Adsorption of Acid Dye on Activated Carbon Prepared from Water Hyacinth by Sodium Chloride Activation

Panupong Tarapitakcheevin, Panomchai Weerayutsil, and Kulyakorn Khuanmar

Abstract— *The adsorption of acid dye (AB80) onto the prepared adsorbents from water hyacinth, Hyacinth Black Carbon (HBC) and Hyacinth Activated Carbon (HAC), were investigated. Batch isotherm studies were carried out under varying experimental conditions of contact time, temperature, and pH. The adsorption efficiency study was also compared to the Commercial Activated Carbon (CAC). The study results indicated that the prepared adsorbents from hyacinth, HBC and HAC, could be substantially used for the adsorption of acid dye (AB80) as compared with the commercial activated carbon, CAC. The HAC also presented the comparable efficiency to CAC. Base on the Langmuir isotherm, the monolayer adsorption capacity was determined to be 5.75, 56.50, and 100.00 mg/g for HBC, HAC, and CAC, respectively. The* R_L *values showed that all adsorbents were favourable for the adsorption of acid dye (AB80). Base on Freundlich isotherms, the magnitudes of 1/n for Freundlich isotherms were revealed to lie between zero to one, indicating that acid dye (AB80) is favorably adsorbed by all three adsorbents. The results of isotherm adsorption study elucidated that HBC was fitted to Langmuir model with high correlation* (R^2) *of 0.997 while HAC and CAC were well fitted to Freundlich model with favorable correlation* (R^2) *of 0.990 and 0.991, respectively.*

Keywords— **Adsorption, acid dye (AB80), water hyacinth, sodium chloride activation, activated carbon.**

1. INTRODUCTION

Water hyacinth (*Eichhornia crassipes*) is a free-floating perennial aquatic plant and it was introduced to Thailand in 1901 during the reign of King Rama V from Indonesia as ornamental plant. Nowadays, water hyacinth changed itself form the decorated flower to problematic weed due to its fast spread and congested growth (over 60 kg/m^2). The floating mats of water hyacinth obstruct navigation and clog irrigation works. Although water hyacinth is seen as a weed and worthless, there are many researches reported its application for water tretment due to its dominant structure is fibrous tissue which is capable to be an adsorbent for pollutants removal from water [1-5].

Water pollution from textile industry is a challenge problem due to large volume of colored wastewater and its low biodegradability. Effluents discharged from textile industry into recieving water might be toxic to aquatic life, and colored water reduce sunlight transmission through water. Especially when even just 1.0 mg/L of dye concentration in water supply, it could be inappropriate for human consumption [6, 7]. Adsorption is an effective process for removal of contaminants from wastewater. Activated carbon is the most widely used as an adsorbent because of its advantage on high adsorption capacity for both organic and inorganic compounds. The adsorption capacity of activated carbon is usually related to their specific surface area and porosity. In addition, the adsorption property of activated carbon is found to strongly depend on the activation process [8]. Chemical activation has been recognized for the production of activated carbon with high developed porosity. Furthermore, this procedure leads to high yield by activating at low temperture as well [9]. Activating agents used in the chemical process are normally KOH, NaOH, H_3PO_4, $ZnCl_2$, Na_3PO_4, NaCl, $KMnO_4$ for various raw materials to yield for activated carbon [10]. Among of these chemical agents, NaCl shows attractive property because of inexpensive and non toxic.

This study aimed to investigate the possibility of activated cabon prepared from water hyacinth by chemical activation using sodium chloride (NaCl) as an activating agent for removal of color from acid dye in aqueous solution.

2. MATERIALS AND METHODS

2.1 Preparation of adsorbent

Water hyacinth was collected from Sritan Pond at Khon Kaen University, Khon Kaen, Thailand. It was thoroughly washed to remove dirt particles and its spongy inflated petioles (leaf stalks) and separated as a piece to prepare for an adsorbent. Then it was dried in sunlight for a week and dried in an oven at 103 ^{o}C for 24 hours. The dried material was burnt without oxygen at 600 ^{o}C for 2 hours to obtain Hyacinth Black Carbon (HBC). To prepare hyacinth activated carbon (HAC), HBC was chemically activated using 1:1 of NaCl and HBC by weight and followed by carbonization at 800 °C for 2 hours. Then, HAC was washed with distilled water for several times. Both HBC and HAC were crushed to pass a *sieve* with apertures of *125* μm and kept in an airtight container for adsorption studies. To compare the adsorption properties between prepared carbons and Commercial Activated Carbon (CAC), the powder activated charcoal Fluka 0512 supplied from Sigma Aldrich was selected to use in this study.

