



Hydrogen sulphide removal on carbonaceous adsorbents prepared from coffee industry waste materials



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HIGHLIGHTS

- The alternative method of utilisation of coffee industry waste materials is proposed.
- Very effective H₂S adsorbents were prepared from coffee industry waste materials.
- The adsorbents prepared show greater efficiency of H₂S removal than commercial ones.
- Sorption capacity depends mainly on mineral matter content and adsorption conditions.

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ABSTRACT

The sorption properties of chars and activated carbons obtained from coffee industry waste materials toward hydrogen sulphide are characterised. The effects of pyrolysis temperature and method of activation as well as porous structure, acid–base character of the surface and mineral matter content on the efficiency of H₂S removal are checked. Moreover, four different variants of adsorption test are applied, in order to estimate the optimal conditions of hydrogen sulphide capture. Depending on the method of activation, the adsorbents prepared are characterised by diverse textural parameters, strong basic or medium-acidic character of the surface and various mineral matter content, varying from 1.2 to 58.4 wt.%. The results obtained in our study have proved that through an appropriate choice of pyrolysis conditions and activation procedure for coffee industry waste materials it is possible to obtain adsorbents with high capacity of hydrogen sulphide, reaching to 281.5 mg H₂S/g_{ads}. The results of our study have also shown that the adsorption ability of activated carbons prepared depends first of all on the conditions of adsorption test, mineral matter content and basicity of the surface and only to a small degree on porous structure development.

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1. Introduction

Everyday huge amounts of toxic gas pollutants are released to the atmosphere. The dominant among them are volatile organic compounds, carbon and nitrogen oxides, ammonia, methane as well as sulphur compounds [1]. Particularly hazardous for human health and for the natural environment are the inorganic sulphur compounds such as SO₂, CS₂ or H₂S. They originate from the economic and industrial activity of man (in particular hydrogen sulphide), including electric power plant emission, industrial plants emission, animal farms, septic tanks, waste purification plants as well as from natural sources such as volcano eruptions, thermal springs and bogs [2]. As the emission from the natural sources is uncontrollable, it is very important to work on limiting the

pollutants from anthropogenic sources. Much attention has been paid to this problem and it is a subject of studies all over the world. Some of the recommendations are to use desulfurized fuels, to improve efficiency of their combustion and use of the energy from this combustion, to purify the exhaust gases formed in the process [3].

Sulphur compounds can be effectively removed by many ways, e.g. by wet scrubbing, catalytic oxidation or combustion [4–5]. An important role in limitation of the emission of sulphur compounds (in particular H₂S) to the atmosphere has been played by adsorbents [6–8], especially activated carbons [9–14]. Thanks to their unique physicochemical properties they can not only be effective adsorbents, but also as catalysts or their carriers, so the removal of gases containing sulphur can take place by physical or chemical adsorption or by catalytic oxidation on the carbon surface [15–18].

The effectiveness of H₂S removal by activated carbons can be improved by their impregnation with caustic materials such as

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NaOH or KOH, copper(II) ions and by incorporation of nitrogen, sulphur and oxygen functional groups into the carbon structure [16,19–22]. Important positive influence on the effectiveness of H₂S removal has the presence of steam in the gas flux during H₂S adsorption, the presence of inorganic compounds in the carbon structure (such as iron oxide, calcium oxide, magnesium) and the proper choice of textural parameters [3,16,23–26].

In our earlier studies on the synthesis of activated carbons from waste products obtained in production of coffee and their potential use in NO₂ adsorption [27], we obtained carbon adsorbents showing strongly basic surface, different degrees of surface development, high content of mineral substances (including alkali metals) and a considerable content of heteroatoms (mainly nitrogen and sulphur) in their structure. As mentioned above all these parameters have significant influence on the effectiveness of H₂S adsorption by activated carbons, so the aim of this study was to evaluate the adsorbents obtained from the coffee industry waste products in adsorption of hydrogen sulphide from the stream of gases and to establish the optimum conditions of this gas removal.

2. Experimental

2.1. Sample preparation

The starting material – coffee industry waste materials (C) in the form of pellet was subjected to pyrolysis process (P) followed by physical activation with CO₂ (PA) or chemical activation with KOH (CA), according to procedures described in detail in our earlier work [27] and presented briefly in Scheme 1.

