Adsorption characteristics of benzene–chlorobenzene vapor on hypercrosslinked polystyrene adsorbent and a pilot-scale application study

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ABSTRACT

The benzene and chlorobenzene is the representative of VOCs and widely exist in the industrial waste gas. In this paper, the removal characteristics of benzene and chlorobenzene vapor using a microporous hypercrosslinked polystyrene adsorbent (HPsorbent) were studied. The HPsorbent had the similar equilibrium adsorption capacities for benzene and chlorobenzene vapors with commercial granular activated carbon (GAC). The breakthrough adsorption capacities of benzene and chlorobenzene in the single and binary vapor system were also investigated. Although there exist a competitive adsorption between benzene and chlorobenzene vapors on HPsorbent, benzene and chlorobenzene removals of above 99% in the both system was attained before significant breakthrough occurred. On the other hand, a pilot-scale experiment was carried out to investigate the effectiveness of using HPsorbent to remove benzene–chlorobenzene vapors mixture from industrial byproduct hydrogen chloride gas. The results show that the hydrogen chloride gas did not have an adverse effect on the adsorption of benzene and chlorobenzene. In sum, HPsorbent should be potentially an effective adsorbent for removal of benzene–chlorobenzene vapors not only from air stream but also from hydrogen chloride gas.

1. Introduction

Chlorobenzene is an important industrial solvent and a widely used intermediate in production of commodities such as herbicides, dyestuffs, and rubber. In china, about 600,000 tons of Chlorobenzene is produced every year, accounting for above half of the annual output in the whole world. Presently it is manufactured by chlorination of benzene in the presence of a catalytic amount of Lewis acid such as ferric chloride. Therefore, the byproduct hydrogen chloride gas containing benzene–chlorobenzene vapor mixture is produced during the production of chlorobenzene. The concentrations of benzene and chlorobenzene are still kept at about 25–50 and 5–15 g/N m^3, respectively, after the hydrogen chloride is treated by the process of condensation and absorption. Generally, the resulting hydrogen chloride gas is absorbed in water, resulting in hydrochloric acid of industrial grade. If the benzene and chlorobenzene would be further removed from the resulting hydrogen chloride gas, however, hydrogen chloride gas could be used as raw material to manufacture other chemicals, such as vinyl, alkyl

chlorides and 3-chloro-1,2-epoxypropane, then more economical benefit was attained.

It is well known that adsorption is one of the most practical methods for separating and recovering volatile organic compounds (VOCs) from industrial waste gas. In order to reuse the above-mentioned hydrogen chloride gas, some factories had made an attempt to remove benzene and chlorobenzene using carbonaceous adsorbent from the hydrogen chloride in China, but it failed due to low adsorption capacity and sharp rise of bed temperature, resulting from the strong interaction of hydrogen chloride with functional groups on the surface of carbonaceous adsorbent [1,2]. Therefore, the removal of benzene and chlorobenzene from hydrogen chloride gas is serious challenge.

In the past few decades, permanently porous polymeric adsorbent has emerged as a potential alternative to activated carbon for removing the organic pollutants due to its controllable pore structure, stable physical, chemical properties as well as regenerability on site. Of the porous polymers, hypercrosslinked polymeric resin, which is produced by crosslinking polymers of macroporous resin in a good solvent, represents a class of predominantly microporous organic materials with high surface areas and high micropore volume [3,4], and gained popularity as excellent adsorbing materials for solid-phase extraction of organic contaminants from aquatic environment [5–9]. More recently, a few studies have been carried to investigate the adsorption characteristics of hypercrosslinked

Table 1
Salient properties of HPsorbent and GAC.

Adsorbent	S_{BET} (m^2/g)	S_{meso} (m^2/g)	V_{micro} (mL/g)	V_{meso} (mL/g)	Acidic groups	Basic groups
HPsorbent	1020.7	214.27	0.394	0.185	0.224	0
GAC	1015.2	102.9	0.407	0.081	0.887	0.419

polymeric resin as adsorbents for removing the VOCs from gas steam [10–13]. These studies have shown that hypercrosslinked polymeric resin is a promising adsorbent for removing and recovering VOCs from polluted vapor streams.

