

## Adsorption of Flavonoids on Resins: Hesperidin

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Adsorption of hesperidin from aqueous solutions on styrene–divinylbenzene (SDVB) and acrylic resins was investigated at different pH values (1.5–5.5) and temperatures (10–40 °C). Adsorption was not affected by pH variation, whereas it increased on increasing temperature for the SDVB resins and remained substantially unchanged for the acrylic ones. The different behavior of the two types of resins was ascribed to the different wetting, because of their hydrophobic or partially hydrophilic properties, respectively. The equilibrium data at 20 °C were determined on 13 commercial resins displaying a wide range of surface areas ( $S_A$ , 330–1200 m<sup>2</sup>/g) and pore radii ( $P_R$ , 20–260 Å). Data were well fitted to the Freundlich isotherm, and its parameters were used to compare the adsorption capacity of different resins. The most effective resin is a SDVB copolymer with the largest  $S_A$  (1200 m<sup>2</sup>/g) and an intermediate  $P_R$  (90 Å). The Freundlich constants ( $K_F$ ) were rationalized in terms of a two parameter equation, including  $S_A$  and  $P_R$  as independent variables. The adsorption constant increased on increasing both  $S_A$  and  $P_R$  for the resins having  $P_R \leq 90$  Å; beyond this limit, the contribution of  $S_A$  was predominant and that of  $P_R$  was slightly negative.

**KEYWORDS:** Acrylic resins; adsorption; Freundlich isotherm; hesperidin; styrene–divinylbenzene resins

### INTRODUCTION

Flavonoids have found applications in food and pharmaceutical industries for their valuable properties (1–3), and adsorbent resins have been utilized to separate and concentrate these products from the natural matrixes (4–6). In particular, the high porous and low cost styrene-divinylbenzene copolymers (SDVB) have been employed for recovering hesperidin (7, 8) and anthocyanins (9) from byproducts of citrus processing and for purifying citrus juices (10–16) and aspartame (17).

Adsorption capacity of an adsorbate/adsorbent system cannot be easily predicted, because various interactions occur at the solid–liquid interface (hydrophobic, dipole–dipole, and hydrogen bonding). Physical properties of the resin (surface area, pore radius, and porosity) and chemical characteristics of the solution (solvent, pH, and temperature) can also play an important role in determining rates and equilibria of adsorption. In addition, the study of a multicomponent system requires the knowledge of each single component system. For these reasons, the adsorption mechanism of flavonoids on resins today remains largely unknown.

The present work reports experimental data on the batch equilibrium adsorption of hesperidin (the dominant flavanone of the orange fruit) from aqueous solutions at various pH values and temperatures, using several commercial polymers differing in chemical and physical properties. The objectives of this study are to compare the adsorption capacity of different resins in terms of Freundlich parameters and to correlate the constant

$K_F$  with the physical properties of the resin. The availability of reliable mathematical expressions describing the experimental system allows one to better assess the efficiency of commercial adsorbents used for separation, purification, and other industrial processes and makes its design more rational.

### EQUILIBRIUM MODELS

Kinetic measurements in batch experiments give accurate information that is isolated from the chromatographic and pseudo-equilibrium effects encountered in column studies (18). Basically, three consecutive steps describe the adsorption mechanism: (i) mass transfer of solute molecules from the solution to the sorbent particle surface; (ii) diffusion within internal structure to the sorption site; and (iii) rapid uptake. There are different opinions on the mode of intraparticle diffusion (step ii) that give rise to several mathematical models to describe the adsorption process. Kinetic studies describe the change of solute concentration as a function of time, and equilibrium data give information about the affinity between solute and adsorbent. The relationship between the concentration of solute in the solid and liquid phases at equilibrium is described by adsorption isotherms.

The simplest theoretical model used to describe monolayer adsorption is the Langmuir isotherm (18, 19). It assumes a uniform adsorbent surface with energetically identical sorption sites. The Langmuir equation is

$$q_s = \frac{K_L C_s}{1 + a_L C_s}$$

where  $q_s$  (mg/g) is the adsorbate concentration per unit of weight

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of adsorbent (solid phase),  $C_s$  (mg/L) is the concentration of adsorbate in solution (fluid phase) at equilibrium, and  $K_L$  (L/g) and  $a_L$  (L/mg) are the Langmuir constants.  $K_L$  reflects the solute adsorptivity, and  $a_L$  is the ratio between sorption and desorption rate constants.  $K_L/a_L$  (mg/g) is defined as the monolayer adsorbent capacity; in fact, when graphically plotted, this isotherm is characterized by a "plateau" that shows the monolayer adsorption implied by the energetically identical sites. The Langmuir isotherm well describes the adsorption data of gases on solid surfaces, but it is less accurate for equilibria involving the solid-liquid interfaces where adsorption continues beyond a monolayer.

