

## Adsorption of phenol and 2,4-dichlorophenol on carbon-containing sorbent produced from sugar cane bagasse

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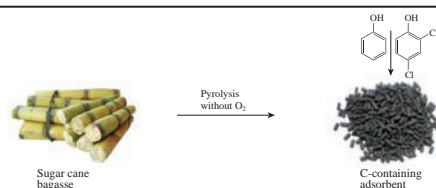
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An adsorbent prepared from carbonized sugar cane bagasse shows high adsorption capacity to phenol and 2,4-dichlorophenol that is equal to 2.24 and 2.45 mmol g<sup>-1</sup>, respectively.



**Keywords:** phenol, 2,4-dichlorophenol, adsorption, carbon-containing sorbent, lignin, sugar cane bagasse, plant waste treatment, carbonization.

Producing adsorbents based on the plant raw materials is an important direction in modern chemistry due to the wide availability and the porous structure of vegetable matter. The main components of plant biomass are well known to consist of lignocellulose, which stiffens the cell walls of plants and acts as an intercellular binder. Its widespread availability makes this biomass feedstock a renewable raw material for the modern chemical industry.<sup>1–5</sup> The most important sources of lignocellulosic biomass are forestry (hardwood and softwood) and agricultural (*e.g.*, comcob, corn stover, rice straw and wheat straw) wastes along with fast-growing perennial grasses like switchgrass.<sup>6</sup> An impeding factor, however, is lignocellulose's resistance towards chemical and biological conversion.<sup>7,8</sup> This chemical stability originates mainly from the strong covalent and non-covalent interactions between three major biopolymers, *i.e.*, cellulose, hemicellulose and lignin, which all together form the lignocellulose matrix. Lignin is a type of complex organic polymers that form key structural materials in the supporting tissues of vascular plants and some algae. From the chemical viewpoint, lignin is a cross-linked phenolic polymer.

The structure of plant material contains heterogeneous pores whose radius of curvature varies in a wide range. In such materials, there are cavities between structural elements, *i.e.*, open pores or channels that permeate the entire volume of the material.<sup>9</sup>

Various methods based on physical and chemical activation are used to obtain adsorbents from plant raw materials.<sup>10</sup> The physical activation is usually carried out in two stages, which include carbonization of the raw material followed by activation of the carbonized product with water vapor or carbon dioxide. The resulting porous carbon material, carbonizate, has a structure similar to that of graphite, but there is an alternation of ordered and disordered regions containing hexagonal carbon rings. Unlike graphite, the carbonizate has a porous structure characterized by three-dimensional labyrinths consisting of interconnected expansions and constrictions showing various sizes and shapes. As a result, the obtained carbon-containing material accommodates pores of different sizes, *i.e.*, micropores, mesopores and macropores

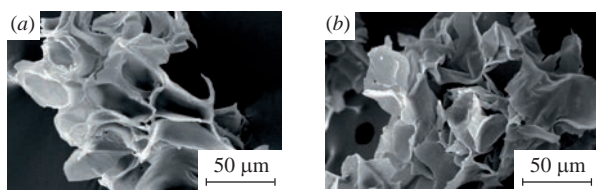
with sizes of  $\leq 2$ , 2 to 50 and  $> 50$  nm, respectively. Due to the porous structure this carbon-containing material has a high specific surface area and can adsorb various substances from liquid and gaseous phases.

To create functional groups on the surface of the carbonized porous carrier that increase its capacity for the specific adsorption of harmful pollutants, in particular aromatic alcohols and chloro-aromatic substances, chemical activation is additionally used. The chemical activation is based on the single-stage heat treatment of the initial raw carbon material with some chemicals, *e.g.*, H<sub>3</sub>PO<sub>4</sub>, KOH, NaOH, ZnCl<sub>2</sub>, *etc.* Moreover, the chemical activation leads to the formation of porous carbon material with a larger surface area and micropore volume as compared to those of the material formed by physical activation.

In this work, sugar cane bagasse is used as plant raw material. This waste of sugar production in Vietnam is accumulated in the amount of up to 4.2 million tons according to the official statistics.<sup>11</sup> The main objective of this work was to develop the method for sugar cane bagasse carbonization, which would allow us to prepare the adsorbents capable of purifying water from phenol and 2,4-dichlorophenol, whose permissible concentration is 0.001 mg dm<sup>-3</sup> (11 and 6 nmol dm<sup>-3</sup>, respectively).