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2.2 Characterization of the activated carbons

Adsorbent was characterized as a specific surface area (S_{BET}) by the conventional adsorption of N_2 at 77 K (Autosorb I MP, Quantachrome). The morphology of the adsorbents, after being coated with gold, was characterized by SEM (LEO SEM 1450VP, U.K.).

2.3 Preparation of dye solution

The adsorption studies were carried out with color of Acid Blue 80. The acid dye (AB80) was used without further purification. Acid Blue dye has an empirical formula of $C_{32}H_{28}N_2Na_2O_8S_2$, molecular weight of 678.68 g/mol, and its chemical structure of the acid dye is shown in Fig.1. The dye solution of 1000 mg/L was prepared from Acid Blue 80 (dye content 40 %) for single solution which was dissolved in heated deionized water and made up to 1000 ml for the concentrated stock solution. The concentration of acid dye was analyzed by Shimadzu-1601 UV-visible using the maximum UV absorption (λ_{max}) of acid dye solution that was fixed for measuring its color concentrations.

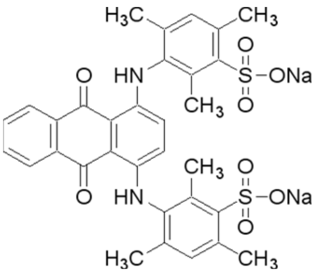


Fig. 1. The chemical structure of Acid Blue 80.

2.4 Effect of contact time

The effect of contact time of three adsorbents (HBC, HAC, and CAC) was investigated at 20 mg/L initial concentration of dye solution. A constant mass 0.1 g of adsorbent materials was mixed with a 50 ml dye solution at neutral pH. The mixture of each batch was constantly agitated as a function of time by orbital shaker at speed of 200 rpm and controlled temperature 25 °C. At various time intervals (5, 10, 15, 20, 30, 40, 50, 60, 90, 120, 180, 240, 300, and 360 minutes), samples were taken and filtered with filter disk 0.45 µm to remove the adsorbent, then the dye concentrations were measured by UV-Vis Spectrophotometer.

2.5 Effect of temperature and pH

The effects of temperature and pH on the amount of dye solution on three adsorbents (HBC, HAC, and CAC) were examined at 60 mg/L initial concentration of dye solution. A constant mass 0.1 g of adsorbent materials was mixed with a 50 ml dye solution and 200 rpm agitation speed for 6 hours. The effect of temperature study, different adsorption temperatures for each batch of the experiment was controlled from 20-50 °C. The effect of the solution pH on the adsorption of dye solution was examined at the controlled temperature of 25 °C. The solution pH range was adjusted between 2 and 10 by adjusting the pH of the solution with 0.1 M HCl and 0.1 M NaOH solutions.

2.6 Adsorption isotherms

The adsorption isotherm studies were determined by contacting a constant mass 0.1 g of adsorbent material with a range of different concentrations of dye solutions from 5, 10, 20, 40, 60, 80, 120, 160, and 200 mg/L and the solutions were adjusted to neutral pH. All experiments were conducted in 250 ml of glass bottle with working volume of 50 ml. The mixture of each batch was constantly agitated by orbital shaker at speed of 200 rpm and controlled temperature at 25 °C. After equilibrium time shaking, water samples were filtered with filter disk 0.45 µm to remove the adsorbent and the water samples were measured concentration by UV-Vis Spectrophotometer. The experimental results were evaluated in terms of fitting with Langmuir and Freundlich model.

