Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Separation of Hydroxycitric Acid Lactone from Fruit Pectins and Polyhydroxyphenols on Poly(4-Vinylpyridine) Weak-Base Resin

M. Chanda[a]; G. L. Rempel[a]
[a] DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF WATERLOO, WATERLOO, CANADA

Online publication date: 17 April 2000

To cite this Article Chanda, M. and Rempel, G. L.(2000) 'Separation of Hydroxycitric Acid Lactone from Fruit Pectins and Polyhydroxyphenols on Poly(4-Vinylpyridine) Weak-Base Resin', Separation Science and Technology, 35: 6, 869 — 902
To link to this Article: DOI: 10.1081/SS-100100199
URL: http://dx.doi.org/10.1081/SS-100100199

SEPARATION SCIENCE AND TECHNOLOGY, **35**(6), pp. 883–902, 2000

Separation of Hydroxycitric Acid Lactone from Fruit Pectins and Polyhydroxyphenols on Poly(4-Vinylpyridine) Weak-Base Resin

M. CHANDA* and G. L. REMPEL†
DEPARTMENT OF CHEMICAL ENGINEERING
UNIVERSITY OF WATERLOO
WATERLOO, ONTARIO N2L 3G1, CANADA

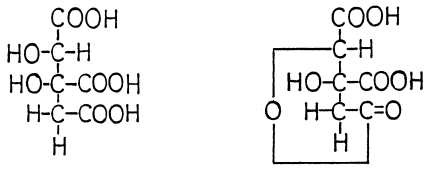
ABSTRACT

Poly(4-vinylpyridine) (PVP) has been used for the separation of hydroxycitric acid lactone (HCAL) from polyhydroxyphenols and fruit pectins, as the study has relevance to the problem of extraction of the antiobesity substance hydroxycitric acid from *Garcinia cambogia* fruits, a rich source of the acid. PVP has been used both in free-base form and in protonated or salt form as a sorbent, while catechol and pyrogallol have been used as representative polyhydroxyphenols. Though the protonated form, used as PVP(HCl), has a low sorption capacity (96 mg/g dry resin) and low selectivity for pectin (at pH 8), its higher, but comparable, sorptions (at pH 8) of HCAL, catechol, and pyrogallol, with respective saturation values of 354, 349, and 366 mg/g dry resin, coupled with high selectivity for the hydroxyphenols, make the sorbent unsuitable for the desired separation of HCAL. On the other hand, PVP free-base resin has significantly high sorption of HCAL as compared to catechol and pyrogallol in mildly acidic media (pH 1.8–2.8), the respective saturation values being 576, 206, and 303 mg/g dry resin, but the free-base resin also shows high saturation capacity (500 mg/g dry resin) for pectin. However, at low substrate concentrations (<1 g/L) or relatively low pH (<2), pectin has an order of magnitude lower sorption than HCAL, making separation of the latter possible on PVP free-base resin. Column operation using PVP free-base resin with influent maintained at pH 1.8, followed by stripping with less than the theoretical amount of alkali, produces good separation and high yield of HCAL from the mixed influent. Reillex HP, a macroporous PVP resin, used in free-base form, has relatively fast kinetics for HCAL sorption, with a $t_{1/2}$ value of about 5 minutes and diffusivity of the order of 10^{-6} cm^2/s.

* On leave from Indian Institute of Science, Bangalore, India.
† To whom correspondence should be addressed.

INTRODUCTION

Garcinia cambogia, grown extensively in the coastal regions of southern India, has gained considerable attention in recent years as more research focuses on antiobesity drugs, both natural and synthetic. Described as a "weight-loss wonder" (1), *G. cambogia* is a rich source of (−)hydroxycitric acid (**I**), which has been identified as the principal antiobesity substance and is abundantly present in the rind of the fruit. Antiobesity drugs belong to one or more of the following categories: (a) drugs which can reduce the amount of fat produced in the body or absorbed in the gut; (b) thermogenic drugs, which increase the amount of fat that is metabolized in the body by burning off excess calories; and (c) satiety drugs which reduce the appetite. *G. cambogia* is known to perform all three roles (2). It inhibits lipogenesis, lowers the production of cholesterol and fatty acids, increases the production of glycogen in the liver, suppresses appetite, and increases the body's production of heat by activating the process of thermogenesis. There are many weight loss products on the market that work by stimulating the central nervous system. There are often side effects associated with these products, such as nervousness and agitation. *G. cambogia* is a new approach in that it does not influence the central nervous system and works with the body naturally.



(I) (II)

There are approximately 200 different species of garcinia but only a few contain the necessary component, (−)hydroxycitric acid (HCA). *G. cambogia*, grown in the coastal regions of southern India and popularly known as "Malabar Tamarind," is a rich source of (−)HCA, containing about 30% of the acid (3). HCA cannot, however, be crystallized because evaporation results in the formation of the lactone (**II**) in the form of needle-shaped crystals. Pure (−)HCA in aqueous solution can be obtained from the lactone by treating the latter with equivalent amounts of alkali and further treating the salt solution with cation-exchange resins.

Besides (−)HCA (and its lactone), the other major solute components in aqueous extracts of garcinia are pectins and polyphenols (4). Because of the relatively low pK_a value of (−)HCA compared to the other main components, ion-exchange separation on weak-base resins would appear to be the most convenient approach. Such a process has already been claimed in a patent by Moffett et al. (5) for the preparation of (−)HCA concentrate. The process uses conventional weak-base resins for concentrating HCA in sodium salt form,

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

and a strong acid resin to generate HCA as the free acid. However, no detailed studies have been made to evaluate the equilibrium and kinetic factors involved in ion-exchange separation of HCA on different weak-base resins.

In continuation of our earlier studies (6, 7) on relatively new and unconventional weak-base resins, poly(4-vinylpyridine) and polybenzimidazole, which have shown capacity to adsorb both carboxylic acids and simple phenols from aqueous solutions, we undertook a systematic investigation of the possible use of such weak-base resins for the separation of (−)HCA lactone from fruit pectins and polyhydroxyphenols in aqueous solutions in an effort to find an economic method of extracting HCA and its lactone directly from the aqueous extracts of garcinia fruits and rinds. The present paper deals with such a study made with the commercial resin Reillex HP.

EXPERIMENTAL

Sorbent

The crosslinked poly(4-vinylpyridine) (PVP) used in this work was Reillex HP, obtained from Reilly Industries, Inc., Indianapolis, Indiana, USA. It is a spherical bead-form macroporous resin of average pore size 600 Å and particle size −30+60 (US mesh) with a divinylbenzene content of 25% and a bulk density of 25 kg/ft^3. The resin was washed thoroughly with distilled water and partially dewatered and stored in wet condition with a 55 wt% moisture content. The capacity of the resin as determined by converting a weighed amount into the chloride salt by treatment with HCl followed by estimation of the amount of acid consumed was 5.8 meq/g dry resin.

For sorption studies, PVP was also converted to the chloride form followed by washing with water to remove the unreacted acid. The product was partially dewatered by pressing it between filter sheets. The resulting product, PVP(HCl), had 60% moisture and a proton content of 3.8 meq/g dry.

