

## Adsorptive separation of fumaric acid and glucose from the mixed aqueous solutions by anion exchange resin Amberlite IRA-400

Yong-Qian Fu\*, Hua-Yue Zhu, Ru Jiang, Long-Fei Yin, An-Guo Ying, Shi-Bin Ren and Qi-Cheng Ruan

College of Life Science, Taizhou University, Linhai 317000, Zhejiang, People's Republic of China

E-mail : fuyq@tzc.edu.cn Fax : 86-0576-85137066

Manuscript received on line 17 March 2012, revised 06 April 2012, accepted 07 April 2012

---

**Abstract :** The adsorption and separation of fumaric acid and glucose from synthetic single and mixed aqueous solutions by Amberlite IRA-400 resin under batch equilibrium and dynamic column experimental conditions were presented in this work. The equilibrium adsorption data of fumaric acid and glucose from single component solutions were fitted well with the Freundlich and linear adsorption isotherm models. The batch adsorption indicated that IRA-400 resin had higher affinity for fumaric acid than glucose even at higher glucose concentrations. The breakthrough capacity and total capacity of the resin for the adsorbates at different flow rates were evaluated through column adsorption studies. Attempts were also made to separate and recovery fumaric acid and glucose. The results showed that both of them could be separated effectively when the IRA-400 resin is eluted by deionized water and 1 M NaOH alternately.

**Keywords :** Adsorption, fumaric acid, glucose, IRA-400 resin, separation.

---

### Introduction

Fumaric acid is a four-carbon unsaturated dicarboxylic acid that is widely used as a food acidulant and beverage ingredient<sup>1</sup>. It is derived exclusively from petroleum-based materials. There is no current commercial biologic process for the production of fumaric acid. In typical fumaric acid fermentation with *Rhizopus oryzae*, the presence of a neutralizing agent is required to remove fumaric acid produced from fermentation broth<sup>2</sup>. Recovery of calcium fumarate and regeneration of free acid from fumarate are complicated, tedious, and expensive<sup>3</sup>. In the downstream processing field, adsorption of ion exchange resin is gaining wider acceptance for large-scale separation from liquid due to the low energy nature of adsorptive separation processes when compared to other separation methods. Especially this separation method can be coupled with fermentation process<sup>4,5</sup>.

Glucose is the main component of organic acid fermentation broth. Frequently the glucose is included in the fermentation medium for competitive sorption. Especially in an extractive fermentation, the continuous removal of the resin would also remove a significant amount of glucose. This may decrease the total capacity available and the product purity<sup>6,7</sup>. Some researchers have reported

the effect of glucose on organic acid adsorption by anion exchange resins<sup>8-10</sup>. These studies were mainly focused on improving fermentation yield. The effect of glucose on fumaric acid adsorption as well as the separation and recovery between the two by anion exchange resin was not studied. In this work, Amberlite IRA-400 anion exchange resin is selected from six anion exchange resins to investigate the effects of glucose on fumaric acid adsorption, as well as the effective separation and recovery between the two.

### Experimental

#### Materials :

Six resins are used in this study and parts of the characteristics are given in Table 1. Before the resins are used in the experiments, they are pretreated<sup>8</sup>.

#### Adsorption isotherms :

A known concentration of single aqueous solution of fumaric acid or glucose is prepared by dissolving required amounts. The equilibrium adsorption data are obtained by contacting a known weight of resin (1.0 g wet wt) with 50 ml of single adsorbate solution at different initial concentrations in 250 ml conical flasks. The flasks are completely sealed, placed in an incubator and shake for

24 h, which are enough to establish equilibrium. The fumaric acid and glucose concentrations are determined by using HPLC<sup>10</sup>. The amount of adsorbate absorbed by resins is calculated using the following equation :

$$Q_e = \frac{(C_0 - C_e)V}{MW} \quad (1)$$

*Batch adsorption of fumaric acid and glucose :*

The IRA-400 resin (1.0 g wet wt) is introduced directly into each series of 250 ml conical flasks and 50 ml of the adsorbate solution added to each flask. The mixed aqueous solution of fumaric acid (5.0 mg/ml) and glucose with concentrations ranging from 25.0 to 100.0 mg/ml at different pH ranging from 2.0 to 5.0 are used as an initial solution. The flasks are completely sealed, placed in an incubator and shake for 24 h. The fumaric acid and glucose concentrations are determined by HPLC.

