Electronic supplementary materials *Mendeleev Commun.*, 2022, **32**, 828–830

Efficient carbon adsorbent for hydrogen sulfide produced from sugar cane bagasse

Alexander A. Greish, Pavel V. Sokolovskiy, Elena D. Finashina, Leonid M. Kustov, Alexander I. Vezentsev, Dinh Chien Nguyen and Hoai Chau Nguyen

Experimental

The runs related with testing carbon adsorbents in its ability to adsorb H_2S both in the gas and aqueous media were carried out in the pulse mode that can be considered as the express method to study such research problems.

The carbon-based adsorbents preparation

The initial carbon adsorbent was produced from sugarcane bagasse by its carbonization at 600°C for 3 hours without oxygen access[5]. Then the two-stage oxidative-alkaline activation of the carbon adsorbent was carried out. At the first stage, the adsorbent was placed in a solution consisting of 100 ml of 8% HNO_3 and 1.4 g of urea, and it was stirred for one hour at 90° C. The urea was added to reduce a quantity of NO_2 emitted during a carbon oxidation by HNO_3. The oxidized sample was washed with distilled water till pH=7. After that, the sample was filtered and dried at 100° C for 1 hour. At the second stage of the activation procedure the sample was impregnated with the 1mol KOH solution and left to stay in it for 48 hours at room temperature. Then the sample was washed secondary with distilled water till pH = 7, dried at 100 °C for 1 hour and was calcined in the muffle furnace at 300 °C for 1 hour.

Testing of the carbon adsorbents in H_2S adsorption in the gas phase

The study of adsorption of gaseous H_2S on the carbon adsorbents was carried out in a pulse mode in the U-shape micro-reactor (made from stainless steel, d = 4 mm) in the inert gas flow (He). The outlet of the micro-reactor was connected with the GL chromatograph injector. Due to this one and the same carrier-gas flow passed through both the micro-reactor and a GL chromatograph column. The amount of the adsorbent loaded to the micro-reactor was 150 mg (fraction 0.25 - 0.50 mm). In the each run small amount of H_2S (0.015-0.1 cm3) were input by a micro-syringe into the micro-reactor being with the inert carrier-gas flow passing through. The H_2S pulse went at first through the adsorbent bed, and then it entered into the chromatographic packed column. The GLC analysis of H_2S was carried out with the use of the LChM-8MD chromatograph, which allowed us to determine two important values characterized the adsorption process: 1 - the amount of H_2S left in the carrier-gas after passing through the adsorbent bed; 2 - the quantity of H_2S kept by the adsorbent loaded in the reactor. The pressure in the micro-reactor

was 2.25 atm., the volume rate of the carrier-gas was 15.8 cm3/min (ambient conditions). The free space of the micro-reactor was filled with crushed quartz (0.5 – 1.0 mm). The GLC analysis was carried out on the packed column (2 m x 3 mm) filled with Chromaton support with 15%SE-54 as a liquid phase, the temperature of a column was 38° C, the detector was a catarometer.

Testing of the carbon adsorbents in the H_2S adsorption in the aqueous solution

To study the adsorption of H_2S dissolved in water on the carbon adsorbents, it was used a pulse mode too, but unlike experiments related with the pulses of gaseous H_2S, we applied the vertical micro-reactor (made from stainless steel, d=4 mm) which was not connected with the chromatograph equipment. In this case the aqueous samples with a volume of 2 ml and containing 50 μl of dissolved H_2S were injected by a syringe for 1 min into the micro-reactor in which the carbon adsorbent with a weight of 150 mg was loaded. The concentration of H_2S in the aqueous solution was of 1.1 mmol/L. Together with a liquid sample a slow carrier-gas flow (with a rate of 5 ml/min) was fed also into the reactor, the purpose of that was to facilitate passage of a liquid sample through the adsorbent bed consisting of small grains, as well its collection in the products receiver that was a small glass vial. After the sample injection the reactor was purged with inert gas for 1 min.

To determine the amount of H_2S caught by the carbon adsorbent it was used the GLC method also. In order to perform the GLC analysis of H_2S dissolved in water, it has made some changes in the entering part of the carrier-gas line of the chromatograph. Thus, when carrying out the GLC analysis of the H_2S solution, the liquid sample of about 100 μl was injected into the injector-evaporator, the temperature of which was 250°-300°C. Due to the high temperature in it, the water being in the sample quickly turned into a vaporous state and, together with the carrier-gas, entered the freezer (made from stainless steel, d=4 mm), the temperature of which was maintained at the level of -30° - 40°C. In the freezer the water contained in the liquid sample turned into ice, which settled on the freezer walls, while gaseous H_2S passed to the chromatographic column, where there was its separation from the air admixture. As a result, the H_2S concentration in the analyzed aqueous sample was determined that was the quantity of the non-adsorbed H_2S. And as for the concentration of H_2S in the initial solution was known one could calculate the quantity of H_2S kept by the carbon adsorbent. The scheme of the experimental setup for study of adsorption of H_2S dissolved in water on the carbon adsorbents is shown in Fig. 1S.