The Freundlich isotherm is an empirical equation for nonideal adsorptions (18, 20). It describes the equilibrium conditions on heterogeneous surfaces and therefore does not assume the monolayer capacity. It is expressed by the formula below:

$$q_s = K_F C_s^{b_F}$$

where  $q_s$  and  $C_s$  are as defined above and  $K_F$  (L/g) and  $b_F$  (dimensionless) are the empirical constants dependent on several environmental factors;  $K_F$  provides an indication of the adsorption capacity of the adsorbent, and  $b_F$  represents the adsorption intensity. A larger value for  $b_F$  indicates a larger change in effectiveness over different equilibrium concentrations; when  $b_F$  is  $> 1$ , the change in adsorbed concentration is greater than the change in the solute concentration. This equation is usually applied in the linear form

$$\log q_s = \log K_F + b_F \log C_s$$

Plotting the equation on a log-log scale,  $K_F$  and  $b_F$  can be evaluated from the intercept and the slope, respectively.

## MATERIALS AND METHODS

Hesperidin (97% purity) for batch experiments and citric acid and potassium citrate monohydrate for buffer solutions were supplied by Sigma Aldrich (Milan, Italy); *N,N*-dimethylformamide was from Merck (Milan, Italy); 96% ethanol for resins activation was provided by Panreac Quimica (Barcelona, Spain).

The tested resins were Sepabeads SP-70, Relite EXA-31, EXA-32, EXA-45, EXA-50, EXA-90, EXA-117, EXA-118 (Resindion, Mitsubishi Chem. Co., Milan, Italy), and Amberlite XAD-2, XAD-4, XAD-7, XAD-16, XAD-1180 (Sigma Aldrich). Apart from EXA-31 and XAD-7, which are methacrylic and acrylic polymers, respectively, all other resins were SDVB copolymers. These resins may be used for the removal of organic substances from aqueous food under prescribed conditions of preparation and should be pretreated with water according to the manufacturer's recommendation to guarantee food grade purity at time of use, in accordance with current good manufacturing practice. The resins were characterized by a wide range of surface areas (330–1200 m<sup>2</sup>/g), pore radii (20–260 Å), and porosities (0.65–2.30 mL/g). Their chemical and physical properties, together with the European or FDA code of regulation, are shown in Table 1.

**Hesperidin Adsorption Studies.** All adsorption experiments were carried out utilizing weighed quantities of resins based on dry weight from each commercial lot. Such a quantity was previously determined by drying the beads at 70 °C up to constant weight in an electric oven for over 24 h and by putting them in a desiccator for cooling. The resins were activated by overnight treatment with 2 bed volumes (BV) of 96% ethanol and then rinsed with 5 BV of deionized water before use.

Different weighed quantities of hesperidin ranging from 35 to 170 mg were dissolved in the minimum quantity of *N,N*-dimethylformamide (7, 8) and diluted to 1 L with citric acid/citrate buffer solution at pH 3.5. The hesperidin solution was placed in a constant temperature bath at 20 ± 0.5 °C, and 1 g (dry basis) of pretreated resin was added under constant stirring at 300 rpm. Aliquots of 1 mL were drawn from the

**Table 1.** Chemical and Physical Properties of Resins Reported by Manufacturers

trade name	structure	surface area (m <sup>2</sup> /g)	pore radius (Å)	porosity (mL/g)	particle size (mm)	density (g/mL)	code of regulations
XAD-2	SDVB	330	45	0.65	0.25–0.84	1.08	a
XAD-7	acrylic	450	45	1.14	0.25–0.84	1.24	a
EXA-31	methacrylic	470	170	1.20	0.35	1.09	b
EXA-117	SDVB	570	80	1.10	0.25		b
XAD-1180	SDVB	600	150	1.68	0.25–0.84	1.04	a
EXA-32	SDVB	600	260	1.30	0.25	1.01	b
EXA-90	SDVB	630	105	1.30	0.25	1.18	b
SP-70	SDVB	700	65	1.10	>0.25	1.01	a
XAD-4	SDVB	725	20	0.98	0.25–0.84	1.02	a
XAD-16	SDVB	800	50	1.82	0.25–0.84	1.08	a
EXA-45	SDVB	1000	38	1.20	0.25	1.01	b
EXA-50	SDVB	1000	57	1.40	0.25	1.01	b
EXA-118	SDVB	1200	90	2.30	0.25	1.04	b

<sup>a</sup> Council of Europe, Resolution AP (97) 1 on Ion Exchange and Adsorbent Resins used in the Processing of Foodstuffs, adopted by the Committee of Ministers on 30 September 1997. <sup>b</sup> U.S. Food and Drug Administration, Code of Federal Regulation Title 21—Food and Drugs—Revised as of April 1, 2002. Part 173.65: divinylbenzene copolymers. Part 173.5: acrylic resins.

