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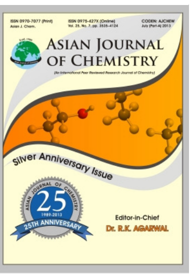

Influence of pH on Fumaric Acid Adsorption by Basic Ion-Exchange Resins

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The effects of pH on the adsorption of fumaric acid by basic ion-exchange resins were investigated. The adsorption isotherms of the strong-base resin IRA-400 and the weak-base resin IRA-94 were investigated with aqueous solutions of fumaric acid at different pH and the equilibrium adsorption data obtained being very well fitted by the Freundlich model. The pseudo-first-order and pseudo-second-order kinetic models were applied to describe the kinetic data, with the pseudo-second-order model providing a perfect fit. The value of equilibrium rate constant k_2 indicated that the equilibrium rate of IRA-400 resin was much faster than that of IRA-94 resin, but there was no evident discrepancy at different pH for each resin. Breakthrough curves of two resins at different pH were also investigated. The efficiency of adsorption column of IRA-400 resin had no evident correlation with the pH; while the efficiency of adsorption of IRA-94 resin decreased from 64-31 % as the pH increased from 2.0-5.0.

Key Words: Breakthrough curve, Basic ion-exchangers, Fumaric acid, Isotherms, Kinetics.

INTRODUCTION

Fumaric acid is a four-carbon unsaturated dicarboxylic acid that is widely used as a food acidulant and beverage ingredient. Because of its double bond and two carboxylic groups, fumaric acid has many potential industrial applications, ranging from the manufacture of synthetic resins and biodegradable polymers[1] to the production of intermediates for chemical syntheses[2]. Fumaric acid is derived exclusively from petroleum-based materials. As the world's crude oil resources diminish and the prices of petroleum products continue to increase, the production of chemicals by biological processes is becoming more competitive.

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 not only to neutralize the acid but also to remove fumaric acid produced from fermentation broth[3]. Recovery of calcium fumarate and regeneration of free acid from fumarate are complicated, tedious and expensive[4]. In the downstream processing field, recovery techniques have not so much been studied for fumaric acid producers in submerged cultivations as it has been done for related fermentation products like succinic acid[5], citric acid[6] and lactic acid[7]. Recovery systems like reactive extraction and membrane electrodialysis have not been studied yet. However, simultaneous fermentation and adsorption have been studied to remove fumaric acid during its formation to control fermentation pH at desired values and avoid product inhibition[8,9].

The adsorption of fumaric acid and carboxylic acids in general, on basic ion-exchange resins is strongly affected by the pH of the process stream. This is because the pH effects on the equilibrium of the undissociated and dissociated acid forms. Therefore, the resins that will maximize the recovery of carboxylic acids are expected to depend on the processing pH. King and Tung[10] separated carboxylic acid from carboxylic salt solution at pH closed to or above theirs pK_as. Evangelista and Nikolov[11] recovered lactic acid from fermentation broth by weak-base polymer adsorbents MWA-1, IRA-35 and VI-15. The pH for the lactic acid adsorption was below its pK_a and fermentation broth was acidified before the recovery of lactic acid. Kulprathipanja and Oroshar[12] separated lactic acid from fermentation broth by using anion polymeric adsorbents, which were strong, moderate or weak basic anion exchange resins adsorbing lactic acid below its pK_a. Fuamric acid was dicarboxylic acid and the two pK_as values of fumaric acid were 3.03 and 4.44[13]. Cao *et al*,[9] separated fumaric acid by using an adsorption column coupled with fermentor. This study was focused on improving fermentation yield and the effects of pH on fumaric acid adsorption by basic ion-exchange resins had not been studied. In this study, the effects of pH below, between and above the pK_as of fumaric acid on fumaric acid adsorption by basic ion-exchange resins were studied. It was hoped that the results obtained will be useful for understanding the physical and thermodynamic properties of the fumaric acid adsorption on basic ion-exchange resins.

EXPERIMENTAL

The base resins Amberlite IRA-94, IRA-400, IRA-900 and D315 (Table-1) were used for this study. The resins are pretreated by washing with distilled water several times. Then the resins are immersed in 1 M NaOH solution for 48 h and finally washed again with distilled water.

