Utilization of spent dregs for the production of activated carbon for CO₂ adsorption

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The objective of this work was preparation of activated carbon from spent dregs for carbon dioxide adsorption. A saturated solution of KOH was used as an activating agent. Samples were carbonized in the furnace at the temperature of 550°C. Textural properties of activated carbons were obtained based on the adsorption-desorption isotherms of nitrogen at −196°C and carbon dioxide at 0°C. The specific surface areas of activated carbons were calculated by the Brunauer – Emmett – Teller equation. The volumes of micropores were obtained by density functional theory method. The highest CO₂ adsorption was 9.54 mmol/cm³ at 0°C – and 8.50 mmol/cm³ at 25°C.

Keywords: activated carbon, biomass, CO₂ adsorption.

INTRODUCTION

The development of industry and civilization has contributed to improving the quality of social life. Unfortunately, over the years the negative effects of anthropogenic activities have been more pronounced including global warming. Recent reports indicate that in the years 1901–2012 there was an increase in an average global temperature of approximately 0.89°C, with an increase of 0.72°C in the years 1951–2012.[1–6]

The consequences of global warming cause serious and irreversible changes such as the melting of ice shelves and raising sea levels, thus counteracting the effects of global warming has become an important issue of environmental policy and has contributed to the establishment of the IPCC[7]. According to the Kyoto Protocol (1988), the main culprits inducing the global temperature increase are: carbon dioxide, methane, nitrogen oxide, hydrofluorocarbons, perfluorocarbons, sulfur hexafluoride, which absorb infrared radiation emitted by the land surface.[8]

Most responsible for increasing the concentration of carbon dioxide are power plants, refineries, chemical, petrochemical, steel and cement industries. Great efforts have been directed towards finding new approaches for CO₂ sorbents such as activated carbons[9–14] and other carbonaceous materials[15], zeolites[16–18], metal–organic frameworks[19–21], porous polymers[22–24], and others.[25–27]. Photocatalytic CO₂ reduction into green solar fuels such as methane, formic acid, formaldehyde and methanol[28–33] has been known as the most promising technology. The generation of energy from non-fuel sources such as hydrogen[34–38], nuclear energy and renewable energy[5, 39] is also very important. Much work has been done in methane utilization. Good CH₄ sorbents are very important because methane can be an alternative fuel vehicle. The main possibility to reduce CH₄ emission is methane conversion to more valuable products such as formaldehyde[41–43], syngas via dry reforming[44], methanol[41, 43, 45, 46], methyl bisulphate[47–49], carbon nanotubes[50–58], hydrogen[55, 59–61].

Nowadays, one of the most popular options of the mitigation of carbon dioxide emission is the amine-based chemical absorption, the most commonly used absorbent is MEA[5, 39, 62]. However, this technique has serious drawbacks such as high energy penalty, volatility of the amines, solvent and regeneration cost or equipment corrosion, and therefore alternative approaches are still desirable[5, 6, 62]. There are several ways to reduce carbon dioxide emissions from the use of separation methods: pre-combustion, post-combustion, oxy-fuel combustion or chemical looping combustion[62]. Among them for particular interest deserve the post-combustion strategy, including adsorption processes[63].

In general, highly attractive CO₂ sorbents are carbonaceous materials, especially activated carbons because of their easy-to-design pore structure determining high adsorption capacity and large specific surface area, selectivity, uncomplicated regeneration of the materials and insensitive to moisture.[5, 6, 62–64]. Various properties of activated carbons are caused mainly by the activation conditions and used reagents[65, 66]. Activated carbons are very good sorbents of gases[9–14, 40, 67–69], organic[69–70] and inorganic water pollutants[71, 72] but can be used as catalyst supports[73] or even catalysts[74, 75].

In order to reduce that costs, waste or different raw materials are used to obtain activated carbons (ACs). More economical and environmentally friendly is to use waste material[5, 76, 77]. To date, it has been reported that activated carbons have been prepared from agricultural residues such as sawdust[76], coconut shell[78], olive stone[79], beet molasses[80], fungi[80], corn syrup[76, 81], kraft lignin[82], ebony wood[83, 84], mahogany wood[82] and food waste[85, 86].

The main objective of my work was to evaluate the utility of waste spent dregs as an abundant and accessible precursor for activated carbon production at low carbonization temperature of 550°C. Potassium hydroxide was used as the activating agent.

MATERIAL AND METHODS

Preparation of activated carbon

The material used for activated carbon production was coffee (CG), tea (TG), mint (MG) and rock rose (RG) grounds. Grounds were mixed with a saturated solution of potassium hydroxide at 1:1 values of the mass ratio. Mixtures were left for 1h at room temperature. Then they were dried at 200°C for 19 h. The next step was...
Carbonization of all samples at 550°C for 1h under nitrogen gases. Carbonization was performed in a horizontal oven under insert gas flow of 15l/h. Activator potassium hydroxide was removed by washing samples with deionized water and a solution 1M HCl and after that again with deionized water until neutral pH was obtained for all samples. After washing activated carbons were dried at a temperature 200°C for 19 h. After this time the material was grounded into powder and tested.

Characterization of activated carbons

Textural characterization

The specific surface area and porous texture characterization of all the ACs was carried out by physical N₂ adsorption and desorption at –196°C using a Quadrasorb automatic system (Quantachrome Instruments). Before the analysis samples were degassed overnight (16 h) under high vacuum of 1 × 10⁻⁶ mbar at 250°C. The Brunauer–Emmett–Teller (BET) equation was used to determine surface areas (S_BET). The total pore volume (Vtot) was determined at relative pressure (p/p₀ = 0.99). The volume of micropore (Vmic(N₂)) in the range of 1.8–2 nm was obtained using the density functional theory (DFT). The volume of micropore (Vmic (CO₂)) in the range of 0.3–1.4 nm and submicropore (Vsubmic(CO₂)) in the range of 0.3–0.8 nm was obtained using DFT.

