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Adsorption and separation of lignin-based aromatic aldehydes using macroporous resins

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Abstract−Lignin-based aromatic aldehydes (p-hydroxybenzaldehyde, vanillaldehyde and syringaldehyde) have wide applications in flavoring. However, their separation using chromatographic methods has not been explored. We studied the adsorption and desorption behaviors of aromatic aldehydes on macroporous resins and four macroporous resins X-5, CAD-40, AB-8 and D101 were screened for separation of aromatic aldehydes. The results demonstrated that X-5 showed the highest adsorption and desorption capacities. The adsorption capacities for p-hydroxybenzaldehyde, vanillaldehyde and syringaldehyde on X-5 were 33.5 mg/g, 46.6 mg/g and 47.0 mg/g at 20 °C, respectively, higher than that of CAD-40, AB-8 and D101. Adsorption isotherms of aromatic aldehydes on X-5 were confirmed to fit to Freundlich equation which was calculated by $\ln Q_e = 0.6933\ln C_e + 6.788$, $\ln Q_e = 0.7031\ln C_e + 7.7358$ and $\ln Q_e = 0.7107\ln C_e + 8.2412$ for p-hydroxybenzaldehyde, vanillaldehyde and syringaldehyde, respectively. The results of dynamic adsorption and desorption experiments demonstrated that 50% (v/v) ethanol solution was an effective elution solvent for aromatic aldehydes. The maximum concentration of the three kinds of aromatic aldehydes in eluent reached 3.74 g/L, 5.44 g/L and 7.03 g/L, which indicated that the elution process was also an effective enrichment process for sorbate.

Keywords: Aromatic Aldehydes, Macroporous Resin, Adsorption, Desorption, Adsorption Isotherms

INTRODUCTION

Plant biomass is an important part of biological resources. Cellulose and hemicellulose are usually used to prepare for bio-ethanol, which is of vital importance in alleviating the energy crisis and for environmental protection. Lignin offers possibilities for higher value-added renewable products applications based on its phenolic functionalities and properties [1,2]. Moreover, lignin constitutes up to 30% of the weight and 40% of the fuel value of biomass; it can be used to increase fuel production. Lignin is an extremely complex three-dimensional macromolecule with irregular structure, which results from random dehydrogenative polymerization of phenylpropane building units, including guaiacyl, syringyl and p-hydroxyphenyl [3,4]. These structural units can be converted into aromatic aldehydes such as p-hydroxybenzaldehyde, vanillaldehyde and syringaldehyde, which have wide applications in flavoring, as chemical intermediates for pharmaceutical drugs and agricultural pesticides by oxidative degradation.

The oxidative degradation products of lignin are extremely complex [5]. Separation and purification of p-hydroxybenzaldehyde, vanillaldehyde and syringaldehyde from degradation products are technological difficulties in higher-added value application of lignin. P-hydroxybenzaldehyde, vanillaldehyde and syringaldehyde have similar physicochemical properties because of their similar chemical structure that the number and location of the methoxyl attached to the benzene ring of the three kind of aromatic aldehydes are different (Fig. 1).

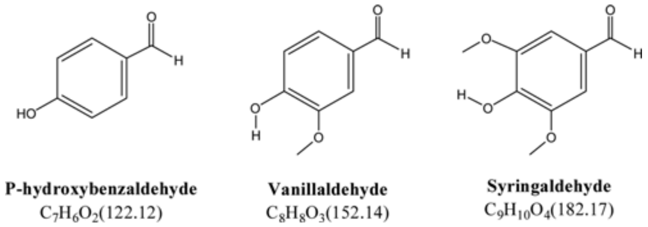

Fig. 1. Molecular structure, chemical formula (molecular weight) of lignin-based aromatic aldehydes.

It is virtually impossible to separate the aromatic aldehydes by ordinary distillation because of their extremely close boiling points, and many methods such as solvent extraction, molecular distillation, membrane separation have been developed [6-8]. However, these methods have disadvantages such as high production costs and formation of toxic compounds [9]. It is necessary to establish reliable, efficient and economical methods. Recently, macroporous resins have been used as adsorbents due to their high efficiency, long life, environmental friendliness, high adsorption capacity and selectivity, favorable physicochemical stability and convenient regeneration treatments [10-12]. Macroporous resins have been applied to separate benzaldehydes due to characteristics including high mechanical strength, various functional groups, porous ability, and long life times [13,14]. Most of these resins can adsorb organic constituents because they are hydrophobic and weakly polar. Separation and purification of benzaldehydes by macroporous resins have been

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Table 1. Physicochemical properties of screened macroporous resins

