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Efficient carbon adsorbent for hydrogen sulfide produced from sugar cane bagasse

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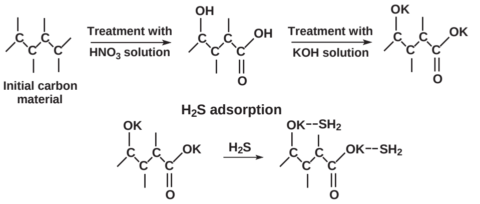
It was found that a carbon-containing adsorbent produced from sugar cane bagasse and activated by oxidative alkaline treatment has rather high adsorption activity towards H_2S impurities polluting environment.



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Hydrogen sulfide is one of the most common pollutants that cause great harm to the environment. The permissible concentration of H_2S in the air does not exceed 0.008 mg m^{-3}. Activated carbons are often used to remove H_2S impurity from the air; moreover, they are also widely applied as adsorbents for cleaning various gas emissions and water effluents from acid gases admixtures.[1–3] In this regard, the use of carbon-containing adsorbents to remove acid gases from shrimp pools located in Vietnam and intended for artificial cultivation of shrimp aquaculture is of great interest.

The formation of acid gases in shrimp pools occurs mainly due to the decomposition of bottom sediments containing both food residues and waste products of the shrimp vital activity by anaerobic bacteria. Hydrogen sulfide and ammonia are the primary gaseous decomposition products of organic substances in shrimp pools. In turn, these gases are oxidized by aerobic bacteria producing sulfur and nitrogen oxides, which, no doubt, can provide a detrimental effect on the shrimp colony living in the pool and the environment where the shrimp pool is located.

Due to their hydrophobic properties and very high surface areas, the carbon-containing adsorbents can be used to remove harmful gases from both air environment and water media, herewith they are able to adsorb not only H_2S, but also other gases polluting the environment. The use of the carbon-containing adsorbent can be considered as the most suitable way to reduce the concentration of harmful gases in shrimp pools located in Vietnam. The main advantages of the adsorption removal of harmful gases in shrimp pools and their environment are, on the one hand, the technological simplicity of the adsorption process, which does not require large energy consumption, and on the other hand, the high efficiency of the removing of harmful gaseous impurities with carbon-containing adsorbents. At the same time, it must be taken into account that the adsorption properties of activated carbons depend in large extent both on the textural characteristics of the carbon-containing materials which they are produced from and on the activation methods intended to increase the adsorption capacity of initial carbon material. The use of sugar cane bagasse to produce carbon-containing adsorbents destined for cleaning the aqueous media from harmful gases in the shrimp pools located in Vietnam is of great interest. Sugar cane bagasse is a waste of sugar production, which takes a remarkable place in the Vietnamese agriculture.[4] Indeed, the total amount of sugar cane bagasse accumulated annually on the sugar plantations in Vietnam can exceed four hundred million tons. Moreover, as shown in the previous studies,[5,6] sugar cane bagasse, like most wood materials of the natural origins, consists mainly of such compounds as cellulose, hemicellulose and lignin. Then, the use of sugar cane bagasse as a feedstock for the production of carbon-containing adsorbents can be considered as a practically suitable way to utilize these agricultural wastes. The transformation of sugar cane bagasse into carbon form can be carried out by carbonization or firing sugar cane bagasse in an oxygen-free atmosphere at 550–650 °C.[5]

To increase the adsorption capacity of the carbon-containing adsorbent towards hydrogen sulfide to be removed, the carbon material is usually activated by appropriate chemicals, that can functionalize the surface of carbon-containing adsorbent, making it capable of interacting with pollutants molecules to be removed from the environment. Thus, to increase the ability of carbon-containing adsorbents to remove acid gases, they are often treated with alkali metal hydroxides (NaOH and KOH).[1,7,8] This leads to the formation of basic functional groups on the carbon-containing adsorbent surface which in turn increases its adsorption activity towards substances having acidic properties.

The purpose of the present work was to prepare carbon adsorbents based on sugar cane bagasse, which have high adsorption activity towards H_2S impurity, located in both gaseous and aqueous environments.