**Table 2.** Freundlich Parameters Obtained from  $q_s$  and  $C_s$  Values at 150 and 200 min of the Run

calculated constants <sup>a</sup>	at 150 min	at 200 min	Δ %
	XAD-4		
$K_F$	1.93	2.07	6.8
$b_F$	0.457	0.467	2.1
	EXA-118		
$K_F$	42.15	41.64	-1.2
$b_F$	0.288	0.306	-5.9
	XAD-16		
$K_F$	22.40	23.40	4.3
$b_F$	0.294	0.275	-6.5

<sup>a</sup> From six to seven experiments were carried out at different initial concentrations of hesperidin.

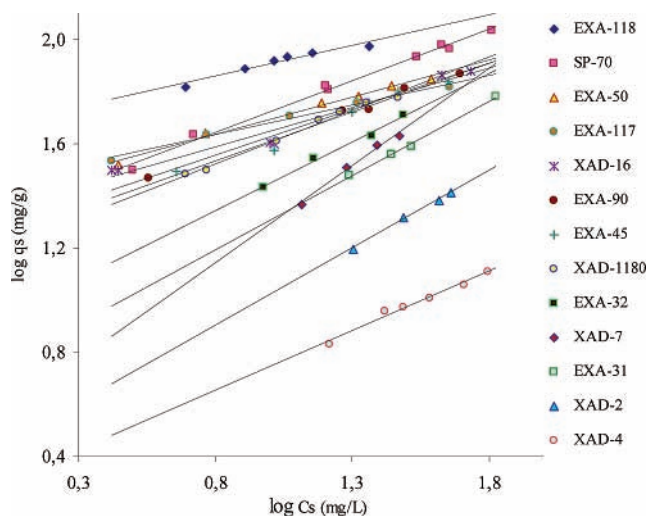
batch periodically, and the hesperidin concentrations in the aqueous solution were determined by UV spectrophotometry at 283 nm (Shimadzu UV 2401) using a calibration line. The resin phase concentration of hesperidin was estimated by mass balance according to the following equation:

$$q_t = \frac{(C_0 - C_t)V}{m}$$

where  $q_t$  is the quantity (mg) of hesperidin adsorbed at time  $t$  onto a unit amount (g) of dry resin,  $C_0$  and  $C_t$  are the concentrations of hesperidin in the aqueous solution (mg/L) at the initial stage and at  $t$  time,  $V$  is the volume of the solution (L), and  $m$  is the amount (g) of adsorbent.  $q_t$  and  $C_t$  values at equilibrium are the  $q_s$  and  $C_s$  values used in the Freundlich isotherm. It usually took approximately 150–200 min for the adsorption to reach equilibrium. In some cases, precipitation of hesperidin was observed over 160 min of contact time. Therefore, the batch equilibrium tests were run for 150 min, when the hesperidin concentration into solution usually varied less than 2% per a quarter of an hour. However, where it was possible to calculate Freundlich parameters at 200 min of run, the difference in the calculated  $K_F$  and  $b_F$  values was negligible as well as for the resins at achieving slowest equilibrium (Table 2).

Hesperidin adsorption data on some resins were also determined at different resin amounts (0.5, 1, and 1.5 g/L), temperatures (10, 20, 30, and 40 °C), and pH values (1.5, 2.5, 3.5, 4.5, and 5.5). Each experiment was carried out in duplicate. A control sample was employed to monitor any change in the initial concentration values, to exclude effects on measured absorbance.

**Microscope Observations.** Hesperidin solution microdrops together with some beads of activated XAD-16 and EXA-31, taken as models of SDVB and acrylic resins, respectively, were observed under an



**Figure 1.** Linearized Freundlich adsorption isotherms at 20 °C and experimental equilibrium data.

**Table 3.** Freundlich Parameters at pH 3.5 and 20 °C for Different Resins<sup>a</sup>

trade name	no. of experiments	$K_F$ (L/g)	$b_F$ (dimensionless)	$r^2$
XAD-2	4	2.66	0.594	0.998
XAD-7	4	3.52	0.744	0.989
EXA-31	4	5.45	0.569	0.997
EXA-117	5	28.24	0.228	0.991
XAD-1180	7	15.71	0.407	0.989
EXA-32	4	8.42	0.523	0.995
EXA-90	5	18.66	0.353	0.991
SP-70	8	23.46	0.366	0.997
XAD-4	6	1.93	0.457	0.983
XAD-16	7	22.40	0.294	0.970
EXA-45	6	18.27	0.357	0.990
EXA-50	6	25.46	0.286	0.992
EXA-118	6	42.15	0.288	0.998

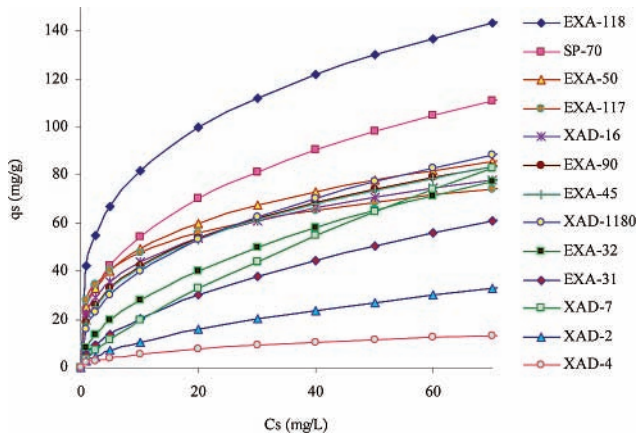
<sup>a</sup> The mean standard error does not exceed  $\pm 6\%$  of the estimate.

optical microscope (Olympus B 201: Camera DP10, Plan 10x/0.25 Ph1; Japan) to verify the occurrence of different wetting on increasing the temperature from 20 to 40 °C.