The purpose of this study was to exploring the effectiveness of benzene–chlorobenzene vapors mixture removal from polluted gas by a hypercrosslinked polymeric adsorbent (HPsorbent), which was prepared through Friedel–Craft modification of macroreticular type polymer beads. First, adsorption equilibrium of benzene and chlorobenzene vapors onto HPsorbent at 303, 318, and 333 K, respectively, were measured to elucidate the adsorption mechanism. Then, column adsorption of benzene–chlorobenzene vapors mixture was carried out in bench-scale systems using nitrogen as a carrier gas. Guided by the bench-scale findings, pilot-scale tests were conducted for removing benzene and chlorobenzene vapors mixture from hydrogen chloride at the Yangnong Chemical Group Corporation Limited, which is one of the largest manufacturers of chlorobenzene in China.

2. Materials and methods

2.1. Materials

The hypercrosslinked polymeric adsorbent (HPsorbent, 0.6–1.0 mm in diameter) was prepared via a post-crosslinking step involving the Friedel–Crafts reaction between the chloromethylated copolymer of styrene–divinylbenzene, the synthetic process had been described in detail in our previous paper [7]. The coconut-shell granular activated carbon (GAC) purchased from Liyang Tianlun Environmental Materials Ltd., China was chosen as a reference. The porous texture of two adsorbents was determined by N$_2$ isotherms data at 77 K, using an adsorption analyzer ASAP 2020 (Micromeritics Instrument Co., USA). Their specific surface area (S_{BET}), micropore volume (V_{micro}), mesopore surface area (S_{meso}) and mesopore volume (V_{mero}) were calculated from the N$_2$ isotherm data at 77 K by Brunauer–Emmett–Teller (BET) and Dubinin–Astakov (DA), and Barrett–Joyner–Halena (BJH) methods, respectively. The surface functional groups of two adsorbents were evaluated by the method of Boehm [14]. Characteristics of HPsorbent and GAC were listed in Table 1; the pore size distribution of two adsorbents was shown in Fig. 1.

Two volatile organic compounds including analytic grade chlorobenzene (99.5%) and benzene (99.5%) were purchased from Nanjing Chemical Reagent station (Nanjing, China) and used in this study without further purification.

2.2. Adsorption experiments

The adsorption of benzene and chlorobenzene vapors from the nitrogen stream was determined by the column adsorption method. The detailed experimental apparatus and adsorption procedure have been described previously [13]. Briefly, about 1.000 g of HPsorbent or GAC was precisely weighed out and charged into the adsorption column made of glass. 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 com-

puter. 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.

2.3. Pilot-scale test

To investigate the effectiveness of benzene–chlorobenzene vapors removal using HPsorbent from the hydrogen chloride gas, a pilot-scale device was built at the Yangnong Chemical Group Corporation (China). The environmental temperature was about 10–15 °C during the experiment. The schematic process chart of the pilot-scale facility is shown in Fig. 2. The hydrogen chloride was piped from the manufacture device of chlorobenzene. The packed column was 0.30 m in diameter, contained 65 kg (in dry weight) of hypercrosslinked polymeric adsorbent (HPsorbent), and the superficial gas flow velocity in the packed bed was about 0.2 m/s. Benzene and chlorobenzene concentration were measured at the inlet and outlet of adsorption column using gas chromatography method [15]. The adsorbent was regenerated using the water vapor of about 120 °C. Additionally, the pilot-scale device was equipped with cooler to cool the water vapor and recover the benzene and chlorobenzene.