Fumaric acid used in this study is of chemical grade and is purchased from the Sinopharm Chemical Reagent Co., Ltd. (Shanghai, P. R. China). Fumaric acid concentration was measured by a high performance liquid chromatography system (Summit P 680 HPLC, Dionex, USA), equipped with a tunable UV detector (UVD 170U, Dionex, USA) at 210 nm. An organic acid analysis column (Aminex HPX-87H 300 mm × 7.8 mm, Bio-Rad, USA) was used with 0.005 M H_2SO_4 as a mobile phase at a flow rate of 0.8 mL/min and the column temperature was maintained at 333 K.

Adsorption equilibrium experiments: Equilibrium adsorption studies of fumaric acid were performed at 298, 308 and 318 K, respectively. Thus, a known amount of resin (1.00 g wet wt) was introduced directly into each of a series of 250 mL conical flasks and 50 mL aqueous fumarate added to each flask. Aqueous fumarate with concentrations ranging from 1-20 mg/mL at three pH 2, 3.5 and 5 was used as an initial solution. The flasks were completely sealed, placed in an incubator and shaked for 24 h, which was enough to establish equilibrium. The fumaric acid concentrations were determined by HPLC.

The amount of fumaric acid absorbed by the resins was calculated using the following equation:

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

where Q_e is the equilibrium adsorption capacity (mmol/g), C_0 is the initial concentration (mmol/L), C_e is the equilibrium concentration (mmol/L), V is the volume of solution (L), W is the weight of wet resin (g) and M is the molecular weight of fumaric acid (mg/mmol).

Fixed-bed adsorption: The fixed-bed adsorption experiments are performed in a glass column (1 cm internal diameter and 30 cm length). Every column is packed with resin. A water jacket is used to maintain a desired constant operation temperature. A water jacket is used to maintain a desired constant operation temperature. The solution with a known concentration of fumaric acid is fed to the top of the column at a desired flow rate regulated by a HL-2D constant-speed pump (Shanghai, P. R. China). From the outlet of the column, each successive fractions of the effluent is collected using DBS-100 fraction collector (Shanghai, P. R. China). Breakthrough curves are obtained by analysis of each fraction by HPLC. Column studies are terminated when the column reaches exhaustion.

RESULTS AND DISCUSSION

Effect of initial pH on adsorption of fumaric acid: All the four resins have a common styrene-divinyl matrix but they differ in functional groups. IRA-94 and D315 resins have *tert*-amino functional groups, while IRA-400 and IRA-900 have quaternary ammonium functional groups. The capacities of the four resins for fumaric acid-fumarate adsorption at three initial pH 2, 3.5 and 5 which was below, between and above the pK_as of fumaric acid were showed in Table-1.

As seen from Table-1, the IRA-94 and D315 resins, which contain *tert*-amino functional groups, have the fumaric acid adsorption of 1.466 and 1.219 mmol/g, respectively, while the IRA-400 and IRA-900 resins, which contain quaternary ammonium groups, show much lower acid adsorption of 0.914 and 0.655 mmol/g at pH 2 and fumaric acid mainly exists in the form of molecular. An equilibrium exists between the molecular fumaric acid and its dissociated form at a given pH condition. The strong-base ion-exchange resins should interact mainly with the ionized fumarate ions through electrostatic forces but should show relatively poor attractive interaction with the molecular form of the acid. But with the increasing of pH, the degree of ionization of fumaric acid increased, meanwhile, the adsorption of fumaric acid of the weak-base resins decreased and the strong-base resins exhibited the tendency of firstly increasing and then decreasing. In order to study the influence of pH on basic ion-exchangers more deeply, the static adsorption isotherms, adsorption dynamics and adsorption breakthrough curve of the resins IRA-400 and IRA-94 at different pH was studied.

Static adsorption isotherms: The adsorption isotherms of the IRA-400 resin and the IRA-94 resin were generated with fumaric acid solutions of different initial pH (Figs. 1 and 2).

