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Production of activated carbons from waste carpets and its application in methylene blue adsorption: Kinetic and thermodynamic studies

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Asaad F. Hassan[a,b,*], Hassan Elhadidy[b]

[a] Chemistry Department, Faculty of Science, Damanhour University, Damanhour, Egypt
[b] Central European Institute of Technology, Institute of Physics of Materials, Žižkova 22, CZ 61662 Brno, Czechia

A B S T R A C T

This work reports synthesis of three H_3PO_4-activated carbons from waste carpets (pre-and/or post-consumer wastes) with different weight ratios of solid waste: H_3PO_4 (1:1, 1:2 and 1:3) to obtain CP11, CP12 and CP13, respectively. Thermal, textural and chemical characterizations were used to compare between the properties of the prepared samples. TGA confirms thermal stability of the prepared adsorbents compared with carpet sample and ash content increases with increasing the percentage of H_3PO_4. SEM confirms the presence of nanopores created with chemical activation. Nitrogen adsorption showed that surface area in the range 330–953 m^2/g with pore radius in the range 1.40–1.48 nm. FTIR, pH_{PZC} and base adsorption capacities confirm the presence of acidic surface function groups. It was observed that the optimum conditions for methylene blue adsorption were confirmed at adsorbent dosage of 8 g/L, pH8, equilibrium time about 12 h and the adsorption follow pseudo-second order kinetic model. Maximum adsorption capacities calculated using Langmuir model were 403.2, 704.2 and 769.2 mg/g for CP11, CP12 and CP13, respectively at 35 °C. Thermodynamic parameters indicate the physical and spontaneous nature of adsorption. Maximum desorption efficiency of methylene blue was confirmed by ethanol solvent and increased with temperature.

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1. Introduction

Wastes are materials that play a main role in the issue of climate change, especially that its disposal produces several greenhouse gas emissions which are responsible for global climate change [1]. Carpets are complex composite materials often made from synthetic and natural materials with high carbon content. Carpets consist of four layers: face fiber, primary backing, adhesive, and secondary backing [2]. The first layer or the face fiber layer which made from nylon, polypropylene, or wool represents the main component in the carpet waste [3]. Waste carpets contain post-consumer waste where the average life expectancy of carpets ranged between 8 and 12 years [4] and pre-consumer waste coming from cuts or trimmings which represents about 12% of the total production [5]. In UK according to Carpet Recycling about 400,000 tons of waste carpets are sent annually to landfill [6]. There are many options for carpet waste (i) carpet waste to energy through incineration and represent about 58% from waste

processing. (ii) The use of carpet waste for equestrian applications and represent about 35%, (iii) plastic processing and act as 4% from carpet waste processing. (iv) Fiber reprocessing which act as 2% only from the total carpet waste processing and (v) carpet waste reuse which represent only 1% [7]. The conversions of solid waste into activated carbons take attentions from many researchers in the past decades. The only trial in preparation of KOH-activated carbon from waste carpet for gas adsorption was achieved by M. Olivares-Marine [3,8].

There are many methods to remove pollutants from aqueous medium such as, flocculation and coagulation [9], precipitation [10], degradation (photo, oxidative, and biochemical) [11–13], and adsorption [14]. Adsorption has been proven more attractive and effective for organic and inorganic pollutants removal where, it is simple, cheap, fast, effective and selective after adsorbent modification. Methylene blue is a basic cationic dye and considered as the most commonly used dye in industry [15]. Methylene blue has various dangerous effects on animals and human where, it can cause vomiting, nausea, and heart rate increasing [16].

The aim of the present work focuses on the conversion of solid waste carpets into H_3PO_4-activated carbons with different ratios of carpet weight: weight of H_3PO_4. The synthetized activated carbon samples will be characterized by thermal analysis, textural and

* Corresponding author at: Chemistry Department, Faculty of Science, Damanhour University, Damanhour, Egypt.
E-mail address: asmz68@yahoo.com (A.F. Hassan).

chemical characterization. The optimum conditions for methylene blue adsorption are tested for the effect of adsorbent dosage, time, pH, temperature and initial dye concentration. Thermodynamic and kinetic studies will be considered to investigate the nature of MB adsorption on the surface of activated carbon. Methylene blue desorption using different solvents at different temperatures will be carried out.

2. Materials and methods

2.1. Materials

Post-consumer waste was collected from private house. H_3PO_4, methylene blue (MB), ethanol, propanol, carbon tetrachloride, and benzene were purchased from Alfa Aesar Co. All of the other chemical reagents used in the experiments are of analytical grade were purchased from El-Nasr for pharmaceutical and chemical industry Co., Egypt. All chemicals were used without further purification.

2.2. Preparation of activated carbon

Carpets were cut manually into pieces (about 2×2 cm) with average weight of 1.9 g/piece. A certain weight of dried carpet pieces was impregnated with phosphoric acid solution for 24 h at room temperature with ratios 1:1, 1:2 and 1:3 (weight of dried carpet: weight of H_3PO_4) to obtain the designated activated carbon samples CP11, CP12 and CP13. After soaking the carpet in H_3PO_4, the solid mixture is dried at 110 °C for 24 h followed by gentle grinding. The grinded solid is activated in stainless steel tube (60×5 cm) in presence of nitrogen gas, using tubular muffle with temperature rate 10 °C/min up to 700 °C and kept at the final temperature for 4 h. Cooled at room temperature and washed with distilled water several times till neutral filtrate and dried at 110 °C for 24 h. The dried sample was sieved and stored in stoppered tube with mean particle diameter of 1.5–1.7 mm (8–20 mesh size).