The carbon-containing material used in this work for H_2S adsorbent production was obtained by carbonization of sugar cane bagasse at 550 °C for 3 h without oxygen access. The appearance of the produced carbon containing material (see SEM images in Online Supplementary Materials) indicates that we are dealing with a rather loose structure, significantly different from that of the birch activated carbon or the activated carbon produced from coconut shells, despite the fact that all these materials are derived from related structures of natural origins having similar chemical compositions. The main target of this research was to develop an efficient method to increase the adsorption activity of the carbon-containing adsorbent based on sugar cane bagasse, particularly towards H_2S, which is known to exhibit not so strong acidic properties. We considered the use of the two-stage oxidative alkaline activation as an optimal solution, namely, the sequential treatment of the carbon-containing adsorbent at first with a solution of a strong oxidizer and then, after washing and drying, the treatment with a solution of a strong alkali. A solution of nitric acid with a small addition of urea was chosen as an oxidizer, and KOH solution was used as an alkaline one. We proceeded from the fact that oxidation of a carbon-containing adsorbent with nitric acid can lead to the formation of oxygen-containing functional groups connected with surface carbon atoms, such as hydroxyl (C–OH) and carboxyl (C–COOH) groups. Then, during the subsequent treatment of the adsorbent with an alkali (KOH) solution, the formation of functional groups containing an alkali metal (C–OK, C–COOK) can occur, which should lead in turn to the adsorption interaction of the adsorbent with an acidic substance, namely hydrogen sulfide. The appearance of C–OH and C–COOH groups on the adsorbent surface after the treatment with nitric acid was confirmed by diffuse reflectance IR Fourier transform (DRIFT) spectroscopy. It is obvious that C–OK and C–COOK groups can act as the sites of irreversible chemisorption of H_2S, so they can be responsible for the adsorption activity of the carbon-containing adsorbent towards acidic gases including H_2S. Additionally, the SEM micrographs showed that the treatment of the carbon-containing adsorbent with concentrated HNO_3 solution leads to the partial destruction and apparently to the decrease in the adsorbent hardness.

Figure 1 shows the results of H_2S adsorption carried out in the pulse mode on the two adsorbents obtained from sugar cane bagasse: the initial sample of carbonized sugar cane bagasse (CSB) and the CSB sample subjected to the sequential oxidative alkaline activation (designated as CSB-A) that could lead to increase in its adsorption activity towards H_2S.

Comparison of the results on the H_2S absorption obtained for CSB and CSB-A samples clearly demonstrates that oxidative alkaline activation of CSB adsorbent significantly increases the adsorption activity of the initial adsorbent towards H_2S. According to the data presented in Figure 1(*a*), only 120 μl from total 1200 μl of H_2S (24 pulses of H_2S of 50 μl each) supplied to the reactor loaded with the CSB adsorbent, were adsorbed, that is only 10% of the total quantity of H_2S input into the reactor. It is rather typical that even in the first H_2S pulse, about 40% of the H_2S passes through the adsorbent bed without any interaction with it. Moreover, the adsorption capacity of the CSB adsorbent is reduced very fast from pulse to pulse. At the same time, the CSB-A sample exhibits remarkably higher adsorption activity towards H_2S [see Figure 1(*b*)]. Indeed, the CSB-A adsorbent adsorbed about 121 μl from 360 μl of H_2S (24 pulses of 15 μl each) passed through reactor, that is about 33.5% of the total amount of H_2S. The high adsorption activity of the CSB-A sample towards H_2S, is apparently caused by the irreversible interaction of H_2S molecules with the functional groups on the carbon-containing adsorbent surface which include alkali metal in their compositions (C–OK, C–OOK), that resulted from the sequential oxidative alkaline treatment of the initial CSB adsorbent.

For comparative purpose, the similar experiments were carried out with the carbon adsorbents produced from coconut shells (CAC). Figure 2 depicts the adsorption capacity of the initial CAC sample and the one prepared from the CAC sample activated by the oxidative alkaline treatment (CAC-A) similar to that was done in the case of the CSB adsorbent.

It should be noted that the oxidative alkaline activation of the CAC sample also increases its adsorption activity towards H_2S, even to greater extent than that in the case of the carbon-containing adsorbents produced from sugar cane bagasse (CSB *vs.* CSB-A). Indeed, the results show that the CAC-A sample adsorbed 1860 μl from 2220 μl of H_2S (37 pulses of 60 μl each), *i.e.* 83.7% of the total H_2S amount supplied to the reactor. Thus, the CAC-A sample demonstrates rather high adsorption capacity towards H_2S.

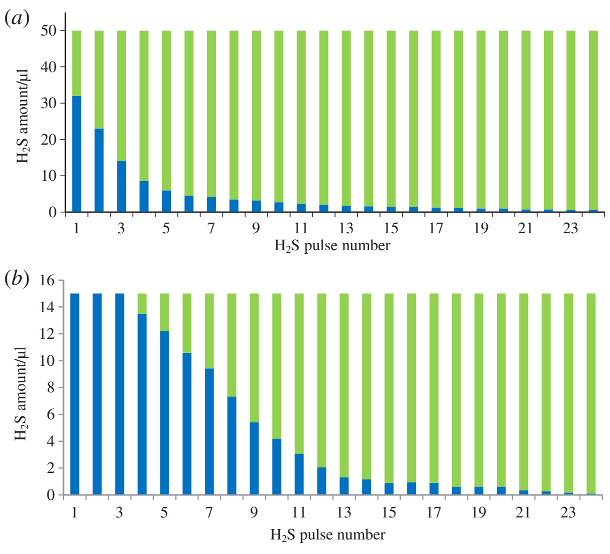

Figure 1 The pulse mode H_2S adsorption by the two adsorbents produced from sugar cane bagasse: (*a*) CSB sample; 50 μl H_2S pulses, total H_2S amount 1200 μl; (*b*) CSB-A sample, 15 μl H_2S pulses, total H_2S amount 360 μl.; 🟦 indicates the amount of adsorbed H_2S, 🟩 indicates the amount of non-adsorbed H_2S.