*Column experiments :*

The column adsorption experiments are performed in a glass column (1.0 cm internal diameter and 30.0 cm length). The solution with known concentration of fumaric acid or glucose is fed to the top of the column at a desired flow rate. From the outlet of the column, each successive fractions of the effluent is collected by DBS-100 fraction collector. Breakthrough curves are obtained by analysis of each fraction.

Dynamic column adsorption and desorption characteristics of fumaric acid at the concentration of 5.0 mg/

ml in the presence of glucose at concentration of 20.0 mg/ml are studied. The flow rate was 60 ml/h. The column elution experiment was performed at 60 ml/h flow rate by using deionized water and 1.0 M NaOH alternately. The effluent samples are collected at intervals. The amount of adsorbate dynamic absorbed by resins is calculated using the following equation<sup>11</sup> :

$$Q_t = \int_0^{V_t} \frac{(C_0 - C_t) dV}{m} \quad (2)$$

## Results and discussion

*Selection of the resins :*

The capacities of six resins for fumaric acid or glucose adsorption are showed in Table 1.

As seen from Table 1, the fumaric acid adsorption capabilities of strongly basic resins firstly increase and then decrease with increasing pH, and exhibit the highest fumaric acid adsorption capability at pH 3.5. The fumaric acid adsorption capabilities of the weakly basic resins decrease gradually with the increase of the pH. The strongly basic resin Amberlite IRA-400 exhibits the greatest fumaric acid adsorption capacities at pH 5.0 which is typically required for the fermentation. At the same time, relatively less glucose is adsorbed by IRA-400 resin. So IRA-400 resin was chosen for the following research.

*Adsorption isotherms :*

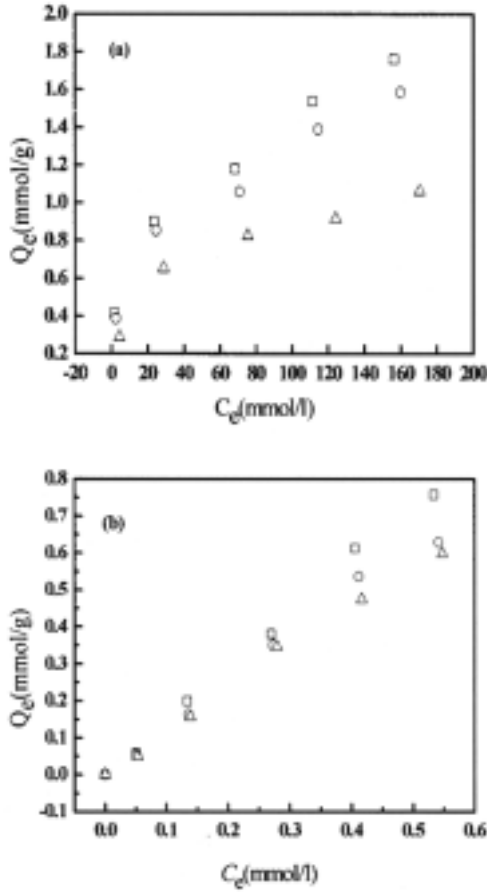
The equilibrium adsorption isotherms of fumaric acid