Physico-Chemical methods used in the work. The observations were carried out using Hitachi SU8000 field-emission scanning electron microscope (FE-SEM). Images were acquired in secondary electron mode at 10 kV accelerating voltage and at working distance 8-10 mm. EDX studies were carried out using Oxford Instruments X-max EDX system. The presence of different functional groups on the carbon-containing adsorbebts surfaces was studied by the diffuse

scattering IR method (DRIFT). The DRIFT spectra were recorded at room temperature on a NICOLET «Protege – 460» spectrometer equipped with a diffuse scattering prefix in the range of wave numbers 4000-1000 cm^{-1}, in increments of 4 cm^{-1}. The intensity of the IR absorption bands in the spectra was represented in Kubelka-Munk units. CaF_2 powder was used as a standard. IR spectra were processed according to the OMNIC program.

Comparing the concentrations of H_2S in the initial solution and that one in the solution obtained after passing through the adsorbent bed, it was could be determined the amount of H_2S that was absorbed by the carbon adsorbent. The scheme of the experimental setup is shown in Figure 1S.

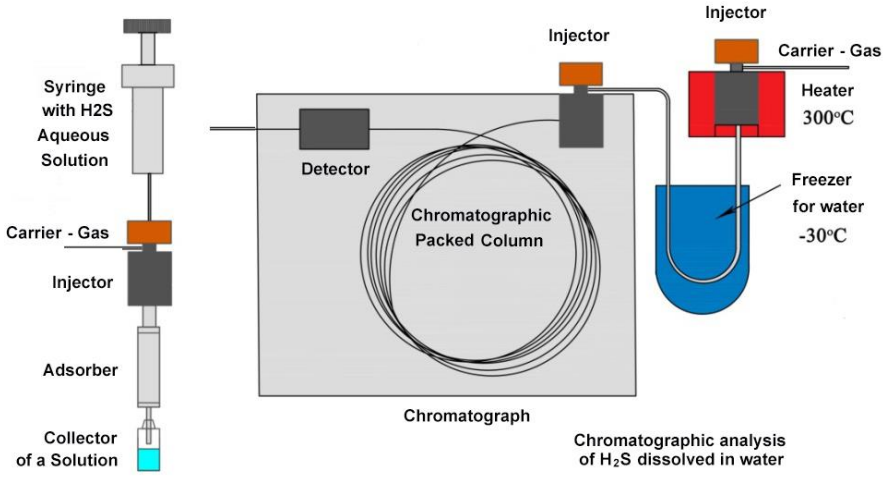
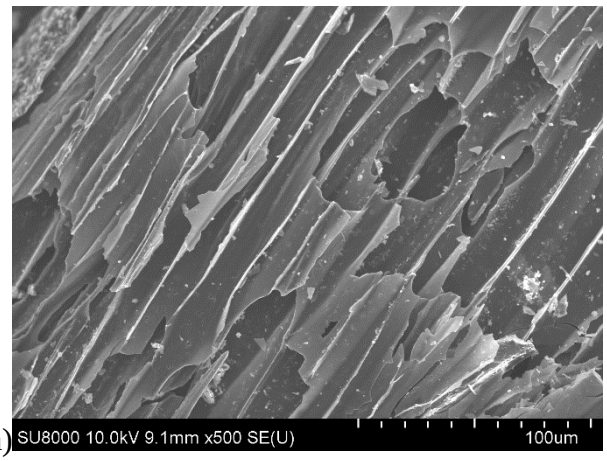


Figure S1. Experimental setup for testing carbon adsorbents for its ability to adsorb H_2S dissolved in the aqueous solution in the pulse mode.

The microstructure of the carbon adsorbent obtained from sugarcane bagasse during oxygen-restricted carbonization is represented by parallel fibrous aggregates 20–25 μm wide, permeated with micropores up to 1 μm in size (Fig. 2S). The micropores have a fairly narrow size distribution. The microphotographs show that the heat treatment of sugarcane bagasse does not destroy the structure of parallel-fibrous aggregates; no cracks are observed in the structure.

Acid-alkaline treatment of sugarcane bagasse with HNO_3 and KOH solutions makes it possible to obtain a completely different microstructure. The fibrous structure is preserved, but the number and size of micropores increase significantly. The size of micropores is in the range of 1.5 - 2 microns, the edges of micropores are uneven. Micropores are formed on the outer and inner surface of the carbonized bagasse fibers of sugar cane, which can significantly increase the adsorption characteristics of the resulting carbon.

a) 

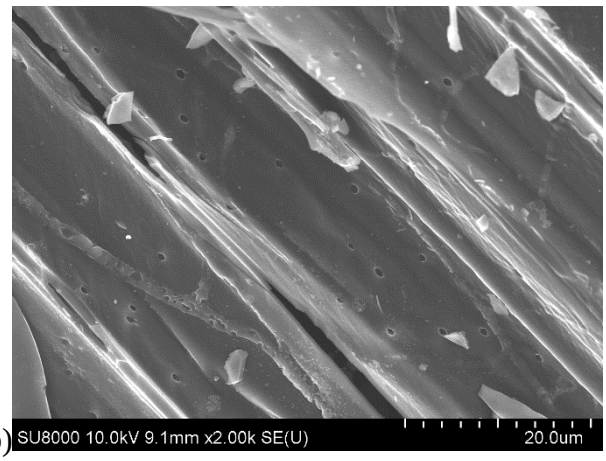
b) 

Figure S2. Microstructure of the CSB sample: a) the initial CSB sample b) the CSB sample sequentially treated with the HNO_3 and KOH solutions.