2.2. Analytical procedures

The elemental analysis of the all samples under investigation was performed on an Elementar Analysensysteme instrument, model Vario EL III. The contribution of metals in the precursor was measured on an emission spectrophotometer Varian ICP-OES VISTA-MPX. The content of mineral matter for all samples obtained was determined according to the DNS ISO 1171:2002. The textural characterisation of the samples was based on the nitrogen-adsorption isotherms determined at –196 °C with a Quantachrome Autosorb iQ surface area analyzer. The content of surface oxygen functional groups of acidic and basic character was determined

using potentiometric titration experiments, according to procedure described earlier [27].

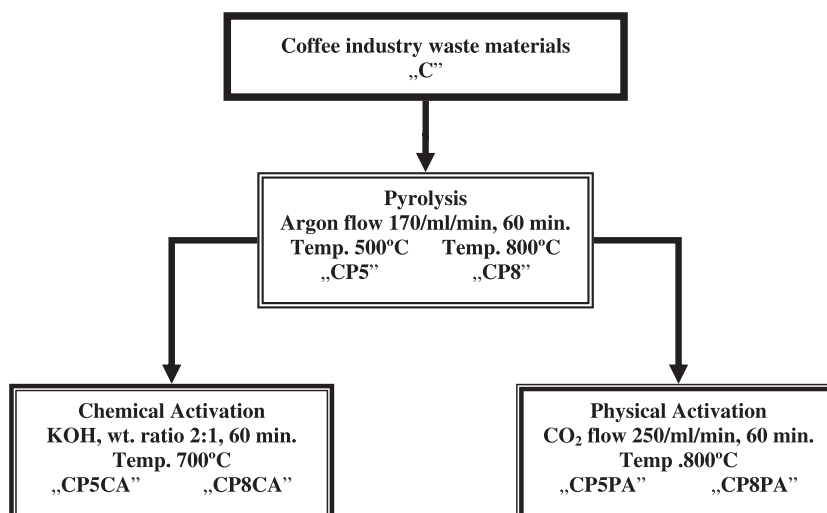
2.3. Evaluation of hydrogen sulphide sorption capacity

The chars and activated carbons (in the form of grains of 0.75–1.5 mm in diameter) were packed into a glass column (internal diameter 9 mm, bed volume 3 cm³). Dry (D) or wet (M, 70% humidity) air with 0.1% of H₂S was passed through the dry bed of the adsorbent at 450 cm³/min. All adsorption tests were performed at room temperature. Moreover, additional variant of H₂S adsorption were used: the samples were wetted before the adsorption tests by the air of 70% humidity for 30 min and then the tests were performed either in dry (referred as mix-dry – MD) or in wet (referred as mix-wet – MW) conditions. The breakthrough of H₂S were monitored using Multi-Gas Monitor Q-RAE PLUS PGM-2000/2020. The tests were stopped at the breakthrough concentration of 100 ppm, because of the electrochemical sensor limit. The capacities of each material in terms of milligram of hydrogen sulphide per gram of adsorbent were calculated by integration of the area above the breakthrough curves, and from the breakthrough time, H₂S concentration in the inlet gas, flow rate as well as mass of adsorbent.

3. Results and discussion

3.1. Sorption properties of chars toward hydrogen sulphide

As follows from the data collected in Table 1, the main components of the inorganic substance in the coffee industry waste materials are the compounds of potassium, calcium, magnesium, sodium and iron, whose presence is known to have beneficial influence on the sorption properties of carbon adsorbents. The presence of such compounds suggests that the chars and first of all activated carbons obtained by chemical or physical activation, will show high sorption capacity not only towards NO₂ [27] but also towards H₂S. To verify this supposition, each of the materials obtained was subjected to adsorption tests in four variants. The results, collected in Table 2, reveal that the sorption capacity towards H₂S significantly depend on the thermal conditions of pyrolysis and the variant of activation, however, the greatest influence on the effectiveness of H₂S removal from the gas stream have the conditions of adsorption process.



Scheme 1. Preparation conditions of activated carbons.

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