Modified Carbonized Rice Husk as Low-Cost CO\textsubscript{2} Adsorbent: Perspectives and Possible Improvements

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Abstract. The international scientific community in the recent years deserves great attention to the problem of greenhouse gases emissions into the atmosphere. Particular importance was given to the development of CO\textsubscript{2} capture and storage strategies. This work investigates the possibility to use carbonized rice husk as a low cost starting materials for the production of CO\textsubscript{2} sorbents. The performances toward CO\textsubscript{2} capture of materials based on rice husk were carried out in a static micro-reactor showed high efficiency up to 60\% with respect to the previously studied carbon-based sorbents.

Introduction

Recently the international scientific community pays a great attention to environmental issues, especially climate change and global warming. Both these issues require global efforts to reduce the concentration of greenhouse gases, particularly carbon dioxide (CO\textsubscript{2}). To this aim, CO\textsubscript{2} capture and storage (CCS) is still considered the main strategy for achieving CO\textsubscript{2} emission reduction targets [1].

Three major CCS approaches are currently applied: post-combustion capture, pre-combustion capture and oxy-fuel combustion [2]. Post-combustion is the most advantageous CO\textsubscript{2} capture strategy, as it does not imply substantial modifications to the combustion process technologies at the present days used. Among the many CO\textsubscript{2} separation processes proposed, adsorption is the most mature and commonly adopted due to its high efficiency and lower cost. The use of solid sorbents offers remarkable advantages over the other separation methods because it is characterized by great capacity, ease of handling, selectivity and lower energy for regeneration [3].

A lot of materials have been explored as CO\textsubscript{2} sorbent, including amine-impregnated solids [4], carbon-based and graphite/graphene-based materials, zeolite-based materials, MOF-based sorbents, silica-based sorbents, polymer-based adsorbents, clay-based adsorbents, alkali metal carbonate-based adsorbents, immobilized ionic liquid-based adsorbents, LDH-based sorbents, MgO-based sorbents, CaO-based sorbents, alkali zirconate-based sorbents, alkali silicate-based sorbents etc. [5-7]. This work describes the preparation of solid CO\textsubscript{2} sorbents from biomass waste resources, more precisely sorbents based on carbonized rice husk (cRH).

Rice is the one of most important cultivated food crop worldwide. It accounts for more than 20\% of the world’s crop feeds and productions for approximately 50\% of the world’s population. Rice husk (RH) is the hard protecting covering of rice grains. RH protects the seed during all growing season, since it is formed from hard materials, including lignin and opaline silica. Lignocellulosic materials, such as vegetable wastes, if properly treated under controlled conditions are an inexhaustible and renewable source of carbonaceous materials with reproducible chemico-physical characteristics exploitable in CCS approaches. Moreover lignocellulosic materials have a more even geographic distribution compared to that of oil or coal representing recyclable natural alternative to traditional fuel in the production of carbon materials. RH is a large-scale agricultural waste abundantly available in rice producing countries, obtained during the milling of paddy (22 wt. % of the weight of unmilled rice is received as husk) [8, 9] and various methods to produce carbon materials from this are well investigated.

RH being the outer shell of rice kernels protects the internal components from external attacks of
insects and bacteria, but also RH need to get air and moisture for the growth of corn. Due to this peculiar function, rice in the process of natural evolution has created in its husk characteristics shapes with nanoporous layers. These properties let us applying RH in different field of science: in biomedicine and environmental applications, as fertilizer, as a mineral admixture in concrete, Li-ion battery anodes, petroleum adsorption etc. When RH is carbonized under controlled conditions its surface area and porosity increase making carbonized RH a good candidate for CCS approaches.

The adsorption properties of cRH are an interesting research subject in industrial and environmental context. Annually about 200 million tons of RH are produced in the world. The production and use of adsorbent materials based on RH can contribute to mitigate two environmental problems: utilization of agricultural wastes and CO\textsubscript{2} abatement. There are many studies on cRH used for waste water remediation, also have a lot of adsorbent for oil products and blood [10-15]. In this work we investigate adsorption behavior of materials based on RH for CO\textsubscript{2} capture.

**Experimental**

Carbonization of RH was performed in auger furnace in the 500° - 800°C temperature range for 3 hours. More than 350 kg at day of carbonized rice husk (cRH) in Innovative Enterprises “Zhaly” in Almaty, Kazakhstan can be obtained. Carbonized rice husk features are presented at the Figure 1. high surface area, good porosity and a carbon content around 66 wt.% (EDAX) (RH was investigated in Nanolaboratory, al-Farabi Kazakh National University, Almaty, Kazakhstan). The presence of silica, revealed by EDAX, indicates that cRH can be stored for long time, without significant degradation.

![Characterization of cRH (SEM and EDAX).](image)

Sorbents based on cRH were produced by a base-leaching procedure [16]. We prepared 2 samples by treating cRH with two different strong bases: NH\textsubscript{4}OH (28% water solution) and NaOH (5M). The obtained samples were labeled as cRH-NH\textsubscript{4}OH and cRH-NaOH, respectively. Briefly, cRH was suspended into 200 mL of de-ionized water by sonication for 20 min. The mixture was kept at 30° C for 30 min under stirring. After that, 10 mL 28% ammonia solution or 5M solution of NaOH was added. The mixture was kept for 1 h at 90° C under stirring. The schematically workup of the reaction represent below in Figure 2.