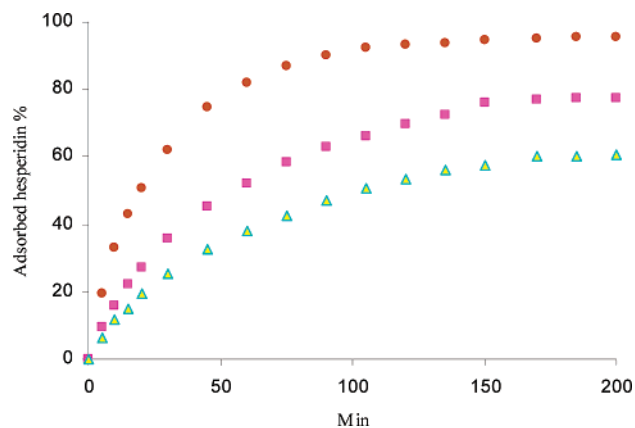
**Statistical Analyses.** Simple and multiple regressions of  $K_F$  values (the dependent variable) against the  $S_A$  or/and  $P_R$  values (the independent variables) were performed using "Statgraphic Plus" software for Windows 98 (Manugistic Inc., Rockville, MD); the coefficients of variables and the constant term were obtained, together with standard errors, correlation coefficients,  $P$  values, and  $F$  test values.

## RESULTS AND DISCUSSION

**Application of the Freundlich Model to Hesperidin Adsorption.** The Freundlich isotherm is perhaps the most popular adsorption model for a single solute system, and it has been used in several studies to compare the adsorption of commercial resins (21) and activated carbons (22). The linearized Freundlich adsorption isotherms of resins obtained from the  $q_s$  and  $C_s$  values at 20 °C and pH 3.5 are given in **Figure 1**. The adsorption constants  $K_F$  and  $b_F$  together with the correlation coefficients are listed in **Table 3**. The high correlations showed that the model is very suitable for describing the tested adsorption system in the studied concentration range. To compare different resins, usually the one with the highest amount of solute adsorbed ( $q_s$ ) at a specified residual concentration ( $C_s$ ) would be preferred for the particular application. The amount of hesperidin adsorbed (mg/g) at different  $C_s$  was calculated on the basis of the constants given in **Table 3** for each resin. The resulting curves (**Figure 2**) show that EXA-118 has greater



**Figure 2.** Adsorption equilibrium curves calculated on the basis of the Freundlich constants at 20 °C.



**Figure 3.** Adsorption kinetics of hesperidin on XAD-16 (pH 3.5, 20 °C) at different resin concentrations: 0.5,  $\Delta$ ; 1,  $\blacksquare$ ; and 1.5 g/L,  $\bullet$ .

$q_s$  values than the other resins at all hesperidin residual concentrations and is the most appropriate one for removing hesperidin from aqueous solutions. The least effective resin in hesperidin removal is XAD-4. XAD-7 resin, with the greater  $b_F$  value, shows a low efficiency for removing trace amounts of hesperidin, but it has an intermediate adsorption capacity at higher  $C_s$  values.

**Effects of Resin Amount, pH, and Temperature.** The effect of the resin amount from 0.5 to 1.5 g/L was tested on XAD-16 resin at a constant concentration of hesperidin ( $C_0$ ,  $50.1 \pm 0.6$  mg/L). **Figure 3** shows the adsorption kinetics performed at pH 3.5 and 20 °C. The kinetic and equilibrium data increase as the concentration of adsorbent increases. In particular, adsorption onto 0.5 g/L is 60.5% at equilibrium, while onto 1.0 and 1.5 g/L the percentages of adsorption increase to 77.5 and 95.5%, respectively. Increasing the resin dosage of 0.5 g, hesperidin removal increases by 17.5 percentage points.

