Journal of Hazardous Materials 166 (2009) 46–51

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

Adsorption of trichloroethylene and benzene vapors onto hypercrosslinked polymeric resin

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ARTICLE INFO

Article history:
Received 26 August 2008
Received in revised form 31 October 2008
Accepted 31 October 2008
Available online 11 November 2008

Keywords:
Hypercrosslinked polymeric resin
VOCs
Adsorption
Isosteric enthalpy
Kinetic

ABSTRACT

In this research, the adsorption equilibria of trichloroethylene (TCE) and benzene vapors onto hypercrosslinked polymeric resin (NDA201) were investigated by the column adsorption method in the temperature range from 303 to 333 K and pressures up to 8 kPa for TCE, 12 kPa for benzene. The Toth and Dubinin–Astakov (D–A) equations were tested to correlate experimental isotherms, and the experimental data were found to fit well by them. The good fits and characteristic curves of D–A equation provided evidence that a pore-filling phenomenon was involved during the adsorption of TCE and benzene onto NDA-201. Moreover, thermodynamic properties such as the Henry's constant and the isosteric enthalpy of adsorption were calculated. The isosteric enthalpy curves varied with the surface loading for each adsorbate, indicating that the hypercrosslinked polymeric resin has an energetically heterogeneous surface. In addition, a simple mathematic model developed by Yoon and Nelson was applied to investigate the breakthrough behavior on a hypercrosslinked polymeric resin column at 303 K and the calculated breakthrough curves were in high agreement with corresponding experimental data.

1. Introduction

Volatile organic compounds (VOCs) are among the most common air pollutants emitted by the chemical process industries, which include thinner, degreasers, cleaners, lubricants, liquid fuels, and so on. Due to ubiquity in the environment and risk to human health [1,2], VOCs have already received great attention in the field of environmental control. For an environmental point of view, it's necessary to limit and control VOC emissions. So far, add-on control techniques [3,4] are broadly classified into two types: destruction (biofiltration, thermal oxidation, catalytic oxidation) and recovery (adsorption, condensation, membrane separation). Among these methods, activated carbon adsorption [5–10] has been considered to be one of the promising methods for controlling VOCs of low concentrations with potential to recover valuable vapors. However, it has been recognized that activated carbon adsorption always encounters some problems such as combustion, pore blocking, inefficiently desorption of high-boiling solvents, and hygroscopicity. Therefore, it is significant to develop new adsorbent materials to separate and recover VOCs from polluted air streams.

In the past few decades, polymeric adsorbent has emerged as a potential alternative to activated carbon for removing the organic pollutants from aqueous solution due to its controllable pore structure, stable physical, chemical properties as well as regenerability on site. More recently, hypercrosslinked polymeric resin [11–13], which is produced by crosslinking polymers of macroporous resin in a good solvent and represents a class of predominantly microporous organic materials with high surface areas and high micropore volume, has gained increasing interest. Now hypercrosslinked polymeric resin produced by many manufactures worldwide is finding increased application as sorbents for separation or analytical purposes and water pollution control [14,5]. However, to the best of our knowledge, there are relatively limited studies done on hypercrosslinked polymeric resin as adsorbents for removing the VOCs from gas steam currently.

This study aims at exploring the possibility to remove VOCs from air streams by hypercrosslinked polymeric resin. For that reason, the hypercrosslinked resin was chosen as an adsorbent to evaluate the adsorption characteristics. Apparently, benzene is a typically non-polar and inert aromatic hydrocarbon; trichloroethylene (TCE) is a common polar chlorinated VOC. Both of them are considered priority pollutants in view of their high toxicity and volatility [15]. Thus, benzene and TCE were selected as model adsorbates in this study. Adsorption equilibria of TCE and benzene vapors onto hypercrosslinked polymeric resin (NDA-201) at 303, 318, and 333 K were

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doi:10.1016/j.jhazmat.2008.10.124

Table 1
Physical properties of the hypercrosslinked polymeric resin (NDA-201).

