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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 investiga

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 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

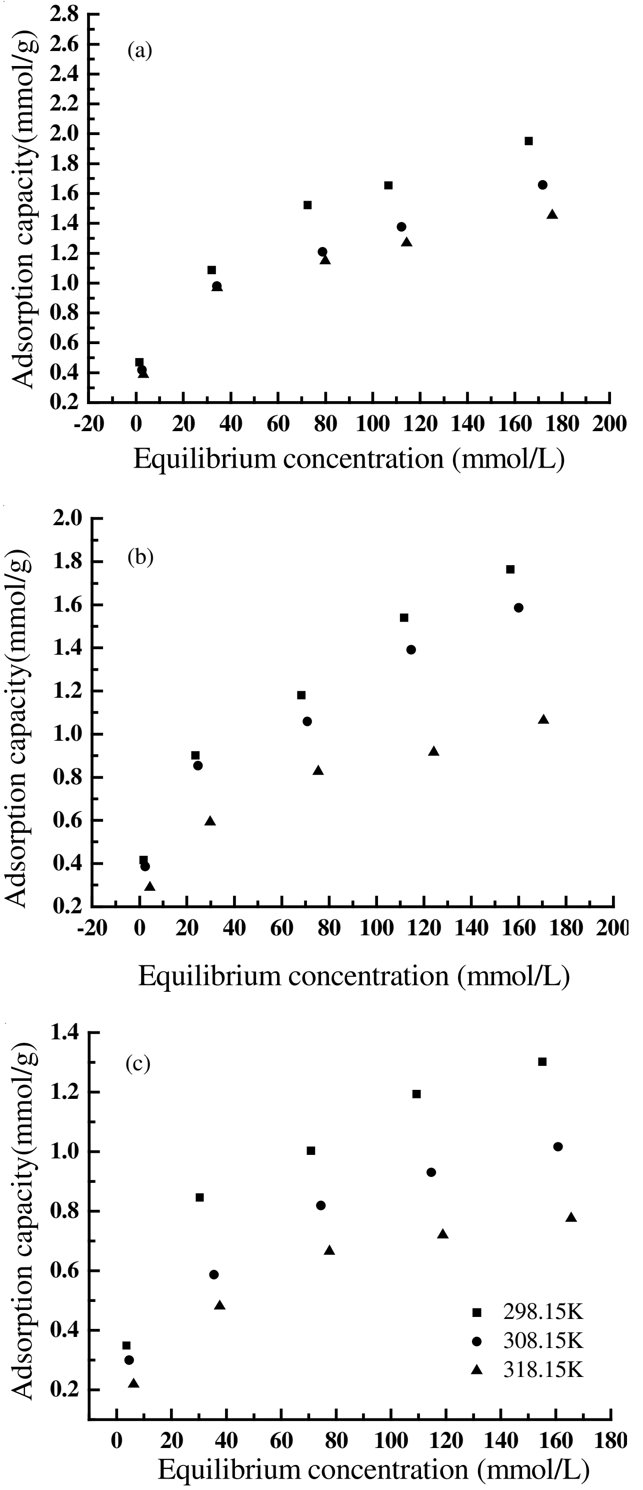


Fig. 1. Equilibrum adsorption isotherms of fumaric acid onto IRA-400 resin at different pH (a) pH 2.0, (b) pH 3.5, (c) pH 5.0; ■ 298 K, ● 308 K, ▲ 318 K

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

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.

