Chemical Engineering Journal 221 (2013) 105–110

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Adsorption of n-hexane vapor by macroporous and hypercrosslinked polymeric resins: Equilibrium and breakthrough analysis

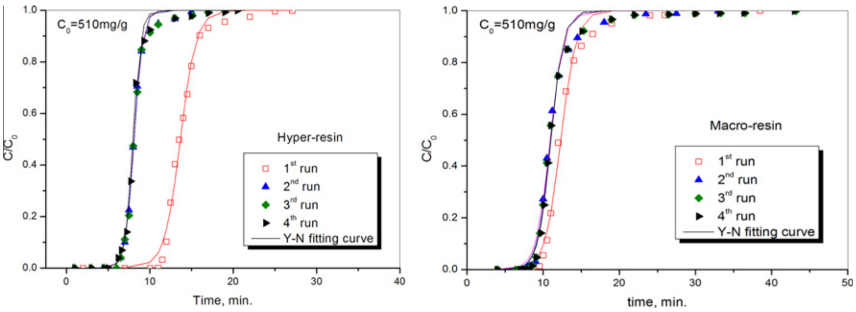
Chao Long *, Weihua Yu [1], Aimin Li

State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, No. 163 Xianlin Avenue, Nanjing 210023, China

HIGHLIGHTS

- ▶ Dubinin–Astakov equation described the adsorption isotherms well.
- ▶ Hyper-resin showed good adsorption capacities for low concentration of hexane.
- ▶ Macro-resin had a potential advantage to adsorb high concentration of hexane.
- ▶ Macro-resin can be regenerated more efficiently than Hyper-resin.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 26 November 2012
Received in revised form 26 January 2013
Accepted 28 January 2013
Available online 6 February 2013

Keywords:
Polymeric adsorbent
Macroporous
Hypercrosslinked
Adsorption
VOCs

ABSTRACT

The adsorption behaviors of n-hexane vapor onto macroporous and hypercrosslinked polymeric resins were investigated. All adsorption isotherms were nonlinear and well fitted with Dubinin–Astakov equation. The equilibrium adsorption data showed that the adsorption capacities of hypercrosslinked polymeric resin (Hyper-resin) were superior to macroporous polymeric resin (Macro-resin) for lower concentration of n-hexane; however, Macro-resin had higher adsorption capacities than Hyper-resin for higher concentration of hexane. The isosteric enthalpies of adsorption for n-hexane were calculated. The Hyper-resin exhibited much higher values of $\triangle H_{st}$ for n-hexane than Macro-resin at the whole loading studied, indicating that the interaction force of n-hexane adsorption onto Hyper-resin was larger than Macro-resin. The consecutive column adsorption–desorption cycles were carried out to investigate the dynamic adsorption characteristics. The results revealed that the breakthrough adsorption capacities of n-hexane onto the virgin Hyper-resin were about 105% and 43% higher than those onto the virgin Macro-resin when the initial concentrations of n-hexane were 85 mg/g and 510 mg/g, respectively. Due to higher regeneration efficiency, however, the breakthrough capacities of the regenerated Macro-resin were higher than those of the regenerated Hyper-resin for the adsorption of higher concentration n-hexane.

1. Introduction

The emission of solvent vapors from industrial processes has caused not only severe air pollution but also great loss of valuable chemicals. Therefore, proper recovery of volatile solvent vapors from industries will help in reducing production costs, saving energies, and protecting the environment. Adsorption is proved to be one of the most attractive and effective techniques to remove and recover volatile organic compounds (VOCs) from gas streams [1,2]. The core of adsorption process technology is to develop suitable adsorbents with high specific surface, stable physical, chemical properties and regenerability on site, etc. [3]. Activated carbon is applied extensively for the removal of VOCs from gas streams

---

* Corresponding author. Tel.: +86 25 89680380.
E-mail address: clong@nju.edu.cn (C. Long).

[1] Present address: Nanjing University & Yancheng Academy of Environmental Protection Technology and Engineering, No. 188 Yingbin Avenue, Yancheng 22400, China.

http://dx.doi.org/10.1016/j.cej.2013.01.083

with subsequent solvent recovery or incineration [4–6]. However, it has been recognized that activated carbon adsorption always encounters several disadvantages such as pore clog (due to polymerization of some VOCs catalyzed by ashes present on activated carbon surfaces), fire risk, and hygroscopicity [7–9]. Hence, much effort has been focused at finding an alternative adsorbent to activated carbons for separating and recovering VOCs from polluted air streams.