Resins	X-5	CAD-40	AB-8	D101
Matrix structure	Crosslinked polystyrene	Crosslinked polystyrene	Crosslinked polystyrene	Crosslinked polystyrene
Polarity	Non	Mid	Low	Non
Bead size (mm)	0.3-1.25	0.3-1.25	0.3-1.25	0.3-1.25
Moisture (%)	64.23	68.20	67.73	66.81
Ture density (g/mL) (wet)	1.04	1.07	1.05	1.03
Apparent density (g/mL) (wet)	0.68	0.70	0.69	0.68
Surface area (m^2/g)	660	500	490	520
Average pore diameter (nm)	28	5.5	14	9.5
Porosity (%)	54.47	61.03	50.86	56.58

widely investigated; however, adsorption and desorption properties on lignin-based aromatic aldehydes have not been explored.

The aim of the present work was to investigate the adsorption and desorption behaviors of aromatic aldehydes on macroporous resins and to develop an efficient process for enrichment and purification of aromatic aldehydes using macroporous resins. The Freundlich adsorption isotherms were used to fit the experimental data and the associated constants were evaluated.

EXPERIMENTAL

1. Materials and Methods

The macroporous resins X-5, CAD-40, AB-8, D101 were supplied by Anhui Sanxing Resin Technology Co. Ltd. (Anhui, China). Some properties of the resins are given in Table 1. The resins in the wet form were soaked in 95% (v/v) ethanol solution for 24 h, then loaded into glass columns (20 mm×300 mm), drip washed with 95% (v/v) ethanol solution until there was no precipitation when deionized water was added into eluent, then alcohol was washed away with deionized water. The resins were pretreated with 5 wt% HCl solution at the flow rate of 3-5 times bed volume per hour (BV/h), and then pretreated with 5 wt% NaOH solution at the same flow rate, washed adequately with deionized water. All the chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China) and used without further purification.

Lignin-based aromatic aldehydes were prepared by catalytic wet oxidation (CWO) of enzymatic hydrolysis lignin [15,16]. Reaction was carried out in an autoclave. Concentration of NaOH was 8 wt% and 1 wt% $CuSO_4$ was used as catalyst. Concentration of enzymatic hydrolysis lignin used as substrate was 5 wt%. Oxygen pressure was 1.5-2.0 MPa, 200 rpm, 180 °C for 240 min, then filtered. The filtrate was neutralized to pH=2-3 with hydrochloric acid and flocculent generated, filtered and the residue was extracted with chloroform, the organic phase vacuum evaporated and the residue dissolved with water; then the aromatic aldehyde solution was ready for further investigations. High performance liquid chromatography (HPLC) was conducted to analyze the composition of the aromatic aldehydes solution and determine the contents of p-hydroxybenzaldehyde, vanillaldehyde and syringaldehyde with external standard method.

2. Static Adsorption and Desorption Experiments

The static adsorption and desorption tests for the separation of aromatic aldehydes using the macroporous resins were performed as follows: 2 g of the pre-weighed resins was put into four Erlenmeyer flasks with lid, respectively, and 150 mL of aromatic aldehyde solution was added to each flask. The flasks were sealed tightly and shaken using the shaking incubator (200 rpm) at 20 °C for 12 h to reach adsorption equilibrium. After adsorption, resins were washed three times with deionized water. For desorption, 100 mL of 50% (v/v) ethanol solution was added to the flasks containing the resins. The flasks were shaken (200 rpm) at 20 °C for 12 h to reach desorption equilibrium. After adsorption and desorption, the solutions were filtered and the concentrations of aromatic aldehydes were analyzed. The adsorption capacity of resins (Q_e, mg/g) and adsorption rate (E, %) were calculated according to the following equations:

$$Q_e=(C_0-C_e)V_1/m \tag{1}$$

$$E(\%)=(C_0-C_e)/C_0 \tag{2}$$

where Q_e is the adsorption capacity at the adsorption equilibrium (mg/g dry resin), C_0 is the initial concentration (g/L), C_e is the equilibrium concentration (g/L), V_1 is the volume of the initial sample solution (L), m is the dry weight of resin (g), E is the adsorption rate (%).

