Sorption of Pyruvic Acid with Weakly Basic Polymer Sorbents[*]

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Abstract Uptakes of pyruvic acid for two types of commercially available weakly basic polymer sorbents, D301G and D301R, have been measured over a wide pH range and at various salinities of $MgSO_4$. The results show that the overloading adsorption of pyruvic acid occurs on both weakly basic polymer sorbents, and the overloading models can predict the experimental data of uptake very well. The overloading value for D301G is larger than that for D301R. The adsorption isotherm of pyruvic acid for both polymeric sorbents is greatly affected by the solution pH and $MgSO_4$ concentration in the aqueous phase, and a high recovery efficiency of pyruvic acid from aqueous solution can be obtained at the solution pH around 2.
Keywords pyruvic acid, weakly basic polymer sorbents, adsorption, pH

1 INTRODUCTION

Carboxylic acids are among the most attractive substances that can be manufactured from biomass[1,2]. Recovery of carboxylic acids from fermentation broths presents a challenging separation problem. To avoid producing waste salts and net consumption of chemical agents in calcium carboxylate salt process[3], the reversible chemical complexation with polymeric sorbents and extractants are attractive for the recovery of carboxylic acids[4—6].

For the extraction and adsorption on the basis of the reversible chemical complexation, the mass transfer driving force is the concentration of unionized form of acid[7—10]. Many fermentation processes producing carboxylic acids operate most effectively at pH above pK_a of the acid product[11—13]. For example, pyruvic acid ($pK_a = 2.49$) is typically produced at pH=4.5—6.5[14]. One approach for recovering carboxylic acids from such solutions is to use agents that are sufficiently basic to retain a substantial capacity at several pH units above the pK_a of the carboxylic acid. Tung and King[5] investigated the extraction and sorption of lactic and succinic acids by using different basic extractants and polymeric sorbents. It was found that the uptake in the pH range of 5—6 varied substantially from one agent to another, and was strongly dependent upon the basicity and capacity of the agent. Similar results have been reported by other researchers[7,15—18] To avoid desorption difficulty of strongly basic sorbent, the sorbents used to separate carboxylic acid are mainly the basic macroporous sorbent.

Pyruvic acid is widely used for manufacturing medicine, pesticide and foodstuff[19], and can be produced by fermentation. As the acidity of pyruvic acid is stronger than that of normal carboxylic acids, and few reports of recovering pyruvic acid can be found. In this article two types of weakly basic polymeric sorbents with tertiary amine functional group were selected, D301R and D301G, to investigate the uptake of pyruvic acid from aqueous solution over a wide pH range and at various salinity of $MgSO_4$.

2 EXPERIMENTAL

2.1 Materials

Two types of weakly basic polymer sorbents, D301R and D301G (tertiary amine), are from Nankai Chemicals Factory. Their properties are listed in Table 1. Obviously, the structure and functional group is same for both sorbents, while the exchange capacity, particle diameter and porosity are different. They were washed successively with water, methanol, 5% NaOH solution, 5% HCl solution, and then dried to a constant mass in a vacuum oven at 60℃ and 60kPa. Both sorbents were initially in the dry form. Analytical grade pyruvic acid (Arcros Corp.) was used to prepare the aqueous solutions of various concentrations.

2.2 Methods

2.2.1 *Pyruvic acid sorption*

Uptake of pyruvic acid onto various sorbents were conducted in a 20-ml flask sealed with foil-line caps at $(25\pm0.5)℃$. The sorbent (typically 0.25g, 0.5g, 1.0g, dry basis) and pyruvic acid solution (typically 10ml) were added to a flask without or with

Table 1 The Properties of Sorbents

Sorbent	Functional group	Exchange capacity (dry), $mmol \cdot g^{-1}$	Particle diameter, mm	Porosity, $ml \cdot ml^{-1}$	Density (dry), $kg \cdot m^{-3}$	Density (wet), $kg \cdot m^{-3}$
D301R	—$N(CH_3)_2$	⩾4.8	0.315—1.25	0.45	650—720	1030—1070
D301G	—$N(CH_3)_2$	⩾4.2	0.6—1.6	0.55	650—720	1030—1070

adjustment of solution pH by NaOH or H_2SO_4 solution. The flask was shaken for about 24h in a shaker bath with a vibration rate of 120r·min^{-1}, under which the adsorption is guaranteed to reach equilibrium as proved in preliminary tests. The aqueous solution was separated from the sorbents by a vacuum filtration, an aqueous phase sample was taken for pH and solute concentration analyses, and the impregnated sorbents sample was obtained for weighing.