3. Results and discussion

3.1. Equilibrium adsorption of single vapor

Adsorption isotherms of benzene or chlorobenzene vapor on HPsorbent at 303, 318, and 333 K were shown in Fig. 3. As shown in Fig. 3, HPsorbent had good adsorption ability for benzene and chlorobenzene vapor; favorable adsorption isotherms were exhibited for benzene and chlorobenzene vapor with the extent of adsorption increasing as the equilibrium pressure of the adsorbate increased. The results also show that HPsorbent had greater adsorption capacities for chlorobenzene than that for benzene in the present concentration range. This is due to the higher boiling
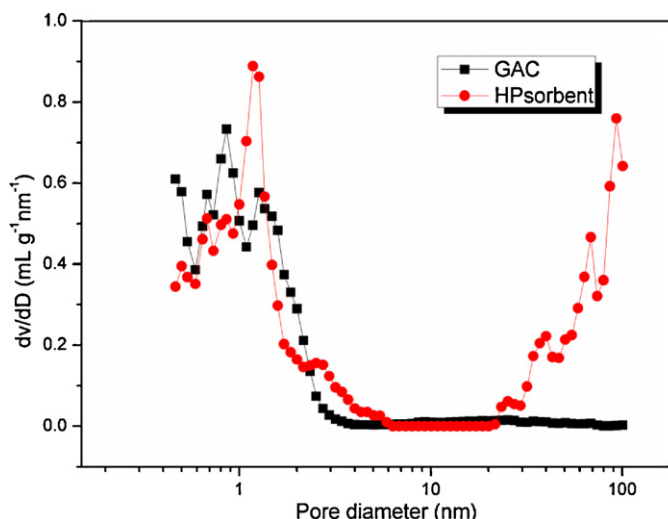

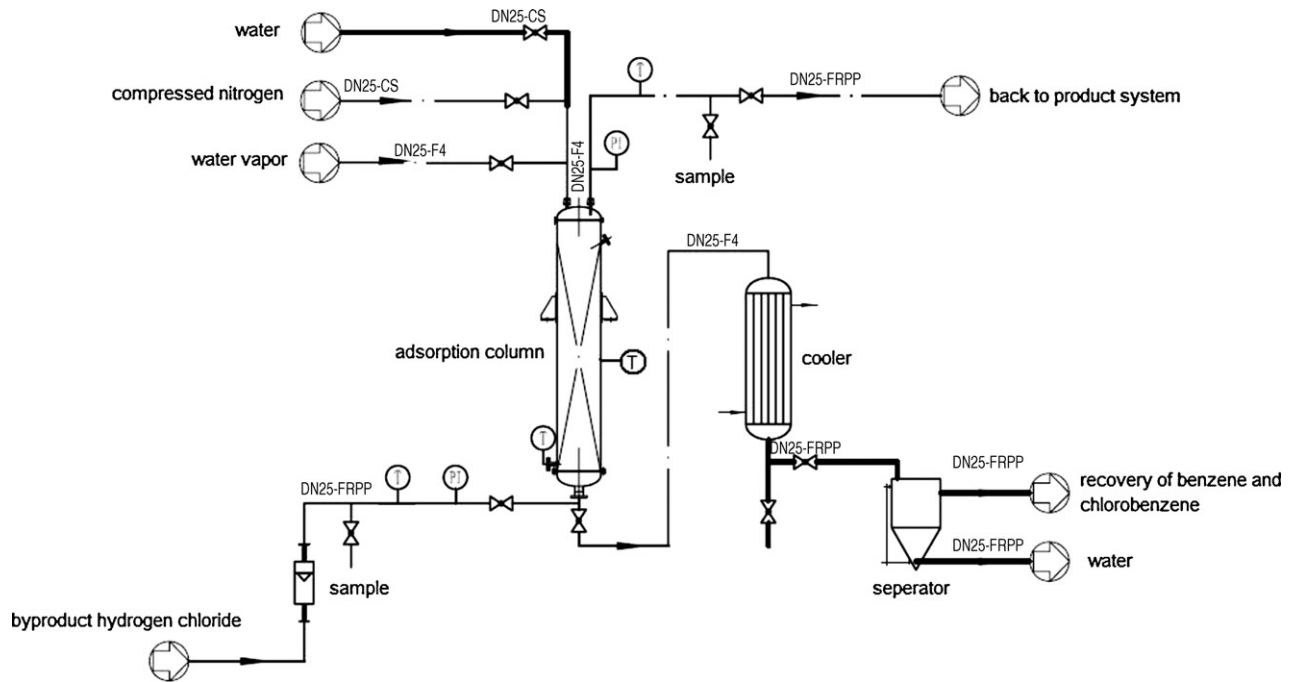**Fig. 1.** The pore size distribution of HPsorbent and GAC.

Fig. 2. The schematic process chart of the pilot-scale facility for removing the benzene and chlorobenzene from hydrogen chloride gas.

point and higher saturation vapor pressure of chlorobenzene compared to benzene.