3. Static Adsorption Isotherms

The tests to determine the adsorption isotherms of aromatic aldehyde separation by screening macroporous resin were conducted using 100 mL of the sample solution at different initial concentrations of aromatic aldehydes (0.1, 0.2, 0.3, 0.4 and 0.5 g/L) with 1 g of dried resins in the shaker (200 rpm) at 20 °C for 12 h. After adsorption, the concentrations of aromatic aldehydes were measured, and their degrees of fitness to the Freundlich equation were evaluated. The Freundlich model can be expressed by the following mathematical formula [17,18]:

$$\ln Q_e(\mathrm{mg/g})=\ln K_f+\left(\frac{1}{n}\right)\ln C_e \tag{3}$$

where Q_e is the adsorption capacity at the adsorption equilibrium which can be evaluated by formula (1), C_e is the equilibrium concentration, K_f is the Freundlich constant that is an indicator of adsorption capacity, and 1/n is the empirical constant that is dependent on temperature and the adsorption system.

4. Dynamic Adsorption and Desorption Experiments

The dynamic adsorption and desorption properties of screened macroporous resin were evaluated by using glass columns (20 mm× 300 mm) at 20 °C. The bed volume (BV) of resin was 85 mL. The sample solution was loaded on 20 g of resin in a glass column at a flow rate of 1 BV/h. After adsorption, desorption was investigated at a flow rate of 1 BV/h. The elution solvent was 50% (v/v) ethanol solution. During adsorption and desorption, aliquots were collected in 1 BV and 0.5 BV intervals by an auto-fraction collector, respectively.

5. Reuse and Regeneration of the Macroporous Resins

The macroporous resins could be used repeatedly for the adsorption of aromatic aldehydes after being eluted, except that the adsorption capacities of the resins declined significantly. The the regeneration of the macroporous resins was required, which was conducted as follows: the resins used were soaked in 3 wt% HCl solution for 4 h, then loaded into glass columns, drip washed with 3 wt% HCl solution of 3 BV at the flow rate of 3 BV/h, washed adequately with deionized water to neutral, then treated with 5 wt% NaOH solution and the procedures were basically identical to those of HCl solution. Finally, the macroporous resins were drip washed with 95% (v/v) ethanol solution of 3 BV, then alcohol was washed away with deionized water.

6. HPLC Analysis

HPLC analysis of aromatic aldehydes was performed on an Agilent R60 infinity chromatographic work station equipped with an Eclipse Plus C18 column (4.6 mm×150 mm) and a UV detector at 280 nm to quantitatively determine the content of p-hydroxybenzaldehyde, vanillaldehyde and syringaldehyde. The injection volume was 5 μL and a mixture of acetonitrile (10%, v/v), deionized water (88.5%, v/v) and acetic acid (1.5%, v/v) was used as the mobile phase at a flow rate of 0.9 mL/min.

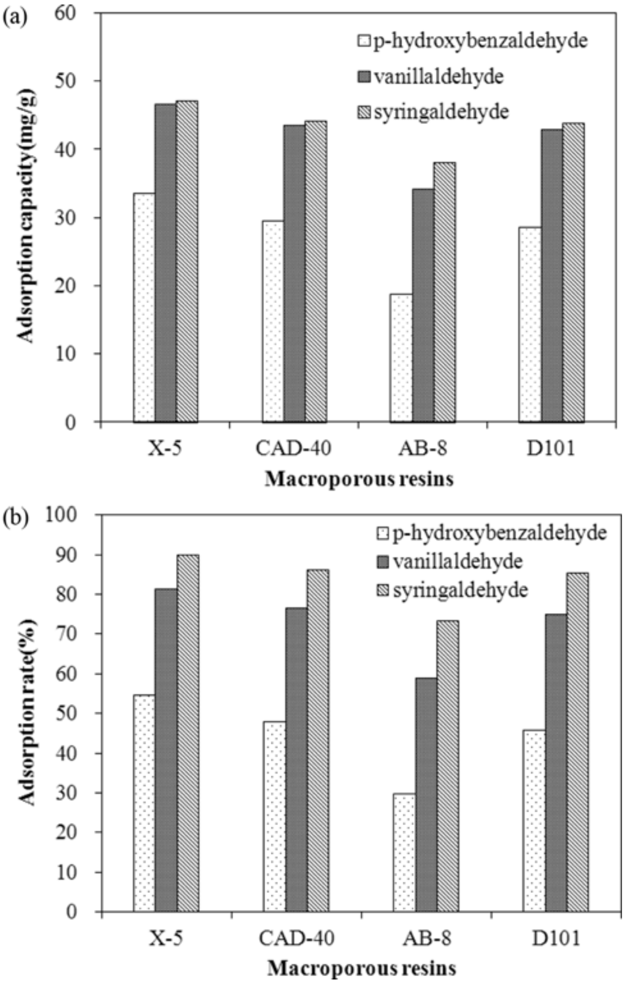

Fig. 2. The static adsorption capacities of different macroporous resins.