S_{BET} (m^2/g)	S_{micro} (m^2/g)	S_{mero} (m^2/g)	V_t (ml/g)	V_{micro} (ml/g)	V_{mero} (ml/g)
855.6	508.1	208.9	0.521	0.303	0.242

investigated. For better understanding of adsorption properties, Toth [16,17] and D–A equations [18–20] were employed to correlate the experimental data. Henry's constant and isosteric enthalpy of adsorption were calculated, which is very important to evaluate the molecular scale interactions between adsorbate molecules and adsorbent. In addition, an experiential model with two parameters was applied to model the breakthrough curves of adsorbates through beds of NDA-201 with the consideration of the effect of inlet concentration.

2. Experimental

2.1. Materials

A commercial available hypercrosslinked polymeric resin (NDA-201) with poly (styrene-divinylbenzene) matrix was adopted in this study. The NDA-201 was purchased from Jiangsu N & G Environmental Technology Co. Ltd. (Jiangsu, China). The pore texture of the polymeric adsorbents were determined by N_2 isotherms data at 77 K, using an adsorption analyzer ASAP 2020 (Micromeritics Instrument Co., USA). The physical properties of the sample are listed in Table 1. It is clear from Table 1 that NDA-201 has a significant proportion of surface area and pore volume in the microporous regions.

Before use, the samples were pretreated at 80 °C in an oven purged with pure nitrogen gas in vacuum overnight for removing the moisture and other contaminants prior to experiments. Two volatile organic compounds including analytic grade trichloroethylene (C_2HCl_3, 99.5%) and benzene (C_6H_6, 99.5%) were purchased from Nanjing Chemical Reagent station (Nanjing, China) and used in this study without further purification.

2.2. Adsorption apparatus and procedure

The equilibrium relations for adsorption of TCE and benzene vapors from the nitrogen stream were determined by the column adsorption method. The experimental apparatus used is illustrated in Fig. 1. It consisted of two gas/vapor feed lines, evaporator, an adsorption column (Ø 5 mm × 100 mm) and analytical equipment. About 0.5000 g of hypercrosslinked polymeric adsorbent was precisely weighed out and charged into the adsorption column made of glass. The nitrogen steam was divided into two lines by mass flow control valves. One line was introduced into VOCs evaporator to make VOCs-saturated steam at the controlled temperature. The VOCs-saturated stream was mixed with the other line at the mixer to make different VOCs concentration. Then, the carrier gas containing a scheduled concentration of VOCs vapor was passed through the column until the VOCs concentration become constant and stable, the changes of VOCs concentration in the effluent steam from the adsorption column was measured by using gas chromatography with a FID detector (SP-6890, Nunan, China) and recorded by a computer. The equilibrium amount adsorbed was equal to the weight change of adsorbent before and after the adsorption process. Here, a high precision microbalance (BS224S, Sartorius, Germany) was adopted as the weighing device.

3. Results and discussion

3.1. Adsorption equilibrium

The adsorption equilibrium data of TCE and benzene vapors onto hypercrosslinked polymeric resin (NDA-201) were obtained. Measurements were done at 303, 318, and 333 K and pressures up to 8 kPa for TCE and 12 kPa for benzene, respectively. Fig. 2 shows the adsorption equilibrium isotherms of TCE and benzene onto NDA-201 at various temperatures. Favourable adsorption isotherms were exhibited for TCE and benzene with the extent of adsorption increasing as the equilibrium pressure of the adsorbate increased. It appears clearly that NDA-201 adsorbed TCE and benzene more effectively at low pressures, and the adsorption isotherms were found to be type laccording to the IUPAC classification, which corresponds to the high micropore volume of hypercrosslinked polymeric resin [21].

Information concerning the relevant adsorption equilibrium is generally an essential requirement for analysis and design of an adsorption separation process [22,23]. In this study, Toth and Dubinin–Astakov (D–A) were used to correlate the experimental equilibrium data of TCE and benzene vapors onto hypercrosslinked polymeric resin.

