Binary adsorption equilibrium and breakthrough of toluene and cyclohexane on macroporous and hypercrosslinked polymeric resins

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ABSTRACT

Adsorption-based separation is one of the most widely used methods in treating gasoline vapor. For effective control of gasoline vapor emission, the total concentration of non-methane hydrocarbons (NMHC) and the specific component such as toluene must meet the emission limit values. In this study, hypercrosslinked polymeric resin (Hyper-resin) and macroporous polymeric resin (Macro-resin) were selected as adsorbents. Toluene and cyclohexane were chosen as the representative of alkanes and aromatic hydrocarbons components of gasoline vapor. Pure and binary component adsorption isotherms of toluene and cyclohexane on two resins were measured by head space analysis method. Breakthrough data for binary system were obtained at the different concentrations of toluene (12–46 mg/L) and cyclohexane (15 mg/L and 102 mg/L) using a fixed-bed reactor. The results indicate that adsorption equilibria of binary component can be predicted by ideal adsorbed solution theory (IAST) with the average relative error lower than 15% using the pure component adsorption isotherm data. Hyper-resin provides higher selectivity to toluene than Macro-resin in binary equilibrium and breakthrough system. Moreover, the breakthrough adsorption capacities of pure component (toluene and cyclohexane) and their mixture on Hyper-resin are higher than those on Macro-resin, suggesting Hyper-resin would be a promising adsorbent for treating gasoline vapor.

1. Introduction

The gasoline vapor, which mainly comes from gasoline production, transportation and usage, is a common source of volatile organic compounds (VOCs). The emission of gasoline vapor can lead to photochemical smog [1–3], endanger human's health [4,5] and lower fuel quality [6]. Therefore, removal and recycle of gasoline vapor are important from both economic and environmental perspectives.

Adsorption-based separation is one of the most widely used methods in treating volatile organic gas. Among all commercially available adsorbents for gasoline vapor removal, activated carbon is the most common adsorbent which has been applied and studied extensively. He et al. studied the effect of pressure on the adsorption rate for gasoline vapor on pitch-based activated carbon [7]. El-Sharkawy et al. did research on adsorption equilibrium and kinetics of gasoline vapors onto carbon-based adsorbents [8]. Ryu et al. studied equilibrium of toluene and gasoline vapor separately on activated carbon [9]. Nevertheless, the disadvantages are still being noticeable for activated carbon adsorption: its adsorption capacity is susceptible to humidity; also its poor regenerability and weak mechanical strength usually results in short

lifespan [10–14]. Aiming at these issues, some researchers focused on improving activated carbon performance [15–18] or looking for alternative adsorbents.

On the other hand, it is well known that gasoline vapor consists of mostly light hydrocarbons (C4's – C7's) and aromatic hydrocarbon, such as butane, pentane, cyclohexane, toluene and so on. However, researchers often simplified gasoline as pure substance or studied on a particular component of gasoline vapor [19]. Seldom did people study multi-components adsorption of gasoline vapor. In fact, the adsorption behavior in a multicomponent system is much more complex than that in a single component system due to inter-adsorbate and adsorbent-adsorbate interaction. Typically, the existence of competitive adsorption will lead to the distinctive adsorption behavior for a specific adsorbate in the multi-components and single component system. For example, Lashaki et al. [20] and Xu et al. [21] studied several kinds of VOCs adsorption from automotive painting operation by activated carbon. They found the higher boiling point compounds were preferentially adsorbed and would displace the lower boiling point compounds. Hence, it is necessary to figure out the adsorption behavior of the particular components of gasoline vapor in mixture system for

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controlling the emission of toxic pollutants. According to Chinese environmental regulation "Integrated Emission Standards of Air Pollutants" (GB16297-1996), the total emission concentration of non-methane hydrocarbons (NMHC) should be less than 25 g/m^3. The emission of aromatic compounds, however, has the lower concentration limits, e.g., the emission concentration of toluene must not exceed 40 mg/m^3. In brief, the treatment of gasoline vapor should meet the concentration limits of both NMHC and the specific pollutants. Therefore, for effective control of toxic pollutants emission and oil restoration, the study on multi-components VOCs adsorption in gasoline vapor becomes necessary.

Recently, polymeric resin has gained much attention as a potential alternative to activated carbon due to its large specific surface area, stable physical and chemical properties, controllable pore structure and hydrophobic surface [22–24]. Simpson et al. studied the properties of hypercrosslinked resin for adsorbing toluene, chlorobenzene, benzene and other VOCs vapors [25,26]. Long et al. investigated adsorption equilibrium of typical VOCs such as benzene, chlorobenzene, trichloroethylene, etc. on hypercrosslinked resin [27–29]. They found that the hypercrosslinked resin had similar adsorption capacity to activated carbon. Also, the studies showed that the hypercrosslinked resin adsorption performance was barely influenced by humidity due to its hydrophobic surface [30,31]. Hence, polymeric resin would be an ideal target as VOCs adsorbents. However, to the best of our knowledge, no research about multi-components adsorption of gasoline vapor on polymeric resin has been reported.

