Carbon – Science and Technology

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RESEARCH ARTICLE

Study of adsorption behavior of methyl orange dye on activated carbon prepared from sugarcane bagasse via chemical activation

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Two activated carbon (AC) samples were produced from sugarcane bagasse using different chemical activation substances (H_2SO_4 and NaOH). The AC sample activated by H_2SO_4 presented enhanced surface properties compared to the NaOH activated sample, with higher specific surface area and porosity determined by BET and SEM analysis were also tested for methyl orange (MO) adsorption. The adsorption efficiency decreased as MO concentration increased. Experimental data including adsorption isotherms and the Gibbs free energy ($\Delta G°$) thermodynamic potential were analysed. Adsorption experimental results agreed well with the Langmuir adsorption isotherm with a high correlation coefficient (R^2) and the chemisorption process formed spontaneously adsorbed monolayers. Therefore, sugarcane bagasse waste was considered as a low cost precursor to prepare AC adsorbents with high pollutant removal efficiency through spontaneously adsorbed monolayers.

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1. Introduction: Contamination of surface water containing organic pollutants including sewage, sludge pesticides and organic dyes is a serious environmental problem [1]. Organic dyes have a negative impact on overall water quality which affects both people and the whole ecosystem. Methyl orange (MO) is an extremely toxic organic dye released into soil and water as industrial waste from the textile and silk painting industries (Batik) [2]. Organic dyes present toxicity to human cells and the central nervous and respiratory systems [3]. Therefore MO dye contained in wastewater must be eliminated before release into the environment. Currently, many methods are utilised to remove organic dyes from aqueous solution including membrane separation, photocatalysis, reverse osmosis and adsorption [4, 5]. The later one offers a cost-effective method for removing various pollutants from water [6]. Recently, activated carbon (AC) prepared from waste biomass of apricot stones cedar sawdust, crushed brick, palm shells, coffee grounds, coconut shells, corn cobs, peach stones, and rice husks has attracted increasing interest as an adsorbent for water and air purification with low-cost precursors, high carbon value and low inorganic content [7 - 11]. In the process of preparation of activated carbon from biomass, many studies have identified the benefits of chemical activation adsorption efficiency over physical activation with higher yields, higher porosity, increased surface area and hence greater adsorption capacity. There are many types of chemical activating agents including zinc chloride ($ZnCl_2$), phosphoric acid (H_3PO_4), aluminum chloride ($AlCl_3$), potassium carbonate (K_2CO_3) and potassium hydroxide (KOH) which change the carbon structure in biomass to form a porous framework during the activation and carbonisation processes [12 - 18].

Here, a local waste by-product as sugarcane bagasse was used to produce AC. The effects of different activating agents (NaOH and H_2SO_4) have been thoroughly investigated. Morphology, porosity and surface properties were analysed using SEM technology and BET N_2 adsorption-desorption, respectively. Adsorption efficiency and adsorption isotherms of AC produced from sugarcane bagasse were determined with regards to the MO adsorption from aqueous solution. Gibbs free energy ($\Delta G°$) was also defined in terms of the thermodynamic adsorption process.

2.   Experimental

2.1 Preparation of activated carbon (AC) from sugarcane bagasse: Sugarcane bagasse was collected from Rong Kluea Market, Pathum Thani Thailand. The bagasse was cleaned with tap water and dried at 120 °C for 6 h before impregnation with chemicals. For comparison, a small piece of sample was soaked in 28 % v/v H_2SO_4, or 28 % v/v NaOH for 24 h. The impregnated samples were then pyrolised at 600 °C for 2 h.