To understand the adsorption mechanism, the equilibrium adsorption data of benzene and chlorobenzene on HPsorbent at different temperatures were fitted using Dubinin–Astakov equation (DA), which is based on the potential theory and is useful for describing the adsorption on microporous adsorbent. The DA equation can be defined as Eqs. (1)–(3):

$$q_v = q_0 \exp\left[-\left(\frac{\varepsilon}{E}\right)^r\right] \tag{1}$$

$$\varepsilon = RT \ln\left(\frac{P_s}{P}\right) \tag{2}$$

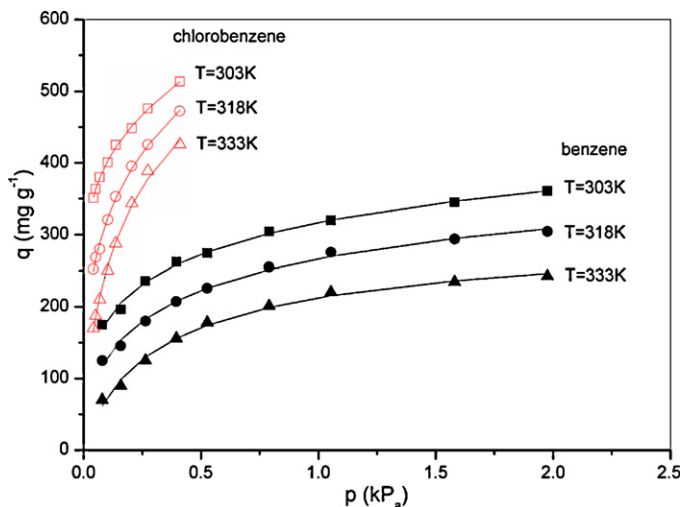$$q_v = \frac{q}{\rho} \tag{3}$$

Fig. 3. Equilibrium adsorption data of benzene and chlorobenzene onto HPsorbent and fitting curves of Dubinin–Astakov equation as solid lines.

where q_v is volume adsorbed capacity (mL/g), q_0 is the limiting microporous volume, ε is the adsorption potential (J/mol) written by Eq. (2), 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 adsorption amount (mg/g), ρ is the adsorbate density in the adsorbed phase assumed to be the same as that in the liquid phase.

The experimental data of benzene and chlorobenzene onto HPsorbent at 303, 318, and 333 K in Fig. 3 are represented as symbols and isotherm fittings using the DA equation as solid lines. Clearly, the experimental data were well fitted by the DA equation. According to potential theory, for the adsorption of different adsorbates on a given adsorbent, it is certain that plots of adsorbed volume q_v against the ratio of the adsorption potential to molar volume (ε/V_s) at different temperature should yield a unique curve that is independent on temperature and adsorbate [16]. To further examine whether DA equation mechanistically captures the adsorption process of compounds by adsorbent, the plots of adsorbed volume (q_v) vs. adsorption potential density (ε/V_s) of benzene and chlorobenzene onto HPsorbent are shown in Fig. 4. As the Polanyi potential theory would predict, they all fell essentially onto a single curve with the larger correlation coefficient $R^2 \geq 0.95$, indicating usefulness of DA equation to describe the adsorption of benzene and chlorobenzene on HPsorbent, and that micropore filling is the dominating mechanism for the adsorption of benzene and chlorobenzene.

Although activated carbon adsorption sometimes encounters some problems such as combustion, pore blocking, inefficiently desorption of high-boiling solvents, and hygroscopicity [17–19], activated carbon is one of the most effective adsorbent materials and is widely used to elimination and recovery of VOCs. Therefore, for the better understanding of the adsorption capacities of HPsorbent, comparison of the adsorption of benzene and chlorobenzene vapor on HPsorbent and a commercial GAC were made in the present study. From Fig. 5, it is clearly known that HPsorbent had the comparative adsorption capacities with GAC. Moreover, it should be noticed that the adsorption capacities of HPsorbent were much larger for benzene and chlorobenzene than that of GAC at the
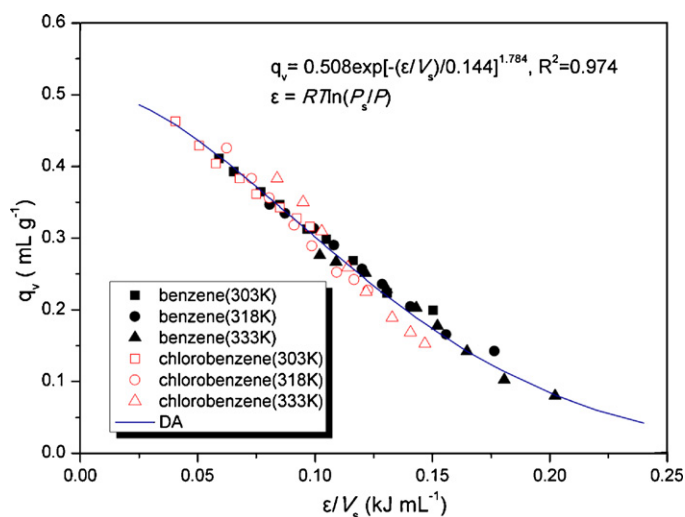
Fig. 4. Plots of adsorbed volume (q_v) vs. adsorption potential density (ε/V_s) for benzene and chlorobenzene on HPsorbent.