It is obvious from the Figs. 1 and 2 that the equilibrium adsorption capacities of both resins towards fumaric acid decreased with temperature increasing at all pH level. In addition, favorable adsorption isotherms were exhibited by both resins for fumaric acid with the extent of adsorption increasing as the equilibrium concentration of the fumarate ion increased in the aqueous solution. In order to evaluate the pH effects on fumaric acid adsorption, the adsorption isotherm of fumaric acid on IRA-400 and IRA-94 resins at different pH and temperatures were examined using the empirical Freundlich adsorption model[14] which may be expressed as:

TABLE- 1
EQUILIBRIUM ADSORPTION QUANTITY OF FUMARIC ACID AT DIFFERENT pH

Resin	Capacity Q_e (mmol/g)				
	Source	Type	pH 2.0	pH 3.5	pH 5.0
IRA-400	Sigma Chemical Co.	Strong base	0.914	1.052	0.750
IRA-900	Sigma Chemical Co.	Strong base	0.655	0.793	0.552
IRA-94	Sigma Chemical Co.	Weak base	1.466	1.181	0.414
D315	Huazhen Sci. & Tech. Co	Weak base	1.219	0.886	0.125

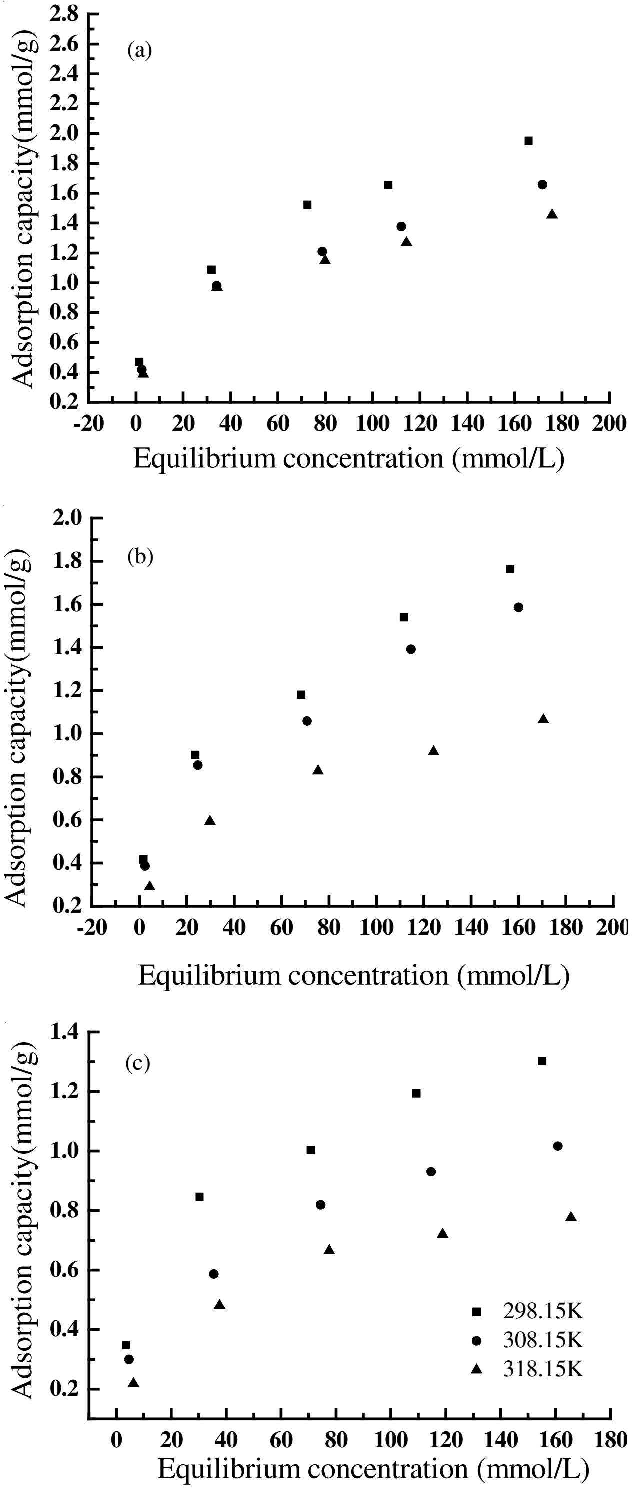


Fig. 1. Equilibrum adsorption isotherms of fumaric acid onto IRA-400 resin at different pH (a) pH 2.0, (b) pH 3.5, (c) pH 5.0; ■ 298 K, ● 308 K, ▲ 318 K