2.3. Characterization of activated carbon samples

2.3.1. Thermal characterization

Thermogravimetric curve was performed to identify the thermal decomposition of precursor, CP11, CP12 and CP13 using differential thermal analyzer ShimadzuDTA-50, Japan under heating rates of 10 °C/min. Weight loss on drying was determined for raw material and activated samples by weighing 0.5 g of the sample and heating for 24 h in oven at 110 °C till constant weight. Ash content for adsorbents was determined by burning a 1.0 g of sample in a crucible at 650 °C till a constant weight is attained and the residual% ash content was determined in relation to the initial sample weight (Eq. (1))

$$\%Ash \ content = \frac{weight \ ofash(g)}{1.0} \times 100 \tag{1}$$

2.3.2. Textural characterization

Scanning electron micrographs for CP11, CP12 and CP13 were obtained using JEOL 6400. Prior to the measurement, the sample was dried at 110 °C for 4 h. The sample was coated with a thin layer of gold for charge dissipation. Specific surface area (S_{BET}, m^2/g), total pore volume (V_T, mL/g), and pore radius ($\bar{r}$, nm) for the investigated carbon samples were determined through nitrogen adsorption at -196 °C using NOVA2000 gas sorption analyzer (Quantachrome Corporation, USA) system. Average pore radius ($\bar{r}$,

nm) was calculated using the following equation:

$$\bar{r}(nm) = \frac{2V_T(mL/g)}{S_{BET} \ (m^2/g)} \times 10^3 \tag{2}$$

where, V_T is the adsorbed volume near saturation, i.e. at $p/p^o \approx 0.95$ multiplied by the factor 15.5×10^{-4}.

2.3.3. Chemical characterization

Point of zero charge was determined by: initially, 40 mL of NaCl (0.01 M) was placed in several closed flasks. The pH within each flask was adjusted to a value between 2–12 using 0.01 M NaOH and/or 0.01 M HCl. Then, 0.14 g of activated carbon sample was added to each flask, the flasks were agitated for 48 h, the final pH was then measured. The pH_{PCZ} was defined as the point where the curve pH_{final} versus $pH_{initial}$ crossed the line $pH_{final} = pH_{initial}$ [15]. Base neutralization capacities were determined by the adsorption of NaOH, Na_2CO_3, and $NaHCO_3$ by shaking 0.25 g of adsorbent with 50 mL of 0.1 N base solution in a closed glass bottle for 48 h and 10 mL of supernatant was titrated against 0.1N HCl solution in presence of suitable color indicator. Fourier transform infrared spectra were recorded on a Mattson 5000 FTIR spectrometer in the range between 4000 and 400 cm^{-1}.

2.4. Adsorption of methylene blue

Batch equilibrium adsorption experiments were performed at 25 °C by mixing a 0.05 g activated carbon with 50 mL solution (pH 7.5) of definite concentration of methylene blue (50–800 mg/L) in 250 mL Erlenmeyer flask, and were shaken for 20 h to reach equilibrium. Then the mixture was filtered and the residual methylene blue concentrations were measured at a wavelength of 662 nm using UV–vis spectrophotometer Unicam UV/VIS 5625. Adsorbed amount q_e (mg/g) was calculated as follows:

$$q_e = \frac{(C_o - C_e)V}{W} \tag{3}$$

where, C_o and C_e (mg/L) are the concentrations of methylene blue solution before and after adsorption, V is the volume of solution (L), and W is the mass (g) of dried activated carbon.

The effect of adsorbent dosage on uptake was determined by shaking 2, 4, 6, 8, 10, and 12 g/L of activated carbon with 50 mL of 700 mg/L methylene blue. The mixtures were shaken at 25 °C and pH 7.5. The reduction in methylene blue concentrations (removal%) was calculated.

Effect of pH was carried out via batch adsorption process using methylene blue solutions with pH ranged between 2 and 12, 700 mg/L as initial concentration, 50 mL volume and 0.05 g of the activated carbon samples.

Effect of contact time was investigated by contacting 0.1 g of the adsorbent, 100 mL volume of 700 mg/L MB solution with pH8 and the residual concentration was determined after certain time intervals (0.25–20 h). The adsorption capacity at time t; q_t (mg/g) was calculated using:

$$q_t = \frac{(C_o - C_t)V}{W} \tag{4}$$

C_t (mg/L) is the liquid-phase concentration of MB at time t.

Effect of temperature was examined by methylene blue adsorption at two different temperature 25 and 35 °C at pH of 8.0 and 8 g/L as adsorbent dosage.

2.5. Desorption studying of methylene blue

Desorption of MB from the surface of activated carbon using different solvents was investigated by; 0.2 g of CP13 pre-loaded with MB was shaken with 100 mL of pure solvent (distilled water,