Sorbates

Since pure (−)HCA was not available and is difficult to obtain as a solid because of its easy conversion to the lactone, the extracts of *G. cambogia* fruit rinds commercially available as calcium salts were used to obtain (−)HCA as the lactone (HCAL). The calcium salt supplied by Natural Remedies India, Bangalore, was dissolved in 2 N HCl and neutralized with a calculated quantity of Na_2CO_3 to remove the calcium as carbonate, which also carried with it some insoluble resinous material. The filtrate, which had the dissolved sodium salts of *G. cambogia* extracts, was treated with the sulfonic acid resin Dowex 50W-X8(H^+) to liberate free acids. The reddish brown filtrate was treated with activated charcoal and concentrated to a thick syrup (light brown in

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

color) on a water bath. It was seeded with a few crystals of the lactone of HCA and left overnight in a desiccator. A light brown, crystalline material was obtained. The yield was about 18% based on the starting calcium salt. For further purification the material was repeatedly extracted with ether, and the combined extracts were dried over anhydrous sodium sulfate. A considerable proportion of the color was removed in this way as it was ether insoluble. Ether was removed by distillation, and the syrupy mass thus obtained was heated as a thin layer on a water bath to remove traces of ether. Seeding with HCA lactone resulted in a needle-shaped crystalline solid in about 12% yield based on the starting calcium salt of *G. cambogia* extracts.

The crystalline solid obtained by the above procedure was found to have an equivalent weight of 95 from alkali titrations; an elemental composition of C 38.2%, H 3.1%, and O 58.2%, in good agreement with $C_6H_6O_7$ (C 37.9%, H 3.2%, O 58.9%) for hydroxycitric acid lactone (HCAL); and a melting point of 175°C, in fair agreement with the reported value of 178°C for the lactone (4). Because it is a γ-hydroxy acid, HCA is easily converted to the lactone on evaporation of its solution to recover the solid.

The two polyhydroxyphenols used in the work, viz., catechol and pyrogallol, of >99% purity, were obtained from Aldrich Chemical Company, Milwaukee, Wisconsin, USA. Pectin from natural fruit peel, available as Certo brand product of Kraft Canada, Don Mills, Ontario, Canada, was used. Its acid content from alkali titration was determined to be 1.26 meq/g dry weight.

Analysis

A colorimetric method was used for measuring the concentration of HCAL in aqueous solution. To 1 mL of glacial acetic acid in a 50-mL volumetric flask was added 4 mL of 2.5% (w/v) clear aqueous sodium metavanadate solution. A measured volume of solution containing 4 to 30 mg HCAL was then added, and the volume made up with water. (The sodium metavanadate was conveniently dissolved in water at 50–60°C, made up nearly to volume, allowed to cool, and then filtered.) A scan of the visible range spectrum (Varian Spectrophotometer Model Cary 219) after color development for 4 to 5 hours at 25°C showed absorption maxima at 500 and 570 nm (Fig. 1). Absorbance was measured at these wavelengths after color development for 4 hours at 25°C, and a calibration curve was prepared using known concentrations of HCAL.

For the estimation of pectin the anthrone method of Jermyn (8) and the carbazole method of Dische (9) were adopted with slight modifications. Both methods gave similar results. The anthrone and carbazole reagents were made by dissolving 100 mg of the respective material in 500 mL of 80% (v/v) sulfuric acid. An amount of pectin solution was added to the reagent such that the pectin concentration in the final solution was in the 1 to 5 mg/100 mL range.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

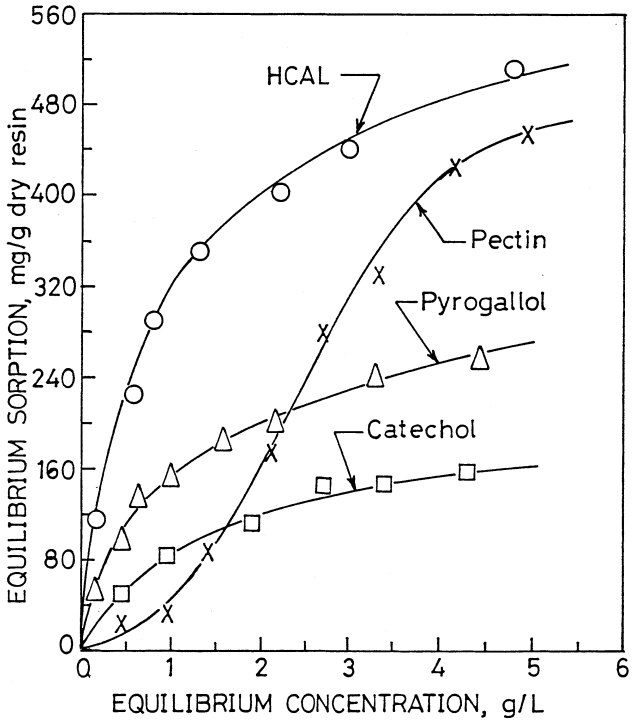


FIG. 1 Sorption isotherms of hydroxycitric acid lactone (HCAL), catechol, pyrogallol, and pectin on PVP free-base resin in mildly acidic media: HCAL (pH 2.2–2.5); catechol (pH 4.2–4.6); pyrogallol (3.7–4.3); pectin (pH 2.3–2.5). Resin loading 4 g (wet)/L; temperature 25°C.

The absorbance was measured at 630 nm in the anthrone method and 530 nm in the carbazole method, after color development for 4 hours at 25°C.

For the estimation of catechol and pyrogallol, a colorimetric method based on color development with hydroxylamine–Fe(III) in aqueous solution was used. The reagent was made by dissolving 10 g of $NH_2OH{\cdot}HCl$ and 10 g $FeCl_3{\cdot}6H_2O$ in 1 L of water and filtering. No adjustment of pH was made. An amount of phenolic solution was added to a definite volume (20 mL) of the reagent such that the concentration of phenol was 100 to 500 μg in the final volume (25 mL) made up in a volumetric flask. Absorbance was measured at 630 nm for catechol and 460 nm for pyrogallol after color development for 4 hours at 25°C. Calibration curves were prepared using known concentrations of catechol and pyrogallol.

Sorption Experiments

Sorption measurements for the four sorbents (HCAL, catechol, pyrogallol, and pectin) were used both individually and in binary mixtures of HCAL with the other three sorbates. In view of the oxygen sensitivity of polyhydroxyphe-

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

nols, deaerated water was used for making the solutions, and air was displaced by nitrogen in the sorption vessels. Since all the sorbates are acidic and differ significantly in their pK_a values, the possibility of separating them in sodium salt form by ion exchange on protonated PVP has been explored for comparison with the other approach in which the acidic sorbates are sorbed on the free-base resin by acid–base interaction. For equilibrium sorption measurements in both these series of experiments, a measured amount of the resin was vigorously shaken with a definite volume of the sorbate for 12 hours in a tightly stoppered flask at 25°C and the concentration of the residual sorbate was measured. A range of concentrations was employed for each sorbate. The sorption was also measured at different pH values of the aqueous medium for the sorbates individually and in binary mixtures of HCAL and the other three sorbates.