$$\ln Q_e = \ln K + \frac{1}{n}\ln C_e \quad (2)$$

where k and n are the Freundlich constants characteristic on the system. C_e in the liquid phase was measured after the adsorption equilibrium was reached. With a known initial fumaric acid concentration (C_0), the isotherm parameters can be obtained by plotting ln Q_e against ln C_e according to Freundlich equation. Resins IRA-400 and IRA-94 were compared for the experimental equilibrium fumaric acid adsorption capacities.

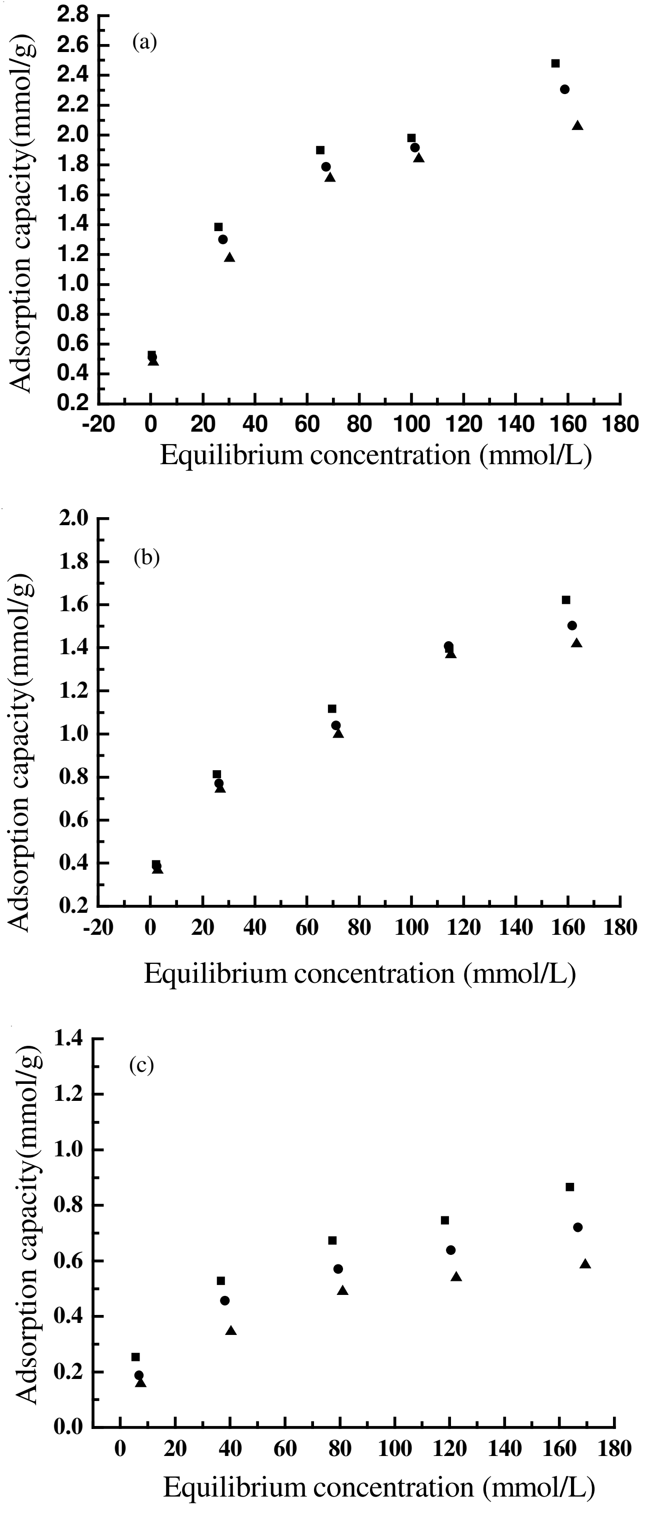


Fig. 2. Equilibrum adsorption isotherms of fumaric acid onto IRA-94 resin at different pH (a) pH 2.0, (b) pH 3.5, (c) pH 5.0; ■ 298 K, ● 308 K, ▲ 318 K

The corresponding correlation coefficients, r^2 and correlation equations derived from such an analysis together with the values of the Freundlich constants k and n obtained in the present studies are listed in Table-2.

