Advanced Powder Technology xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Advanced Powder Technology

journal homepage: www.elsevier.com/locate/apt

Original Research Paper

Role of optimization parameters in the production of nanoporous carbon from mandarin shells by microwave-assisted chemical activation and utilization as dye adsorbent

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ARTICLE INFO

Article history:
Received 30 November 2017
Received in revised form 15 May 2018
Accepted 18 May 2018
Available online xxxx

Keywords:
Mandarin shell
Nanoporous carbon
Microwave-assisted chemical activation
Characterization

ABSTRACT

In this study, mandarin (*Citrus reticulata*) shells (MS) were used as a new precursor material for preparation of nanoporous carbon by chemical activation method with H_3PO_4 in the presence of microwave radiation. The obtained nanoporous carbon (MNC) was characterized using nitrogen adsorption-desorption isotherms, scanning electron microscopy, powder X-ray diffraction, X-ray photoelectron spectroscopy, Raman spectroscopy, Fourier transform infrared spectroscopy and Boehm titration analysis. When using impregnation ratio of 2.0 at 500 °C for 1 h, specific surface area of prepared MNC reached the maximum value, which is 1021 m^2/g. Pore properties of MNC were strongly influenced by impregnation ratio, activation temperature and activation time. For industrial and environmental applications, MNC was tested towards the removal of basic blue 9 (BB9) and acid yellow 36 (AY36) dyes in aqueous media and compared with other carbon adsorbents. The high sorption capacities were 294 mg/g for BB9 and 417 mg/g for AY36. The results indicate that MNC could be regard as a valuable adsorbent to treatment dye pollutants.

1. Introduction

Nanoporous carbons (NCs) are a group of established, universal and versatile adsorbents because of their high surface area, controllable pore size distribution, high adsorption capacity and high degree of surface reactivity [1]. NCs are extensively used in many fields, including organic and inorganic pollutions removal, catalyst support, energy storage, gas storage and electrochemical capacitors [2]. Therefore, they have a central location between other nanoporous adsorbents.

NCs have specific properties depending on the precursor materials and activation methods. There are two activation methods for producing NCs: physical or chemical. Physical activation includes carbonization of the precursor in an inert atmosphere and activation of resulting char by an activation agent such as CO_2, steam or air [3]. In a chemical activation, a precursor is impregnated with an activating agent and impregnated material is heated in an inert atmosphere. Several chemical activating agents, such as $ZnCl_2$, H_3PO_4, KOH, NaOH, $AlCl_3$, $CaCl_2$, etc., are widely used. These generally act as dehydrating materials and promote the formation of crosslinks [4]. However, H_3PO_4 is eco-friendly as it is non-polluting, easy to recover by simply solubilizing salts of H_3PO_4 in water and can be recycled back into the process [5]. H_3PO_4 has two important functions such as promote the pyrolytic decomposition of precursor and formation of cross-linked structure [6]. Besides, using phosphoric acid allows the development of both micropores and mesopores in resulting NC structure [7]. Therefore, H_3PO_4 was used as chemical activating agent in present study.

It is well known that the precursors for production of NCs are mainly exhausted non-renewable resources, such as coals, pitch, and phenol-resin [2]. These types of precursors are quite expensive and often imported, in many places; hence making it necessary, particularly for developing countries, to find a cheap and available precursor for production of NC for use in industry, drinking water purification and wastewater treatment [8]. In addition, high cost (including production from expensive and non-renewable

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https://doi.org/10.1016/j.apt.2018.05.019
0921-8831/

Please cite this article in press as: F. Koyuncu et al., Role of optimization parameters in the production of nanoporous carbon from mandarin shells by microwave-assisted chemical activation and utilization as dye adsorbent, Advanced Powder Technology (2018), https://doi.org/10.1016/j.apt.2018.05.019

Nomenclature

Abbreviations

C_e	equilibrium concentration of dye, mg/L
C_i	initial dye concentration, mg/L
d_p	particle size, mm
D_p	average pore diameter, nm
FT-IR	fourier transform infrared
K_F	constant in Freundlich model, (mg/g) $(L/mg)^{1/n}$
K_L	constant in Langmuir isotherm model, L/mg
n_F	Freundlich power constant
pH_{pzc}	zero point charge of adsorbent
q_e	adsorbed dye amount per gram of adsorbent at equilibrium, mg/g
q_m	monolayer adsorption capacity; mg/g;
R^2	correlation coefficient;
R_L	separation factor or equilibrium parameter
S_{BET}	BET (Brunauer-Emmett-Teller) surface area, m^2/g
SEM	scanning electron microscopy;
TG/DTA	thermogravimetric and differential thermal analysis
V_{mes}	mesopore volume, cm^3/g
$V_{mes}(\%)$	mesopore contribution
V_{mic}	micropore volume, cm^3/g
$V_{mic}(\%)$	micropore contribution
V_{tot}	total pore volume, cm^3/g
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
λ_{max}	maximum wavelength, nm