3.1.1. Correlation by Toth equation

Because of its simplicity in form and its correct behavior at low and high pressure, the Toth equation (Eq. (1)) is popularly used for heterogeneous adsorbents such as activated carbon.

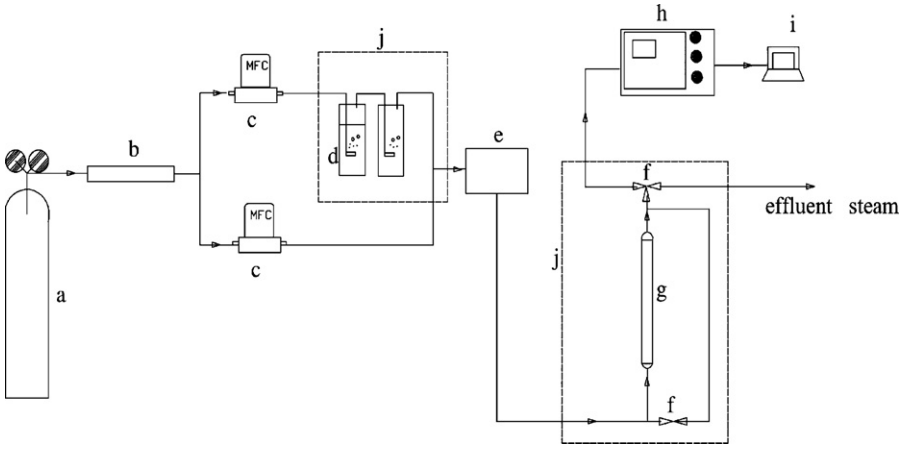

Fig. 1. Experimental apparatus for column adsorption of TCE and benzene vapors: (a) nitrogen gas cylinder, (b) gas purifier, (c) mass flow control valve, (d) vapor evaporator, (e) mixer, (f) switching valve, (g) adsorption column, (h) gas chromatography, (i) recorder, (j) constant temperature water bath.

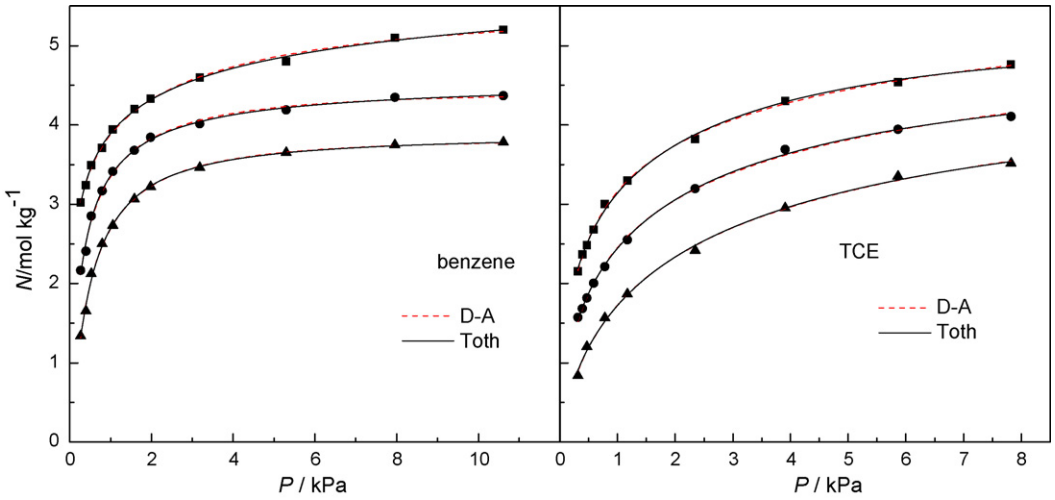

Fig. 2. Adsorption equilibrium isotherms of TCE and benzene vapors onto hypercrosslinked polymeric resin at various temperatures: (■) 303.15 K; (●) 318.15 K; (▲) 333.15 K.

$$N = \frac{mP}{(b + P^t)^{1/t}} \quad (1)$$

where P is the equilibrium pressure (kPa) , N is the adsorbed moles (mol/kg), and m, b, and t are isotherm parameters.