**Table 1.** Equilibrium adsorption quantity of fumaric acid and glucose at different pH<sup>a</sup>

Resin	Type	Matrix structure	Capacity $Q_e$ (mmol/g)					
			pH 2.0		pH 3.5		pH 5.0	
			FA <sup>1</sup>	GLU <sup>2</sup>	FA <sup>1</sup>	GLU <sup>2</sup>	FA <sup>1</sup>	GLU <sup>2</sup>
IRA-400	Strong base	Styrene	0.91	0.34	1.05	0.35	0.75	0.32
IRA-900	Strong base	Styrene	0.66	0.39	0.79	0.40	0.55	0.38
	macroporous							
HZ202	Strong base	Styrene	0.35	0.41	0.62	0.43	0.48	0.40
IRA-94	Weak base	Styrene	1.47	0.76	1.18	0.64	0.41	0.60
	macroporous							
D315	Weak base	Propylene	0.82	0.71	0.59	0.62	0.09	0.59
	macroporous							
D318	Weak base	Propylene	1.09	0.81	0.7	0.79	0.10	0.64
	macroporous							

<sup>a</sup>FA : Fumaric acid; GLU : Glucose; 1 : Initial concentration of fumaric acid in the absence of glucose is 5.0 mg/ml; 2 : Initial concentration of glucose in the absence of fumaric acid is 50.0 mg/ml.

from aqueous solution onto IRA-400 resin at different temperatures are depicted in Fig. 1(a).



**Fig. 1.** Adsorption isotherms of (a) fumaric acid and (b) glucose onto IRA-400 resin : (□) 298 K, (○) 308 K, (Δ) 318 K.

It is obvious that the equilibrium adsorption capacities of IRA-400 resin towards fumaric acid decreased with increasing the temperature. In addition, the fumaric acid adsorption capacities increased with the equilibrium adsorbate concentration increased. In order to investigate the adsorption isotherms, the Freundlich isotherm model<sup>12</sup> is used to fit the equilibrium adsorption data and the results are listed in Table 2. As shown by the data listed, the correlation coefficients for the Freundlich model are larger than 0.99, which indicated that the Freundlich equation fitted the experimental results well.

The equilibrium adsorption isotherms of glucose from aqueous solution onto IRA-400 resin at different temperatures are depicted in Fig. 1(b). From Fig. 1(b) we can see that the equilibrium adsorption isotherms of glucose are essentially linear. So linear equation<sup>13</sup> is used here to fit the equilibrium adsorption data and the results are listed in Table 2. As shown by the data listed, the correlation coefficients for the linear equation are larger than 0.99 indicated that linear equation fitted to the experimental results well.

*Effect of glucose concentrations on fumaric acid adsorption :*

The results of glucose and fumaric acid adsorption by IRA-400 resin at different glucose concentrations and different pH are shown in Table 3. It can be clearly observed that the glucose adsorption has no conspicuous

**Table 2.** Simulated results between isothermal adsorption curve of fumaric acid and glucose

Adsorbate	T (K)	Simulation equation	$K_F$	$n$	$K_e$ (ml/g)	$R^2$
Fumaric acid	298	$\ln Q_e = 0.317 \ln C_e - 1.090$	0.336	3.155		0.996
	308	$\ln Q_e = 0.325 \ln C_e - 1.241$	0.289	3.077		0.995
	318	$\ln Q_e = 0.353 \ln C_e - 1.745$	0.175	2.833		0.998
Glucose	298	$Q_e = 1.455 C_e - 0.004$			1.455	0.998
	308	$Q_e = 1.214 C_e - 0.003$			1.214	0.996
	318	$Q_e = 1.118 C_e - 0.003$			1.118	0.997

**Table 3.** Adsorption of fumaric acid and glucose by IRA-400 at different pH and glucose concentration

Concentration of glucose (mg/ml)	pH 2.0		pH 3.5		pH 5.0	
	Fumaric acid (mg/g)	Glucose (mg/g)	Fumaric acid (mg/g)	Glucose (mg/g)	Fumaric acid (mg/g)	Glucose (mg/g)
25.0	104.3	25.4	118.4	28.5	83.4	24.7
50.0	102.7	45.6	113.9	49.2	78.5	46.3
100.0	98.5	67.3	109.6	70.2	75.8	63.3