It is quite obvious from the data that the Freundlich equation provided a perfect fit to the experimental results, since the correlation coefficients were larger than 0.99 in all cases. The parameter k, one of the Freundlich constants, has been

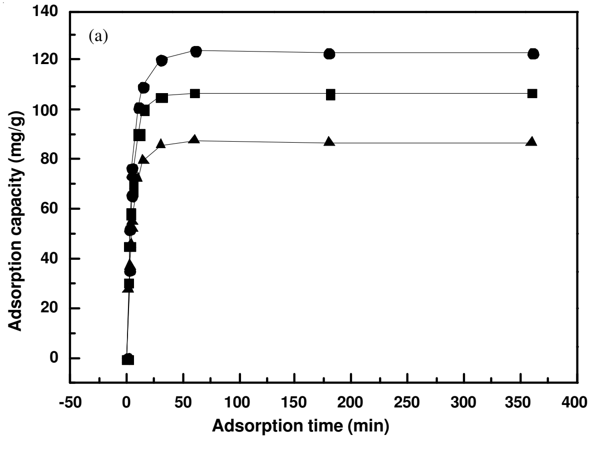
TABLE- 2
REGRESSION EQUATIONS AND ASSOCIATES FREUNDLICH ISOTHERMS FOR SYSTEMS STUDIED

Resin	pH	Temperature (K)	Regression equation	k	n	r^2
IRA-400	2.0	298	$\ln Q_e = 0.304 \ln C_e - 0.909$	0.403	3.289	0.996
		308	$\ln Q_e = 0.320 \ln C_e - 1.174$	0.309	3.125	0.998
		318	$\ln Q_e = 0.327 \ln C_e - 1.289$	0.276	3.058	0.994
	3.5	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
	5.0	298	$\ln Q_e = 0.351 \ln C_e - 1.467$	0.231	2.849	0.994
		308	$\ln Q_e = 0.356 \ln C_e - 1.754$	0.173	2.809	0.996
		318	$\ln Q_e = 0.399 \ln C_e - 2.223$	0.108	2.506	0.997
IRA-94	2.0	298	$\ln Q_e = 0.249 \ln C_e - 0.424$	0.654	4.016	0.998
		308	$\ln Q_e = 0.272 \ln C_e - 0.585$	0.557	3.676	0.997
		318	$\ln Q_e = 0.279 \ln C_e - 0.698$	0.498	3.584	0.995
	3.5	298	$\ln Q_e = 0.323 \ln C_e - 1.214$	0.297	3.096	0.997
		308	$\ln Q_e = 0.326 \ln C_e - 1.274$	0.280	3.067	0.994
		318	$\ln Q_e = 0.338 \ln C_e - 1.373$	0.253	2.959	0.993
	5.0	298	$\ln Q_e = 0.359 \ln C_e - 1.971$	0.139	2.786	0.998
		308	$\ln Q_e = 0.422 \ln C_e - 2.432$	0.088	2.370	0.994
		318	$\ln Q_e = 0.434 \ln C_e - 2.695$	0.068	2.304	0.995

used as a relative measure of adsorption capacity. A greater value of k indicates a higher capacity for adsorption. It is obvious from the measured values of k that the capacities of resins IRA-400 and IRA-94 decreased with increasing temperature at same pH.

The n, the other Freundlich constant, is an empirical parameter that varies with the degree of heterogeneity indicating the degree of non-linearity between fumaric acid adsorption capacity and unadsorbed fumaric acid concentration and is related to the distribution of bonded ions on the adsorbent surface. In general, n > 1 illustrates that adsorbate is favorably adsorbed on an adsorbent and the higher the n value the stronger the adsorption intensity. Table-2 also indicated that n is greater than unity, indicating that fumaric acid is favorably adsorbed by two resins at all temperatures and pH studied.

