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Equilibrium adsorption of ethyl mercaptan and thiophene using molecular sieve 13X

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A B S T R A C T

In the present study, adsorption of the sulfur compound onto two types of molecular sieve (HYD10B and LQ-MS-13X) in a batch system was investigated. It has been illustrated that HYD10B type has more adsorption capacity than LQ-MS-13X type to separate ethyl mercaptan from simulated liquid mixture. Selected as the better adsorbent, the isotherm equilibrium adsorptions of ethyl mercaptan and thiophene in liquid phase had been carried out by using this type of molecular sieve in the temperature range of 25−65 °C. HYD10B-MS-13X brought out the highest adsorption capacity for adsorption of ethyl mercaptan component. Diminution of adsorption capacity with temperature increment has been found and it was shown that adsorption of ethyl mercaptan is less affected by temperature changes. Using four more common isotherm models (Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich), Freundlich isotherm was found to be the best representative model for describing ethyl mercaptan and thiophene equilibrium data.

1. Introduction

Acid rain is one of the devastating consequences of environmental pollution due to sulfur emission into the air atmosphere. Moreover, presence of this type of material in hydrocarbon fuels causes corrosion problems and reduces the performance of those engines that uses such fuels. Therefore, enhancement in air quality can be achieved by decreasing sulfur emissions when sulfur compounds are not accessible to machines [1,2]. Consequently, sulfur removal is one of the most important separation processes in petroleum refineries to clean-up of transportation fuels.

One of the most practical desulfurization technique in most modern refineries is hydro-desulfurization (HDS). This method uses expensive molybdenum-based metal sulfide catalysts at high temperatures and hydrogen pressure to break the C-S bonds to remove the sulfur molecules as hydrogen sulfide (H_2S) [3]. Therefore, using this relatively expensive technique is not lucrative to perform in developing countries [4]. HDS method also hydro treats all aromatic compounds, which reduces the octane number of the gasoline fuel [5].

Other technologies of treatment with distinct successful levels significantly developed as results of recently developing research.

Using little or no hydrogen, running at low temperatures and selectivity to sulfur removal, which is highly advantageous lead to recognizing of adsorption method as the most efficient and promising solution technique. Therefore, recently adsorption methods for removing sulfur from fuels are taken attractively into consideration. Ease of operation at normal pressure and temperature, ease of process controlling and minimum requirement of energy and chemical for easy regeneration of used adsorbent are expected to be offered by a typical adsorption process.

Many reports of various materials starting from activated carbon (AC), silica-based adsorbents, zeolites, and metal exchanged/impregnated AC/zeolites/mesoporous materials have been presented in the literature for adsorption processes [6–11]. High internal and external surface areas [12], layered structure [13] and chemical and mechanical stability [14] which are the most important characteristics of zeolites lead to recognizing it as an excellent adsorbent material. In addition, adsorption on zeolites can be described as physical adsorption [15].

The present study is dedicated to make an investigation on equilibrium isotherms adsorption of sulfur compound understudy (ethyl mercaptan and thiophene). Having high surface area, pore volume and commercial availability of zeolite 13X lead to using two

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types of this zeolite to perform experiments. Moreover, this type of molecular sieve came out as an capable adsorbent among some studied material [16].

In this study, comparison between two types of Molecular seives 13X for adsorption of the sulfur compound was conducted. The study was followed to investigate the adsorption behavior of selected molecular sieve 13X on mentioned adsorbates in the liquid phase mixture of n-hexane as solvent at three different temperatures of 25, 45 and 65 °C. Regarding to obtain results the best isotherm model to predict the equilibrium conditions on the process of adsorption was proposed.

2. Experimental section

2.1. Material

2.1.1. Adsorbates

Ethyl mercaptan and thiophene both with a purity of more than 99% were supplied from Merck (Germany). N-hexane supplied from BIPC Co. (Iran) with a purity of 97% which was used as a solvent to prepare simulated liquid fuel.

2.1.2. Adsorbents

Two type of Molecular sieves 13X in granular form were used. LQ-MS-13X and HYD10B-MS-13X were prepared from SHLQ Co., Ltd (China) and SHMS Co., Ltd (China), respectively. Some physical properties of solid adsorbents are presented in Table 1.

