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Determination of adsorption isotherms of chlorinated hydrocarbons on halloysite adsorbent by inverse gas chromatography☆

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ABSTRACT

Inverse gas chromatographic methods of isotherm determination peak maximum (PM) and peak division (PD) were compared. These methods were applied to determine adsorption isotherms of dichloroethylene, trichloroethylene and tetrachloroethylene on acid-activated halloysite and adsorption enthalpy.

1. Introduction

Halloysite belongs to a sub-group of kaloinite minerals. Their basic structural element is a halloysite pack with the crystallochemical formula $Al_4Si_4O_{10}(OH)_8$. It is composed of two layers: tetrahedric and octahedric. The tetrahedric layer is formed by tetrahedrons interconnected with three vertexes, where Si^{4+} is a central ion, surrounded by four oxygen anions O^{2-}. The octahedric layer, called the metal–oxygen–hydroxide layer, is composed of octahedrons interconnected with edges, in centre of which the Al^{3+} ion is located, coordinated by OH^- and O^{2-} anions, with O^{2-} anions being shared by the tetrahedirc and octahedric layers. Both layers form a pack structure [1,2].

Acid activation, or less commonly – alkaline activation, is performed in order to obtain a mineral sorbent of halloysite.

Acid activation takes place as a result of partial dissolution of halloysite. The process follows the pseudo-primary mechanism and is characterized by initial exchange of interlayer cations with protons, followed by dissolution of tetrahedric and octahedric layers and desorption of interlayer cations.

The analyzed halloysite samples come from strip mine *Dunino* in the vicinity of Legnica (Poland). This is one of three active halloysite mines in the world, besides the deposits in New Zealand and USA. The Polish deposit belongs to the largest in the world, supplying about 12 million tons of this raw material.

Mineral adsorbent obtained from acid-activated halloysite may be used for adsorption of airborne chlorinated hydrocarbons. Sources of those hydrocarbons are: chemical and petrochemical industry, use of solvents and solvent-containing agents.

This paper presents results of adsorption measurement of dichloroethylene (DiCE), trichloroethylene (TriCE), and tetrachloroethylene (TetraCE) on mineral adsorbent obtained from acid-activated halloysite basalt eluvium from the Dunino strip mine. The fast method of adsorption measurement by use inverse gas chromatography was tested, also.

2. Theory

Inverse gas chromatography (IGC) is a gas chromatographic technique in which the adsorbent is placed in the chromatographic column as stationary phase and known solutes are injected into the carrier gas stream. Retention time and shape of the chromatogram are a function of the interactions between the solute and stationary phase, and can be used to determine several physico-chemical properties of the adsorbate–adsorbent system, such as adsorption properties, heat of adsorption, interaction parameters, and diffusion coefficients [3].

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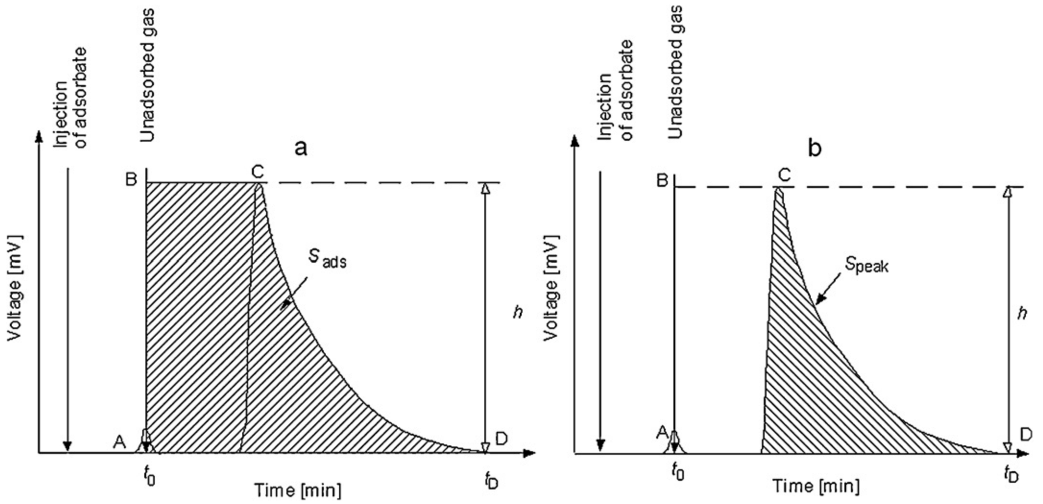

Fig. 1. Application of peak maxima PM method to the chromatographic peak profile: (a) the total adsorption surface area, S_s, i.e. the area between the points A, B, C and D and (b) the total surface area of the chromatographic peak, S_p.