Static adsorption dynamics: Generally, the resins with different physical and chemical properties show the different dynamics of adsorption. So it is necessary to investigate the factors involved in dynamics of adsorption. Fig. 3 depicts the influence of time on the uptake of fumaric acid at different pH onto the two resins. The data depicted shown that the most of the fumaric acid adsorption occurred during the first 25 min of contact with IRA-400 resin which was more rapid than IRA-94 resin at the same pH.



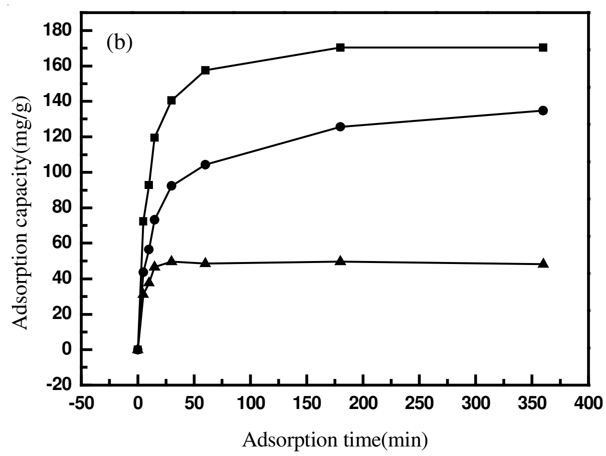


Fig. 3. Dynamics curve of fumaric acid adsorption onto (a) IRA-400 and (b) IRA-94 with 1 g adsorbent, 5 mg/mL inlet concentration in different pH and at 308 K ■ pH 2.0, ● pH 3.5, ▲ pH 5.0

In order to explore the kinetic adsorption processes more fully, the pseudo-first-order and pseudo-second-order equations were used to fit the experimental data for the two adsorbents at different pH. The pseudo-first-order rate expression of Lagergren may be written as[15]:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \qquad (3)$$

where Q_t is the equilibrium capacity of the resin (mg/g) at time t, Q_e (mg/g) is the equilibrium adsorption capacity of the resin and k_1 (min^{-1}) is the rate constant arising from the first-order model. A linear plot of ln (Q_e-Q_t) *versus* t would endorse the applicability of this kinetic model for fitting the experimental data. The slopes and intercepts of such linear plots would enable the first-order rate constant, k_1 and the equilibrium adsorption capacity, Q_e, to be determined.

The pseudo-second-order kinetic model may be expressed by the following relationships[16]:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}; \quad h = k_2 Q_e^2; \quad t_{1/2} = \frac{1}{k_2 Q_e} \qquad (4)$$

where k_2 is the rate constant arising from the second-order adsorption process, h is the initial adsorption rate [mg/(g min)] and $t_{1/2}$ (min) is the time at which the adsorption capacity Q_t reaches half of the equilibrium adsorption capacity Q_e. In this case, a linear plot of t/Q_e *versus* t would endorse the applicability of this kinetic model for fitting the experimental data. The slopes and intercepts of such linear plots would enable the second-order rate constant, k_2 and the equilibrium adsorption capacity, Q_e, to be determined.

The calculated results obtained by applying these various kinetic equations are listed in Table-3, together with a comparison of results for the correlation coefficients (r^2) obtained from the two kinetic models. As shown by the data listed, the correlation coefficients of two resins at pH 2.0, 3.5 and 5.0 for the pseudo-first-order kinetic model were quite low whereas, in contrast, those for the pseudo-second-order kinetic model were larger than 0.99 in virtually every case. In addition, the linear plot of t/Q_e *versus* t showed good agreement between the experimental data and the pseudo-second-order kinetic model. Furthermore, the calculated values of Q_e obtained from the pseudo-second-order kinetic model were generally more reasonable than those obtained from the pseudo-first-order model.