Recently, there has been increasing interest in permanently porous polymeric resins as a potential adsorbent for removal of VOCs from polluted gas streams. Permanent porous polymeric resins may be classified into two categories: macroporous and hypercrosslinked [10]. Macroporous resin is typically produced by suspension copolymerization of a monomer (styrene) and a crosslinking agent (divinylbenzene) and also a porogen that is miscible with monomers. It should be noted that the pore diameter of the "macroporous" styrene–DVB copolymer used as adsorbent mainly lies in the regions of mesopore (2–50 nm) [11,12], though it is more common to refer to "macro" pores as larger than 50 nm in diameter. Hypercrosslinked resin is produced by further crosslinking macroporous polymers swelling in a good solvent [13]. As compared to the macroporous polymeric resin, hypercrosslinked polymeric resin represents a class of predominantly microporous organic materials in the regions of pore size 0.5–2 nm, whose inner specific surface area is exceptionally high (up to 1000–1500 m^2/g) [14,15]. Recently, some researchers including our group investigated polymeric resins as adsorbent for removing the VOCs from gas steam. Simpson et al. discovered that the synthesized hypercrosslinked polystyrene had competitive VOCs sorption capacities in vapor streams, was insensitive to humidity, and possessed remarkably high ultimate sorption capacities ($\sim$2 mL/g) [16]. Podlesnyuk et al. investigated the adsorption properties of hexane, 1, 2-dichloroethane, tetrachloromethane and pyridine on hypercrosslinked polymeric adsorbents [17]. Baya et al. investigated the adsorption capacities of 8 volatile organic compounds (pentane, octane, etc.) on hypercrosslinked polystyrene, MN-200 [18]. In our group, the adsorption of benzene, chlorobenzene, methyl ethyl ketone and chlorinated VOCs on hypercrosslinked polymeric adsorbents has been investigated [19–23]. These studies have proved that hypercrosslinked polymeric adsorbents have a good sorption capacity for VOCs from polluted gas streams. However, few studies have been carried out to compare the adsorption properties of macroporous and hypercrosslinked polymeric adsorbents for removing the VOCs from gas steam. Moreover, it is generally believed that the higher adsorption capacity of hypercrosslinked resin than macroporous resin is due to their higher specific surface area and micropore volume [16,17]. On the other hand, all those studies paid more attention to adsorption equilibrium of polymeric adsorbents; dynamic data of VOCs on polymeric adsorbents are scarce in the literature. However, from the viewpoint of engineering application, a dynamic analysis and desorption properties is the most important fundamental information required to determine the residence time for completion of the adsorption process. Therefore, much further research is still needed for a better understanding of adsorption equilibrium and dynamic characteristics of macroporous and hypercrosslinked polymeric resins.

In this study, adsorption of organic vapors by commercial macroporous and hypercrosslinked polymeric resins was studied with model compounds n-hexane. Equilibrium adsorption isotherms of n-hexane vapor onto two resins at 293, 303, and 328 K were investigated; isosteric enthalpies of adsorption were measured to examine the interaction between VOCs and adsorbents. Finally, the breakthrough curves of n-hexane at the consecutive adsorption cycles under the same condition were obtained to evaluate the dynamic adsorption performance of two adsorbents.

2. Material and methods

2.1. Materials

The macroporous polymeric resin (Macro-resin) and hypercrosslinked polymeric resin (Hyper-resin) were supplied by N&G Environmental Technology Co. Ltd. (Jiangsu, China). 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). Their specific surface area (S_{BET}), micropore volume (V_{micro}) and mesopore volume (V_{meso}) were calculated from the N_2 isotherm data at 77 K by Brunauer–Emmett–Teller (BET), Dubinin–Astakov (DA) and Barrett–Joyner–Halena (BJH) methods, respectively. The salient properties of Macro-resin and Hyper-resin were listed in Table 1. The pore size distributions of two resins are shown Fig. S1 of Supplementary data. Hyper-resin is typical of micropore adsorbent with a small proportion of macropores and mesopores. In comparison with Hyper-resin, the pore size of Macro-resin is mainly distributed in the regions of mesopores.

2.2. Adsorption experiments

The adsorption of n-hexane vapors was determined by the column adsorption method. The detailed experimental apparatus and adsorption procedure have been described previously [20]. Briefly, Macro-resin or Hyper-resin was precisely weighed out and charged into the adsorption column made of glass. The carrier gas containing a scheduled concentration of n-hexane vapor was passed through the column until the n-hexane concentration become constant and stable; the n-hexane concentration in the effluent steam from the adsorption column was measured by using gas chromatography and recorded by a computer. The breakthrough curves were obtained by recording the concentration of n-hexane consecutively at the outlet of adsorption column. In this study, it was recognized that the adsorption equilibrium was reached when the exit concentration became equal to the inlet concentration and stable over a continuous 60 min. So, the equilibrium amount adsorbed was equal to the weight change of adsorbent before and after the adsorption process. Regeneration of n-hexane loaded resin was carried out in the same fixed-bed column configuration and in the down-flow mode. After the adsorption procedure, the adsorption column was connected to a vacuum pump and regenerated under vacuum at 0.005 MPa. Here, a high precision microbalance (BS224S, Sartorius, Germany) was adopted as the weighing device.

3. Result and discussion

3.1. Adsorption equilibrium and modeling

The adsorption equilibrium data of n-hexane vapor onto Hyper-resin and Macro-resin at 293, 308, and 323 K were obtained. Fig. 1 shows that favorable adsorption isotherms were exhibited for n-hexane vapor with the extent of adsorption increasing as the equilibrium pressure of the adsorbate increased. It appears clearly that the adsorption isotherms of n-hexane onto Hyper-resin were type I according to the IUPAC classification, which is typical of

Table 1
Selected properties of Macro-resin and Hyper-resin.

Adsorbent	S_{BET} (m^2/g)	S_{meso} (m^2/g)	V_{micro} (mL/g)	V_{meso} (mL/g)
Hyper-resin	1194.6	140.8	0.547	0.185
Macro-resin	850.3	536.9	0.125	1.291