The sorption of HCAL was measured as a function of time under conditions of vigorous agitation using wet sieved resins of narrow size range and a rectangular basket made of a polypropylene screen (0.45 mm openings) to hold the resin beads. The basket was fitted to the shaft of a rotor and rotated while the sorbate solution was brought into contact for a specified period. In this way the sorbent could be instantly separated from the sorbate solution at any specified time. To determine the minimum speed above which the kinetics are not influenced by the degree of agitation (and hence are not controlled by film diffusion), dynamic contacts between sorbent and solution were effected at different stirring speeds using a low solution concentration of HCAL (2 mmol/L). Kinetic measurements were always performed at stirring speeds much above this minimum.

The performance of the PVP resin in continuous operation was studied by conducting column runs for the separation and recovery of HCAL from mixtures containing polyhydroxyphenols and pectin besides HCAL. The study was aimed at determining the breakthrough capacity of the resin for HCAL sorption in column runs and the enrichment that can be achieved by the process.

RESULTS AND DISCUSSION

Sorption Isotherm

The PVP resin was used both in free-base form and in protonated form as PVP(HCl) in order to determine the sorption isotherms. With the PVP free-base resin the sorbates, which are all acidic, were used in mildly acidic solutions to promote sorption by acid–base or hydrogen-bonding interactions:

$$\overline{\text{Py}} + \text{RCOOH} \rightleftharpoons \overline{\text{Py}}\text{H}^{+-}\text{OOCR} \quad (1)$$

$$\overline{\text{Py}} + \text{PhOH} \rightleftharpoons \overline{\text{Py}}\cdots\text{HOPh} \quad (2)$$

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

where $\overline{Py}$ represents a pyridinium unit and $Py^{-}H^{+}$ a protonated pyridinium unit in the resin. For sorption on PVP(HCl), the sorbates were converted to sodium salts by treating with NaOH to a pH value of 8 to promote sorption by ion exchange:

$$\overline{Py}H^{+}Cl^{-} + RCOO^{-}Na^{+} \rightleftharpoons \overline{Py}H^{+-}OOCR + Na^{+}Cl^{-} \quad (3)$$

$$\overline{Py}H^{+}Cl^{-} + PhO^{-}Na^{+} \rightleftharpoons \overline{Py}H^{+-}OPh + Na^{+}Cl^{-} \quad (4)$$

The equilibrium sorption data on PVP free-base resin and PVP(HCl) obtained in this way are compared in Figs. 1 and 2. While for catechol (pK_1 = 9.45, pK_2 = 12.8) and pyrogallol (pK_1 = 9.0, pK_2 = 11.2, pK_3 = 14.0) the sorptions by hydrogen-bonding interaction on free-base PVP in mildly acidic media and the ion-exchange reaction on PVP(HCl) at pH 8 are fairly comparable, for HCAL (pK_1 = 3.14, pK_2 = 4.77 for citric acid), however, the acid–base interaction on PVP free-base resin produces significantly greater sorption than ion exchange on PVP(HCl).

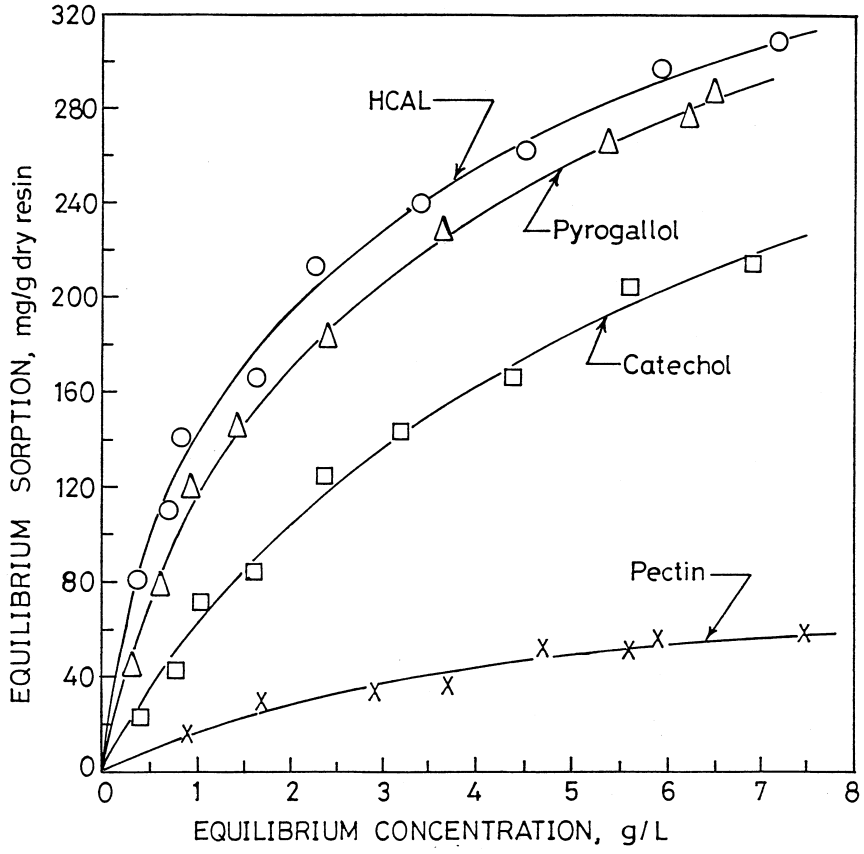


FIG. 2 Sorption isotherms of hydroxycitric acid lactone (HCAL), catechol, pyrogallol, and pectin on PVP(HCl) resin at pH 8.0. Resin loading 20 g (wet)/L; temperature 25°C.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

TABLE 1
Langmuir Isotherm Parameters for Sorption of HCAL, Catechol, Pyrogallol, and Fruit Pectin on PVP Free-Base and Protonated Resins

	Free-base resin			Protonated resin		
Sorbate	A_s (mg/g of dry resin)	K_b (L/g)	Correlation Coefficient	A_s (mg/g of dry resin)	K_b (L/g)	Correlation Coefficient
HCAL	576	1.34	0.999	354	0.67	0.996
Catechol	206	0.72	0.999	349	0.22	0.994
Pyrogallol	313	1.03	0.997	366	0.46	0.997
Pectin	—	—	—	96	0.22	0.999

The comparison between free-base PVP and PVP(HCl) is more striking in the case of pectin, which is a group of polysaccharides, mainly partially methylated polygalacturonic acids. Pectin sorption by ion exchange on PVP(HCl) is very low in comparison to sorption by acid–base interaction on PVP free-base resin, indicating the advantage of the ion-exchange process for separating HCAL from pectins. However, the situation is reversed in the case of phenols, which exhibit relatively high sorptions by ion exchange on PVP(HCl), with HCAL and pyrogallol sorptions being almost comparable (Fig. 2), while, in contrast, HCAL sorption on PVP free-base resin is significantly higher than the sorptions of both catechol and pyrogallol. The difference between HCAL and pectin sorptions on PVP free-base resin is large at low concentrations, with HCAL having 3 to 8 times higher sorption, while at higher concentrations the sorptions are comparable. So, on the whole, PVP free-base resin would be preferred for separating HCAL from both pectin and polyhydroxyphenols in mildly acidic media, especially at relatively low substrate concentrations.