Numeric methods of adsorption isotherm calculation based on a chromatographic peak are known. In this study calculations were completed using two methods: peak maximum (PM) and peak division (PD). Results of adsorption measurements completed with both methods were also compared.

Determination of adsorption data from the chromatographic peak area using the peak maximum (PM) method was described in [4].

Weight of an adsorbed substance at a given temperature is determined from a chromatogram based on Eq. (1):

$$a = \frac{m_a S_{ads}}{m S_{peak}} \tag{1}$$

and calculation of equilibrium pressure corresponding to the weight of adsorbed substance is made using Eq. (2):

$$p = \frac{m_a h}{F S_{peak}} RT \tag{2}$$

where a is the adsorption coefficient in mg/g, m_a is the amount of injected adsorbate in mg, m is the adsorbent mass in the column in g, S_{ads} is the area bounded by the height between the outflow of the non-adsorbing gas and the diffuse side of the chromatogram in mV min, S_{peak} is the adsorbate peak area in mV min, p is the partial pressure in Pa, h is the peak height in mV, R is the ideal gas constant in (cm^3 Pa)/(K mol), T is the temperature in K, and F is the volumetric flow-rate of carrier gas in the column in cm^3/min [4]. Method of determination of those values is presented in Fig. 1.

The use of the peak division method (PD), exactly described in [5], needs dividing the adsorption area S_{ads} into I – parts parallel to the basic line (Fig. 2) and measuring the area of individual surface segments.

The areas of individual segments satisfy the dependence:

$$S_{ads} = \sum_{1}^{I} S_{ls} \tag{3}$$

where S_{ls} is the area of I part of total adsorption surface (mV min).

The part of the quantity of adsorbed substance a_l is measured according to the formula:

$$a_l = \frac{m_a \sum_{1}^{I} S_{ls}}{m S_{peak}} \tag{4}$$

which is obtained after inserting Eq. (3) into Eq. (1).

The quantity of adsorbed substance a_l corresponding with the fraction of partial pressure p_l is calculated by dividing the height of the chromatographic peak (Fig. 2) into l – parts, according to the relation

$$h = \sum_{1}^{l} h_l \tag{5}$$

where h_l is the height of part l of peak (mV).

After inserting Eq. (5) into Eq. (2), the following is obtained:

$$p_l = \frac{n_a \sum_{1}^{l} h_l}{F S_{peak}} RT \tag{6}$$

The method of calculation of adsorption volume and partial pressure of adsorbates described in [5] was modified in [6], so that formulas used for those calculations included a computer-based method of chromatographic peak area determination. Preserving their physical sense, the modification consisted in insertion of values characterizing area of a chromatographic peak in units of voltage product (mV) and registration time (min) of the chromatogram (mV min) to those formulas. Simultaneously, values used for registration of chromatograms in analogue recorders were removed from those formulas.

In order to measure the adsorption surface, the areas of its individual segments, the area and the segments of the adsorption peak and the retention time, the computer program KSPD [7], was used. The program makes it possible to select the number of segments into which the surface of the elution peak can be divided. Measurements of the partial pressure p_l and the quantity of adsorbed adsorbate a_l were taken on the basis of data on the division of the profile peak listed in the data base of the program KSPD. As a result, the dependence $a = f(p)$ being the function of the adsorption isotherm was obtained. The number of points defining this isotherm depends on the selected number of the division of the adsorption surface into l-segments. The peak division method mentioned above makes it possible to determine an adsorption isotherm even on the basis of one chromatographic peak.

The applied Langmuir's equation was modified to the involution form [8]. The power factor n defines model of adsorption. For $n = 1$ adsorption takes course according to a single-centre model, for $n \neq 1$ adsorption is consistent with a multi-centre model. The factor of proportionality b is used for adjustment of the curve