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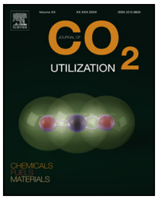

Highly microporous activated carbons from biomass for CO_2 capture and effective micropores at different conditions

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ABSTRACT

This work reports on the preparation and examination of biomass-derived activated carbons featuring high CO_2 adsorption capacity. A detailed micropore structure analysis and surface characterization were performed using nitrogen adsorption isotherms at 77 K and carbon dioxide isotherms at 273 K. At 273 K and 1 bar only micropores in the range of 0.30–0.86 nm were mainly effective for CO_2 adsorption. When the temperature increased to 298 K, the ranges of effective micropores for CO_2 adsorption at 1 bar decreased to 0.30–0.33 nm. For the typical flue gas conditions (partial pressure of CO_2 0.15 bar), micropores in the range of 0.30–0.57 nm were mainly effective for CO_2 adsorption. The precursor had a strong effect on the textural properties of the resulting carbon and CO_2 adsorption. Activated carbon prepared from pomegranate peels showed the highest CO_2 adsorption and selectivity (CO_2/N_2). The experimental isotherm data of activated carbon produced from pomegranate peels were analysed using Langmuir, Freundlich, Sips, and Toth isotherm equations. The fitting details showed that the multitemperature Toth equation is a powerful tool to mathematically represent CO_2 isotherms on activated carbon produced from pomegranate peels. The isosteric heat of adsorption was calculated by fitting the Toth equation to the adsorption isotherms and applying the Clausius–Clapeyron equation. The value of the heterogeneity coefficient and isosteric heat of adsorption suggested heterogeneous interactions between CO_2 and sorbent surface.

1. Introduction

Anthropogenic carbon dioxide, methane, ozone and chlorofluorocarbons cause global warming effects [1]. Methane can be transformed to various chemicals [2,3] whereas conversion of carbon dioxide to organic compounds takes place with low yield with the exception of urea [4]. The report published in 2015 by the Intergovernmental Panel on Climate Change stated that CO_2 is the main greenhouse gas emitted following human activities [5]. CO_2 is mainly released to the atmosphere from the combustion of fossil fuels (coal, natural gas, and oil) for energy and transportation, although certain industrial processes (cement production, chemical, petrochemical, and refining processes) and land-use changes also emit CO_2. Reducing emissions of CO_2 is of great importance to the scientific community.

The potential new technologies and improvements have to be economically rational. CO_2 absorption in amine solutions [6] is utilized in industry nowadays. The adsorption on solids is environmentally friendly and can be more cost effective on the condition that an efficient sorbent is found [7,8]. Carbonaceous materials, zeolites, metal-organic frameworks, alkali-metal based materials, amine-based solid adsorbents are mainly described in reviews as potential CO_2 sorbents [9–11].

Carbonaceous sorbents present a variety of advantages: high specific surface area, large pore volume, favorable surface chemistry, high chemical and thermal stability, ingrained reversibility, fast kinetics, stability to moisture, and high recyclability [12]. As CO_2 sorbents with high adsorption capacity various sophisticated carbon materials were described: hierarchical porous polyacrylonitrile-based activated carbon fibers (4.4 mmol CO_2/g at 1 bar, 25 °C) [13], porous carbon nanosheets (18 mmol CO_2/g at 40 bar, 40 °C) [14], FAU-type zeolite nanocasted carbon replicas (22 mmol CO_2/g at 40 bar, 25 °C) [15], and carbon spheres (8.05 mmol CO_2/g at 1 bar, 0 °C) [16], (4.7 mmol CO_2/g at 1 bar,

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25 °C) [7]. Their large-scale application cannot be recommended for economic reasons.

Activated carbons obtained from renewable inexpensive precursors such as biomass sources are highly desirable [17,18]. It is very important especially because of the expected scale of production. This can be achieved using various kinds of biomass as precursors for the production of carbon sorbents [19]. An extensive description of carbonaceous adsorbents prepared from various biomass sources was presented elsewhere [20,21]. Activated carbons produced from molasses are very useful for the adsorption of both greenhouse gases: methane [22] and carbon dioxide [23,24].

Our work focuses above all on activated carbons derived from biomass for the production of very good CO_2 sorbents. Pomegranate peels (PP), tinder fungus: Piptoporus betulinus (TF1), Trametes versicolor (L.) Lloyd (TF2), mistletoe branches (MB) and leaves (ML), carrot peels (CP), kiwi fruit peels (KP), fern leaves (FL), sugar beet pulp (SP) were used as carbon precursors.

Tinder fungus, mistletoe and fern have not been described as carbon precursors up to now. None of the materials listed above were described as raw material for CO_2 sorbent preparation. The effective micropore ranges for CO_2 adsorption at 273 and 298 K and pressures of 0.15 and 1 bar were investigated.

2. Experimental

2.1. Synthesis of porous carbons

Activated carbons were prepared from biomass by KOH chemical activation. Biomass was dried at 200 °C for 24 h to remove moisture. Then materials were grounded to a particle size in the range of 1–3 mm. A one-step method was applied: carbonization with activation. The impregnation with a saturated solution of potassium hydroxide was performed for 3 h. The mass ratio of dry biomass: KOH was equal to 1:1. After that materials were dried at 200 °C for 19 h and carbonized at 700 °C for 1 h under nitrogen flow. After carbonization, activated carbons were washed several times with distilled water and then soaked in 1 M HCl and again with water until the filtrate was neutral and free of chloride ions. Finally, the samples were dried at 200 °C for 12 h.

