



Preparation and characterization of surface functionalized activated carbons from date palm leaflets and application for methylene blue removal



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ABSTRACT

The objective of this research is to produce acidic, basic and hydrophobic activated carbon and to test them for methylene blue removal. Activated carbon (AC) was prepared from date palm leaflets using KOH activation followed by nitric acid oxidation to produce oxidized activated carbon (OAC) which possesses acidic surface. Basic activated carbons (BACs) were prepared via surface functionalization of OAC using ethylene diamine (EDA) and propylene diamine (PDA) producing basic activated carbons BAC-EDA and BAC-PDA, respectively. Hydrophobic activated carbons (HACs) were also prepared via OAC surface functionalization using ethylamine (EA) and aniline (AN) producing hydrophobic activated carbons HAC-EA and HAC-AN, respectively. AC surface area is high (823 m²/g) with microporosity domination, however, after oxidation and surface functionalization, both the surface area and surface microporosity decrease tremendously. FTIR spectra show that —COOH group on OAC almost disappeared after surface functionalization. Methylene blue adsorption follows pseudo second order model more than pseudo zero or pseudo first order models with faster adsorption on HACs. Equilibrium adsorption data fit the Langmuir model more than the Freundlich model with HAC-EA showing the largest adsorption capacity of methylene blue. Dominating adsorption forces of methylene blue most probably are hydrophobic for HACs, hydrogen bonding for BACs, electrostatic attraction for OAC and van der Waals forces for AC.

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1. Introduction

Activated carbon is considered as the most commonly used adsorbent in water and wastewater treatment worldwide [1]. Charcoal was used as early as 1500 B. C. for medical and purification purposes [2]. Carbon filters were used in England in the mid-19th century in the treatment of drinking waters for the removal of odors and tastes [3]. Activated carbon possesses different functional groups on its surface including carboxyl, lactone, phenol, carbonyl and quinones. The adsorption properties of activated carbon are strongly influenced by the type and amounts of functional groups on its surface. The presence of functional groups on carbon surface depends on the precursor materials, preparation conditions and activation methods used [4]. In general, activated carbon is more efficient for the removal of organic compounds than metal ions, nitrate, fluoride, and other inorganic pollutants from aqueous solutions. Research efforts have

continued to improve and diversify the carbon surface functionality via different treatment methods to enable activated carbon to remove efficiently specific pollutants from wastewater [5]. Surface modification of activated carbon has been carried out chemically, physically and biologically after preparation [6–9]. Generally, London dispersion forces or van der Waals adsorption forces dominate the adsorption processes of non-modified activated carbon for the removal of organic compounds from aqueous solutions [10]. Surface functionalization can introduce other dominating adsorption forces such as H-bonding, electrostatic interaction and hydrophobic bonding. Activated carbon surface can be tailored to utilize such powerful adsorption forces via chemical modification. In previous studies, activated carbon was modified to enhance its adsorption capacity towards some pollutants. Surface oxidation of carbon is generally employed to increase the surface acidic property and its hydrophilic nature. Oxidation with HNO₃, persulfate and hydrogen peroxide [11] has increased the surface acidic functionality and improved heavy metal removal [11]. Activated carbon was also modified via its impregnation with metals such as silver [12], aluminum [13] and copper [14] to obtain carbons with high adsorption capacities. Cationic surfactant

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(cetyltrimethylammonium chloride (CTAC)) was employed to modify granular activated carbon for bromate enhanced removal [15]. Activated carbon modified with tetrabutyl ammonium iodide [5] showed improved cyanide removal from water. Surface modification of activated carbon with sodium diethyl dithiocarbamate [5] has also improved the removal of some heavy metals. Surface modification with ammonia has increased the adsorption capacity of phenol [16] and 2,4-dichlorophenol [17]. The impregnation of activated carbon with aluminium nitrate solution, followed by calcinations in an inert atmosphere led to improved fluoride removal [18]. Surface modification using ethylene diamine showed enhanced removal of Cr(VI) from aqueous solution [19]. Activated carbon modified with tris (hydroxymethyl) amino-methane was used for selective separation of Au(III) [20]. Activated carbon treated with nitrogen in microwave has shown enhanced removal of methylene blue [21]. Surface functionalized dehydrated carbon with ethylene diamine showed improvement in the sorption of Zn(II) and SO_4^{2-} from aqueous solution [22].

Date palm leaflets, agricultural waste, are produced in Oman in large quantities with a rate of ~180 000 ton per year with no actual use [23]. In this study, AC was prepared from Omani date palm leaflets using KOH activation. After oxidation, OAC surface was functionalized to produce basic and hydrophobic activated carbons. The different activated carbons were surface characterized and tested for methylene blue adsorption in terms of kinetics and equilibrium.

2. Experimental methods

2.1. Materials

All chemicals used were of analytical grade. Dry date palm leaflets (*Phoenix Dactylifera* L.), collected from a local farm in Muscat, were carefully washed with deionized water to remove dust and other surface impurities. The leaflets were left to dry in open air at room temperature to constant weight. Clean dry leaflets were cut to small pieces (1 cm length) before use in carbon preparation.