2.2.2 *Sample analysis*

The aqueous samples were analyzed for solute concentration by using a high- performance liquid chromatography (HPLC) system (Waters), with each measurement being performed in duplicate, and the pH value of the solution was measured with a Hanna 201 pH-meter. Pyruvic acid uptake in the sorbents (Q_m) was calculated by material balance on the basis of the volume of aqueous phase, the amount of sorbent and the acid concentration at equilibrium:

$$Q = \frac{W_0(C_0 - C_e)}{m} \quad (1)$$

where Q represents the uptake of acid on the sorbent, W_0 and m is the mass of aqueous phase and sorbent, respectively. C_0 and C_e is the total acid concentration in initial solution and equilibrium aqueous solution, respectively.

2.3 Theory

When the initial acid concentration is high, the overloading adsorption, that is, multilayer adsorption, can occur. A model based on the mass action law can be used to describe the overloading of the basic sites on the sorbent. In the models, the formation of (2,1) stoichiometric acid-base complex is postulated, namely, a normal (1,1) acid-amine complex may combine one more acid to further form a (2,1) acid-amine complex. In this situation, the uptake of acid at equilibrium is then given as[20]

$$\frac{Q}{Q_m} = \frac{K_{11}C + 2K_{11}K_{21}C^2}{1 + K_{11}C + K_{11}K_{21}C^2} \quad (2)$$

where Q_m represents the acid adsorption capacity of the sorbent for monolayer coverage. C is the undissociated acid concentration in equilibrium aqueous solution. K_{11} and K_{21} are the apparent sorption equilibrium constant of (1,1) and (2,1) acid-amine complex, respectively.

3 RESULTS AND DISCUSSION

3.1 Equilibrium behavior

As shown in Fig.1, the uptake of pyruvic acid for both sorbents increased with the equilibrium acid concentration in aqueous phase, and no constant uptake appeared at the high acid concentration in the aqueous phase (>0.4mol·L^{-1}). Obviously, overloading adsorption occurred, which could result from hydrogen bonding of a second acid to the carbonyl oxygen of the first acid uptaken on sorbent. Husson and Judson[21] found similar results in their experimental data for succinic acid on Dowex MWA-1.
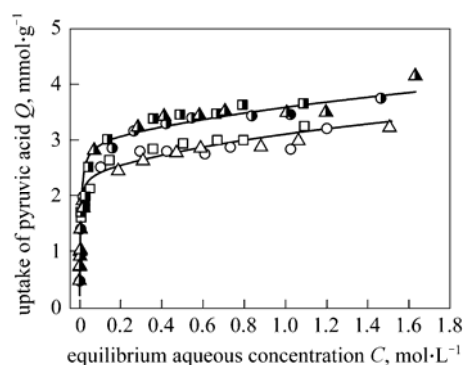

Figure 1   Sorption isotherm for pyruvic acid onto D301R and D301G at 25°C
□ 0.25g D301R; ○ 0.50g D301R; △ 1.00g D301R;
◨ 0.25g D301G; ◕ 0.50g D301G; ▲ 1.00g D301G

Fitting all the experimental data to Eq.(2), Q_m, K_{11} and K_{21}, can be obtained and are listed in Table 2. The solid line in Fig.1 represents the predicted value with Q_m, K_{11} and K_{21} as given in Table 2. It can be found that the predicted data fitted the experimental data very well. In comparison, both the apparent equilibrium constants K_{11} and K_{21} of pyruvic acid for D301R were larger than that for D301G. The maximum uptake capacities (Q_m) of D301G was higher than that of D301R, which may have resulted from the larger porosity of sorbent D301G.

Table 2   The fitted parameters of sorption at 25°C

	Q_m	K_{11}	K_{21}
D301R	2.40	330	0.45
D301G	3.00	200	0.25

It should be noted that the value of K_{21} of D301R sorbent is close to that of D301G sorbent, that is, the overloading of D301R is similar to that of D301G. And K_{21} is less than K_{11} for both sorbents, which might be attributed to hindrance of tertiary amine on the sorbents preventing hydrogen-bonding formation of the complex from a second acid at this site.