2.2. Characterization

A QUADRASORB evo^{TM} Gas Sorption Surface Area and Pore Size Analyzer was used for textural characterization. Nitrogen adsorption isotherms were measured at 77 and carbon dioxide isotherms at 273 K. Before adsorption measurements all samples were outgassed at 250 °C for at least 20 h. The specific surface area was calculated using the Brunauer–Emmett–Teller (S_{BET}) equation from nitrogen adsorption isotherms. The total pore volume (V_{tot}) was evaluated from the nitrogen volume adsorbed at a relative pressure of ~0.98. The volumes of larger micropores (supermicropores) and small micropores (ultramicropores) were calculated by the DFT method on the basis on nitrogen and carbon dioxide adsorption. The pore size distribution (V mic(N2)) was obtained from the DFT model in the QuadraWin software package based on the N2 sorption isotherm. DFT kernel used: N_2 at 77 K on carbon (cylinder. Pores, ASDFT adsorption). For the pore size distribution Vmic CO_2 a different model of the same software was used: CO_2 at 273 K on carbon (NLDFT model).

Carbon dioxide adsorption isotherms series at the highest temperatures (25–80 °C) for the best sorbent were measured utilizing MI-HTP (Hiden Isochema) static volumetric analyser. Before adsorption measurements each sample was degassed as described above. The volumetric method was described in [25,26].

3. Results and discussion

Fig. 1 shows nitrogen adsorption–desorption isotherms for all activated carbons. The adsorption isotherms are of Type I according to the IUPAC classification [27]. Type I is typical for microporous materials. The isotherms do not flatten at a $p/p_0 \sim 0.1$. This indicates that all the carbons have large micropores and/or small mesopores [28]. All materials show high and increasing adsorption below relative pressure 0.1 indicating that the pore structure is composed mainly of micropores. All samples except TF showed hysteresis loops at relative pressures >0.4, indicating the presence of mesopores. The branches of hysteresis were almost horizontal and parallel over a wide range. The isotherm reveals a type H4 hysteresis loop indicating narrow slit-like pores. The combination of H4 and isotherms Type I suggests high microporosity of the materials.

Table 1 summarizes the textural properties for all activated carbons which have surface area values in the range of 585–1593 m^2/g and total pore volume values of 0.28–0.80 cm^3/g. The micropore volume of narrow pores (0.3–1.4 nm) ranged from 0.31 to 0.42 cm^3/g and micropore volume estimated on the basis of N_2 adsorption ranged from 0.20 to 0.54 cm^3/g.

Fig. 2 shows the pore size distribution (PSD) of the activated carbons produced from biomass using the N_2 adsorption results at 77 K. Fig. 3 shows PSD from CO_2 adsorption at 273 K. Both PSDs were calculated using the DFT method. On the basis of Fig. 2 it was found that all activated carbons consist mainly of micropores (pores up to 2 nm). Mesopopres not higher than 3.5 nm were present. These pores are formed by the release of non-carbon components such as N and O during carbonization, and due to KOH the activating agent.

The narrow micropore size distribution curves (Fig. 4) for most produced activated carbons contained three peaks at about 0.35, 0.55 and 0.78 nm. For MB and FL activated carbons narrow micropore size distribution curves were different from the others but still the highest pore volume was within 0.3–1.1 nm.

Carbon dioxide adsorption data at 273 and 298 K were fitted to Langmuir, Freundlich, Sips, and Toth models by means of Microsoft Excel and a tool called Solver program. Error Sum of Squares (SSE) was used to evaluate the performance of the models [25]. The Toth isotherm fitted the experimental data better than the others. Fig. 4 presents CO_2 experimental adsorption isotherms of the activated carbons investigated by the volumetric method at temperatures of 273 and 298 K (points) and fitting curves to Toth models.

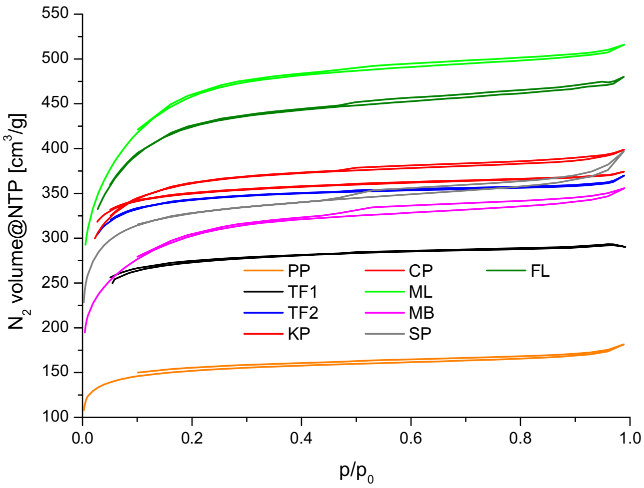

Fig. 1. Nitrogen adsorption–desorption isotherms for activated carbons derived from biomass.