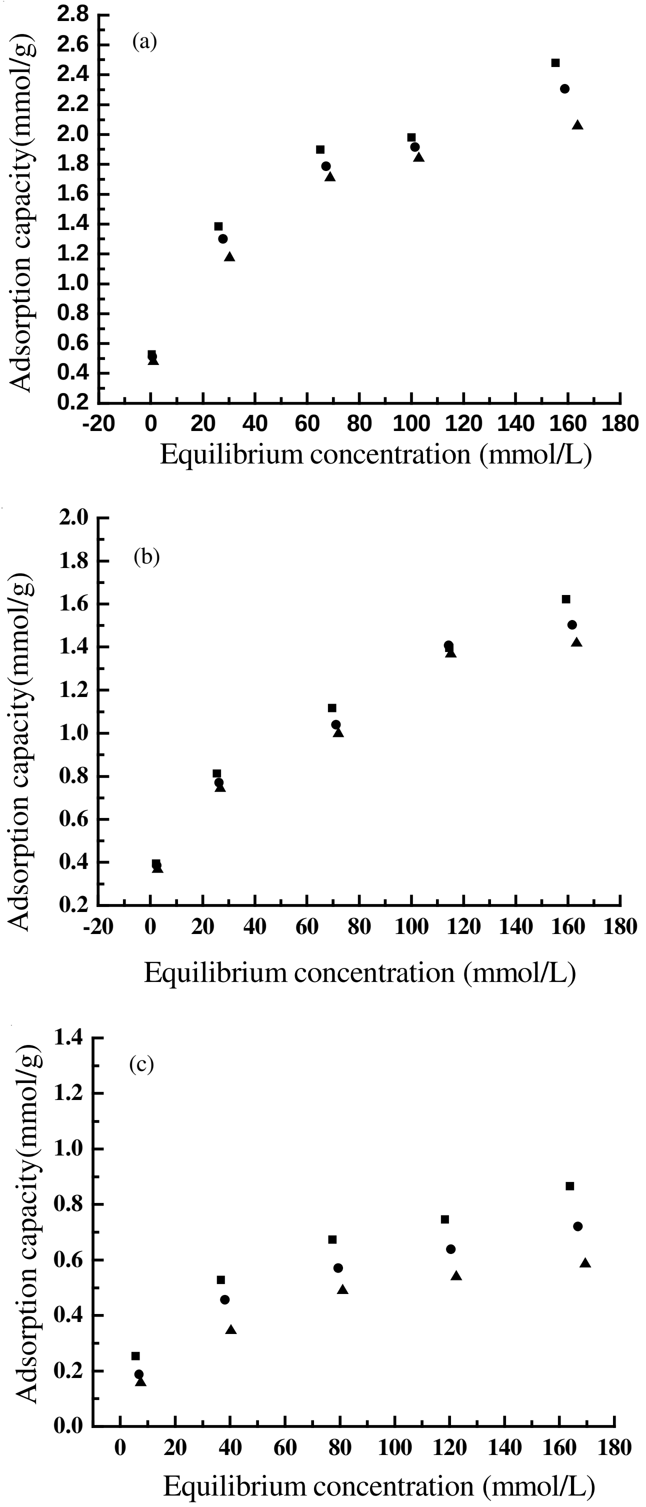


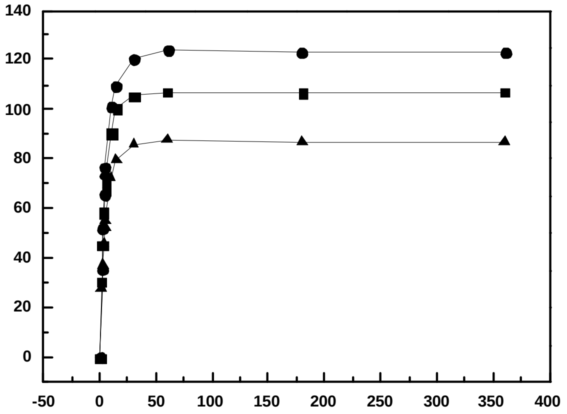
Fig. 2. Equilibrum adsorption isotherms of fumaric acid onto IRA-94 resin at different pH (a) pH 2.0, (b) pH 3.5, (c) pH 5.0; ■ 298 K, ● 308 K, ▲ 318 K

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 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.



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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REFERENCES

1. W.Y. Tao, J.R. Collier, B.J. Collier and I.I. Negulescu, *Textile Res. J.*, **63**, 162 (1993).
2. T.K. Ng, R.J. Hesser, B. Stieglitz, B.S. Griffiths and L.B. Ling, *Biotechnol Bioeng. Symp.*, **17**, 355 (1986).
3. Y. Zhou, J. Du and G.T. Tsao, *Bioprocess Biosyst. Eng.*, **25**, 179 (2002).
4. I.C. Gangl, W.A. Weigand and F.A. Keller, *Appl. Biochem. Biotechnol.*, **24/25**, 663 (1990).
5. J.G. Zeikus, M.K. Jain and P.B. Elankovan, *Appl. Microbiol. Biotechnol.*, **51**, 545 (1999).
6. J.L. Wang, X.H. Wen and D. Zhou, *Bioresour. Technol.*, **75**, 231 (2000).
7. H.G. Joglekar, I. Rahman, S. Babu, B.D. Kulkarni and A. Joshi, *Sep. Purif. Technol.*, **52**, 1 (2006).
8. Y. Zhou, Ph.D. Thesis, Fumaric Acid Fermentation by Rhizopus Oryzae in Submerged Systems, Purdue University, West Lafayette, Indiana, USA (1999).
9. N.J. Cao, J.X. Du, C.S. Gong and G.T. Tsao, *Appl. Environ. Microbiol.*, **62**, 2926 (1996).
10. C.J. King and L.A. T02 0 Td (ter)Tj