higher relative pressure range. It may be attributed to larger meso-pore volume of HPsorbent despite of the similar BET surface area of two adsorbents, 1020.7 and 1015.2 m^2/g for HPsorbent and GAC, respectively. It is clearly shown from Fig. 1 that GAC is typical of micropore adsorbent with a unimodal pore distribution between 0.4 and 2.0 nm, while HPsorbent is of coexisting pore structures of micropore and mesopore called a "bimodal pore system". There-fore, it is expected that HPsorbent would be a promising adsorbent for removal of benzene–chlorobenzene mixture vapor; specially for adsorbing the benzene and chlorobenzene vapor of higher concen-tration.

3.2. Dynamic adsorption for the benzene–chlorobenzene mixture

Breakthrough experiments for binary vapor system of benzene–chlorobenzene mixture at 303 K have been carried out to study the adsorption capacity of HPsorbent up to the break-through time. Inlet concentration of benzene in the experiments for a binary vapor was 16.33 and 32.67 $g/N\,m^3$, respectively, while the concentration of chlorobenzene was fixed at 6.1 $g/N\,m^3$. As shown in Fig. 6, it was noted that benzene was the first breakthrough gas, and the breakthrough time of benzene and
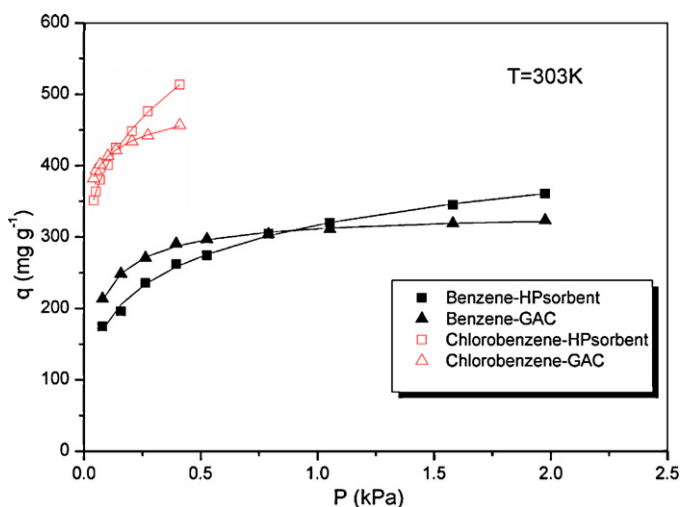

Fig. 5. Comparison of adsorption capacities of benzene and chlorobenzene onto HPsorbent and GAC.
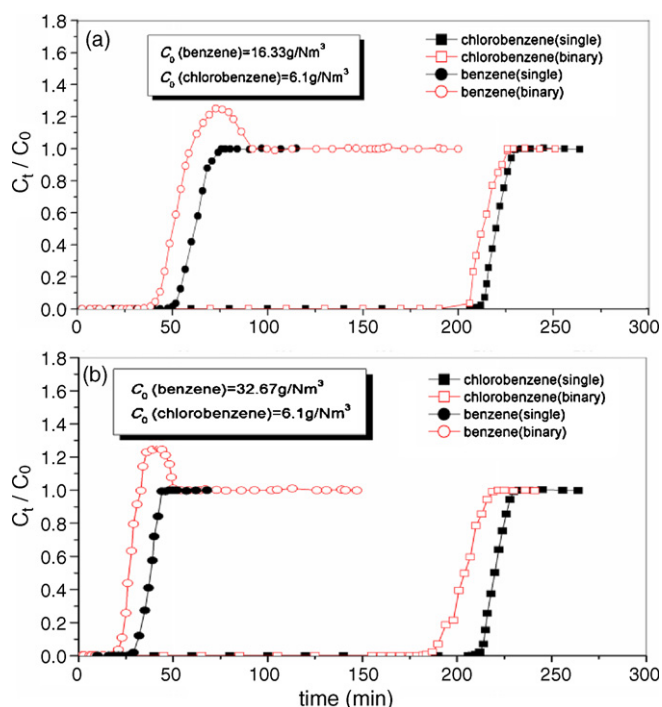