2.2 Adsorption equilibrium experiments: Batch experiments were conducted by varying the AC adsorbent dosage (50, 100, 150, 200, 250 and 300 mg). For each run, 100 mL of 5, 10, 15, 20, 25 and 30 ppm MO concentration was placed in a beaker and mixed with the desired dosage of AC. Each sample was kept in an isothermal condition (30°C) for 120 min to ensure adsorption-desorption equilibrium. During the adsorption process, 5 mL of suspension was removed for analysis at regular intervals using a syringe with a 0.45 μm membrane filter to remove the sediment. The MO concentration remaining at each contact time (t) was determined by measuring the UV-Vis spectra (UV-6100 Double Beam Spectrophotometer) at 466 nm. A calibration curve was plotted to calculate the concentration of MO after adsorption at different contact time intervals (Figure 1).
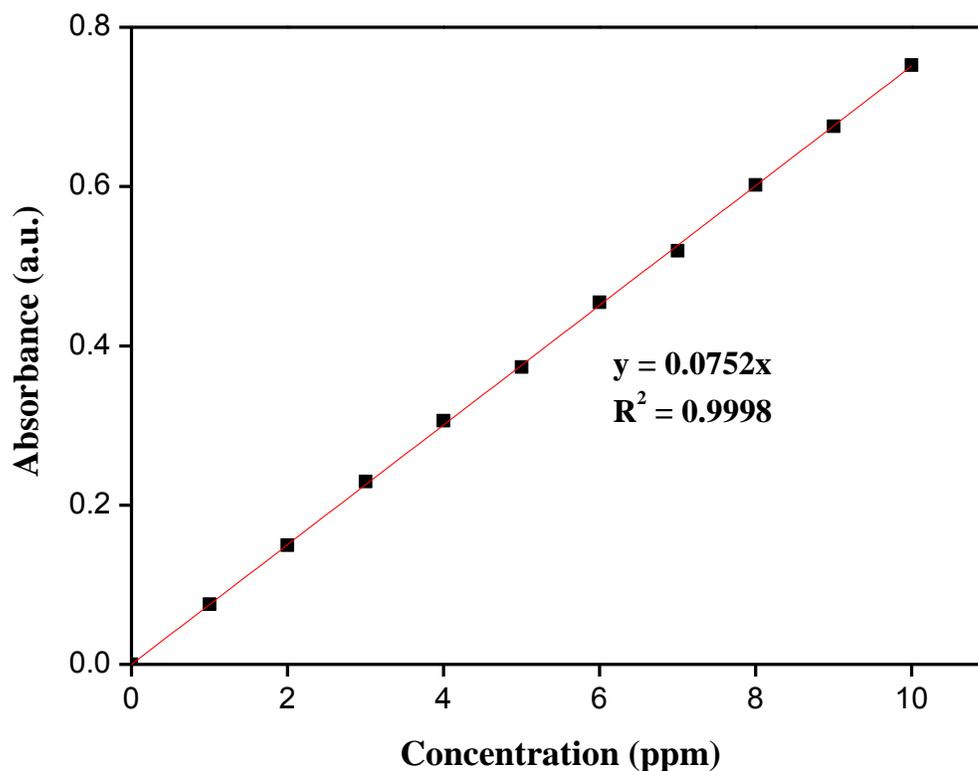

y = 0.0752x
R^2 = 0.9998

Figure (1): the spectrophotometer calibration curve of MO dye at 466 nm.

2.3   Characterizations: A scanning electron microscope (SEM, Leo1455VP) was utilised to study the morphology and porosity of the samples. Surface properties of specific surface area and pore volume were analysed by BET N_2 gas adsorption (Adtosorb 1 MP, Quantachrome).

3. Results and discussion

3.1. Material characterization: BET surface area, pore volume and pore size diameter of AC prepared under NaOH activation were 454.43 m²/g, 0.22 cm³/g and 3.1210 nm respectively, while BET surface area, pore volume and pore size diameter attained under H_2SO_4 activation were 663.18 m²/g, 0.34 cm³/g and 3.1286 nm respectively. Impregnation with H_2SO_4 followed by thermal treatment resulted in an increase in surface area. H_2SO_4 performed as both a chemical activating agent and a template by supporting the decomposition of raw materials during the carbonisation process, preventing tar generation and hence increasing the specific surface area [19]. Average molecular size of MO in aqueous solutions is 2.614 nm in the form of ionic micelles [20], thus MO molecules were able to penetrate the mesopores of the prepared activated carbon with pore size diameter of 3.1286 nm.

Figure (2) shows SEM images of the different samples. The porosity and pore size distribution of AC prepared by H_2SO_4 were higher than AC produced using NaOH, corresponding to the larger surface area obtained from BET analysis. Therefore, AC prepared using H_2SO_4 was found to be a good adsorbent, providing abundant active sites to adsorb dye molecules with high surface area, pore volume and porosity.

