsorption rate constant. As can be seen from these graphs, the trend obtained for all dosage almost equals, negative slopes and positive intercepts. The R^2, constant k_1 and $q_{e,calc}$ for pseudo-first order kinetic model were summarized in Table 2.

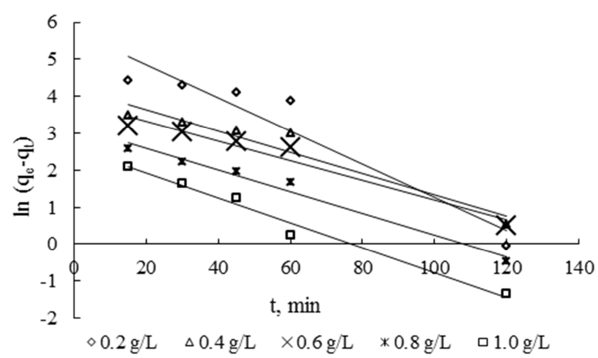

Fig. 4. Pseudo first-order kinetic model for different adsorbent dosage.

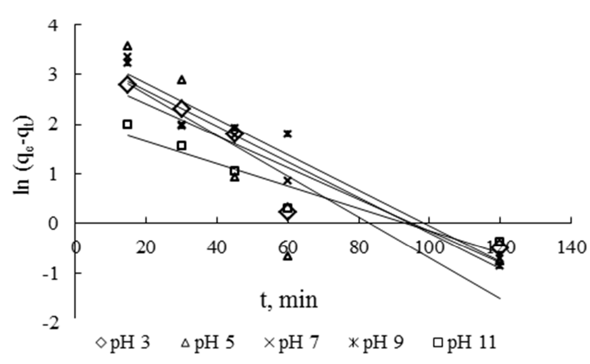

Fig. 5. Pseudo first-order kinetic model for different pH.

Table 2. Pseudo First-order Kinetics Models.

Adsorbent dosage, g/L	Constants			R^2	pH	Constants			R^2
	$q_{e,exp}$, mg/g	$q_{e,calc}$, mg/g	k_1			$q_{e,exp}$, mg/g	$q_{e,calc}$, mg/g	k_1	
0.2	456	316.7	0.05	0.90	**3**	41.3	21.2	0.03	0.87
0.4	232	68.4	0.03	0.93	**5**	67.7	30.4	0.04	0.71
0.6	159	46.8	0.03	0.95	**7**	79.4	29.5	0.03	0.94
0.8	122	24.1	0.03	0.99	**9**	86.2	34.6	0.03	0.95
1.0	98	13.4	0.03	0.98	**11**	95.3	8.3	0.02	0.91

Figures 6 and 7 show the graph of pseudo-second order kinetic models. A straight line was obtained when t/q_t was plotted against t. From the graph showns in Figs. 6 and 7, the slopes are k_2 and the intercept are $1/k_2q^e{}_2$, where k_2 is second order adsorption rate constant. The trends for all graphs are almost same, positive slopes. The R^2, constant k_2 and $q_{e,calc}$ for pseudo-second order kinetic model were summarized in Table 3.

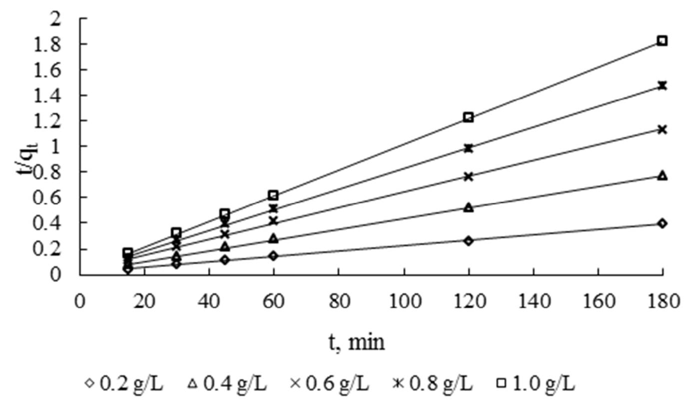

Fig. 6. Pseudo second-order kinetic model for different adsorbent dosage.

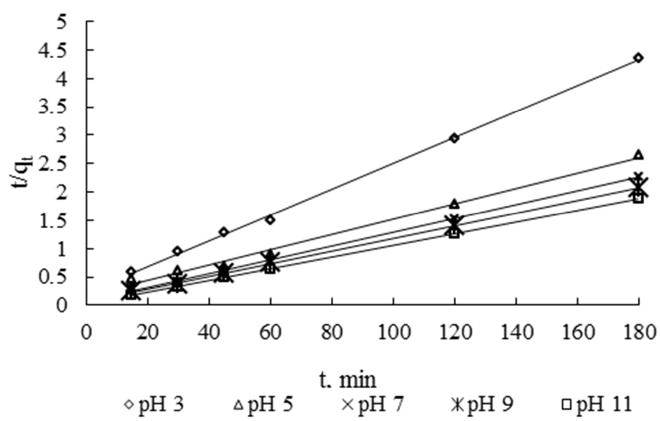

Fig. 7. Pseudo Second-order kinetic model for different pH.

Table 3. Pseudo Second-order Kinetics Model.

Adsorbent dosage, g/L	$q_{e,exp}$, mg/g	Constants		R^2	pH	$q_{e,exp}$, mg/g	Constants		R^2
		$q_{e,calc}$, mg/g	k_2				$q_{e,calc}$, mg/g	k_2	
0.2	456	476.2	0.0003	0.99	**3**	41.3	44.1	0.002	0.99
0.4	232	238.1	0.0009	0.99	**5**	67.8	72.9	0.001	0.99
0.6	159	163.9	0.0011	0.99	**7**	79.4	82.6	0.002	0.99
0.8	122	125.0	0.0027	0.99	**9**	86.3	89.3	0.002	0.99
1.0	98	100.0	0.0056	1	**11**	95.3	96.1	0.007	1

From the experimental data as shown in Tables 2 and 3, it shows that pseudo-second order model give very high values of R^2 in addition of good agreement between the values of experimental and calculated dye uptake of BR46 onto COAC. The different between $q_{e,exp}$ and $q_{e,calc}$ in pseudo-second order model was not so far compared to pseudo-first order model. Moreover, R^2 in pseudo-second order also closed 1. Higher value of R^2> 0.99 and good correlation between the experimental and calculated equilibrium described properly the adsorption kinetics [24]. According to Al-Ghouti et al. [25], the mechanism of the process could be chemisorptions as it is obeyed pseudo-second order kinetic model. It suggested that chemical bonding between cationic groups of dye and active functional groups such as hydroxyl and carboxyl occurred at the surface of *Cerbera odollam* activated carbon. Therefore, it can recommend that the pseudo-second order model described the adsorption kinetics better than pseudo-first order model.

4. Conclusion

This study reveals that *Cerbera odollam* is a novel source for activated carbon prepration as it has never been used in any other researches. *Cerbera odollam* activated carbon has possibly becomes an excellent precursor to produced activated carbon.

- BR46 was strongly adsorbed onto COAC by different adsorbent dosage and pH of solution.
- Maximum removal of BR46 was 1.0 g/L for adsorbent dosage and pH 11 for pH of solution.
- The adsorption is well described by the pseudo-second-order kinetic model as the R^2> 0.99.

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