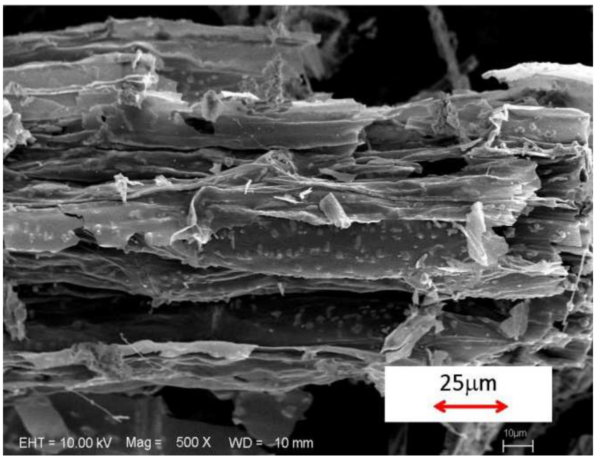
3. RESULTS AND DISCUSSION

3.1 Characterization of adsorbents and adsorbate

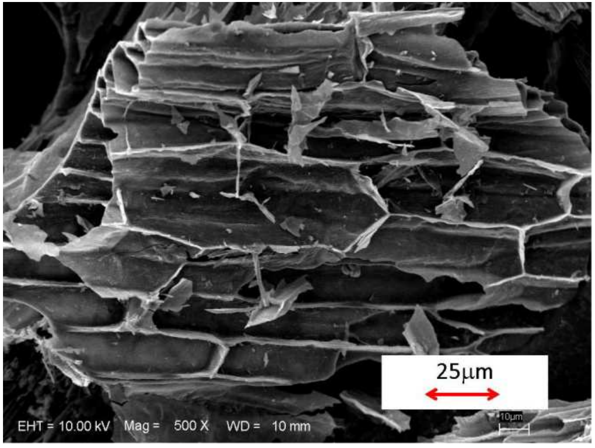
The prepared adsorbents as Hyacinth Black Carbon (HBC) and Hyacinth Activated Carbon (HAC), characterized for the specific surface area (S_{BET}) and morphology are shown in Table 1. Specific surface areas (S_{BET}) of prepared adsorbents without and with activation were found to be 158.22m^2/g and 745.13m^2/g, respectively. Fluka 05120 selected as the representative of Commercial Activated Carbon (CAC), with BET results from other researchers reported that its surface area is in the range of 788-1110 m^2/g.

Table 1. Physical properties of adsorbents

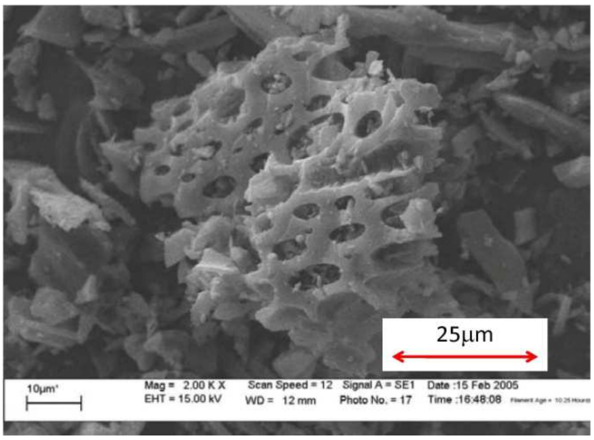
Samples	Surface area (m^2/g)	Total pore volume (ml/g)	Mean radius (nm)	References
HBC	158.22	0.098	2.48	This work
HAC	745.13	0.558	2.99	This work
CAC	1110	-	-	[11]
	930	-	-	[12]
	788	0.74	-	[13]



(a) HBC with magnification 500X



(b) HAC with magnification 500X



(c) CAC with magnification 2000X [14]

Fig. 2. Scanning electron micrograph (SEM) of (a) HBC, (b) HAC, and (c) CAC

The morphology examinations of adsorbent particles using the scanning electron microscopy (SEM) images are shown in Fig.2 (a)-(c). Fig 2 (a) presents the SEM image for HBC, indicating the surface texture was rough and irregular. The SEM image for HAC shown in Fig 2 (b), reveal the texture having the pores within the adsorbent particles with highly heterogeneous and honeycomb shape gabs with different sizes. The commercial adsorbent texture image shown in Fig 2 (c) indicate that CAC appearing to have numbers of microporous structure which offers more adsorption sites. It also indicated that CAC having a good possibility for dye to be trapped and adsorbed into these pore more than HBC and HAC.

The scanning wavelength was observed to locate the maximum absorbance of acid dye (AB80) by Spectrophotometer. The absorption spectra illustrates in Fig.3. The spectra indicated two peaks of λ_{max} that were 584 and 625 nm, so the higher absorbance was selected. The fixed wavelength at λ_{max} 625 nm was used for measuring concentrations of dye solution for all experiments.