3.2 Effect of pH

Tertiary amine associates most Lewis acid functional groups by forming a complex with the neutral molecule. Because the neutral molecule concentration of pyruvic acid is a function of pH, the uptake of pyruvic acid will greatly depend on the pH of the aqueous phase. As is already shown in Fig.2, the uptake of pyruvic acid with two kinds of polymeric sorbents is greatly affected by the pH value. The uptake value increased with an increase in the pH value and then decreased. There was a maximum uptake at a pH value of around pK_a of pyruvic acid (pH=1.5—2.5), and the maximum uptake of D301G was larger than that of D301R, which is the same as the adsorption isotherm. Effect of pH can be explained by two aspects, one is pyruvic acid dissociation and another is competing effect of H_2SO_4 and pyruvic acid to amine functional group.
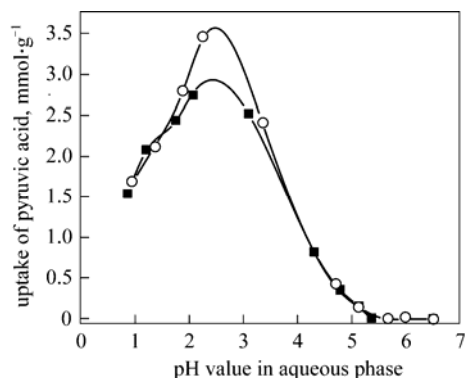
Figure 2   Effect of pH on composite uptakes of pyruvic acid at 25℃
$(C_0=0.7652\text{mol·L}^{-1}, W_0/m=20\text{ml·g}^{-1})$
■ D301R; ○ D301G

In order to provide a suggestion of initial solution pH value with high recovery efficiency, the plot of the equilibrium pH *vs*. the initial solution pH (pH$_0$) is shown in Fig.3. It can be found that the equilibrium pH was always higher than the initial pH for both sorbents. Its value depended on the sorbents type and the extent of acid adsorption, and the equilibrium pH for D301G was larger than that of D301R. Obviously, because the acid concentration in the aqueous phase at the equilibrium was lower than that in the initial, the solution pH values at the equilibrium should be higher than that in the initial. Also, because the uptake of D301G was larger than that of D301R, the acid concentration residual in the aqueous phase for D301G was less than the one for D301R, then; the equilibrium pH for D301G was larger than that of D301R. According to Figs.2 and 3, if weakly basic sorbent D301R or D301G is used to recover pyruvic acid from aqueous solution, especially the fermentation broth, the initial solution pH should be adjusted at around 2.
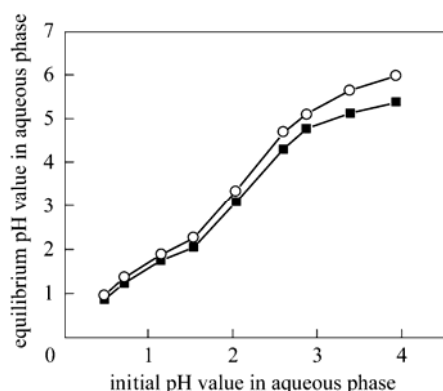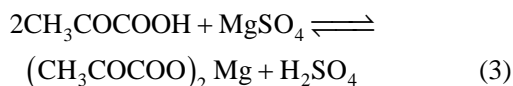

Figure 3   Comparison of the initial solution pH with the equilibrium pH at 25℃
$(C_0=0.7652\text{mol·L}^{-1}, W_0/m=20\text{ml·g}^{-1})$
■ D301R; ○ D301G

3.3   Effect of MgSO$_4$

In MgSO$_4$ solution, pyruvic acid is present.

$$2CH_3COCOOH + MgSO_4 \rightleftharpoons$$
$$\left(CH_3COCOO\right)_2 Mg + H_2SO_4 \qquad (3)$$

It is clear that the effective concentration of neutral molecule of pyruvic acid is a function of the salt concentration, and that the sorption of pyruvic acid will greatly depend on the salt concentration in aqueous phase.