When the parameter t is unity, the above equation is identical with the Langmuir equation. Also, although the Toth equation is an empirical equation, it reduces to the Henry's law at low pressures (Eq. (2)) and approaches the saturation limit at high pressures (Eq. (3)). In order to compare the correlation results with experimental data, a deviation parameter on the adsorbed amount, D, was utilized (Eq. (4)).

$$H = \lim_{P\to 0}\frac{N}{P} = \lim_{P\to 0}\frac{dN}{dP} = \frac{m}{b^{1/t}} \quad (2)$$

$$\lim_{P\to\infty} N = m \quad (3)$$

$$D = \frac{1}{k}\sum_{i}^{k}\left|\frac{N_i^{obs} - N_i^{cal}}{N_i^{cal}}\right| \quad (4)$$

where k is the number of data, N_i^{obs} is the experimental adsobed moles (mol/kg), and N_i^{cal} is the calculated adsobed moles (mol/kg).

The experimental data are represented as symbols and isotherm fittings using the Toth equation as solid lines in Fig. 2, and the isotherm parameters for the Toth equation are given in Table 2. It is quite obvious that all the equilibrium data were successfully correlated by the Toth equation, supported by larger $R^2 \geq 0.99$ and low D value.

It is valuable to evaluate the Henry's constant because it has been used as a criterion of the adsorption affinity. By using Eq. (2), the Henry's constant was calculated and given in Table 2. As shown in Table 2, the order of adsorption affinity is benzene > trichloroethylene. We know that the hypercrosslinked polymeric resin (NDA-201) is poly (styrene-divinylbenzene) matrix, the larger adsorption affinity of benzene may be due to the specific adsorbate–adsorbent interactions between the aromatic rings of NDA-201 matrix and aromatic rings of benzene.

3.1.2. Correlation by D–A equation

It has been reported that the potential theory is useful for adsorption on microporous materials such as activated carbon. According to potential theory, the simplified Dubinin–Astakov equation (D–A equation) written by Eqs. (5)–(7) was employed for data correlation.

$$W = W_0 \exp[-(\varepsilon/E)^r] \quad (5)$$

$$\varepsilon = RT\ln(P_s/P) \quad (6)$$

$$W = q/\rho^* \quad (7)$$

where W is the pore volume filled with adsorbate (ml/g), W_0 is the limiting W, ε is the adsorption potential (J/mol) written by Eq. (6), E is the adsorption characteristic energy (kJ mol^{-1}), R is a gas constant, T is the absolute temperature (K), P_s is the saturation vapor pressure (kPa), P is the equilibrium vapor pressure, q is the equilibrium amount (mg/g), ρ^* is the adsorbate density in the adsorbed phase assumed to be the same as that in the liquid phase.

As shown in Fig. 2, the experimental data at 303, 318, and 333 K are represented as symbols and isotherm fittings using the D–A equation as dash lines. Clearly, the experimental data were well fitted by the D–A equation, and the isotherm parameters for the D–A equation are given in Table 3. In terms of the Polanyi potential theory, plots of adsorbed volume $W(\varepsilon)$ against ε will form a "characteristic" adsorption curve that will be a temperature-independent function, and this function can be employed to examine whether the Polanyi theory mechanistically captures the adsorption process of compounds by adsorbent. The characteristic curves of each

Table 2
Toth equation parameters for the adsorption of TCE and benzene vapors onto hypercrosslinked polymeric resin.

Adsorbate	T (K)	m (mol kg^{-1})	b (kPa)	t	H (mol kg^{-1} kPa^{-1})	100D	R^2
TCE	303.15	6.724	0.374	0.421	69.22	0.765	0.998
	318.15	6.332	0.537	0.453	24.91	1.097	0.998
	333.15	5.730	0.928	0.547	6.56	2.413	0.997
Benzene	303.15	6.795	0.201	0.328	895.92	0.676	0.998
	318.15	5.452	0.211	0.394	279.67	2.050	0.996
	333.15	4.382	0.344	0.613	24.94	2.739	0.997

Table 3
D–A equation parameters for the adsorption of TCE and benzene vapors onto hypercrosslinked polymeric resin.