RESULTS AND DISCUSSION

1. Screening of Macroporous Resins for Separation of Aromatic Aldehydes

For the separation of aromatic aldehydes, we screened adsorption and desorption capacities of four macroporous resins (X-5, CAD-40, AB-8 and D101) which were used in the purification of benzaldehydes in previous studies. The static adsorption and desorption capacities of different macroporous resins are shown in Figs. 2(a) and 2(b), respectively. As can be seen, adsorption capacities of aromatic aldehydes ranked as syringaldehyde>vanillaldehyde>p-hydroxybenzaldehyde on all kinds of macroporous resins. This is probably because these resins can adsorb organic constituents by virtue of their hydrophobicity and weak polarity. Syringaldehyde has the weakest polarity, which leads to the maximum adsorption capacity on macroporous resins. For p-hydroxybenzaldehyde, adsorption capacity of X-5 (33.5 mg/g) was higher than that of CAD-40 (29.4 mg/g), D101 (28.4 mg/g) and AB-8 (18.7 mg/g). It showed the same certain law for vanillaldehyde and syringaldehyde adsorbed on X-5 with the maximum adsorption capacities of 46.6 mg/g and 47.0 mg/g, respectively. The adsorption rate of p-hydroxybenzaldehyde, vanillaldehyde and syringaldehyde adsorbed on X-5 was 54.4%, 81.1% and 89.6%, respectively, which was higher than that of CAD-40 (47.6%, 76.3% and 86.0%), D101 (45.6%, 74.7% and 85.1%) and AB-8 (29.6%, 58.6% and 73.0%). This could be related to the physicochemical properties of macroporous resins. Polarity and surface area of the macroporous resins might be the dominant reason. X-5 with non-polarity and larger surface area was more likely to adsorb aromatic aldehydes (see Table 1). Among the resins, X-5 exhibited the highest adsorption capacity for aromatic aldehydes and was selected for further investigations.

2. Static Adsorption and Desorption Kinetics on Macroporous Resins

Static adsorption and desorption experiments were conducted at 20 °C to understand the separation of aromatic aldehydes by X-5, CAD-40, AB-8 and D101. In the kinetic adsorption tests (Figs. 3(a)-3(d)), the adsorption capacities of macroporous resins increased rapidly in the first 10 min, then reached equilibrium after 60 min and the adsorption rate of aromatic aldehydes reached to maximum value for all kinds of macroporous resins adopted. Meanwhile, the concentrations of aromatic aldehydes in eluent increased sharply in the first 20 min, then reached equilibrium after 90 min for all kinds of macroporous resins adopted (Figs. 4(a)-4(d)). The results of desorption experiments indicated that aromatic aldehydes adsorbed on macroporous resins could be eluted effectively by 50% (v/v) ethanol solution that could be used as elution solvent of aro-