Fig. 6. Comparison of breakthrough curves in the single and binary vapor system composed of benzene and chlorobenzene.

chlorobenzene vapor in the binary vapor was faster than that in the single benzene or chlorobenzene vapor system. Additionally, the breakthrough curves of benzene in the binary vapor were quite different from that of single vapor, the phenomenon of "roll-up" was observed in the breakthrough curves, the outlet concentration of benzene vapor in the binary vapor reached to the inlet concentration rapidly and then increased to approxi-mate 1.3 times than inlet concentration. This is a consequence of competitive adsorption of benzene and chlorobenzene on the HPsorbent. Owing to the stronger adsorption of chlorobenzene on the HPsorbent surface and the lower volatility of chlorobenzene, the more strongly adsorbed chlorobenzene displaces the weaker adsorbate benzene, leading to a rise in the outlet concentration of the less strongly adsorbed benzene above the inlet concentration. However, it should be noted from Fig. 6 that the benzene was not displaced completely by the chlorobenzene in the binary vapor system.

The total breakthrough adsorption capacities of HPsorbent for the mixture of benzene and chlorobenzene were calculated as the outlet concentration of the first breakthrough component of the mixture in the outlet gas was 1% of the inlet concentration. This is one of the most important design parameters for an adsorp-tion system, since bed replacement or the regeneration step do not occur when the equilibrium is achieved and the adsorbent is exhausted, but when the first breakthrough component is detected in the outlet gas stream. The quantification of adsorption capacities of benzene and chlorobenzene up to the breakthrough time is pre-sented in Table 2. It is known from Table 2 that the breakthrough adsorption capacities of the first breakthrough component benzene in the binary vapor system decreased by 21.1% and 22.4%, respec-tively, compared with that in the single vapor system. In additional, as the benzene concentration increased from 16.33 to 32.67 $g/N\,m^3$ in the binary vapor, it was noted that the breakthrough adsorption capacity of benzene was increased from 200.9 to 220.4 mg/g, but the adsorption capacities of chlorobenzene until the breakthrough time of benzene was decreased from 95.2 to 42.1 mg/g, and that of benzene–chlorobenzene mixture was also decreased from 296.1

Table 2
Adsorption capacities of the benzene and chlorobenzene until the breakthrough time.

| Inlet concentration (g/N m³)	Single vapor		Binary vapor		
	Benzene	Chlorobenzene	Benzene	Chlorobenzene	Benzene + chlorobenzene
16.33 (benzene) + 6.1 (chlorobenzene)	254.7	389.8	200.9	95.2	296.1
32.67 (benzene) + 6.1 (chlorobenzene)	284.2	389.8	220.4	42.1	262.5

to 262.5 mg/g. The decrease of the breakthrough adsorption capacities of chlorobenzene and mixture was owing to the decrease of breakthrough time of the first breakthrough component benzene.

To sum up, although the stronger adsorption of chlorobenzene can displace the weaker adsorption of benzene, there is co-adsorption of benzene and chlorobenzene before the breakthrough of first component occurred. The breakthrough adsorption capacities of HPsorbent for benzene–chlorobenzene mixture were as high as 267.5 and 296.1 mg/g in the current conditions, respectively, and HPsorbent should be effective adsorbent for removing the mixture of benzene and chlorobenzene.

