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Research paper

Determination of adsorption isotherms of aniline and 4-chloroaniline on halloysite adsorbent by inverse liquid chromatography

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A B S T R A C T

Infrared spectroscopy (ATR FT-IR), X-ray fluorescence (WDXRF), and X-ray powder diffraction (XRPD) methods were used to investigate the structure and composition of halloysite mineral. On the basis of the results, we found that the chemical composition of Hal samples is typical as regards clay minerals with the exception of the high levels of iron and titanium oxides. The FTIR spectra of halloysite samples, before and after modifying, with aniline and 4-chloroaniline indicate successive incorporation of these compounds to the halloysite sample. Inverse chromatography is a quick and accurate method to determine adsorption equilibrium constants. The division peak method used previously to inverse gas chromatography was adapted in inverse liquid chromatography. Inverse liquid chromatography was used for aniline and 4-chloroaniline adsorption measurements on halloysite, which was an applying method of division peak. Both adsorption isotherms and enthalpy were determined. Physical significance of adsorption enthalpy was checked by the Boudart's criterion of entropy. In this paper proved that the division peak method of inverse liquid chromatography is useful because adsorption equilibrium constant can be determined with a single adsorbate dosage.

1. Introduction

Clay minerals have many applications in pharmaceutics, cosmetology, and environmental protection technologies as active principles, excipients, for drug delivery and adsorbents (López-Galindo et al., 2007; Joshi et al., 2010).

Halloysite (Hal) is a 1:1 layered clay mineral with one silica tetrahedron sheet and one alumina octahedron sheet (Brigatti et al., 2006). Due to its unique tubular structure in the nano-scale and many physicochemical properties (such as good mechanical properties, excellent chemical stability, high specific surface area and porosity, and large adsorption capacity), Hal has wide range applications in many areas and is a potential promising cheap alternative to expensive carbon nanotubes. This mineral is mainly used to produce porcelain products and as additive fillers in polymers, plastics and other similar composites. The studies have focused mostly on Hal as a microfiber reinforcement in polymer systems, where the internal lumen of the tube is used to store and control the release of active agents (Soma et al., 1992; Guo et al., 2009; Du et al., 2010; Vergaro et al., 2010; Dong et al., 2012). Chemically modified Hal (activated with sulfuric acid (VI)) was proved to be an effective adsorbent for the pesticide chlorpropham, 3- and 4-chloroaniline from an aqueous solution (Szczepanik et al., 2014a,b).

Aniline and its derivatives are important compounds that are used as intermediates in the production of many synthetic organic chemicals including polyurethanes, rubber additives, dyes, pharmaceuticals, pesticides and herbicides (Jen et al., 2001). Their presence in the environment not only is associated with the use in industrial manufacture, but also is a result of the biodegradation concerning xenobiotic compounds, including certain azo dyes and herbicides (e.g., acylanilides, phenylureas and phenylcarbamates) (Matsumoto et al., 1995; Emtiazi et al., 2001; Loos et al., 2003; Sørensen et al., 2003; Gosetti et al., 2010). Aniline and 4-chloroaniline are frequently found in industrial effluents and surface water, which induce serious environmental problems. Due to their high toxicity and accumulation in the environment, these compounds have been identified as potential carcinogens (Chu et al., 2007) that possess the ability of preventing oxygen uptake in the blood and thus causing damage the spleen (Goonewardena et al., 1992; Asakura and Okazaki, 1995; Göb et al., 1999; Karunakaran et al., 2005b; Wang et al., 2007a,b). Many methods, including biological and chemical (Sarasa et al., 2002; Gomes et al., 2005; Han et al., 2006; Jagtap and Ramaswamy, 2006), and photochemical ones (David et al., 1998; Augugliaro et al., 2000; Emtiazi et al., 2001; Sauleda and Brillas, 2001; Sanchez et al., 2002; Kumar and Mathur, 2004; Canle et al., 2005; Kamble et al., 2003; Karunakaran and Senthilvelan, 2005a; Karunakaran et al., 2005b; Chu et al., 2007; Wang et al., 2007a,b; Tang et al., 2010) have been used to remove this kind of pollutant.

Adsorption technology is one of the most effective techniques in the separation and removal of a wide variety of organic pollutants including

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aniline and its derivatives from wastewater (Cai et al., 2005; Laszlo, 2005; Villacanas et al., 2006; An et al., 2010; Al-Johani and Salam, 2011). The development of adsorption technologies requires the use of new adsorbents which could successfully remove organic pollutants, such as aniline and 4-chloroaniline from aqueous solutions.

Inverse chromatography is a quick and accurate method to determine adsorption equilibrium constants. Investigations on adsorption made by this method consist in introducing a specimen of adsorbate onto the adsorbent placed in a chromatographic column and in analyzing the chromatogram obtained. On the basis of quantities characteristic as regards the position and profile shape of the chromatographic peak can be calculated physical and chemical properties of adsorption. Inverse liquid chromatography (ILC), apart from inverse gas chromatography (IGC), is used more often for these measurements. The method used is based on ILC in paper (Bednar et al., 2012), where the retention of the molecular probes serves as a measure for the strength of interaction. The authors used two different methods to evaluate the retention data: one is kind of simple measure to deconvolute the peak and the other is called second peak maximum method, while researches observed that all methods gave similar results.