2.1.1. Activated carbon preparation

~ 25 g of clean dry leaflets were charred in a carbon steel tube (internal diameter 5.1 cm and length 61 cm) that was heated in a tube furnace (GSL-1100X-110 V, MTI Corporation, USA) under nitrogen atmosphere at 500 °C for 2 h. The char was impregnated in saturated KOH solution in a weight ratio of 1:3. The mixture was left in the oven (Hobersal Mon X B2-125 furnace, Hobersal, Spain) overnight at 120 °C before being transferred to the tube furnace described above. The temperature was raised from room temperature to 550 °C in a heating rate of ~8.6 °C/min and was kept at 550 °C for 1 h under nitrogen for activation. AC produced was washed thoroughly with deionized water to remove residual alkalinity. To keep the acidic functional groups on the carbon in H-form, AC was washed with 0.1 M HCl followed by deionized water until no acidity was detected in wash water. AC was left to dry at 120 °C until constant weight was obtained. After cooling in a desiccator and grinding, a size range between two sieves of 1.19 mm and 0.25 mm was selected for characterization and adsorption experiments.

2.1.2. Surface modification of activated carbon

AC surface was heated with concentrated HNO_3 (1 g AC: 10 mL acid) at 80 °C to almost dryness to produce OAC that was washed thoroughly until no acidity was detected in wash water. OAC was dried at 120 °C until constant weight was achieved. OAC surface

was functionalized to produce basic activated carbons (BACs) as follows. 15 g of dry OAC was allowed to react with 25% thionyl chloride in toluene (100 mL) under reflux for 6 h at 70 °C. During this stage, surface carboxylic groups were converted to acetyl chloride groups. The carbon was left to dry in the oven at 85 °C for 2 h and the carbon product was allowed to react with 100 mL 0.75 M 1,2-diaminoethane (ethylene diamine, EDA) or 1,3-diaminopropane (propylene diamine, PDA) at 90 °C under reflux for 24 h. By the end of the reaction, nitrogen-containing functional groups were immobilized on the carbon surface via amide coupling. For the preparation of hydrophobic activated carbons (HACs), 15 g of dry OAC was allowed to react with 50% thionyl chloride in toluene under reflux for 2 h at 70 °C. The product was allowed to cool and the solvents were dried using rotary evaporator. After evaporation, the product was immediately mixed with 100 mL of ethylamine (EA) or aniline (AN) and the mixture was kept at 90 °C for 2 h under reflux. By the end of the functionalization steps for both types of surface functionalized carbons (BACs and HACs), the carbons were purified via Soxhlet extraction using 150 mL of acetone for 6 h followed by washing with deionized water. Further washing using 2 M HCl was carried out to remove residual amines from carbon surface. Finally, the carbon was thoroughly washed with deionized water to remove residual acid. The carbon was allowed to dry at 70 °C in an oven under vacuum until constant weight was reached. Surface functionalization using EDA and PDA produced BACs designated as BAC-EDA and BAC-PDA, respectively. For hydrophobic carbons, surface modification using EA and AN produced HACs namely HAC-EA and HAC-AN, respectively. A schematic representation of the functionalization processes is presented in Fig. 1.

Physico-chemical characterization

Surface area of activated and modified activated carbons were determined using ASAP 2020 instrument (Micrometrics, USA) via nitrogen adsorption at 77 K. Degassing was carried out for 4 h at 200 °C for AC and OAC, and at 70 °C for 8 h under vacuum (0.1 atm) for other functionalized carbons. Higher degassing temperature for surface functionalized carbons was avoided to protect their surface structure from being destroyed. Scanning electron microscopy (SEM) was utilized to investigate surface morphology of carbons by a JEOL/EO JSM 5600 scanning electron microscope (Jeol, Japan) at a 20 kV accelerating voltage. Energy dispersive x-ray microanalysis (EDX) of carbon surface was carried out using JEOL/O JSM 5600 editor energy disperse analysis system (Joel, Japan). CHN analysis was carried out using Euro EA 3000 elemental analyzer (UK) with acetanilide as a standard. Apparent density was determined using standard method [24]. X-ray powder diffraction was carried out using a Philips PW 1830 generator with a Philips PW 1050 powder goniometer (Philips, USA) using copper $K\alpha$ as the incident radiation. Infrared analysis was carried out using FT-IR spectrometer (Spectrum BX, Berkin Elmer, Germany) for carbons after drying for 2 h (AC and OAC at 120 °C and other carbons at 70 °C under vacuum). Thermogravimetric analysis was carried out using SDT Q600 Simultaneous DSC-TGA apparatus (TA instruments, USA). Heating was conducted under nitrogen with a flow rate of 100 mL/min and a heating rate of 20 °C/min from room temperature to 800 °C. Zero point of charge (pH_{zpc}) for carbons was determined following the procedure of Moreno-castilla et al. [25]. Base neutralization capacity was determined using Boehm titrations [26]. The basic sites on carbons were determined as follows. 0.1 g of carbon was mixed with 50 mL HCl (0.1 M) and the mixture was left for 48 h under agitation. Aliquots of residual acid were analyzed using standardized 0.1 M NaOH. Cation exchange capacity (CEC) was determined following a standard method [27]. Zeta potential was measured as a function of pH using SurPASSTM electrokinetic analyzer (UK). ~0.05 g of carbon (1.19–0.25 mm size)

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