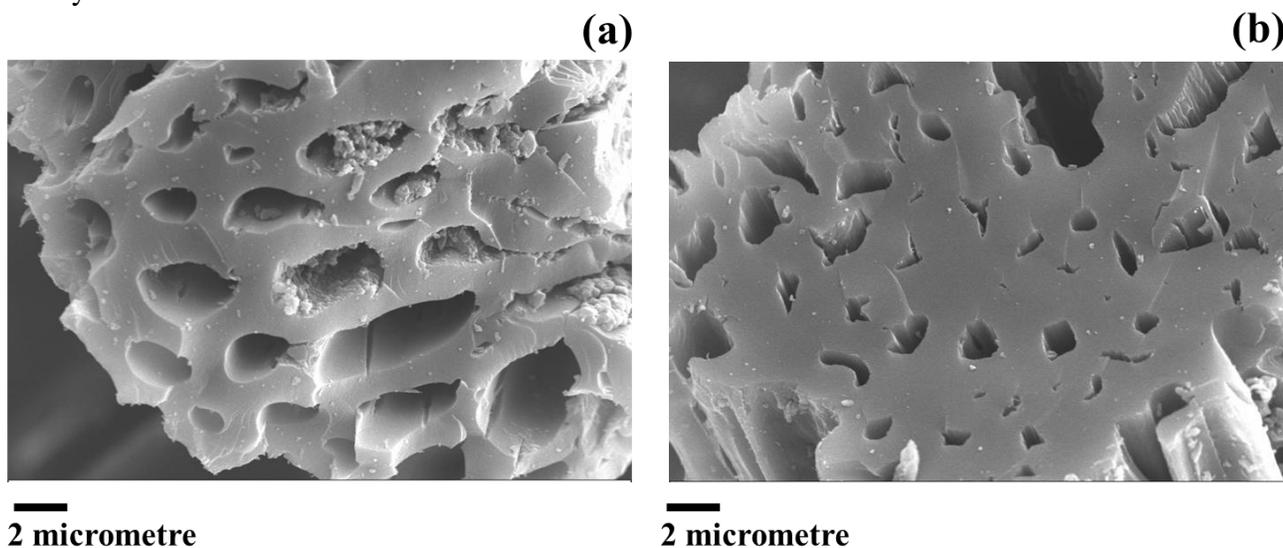**(a)** **(b)**

2 micrometre   **2 micrometre**

Figure (2): SEM images of AC samples activated by (a) H_2SO_4 and (b) NaOH.