3.3. Pilot-scale study: removal of benzene–chlorobenzene mixture from hydrogen chloride gas

Since the bench-scale results have shown that hypercrosslinked polymeric adsorbent could be effective adsorbent for removing the benzene and chlorobenzene vapor from the nitrogen stream. To investigate the effectiveness of benzene and chlorobenzene vapor removal from the industrial byproduct hydrogen chloride, a pilot-scale experiment was conducted at the Yangnong Chemical Group Corporation, China.

Fig. 7 shows the benzene and chlorobenzene vapor removal efficiency by HPsorbent as a function of adsorption time for the 1st and 25th run, respectively. Continuous adsorption–regeneration runs of an identical HPsorbent bed were performed to test its feasibility for field application. As depicted in Fig. 7, both of benzene and chlorobenzene removals of above 98% before significant breakthrough occurred for each run were achieved in spite of an obvious inlet concentration fluctuation. The total breakthrough
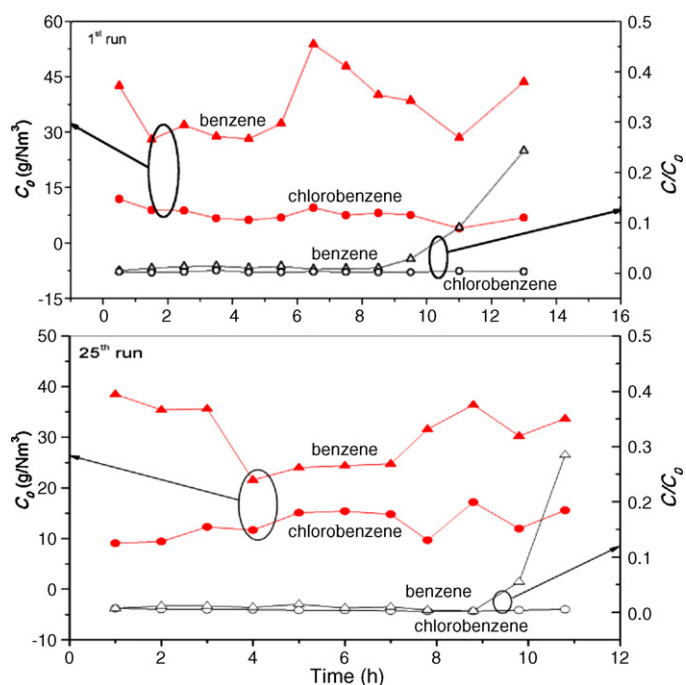
adsorption capacities of the 1st and 25th run determined at leakage of 0.5 g/N m³ of benzene in effluent were 283.8 and 291.9 mg/g, respectively. Comparison of the pilot- and bench-scale experimental results showed that both of the breakthrough adsorption capacities was basically similar, indicating hydrogen chloride did not have an adverse effect on the adsorption of benzene and chlorobenzene on the HPsorbent. The result of pilot-scale experiment clearly show that benzene and chlorobenzene can be removed effectively from hydrogen chloride by hypercrosslinked polymeric adsorbent, and that HPsorbent can be completely regenerated for repeated use with no capacity loss.

The adsorbed benzene and chlorobenzene was desorbed using water vapor of 120 °C. Then, the vapor steam containing high-content benzene and chlorobenzene was cooled to recover the benzene and chlorobenzene. Continuous 6-month runs indicated that about 95–98% of benzene and chlorobenzene was recovered in the pilot scale.

4. Conclusions

The breakthrough adsorption capacities of benzene and chlorobenzene in the binary vapor system were lower than those in the single vapor system. However, there is co-adsorption of benzene and chlorobenzene, and benzene–chlorobenzene mixture removal efficiency of column adsorption was above 99% before the breakthrough of first component occurred. On the other hand, hydrogen chloride did not have an adverse effect on the adsorption of benzene and chlorobenzene on the HPsorbent. The total breakthrough adsorption capacities of benzene and chlorobenzene determined at leakage of 0.5 g/N m³ of benzene in effluent were above 280 mg/g in the current pilot-scale experiment. Therefore, it is concluded that hypercrosslinked polymeric adsorbent (HPsorbent) is a potential adsorbent for the removal of benzene and chlorobenzene not only from the nitrogen stream but also from hydrogen chloride gas.

Fig. 7. Breakthrough curves of benzene and chlorobenzene in a pilot-scale experiment.

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