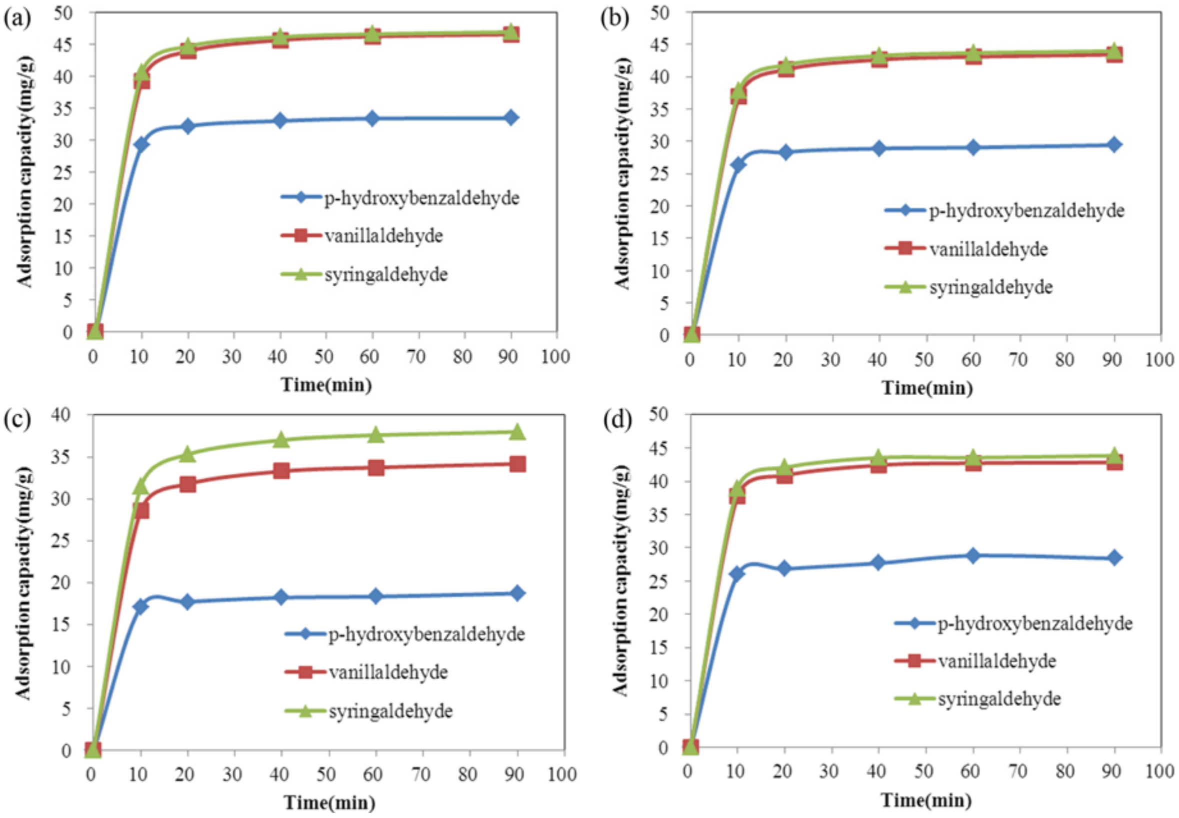

Fig. 3. The static adsorption kinetics of aromatic aldehydes on X-5 (a), CAD-40 (b), AB-8 (c) and D101 (d) at 20 °C.

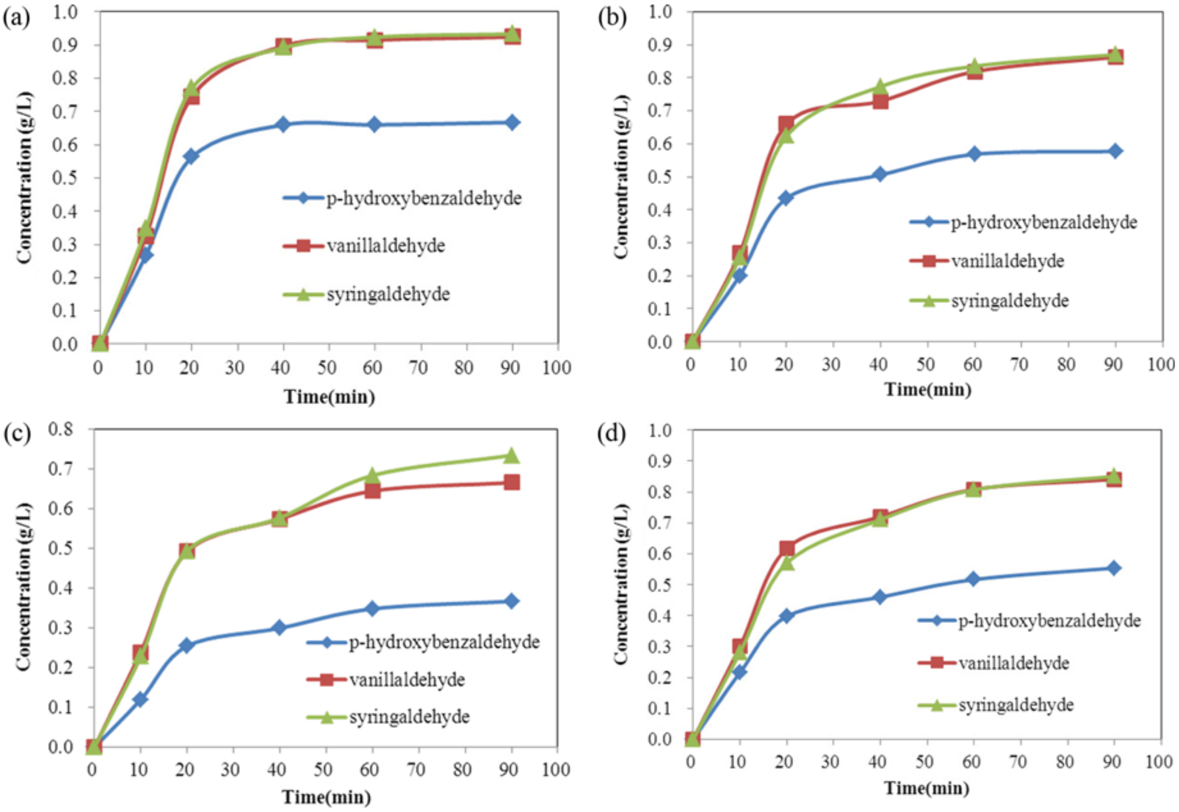

Fig. 4. The static desorption kinetics of aromatic aldehydes on X-5 (a), CAD-40 (b), AB-8 (c) and D101 (d) at 20 °C.

