

Preparation of Activated Carbon from Beet Molasses and TiO₂ as the Adsorption of CO₂

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The objective of this work is to produce activated carbon from sugar beet molasses containing TiO₂ for CO₂ adsorption and reduction. Textural properties of activated carbons were obtained based on the adsorption-desorption isotherms of nitrogen at 77 K. The specific surface areas of activated carbons were calculated by the Brunauer-Emmett-Teller method. The volumes of micropores were obtained by density functional theory method. The adsorption isotherms of CO₂ were measured up to the pressure of 1 atm at a temperature of 40 °C. The best activated carbon adsorbed 1.9 mmol/g of CO₂.

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1. Introduction

Over the last decades a systematic increase of CO₂ emissions worldwide was noticed. The reduction of CO₂ emissions is dependent on new technological systems as CO₂ conversion to useful chemicals [1] as well as carbon capture and storage (CCS) [2, 3]. Hence, to achieve a high level of CO₂ removal, high cost operational technologies are used. In this case, activated carbons (ACs) seem to be a very promising solution. Activated carbons generally are less costly than other sorbents (e.g. zeolites, ordered mesoporous silicas, etc.) [4–6] due to a low heat of adsorption, low cost raw materials and cost-effective regeneration. Regeneration can be performed either by increasing the temperature (temperature swing adsorption, TSA) or by decreasing the pressure (pressure swing adsorption, PSA) or even using under vacuum (vacuum swing adsorption, VSA) [7, 8].

Activated carbons are microporous and mesoporous materials widely studied as potential CO₂ adsorbents [9–14]. In common opinion, the advantages of activated carbons are their low cost and flexibility in terms of porous texture, regeneration and surface properties [15, 16].

The control of porous texture and surface properties in activated carbon depends upon the type of raw materials and the method of activation. The preparation of activated carbon by activation is very important from the industrial and economic points of view [17, 18]. Activated carbons can be obtained from carbonaceous materials but increasingly more often from cheap agricultural wastes [15, 19, 20].

For this reason the new precursor which is beet molasses was used. Beet molasses is an abundant waste

material from the production of sugar [16, 21–23]. In addition to determining the proper raw materials, the selection of certain properties of suitable substances is important. TiO₂ was described as photocatalyst for CO₂ conversion [1] and was chosen by us as additive in the preparation of activated carbon.

The primary objective of this work is to produce material for the reduction of CO₂ which is the activated carbon from sugar beet molasses containing TiO₂. The preparation of activated carbon was performed by combining carbonisation and chemical activation.

2. Materials and methods

2.1. Preparation of activated carbon

The material used for activated carbon production was a vegetable waste from sugar production. A commercial titanium dioxide P25 (Commercial Aeroxide® TiO₂) was supplied by Evonik in Germany. The beet molasses (Mb) was delivered by a Polish sugar factory.

Molasses was mixed with TiO₂ and KOH at different amounts and at different values of the mass ratio. The mass ratios are shown in Table I. Mixtures were left for 3 h at 25 °C and atmospheric pressure. Then mixtures were dried for 19 h at 200 °C.

Activated carbons were obtained by carbonising all the mixtures at 750 °C for 1 h under nitrogen. Carbonisation was performed in a horizontal tube oven with an inner diameter of 100 mm under inert gas flow of 15.2 l/h. AC1 and AC2 activated carbons were prepared from mixed molasses and TiO₂ with a different value of the mass ratio molasses (Mb), while TiO₂ and AC3 and AC3 were prepared from TiO₂ and KOH with a different value of the mass ratio Mb:TiO₂ and mass ratio Mb:KOH. Different amounts of TiO₂ and KOH as the value of the mass ratio molasses Mb:TiO₂ and Mb:KOH are shown in Table I.

The activating agent was removed by washing samples with water and a solution of 5N HCl and with water again

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until all samples reached pH = 7. The washed activated carbons were dried at 200 °C for 19 h. Then, they were triturated in a mortar to a powder.

TABLE I
Amounts of TiO₂ and KOH as the ratio of mass Mb:TiO₂ and Mb:KOH.

Name of material	Mb:TiO ₂	Mb:KOH
AC1	0.08	
AC2	0.16	
AC3	0.08	1
AC4	0.32	1

2.2. Characterisation of activated carbons

2.2.1. Nitrogen adsorption isotherms and their analysis

Textural properties of ACs were obtained based on the adsorption and desorption isotherms of nitrogen at its normal boiling point of 77 K, using an automated adsorption system Quadrasorb (Quantchrome Instruments). Before analysis, all samples were degassed at 250 °C (16 h). N₂ adsorption isotherms were used to determine the total micro- (V_m) and mesopore volume (V_t), the Brunauer–Emmett–Teller (BET) surface area, and microporosity development. The specific surface areas of the activated carbon were calculated by the BET method (S_{BET}). The volume of micropores (V_m) was obtained from the application of the density functional theory (DFT) method.

