

# Metals Hydroxide Activation of Casuarina Empty Fruit for Methylene Blue and Congo Red Removal

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## ABSTRACT

Casuarina equisetifolia empty fruit has been utilized as activated carbon material because it is abundantly available in nature. The fruit was activated by metals hydroxide, namely potassium hydroxide and sodium hydroxide for dyes adsorption. The present work was aimed to evaluate the adsorption properties of activated carbons towards cationic dye (methylene blue) and anionic dye (congo red). Results show that KOH activation yields activated carbon with excellent maximum adsorption capacities of 614 mg/g and 340 mg/g for methylene blue and congo red, respectively. The adsorption data were analysed using isotherm and kinetic models and displayed a good regression with Langmuir and pseudo-second-order kinetic models.

**Keywords:** Metals hydroxide, adsorption, chemical activation, dye removal, wastewater treatment

## 1. INTRODUCTION

Adsorption on solid surface is effective for the removal of pollutants especially dyes in wastewater treatment. Activated carbon is the commonly used adsorbent to remove colours, contaminants and odors from industrial wastewater [1]. Commercially available activated carbon is effective to apply, but it is very expensive. Therefore, low-cost and environmental friendly activated carbons have been developed to further decrease the cost. Various adsorbents from agricultural and industrial by-products such as amberlite Ira-938 resin [2], corn cob [3], palm oil mill effluent sludge [4] and oil palm empty fruit bunch [5] have been synthesized into activated carbons. Large amount of casuarina equisetifolia fruit is available as an underutilized natural resource in Malaysia. Hence, there are several reported studies on the use of the fruit as activated carbon precursor to remove water pollutants such as methylene blue [6], chromium [7], copper [8], malachite green [9] and lead [10]. In general, the preparation of activated carbon involved physical or chemical activation. However, chemical activation is preferable due to several advantages such as lower activation temperature, shorter activation time, higher carbon yield and surface area. Pre-carbonization step is usually introduced prior to chemical impregnation and activation because it initially develops rudimentary channels that offers larger specific surface area upon activation. Among various chemical activating agents, metals hydroxide, i.e., potassium hydroxide (KOH) or sodium hydroxide (NaOH) are commonly used to activate the carbonaceous precursor. Activated carbon obtained by

this activation often possesses unique characteristics such as lower ash content, narrow porosity distribution, high surface area and adsorption capacity. For example, KOH-activated rice husk displays an increase of surface area from 173 m<sup>2</sup>/g in char to 1320 m<sup>2</sup>/g, that brings about an improved maximum adsorption capacity to 1919 mg/g of phenol [11]. In a related study, a removal of 90 % of malachite green was reported using NaOH/KOH-activated banana peel with an improved of 95 % surface area as compared to char [12]. To date, the utilization of casuarina equisetifolia empty fruit as activated carbon precursor is not widely explored and reported in literature. This study was embarked to evaluate metals hydroxide activation of casuarina fruit for dyes removal. The adsorption data were analysed and discussed from the perspectives of equilibrium and kinetics to shed valuable insights into feasible industrial wastewater treatment.

## 2. EXPERIMENTAL

Casuarina equisetifolia fruit was collected from Teluk Mak Nik beach, Kemaman, Terengganu. Potassium hydroxide (KOH, MW=56.11 g/mol) and sodium hydroxide (NaOH, MW= 40.00 g/mol) were purchased from R&M Chemicals. Methylene blue (MB, MW=319.86 g/mol) and Congo red (CR, MW=696.65 g/mol) dyes were supplied by Quality Reagent Chemicals (QReC) and R&M Chemicals, respectively.

The fruit was pre-carbonized in a muffle furnace at 300 °C for 1.5 h prior to chemical activation. Then, the pre-carbonized sample was impregnated with KOH solution in 1.5 ratio (w/w, KOH pellet : casuarina fruit). The

impregnated sample was oven-dried prior to carbonization. The activation was conducted in a muffle furnace at 600 °C for 1.5 h. The sample was refluxed multiple times with hot water for 6 h. After that, the sample was dried and stored prior to use. The same procedures were repeated for NaOH activation. The casuarina fruit-based activated carbons were defined as AC-KOH and AC-NaOH by KOH and NaOH activation, respectively. For comparison, casuarina fruit char was prepared at 600 °C for 1.5 h in the absence of activating agent.