Adsorbate	T (K)	W_0 (mol g^{-1})	E (kJ mol^{-1})	r	100D	R^2
TCE	303.15	0.435	10.56	1.563	0.929	0.998
	318.15	0.406	10.84	1.790	0.859	0.999
	333.15	0.387	10.86	1.988	2.44	0.998
Benzene	303.15	0.466	14.84	1.591	0.775	0.997
	318.15	0.395	13.91	2.990	1.192	0.997
	333.15	0.387	14.41	3.857	1.176	0.998

adsorbate are represented in Fig. 3. As the Polanyi potential theory would predict, they all fell essentially onto a single curve with the larger correlation coefficient $R^2 \geq 0.995$ for the adsorption of TCE and benzene onto NDA-201, indicating mechanistic usefulness of Polanyi theory to describe adsorption of TCE and benzene onto hypercrosslinked polymeric adsorbents and pore-filling is the dominating mechanism for TCE and benzene adsorption.

3.2. Isosteric enthalpies of adsorption

The isosteric enthalpy of adsorption is evaluated simply by applying the Clausius-Clapeyron equation (Eq. (8)) if one has a good set of adsorption equilibrium data obtained at several temperatures:

$$\frac{q_{st}}{RT^2} = \left[\frac{\partial \ln P}{\partial T}\right]_N \tag{8}$$

where q_{st} is the isosteric enthalpy of adsorption (kJ/mol), R is the gas constant, and N is the moles adsorbed (mol/kg).

The isosteric enthalpy changes accompanying adsorption can be used to examine the molecular scale interactions between adsorbate molecules and adsorbent. Moreover, the isosteric enthalpy may be used as a measure of the energetic heterogeneity of a solid surface. For the heterogeneous adsorption system, the isosteric enthalpy curve varies with the surface loading. In Fig. 4, the isosteric enthalpies of adsorption for TCE and benzene vapors studied were plotted as a function of the moles adsorbed. As shown in Fig. 4, the isosteric enthalpies of adsorption was varied with the surface loading for each adsorbate. This result implies that the hypercrosslinked polymeric resin (NDA-201) has an energetically heterogeneous surface [24,25]. In addition, it should be noted that the isosteric enthalpies for benzene was larger than that for TCE at the same surface loading, namely, the adsorption affinity of NDA-201 for benzene is larger than that of TCE, this result is identical with the order of Henry's constant for each adsorbate.

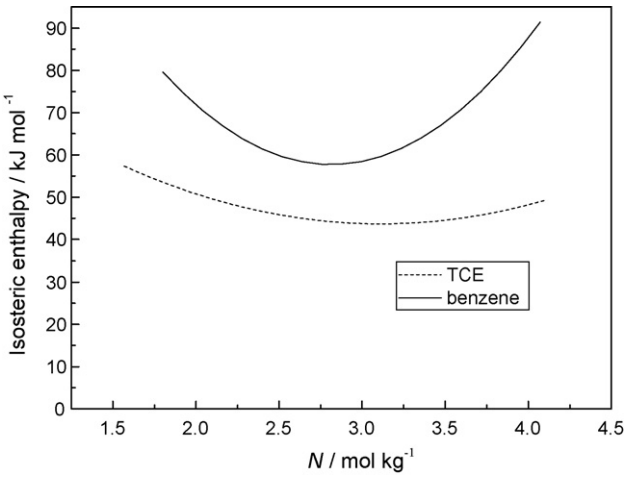

Fig. 4. Variation curves of isosteric enthalpy of adsorption with respect to surface loading.

