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Extractive recovery of *p*-coumaric acid using natural and conventional organic solvents

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p-Coumaric acid is usually found in effluent from olive oil, pulp-paper and winery industries. It degrades slowly and deteriorates the fertility of soil. On the other hand, it has exceptional medicinal properties and has wide application in health, food, and pharmaceutical industries. In this work physical extraction has been carried out with two natural solvents, rice bran oil and soybean oil and two conventional organic solvents, 1-octanol and *p*-ether. To identify the suitable solvent, partition coefficient (*P*), distribution coefficient (K_d), dimerization constant (*D*) and extraction efficiency (*E*%) have been investigated and compared. The results showed that 1-octanol is the most effective solvent with extraction efficiency and distribution coefficient being 43.1% and 0.93, respectively.

Keywords: Phenolic acids, reactive extraction, partition coefficient, dimerization constant, extraction efficiency.

Introduction

p-Coumaric acid being a hydroxycinnamic acid, subgroup of phenolic acids, has an important role in human immune regulations. *p*-Coumaric acid is phenolic acid, present in various food items and possesses different physiological properties like antioxidant, anti-allergic, anti-cancerous, anti-microbial, anti-inflammatory etc.[1]. The studies have confirmed its protective effect in doxorubicin-induced oxidative stress in rats and also formation of ultra-violet B induced oxidative damage in SIRC cells[2]. It has many uses in pharmaceutical, cosmetic, chemical, food and health industries[3]. *p*-Coumaric acid could be obtained either from plant source directly, chemical synthesis or bio-synthesis. Direct extraction from the plant source is difficult whereas bio-synthesis is economic and can be used to fulfill the demand of the acid as it has vivid applications. *p*-Coumaric acid is present in effluent from paper, olive oil, grapes-based wine industry[4,5]. Its degradation is very slow and hence it stays for long time in the soil. The untreated effluent discharged over a land severely damages the fertility of soil[6,7]. Hence, removal of *p*-coumaric acid not only provides a valuable product, because of its physiological properties, but also mitigates soil pollution.

Among various separation techniques, reactive extraction is energy incentive and convincing technique for the efficient separation, especially from the dilute solutions[8]. Reactive extraction is a proven technique for effective extraction of carboxylic acids such as, lactic, picolinic, glycolic, phosphoric, itaconic acid[9–13] and phenolic acids like gallic acid, 4-hydroxy benzoic acid[14,15]. The technique uses three different types of extractants, the oxygen donor extractants namely carbon bonded and phosphorous bonded and the aliphatic amine extractant and the diluents, polar protic, dipolar aprotic and non-polar[16].

Exploring the different physical extraction parameters helps in finding the suitable and most efficient diluents for the particular solute. In this context, two conventional solvents; 1-octanol and *p*-ether; and two natural solvents; rice bran and soyabean oil have been used and the physical parameters were explored experimentally to identify the suitable solvent among them.

Experimental

The laboratory grade *p*-coumaric acid (98% pure) was acquired from Sigma Aldrich and its solution of different concentrations (0.45–0.731 mmol/lit) was prepared using distilled water. 10 ml of this solution was mixed with an equal amount of solvent in a 100 ml volumetric flask and kept in orbital shaker (Remi, India) for 4 h at 303±1 K and atmospheric pressure. The chemical solvents (1-octanol 98% pure, *p*-ether 98% pure) were purchased from Merck, India. After, the mixture was centrifuged for 5 min for the effective separation of two phases. The phase volume was checked and found no change. The aqueous and organic phase was separated and the concentration of solute in aqueous phase was determined through titration. The solute in organic phase was determined through mass balance. For the maximum recovery of unionized acid molecules by extraction, the solutions of pH less than the pK_a value (= 4) of acid were made. Method of titration with standardized NaOH solution (0.0007 *N*) was adopted for the analysis. The reproducibility and reliability of the experiments was found within ±2%.

Theory of extraction:

The complete extraction mechanism can be divided into three steps[16,17];

(i) acid dissociation in aqueous phase

$$HP \overset{k_{HP}}{\longleftrightarrow} H^+ + P^-$$

$$k_{HP} = \frac{[H^+][P^-]}{[HP]} \qquad (1)$$

where HA is the *p*-coumaric acid concentration.