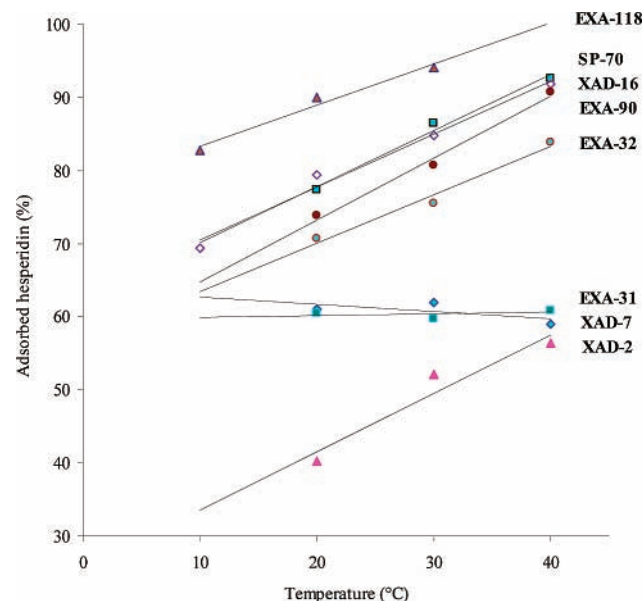
Some experiments were performed at different pH values ranging from 1.5 to 5.5 at 20 °C; the tested resins were a SDVB polymer (XAD-16) and a methacrylic one (EXA-31). The equilibrium data are summarized in **Table 4**. Kinetics on XAD-16 were carried out using  $121.5 \pm 0.1$  mg/L of hesperidin, while for experiments on EXA-31 an initial concentration of hesperidin of  $48.1 \pm 1.5$  mg/L was chosen; in both cases, 1 g/L of resin was used. The mean value for adsorbed hesperidin at equilibrium is 70.2% for XAD-16 and 61.2% for EXA-31. Kinetics appear to be superimposable for each resin, and equilibrium data show no effect on adsorption by changing pH.

Equilibria of adsorption for six SDVB (XAD-2, EXA-32, EXA-90, XAD-16, SP-70, and EXA-118) and two acrylic

**Table 4.** Adsorption of Hesperidin on XAD-16 and EXA-31 Resins at Various pH Values and 20 °C<sup>a</sup>

pH	XAD-16 <sup>b</sup>			EXA-31 <sup>c</sup>		
	$q_s$ (mg/g)	$C_s$ (mg/L)	adsorption (%)	$q_s$ (mg/g)	$C_s$ (mg/L)	adsorption (%)
1.5	85.8	35.7	69.5	29.5	18.2	61.8
2.5	86.5	35.0	71.2	28.3	17.7	61.7
3.5	83.1	38.5	68.3	29.9	19.5	60.5
4.5	83.7	37.8	68.9	30.4	19.4	61.0
5.5	89.2	32.4	73.3	28.9	18.4	61.2
mean <sup>d</sup>	85.6 (2.4)	35.9 (2.4)	70.2 (2.0)	29.5 (0.7)	18.6 (0.8)	61.2 (0.5)

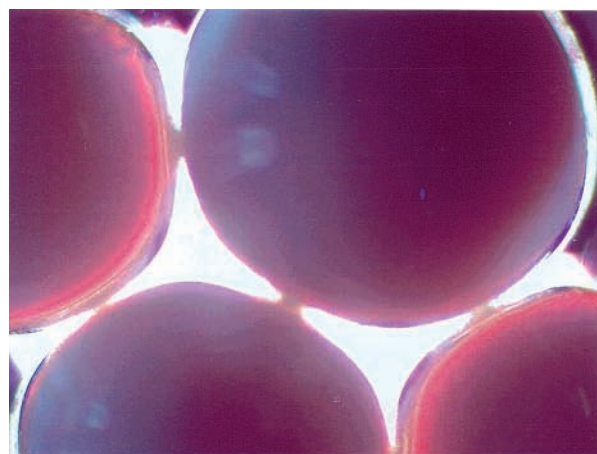
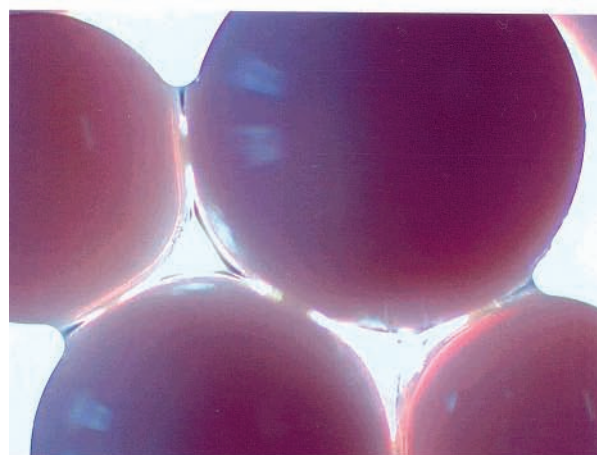
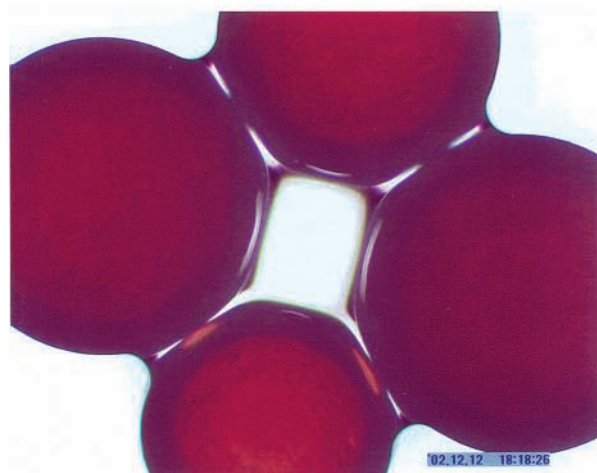
<sup>a</sup> Resin, 1 g/L. <sup>b</sup>  $C_0$ , 121.5 ± 0.1 mg/L. <sup>c</sup>  $C_0$ , 48.1 ± 1.5 mg/L. <sup>d</sup> Standard deviation in parentheses.