With the pseudo-second-order model, at the same pH, the equilibrium rate of IRA-400 resin was much faster than IRA-94 resin, but there was no obvious discrepancy at different pH of each resin according to the equilibrium rate constant, k_2. It is also clear from the data listed in Table-3 that the initial adsorption rate onto IRA-400 resin was greater than that onto IRA-94 resin at the same pH, while the magnitude of $t_{1/2}$ was less. This means that fumaric acid adsorption onto IRA-400 resin occurred more rapidly than onto IRA-94 resin at all considered pH.

Fixed-bed adsorption: The effect of pH on the breakthrough points of IRA-400 and IRA-94 resins were determined (Fig. 4). Breakthrough profiles for IRA-400 and IRA-94 resins showed that the breakthrough points and the efficiency of adsorption column of each resin were very different at different pH. According to Table-4, the efficiency of adsorption column of resin IRA-400 had no evident correlation with the pH; while the efficiency of adsorption of resin IRA-94 decreased gradually along with the increasing of pH of fumaric acid, which decreased from 64 % to 31 %.

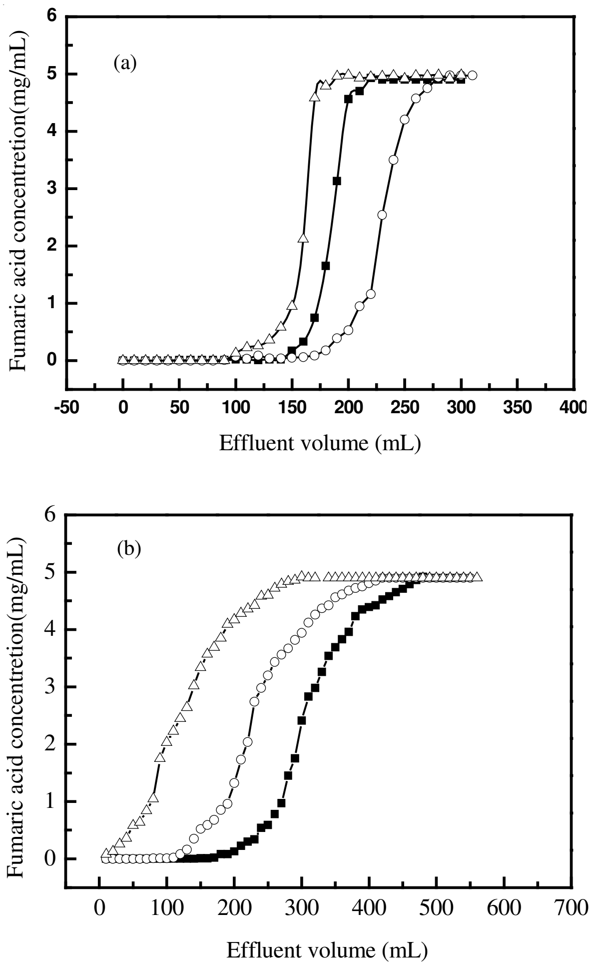


Fig. 4. Breakthrough profiles of fumaric acid (5 mg/mL) at different pH (a) IRA-400, (b) IRA-94 ■ pH 2.0, ○ pH 3.5, □ pH 5.0

TABLE-3
PARAMETERS DERIVE FROM THE APPLICATION OF THE PSEUDO-FIRST-ORDER AND PSEUDO-SECOND-ORDER RATE EQUATIONS TO THE ADSORPTION OF FUMARIC ACID ONTO THE TWO ADSORBENTS STUDIED

Adsorption	pH	Q_e(exp) (mg/g)	Pseudo-first-order model			Pseudo-second-order model				
			K_1	Q_e (calcd.) (mg/g)	r^2	K_2	Q_e(calcd.) (mg/g)	r^2	$t_{1/2}$ (min)	h [mg/(gin)]
IRA-400	2.0	107.50	0.027	23.975	0.735	0.00418	107.99	0.9991	2.22	48.685
	3.5	124.05	0.026	30.661	0.700	0.00323	124.38	0.9983	2.49	49.925
	5.0	87.95	0.024	21.115	0.703	0.00499	87.72	0.9994	2.28	38.417
IRA-94	2.0	170.41	0.019	63.117	0.784	0.00092	173.61	0.9962	6.23	27.855
	3.5	134.76	0.015	36.489	0.932	0.00059	140.45	0.9993	12.05	11.655
	5.0	49.75	0.012	8.697	0.758	0.00480	50.00	0.9973	4.17	11.990