(ii) undissociated acid partition between extract (organic) phase and aqueous phase

$$[HP]_{aqu} \overset{P}{\longleftrightarrow} [HP]_{ex}$$

$$P = \frac{[HP]_{ex}}{[HP]_{aqu}} \qquad (2)$$

where $[HP]_{aqu}$ and $[HP]_{ex}$ are the concentration, in mmol/lit, of *p*-coumaric acid in aqueous phase and extract phase, respectively.

(iii) dimerization of acid in extract phase.

$$2[HP]_{aqu} \overset{D}{\longleftrightarrow} [HP]_{2.ex} \qquad (3)$$

$$D = \frac{[HP]_{2.ex}}{[HP]^2_{aqu}} \qquad (4)$$

The overall distribution coefficient.

$$K_D = \frac{P + 2P^2 D[HP]_{aqu}}{1 + {k_{HP}}/{[H^+]}} \qquad (5)$$

For the dilute solution of pH value of solute, the denominator can be taken as unity and becomes–

$$K_D = P + 2P^2D \qquad (6)$$

Results and discussion

The extraction equilibrium of the *p*-coumaric acid was plotted for two natural diluents and two conventional diluents (Fig. 1). The plot between concentrations of aqueous and extract (organic) phase shows that for lower concentrations it obeys the Henry's law but at higher concentrations it deviates, as it can be seen that linearity diminishes[17].

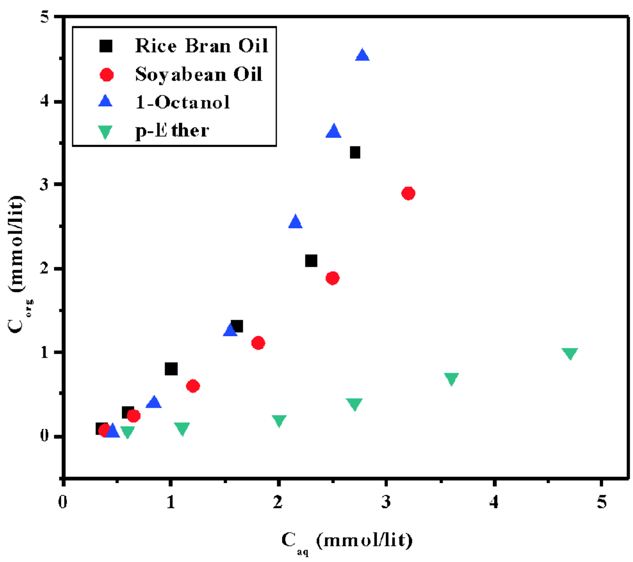

Fig. 1. Extraction equilibrium for recovery of *p*-coumaric acid using different solvents.

The average K_d and *E*% for rice bran oil, soyabean oil, 1-octanol and *p*-ether are 0.76, 41.45%; 0.56, 34.29%; 0.93, 43.1% and 0.14, 12%, respectively (Table 1). This variation in the values of K_d and *E*% owes to different physical properties of solvents like permeability, dipole moment, viscosity, density etc. Natural solvents being non-polar yield less ex-

Table 1. Extraction results for *p*-coumaric acid with different solvents (natural and conventional organic solvents)