**Figure 4.** Effect of temperature on hesperidin adsorption at equilibrium for different resins.

(XAD-7 and EXA-31) resins were investigated at different temperatures (10–40 °C). Hesperidin solutions of 49.5 ± 2.2 mg/L and 1 g/L of activated resin were used, except for the resin EXA-118 where the initial concentration was higher (85.3 ± 2.6 mg/L) to avoid the total hesperidin removal. Results (Figure 4) show that for SDVB resins the percentage of adsorption at equilibrium increases with increasing temperature, whereas no effect is shown by the acrylic resins, which adsorb about 60% of hesperidin at all investigated temperatures.

Positive effects of temperature on equilibrium data were reported for the adsorption of dark compounds from clarified peach juice onto various kinds of activated carbon (23) and for the removal of phenol compounds from apple juices onto a SDVB resin (24). Negative effects of temperature were also reported (17, 25, 26) and explained with the greater mobility of the molecules and the major desorption of those previously adsorbed.

The different effects of temperature on adsorption observed for SDVB and acrylic resins could be ascribed to the different hydrophobicities of the two types of resin; the former is strongly hydrophobic because of its hydrocarbon structure, and the latter is partially hydrophilic due to the presence of polar carboxylic ester groups. An increase in temperature lowers the surface tension at the hydrophobic interface; consequently, the resin wetting increases, thus increasing the solute transfer from the boundary fluid layer to the solid phase. Instead, an increase in temperature in a fully wetted resin does not produce any

**A)** XAD-16 (SDVB) resin at 20°C:  
major surface tension, minor wetting.**B)** XAD-16 (SDVB) resin at 40°C:  
minor surface tension, major wetting.**C)** EXA-31 (acrylic) resin at 20°C and 40°C:  
low surface tension, high wetting.**Figure 5.** Photographs under optical microscope (×100) of XAD-16 and EXA-31 beads in the presence of aqueous solution of hesperidin at pH 3.5.

appreciable difference in the transfer of adsorbate. The increased wetting of hydrophobic XAD-16 resin from 20 to 40 °C was directly observed under an optical microscope (Figure 5A,B);

**Table 5.** Correlation Analysis of  $K_F$  Values by the Equation  $Z = aX + bY + c^a$ 

relationship Nr	Z	X	Y	no. of observations	coefficient of variables				constant term		R	$R^2$ (%) <sup>b</sup>	F test
					a (SE)	P value	b (SE)	P value	c (SE)	P value			
1	$K_F$	$S_A$		13	0.036 (0.011)	0.0038			-8.43 (7.24)	0.2687	0.741	50.8	13.4
2	$K_F$		$P_R$	13			-0.018 (0.054)	0.7462	18.24 (5.95)	0.0107	-0.100	-8.01	0.11
3	$K_F$	$S_A$	$P_R$	13	0.037 (0.011)	0.0058	0.012 (0.039)	0.7566	-10.1 (9.1)	0.2961		46.4	6.20
4	$K_F$		$P_R$	9 <sup>c</sup>			0.544 (0.124)	0.0032	-11.0 (7.22)	0.1732	0.855	69.4	19.2
5	$K_F$		$P_R$	5 <sup>d</sup>			-0.155 (0.087)	0.1726	42.1 (14.4)	0.0617	-0.717	35.3	3.2
6	$K_F$	$S_A$		9 <sup>c</sup>	0.035 (0.013)	0.0291			-7.62 (10.2)	0.4787	0.719	44.8	7.49
7	$K_F$	$S_A$		5 <sup>d</sup>	0.049 (0.007)	0.0058			-16.3 (5.2)	0.0510	0.971	92.5	50.2
8	$K_F$	$S_A$	$P_R$	9 <sup>c</sup>	0.024 (0.004)	0.0009	0.446 (0.053)	0.0002	-24.0 (3.65)	0.0006		94.9	76.0
9	$K_F$	$S_A$	$P_R$	5 <sup>d</sup>	0.042 (0.004)	0.0098	-0.056 (0.018)	0.0879	-2.54 (5.1)	0.6677		98.1	104.5