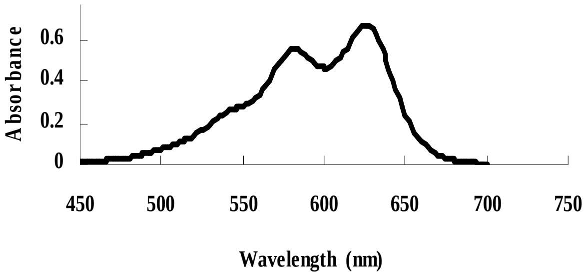


Fig. 3. Absorption spectra for Acid Blue 80 solution.

3.2 Effect of contact time

Various contact time intervals of experiments were performed to optimize the adsorption time at an initial dye concentration of 20 mg/L. The contact time effect of dyes adsorption is presented in Fig.4. The percentage of dye removal by adsorption on HBC, HAC, and CAC were found that HBC shown efficiency of dye removal 28.21 % at the equilibrium of 120 minutes, while HAC and CAC presented favorable removal efficiency of 92.88 % and 97.39 % with the optimum contact time 240 minutes and 40 minutes respectively [15]. Although the HAC and CAC were identified as activated carbon with high surface area, HAC consumed longer time than CAC to achieve the optimum adsorption. This might be due to the surface area and uniformity of pore structure of HAC is less than CAC which is produced for commercial activated carbon.

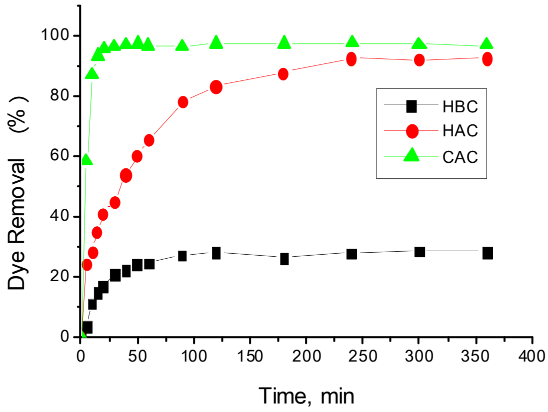


Fig. 4. Effect of contact time of dye removal by HBC, HAC and CAC

3.3 Effect of pH

The pH medium is an important factor in the adsorption process since it controls the magnitude of electrostatic charges. At a high pH solution, the positive charge at the solution interface decrease and the adsorbent surface appears for negative charges. Therefore, the adsorption of cationic dye increases while adsorption of anionic dye decreases. In contrast, at a low pH solution, the positive charges on the solution interface increase and the adsorbent surface appears for positive charges, which results for an increase in anionic dye adsorption and decrease in cationic dye adsorption [7, 16, 17].

According to the general rule, the percentage of anionic dyes adsorption removal will increase at low pH solution, while the percentage of dye removal will decrease at high pH solution. An investigation of the effect of pH adsorption of acid dye was carried out at pH range of 2-10 for 240 minutes. The experimental results illustrated that there was no significant variation in the amount of solute adsorbed on CAC. The adsorption on HAC slightly decreased as increasing pH. Notably, the adsorption on HBC significantly decreased as increasing pH as shown in Fig.5.

The adsorption of both activated carbons, CAC and HAC, seem not to be affected by the charges in the pH of the solution. Similar results were reported for the activated carbon adsorption of tannery dye on which is classified as an acidic dye [18] and Acid Blue (AB25) [16]. An explanation of this behavior might be the presence of both negatively and positively charge function groups in the dye molecules. At low pH solution, more hydrogen ions (H^+) are in the solution making the adsorbent surface more positive, thereby increasing electrostatic attraction between the negative charge SO_3^- anion of the dye and the activated adsorbent. Likewise, at high pH, most favorable adsorption occurred due to interaction of amines groups of Acid Blue (AB80). It is possibly to conclude that both acidic and basic solutions present remarkable adsorption of acid dye on activated carbon which has more active sites (high surface area) due to the presence of both positive and negative groups on Acid Blue (AB80) structure. This substance structure is also known as amphoteric substance [16].

An explanation of HBC adsorption behavior which has lower active sites (low surface area) than others adsorbents, its adsorption followed the general rule. That was a lower adsorption of acid dye at higher pH value while a higher adsorption occurred at lower pH value.