The Langmuir isotherm equation fitted well to the sorption data of all the four sorbates on PVP(HCl) and to the HCAL, catechol, and pyrogallol sorption data on PVP free-base resin, while the pectin sorption data on the latter resin showed good agreement only with the Freundlich isotherm. The parameters of the Langmuir isotherm equation

$$x^* = K_b A_s C^*/(1 + K_b C^*) \tag{5}$$

where x^* is the equilibrium sorption (mg/g dry weight), C^* is the equilibrium sorbate concentration in solution (g/L), A_s is the saturation sorption capacity (mg/g dry weight), and K_b is the binding constant (L/g). The values of A_s and K_b were determined by least-squares fit. These are presented in Table 1.

For pectin sorption on PVP free-base resin, the parameters (p and q) of the Freundlich isotherm

$$x^* = a(C^*)^n \tag{6}$$

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

were determined by least-squares fit, yielding the values $a = 51.0$ and $n = 1.49$ for x^* and C^* as defined above.

A comparison of the Langmuir parameters for the four sorbates on the free-base and protonated PVP resins shows that the sorption by acid–base and hydrogen-bonding interactions produces stronger binding, and hence a higher degree of irreversibility, than sorption by the ion-exchange mechanism.

On PVP free-base resin, pectin is seen to have a relatively high value of saturation sorption in terms of weight (~500 mg/g dry resin), which is comparable to that of HCAL (576 mg/g dry resin). This would, however, be expected in view of the higher molecular weight of pectin per acid group.

Effect of pH

Since the ion-exchange sorption on the protonated PVP resin would be expected to decrease substantially by both the increase and decrease of the substrate pH, the effect of pH variation on sorption was measured only for the PVP free-base resin. The results, presented graphically in Fig. 3, show that the sorption falls at lower pH in all cases. For HCAL this can be explained by the acid–base interaction of the basic resin with the acid to form a complex with carboxylate anion as the associated counterion (Eq. 1), while for phenols this

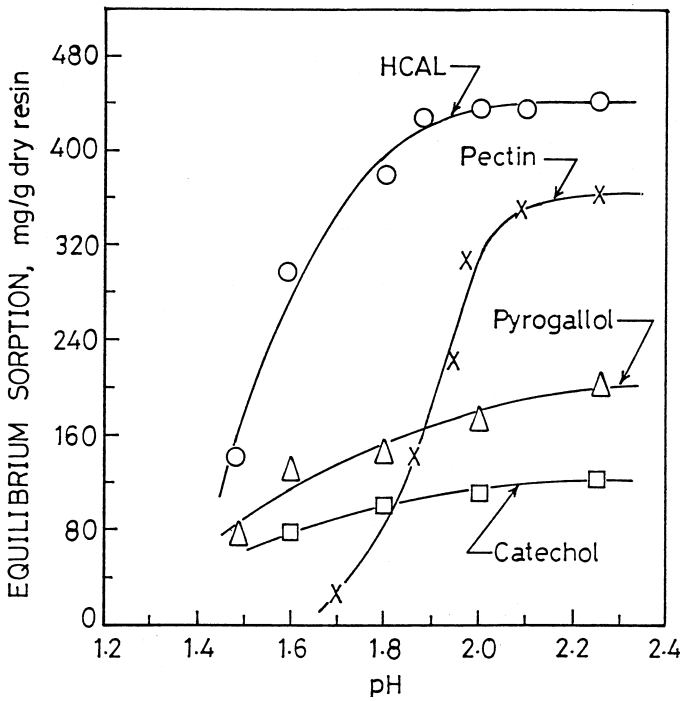


FIG. 3 Effect of pH on the sorption of hydroxycitric acid lactone (HCAL), catechol, pyrogallol, and pectin on PVP free-base resin; initial concentrations 4.0 g/L. Resin loading 4.0 g (wet)/L; temperature 25°C.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

can be explained by the hydrogen bonding mechanism (Eq. 2) of phenolic sorption on weak-base resin (10). Since a decrease in pH in the acidic range reduces the amount of the free-base form of PVP, sorptions by both Eqs. (1) and (2) would be expected to decrease.

The effect of pH is seen to be more drastic on the sorption of HCAL and pectin than on phenolic sorptions. This may be attributed to the greater effect of pH decrease on acid–base interaction than on sorption by hydrogen bonding or chemisorption. In fact, sorption of phenolics on the salt-form resin has also been reported. Chasanov et al. (10) explained the sorption of phenols on strong-base anion-exchange resins in the salt form as being due to chemisorption.

Though the sorptions of both HCAL and pectin are highly sensitive to a decrease in substrate pH, the sorption of HCAL, remains significantly high even at a relatively low pH of 1.7 where pectin has negligible sorption and the phenols also have relatively low sorption. An effective separation of HCAL from the other sorbates would thus be achieved by appropriately controlling the pH of the substrate.

Selectivity for HCAL

Sorption selectivity of HCAL relative to catechol, pyrogallol, and pectin in ion-exchange sorption on PVP(HCl) was measured as a function of the relative concentration of HCAL in binary mixtures with any of the other three sorbates. The results are plotted in Fig. 4 as separation factor α_B^A versus the weight ratio of HCAL and one other sorbate in solution, with α_B^A defined by

$$\alpha_B^A = \frac{x_A^* \times C_B^*}{x_B^* \times C_A^*} \tag{7}$$

where x^* and C^* represent the equilibrium sorption (mg/g dry resin) and equilibrium concentration (g/L), respectively, with A representing HCAL and B any of the other three sorbates, (catechol, pyrogallol, or pectin).

The separation factor values are greater than 1, indicating higher selectivity for HCAL, in the presence of pectin over a wide range of concentration ratios (Fig. 4). However, in relation to both catechol and pyrogallol, the HCAL separation factor is less than 1 over a wide range of concentration ratios, indicating greater selectivity for phenols in ion-exchange sorptions on PVP(HCl).

With PVP free-base resin the equilibrium sorption of HCAL was measured at different pH levels of the substrate, employing binary mixtures of HCAL and one of the other three sorbates, each having an initial concentration of 4 g/L. The separation factor values calculated from Eq. (7) are plotted in Fig. 5 as a function of pH. All the values are significantly greater than 1, indicating that good separation of HCAL from the other three sorbates can be achieved on PVP free-base resin in acidic media. While both HCAL /catechol selectiv-

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

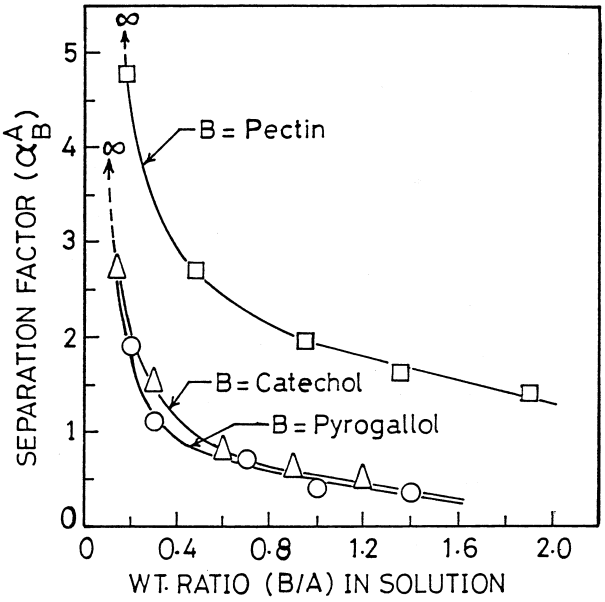


FIG. 4 Selectivity of sorption of hydroxycitric acid lactone (A) relative to catechol, pyrogallol, and pectin (denoted as B) in binary mixtures at pH 8.0 on PVP(HCl) resin; concentration of A in solution 4.0 g/L. Resin loading 20 g (wet)/L; temperature 25°C.