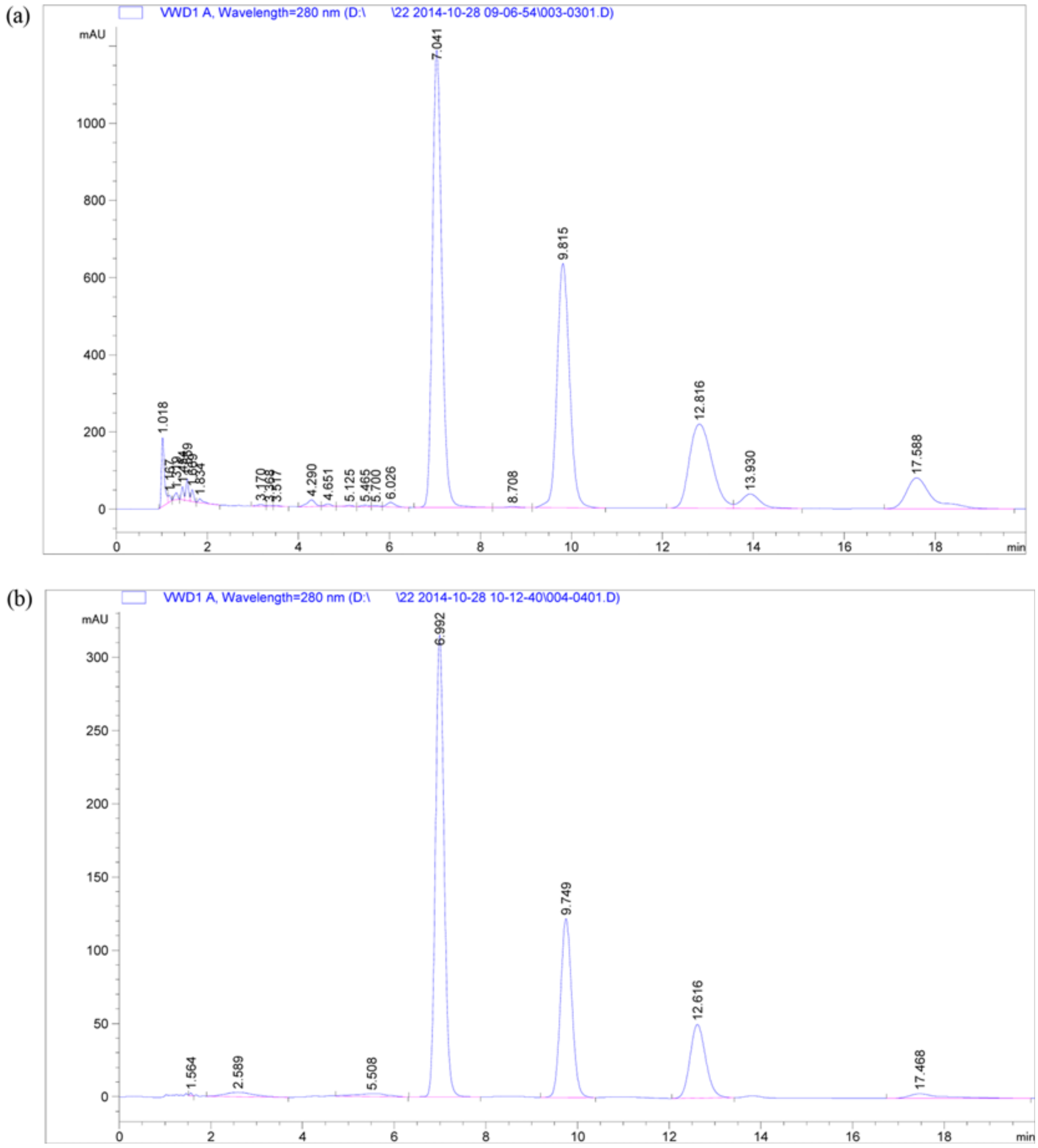

Fig. 5. HPLC spectrums of aromatic aldehydes solution (a) and stripping liquid (b).

matic aldehydes.