3.4 Effect of Temperature

The effect of temperature on the equilibrium of adsorption of AB80 on HBC, HAC, and CAC was carried out at various temperatures including 20, 30, 40, and 50 °C. The result of this effect is given in Fig. 6. The adsorption of acid dye (AB80) on three adsorbents trended to increase as increasing temperature. Especially, HAC and CAC present a likely increased adsorption capacity at temperature beyond 40 °C.

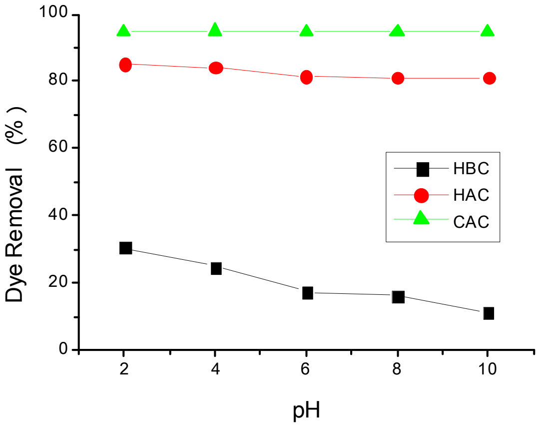


Fig. 5. Effect of pH on acid dye (AB80) adsorption by HBC, HAC, and CAC.

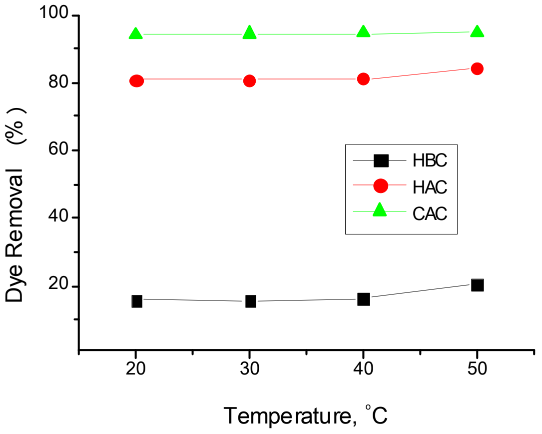
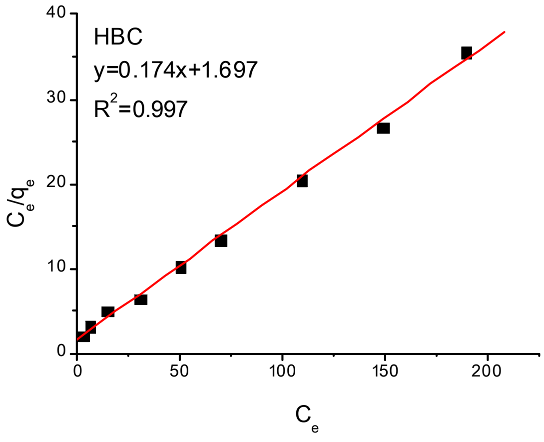


Fig. 6. Effect of temperature on acid dye (AB80) adsorption by HBC, HAC, and CAC

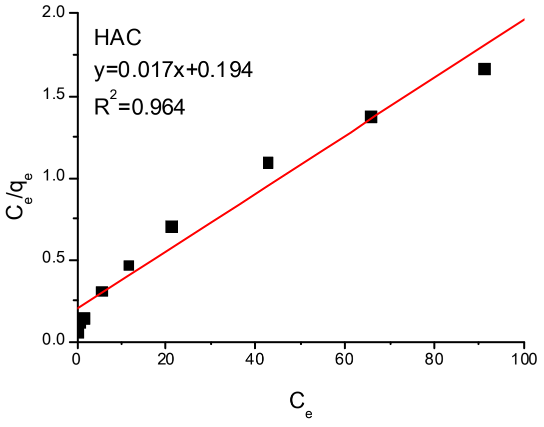
According to the experimental result, the adsorption capacity increased with increasing temperature, so the adsorption was an endothermic process. Because the diffusion process was an endothermic process, the increasing adsorption of dye with temperature might due to the enhance rate of intraparticle of diffusion of the adsorbate. Besides, increasing temperature might also produce a swelling effect within the internal structure of carbons enabling more dye molecules diffuse into carbon [8, 19, 20].