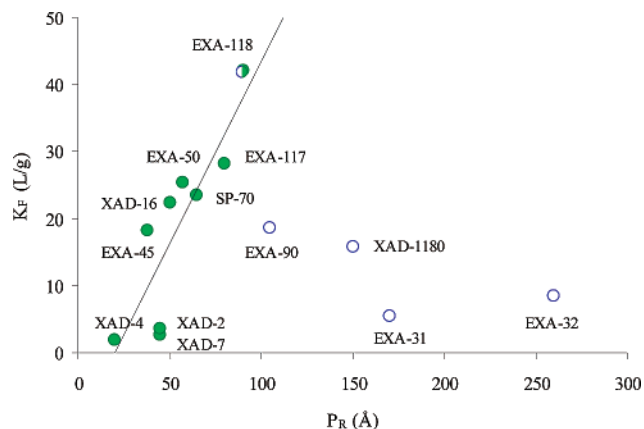
<sup>a</sup> SE, standard error of estimate. <sup>b</sup> Square of correlation coefficient adjusted for freedom degrees. <sup>c</sup> Resins having  $P_R \leq 90$  Å. <sup>d</sup> Resins having  $P_R \geq 90$  Å.

however, no change of wetting occurred for the partially hydrophilic EXA-31 resin (Figure 5C).

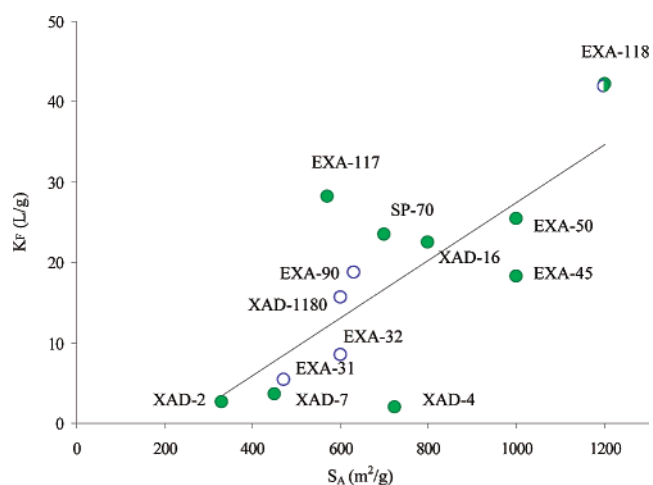
**Correlation Analyses of Freundlich Constant  $K_F$ .** The reasons for the differences in hesperidin adsorption among the tested resins are complex and not well-understood. In general, adsorption involves the accumulation of molecules from a solution onto the exterior and interior surface of an adsorbent. These phenomena are manifestations of various interactions among the three components involved, i.e., the adsorbent, the adsorbate, and the solvent. For hydrophobic compounds such as hesperidin, the amount of surface area associated with the resin may be important because hesperidin has low solubility in aqueous solutions and tends to be pushed from solution to the adsorbent surface. The most effective resin for hesperidin adsorption (EXA-118) has the highest surface area as compared to the other ones. On the other hand, the resin exhibiting the lowest hesperidin adsorption has the smallest pore radius. It is reasonable to expect a correlation between the Freundlich coefficients and the physical properties of the resins. We focused on the relationship between the resin properties ( $S_A$  and  $P_R$ ) and the Freundlich constant  $K_F$  that is related to the adsorption capacity.

The sequence of  $K_F$  values follows strictly neither  $S_A$  nor  $P_R$  values. In fact, the resins EXA-117, EXA-90, XAD-1180, and EXA-32, with the same  $S_A$  ( $600 \pm 30$  m<sup>2</sup>/g) and variable  $P_R$  (80–260 Å), show  $K_F$  decreasing on increasing  $P_R$  values. Moreover, the resins EXA-45 and EXA-50 with an  $S_A$  value of 1000 m<sup>2</sup>/g show  $K_F$  increasing on increasing  $P_R$  values from 38 to 57 Å. These findings suggest that a combination of both  $S_A$  and  $P_R$  variables plays an important role in determining  $K_F$  constants. To rationalize the data set and establish the relative importance of each parameter, a series of simple and multiple regressions was performed using  $S_A$  and/or  $P_R$  as independent variables. The porosity value (Table 1) was not considered as an independent variable because it is linearly related with  $S_A$  values ( $R$ , 0.678;  $P < 0.05$ ), while  $S_A$  and  $P_R$  are not collinear. The results are reported in Table 5.