2.2. Analysis method

An X-ray sulfur meter (RX-360SH) with a high sensitivity was used to determine total sulfur concentration remained in treated solutions. In this device, small-sized X-ray tube and microcomputer to continuous optimizing adjusted conditions are used.

To specify sulfur concentration, a liquid sample is located in a sample cell and is irradiated with the primary X-ray emitted from a small-sized X-ray tube. The resultant X-ray radiation is detected and converted into electrical pulses. Then required pulses, which are temperature-pressure corrected values, are sorted out, and calculated sulfur contents are represented in form of digitized values. It should be mentioned that some primary tests were conducted to provide calibration curve and the sulfur contents were quantified against it. In addition, X-ray analysis method was repeated four times to decrease expected error and obtain average value for concentration, although this device has an acceptable detection limit of 0.005 wt%.

2.3. Experiments

In the present work, a batch system was used to conduct equilibrium isotherm studies where the temperature was adjusted at three different values of 25, 45 and 65 °C. Each test was started with contacting pre-determined amounts of the granular adsorbent with about 4×10^{-5} m^3 of known concentration prepared solution in a special 10^{-4} m^3 glass bottle completely sealed from outside preventing nothing from getting in. In the case of using fuel solutions, competition adsorption between different molecules to occupy sites of solids could be happened that one example was reported by Salem et al. [1]. This is why we used simulated liquid fuel solution as utilized solution in present work. It should be mentioned that to provide fresh adsorbent devoid of any impurities, amounts of solids were transferred to an electrical heater (Oven), heated at the rate of 3 °C min- 1up to 250 °C continuously kept up for two hours, then cooled to ambient temperature.

In the next step, the container was placed in a shaker warmer BenMary, equipped with a digital readout indicator for 2 h where the temperature was adjusted at the range of 25–65 °C. In order to measure the temperature more accurately, a digital thermometer was used continuously. It is a remarkable note that, 2 h for adsorption process time duration was selected as a result of consistency test when the feed concentration reaches to an equilibrium state. At the end of the adsorption process, the solution was filtrated with a Whatman No. 3 filter paper (Sigma - Aldrich) and then total sulfur solution concentration was determined with X-ray sulfur meter (RX-360SH).

After the equilibrium sulfur concentration was attained, the sulfur sorption capacity was computed using the following relationship:

$$q_e = \frac{(C_i - C_e)V}{m} \tag{1}$$

where C_i, C_e, m and V are initial sulfur concentration, equilibrium sulfur concentration, solid adsorbent loaded weight and the solution volume used, respectively.

3. Adsorption isotherms

In order to make a study on adsorbent-adsorbate interaction and identify the behavior of equilibrium, four popular isotherm adsorption models, Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich were used to describe conducted adsorption process.

3.1. Langmuir adsorption isotherm

Langmuir [17] developed an isotherm model for adsorption of gas onto activated carbon solid adsorbent that traditionally has been used to quantify and compare the performance of different bio-sorbent. This model assumes that monolayer adsorption at a finite (limited) number of specific localized sites occurs, that are equivalent, similar and there is not any lateral interaction and steric hindrance between the adsorbed molecules, even on adjacent sites [18]. Longmuir model refers to homogeneous adsorption in which there is constant enthalpy and activated energy of adsorption related to each molecule (all sites have equal affinity for the adsorbate molecule) [19], and transmigration of adsorbate in surface plane does not happen [20].

This model is specified by a plateau graph with an equilibrium saturation point which after that no further adsorption takes place [21,22]. This model is expressed as

$$q_e = \frac{q_m b C_e}{1 + b C_e} \tag{2}$$

can be converted in linearized form as

$$\frac{1}{q_e} = \frac{1}{q_m} \cdot \frac{1}{b C_e} + \frac{1}{q_m} \tag{3}$$

where q_m is the saturation adsorption capacity (mg S g^{-1}) and b

Table 1
Properties of adsorbents under study.

Type	Zeolite	Zeolite
Name	HYD10B-MS-13X	LQ-MS-13X
Size	8–12 mesh	8–12 mesh
Bulk density (kg m^{-3})	640	800
Nominal pore diameter [Å]	9.0	11.0
Pore volume (cm^3/g)	0.20	0.22
Internal surface area (m^2/g)	865	780