CO₂ adsorption

Carbon dioxide sorption measurements were performed using a Quadrasorb automatic system (Quantachrome Instruments). Before analysis samples were degassed at 250°C under high vacuum of 1 × 10⁻⁶ mbar and CO₂ was adsorbed at 0°C and 25°C.

Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) – (model UHR FE-SEM Hitachi SU8020 was used to investigate the morphology of the activated carbons.

RESULTS AND DISCUSSION

The porosity and the accessibility of the active centers have a paramount importance for the adsorption performance. To evaluate the positive effects of the applied modifications, the porous structure of the materials was studied. Surface area, submicropore volume, micropore volume from CO₂ and N₂ and total pore volume of activated carbons derived from BET measurements are presented in Table 1. Chemical activation with solid KOH gave interesting results from the porosity development point of view. The values obtained for the total pore volume were 0.25–0.30 cm³/g, the micropore volume on the basis of N₂ adsorption were 0.20–0.22 cm³/g, the submicropore volume in the range of 0.08 to 0.11 cm³/g and the micropore volume of narrow pores (0.3–1.4 nm) ranged from 0.10 to 0.15 cm³/g. Total surface area (BET) values were within the range of 536–618 cm²/g. The TG sample had a relatively high surface area and large micropore volume. Activated carbons were sorbents with a very well developed porosity. For the RG, CG, TG samples the percentage of micropores was more than 67% of all developed pores.

Adsorption and desorption isotherm plots of nitrogen for CG, TG, MG and RG are shown in Figure 1. The curves of adsorption isotherms increased sharply at low relative pressure and gradually increased at maximum relative pressure. These curves showed a mix of the type I and IV isotherm, characteristic for the micropores and mesopores. The formation of hysteresis loops at relative pressure higher than 0.45 indicated the essential multilayer adsorption process characterizing the mesoporous structures. The hysteresis loops for CG and TG samples was type H4 hysteresis which is also often associated with narrow slit pores. For RG and MG hysteresis loops were type H3 which suggests that the internal porosity of the activated carbons primarily is slit-shaped and panel-shaped.

![Figure 1. Adsorption and desorption isotherm of nitrogen](image)

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<table>
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<th>Sample</th>
<th>S_BET [m²/g]</th>
<th>V_BET [cm³/g]</th>
<th>Vsubmic(CO₂) [cm³/g]</th>
<th>Vmic(CO₂) [cm³/g]</th>
<th>Vmic(N₂) [cm³/g]</th>
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<tr>
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<td>0.15</td>
<td>0.22</td>
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<tr>
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<tr>
<td>RG</td>
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The pore size distribution measured by physical N₂ adsorption-desorption are presented in Figure 2. Pore volume decreased gradually with an increase in pore diameter. Mesopores in the range of 2–2.5 nm were mainly present in materials. Mesopores higher than 5 nm were not observed. These pores were created by the release of non-carbon components such as N and O during carbonization process with the KOH activating agent using.

Figure 3 shows the pore size distribution curves of RG, CG, TG, MG calculated on the basis of CO₂ adsorption at the temperature of 0°C. Narrow micropore size distribution curves were similar. Three dominant peaks were observed for all the materials. One was located in the range of 0.20–0.38 nm, the second in the range of 0.45–0.70 nm and the last one in the range of 0.70–0.90
CO₂ adsorption of RG, CG, TG and MG are shown in Figure 5. The activated carbon CG exhibited the highest adsorption capacity of CO₂ compared to the other ACs. The adsorption value of CG was at 0°C–9.54 mmol/cm³ and at 25°C–8.50 mmol/cm³. It is worth emphasizing that the presence of KOH during activation is associated with developing microporosity of activated carbons. Some authors suggest the importance of submicropores on CO₂ adsorption of CO₂. Recently, some authors studied the validity of submicropores of CO₂ adsorption. On the basis of Figure 2 it was assumed that the highest and the most significant adsorption of CO₂ took place in pores in the range of 0.7–0.9 nm. The pore volume in this range varied as follows CG > TG > RG > MG, and it was correlated with fluctuation of CO₂ adsorption.

CONCLUSIONS

In recent years, low cost materials such as waste biomass have more often been used as a feedstock for environmental, agricultural and industrial purposes. For example, spent dregs are one of the most widely available waste material in the world. Production of activated carbons from these materials is one of the possibilities for utilization. Activated carbons were produced from the different spent dregs. Very low temperature (550°C) was applied in carbonization stage. Obtained results show that activated carbons were good CO₂ sorbents. The maximum surface area was equal to 618 m²/g (TG). The most significant adsorption of CO₂ took place in pores in the range of 0.7–0.9 nm. The highest CO₂ adsorption at 0°C–9.54 mmol/cm³ and at 25°C–8.50 mmol/cm³ was obtained for CG. The submicropore volume of activated carbons was in the range of 0.08 to 0.11 cm³/g, the micropore volume was in the range of 0.20–0.22 cm³/g, total pore volume was from 0.25 cm³/g to 0.30 cm³/g. This work shows that the activated carbons, obtained from different spent dregs during low temperature carbonization, can be a possible alternative for the development of inexpensive adsorbents for environmental applications, such as CO₂ capture.

LITERATURE CITED