3.5 Adsorption Isotherms

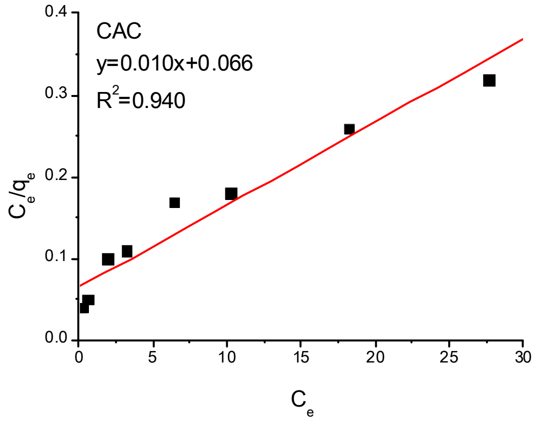
Equilibrium study on adsorption is necessary to establish the most appropriate correlation for the adsorption isotherms. Because the adsorption isotherms not only describe how adsorbates interact with adsorbents but also are basic requirements for design and operation of adsorption systems. The most widely used isotherm equation for the modeling of the adsorption data is Langmuir and Freundlich model [21].



(a) HBC



(b) HAC



(c) CAC

Fig. 7. Langmuir isotherm for acid dye (AB80) adsorption onto (a) HBC, (b) HAC, and (c) CAC.

Table 2. Langmuir Isotherm constants for HBC, HAC, and CAC

Adsorbents	q_m (mg/g)	K_L (L/mg)	R^2	R_L^*
HBC	5.75	0.10	0.997	0.05-0.67
HAC	56.50	0.09	0.964	0.05-0.69
CAC	100.00	0.15	0.940	0.03-0.57

* R_L indicates the shape of isotherm [22].

$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

3.5.1 Langmuir Isotherm

Langmuir equation model is valid for monolayer adsorption onto the adsorbent surface that reflects the limiting adsorption capacity. The model equation is given by Eq (1).

$$q_e = \frac{X}{M} = \frac{q_m K_L C_e}{1 + K_L C_e} \qquad (1)$$

where q_m and K_L are Langmuir parameters related to maximum adsorption capacity (mg/g) and free energy of adsorption (L/mg), respectively. C_e is the equilibrium concentration in the aqueous solution, X is the amount of adsorbate (mg), M is the mass of adsorbent (g), and q_e is the equilibrium adsorption capacity of the adsorbent (mg/g). The linearlized form of Langmuir equation can be written as Eq (2) and (3).

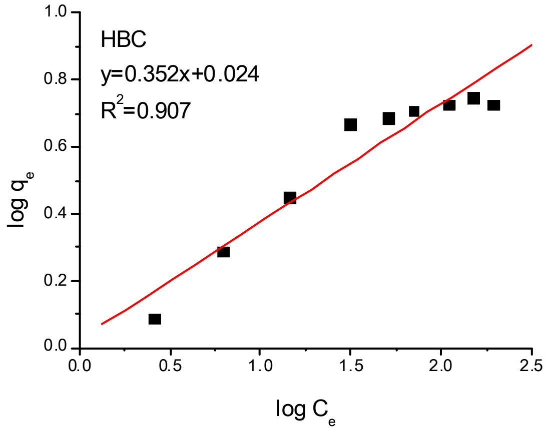
$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L} \cdot \frac{1}{C_e} \qquad (2)$$

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \qquad (3)$$

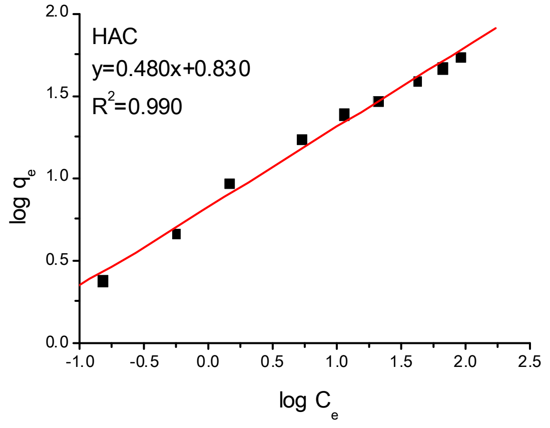
The Langmuir constant q_m and K_L can be calculated by plotting C_e/q_e versus C_e as shown in Fig. 7 (a)-(c). The isotherms of HBC, HAC, and CAC were found to be linear. Table 2 shows Langmuir Isotherm constants for three adsorbents. The maximum sorption capacity of HBC, HAC, and CAC for AB80 was found to be 5.75, 56.50, and 100.00 mg/g, respectively. Nevertheless, the correlation coefficient of HBC was extremely higher than HAC and CAC. This was confirmed that the equilibrium adsorption data of HBC was well fitted to Langmuir model and its behavior also demonstrated that the formation of monolayer coverage of dye molecule on the outer surface of HBC. Furthermore, Langmuir equation can be expressed in term of a dimensionless separation factor (K_L). This factor is defined as Eq. (4) and the calculated values are depicted for the adsorption processes that are favorable or unfavorable for Langmuir model.