3. Component Analysis by HPLC

To preliminarily evaluate the effect of adsorption and desorption, we analyzed and compared the composition of the aromatic aldehydes solution prepared by catalytic wet oxidation of lignin (Fig. 5(a)) and the stripping liquid of aromatic aldehydes on X-5 (Fig. 5(b)) by HPLC. As can be seen from Figs. 5(a) and 5(b), numerous oxidative degradation products of lignin could be detected under the wavelength of 280 nm and the peak time of p-hydroxybenzaldehyde, vanillaldehyde and syringaldehyde was 7.041 min, 9.815 min and 12.816 min, respectively. Most of the impurities peaked before 7 min, while some peaked after 13 min. After being treated by macroporous resin X-5, many impurities disappeared, which proved that adsorption and desorption of aromatic aldehydes using macroporous resin X-5 was an effective way to separate aromatic aldehydes from oxidative degradation products of lignin.

4. Static Adsorption Isotherms of Aromatic Aldehydes on X-5

Analytical isotherm equations such as Langmuir and Freundlich isotherms are widely used for modeling adsorption data [19]. The Langmuir equation requires the assumption that the sorbate forms only a single layer. That is, the adsorption capacity maximizes and maintains with the increasing of equilibrium concentration of the sorbate after the adsorption equilibrium. Whereas, the Freundlich equation requires the assumption that the sorbate forms multilayer adsorption on rough surfaces. So the adsorption capacity increases with the increasing of equilibrium concentration of the sorbate.

As can be seen from Fig. 6(a), the adsorption capacity of X-5 increased with the equilibrium concentration of aromatic aldehydes, which could be explained by Freundlich model. The Freundlich parameters for aromatic aldehydes adsorption are summarized in Fig. 6(b) and Table 2. The Freundlich equations could be expressed by $\ln Q_e=0.6933\ln C_e+6.788$, $\ln Q_e=0.7031\ln C_e+7.7358$ and $\ln Q_e=$

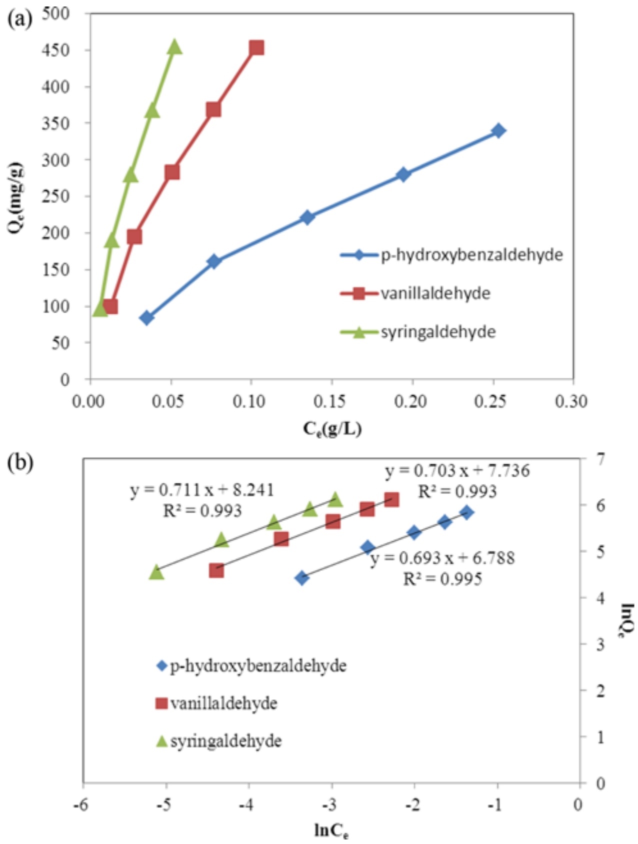

Fig. 6. Adsorption isotherms (a) and Freundlich equations (b) for aromatic aldehydes on X-5 at 20 °C.

Table 2. Fitting results of Freundlich equations

Aromatic aldehydes	n	K_f	R^2
P-hydroxybenzaldehyde	1.4424	887.14	0.995
Vanillaldehyde	1.4223	2288.84	0.993
Syringaldehyde	1.4071	3794.09	0.993

$0.7107\ln C_e+8.2412$ for p-hydroxybenzaldehyde, vanillaldehyde and syringaldehyde, respectively. The correlation coefficients (R^2) of the model were all greater than 0.99, indicating that adsorption isotherms of aromatic aldehydes on X-5 were fitted to the Freundlich equation. The Freundlich constants, K_f, of syringaldehyde and vanillaldehyde were greater than that of p-hydroxybenzaldehyde, observably indicating that adsorption capacities for syringaldehyde and vanillaldehyde on X-5 were greater than that of p-hydroxybenzaldehyde. It was consistent with the results of static adsorption experiments completed.