TABLE- 4
PARAMETERS UNDER DIFFERENT pH AT 308 K

Resin	pH	Breakthrough volume (mL)	Breakthrough capacity (mg/L)	Saturated capacity (mg/L)	Efficiency of adsorption column (% w/w)
IRA-400	2.0	160.0	80.0	106.0	75.5
	3.5	190.0	95.0	122.0	77.8
	5.0	130.0	65.0	87.0	74.7
IRA-900	2.0	220.0	110.0	170.0	64.7
	3.5	140.0	70.0	137.0	51.1
	5.0	30.0	15.0	48.0	31.3

When the fumaric acid adsorption of IRA-400 reached the breakthrough point, the concentration of fumaric acid in effluent increased rapidly and reached a plateau after 50-80 mL which was shorter than IRA-94.

Conclusion

In the present experiments, the fumaric acid adsorption performance of the strong-base resin IRA-400 was compared with that of the weak-base resin IRA-94 at pH above, between and below the pK_as of fumaric acid. It was found that the adsorption equilibrium data at different pH and temperatures with both resins could be fitted perfectly by the Freundlich isotherm model. The results demonstrated that the adsorption capacity of IRA-400 resin did not vary a lot between the pK_as of fumaric acid; while the adsorption capacity of IRA-94 resin sharply decreased as the pH of fumaric acid solution increased. The pseudo-second-order kinetic model agreed very well with the dynamic behaviour for the adsorption of fumaric acid onto the IRA-400 and IRA-94 resins. pH did not influence the resin's adsorption rate and the time necessary to attain equilibrium during the adsorption of fumaric acid onto IRA-400 resin was shorter than that for IRA-94 resin. Breakthrough profiles for IRA-400 and IRA-94 resins show that the quaternary amine structure in IRA-400 resin allows for a much faster diffusion of fumaric acid into the sorbent than in the tertiary amine structure of IRA-94 resin at all pHs.

It shows different adsorption mechanisms in the adsorption of fumaric acid at above, between and below the pKas of fumaric acid. The fumaric acid adsorption by basic resins can thus be attributed to specific interaction of the acid with the basic functional group in the resins. The uptake of the acid is higher for the tertiary amine based basic resin IRA-94 than the strong basic resin IRA-400 with quaternary groups below the pK_as of fumaric acid. The latter should interact mainly with the ionized fumarate ions through electrostatic forces but should show relatively poor attractive interaction with the molecular form of the acid. It may, however, induce a shift in the ionization of the acid locally. For weak base resins, the interaction is influenced by the ease with which the interacting centers approach each other. With an increasing degree of substitution on nitrogen, this ease reduces which indeed is the observation in the case of the resins in tertiary and quaternary groups. The IRA-94 resin, which contain *tert*-amino functional groups, had the fumaric acid adsorption of 1.466 mmol/g, respectively, while the IRA-400 resin, which contains quaternary ammonium groups, showed a much lower acid adsorption of 0.914 mmol/g at pH2.0 which below the pK_as of fumaric acid. Dethe *et al*,[17] has also stated that the nitrogen of the functional quaternary ammonium group, although positively charged, can not be easily approached by the partially negative oxygen of the acid due to the steric hindrance provided by bulky alkyl groups on the nitrogen. The primary and secondary functional groups can give a better uptake than the tertiary group resins but the hydrogen-bonded complexes would be more stable. The *tert*-amino group shows the Lewis acid-base interaction, which is strong enough to take up a large quantity of the acid. So, the fumaric acid adsorption capacity of resin IRA-400 increased, meanwhile that of the resin IRA-94 decreased with the pH increased. When the pH reached a given pH, the OH- of solution began to hold up the bonding between the functional groups of IRA-400 and fumarate ion.

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