3.2 Effect of AC dosage for adsorption efficiency:

To determine the amount of AC prepared using the method above on the adsorption capacity of MO, batch experiments were conducted by varying the AC dosages from 50 - 300 mg with a fixed MO concentration of 5 ppm. Adsorption efficiency increased with increasing AC amounts. MO degradation using H_2SO_4 activated carbon showed higher adsorption efficiency than AC activated by NaOH, corresponding to the higher surface area and porosity determined by BET and SEM. Thus, chemical treatment using H_2SO_4 exposed more sites for MO adsorption onto the AC surface [21] with maximum adsorption at 150 mg which then remained constant. Therefore, an optimal AC dosage of 150 mg was chosen for further experimentation (Figure 3).
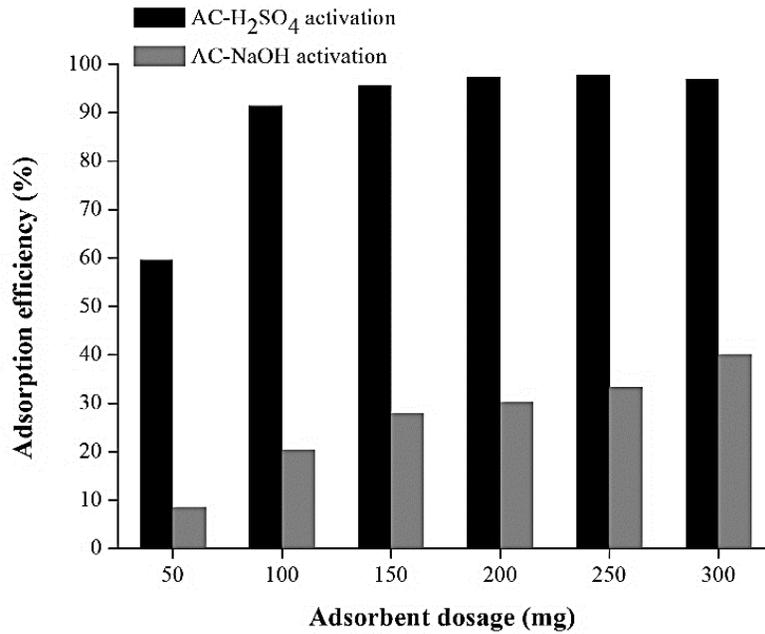
Figure (3): Effect of AC amount on the MO adsorption.
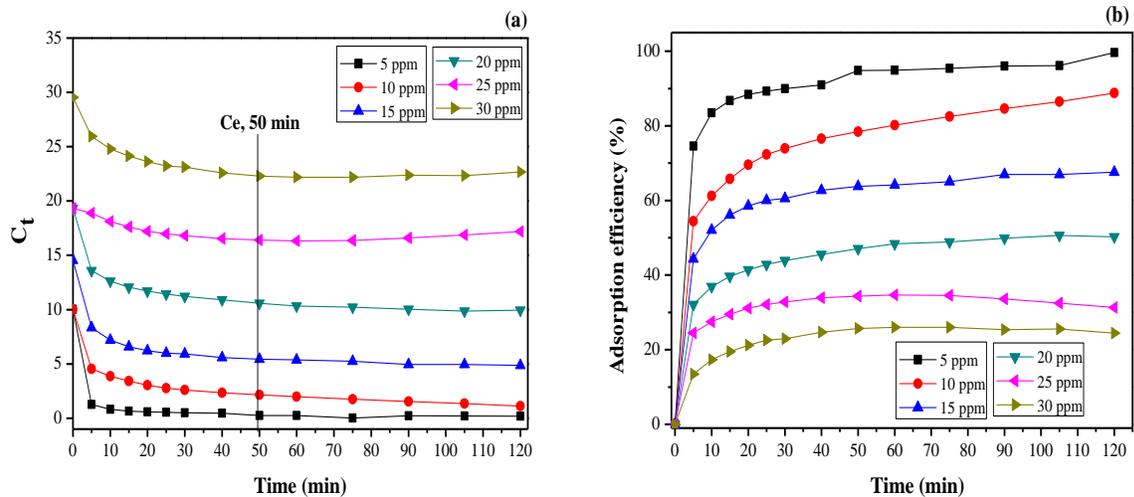
3.3 Initial concentration and contact time:

Figure (4): Initial concentration and contact time (a) C_t and (b) adsorption efficiency. C_t is remaining dye concentration at each contact time (t, min) and C_e is equilibrium dye concentration.

The high porosity of AC impregnated in H_2SO_4 was tested for MO adsorption at different concentrations (5, 10, 15, 20, 25 and 30 ppm). Experiments were conducted until the adsorption capacity reached a constant value (total 120 min). The removal rate increased rapidly in the first 20 min and attained equilibrium within 50 min. There was no significant change with further increase in contact time. The remaining dye concentration (C_t) decreased with decreasing MO concentration from 30 to 5 ppm (Figure 4a) which related to the gradual increase of adsorption efficiency (Figure 4b).

3.4 Adsorption Isotherms:

To explain the adsorption between the adsorbent (AC) and the adsorbate (MO), equilibrium data were evaluated using both the Langmuir and Freundlich models following equations (1) and (2) respectively **[22]**.

$$\frac{C_e}{q_e} = \left(\frac{1}{K_L N_m}\right) + \left(\frac{C_e}{N_m}\right) \qquad (1)$$

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \qquad (2)$$

where N_m is the maximum adsorption capacity with monolayer adsorption, K_L and K_F are the Langmuir and Freundlich constants which corresponded to the quantity of equilibrium adsorption and q_e represents the adsorption capacity at equilibrium which can be calculated following equation (3) [22].

$$q_e = \frac{(C_0 - C_e)V}{W} \qquad (3)$$

where V (L) is the volume of MO solution and W (g) is the weight of AC.