The paper (Arnell et al., 2005) using inverse method to estimate adsorption isotherm parameters in liquid chromatography, which indicates a new experimental approach, that the inverse method on plateaus gives experimental simplicity and low sample consumption. The competitive adsorption of the β-blockers alprenolol and propranolol on a Kromasil C18 stationary phase was used as an investigation model.

Two methods of IGC were used for adsorption in measuring peak maximum (PM) and peak division (PD) (Czech and Słomkiewicz, 2013). The adsorption of dichloroethylene, trichloroethylene and tetrachloroethylene on acid-activated Hal adsorbent was studied. Specifically the PM method requires several dosages of an adsorbate on the adsorbent in a chromatographic column. The PD method allows to determine the adsorption of an isotherm based on a single chromatographic peak obtained after a single dosage of the adsorbate sample. A comparison of both methods demonstrated that the results of adsorption measurements are similar.

As mentioned above, removing aniline from the aqueous phase requires adsorbent testing, and for this purpose, ILC may be useful. Particularly, the developed method can be useful for measuring the adsorption of aniline solution in the aqueous phase. The ILC method compared with the static measurements of the adsorption in water solutions is a less time-consuming method. There is no literature-based data about adsorption measurements performed by the PD method in the liquid phase.

In this work, the Hal mineral from a Polish strip mine “Dunino” has been used. Hal samples were obtained from the strip mine “Dunino” that was located in the vicinity of the town Legnica in south-western part of Poland. Matusik et al. reported that these Hal samples contained kaolinite and the ratio of Hal-(7 Å) to kaolinite was 59:41 (Matusik et al., 2009). The raw Hal mineral usually contains a small amount of hematite, quartz and other minerals in trace amounts. Infrared spectroscopy (ATR FT-IR), X-ray fluorescence (WDXRF), and X-ray powder diffraction (XRPD) methods were used to investigate the structure and composition of the Hal mineral. The research presented in this work was carried out in collaboration with the Intermark Company (Intermark, 2012), which owns the “Dunino” mine.

We plan to apply the PD method in ILC for measuring the adsorption of aniline and 4-chloroaniline on a Hal adsorbent. The verification of the obtained values concerning the enthalpy of adsorption aniline on Hal was checked by Boudart's criterion of entropy.

2. Theory

The method of measuring the quantities of adsorption and partial pressure of adsorbates described in the works (Wigdegrauz, 1978; Paryjczak, 1987) was modified so that the formulas used in such measurements would take the computer method that determines the area of a chromatographic peak into account. However, the values used in registering chromatograms on analog recorders were removed from these formulas and their physical correctness were kept by introduction to these formulas units of voltage (mV) and of registration time (min) in chromatogram.

Adsorption quantity a_i of the substance i at the equilibrium concentration of adsorbate c_i in the liquid phase is expressed by the following equation:

$$a_i = \frac{nS_s}{mS_p} \tag{1}$$

where: a_i — the quantity of the adsorbed substance i on the adsorbent (mg/mg), m — the mass of the adsorbent (mg), n — the quantity of the mass of substance i injected on the adsorbent (mg), S_s — total adsorption surface (mV·min) and S_p — total surface of the chromatographic peak (mV·min) (Fig. 1a).

Total adsorption surface S_s (mV·min) is the area between points A, B, C, and D in Fig. 1b. The area of adsorption surface is defined by the equation below:

$$S_s = \int_0^h (t_D - t_0)\,dh \tag{2}$$

where: t_0 — hold-up time (min), t_D — time from introducing the adsorbate onto the adsorbent to the completion of recording the peak (min) and h — the height of the peak (mV).

The concentration equilibrium of adsorbate c_i (mg/cm^3) in the liquid phase is calculated by the following equation:

$$c_i = \frac{nh}{FS_p} \tag{3}$$

where: F — flow rate of carrier liquid (cm^3/min).

The use of the peak division method (Wigdegrauz, 1978) needs dividing the adsorption area S_s into l — parts parallel to the basic line (Fig. 2a) and measuring the area of individual surface segments.

$$S_s = \sum_1^l S_{ls} \tag{4}$$

where: S_{ls} — the area of l part of total adsorption surface (mV·s).

The part of the quantity of adsorbed substance a_{il} is calculated according to the formula given below:

$$a_{il} = \frac{n\sum_1^l S_{ls}}{mS_p} \tag{5}$$

which is obtained after putting Eq. (4) into Eq. (1).

The quantity of the adsorbed substance a_{il} corresponding with the fraction of equilibrium concentration of adsorbate c_{il} is calculated by dividing the height of the chromatographic peak (Fig. 2b) into I — parts, according to the dependence:

$$h = \sum_1^I h_l \tag{6}$$

where: h_l — height of part I of peak (mV).