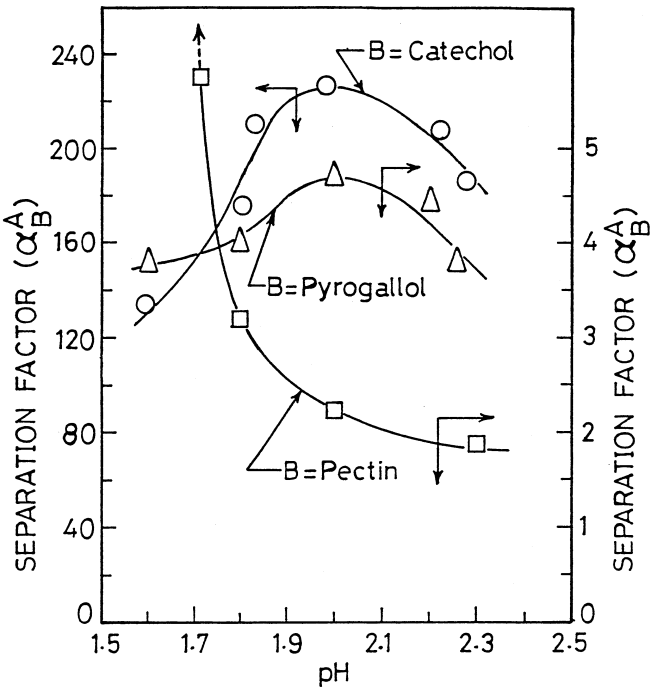


FIG. 5 Selectivity of sorption of hydroxycitric acid lactone (A) relative to catechol, pyrogallol, and pectin (denoted as B) in binary mixtures on PVP free-base resin at different pH levels of the substrate; concentration of each component 4.0 g/L. Resin loading 8.0 g (wet)/L; temperature 25°C.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

ity and HCAL/pyrogallol selectivity show maxima at pH 2.0, the former has 2 orders of magnitude higher α_B^A values, which may be attributed at least partly to a greater difference of pK_a values between HCAL and catechol than between HCAL and pyrogallol.

The HCAL/pectin selectivity increases very rapidly below pH 1.9, becoming nearly infinite at pH 1.7. This agrees well with the effect of pH on pectin sorption presented in Fig. 3, which shows no sorption of pectin below pH 1.7. A substrate pH level of 1.7–1.9 would thus appear to be suitable for recovery of HCAL free of pectin.

Sorption Rate Behavior

In view of the better performance of PVP free-base resin, compared to its protonated form, for the sorption of HCAL from phenolics and pectin, kinetic experiments were performed only with the free-base resin. The sorption of HCAL was measured at stirring speeds (200–300 rpm) much above the experimentally determined minimum for elimination of film diffusional resistance. The "interruption test," described as the best technique for distinguishing between particle and film diffusion control (11), was employed with HCAL as the sorbate. The basket reactor employed for the sorption rate study was especially suitable for such tests. The resin basket was removed from the sorbate solution for a brief period of time (5 minutes) and then reimmersed. A change in the momentary sorption rate following interruption indicated particle diffusion control (pdc) of the sorption rate under the experimental conditions employed.

The effect of the external concentration of HCAL on its sorption rate was measured because knowing it might help in finding the controlling mechanism. The experiments were performed with PVP free-base resin (spherical) beads of a narrow size range under conditions of maximum agitation. The data presented in Fig. 6 as plots of the fractional attainment of equilibrium sorption ($\bar{X}$) vs time (t) show that the external solution concentration in the present case has a pronounced effect on the rate of sorption. Such a concentration effect is not consistent with predictions from the ordinary pdc model, but is in accord with the shell-core or ash-layer model. However, sorption can be assumed to follow a shell-core model only if the reaction is irreversible and is fast as compared to diffusion. Compared to the ion-exchange sorption on the protonated PVP (Fig. 2), the acid–base sorption of HCAL on free-base PVP (Fig. 1) has a significantly higher binding constant (Table 1) and the column sorption, as shown later, exhibits a sharp breakthrough, both indicating a high degree of irreversibility of the sorption reaction. That the sorption is diffusion controlled is, however, shown by the interruption test described above.

A number of researchers have used the shell-core approach for sorption on weak-base resins (12–14). An analytical solution is available for the shell-core mechanism of sorption kinetics with constant bulk concentration (15, 16),

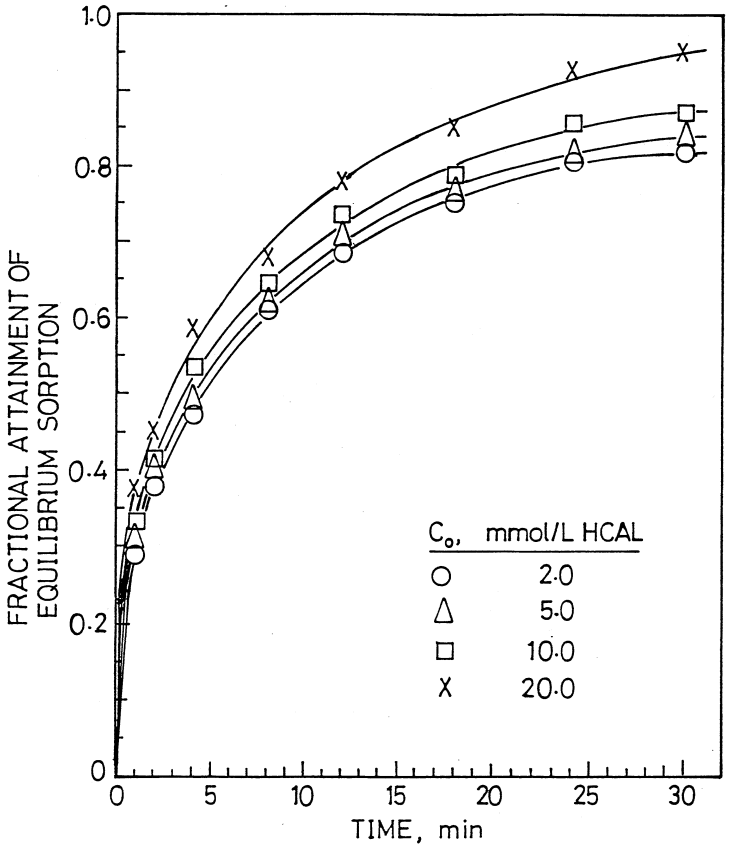


FIG. 6 Rate of sorption of hydroxycitric acid lactone (HCAL) on sieved PVP resin bead of size (diameter) 0.45–0.65 mm in HCAL solutions of different concentrations, C_0. Resin loading 4.0 g (wet)/L; pH 2.3; temperature 25°C; vigorous agitation.