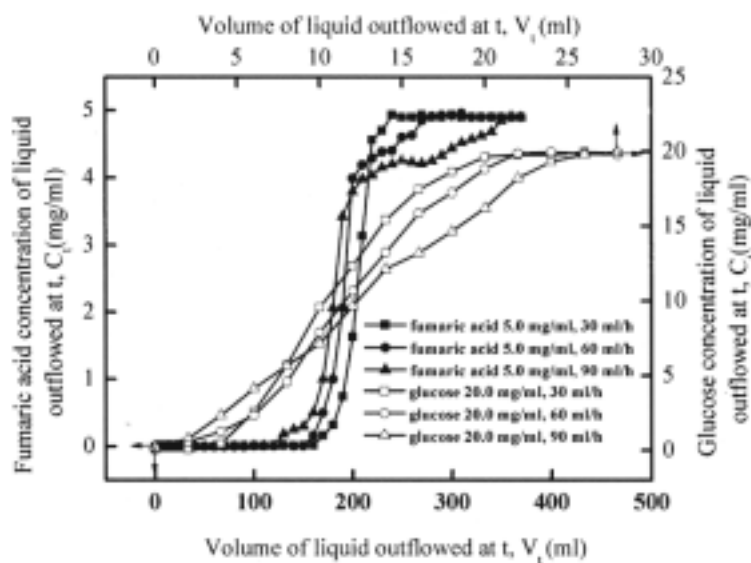


Fig. 2. Effect of flow rates on adsorption breakthrough curve.

change with the increase of the pH at the same glucose concentration, but increases with the glucose concentration increased at the same pH. Although the fumaric acid adsorption by IRA-400 resin decreases slightly with the glucose concentration increased, the resin also has higher affinity for fumaric acid than glucose even at higher glucose concentration. It is possible that the positively charged functional groups on the IRA-400 resin surface would favor the adsorption of negatively charged fumarate anions due to electrostatic attraction which could be the primary mechanism. Glucose exists predominantly as neutral molecule at different pH values. Therefore, the interaction between the IRA-400 resin and glucose is considered mainly as non-polar and the forces responsible for adsorption are physical van der Waals forces. The forces are much smaller than electrostatic forces. Furthermore, IRA-400 resin also has some hydrophobic, in favor of the combination of fumarate anions.

#### Effect of feed flow rate on column adsorption :

The results of dynamic flow experiments are used to obtain the breakthrough curves for fumaric acid or glucose adsorption from the single aqueous solutions. The curves with various flow rates are given in Fig. 2.

The breakthrough adsorption capacity and the total adsorption capacity of IRA-400 are listed in Table 4. As shown by the data listed, the breakthrough adsorption

Table 4. Parameters under different flow rates

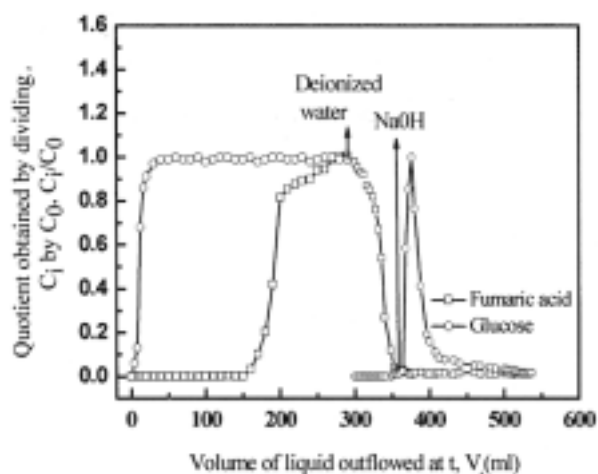
Flow rate (ml/h)	Breakthrough capacity (mg/g)		Saturated capacity (mg/g)	
	Fumaric acid	Glucose	Fumaric acid	Glucose
30.0	87.7	15.4	104.6	20.4
60.0	84.3	10.5	100.8	17.8
90.0	64.8	6.4	94.8	14.2

capacity and the total capacity for fumaric acid as well as glucose decrease gradually with the increase of the flow rate. To promote adsorption, the flow rate must be low so that the liquid-solid contact time is adequate for the absorption and the flow rate should not be too low. In this work, 60 ml/h flow rate is chosen for fumaric acid adsorption.