The relationship Nr 1 shows the linear correlation between  $K_F$  and  $S_A$  using the data of all resins, but it explains only 50.8% of variance; moreover, the standard errors of the variable coefficient and the constant term appear to be unsatisfactory. The corresponding correlation between  $K_F$  and  $P_R$  is not significant (relationship Nr 2), and the introduction of both  $S_A$  and  $P_R$  in the regression makes all statistical parameters worse (relationship Nr 3) as compared to the simple correlation with  $S_A$ ; in particular, the  $P_R$  coefficient is substantially zero, and consequently, it should be removed from the statistical model. This result conflicts with the already indicated influence of  $P_R$ . The plot of  $K_F$  against  $P_R$  (Figure 6) roughly suggests two different trends: the first for those resins having  $P_R \leq 90$  Å,

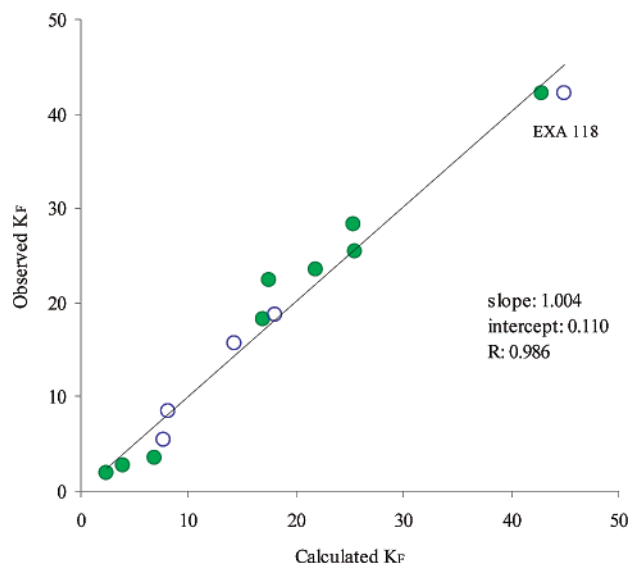


**Figure 6.** Plot of  $K_F$  values at 20 °C against pore radius of resins. Resins having  $P_R \leq 90$  Å, ●; and resins having  $P_R \geq 90$  Å, ○.



**Figure 7.** Plot of  $K_F$  values at 20 °C against surface area of resins. Resins having  $P_R \leq 90$  Å, ●; and resins having  $P_R \geq 90$  Å, ○.

where a significant correlation with positive slope occurs (relationship Nr 4), and the second for those having  $P_R \geq 90$  Å, where the correlation is not significant (relationship Nr 5). The same regressions performed with  $S_A$  (Figure 7) show a low correlation for  $P_R \geq 90$  Å resins (relationship Nr 6) and a fair correlation for those at  $P_R \leq 90$  Å (relationship Nr 7). These single parameter regressions have high standard errors, while the corresponding two parameter regressions (relationships Nr 8 and 9) give the best statistical parameters, explaining 94.9 and 98.1% of  $K_F$  variance in both groups of resins, respectively. In particular, the coefficient of  $S_A$  is always positive, whereas that of  $P_R$  is positive in the first group of resins and slightly negative in the second one. Therefore, the tested resins seem



**Figure 8.** Plot of observed and calculated  $K_F$  values at 20 °C. Resins having  $P_R \leq 90 \text{ \AA}$  (slope, 1.007; intercept, 0.201), ●; and resins having  $P_R \geq 90 \text{ \AA}$  (slope, 0.997; intercept, -0.056), ○.

to act upon a different mechanism, depending on  $P_R$  value. Probably, desorption of hesperidin increases in the resins having  $P_R \geq 90 \text{ \AA}$ , thus lowering the resin adsorption capacity; the negative  $P_R$  coefficient supports this hypothesis. **Figure 8** shows the plot of the observed  $K_F$  against the calculated  $K_F$  on the basis of the following two parameter equations:

$$K_F = 0.024 S_A + 0.446 P_R - 24.0 \quad (\text{for resins having } P_R \leq 90 \text{ \AA})$$

$$K_F = 0.042 S_A - 0.056 P_R - 2.54 \quad (\text{for resins having } P_R \geq 90 \text{ \AA}).$$

The slope obtained is 1.004, and the intercept is very low, showing an excellent fitting of the measured and predicted Freundlich constants, pointing out the strongly predictive value of the proposed model for hesperidin removal.

## CONCLUSIONS

The adsorption equilibria of hesperidin on 13 commercial resins have been studied at 20 °C, and the experimental data were well-fitted to the Freundlich isotherm in the studied concentration range, predicting the capacity of the resins with high accuracy. The SDVB EXA-118, having the highest surface area and a pore radius of 90 Å, proved to be the most efficient among the tested resins for removing hesperidin from aqueous solutions at all residual equilibrium concentrations. Moreover, experimental data have shown that an increase in temperature further increases the hesperidin removal only for the SDVB resins, because of the lowering of the surface tension at the hydrophobic interface. Correlation analysis has demonstrated that the  $K_F$  constant depends on the physical characteristics of the resin. The  $K_F$  constant linearly increases with the increase of the surface area and the pore radius of resins up to a limit value of 90 Å, while beyond this limit the contribution of  $P_R$  is slightly negative.

Although this study focused on the relationship between the resin properties and the Freundlich constant  $K_F$  for the adsorption of hesperidin, the proposed procedure may be applicable to other flavonoids such as anthocyanins (27). This relationship makes it easier to study the adsorption profile of a specific adsorbent/

adsorbate system and can be of help in selecting suitable adsorbents for various processes.

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