which is referred to as the "infinite solution volume condition." The model, however, does not apply to batch experiments with limited solution volume or changing bulk concentration, which are more convenient from a practical point of view. Earlier we derived an analytical solution (17) for a shell-core model which assumes quasi-stationary diffusion but allows a change of bulk concentration with the progressive conversion of resin bead. The model is described by the equation

$$\left(\frac{6\lambda\bar{D}C_0}{r_0^2\bar{C}_r}\right)(t-t_0) = \frac{2}{\alpha}\ln\left[\frac{1-\alpha+\alpha R^{*3}}{1-\alpha+\alpha R_0^{*3}}\right] + \frac{1}{\alpha\beta}\ln\left[\frac{(\beta+R^*)^3(1-\alpha+\alpha R_0^{*3})}{(\beta+R_0^*)^3(1-\alpha+\alpha R^{*3})}\right] + \frac{2\sqrt{3}}{\alpha\beta}\left[\tan^{-1}\left(\frac{2R_0^*-\beta}{\sqrt{3}\beta}\right)-\tan^{-1}\left(\frac{2R^*-\beta}{\sqrt{3}\beta}\right)\right] \quad (8)$$

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

where

$$R^* = (1 - \overline{X})^{1/3} \tag{9}$$

$$R_0^* = (1 - \overline{X}_0)^{1/3} \tag{10}$$

$$\overline{C}_r = x_w^* d_w \tag{11}$$

$$\alpha = \frac{4\pi n \overline{C}_r r_0^3}{3VC_0} = \frac{wx_w^*}{VC_0} \tag{12}$$

$$\beta = \left(\frac{1 - \alpha}{\alpha}\right)^{1/3} \tag{13}$$

The term t_0 in Eq. (8) is the initial time at which a measurable conversion $\overline{X}_0$ of the resin is obtained. In Eq. (12), derived from mass balance for a shell-core system, n is the number of resin beads in each test, r_0 is the radius of the resin bead (cm), $\overline{C}_r$ is the sorption capacity per unit volume of the unreacted resin bead (mmol/mL), w is the weight of resin (wet) suspended in volume V of the sorbate solution (g/mL), d_w is the density of wet resin (g/mL), C_0 is the initial concentration of the sorbate in solution (mmol/mL), and x_w^* is the equilibrium sorption (mmol/g wet resin) for a given C_0. The term λ in Eq. (8) is the molar distribution coefficient. For any given run, λ is assumed to be constant.

The right-hand side of Eq. (8) can be plotted against $(t - t_0)$, and $\lambda\overline{D}$ can be evaluated from the slope of the linear plot. The sorption data for HCAL given in Fig. 6 are thus plotted in Fig. 7. Good fits are seen, however, only for conversions up to about 60%. This shows the limitation of the simple shell-core model which does not include all effects found in the real world. One such effect in the present case may be the decrease in the diffusion coefficient due to Donnan-type interactions of the sorbate with the sorbed species (18), which are likely to be more pronounced at higher resin conversions. Another reason for the variation of diffusivity in the exchanger phase could be the nonuniformity of porosity within the exchanger material, especially between the resin layers close to the surface and those deeper inside the resin bead. The concept of heterogeneity and nonuniformity of structure in ion exchangers has been used by several workers (19, 20) to explain the variation of such properties, as the distribution coefficient in the exchanger phase.

The values of $\lambda\overline{D}$ obtained from the slopes of linear plots up to about 60% resin conversion are recorded in Table 2. The values are seen to increase with a decrease in substrate concentration which would, however, be expected in view of the fact that λ is usually concentration-dependent and has a higher value at lower solution concentration (21).

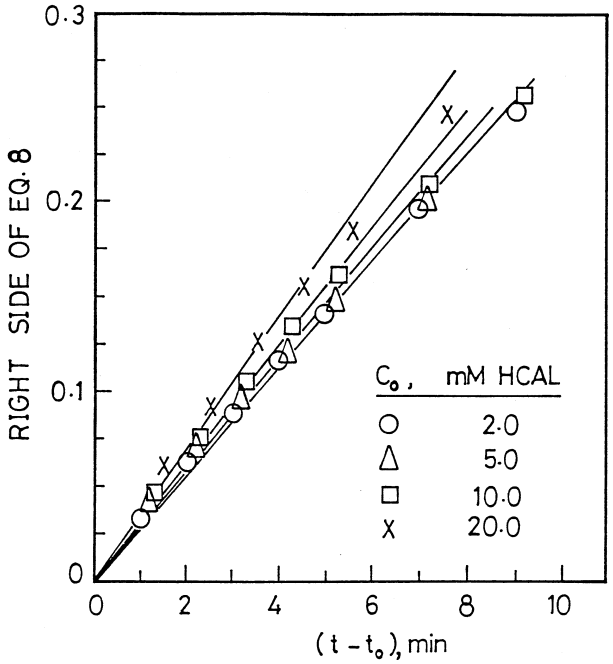


FIG. 7 Test of shell-core model equation (Eq. 8). Data: $w/V = 4.0$ g/L; $r_0 = 0.27$ mm.

Column Operation

The performance of the PVP free-base resin in continuous operation for the separation of HCAL from phenol and pectin was studied by conducting column runs. Figures 8 and 9 show typical breakthrough curves with a 22-cm^3 resin column and an aqueous influent containing HCAL, catechol, and pectin in 2 g/L concentration each. The runs were performed at the same flow rate at different pH values of the substrate. It is seen from Figs. 8 and 9 that distinctly separate breakthroughs are obtained for pectin, catechol, and HCAL, in that order, with pectin appearing almost at the start of the column operation and

TABLE 2
Values of $\lambda\bar{D}$ for Sorption of HCAL on PVP Free-Base Resin

Concentration of HCAL in solution (mmol/L)	$\lambda\bar{D}$ (cm^2/s) calculated from Eq. (8)
2.0	7.0×10^{-6}
5.0	5.5×10^{-6}
10.0	4.6×10^{-6}
20.0	3.3×10^{-6}