The adsorption properties of activated carbons were evaluated by performance of MB and CR removal in water. The adsorption was performed at different concentrations (5-1400 mg/L for MB and 5-800 mg/L for CR) and contact times (5 min-120 h for MB and 5 min-144 h for CR). The residual concentrations were measured using UV-Vis spectrophotometer (752 PRO) at wavelengths of 580 nm ( $x=y/0.0357$ ,  $R^2=0.991$ ) and 495 nm ( $x=y/0.0361$ ,  $R^2=0.999$ ) for MB and CR, respectively. The adsorption was performed in three replicated runs, and the average values were reported. The equilibrium capacity,  $q_e$  (mg/g) was calculated as  $q_e=(C_o-C_e) \times V/m$ , where  $C_o$  (mg/L) is the initial dye concentration,  $C_e$  (mg/L) is the equilibrium dye concentration,  $V$  (L) is the solution volume and  $m$  (g) is the adsorbent mass. The adsorption capacity at time,  $q_t$  (mg/g) was calculated as  $q_t=(C_o-C_t) \times V/m$ , where  $C_t$  (mg/L) is the dye concentration at time.

### 3. RESULTS AND DISCUSSION

#### 3.1. Effect of Initial Concentration

The casuarina equisetifolia precursor was chemically activated at 600 °C, leading to the formation of activated carbon [6]. The yield of char, AC-KOH and AC-NaOH at 1.5 impregnation ratio are 26.35 %, 10.4 % and 22.65 %, respectively. In comparison, the yield of AC-NaOH is higher than that of AC-KOH. In water, KOH is more alkaline than NaOH, showing a weaker K and OH- ionic bond and releasing more hydroxyl ions to attack and weaken the chemical bonds within the char [12].

Figure 1 represents the equilibrium adsorption of MB and CR on adsorbents. In general, the equilibrium adsorption increased as the concentration increases, until the saturation point was obtained. At equilibrium, the quantity of dye desorbed is equivalent to the quantity of dye adsorbed onto the activated carbons. The activated carbon prepared from KOH-activation exhibits excellent performance as demonstrated from the adsorption capacity for both dyes. The effectiveness of both hydroxides depends on the precursor, resulting in different reactivity and structural order of activated carbon [13]. Moreover, the electrostatic attraction between the negatively charged surface as a result of metals hydroxide activation and positively charged dye possibly leads to higher adsorption capacity of MB than that of CR [14]. The comparison of the different samples shows the following adsorption order: AC-KOH > AC-NaOH > char.

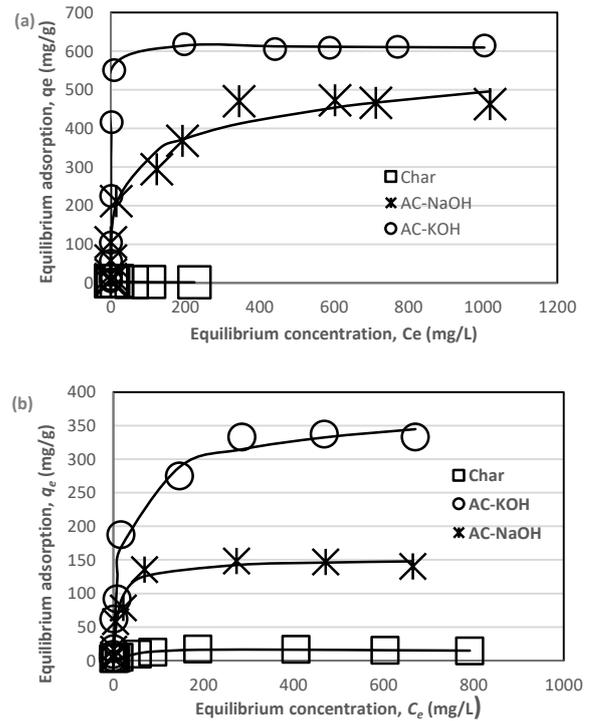


Figure 1 Equilibrium adsorption of (a) methylene blue and (b) congo red by adsorbents

The equilibrium data of all samples demonstrated good correlation with Redlich-Peterson model, describing the adsorption in homogenous or heterogenous surface. The  $R^2$  values are in the range of 0.863 to 0.987. The  $\beta$  values for all samples are close to 1.0, indicating that the Langmuir isotherm model is more preferable than Freundlich model. Table 1 summarizes the isotherm constants for MB and CR adsorption by activated carbons. On a molar basis, maximum adsorption capacity towards MB are 1.92 mmol/g and 1.47 mmol/g for AC-KOH and AC-NaOH, respectively. It is supported with greater affinity of 336 L/mmol for AC-KOH as compared to 16.6 L/mmol for AC-NaOH. However, the affinity value towards CR for AC-NaOH at a value of 57.8 L/mmol is greater than 40.4 L/mmol for AC-KOH. The adsorption is lower instead of higher affinity could be explained by the restriction of the pore size and also the abundance and availability of weaker sites for adsorption [15] [16].