precursors, regeneration and reuse) has limited their widespread use. For this reason, agricultural wastes are the one, which considered being a very important precursor for NC production because there are renewable sources and low-cost materials. Utilization of agricultural wastes for NC production provides a significant contribution, such as reducing solid wastes, adding economic value to them and protecting the environment. Therefore, NC production from agricultural wastes has attracted considerable attention recently in scientific community as they are renewable, low-cost and eco-friendly. Until now, a large number of agricultural by-products have been used in low-cost NC production. Some of these, olive stone [4], bamboo [6], potato peel [8], coffee bean husks [9], rice husk [10], grape stalk [11], coffee grounds [12], almond shell [13], tomato leaves [13], corncob [14], waste tea [15], peanut hulls [16], lotus stalk [17], banana frond [18], grape waste [19], pomelo peel [20], tomato waste [21], waste tea [22], etc. According to our literature reviews, there are no published reports on NC production from mandarin shells (MS). Mandarin fruit is a kind of citrus family that is grown in temperate climates. According to the data of United Nations Food and Agriculture Organization (FAO) in 2013, it is produced about 21 million tons in the world. Most producing countries are China, Spain, Brazil, Turkey, Italy, Egypt, Japan and South Korea. Turkey ranks fourth with 4% share in the world production of approximately 872 thousand tons. It is drinkable squeezing as can be eaten after peeling. When it is used in fruit juice factory, shell as about 8–14% of weight is discharged into the environment. These are usually used as fertilizer, animal feed and solid fuel. The use of waste mandarin shells as a feedstock for production of nanoporous carbon could have a number of advantages and superiority over other agricultural residues. The widespread cultivation of mandarin means that its shell is not only a plentiful feedstock but can also be sourced across the world, whilst the relatively high lignocellulosic content of the shell may offer structural advantages in the resulting nanoporous carbonaceous materials.

The main objective of this study was to determine optimal conditions for NC production from H_3PO_4 impregnated-MS in the presence of microwave radiation. The influences of chemical impregnation ratio, carbonization temperature and time on some pore characteristics of produced NCs were investigated. Optimal produced NC was characterized by a combination of some chemical and spectroscopic techniques including BET, SEM, XRD, XPS, Raman, FT-IR, Boehm titration and pH_{pzc}. The other objective was to test and contrast the adsorption behavior of Basic Blue 9 (BB9) and Acidic Yellow 36 (AY36) on optimal NC.

2. Materials and methods

2.1. Materials

MSs was collected from a local food processing factory. They were washed several times with distilled water in order to remove dust and other inorganic impurities and subsequently dried naturally. Later, dried shells were crushed and then screened to obtain particle size fraction of $0.470 < d_P < 0.570$ mm prior to its chemical activation. H_3PO_4 of purity 99.9% was used as chemical activator agent. The basic dye, BB9 (Trade name: methylene blue, chemical name: 3,7-bis(dimethylamino) phenazathionium chloride trihydrate, type: cationic, chemical formula: $C_{16}H_{18}ClN_3S$, color index: basic blue 9, λ_{max}: 665 nm, M_w: 319.85 g/mol) and acidic dye, AY36 (Trade name: metanil yellow, chemical name: 3-(4-Anilinophenylazo) benzenesulfonic acid sodium salt, type: anionic, chemical formula: $C_{18}H_{14}N_3NaO_3S$, color index: acid yellow 36, λ_{max}: 433 nm, M_w: 375.38 g/mol) were used as adsorbates. The all used chemicals were purchased from Sigma-Aldrich Co. Ltd. (Ankara, Turkey).

2.2. Optimal nanoporous carbon production

The optimal conditions for NC production from MS were determined by examining influences of chemical impregnation ratio (g_{H3PO4}/g_{MS}), carbonization temperature (°C) and time (h).

Firstly, five gram of MS was impregnated with different impregnation ratios (0.0–4.5) of activation agent and then mixtures were heated under microwave radiation by microwave power 900 W for 40 s in a Pyrex glass reactor fixed in a domestic type microwave oven (Bosh, Model HMT84G451/36, 2.45 GHz). Then, carbonization process of activated samples with different ratios H_3PO_4 in the microwave radiation medium were performed by heating in a horizontal stainless-steel tube (7.0 cm diameter ×100 cm length) under nitrogen atmosphere (99.99%) flow (100 mL/min) at the rate of 10 °C/min at different temperature (400–800 °C) and times (0.5–2.0 h). The experimental run of production conditions for NCs from MS are given in Table 1. The resultant NCs cooled down to room temperature under nitrogen flow. They were rinsed several times with hot distilled water until neutral pH values were reached, indicating that the phosphates and ash were eliminated, which helps opening and developing the porosity of carbon and then dried in an oven at 105 °C overnight. Finally, they were sieved to a particle size less than 0.120 mm, and stored in tightly closed bottles for further experimental use.

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