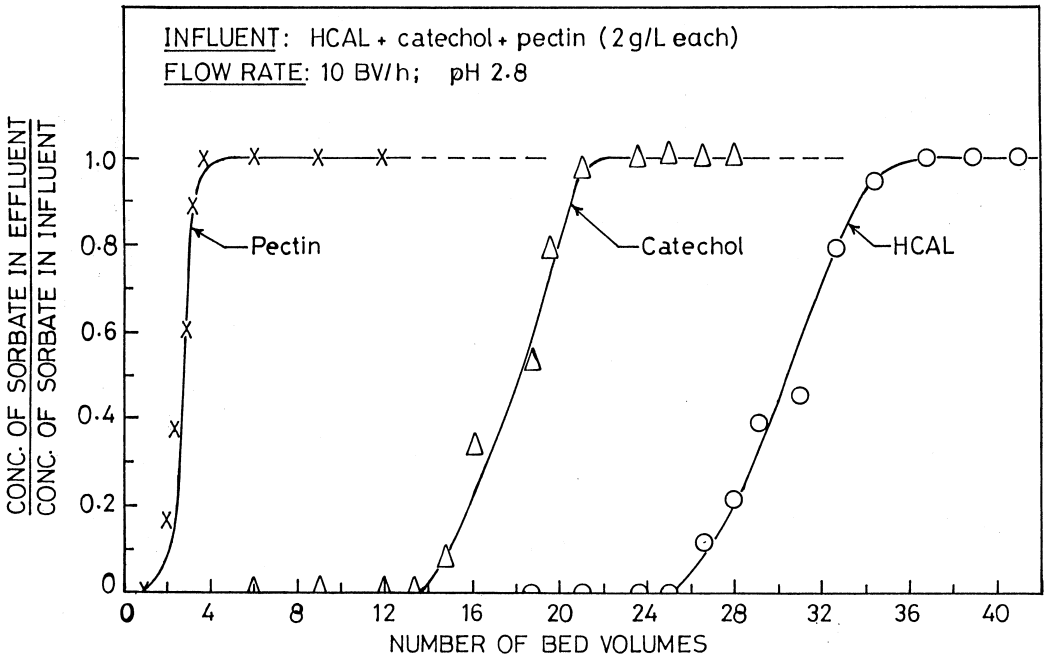


FIG. 8 Breakthrough curves of PVP (free-base) column with relatively high influent pH. Volume of resin bed (wet), 22 mL; resin weight, 15 g (wet); column I.D., 9 mm; resin bed height, 34 cm. (Bed volume = volume of resin bed.)

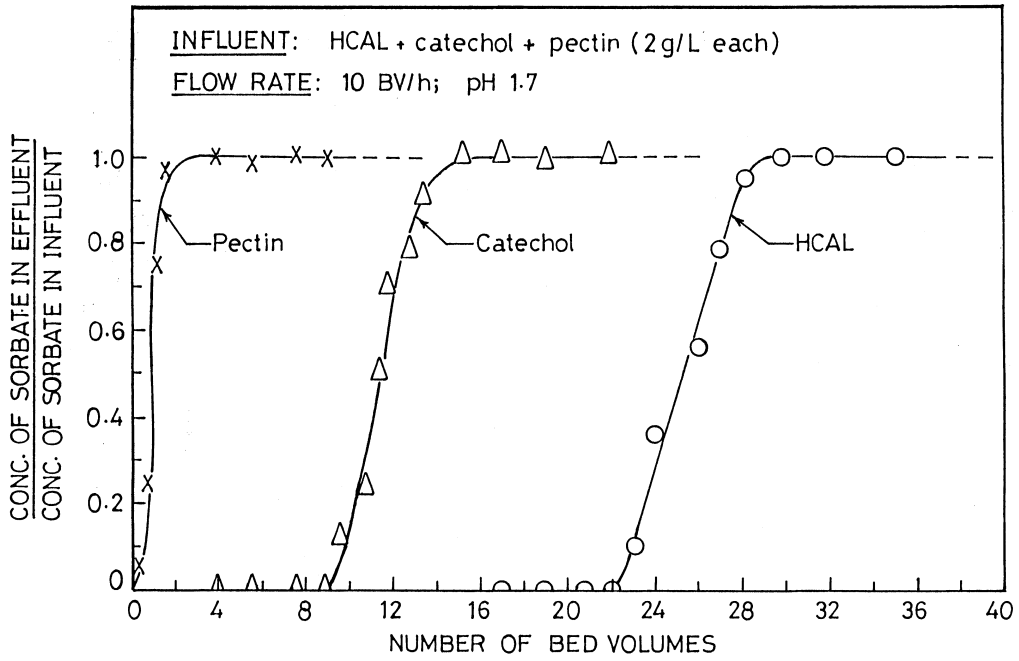


FIG. 9 Breakthrough curves of PVP (free-base) column with relatively low influent pH. Volume of resin bed (wet), 22 mL; resin weight, 15 g (wet); column I.D., 9 mm; resin bed height, 34 cm. (Bed volume = volume of resin bed.)

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

catechol appearing much ahead of HCAL. However, Fig. 8 reveals that at a relatively high pH in mildly acidic media, there is considerable sorption of catechol in the column besides HCAL.

Relatively less sorption of catechol occurs at a lower substrate pH compared to HCAL, resulting in a wider gap between catechol and HCAL breakthrough points. Thus a comparison of the breakthrough curves in Figs. 8 and 9 reveals that the gap between catechol and HCAL breakthrough points increases by about 20% on reducing the substrate pH from 2.8 to 1.7. The column capacity, however, decreases as the pH is lowered.

The HCAL breakthrough capacity for an influent rate of 10 bed volumes (BV) per hour (with the volume of the resin bed considered as 1 BV), the influent pH being 2.8, is determined to be 80 mg HCAL/g wet resin compared to the equilibrium sorption capacity of 148 mg HCAL/g wet resin. With the influent at pH 1.7 and the same flow rate (10 BV/h), the HCAL breakthrough capacity (Fig. 9) is reduced to 64 mg HCAL/g wet resin compared to the equilibrium capacity of 117 mg HCAL/g wet resin.

The stripping performance of the PVP (free-base) resin bed used in the column run of Fig. 9 is shown in Fig. 10. The concentration of NaOH in the stripping solution was fixed at less than the theoretical value calculated on the basis of a stoichiometric amount of NaOH for the sorbed HCAL and 1 BV. As can be seen from Fig. 10, HCAL has a sharper elution profile than the phenolic component (pectin concentration in the effluent, being very low, was not

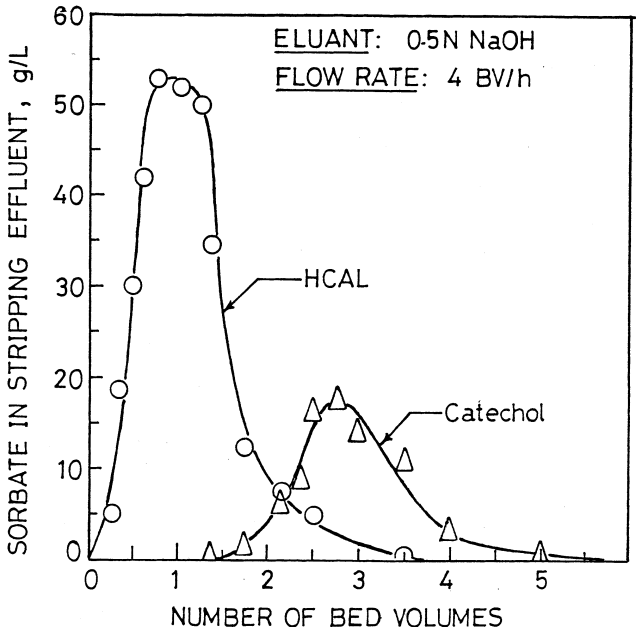


FIG. 10 Stripping of PVP (free-base) column after loading in column run of Fig. 9. (Bed volume = volume of resin bed.)

determined), with practically all the sorbed HCAL being eluted in 2 BV. The stripping produces a good separation of the two sorbates. The peak concentration of HCAL in the effluent is about 27 times the influent concentration, while the average concentration is about 13 times that of the influent (2 g/L).