#### 3.2. Effect of Contact Time

Figure 2 shows the effect of contact time on the dyes adsorption performance of different adsorbents at 5 and 25 mg/L. Overall, the adsorption of dye is rapid at initial contact time and then proceed slowly until the equilibrium is reached. The contact times needed to reach equilibrium for MB and CR adsorption by AC-KOH at 5 mg/L are 30 min and 39 h, respectively. Both dyes are fully adsorbed (100 % removal), where the molecules present are completely attracted by the available binding sites on the

adsorbent. The slow rate of CR adsorption is probably due to the slow pore diffusion of the solute ion into the adsorbent [17]. The pore size might compatible to accommodate MB molecules because the molecular size of CR ( $2.62 \times 0.74 \times 0.43$  nm) is bigger compared to that of MB ( $1.43 \times 0.61 \times 0.4$  nm).

Commonly, an increase in initial concentration enhances the driving force to overcome mass transfer resistance between adsorbate-adsorbent phases as well as their interaction and consequently, higher uptake of dye is obtained. However, longer equilibrium time is needed for higher initial concentration. The pores get filled up with the increase in initial concentration and start offering resistance to the dye molecules to diffuse deeper into the adsorbent structure hence, longer time is required for further adsorption [18].

Tables 2 and 3 summarize the kinetics constants for MB and CR adsorption, respectively by activated carbons. The kinetics data obeyed pseudo-first order and pseudo-second order for MB and CR, respectively. The model was selected based on the higher  $R^2$  and lower sum of squared errors (SSE). However, the MB adsorption for char was controlled by intraparticle or pore diffusion (Table 2). Pseudo-second-order suggested that CR adsorption is likely to be controlled by chemical adsorption [19] [20]. Therefore, the removal of CR could be governed by exchange or sharing of electrons between the surface of adsorbent and the dye molecules.

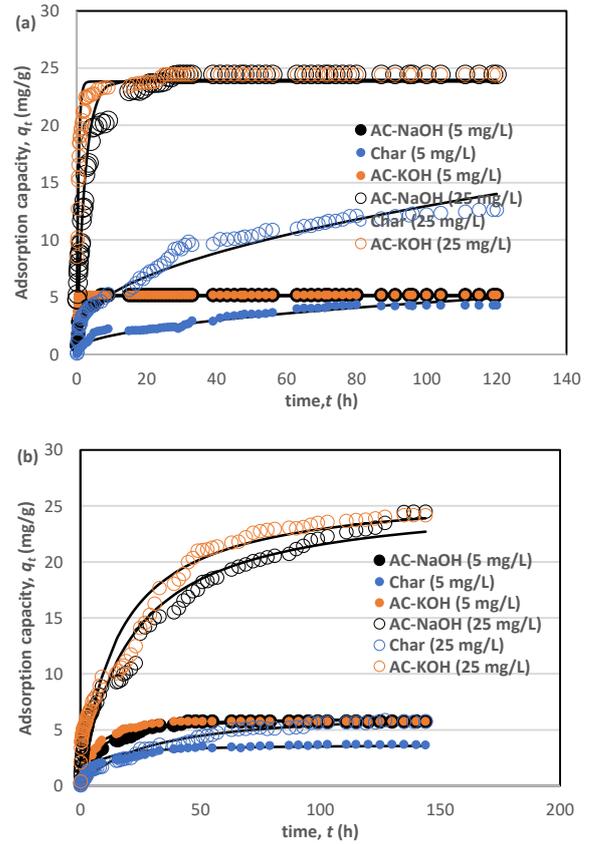


Figure 2 Adsorption rate of (a) methylene blue and (b) congo red for 5 and 25 mg/L by adsorbents

Table 1 Isotherm constants for methylene blue and congo red adsorption by activated carbons