5. Dynamic Adsorption and Desorption of Aromatic Aldehydes on X-5

The dynamic adsorption and desorption processes of aromatic aldehydes on X-5 were designed based on static experiments. Dynamic adsorption of aromatic aldehydes on X-5 was complete within 12 h at a flow rate of 1 BV/h. After adsorption, 50% (v/v) ethanol solution was used for the dynamic desorption of aromatic aldehydes. Fig. 7(a) shows the breakthrough curves of p-hydroxybenzaldehyde, vanillaldehyde and syringaldehyde on X-5 at 20 °C. As illustrated in Fig. 7(a), when the eluent volume increased to 12 BV, adsorption of all the three kinds of aromatic aldehydes achieved equilibrium. The concentration of p-hydroxybenzaldehyde in eluent volume was greater than that of vanillaldehyde and syringaldehyde after 3 BV. The breakthrough of p-hydroxybenzaldehyde was reached at 8 BV, which demonstrated that the adsorption capacities of vanillaldehyde and syringaldehyde were greater than that of p-hydroxybenzaldehyde on X-5. It agreed with the results of static adsorption experiments completed. From Fig. 7(b), the concentrations of p-hydroxybenzaldehyde, vanillaldehyde and syringaldehyde in eluent volume increased sharply after 0.5 BV and peaked soon with a concentration of 3.74 g/L at 1.5 BV for p-hydroxybenzaldehyde, 5.44 g/L at 2 BV for vanillaldehyde and 7.03 g/L at 2 BV for syringaldehyde, then gradually subsided. The aromatic aldehydes were desorbed completely after 5 BV. The results of dynamic adsorption and desorption experiments not only showed that 50% (v/v) ethanol solution was an effective elution solvent for aromatic aldehydes, but also indicated that elution process was also an effective enrichment process for sorbate.

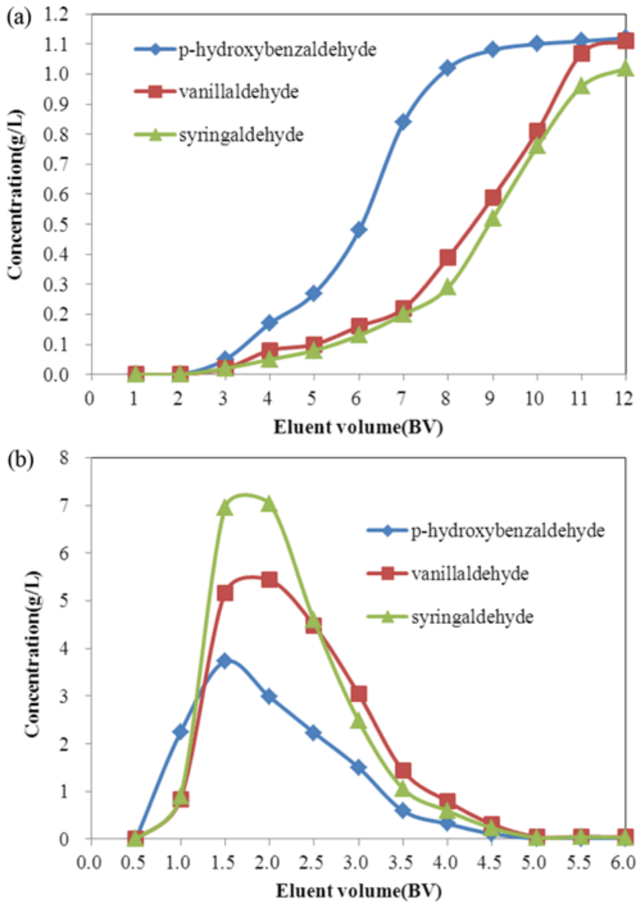

Fig. 7. Profile of breakthrough curves (a) and dynamic desorption (b) of aromatic aldehydes on X-5 at 20 °C.

CONCLUSIONS

We investigated the adsorption and desorption behaviors of lignin-based aromatic aldehydes (p-hydroxybenzaldehyde, vanillaldehyde and syringaldehyde) on macroporous resins X-5, CAD-40, AB-8 and D101. X-5 was selected for adsorption and separation of aromatic aldehydes due to its outstanding adsorption capacity. Static adsorption isotherms of aromatic aldehydes on X-5 were confirmed to fit the Freundlich equation. An efficient desorption method that 50% (v/v) ethanol solution was used to desorb aromatic aldehydes on X-5 has been developed which was also confirmed as an effective enrichment method for sorbate. It is the first time that macroporous resins were systematically investigated for the adsorption and separation of lignin-based aromatic aldehydes.

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