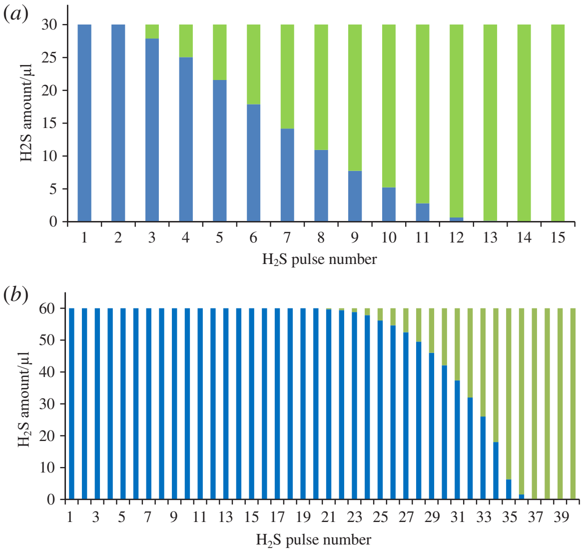

Figure 2 The pulse mode H_2S adsorption by the commercial activated carbon samples obtained from coconut shell: (*a*) CAC sample, 30 μl H_2S pulses, total H_2S amount 390 μl; (*b*) CAC-A sample, 60 μl H_2S pulses, total H_2S amount 2220 μl; 🟦 indicates the amount of adsorbed H_2S, 🟩 indicates the amount of non-adsorbed H_2S.

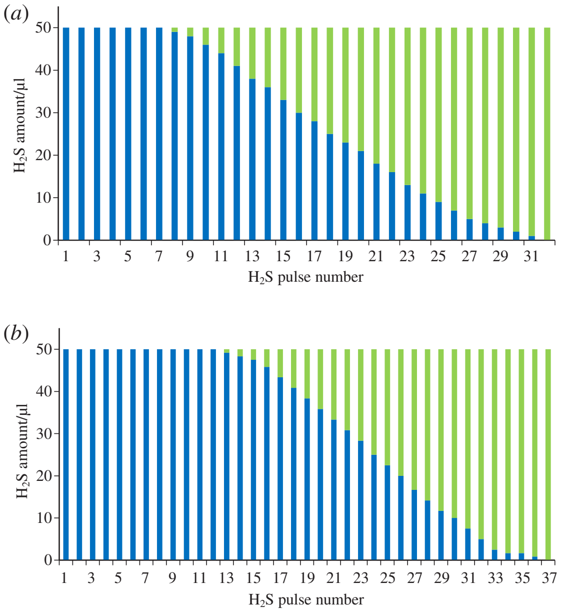

Figure 3 The pulse mode adsorption of H_2S dissolved in water by activated (*a*) CSB-A and (*b*) CAC-A adsorbents. Concentration of H_2S in water solution was 1.1 mM (50 µl H_2S in 2 ml of water); 2 ml of solution was supplied during 1 min in each run; 🟦 indicates the amount of adsorbed H_2S, 🟩 indicates the amount of non-adsorbed H_2S.

Special attention was paid to the adsorption activity of the discussed adsorbents towards H_2S dissolved in water. The experimental installation including a vertical flow microreactor containing 150 mg of the carbon-containing adsorbent was used. In this case, 2 ml of an aqueous H_2S solution were supplied into the reactor during 1 min. The liquid passed through the reactor was collected in the product receiver and the concentration of H_2S in the water solution was determined by GLC. Then the amount of adsorbed H_2S was calculated. The details of the experiments and the GLC analyses are given in Online Supplementary Materials. The initial concentration of H_2S in water solution was 1.1 mM. The results obtained for two adsorbent samples are given in Figure 3.

The results obtained show that the CSB-A and CAC-A adsorbents effectively adsorb H_2S from aqueous solutions. According to the data, when passing 390 µl of H_2S (13 pulses of 30 µl each) through a reactor with the specified adsorbent ~ 194 µl is adsorbed, that is 49.7% of the total amount of H_2S supplied to the reactor.

As can be seen from the above data, H_2S dissolved in water is quite effectively removed by carbon-containing adsorbents based on activated CSB. However, compared with the removal of H_2S impurity in a gaseous medium, the adsorption of this gas in the water solution occurs at a slightly slower rate, and more time is required to achieve adsorption saturation of adsorbents with H_2S impurity. Apparently, the diffusion factors that reduce the rate of dissolved gas molecules passing from aqueous medium to the surface of adsorbent, especially their entrance into its micropores are the main reason for this. It seems that the rate of adsorption of these gases can be increased either by stirring the solution with a mechanical stirrer or by bubbling some inert gas through a liquid layer.

Thus, the results of the work allow us to conclude that the proposed method of carbonation of sugar cane bagasse with subsequent chemical activation can be successfully used to produce rather effective adsorbents for H_2S impurity. In our opinion, the resulting adsorbents are perfectly suitable for removal of H_2S from the water of shrimp aquaculture pools.

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Online Supplementary Materials

Supplementary data associated with this article describing all experimental methods and technique used can be found in the online version at doi: 10.1016/j.mencom.2022.11.040.

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