Dye	Methylene blue			Congo red		
	Char	AC-NaOH	AC-KOH	Char	AC-NaOH	AC-KOH
$q_{m,exp}$ (mg/g)	11.1	473	618	17.0	148	335
Langmuir						
$q_m$ (mg/g)	11.3	469	614	16.6	149	340
$q_m$ (mmol/g)	0.035	1.47	1.92	0.024	0.214	0.488
$\beta$ (L/mg)	0.207	0.052	1.05	0.035	0.083	0.058
SSE	7.81	19627	18504	17.1	673	3542
$R^2$	0.888	0.973	0.987	0.941	0.981	0.983
Freundlich						
$K_f((\text{mg/g})(\text{L/mg})^{1/n})$	4.55	168	370	3.60	38.3	65.4
$n$	5.50	6.38	12.4	4.22	4.48	3.73
SSE	9.27	22674	50400	45.1	3081	9003
$R^2$	0.826	0.965	0.951	0.833	0.904	0.954
Redlich-Peterson						
$K_R$	6.18	33.9	611	0.343	14.3	28.0
$a$	0.924	0.104	0.956	0.007	0.11	0.137
$\beta$	0.897	0.944	1.01	1.17	0.977	0.917
SSE	7.34	18692	18358	14.7	662	3038
$R^2$	0.863	0.975	0.987	0.965	0.981	0.985

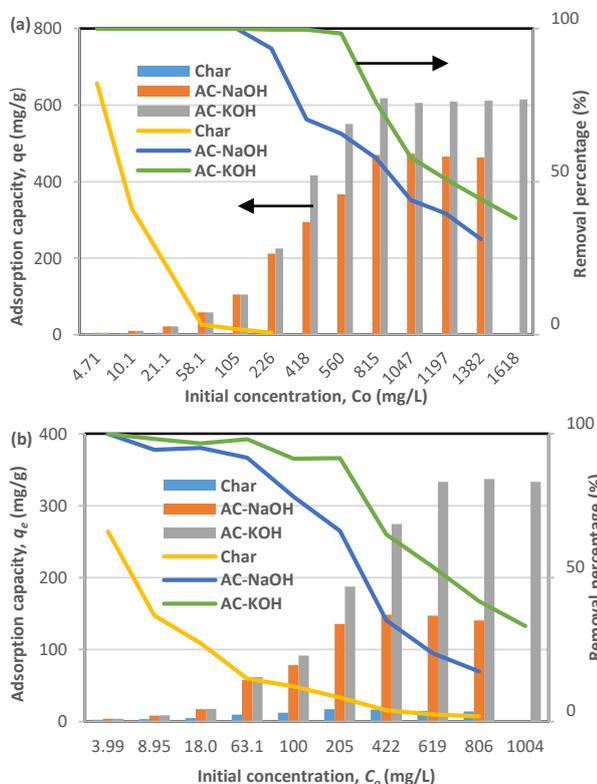
**Table 2** Kinetics constants for 5 and 25 mg/L methylene blue adsorption by activated carbons

Concentration	5 mg/L			25 mg/L		
Activated carbon	Char	AC-NaOH	AC- KOH	Char	AC-NaOH	AC- KOH
Pseudo-first-order						
$k_1$ (h <sup>-1</sup> )	0.038	1.05	9.18	0.060	0.428	1.98
$q_e$ (mg/g)	4.28	5.11	5.18	11.4	24.0	23.8
SSE	12.5	4.98	0.372	115	132	105
R <sup>2</sup>	0.946	0.950	0.950	0.953	0.975	0.919
Pseudo-second-order						
$K_2$ (h <sup>-1</sup> )	0.010	0.318	4.68	0.007	0.026	0.149
$q_e$ (mg/g)	5.03	5.27	5.22	12.7	25.1	24.4
SSE	9.61	1.96	0.916	75.8	49.1	16.4
R <sup>2</sup>	0.949	0.980	0.856	0.953	0.988	0.985
Intraparticle diffusion						
$k_p$	0.422	0.243	0.028	1.11	1.66	0.761
$C$	0.316	3.33	4.98	1.82	11.6	18.6
SSE	6.34	47.7	5.69	46.7	1103	532
R <sup>2</sup>	0.957	0.496	0.0954	0.961	0.677	0.478
Elovich						
$a$	0.634	3.19	4.92	2.50	11.4	18.2
$\beta$	0.707	0.535	0.078	1.92	3.33	1.68
SSE	12.6	17.4	4.66	67.9	254	217
R <sup>2</sup>	0.914	0.816	0.260	0.942	0.926	0.787