![Base-leaching method to obtain sorbents based on cRH.](image)

Carbon dioxide sorption activity of cRH-NH\textsubscript{4}OH and cRH-NaOH was assessed by tests in a
fixed bed reactor (shown below in Figure 3.) with CO₂/N₂ gas mixture (15 Nl/h) at a fixed CO₂ concentration (3% vol), operating under atmospheric pressure. The CO₂ concentration in the inlet and outlet gas streams has been measured by online continuous ABB infrared gas analyzer. A laboratory scale fixed bed Pyrex microreactor (ID = 1 cm, length = 60 cm) operating under atmospheric pressure has been used for the preliminary evaluation of the CO₂ adsorption capacity of different samples. N₂ and CO₂ flowrates have been set by means of mass flow controllers (Bronkhorst), and subsequently mixed before entering the bed (Figure 3.). The CO₂ concentration in the column effluent gas is continuously monitored as a function of time (breakthrough curve) until the gas composition approaches the inlet gas composition value, until bed saturation is reached. The time taken by the gas mixture to flow from the fixed bed to the analyzer has been previously measured by flowing the gas mixture through the empty bed (about 50 s) [3].

Figure 3. Fixed bed micro-reactor for measure CO₂ capture.

These measurements were performed at Institute of Research Combustion IRC-CNR, Napoli, Italy.

Results and Discussion

Preliminary results in terms of absorbed CO₂ moles and time need for saturation of the samples (breakthrough time) are reported in Table 1. As clearly shown by the reported values, the sorption capacity of cRH-NH₄OH was about 33.59 mgCO₂/g better than cRH-NaOH (21.88 mgCO₂/g) and both samples better than raw cRH (11.26 mgCO₂/g and 8 s). Time for saturation better with cRH-NH₄OH and total 25 s, then cRH-NaOH saturated time for this sorbent 13 s. It is better then samples based only RH, which saturation time was 8 s.

Table 1. Preliminary results of CO₂ adsorption tests.

<table>
<thead>
<tr>
<th>Sample</th>
<th>m_{ad} (mgCO₂/g)</th>
<th>t_b (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cRH-NH₄OH</td>
<td>33.59</td>
<td>25</td>
</tr>
<tr>
<td>cRH-NaOH</td>
<td>21.88</td>
<td>13</td>
</tr>
</tbody>
</table>

With reference to carbon based samples investigated in the same conditions at IRC-CNR, Napoli, Italy (Table 2.) we observe an increase of efficiency of sorbents based on cRH more than 60% with respect to the composite materials based on carbon black and magnetite (CB–FM), and about 23% than CB–IL (composite material based on carbon black and ionic liquid) also confirmed by the higher breakthrough times exhibited by the cRH and modified cRH samples [17].

Table 2. Previous results on CO₂ adsorption screening tests in fixed bed reactor on carbon back (CB)-based samples (adapted from [17]).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
<th>m_{ad} (mgCO₂/g)</th>
<th>t* (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB</td>
<td>Carbon black</td>
<td>6.5</td>
<td>2</td>
</tr>
<tr>
<td>CB_{ox}</td>
<td>Oxidized carbon black</td>
<td>6.6</td>
<td>0</td>
</tr>
<tr>
<td>CB_{ox}–NH₂</td>
<td>Oxidized carbon black - amino-groups</td>
<td>12.8</td>
<td>1</td>
</tr>
<tr>
<td>FM</td>
<td>Magnetite</td>
<td>10.8</td>
<td>1</td>
</tr>
<tr>
<td>CB–FM</td>
<td>Carbon black–Magnetite composite</td>
<td>18.3</td>
<td>2</td>
</tr>
<tr>
<td>CB_{ox}–FM</td>
<td>Oxidized carbon black–Magnetite composite</td>
<td>8.0</td>
<td>1</td>
</tr>
<tr>
<td>CB–IL</td>
<td>Ionic liquid supported on carbon black</td>
<td>27.3</td>
<td>18</td>
</tr>
<tr>
<td>CB_{ox}–IL</td>
<td>Ionic liquid supported on oxidized carbon black</td>
<td>9.9</td>
<td>6</td>
</tr>
</tbody>
</table>
Conclusions

CO₂ sorption activity of samples prepared by cRH base-leaching was assessed by tests in a fixed bed reactor. CO₂ capture capacity of the sorbents obtained from cRH by leaching with NH₄OH (cRH-NH₄OH) is higher than Ionic liquid supported on carbon black [17]. Also cRH-NaOH sorption capacity is higher than other composite and hybrids materials based on chemico-physical modification of carbon black [17]. These encouraging preliminary results open up the possibility to widely and profitably use cRH as a low cost biomass-derived materials for CO₂ capture.

References