Polymeric adsorbent can be classified into two categories: macroporous and hypercrosslinked polymeric resin. Hypercrosslinked polymeric resin (Hyper-resin) is a typical microporous adsorbent with a predominant structure in the regions of pore size 0.5–2 nm, while the pore size of macroporous resin (Macro-resin) is distributed largely in the regions of mesopore and macropore [32]. In this study, two commercial polymeric resins (Hyper-resin and Macro-resin) with different pore structure are selected as adsorbents. The binary adsorption equilibrium and breakthrough of cyclohexane and toluene, which are chosen as the representative of alkanes and aromatic hydrocarbons components of gasoline vapor, are investigated on two types of resins. The adsorption selectivity and breakthrough capacities of cyclohexane and toluene in binary system on two resins are evaluated. The present study can be helpful for the application of polymeric resin in the field of gasoline vapor treatment.

2. Materials and methods

2.1. Materials

Cyclohexane and toluene were used as adsorbates supplied by Nanjing Chemical Reagent Company (> 99.5% purity). The macroporous polymeric resin (Macro-resin) and hypercrosslinked polymeric resin (Hyper-resin) were supplied by N&G Environmental Technology Co. Ltd. (Jiangsu, China). Macro-resin was produced by suspension copolymerization of a monomer (styrene) and a crosslinking agent (divinylbenzene), while Hyper-resin was produced by further crosslinking of chloromethylated styrene-divinylbenzene copolymers swelled in a good solvent. The chemical structure of two polymers matrix is shown in Fig. S1 in Supplementary Material. The pore texture of the polymeric adsorbents was determined by N$_2$ isotherms data at 77 K, using an adsorption analyzer ASAP 2010 (Micromeritics Instrument Co., USA). The specific surface area (S$_{BET}$), were calculated from the N$_2$ isotherm data at 77 K by Brunauer–Emmett–Teller (BET) methods. The micropore volume (V$_{micro}$), mesopore volume (V$_{meso}$) and pore size distributions of two adsorbents were calculated by Density Functional Theory (DFT) with silt pores model to the N$_2$ adsorption–desorption isotherms at 77 K. The morphology of two adsorbents was viewed with a scanning electron microscopy (Hitachi-3400 N).
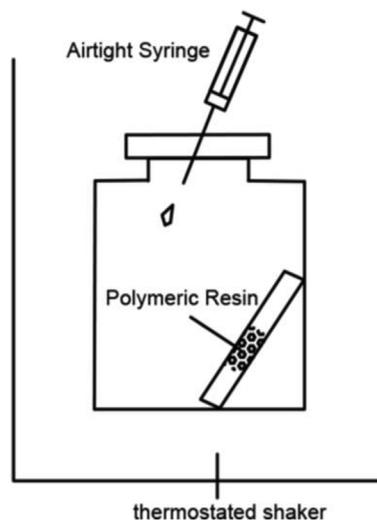

Fig. 1. Adsorption equilibrium apparatus.

2.2. Methods

2.2.1. Adsorption equilibrium

Adsorption isotherms were measured using the head space analysis method [33]. Experimental apparatus is shown in Fig. 1. A known amount of clean resin (0.1 g) was put into glass tube, which was sealed in a 120 mL bottle. A fixed amount of toluene, cyclohexane or toluene-cyclohexane mixture in liquid form was injected into the bottle by a micro syringe. The exact amount of adsorbate was determined by weighing. The sealed bottle was put into the thermostated shaker and was shaken for 48 h to ensure adsorption equilibrium at a constant temperature of 30 °C, 40 °C and 50 °C, respectively. At equilibrium state, 500ul gas was taken from the bottle using an airtight syringe. The gas was then injected into gas chromatography (GC9890, China) and the peak area was observed. The equilibrium concentration of adsorbate in gas phase was got by measuring five times average peak area. According to ideal gas law, the equilibrium concentration can be transformed to equilibrium pressure. The amount adsorbed on the polymeric resin was calculated from the mass balance. An adsorption isotherm was measured by injecting various amounts of adsorbate. The purpose of placing resin inside the glass tube was to prevent direct contact between the liquid adsorbate and polymeric resin.

2.2.2. Adsorption breakthrough

As shown in Fig. 2, The breakthrough experiment setup used was the same as that in the previous study [34]. The VOC vapor obtained using a bubbler was diluted with dry N$_2$ and then went through the column with the clean resin. The VOCs concentration at the outlet of the adsorption column was measured by gas chromatography with a FID detector. The breakthrough curves were obtained by recording the concentration of VOCs consecutively at the outlet of adsorption column.

3. Adsorption theory

3.1. Pure component isotherm

The Dubinin-Radushkevich (D-R) equation, based on Polanyi theory, is described as Equations (1)–(3):

$$Q_v = Q_o \, exp\left[-(\varepsilon/E)^2\right] \tag{1}$$

$$\varepsilon = RTln\,(P_s/P) \tag{2}$$

$$Q_v = q/\rho \tag{3}$$

where Q_v (mL/g) is volume adsorbed capacity, Q_o (mL/g) is the