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Kinetics, equilibrium studies and thermodynamics of methylene blue adsorption on *Ephedra strobilacea* saw dust and modified using phosphoric acid and zinc chloride

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ABSTRACT

In this research, three adsorbents, namely, *Ephedra strobilacea* char (ESC), *E. strobilacea* char modified using phosphoric acid (ESP) and *E. strobilacea* char zinc chloride (ESZ) were prepared for the adsorption of methylene blue. Adsorption was studied as a function of pH (2–11), adsorbent dose (0.01–0.1 g), time (1–120 min), initial MB concentration (30–100 mg/L), agitation speed (120–180 rpm) and temperature (298–338 K). From the results obtained it was observed that with the increase in the pH value, the percentage MB removal increases from 48.62, 68.74 and 46.68% to 92.69, 99.71 and 95.33% for ESC, ESP and ESZ adsorbents, respectively. Hence the optimized pH value for ESC, ESP and ESZ is 8, 6 and 9 respectively. Additionally the percentage MB removal increased from 55.2, 56.19 and 58.25% to 95.81, 99.5 and 95.5% for ESC, ESP and ESZ adsorbents, respectively, by increasing adsorbent dose from 0.01 to 0.1 g. Hence the optimized adsorbent dose for ESC, ESP and ESZ is 0.05, 0.07 and 0.05 g respectively. The experimental data were analyzed by the Langmuir, Freundlich, and Temkin isotherms. Results showed that the maximum monolayer adsorption capacity of ESC, ESP and ESZ adsorbents for the adsorption of MB was 31.152, 21.929 and 37.037 mg/g at 318 K, respectively. The kinetic data were fitted to the pseudo-first-order, pseudo-second-order and intraparticle diffusion models. Adsorption of these adsorbents followed Langmuir adsorption isotherm models and pseudo-second-order kinetics. Thermodynamic parameters were evaluated to predict the nature of adsorption. These results indicate the endothermic and spontaneous nature of the adsorption process.

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1. Introduction

Among the various types of pollution, water pollution has attracted the attention of some researchers. Agricultural activities (such as veterinary and aquaculture drugs, the use of pesticides in agriculture, forestry), the industries (such as textile, rubber, leather, paper, plastics, coal, food, petrochemical, pharmaceutical and dye industries), municipal wastewater, other environmental and global changes are the main sources of water pollution [1,2]. These contaminations (such as dyes, heavy metals, fluoride, phosphate, tetracycline, Cyanide compounds, etc.) are very dangerous in environment even at very low concentrations because of their toxic effects, mutagenicity, carcinogenicity and teratogenicity [3–7]. Different kinds of dyes are used in various industries and wastewater from these industries contains a great amount of synthetic and harmful dyes that are released in rivers and environment without proper treatment [8].

Wastewater treatment containing synthetic dyes is one of the major concerns in environmental cleaning. Various technologies such as electrocoagulation [9], photodegradation [10], oxidative degradation [11], and biochemical degradation [12] have been used worldwide for the elimination of synthetic dyes from wastewater to decrease their impact on the environment. Adsorption is a well-known and superior process for dye removal due to its easy operation, high efficiency, low cost, ability to treat concentrated forms of the dyes, and the possibility of reusing the spent adsorbent via regeneration method [13]. Different kinds of low cost adsorbents have been applied for removal and separation of dyes from the waste water. Activated carbon (AC) are known to be more efficient in adsorbing and removal a greater amount of pollutants by the formation of physical and chemical bonds such as waste rubber tire [2], Rosa canina-L fruits [8], rambutan (*Nephelium lappaceum*) peel [14], shells of Macore fruit [15], papaya stem [16], peanut sticks

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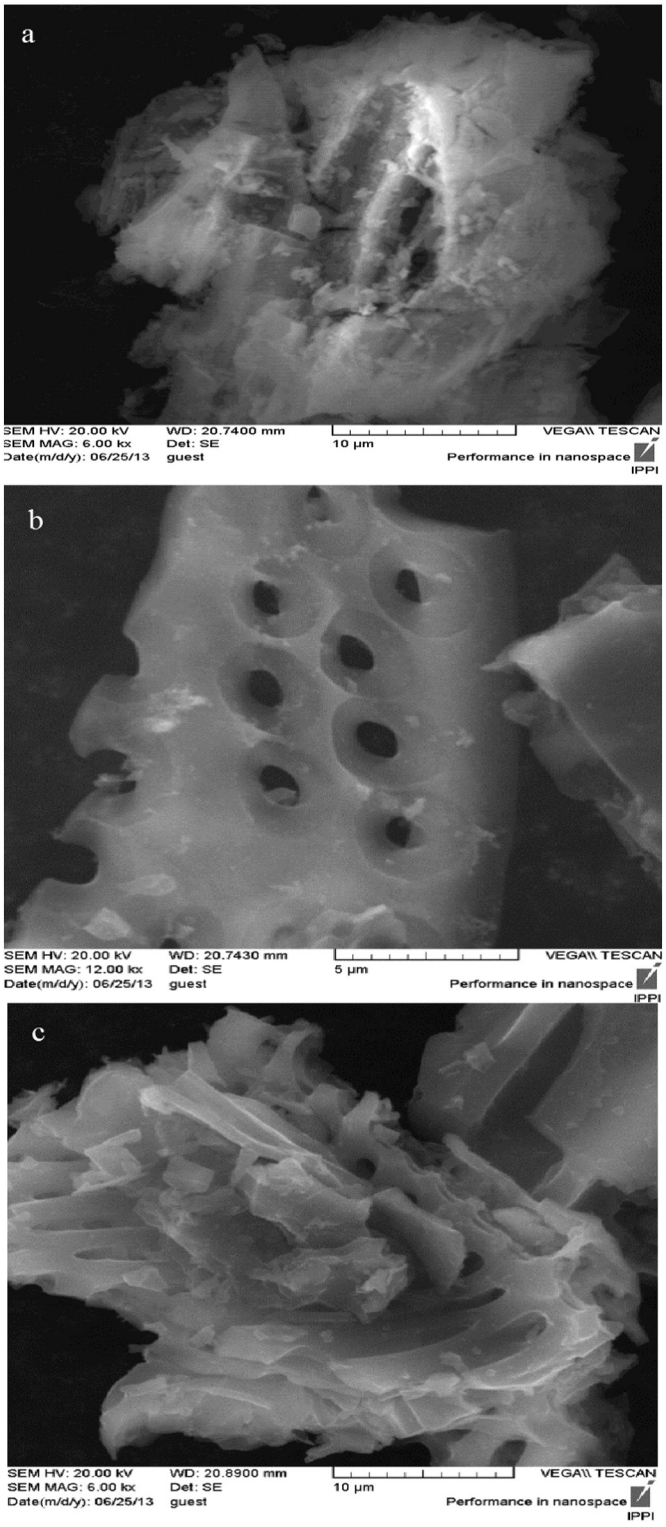