As is shown in Fig.4, the measured uptake of pyruvic acid on both polymeric sorbents decreased with the MgSO$_4$ concentration under the condition of initial pH=0.9, and it approached a constant when the concentration of MgSO$_4$ was higher than 0.1%. If the association of amino functional group and H$_2$SO$_4$ is considered, it can be deduced that the MgSO$_4$ effect is mainly the competitive sorption between SO$_4^{2-}$ and pyruvic acid, and when the association is saturated by sulfuric acid, the uptake of pyruvic acid will not decrease further more. Comparing with D301R, the basicity of D301G is weaker. Hence, the influence of MgSO$_4$ concentration on the uptake of D301G is less than that of D301R.
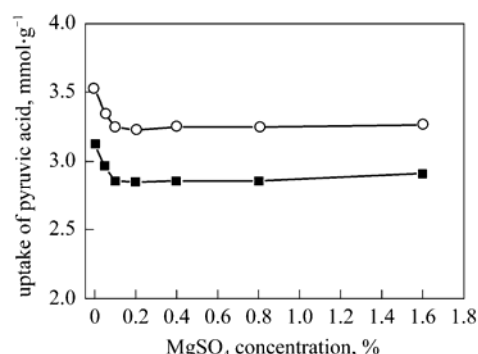

Figure 4   Effect of MgSO$_4$ on composite uptakes of pyruvic acid at 25℃
$(C_0=0.7652\text{mol·L}^{-1}, W_0/m=20\text{ml·g}^{-1})$
■ D301R (pH$_0$=0.9); ○ D301G (pH$_0$=0.9)

3.4   Water uptake and swelling

Generally, the swelling of the polymer sorbent results from two ways: (1) the association with water molecule and functional group on the sorbent, and (2) solvation of the acid-amine complex. Fig.5 shows the measured uptakes of water from pyruvic acid solutions by the two polymeric sorbents. Both polymeric sorbents swelled appreciably. The water capacities of
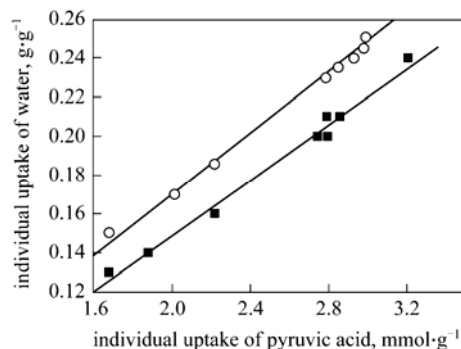

Figure 5   Individual uptakes of water from pyruvic acid solution by D301R and D301G at 25℃
$(W_0/m=20\text{ml·g}^{-1})$
■ D301R; ○ D301G

the two polymeric sorbents increased slightly as the concentrations of pyruvic acid increased. There were linear correlations between the uptakes of pyruvic acid and water for both polymeric sorbents, and the slopes were similar. The intercept, which represents the water uptake for the association with water molecule and functional group on the sorbent, was D301G > D301R, and that is the same as the uptake of pyruvic acid.

4 CONCLUSIONS

The overloading adsorption of pyruvic acid on both weakly basic polymer sorbents occurs, and the overloading of sorbent D301G is larger than that of sorbent D301R. The uptake of pyruvic acid for both polymeric sorbents is greatly affected by the solution pH. There is a maximum uptake at a pH value of around pK_a of pyruvic acid (pH=1.5—2.5), and the maximum uptake of D301G is larger than that of D301R. The uptake of pyruvic acid greatly depends on the $MgSO_4$ concentration in the aqueous phase also. The measured uptake of pyruvic acid on both polymeric sorbents decrease with the $MgSO_4$ concentration, and the approach to the constant at $MgSO_4$ concentration is larger than 0.1%. Both polymeric sorbents swell appreciably.

NOMENCLATURE

C	undissociated concentration of pyruvic acid in the equilibrium aqueous solution, $mol \cdot L^{-1}$
C_e	total concentration of pyruvic acid in the equilibrium aqueous solution, $mol \cdot L^{-1}$
C_0	concentration of pyruvic acid in the initial solution, $mol \cdot L^{-1}$
K_a	dissociation constant of pyruvic acid, $mol \cdot L^{-1}$
K_{11}	apparent equilibrium constant for the (1,1) complex, $L \cdot mol^{-1}$
K_{21}	apparent equilibrium constant for the (2,1) complex, $L \cdot mol^{-1}$
m	mass of dry sorbent, g
Q	composite uptake of pyruvic acid, $mol \cdot g^{-1}$
Q_m	the maximum composite uptake of pyruvic acid, $mol \cdot g^{-1}$
W_0	the amount of aqueous phase, L

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