3.3. Modeling adsorption breakthrough

Knowledge of adsorption kinetics or dynamic behavior in a fixed bed is also valuable in calculating adsorption separation processes. Here, Yoon and Nelson model [26], a semi-empirical gas adsorption model, was tentatively applied to describe the breakthrough curves for adsorption of TCE and benzene vapors onto hypercrosslinked polymeric resin. This model not only is less complicated than other models, but also requires no detailed data concerning the characteristics of adsorbate and physical properties of adsorption bed.

The Yoon and Nelson equation pertaining to a single-component system is expressed as

$$t = \tau + \frac{1}{k'} \ln \frac{C_b}{C_i - C_b} \tag{9}$$

where C_i and C_b are inlet and outlet concentration of adsorbate, t is the breakthrough time, k' is the rate constant, and τ is the time required for 50% adsorbate breakthrough.

Fig. 5 shows breakthrough curves of TCE and benzene under different inlet concentrations in hypercrosslinked polymeric resin (NDA-201) beds at 303 K. There were good breakthrough curve

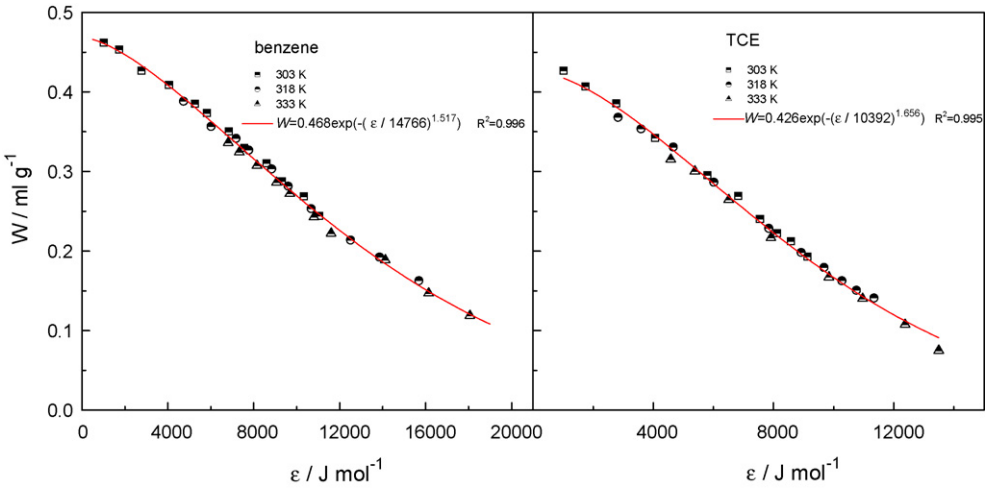

Fig. 3. The Characteristic curves for the adsorption of TCE and benzene vapors onto hypercrosslinked polymeric resin at various temperatures – characteristic curve.

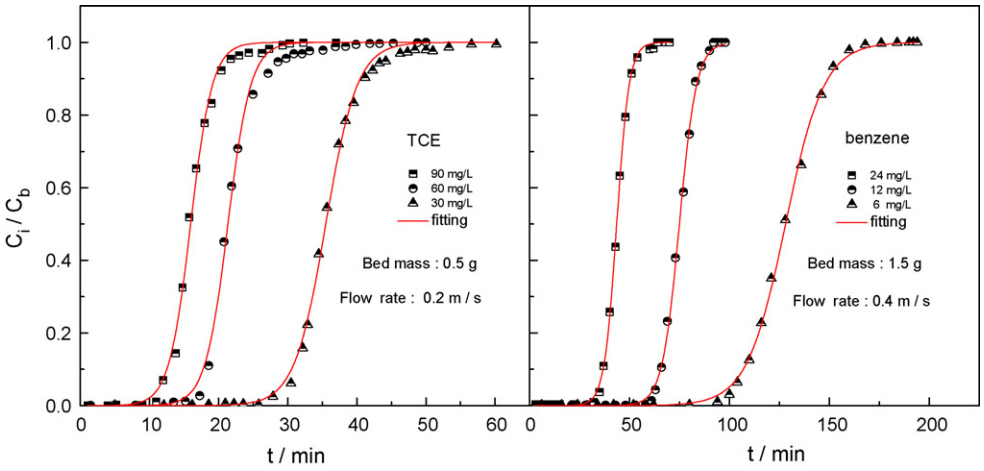

Fig. 5. Breakthrough curves for various concentrations of TCE and benzene adsorption onto NDA-201.