**Table 3** Kinetics constants for 5 and 25 mg/L congo red adsorption by activated carbons

Concentration	5 mg/L			25 mg/L		
Activated carbon	Char	AC-NaOH	AC-KOH	Char	AC-NaOH	AC-KOH
Pseudo-first-order						
$k_1$ (h <sup>-1</sup> )	0.141	0.109	0.156	0.033	0.039	0.047
$q_e$ (mg/g)	3.38	5.64	5.66	5.65	22.2	23.2
SSE	9.42	5.11	2.95	9.49	302	432
R <sup>2</sup>	0.928	0.987	0.991	0.984	0.974	0.970
Pseudo-second-order						
$K_2$ (h <sup>-1</sup> )	0.055	0.024	0.034	0.005	0.002	0.003
$q_e$ (mg/g)	3.67	6.20	6.15	6.87	25.9	26.4
SSE	3.95	1.56	1.54	6.27	196	315
R <sup>2</sup>	0.966	0.995	0.995	0.986	0.975	0.963
Intraparticle diffusion						
$k_p$	0.293	0.515	0.491	0.544	2.08	2.12
$C$	0.878	1.07	1.40	0.137	1.73	2.90
SSE	8.69	48.9	66.6	6.71	69.4	189
R <sup>2</sup>	0.899	0.830	0.766	0.979	0.985	0.961
Elovich						
$a$	1.021	1.25	1.47	0.475	3.04	4.18
$\beta$	0.558	1.01	1.00	0.973	3.70	3.80
SSE	2.31	11.2	13.9	26.5	374	454
R <sup>2</sup>	0.973	0.961	0.951	0.917	0.919	0.908

Figure 3 represents the removal percentage of MB and CR by adsorbents for 120 and 144 h of contact times, respectively. It shows that, from initial concentration of 105 to 1382 mg/L, the removal percentage of MB decreased from 100 to 31.23 % and 100 to 44.27 % using AC-NaOH and AC-KOH, respectively. Similar pattern was also observed for CR adsorption. Dye molecules at lower concentration interact well with the active sites available on the adsorbent surface. While, at higher concentration, the competition exists during dye-adsorbent interaction, leading to saturated binding sites. A lower removal percentage is due to limited binding sites that can accommodate more dye molecules as the concentration increases [21]. AC-KOH exhibits a 100 % removal of MB at 105 mg/L, as compared to 4 mg/L for CR. It implies that different removal percentage will be obtained on the same adsorbent because different dye molecules possess different structures and sizes [22].



**Figure 3** Removal percentage of (a) methylene blue and (b) congo red by adsorbents

Mechanism of dye adsorption giving a deeper insight into influence of hydroxide activator on the physiochemical characteristics of adsorbent and dye removal. The carbonization at 600 °C of the precursor produced aromatic structure of char. The structure could combine with benzene ring in MB molecules through  $\pi$ - $\pi$  stacking, while oxygenated functional groups such as phenolic and carboxylic groups could bind with nitrogen molecules in MB thru hydrogen bonding [10] [23]. Therefore, the

adsorption mechanisms between char and MB are physical interaction,  $\pi$ - $\pi$  stacking, hydrogen bonding and electrostatic interaction. However, hydroxide activation offers larger surface area and developed pore structure. Most of functional groups are absent or limited especially for oxygen-containing groups. Besides, the aromatic structure and  $\pi$ - $\pi$  stacking are important for MB removal. The main adsorption mechanisms are physical interaction, electrostatic attraction and  $\pi$ - $\pi$  stacking. For CR, the mechanism may not be the same as MB because of the opposite electrostatic charge and molecular size. The presence of oxygen-containing functional groups increased electrostatic repulsion instead of electrostatic attraction between anionic dye and negatively charged surface [24].

#### 4. CONCLUSION

Casuarina equisetifolia was converted into activated carbon by KOH and NaOH activation. The influence of different chemical activators was studied and the activated carbon from KOH activation shows a higher adsorption capacity. The maximum adsorption capacity is 614 mg/g for MB and 340 mg/g for CR. MB is more favourably adsorbed than CR by activated carbons. Adsorption of dyes is mainly governed by molecular size and electrostatic charge. This concludes that the activated carbons can be used as adsorbent for the removal of MB and CR from water.

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