$$R_L = \frac{1}{1 + K_L C_0} \qquad (4)$$

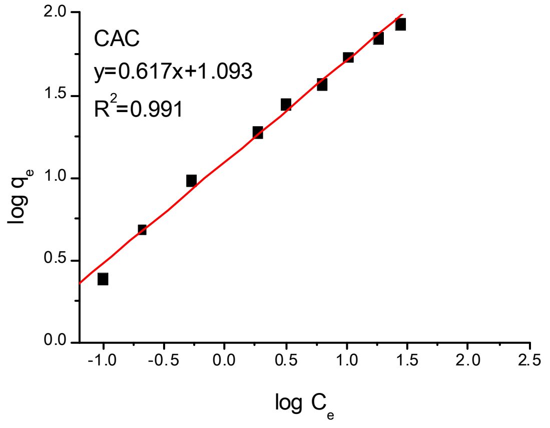
where R_L is a dimensionless separation factor, C_0 is the initial solution concentration and K_L is Langmuir constant (L/mg). Table 2 shows the calculate R_L values of HBC, HAC, and CAC. The values were in the range of 0-1 which confirmed the favorable adsorption of AB80 on the adsorbents.



(a) HBC



(b) HAC



(c) CAC

Fig. 8. Freundlich isotherm for acid dye (AB80) adsorption onto (a) HBC, (b) HAC, and (c) CAC

Table 3. Freundlich Isotherm constants for HBC, HAC, and CAC

Adsorbents	K_F (L/mg)	1/n	R^2
HBC	1.05	0.352	0.907
HAC	6.77	0.480	0.990
CAC	12.39	0.617	0.991

3.5.2 Freundlich Isotherm

The Freundlich model is an empirical equation based on adsorption on the heterogeneous surface and describes reversible adsorption. The adsorption is not restricted to the formation of the monolayer. Likewise, the Freundlich equation predicts that the dye concentration on the adsorbent will increase so long as there is an increased in the dye concentration in the liquid phase [23]. The empirical equation is given as Eq (5).

$$q_e = K_F C_e^{\frac{1}{n}} \qquad (5)$$

where K_F and n are the Freundlich constants that indicate adsorption capacity and adsorption intensity, respectively. The linearized form of Freundlich isotherm can be written as Eq (6).

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (6)$$

The value of K_F and 1/n can be calculated by plotting $\log q_e$ versus $\log C_e$ as shown in Fig. 8 (a)-(c). The logarithmic plots show the deviation from linearity on the Freundlich linear plot for HBC while HAC and CAC were well fitted to the experimental data. Table 3 shows the Freundlich adsorption isotherm constant and correlation coefficients. The values of K_F indicate the degree of the binding capacity between the adsorbent and dye molecules. Thus, the high degree of K_F implies that the affinity between the adsorbent and dye molecules is also high [24]. From the experimental data, the constant K_F of HBC, HAC, and CAC for AB80 were found to be 1.05, 6.77, and 12.39 L/mg, respectively. Likewise the magnitudes of 1/n for Freundlich isotherms were revealed to lie between zero to one, indicating that acid dye (AB80) is favorably adsorbed by all the adsorbents [6].

4. CONCLUSION

The study results elucidated that the prepared adsorbents from hyacinth, HBC and HAC, could be effectively used as an adsorbent for the adsorption of acid dye (AB80). The efficiency of HAC also showed the comparable efficiency to the commercial activated carbon, CAC. The adsorption is an endothermic process due to the adsorption capacity increases with increasing temperature and the adsorption favours acidic pH. The isotherm adsorption study elucidated that HBC was fitted to Langmuir model with high correlation (R^2) of 0.997 while HAC and CAC were well fitted to Freundlich model with favorable correlation (R^2) of 0.990 and

0.991, respectively.

ACKNOWLEDGMENT

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