Fig. 1. SEM images of (a) ESC (b) ESP (c) and ESZ.

wood [17]. These physical and chemical bonds can be electrostatic or non-electrostatic ((i) van der Waals forces; (ii) hydrophobic interactions; and (iii) hydrogen bonding) [18]. The preparation of AC from these low cost adsorbents has been made using both physical activation (PhA) and chemical activation (ChA). Activation involves carbonization of a carbonaceous material followed by the activation of the resulting char at elevated temperature. The AC produced by physical activation did not have satisfactory characteristics in order to be used as adsorbents. While the AC produced by chemical activation is carried out in a single step and at lower temperatures, and therefore resulting in a better porous structure. The most common chemical agents in ChA are $ZnCl_2$, KOH, H_3PO_4 and less K_2CO_3 [19]. From the results, it is very obvious that the two-stage process (two-step chemical activation) was more effective, as it gave ACs with higher porosity. In fact, this two-stage process, gave the higher surface area from all the studies being researched [20–24].

One of the most used basic and cationic dye is Methylene blue (MB) that is widely used for coloring paper, dyeing cottons, wools and temporary hair colorant. MB has formula of $C_{16}H_{18}N_3SCl$, CAS number 61734, FW = 319.86 g/mol with λ_{max} of 656 nm [25].

In the present research, adsorption of aqueous MB onto *Ephedra strobilacea* char (ESC) and *E. strobilacea* char modified using phosphoric acid (ESP) and zinc chloride (ESZ) were synthesized. The kinetics, equilibrium isotherms and thermodynamic of MB adsorption on ESC, ESP and ESZ are also studied.

2. Materials and methods

2.1. Reagents

The chemicals used in this research were $NaHCO_3$ (Merck), NaOH (Merck), HCl (Merck), H_3PO_4 (Merck), KOH (Merck), $ZnCl_2$ (Merck) and Methylene blue of analytical reagent grade. 1000 mg/L of MB as stock solution was prepared by dissolving 1000 mg of MB dye in 1000 mL deionized water. The stock solution was diluted with deionized water to the desired MB concentrations. After adsorption, the supernatant liquids were filtered with Whatman filter paper number 42.

2.2. Instrumentation

The structure of the ESC, ESP and ESZ was examined using the scanning electron microscope (SEM) (model: VGA2TESCAN) under an acceleration voltage of 20 kV with a high resolution of 3.0 nm. The pH measurements were made with a pH meter (model: Sartorious PT-LOP, German). The samples were dried in program controller JEIO TECH (model: CF-02G KOREA). Agitation of the system was carried out on a thermostat-cum-shaking assembly (model Behdad/ROTATOR 2002). The residual MB concentration in the aqueous solution was determined by using a SHIMADZU Model AA-680 UV/Vis spectrophotometer.

2.3. Preparation of adsorbents

2.3.1. Preparation of E. strobilacea char (ESC)

E. strobilacea saw dust was cleaned with tap water and rinsed with distilled water and then were boiled in deionized water three times for 5 h. After that, the boiled samples were dried at 105 °C in an air oven for 5 h in order to evaporate all the moisture. Subsequently, they were crushed and sieved to fine particles. Afterwards, sample was heated to the activation temperature of 450 °C for 5 h. Finally, the char sample was crushed and sieved to the desired particle size (<0.125 mm).

2.3.2. Preparation of E. strobilacea char modified using phosphoric acid (ESP)

Desired weight of ESC impregnated with 95% H_3PO_4 (ESC/H_3PO_4 weight ratio of 1:1) and was activated for 48 h and then was dried at 105 °C for 60 h in the air oven. The acidic sample was heated to the activation temperature of 450 °C for 5 h. Then, the activated carbon was washed in 1 M KOH, 0.1 M $NaHCO_3$ and NaOH solution until the pH of the activated carbon reached 6–6.5. After that, they were washed with distilled water. The activated carbon was dried at 105 °C in an air oven for 17 h and then crushed and sieved to the desired particle size (120 mesh).

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