#### Separation of fumaric acid and glucose on IRA-400 resin :

The breakthrough curve and elution curve of fumaric acid and glucose from the mixed aqueous solution of two at the best flow rate (60 ml/h) are shown in Fig. 3.

As seen in Fig. 3, the breakthrough volume of fumaric acid is 162.3 ml and glucose is only 8.7 ml. Dynamic separation results shows that fumaric acid and glucose could be separated effectively when the resin IRA-400 is eluted by deionized water and 1 M NaOH alternately.



**Fig. 3.** Adsorption breakthrough and elution curve of mixed solution.

### Conclusions :

In the present experiments, Amberlite IRA-400 anion exchange resin was selected from six basic resins to investigate the adsorption and recovery of fumaric acid and glucose from the mixed solution of the two. The results indicated that Amberlite IRA-400, which contains quaternary ammonium groups, mainly interacts with fumarate anions through electrostatic forces and glucose through physical van der Waals forces. So even at higher glucose concentration, the adsorbent IRA-400 had higher affinity for fumaric acid than glucose and both of them could be separated effectively when IRA-400 resin was eluted by deionized water and 1 M NaOH alternately.

### Abbreviations

$C_0$ (mmol/L)	the concentration of adsorbate in the feed solution
$Q_e$ (mmol/g)	the equilibrium adsorption capacity
$C_e$ (mmol/L)	the equilibrium concentration
$Q_t$ (mg/g)	the equilibrium capacity of the resin
$V$ (ml)	the volume of solution

$W$ (g)	the weight of wet resin
$M$ (mg/mmol)	the molecular weight of adsorbate
$V_t$ (ml)	the effluent volume of time $t$
$K_F$ (ml/mg)	the Freundlich constant
$n$ —	the Freundlich constant
$K_e$ (ml/g)	the linear equation constant

### Acknowledgement

This work was financially supported by the National Natural Science Foundation of China (Grant Nos. 21007044, 21106090, 21106091).

### References

1. W. Liao, Y. Liu, C. Frear and S. L. Chen, *Bioresource Technol.*, 2007, **99**, 5859.
2. Y. Zhou, J. Du and G. T. Tsao, *Bioproc. Biosyst. Eng.*, 2002, **25**, 179.
3. C. Gangl, W. A. Weigand and F. A. Keller, *Appl. Biochem. Biotechnol.*, 1990, **24/25**, 663.
4. C. A. Engel, A. J. Straathof, T. W. Zijlmans, W. M. Gulik and L. Wielen, *Appl. Microbiol. Biotechnol.*, 2008, **78**, 379.
5. X. J. Cao, H. S. Yun and Y. M. Koo, *Biochem. Eng. J.*, 2002, **11**, 189.
6. R. L. Evangelista, A. J. Mangold and Z. L. Nikolov, *Appl. Biochem. Biotechnol.*, 1994, **45/46**, 131.
7. E. N. Kaufman, S. P. Cooper, M. K. Budner and C. Richardson, *Appl. Biochem. Biotechnol.*, 1996, **57/58**, 503.
8. B. H. Davison, N. P. Nghiem and G. L. Richardson, *Appl. Biochem. Biotechnol.*, 2004, **113-116**, 653.
9. M. J. Dethe, K. V. Marathe and V. G. Gaikar, *Sep. Sci. Technol.*, 2006, **41**, 2947.
10. N. J. Cao, J. X. Du, C. S. Gong and G. T. Tsao, *Appl. Environ. Microbiol.*, 1996, **62**, 2926.
11. Z. Aksu and F. Gönen, *Process Biochem.*, 2004, **39**, 599.
12. H. L. Maria and A. C. Isabel, *Sep. Purif. Technol.*, 2005, **45**, 232.
13. J. P. Lin, S. D. Ruan and P. L. Cen, *Chem. Eng. Commun.*, 1998, **168**, 59.