CONCLUSIONS

The possibility of using poly(4-vinylpyridine) (PVP) for separation of hydroxycitric acid lactone (HCAL) from mixtures of polyhydroxyphenols and fruit pectins has been explored using catechol and pyrogallol as representative polyhydroxyphenols. PVP has been used in both free-base and protonated (salt) forms. The protonated form, used as PVP(HCl), has comparable saturation capacities for HCAL, catechol, and pyrogallol, the respective values being 354, 349, and 366 mg/g dry resin, while the saturation sorption of pectin is very low (96 mg/g dry resin). In contrast, PVP free-base resin has significantly higher sorption of HCAL than either catechol or pyrogallol, the respective saturation values being 576, 206, and 313 mg/g dry resin. While the saturation sorption capacity of PVP free-base resin for pectin (500 mg/g dry resin) is comparable to that for HCAL, at low concentrations (<1 g/L), however, HCAL has an order of magnitude higher sorption than pectin.

The sorption on PVP free-base resin decreases at lower pH values for all the sorbates. This may be attributed to the protonation of the $\geq$N sites in PVP which reduces sorption by acid–base interaction for HCAL, hydrogen bonding for phenols, and physical as well as acid–base interaction for pectin. Pectin is the most sensitive to pH of all the four sorbates, with sorption reduced nearly to zero at pH less than 1.7.

Selectivity of HCAL sorption relative to catechol and pyrogallol is poor on protonated PVP; the separation factor α_B^A (A = HCAL, B = other component of binary mixture) is less than 1 over a wide range of compositions including a B/A weight ratio of 1:1 in solution. The α_B^A value on PVP free base is, however, greater than 1 under comparable conditions and over a pH range of 1.6 to 2.3, reaching its maximum at pH 2. The α_B^A value for HCAL/pectin is comparable on protonated and free-base PVP resins, becoming infinite at pH $\approx$ 1.7 in both cases. However, because of HCALs greater selectivity relative to phenols on PVP free-base resins as compared to protonated PVP resins, an overall better separation of HCAL from phenols and pectin would be achieved on free-base PVP.

The macroporous PVP resin Reillex HP used in this study has reasonably fast kinetics with a $t_{1/2}$ value of about 5 minutes and 90–95% of the equilibrium sorption of HCAL attained in 30 minutes. The sorption kinetics is dependent on the sorbate concentration in solution and agrees well with a shell-core mechanism involving particle diffusion control, yielding an average $\lambda\overline{D}$ value (where λ is the molar distribution coefficient) of 5×10^{-6} cm^2/s, which

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

in view of λ being greater than 1 indicates a relatively high value of diffusion coefficient in the macroporous resin.

In column operation with an influent mixture of HCAL, catechol, and pectin, pectin breakthrough appears first, followed by catechol and HCAL, resulting in the column being loaded with HCAL in a significantly larger amount than both pectin and catechol. In column operation with the influent at pH 2.8, the breakthrough loading of HCAL is about 1.7 times that of catechol and 12 times that of pectin. The separation is further improved at a lower pH. With the influent at pH 1.7, the gap between HCAL and catechol breakthrough points increases by about 20%, while the large gap between HCAL and pectin remains essentially unaltered. The considerable difference in acidity between HCAL and phenols affords selective recovery of the sorbed HCAL by stripping with a limited volume of sodium hydroxide solution of a relatively low concentration.

ACKNOWLEDGMENTS

The financial support of research from the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged. We thank Dr. R. Seshadri, General Manager (R&D) of Natural Remedies Private Limited, Bangalore, India for a gift of *Garcinia cambogia* extracts (as calcium salt) and Reilly Industries, Indianapolis, USA, for a gift of Reillex HP resin which made this work possible.

REFERENCES

1. D. Tenney, *Garcinia Cambogia: Weight-Loss Wonder*; Woodland Publishing, Vermont, 1997.
2. D. Clouatre and M. Rosenbaum, *The Diet and Health Benefits of HCA* (*Hydroxy Citric Acid*), Keats Publishing, New Canaan, CT, 1994.
3. Y. S. Lewis and S. Neelakantan, *Phytochemistry 4*, 619 (1965).
4. A. K. Bhandari, (Indien Ayurherbs Pvt. Ltd., Bangalore, India), Private Communication, May 1998.
5. S. A. Moffett, A. K. Bhandari, and B. Ravindranath, US Patent (August 24, 1994).
6. M. Chanda, K. F. O'Driscoll, and G. L. Rempel, *Reactive Polym., 1*, 281 (1983).
7. M. Chanda, K. F. O'Driscoll, and G. L. Rempel, *Ibid., 4*, 39 (1985).
8. M. A. Jermyn, *Anal. Biochem., 68*, 332 (1975).
9. Z. Dische, *J. Biol. Chem., 167*, 189 (1947).
10. M. G. Chasanov, R. Kunin, and F. X. McGarvey, *Ind. Eng. Chem., 48*, 305 (1956).
11. F. G. Helfferich, *Ion Exchange*, McGraw-Hill, New York, NY, 1962.
12. M. Gopala Rao and A. K. Gupta, *AIChE Symp. Ser., 78*(219), 96, 103 (1982).
13. F. G. Helfferich and Y.-L. Hwang, "Ion Exchange Kinetics," in *Ion Exchangers* (K. Dorfner, Ed.), Walter de Gruyter, Berlin, 1991, p. 1277.
14. V. M. Bhandari, V. A. Juvekar, and S. R. Patwardhan, *Sep. Sci. Technol., 27*(8&9), 1043 (1992).

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

15. F. G. Helfferich, *J. Phys. Chem., 69*, 1178 (1965).
16. G. Schmuckler and S. Goldstein, "Interphase Mass Transfer Rates of Chemical Reactions with Cross-Linked Polystyrene," in *Ion Exchange and Solvent Extraction, Vol. 7*, (J. Marinsky and Y. Marcus, Eds.), Dekker, New York, NY, 1974, Chapter 1.
17. M. Chanda and G. L. Rempel, *Ind. Eng. Chem. Res., 33*, 623 (1994).
18. D. Petruzzelli, F. G. Helfferich, L. Liberti, J. R. Millar, and R. Passino, *Reactive Polym., 7*, 1 (1987).
19. D. Reichenberg and D. J. McCauley, *J. Chem. Soc.*, p. 2741 (1955).
20. E. Gluekauf, *Proc. R. Soc., A268*, 350 (1962).
21. M. Chanda and G. L. Rempel, *Reactive Polym., 18*, 141 (1992).

Received by editor February 10, 1999
Revision received September 1999

Request Permission or Order Reprints Instantly!