Table 4
Yoon and Nelson model parameters for the adsorption of TCE and benzene vapors onto NDA-201 at various inlet concentrations.

Adsorbate	Concentration (mg/L)	Values of parameters		R^2
		k' (min^{-1})	τ (min)	
TCE	30	0.439	35.5	0.997
	60	0.604	21.4	0.993
	90	0.634	16.0	0.992
Benzene	6	0.103	128.1	0.999
	12	0.233	74.9	0.998
	24	0.439	35.5	0.997

shapes for the adsorption of TCE and benzene onto NDA-201. It is obvious that the breakthrough times decreased with increasing inlet concentrations. Moreover, the breakthrough curves became steep with increasing inlet concentrations, suggesting that intraparticle diffusion affects the overall mass transfer rate greatly at lower flow rate regions. Clearly, the breakthrough curves of TCE and benzene onto NDA-201 was well fitted by the Yoon and Nelson equation. The parameters for the Yoon and Nelson equation are given in Table 4. As can be seen, both k' and τ are depended on the adsorbate inlet concentration. The value of τ decreases with the increasing adsorbate inlet concentration, while the value of k' increases. In a word, the Yoon and Nelson model can predict the whole breakthrough curve in this study, which would be of great benefit to design adsorption engineering process.

4. Conclusions

Adsorption equilibria of TCE and benzene vapors onto hypercrosslinked polymeric resin (NDA-201) were investigated, and favorable adsorption isotherms were exhibited, the adsorption capacities of NDA-201 for each adsorbate were reduced with the increasing temperature. In the analysis, the Toth and D–A equations were employed. The correlations by the Toth and D–A equation were in remarkable agreement with the experiment data. By calculating the Henry's constant and isosteric enthalpies of adsorption, it was found that the order of adsorption affinity was benzene > trichloroethylene. The isosteric enthalpies of adsorption were varied with surface coverage which indicated that hypercrosslinked polymeric resin has an energetically heterogeneous surface. The characteristic curve and its prediction of TCE and benzene vapors adsorption calculated by Polanyi-based isotherm modeling have a potential applicability for field applications.

In addition, Yoon and Nelson model could predict the whole breakthrough curve and provided good correlation of the effects of TCE and benzene concentration on breakthrough curves of adsorption through a NDA-201 column. The calculated theoretical breakthrough curves were in agreement with the corresponding experimental data. In a word, this study is very useful for adsorption process design and hypercrosslinked polymeric resin is a promising adsorbent for removing and recovering VOCs from polluted vapor streams in the chemical process industries.

Acknowledgement

The authors thank to Department of Environmental Protection of Jiangsu Province for financial support through grant no. 2007029.