The carbonization of sugar cane bagasse was performed with limited oxygen access by mixing the feedstock with montmorillonite clay at the temperature of 750 °C for 3 h, followed by activation of the resulting carbonizate with water vapor. To increase the adsorption activity for phenol and 2,4-dichlorophenol, the obtained adsorbent was activated chemically by impregnation with 1 M KOH solution at room temperature for 24 h. Then the adsorbent was washed with distilled water and dried at 100 °C. The samples of the carbonated sugar cane bagasse (CS) and the carbonated sugar cane bagasse with subsequent chemical activation (CS-CA) were thus prepared. Figure 1 shows the SEM micrographs of the activated bagasse in comparison with the raw material.

The porosity parameters of the obtained sorbents were determined by the BET method and the Dubinin–Astakhov method. The results



**Figure 1** SEM micrographs of (a) raw sugar cane bagasse and (b) chemically activated carbon prepared from sugar cane bagasse.

**Table 1** Textural characteristics of the carbonized adsorbent before and after chemical activation.

Sample	BET surface area/m <sup>2</sup> g <sup>-1</sup>	Total pore volume/cm <sup>3</sup> g <sup>-1</sup>	Micropore volume/cm <sup>3</sup> g <sup>-1</sup>	Average pore width/Å
CS	310.1	0.27	0.43	18
CS-CA	889.3	0.32	0.68	25
BAU-A	840.0	0.27	0.54	10

of our calculations are presented in Table 1. For comparison, the parameters of the porous structure of commercial activated carbon known under the brand name BAU-A are given.

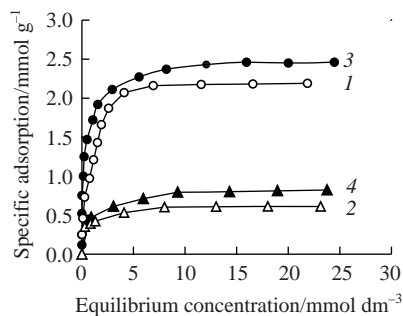
Chemical activation with KOH solution leads to a significant increase in the pore size and volume of the adsorbent. This increase is due to the release of CO and CO<sub>2</sub> gases generated inside the structure during chemical activation. The interaction of these gases with KOH leads to the formation of K<sub>2</sub>O and K<sub>2</sub>CO<sub>3</sub>, which, in turn, make a significant contribution to the formation of a developed porous structure. It should be noted that the average pore width of the prepared CS-CA sample is twice that of the commercial adsorbent.

The adsorption capacity of the obtained samples for phenol and 2,4-dichlorophenol was determined under static conditions using model solutions at a ratio of the weight of the adsorbent (g) to the volume of the model solution (ml) equal to 1 : 50. The concentration of substances was determined using the UV-VIS spectroscopy at the wavelength of 270 nm, a characteristic band for the benzene ring.<sup>†</sup> To determine the maximum adsorption capacity ( $G_M$ ) of the obtained samples, the adsorption isotherms of phenol and 2,4-dichlorophenol were plotted in the coordinates of monomolecular adsorption (Figure 2). These dependencies turned out to be well correlated with the Langmuir equation.

The calculated values of  $G_M$  of the adsorbents are presented in Table 2. For comparison, the measured adsorption capacity of the commercial adsorbent BAU-A is given.

As can be seen, the chemical activation with KOH solution increases the value of  $G_M$  of the obtained adsorbents to phenol by 3.67 times, and to 2,4-dichlorophenol by 2.95 times. Also, the value of  $G_M$  for 2,4-dichlorophenol on both materials was found to be higher than that for phenol. This increase can be explained by the different solubility of the studied adsorbates, namely, the solubility of phenol and 2,4-dichlorophenol is 6.5 and 5.0 g per 100 ml of water, respectively. A substance with lower solubility in an aqueous medium is easier to recover. The data demonstrate that the adsorption capacity of the CS-CA sample is even slightly higher than that of the commercial BAU-A adsorbent.

Thus, the carbonization of sugar cane bagasse allows us to produce highly efficient adsorbents for water purification from phenol and 2,4-dichlorophenol. The values of  $G_M$  for these adsorbents



**Figure 2** Adsorption isotherms of (1,2) phenol and (3,4) 2,4-dichlorophenol on the (2,4) CS and (1,3) CS-CA sorbents.

**Table 2** Parameter  $G_M$  for adsorption of phenol and 2,4-dichlorophenol on the carbon-containing adsorbents.

Adsorbed substance	Adsorbent	$G_M$ /mmol dm <sup>-3</sup>
Phenol	CS	0.61
	CS-CA	2.24
	BAU-A	2.12
2,4-Dichlorophenol	CS	0.83
	CS-CA	2.45
	BAU-A	2.24

reach 0.61 mmol g<sup>-1</sup> with phenol and 0.83 mmol g<sup>-1</sup> with 2,4-dichlorophenol. The chemical activation of the adsorbents with KOH solution enhances these values up to 2.24 and 2.45 mmol g<sup>-1</sup>, respectively.

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