2.2.2. CO₂ sorption isotherm measurement

The sorption isotherms for CO₂ were determined using a volumetric apparatus Sievert-type (IMI Hiden Analytical Ltd.). Before analysis, the activated carbons were degassed at the temperature of 250 °C and under high vacuum.

Then the temperature was decreased to 40 °C to measure gas sorption. The equilibrium time was set at 15–35 min. The adsorption isotherm of CO₂ was measured up to a pressure of 40 atm.

2.2.3. Infrared spectroscopy (FTIR)

Fourier-transformed infrared (FTIR) spectra were recorded on a Nicolet 380 Thermo Scientific, in the transmission mode. FTIR spectrometric analysis was performed in order to investigate the surface composition.

3. Results and discussion

Adsorption–desorption isotherm plots of AC1, AC2, AC3 and AC4 are shown in Fig. 1. The isotherms of AC3 exhibiting type IV indicate a mesoporous structure. The adsorption isotherms of AC1, AC2, AC4 indicate a small amount of adsorbed gas. The porosity of these ACs is much lower than that of AC3.

Figure 2 shows the pore size distribution curves of AC1, AC2, AC3 and AC4. There is a big difference in the pore diameter of activated carbons with KOH and activated carbon without the addition of KOH. The maximum micropore size was between 1.18 and 1.23 nm and

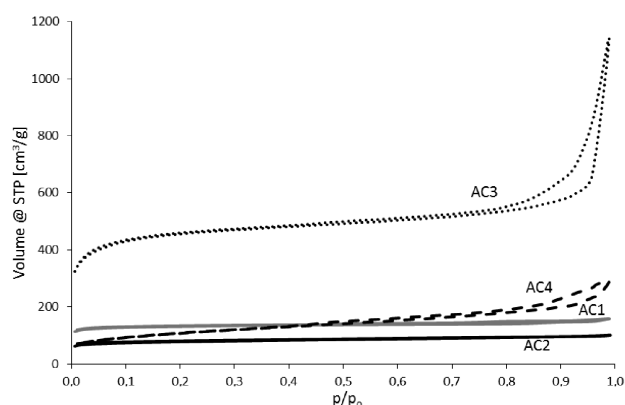


Fig. 1. Adsorption-desorption isotherm of N₂ at ACs [AC1 (—), AC2 (—), AC3 (· · ·) and AC4 (— —)].

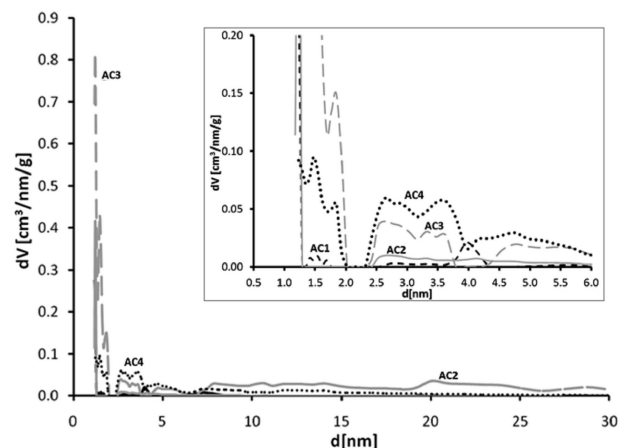


Fig. 2. Pore size distribution for AC1 (—), AC2 (—), AC3 (— —) and AC4 (· · ·).

the presence of mesopores was observed. The micropores present in the range of 1.17–2 nm AC3 were sharp and pointy. AC3 and AC4 had a wide pore size distribution from micropores to mesopores. Micropores and wide mesopores up to 9 nm were dominant in AC1 and up to 5 nm in AC2.

Table II shows the BET surface area, total pore volume, volume and micropore average pore diameter values. The AC3 had a relatively high surface area and large volume micropore which was due to the presence of KOH and a small amount of TiO₂. Such physical properties make AC3 a good candidate for CO₂ adsorption.

TABLE II
Comparison of specific surface area (S_{BET}) and CO₂ adsorption at 1 atm for activated carbons.