References

[1] F.I. Khan, A.Kr. Ghoshal, Removal of volatile organic compounds from polluted air, J. Loss Prevent. Proc. Ind. 13 (2000) 527–545.
[2] N. Nevers, Air Pollution Control Engineering, McGraw-Hill, New York, 1995.
[3] E.N. Ruddy, L.A. Carroll, Select the best VOC control strategy, Chem. Eng. Prog. 89 (1993) 28–35.
[4] D.M. Ruthven, Principles of Adsorption and Adsorption Processes, John Wiley & Sons, New York, USA, 1984.
[5] Chao Long, JunDong Lu, Aimin Li, et al., Adsorption of naphthalene onto the carbon adsorbent from waste ion exchange resin: Equilibrium and kinetic characteristics, J. Hazard. Mater. 201 (2007) 656–661.
[6] M.J. Ruhl, Recover VOCs via adsorption on activated carbon, Chem. Eng. Prog. 89 (1993) 37–41.
[7] Jee-Won Park, Sang-Soon Lee, et al., Adsorption equilibria of toluene, dichloromethane, and trichloroethylene onto activated carbon fiber, J. Chem. Eng. Data. 47 (2002) 980–983.
[8] T. Yasushi, H. Mitsuharu, Removal of single component chlorinated hydrocarbon vapor by activated carbon of high surface area, Sep. Purif. Technol. 15 (1999) 79–90.
[9] M.A. Lillo-Rodenas, A.J. Fletcher, K.M. Thomas, et al., Competitive adsorption of a benzene–toluene mixture on activated carbons at low concentration, Carbon 44 (2006) 1455–1463.
[10] Y. Miyake, M. Suzuki, Removal of trichloroethylene from air stripping off-gas by adsorption on activated carbon fibre, Gas Sep. Purif. 7 (1993) 229–234.
[11] J. Edward, Simpson, J. William, Koros, S. Robert, Schechter, An emerging class of volatile organic compound sorbents: friedel-crafts modified polystyrenes. 1. Synthesis, characterization, and performance in aqueous- and vapor-phase applications, Ind. Eng. Chem. Res. 35 (1996) 1195–1205.
[12] V.A. Davankov, M.P. Tsyurupa, Structure properties of porous hypercrosslinked polystyrene sorbents "styrosorb", Pure Appl. Chem. 61 (1989) 1881–1888.
[13] V.A. Davankov, M.P. Tsyurupa, Structure properties of hypercrosslinked polystyrenes: the first representative of a new class of polymer networks, React. Polym. 13 (1990) 27–42.
[14] R. Kunin, Polymeric adsorbents for treatment of waste effluents, Polym. Eng. Sci. 17 (1977) 58–62.

[15] Tanju, Karanfil, A. Seyed, Dastgheib, Trichloroethylene adsorption by fibrous and granular activated carbons: aqueous phase, gas phase, and water vapor adsorption studies, Environ. Sci. Technol. 38 (2004) 5834–5841.
[16] D.D. Duong, Adsorption Analysis Equilibrium and Kinetics, Imperial, College Press, London, 1988.
[17] D.P. Valenzuela, A.L. Mayers, Adsorption of Equilibrium Data Handbook, Prentice Hall, Englewood Cliffs, NJ, 1998.
[18] Xiaoming Du, Erdong Wu, Application of the adsorption potential theory to hydrogen adsorption on zeolites above critical temperature, Acta Phys. Chim. Sin. 23 (2007) 813–819.
[19] S.J. Tim, E.M. David, Modified dubinin–radushkevich /dubinin –astakhov adsorption equations, J. Colloid Interface Sci. 15 (2002) 263–268.
[20] M.M. Dubinin, H.F. Stoeckli, Homogenous and heterogeneous micropore structures in carbonaceous adsorption adsorbent, J. Colloid Interface Sci. 75 (1980) 34–42.
[21] M.M. Dubinin, Fundamentals of the theory of adsorption in micropores of carbon adsorbents: characteristics of their adsorption properties and microporous structures, Carbon 27 (1989) 457–467.
[22] T.L. Hill, Statistical mechanics of adsorption. V. Thermodynamics and heat of adsorption, J. Chem. Phys. 17 (1949) 520–535.
[23] C.L. Chuang, P.C. Chiang, E.E. Chang, Modeling VOCs adsorption onto activated carbon, Chemosphere 53 (2003) 17–27.
[24] W. Rudzinski, D.H. Everett, Adsorption of Gases on Heterogeneous Surfaces, Academic Press, London, 1992.
[25] D.D. Do, A new adsorption isotherm for heterogeneous adsorbent based on the isosteric heat as a function of loading, Chem. Eng. Sci. 52 (1997) 297–310.
[26] Y.H. Yoon, J.H. Nelson, Application of gas adsorption kinetics i: a theoretical model for respirator cartridge service life, Am. Ind. Hyg. Assoc. J. 45 (1984) 509–516.