Linearised isotherm models fitted well with the Langmuir equation when comparing the correlation coefficient (R^2) between the Langmuir and Freundlich isotherms (Figure 5). The Langmuir model demonstrated that a monolayer adsorption of MO molecules was formed over a surface of AC adsorbent with no interaction of MO molecules in the plane of the adsorption site surface [24]. In addition, many authors considered the slope 1/n from the linearised Freundlich isotherm plot [25, 26]. They reported that 1/n values approaching zero (1/n < 0.5) referred to monolayer adsorption of the systems while a 1/n value > 0.5 was indicative of multilayer adsorption (Freundlich isotherm). From Table (1), Freundlich constants (1/n = 0.0708, 1/n < 0.5) suggested that MO favored monolayer adsorption by AC and corresponded to the Langmuir model.
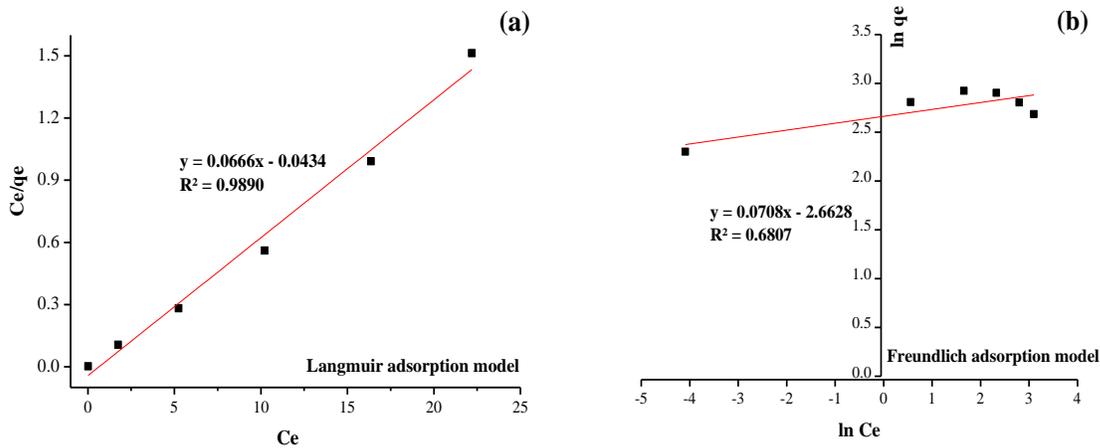

Figure (5): The linearized isotherm models of (a) Langmuir and (b) Freundlich.

Table (1): Adsorption isotherms parameter values.

	R^2	N_m	K_L	1/n	K_F
Langmuir	0.9890	15.015	1.535	-	-
Freundlich	0.6807	-	-	0.0708	14.336

3.5 Gibbs free energy (ΔG°):

As detailed in the literature review, the equilibrium constant or adsorption constant in the Langmuir or Freundlich isotherms can be applied to calculate the change in Gibbs free energy (ΔG°) **[28, 29]**. The relationship between ΔG° of the adsorption process and the Langmuir constant (K_L) is presented by Eq. (4). The ΔG° of MO adsorption on AC adsorbent was determined at -1.08 kJ/mol. Thus, the adsorption processes of MO on the prepared AC in this study was spontaneous in nature **[30, 31]**.

$$\Delta G^\circ = - RT \ln K_L \qquad (4)$$

where T is the reaction temperature (30 ^oC, 303 K) and R is 8.314 J/mol K.

4. Conclusions:

An effective AC adsorbent was successfully prepared from low-cost sugarcane bagasse impregnated with different activating agents including H_2SO_4 and NaOH. AC impregnated in H_2SO_4 effectively removed MO from aqueous solution due to its high surface properties. The adsorption process required only 50 min to reach equilibrium with highest adsorption efficiency recorded at 96 % (5 ppm of MO and 150 mg of AC). The Langmuir isotherm provided the best correlation coefficient $R^2 = 0.9890$, indicating a chemical adsorption with monolayer coverage between the adsorbate (MO) and AC adsorbent. A negative value of ΔG° demonstrated that the adsorption reaction occurred via a spontaneous process.

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