Name of material	S_{BET} [m ² /g]	V_t [cm ³ /g]	V_m [cm ³ /g]	Adsorption of CO ₂
AC1	523	0.245	0.217	1.6849
AC2	298	0.156	0.138	1.1487
AC3	1728	0.176	0.122	1.9285
AC4	385	0.045	0.0399	0.4742

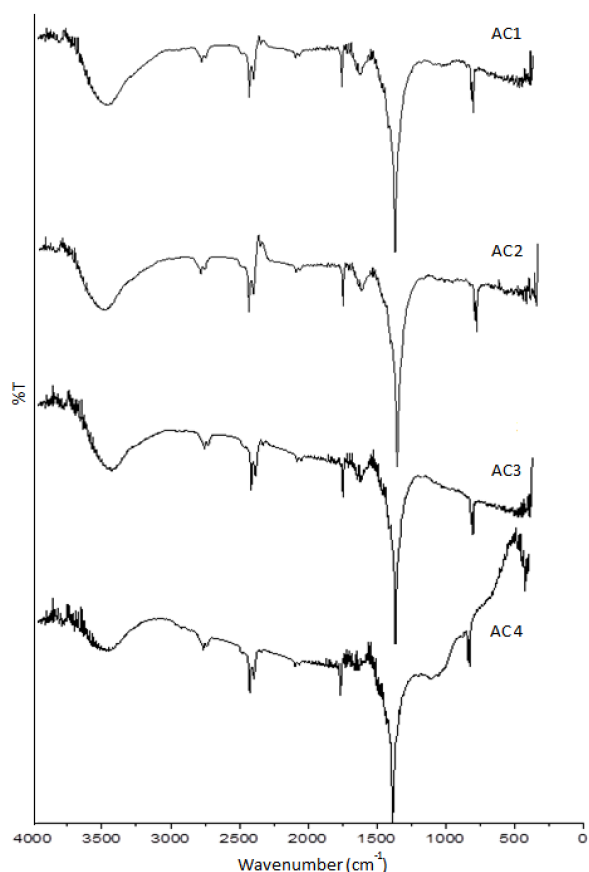


Fig. 3. FTIR spectra of AC1, AC2, AC3 and AC4.

FTIR spectroscopy was used to study qualitative functional groups on an activated surface [24]. Figure 3 shows the FTIR spectra of activated carbons — AC1, AC2, AC3, and AC4. All the studied activated carbons were characterised by the presence of a strong signal which was attributed to C–O vibration at a high wave number (1400 cm^{-1}) and were also characterised by the stretched absorption band in the range of $500\text{--}1000\text{ cm}^{-1}$ for the skeletal O–Ti. An identical spectrum differing only by 2355 cm^{-1} and 668 cm^{-1} bands was observed for AC1 and AC2. Different spectra of AC1 and AC2 may be caused by the value of the mass ratio of TiO_2 .

The band around 1000 cm^{-1} is attributed to the self-absorption of rutile [25] and it was clearly visible for AC4 where it was the largest number of TiO_2 . The band at 1640 cm^{-1} especially with more intensity in the case of AC1, AC2, and AC3 can be attributed to the molecular water bending mode. The broad absorption band in the range of $3400\text{--}3700\text{ cm}^{-1}$ can be assigned to the adsorbed water and hydroxyl groups [26, 27] which were visible in all activated carbons AC1–AC4.

CO_2 adsorption isotherm plots of AC1, AC2, AC3, and AC4 are shown in Fig. 4. The activated carbon AC3 exhibited a much higher adsorption capacity of CO_2 compared to other ACs. It is worth emphasizing that the presence of KOH during activation is associated with de-

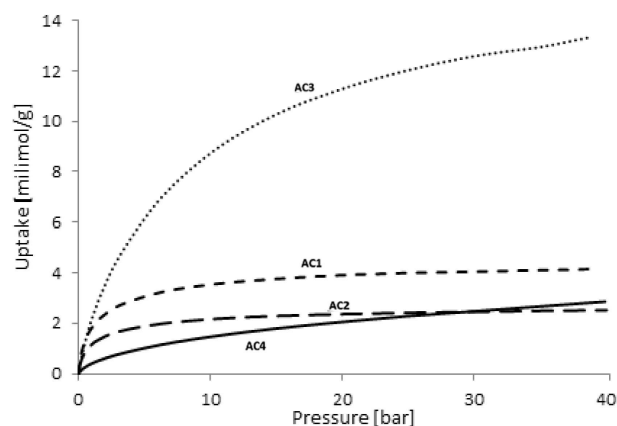


Fig. 3. Isotherms of CO_2 adsorption on AC1 (---), AC2 (— · —), AC3 (····) and AC4 (—).

veloping microporosity of activated carbons. The modification of activated carbons with large quantities of TiO_2 could be the reason of low CO_2 adsorption. Although TiO_2 deteriorated the CO_2 absorption, it was still large for the photocatalyst.

Having in mind the diameter of CO_2 molecules and pore size distribution, the received activated carbons seem to be suitable for the uptake of CO_2 . The activated carbon AC3 adsorbed much more CO_2 than AC1, AC2 and AC4 thanks to the highly-developed porosity of the material.

The adsorption of high amounts of CO_2 proves that AC3 activated carbon can be a good photocatalyst.

4. Conclusions

Activated carbons containing small amounts of TiO_2 are good CO_2 adsorbents. Such materials can be good photocatalysts in conversion reactions for carbon dioxide into organic compounds. The addition of KOH during preparation improves the specific surface area and adsorption capacity of CO_2 .

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