Diluents	C_0 (mmol/lit)	C_{aq} (mmol/lit)	C_{org} (mmol/lit)	K_d	$K_{d\,avg}$	$E\%$	$E\%_{avg}$	P	D (lit/mmol)	R^2
Rice bran oil	0.45	0.35	0.10	0.29	0.76	22.22	41.45	0.28	2.10	0.84
	0.90	0.60	0.30	0.50		33.33				
	1.80	1.00	0.80	0.80		44.44				
	2.92	1.60	1.32	0.83		45.21				
	4.40	2.30	2.10	0.91		47.73				
	6.10	2.70	3.40	1.26		55.74				
Soyabean oil	0.45	0.38	0.07	0.18	0.56	15.56	34.29	0.17	4.00	0.95
	0.90	0.65	0.25	0.38		27.78				
	1.80	1.20	0.60	0.50		33.33				
	2.92	1.80	1.12	0.62		38.36				
	4.40	2.50	1.90	0.76		43.18				
	6.10	3.20	2.90	0.91		47.54				
1-Octanol	0.50	0.46	0.04	0.08	0.93	7.60	43.10	0.77	0.32	0.85
	1.23	0.84	0.39	0.46		31.70				
	2.79	1.55	1.24	0.80		44.40				
	4.70	2.16	2.54	1.18		54.00				
	6.13	2.51	3.62	1.44		59.10				
	7.32	2.78	4.54	1.63		62.00				
p-Ether	0.65	0.60	0.05	0.08	0.14	7.69	12.00	0.05	7.00	0.90
	1.20	1.10	0.10	0.09		8.33				
	2.20	2.00	0.20	0.10		9.09				
	3.10	2.70	0.40	0.15		12.90				
	4.30	3.60	0.70	0.19		16.28				
	5.70	4.70	1.00	0.21		17.54				

C_0 – Initial concentration, mmol/lit; C_{aq} – concentration of aqueous phase, mmol/lit; C_{org} – concentration of organic phase, mmol/lit; P – partition coefficient; K_d – distribution coefficient; D – dimerization constant and $E\%$ – extraction efficiency.

traction, so the K_d value comes to be less than one. Other than their non-polarity, the reason behind the less extraction with the oils may be the lower percentage of arachidic acid, linolenic acid, behenic acid. Moreover, rice bran oil (dielectric constant 3.6) has more permeability compared to soyabean oil (dielectric constant 3.1) hence, it shows more extraction efficiency. 1-Octanol being polar and having high permeability (dielectric constant 10.3), dipole moment 1.68, solvent polarity parameter 48.3, shows the highest extraction. The physical extraction parameters, partition coefficient (P) and dimerization constant (D) were obtained from the linear plot of eq. (6) as intercept and slope respectively.

Conclusion

Extraction of *p*-coumaric acid using two natural and two conventional organic solvents was studied in this work. Different extraction parameters were determined. Among the four solvents, 1-octanol showed the highest extraction. The oils showed less extraction but still they can be recommended because of their non toxicity. The performance of solvents depends on different physical properties, as discussed above, but for some generalization the study of more solvents is warranted.

References

1. N. Balasundram, K. Sundram and S. Samman, *Food Chem.*, 2006, **99(1)**, 191.
2. K. Pei, J. Ou, J. Huang and S. Ou, *J. Sci. Food Agric.*, 2016, **96**, 2952.
3. N. Kumar and N. Goel, *Biotechnol. Rep.*, 2019, **24**, e00370.
4. P. B. Dhamole, S. Chavan, R. G. Patil, H. Feng, M. Bule and P. Kinninge, *Korean J. Chem. Eng.*, 2016, **33(6)**, 1860.

5. M. Ahmedi, M. Mohseni and F. Vahabzadeh, *Iran. J. Chem. Eng.,* 2008, **5(4)**, 23.
6. R. Borja, B. Rincón, F. Raposo, J. Alba and A. Martín, *Biochem. Eng. J.*, 2003, **15(2)**, 139.
7. C. M. L. Santos, M. R. C. Ismael, M. L. F. Gameiro and J. M. R. Carvalho, *Solvent Extr. Ion Exc.*, 2005, **23(2)**, 213.
8. D. Datta, S. Kumar and H. Uslu, *J. Chem.*, 2015, **2015**, 1.
9. K. L. Wasewar, *Chem. Biochem. Eng. Q.*, 2005, **19**, 159.
10. M. D. Waghmare, K. L. Wasewar, S. S. Sonawane and D. Z. Shende, *Sep. Purif. Technol.*, 2013, **120**, 296.
11. D. Datta and S. Kumar, *Int. J. Chem. Eng. Appl.,* 2012, **3(2)**, 141.
12. K. L. Wasewar, D. Shende and A. Keshav, *Ind. Eng. Chem. Res.,* 2011, **50(2)**, 1003.
13. B. Mizzi, M. Meyer, L. Prat, F. Augier and D. Leinekugel-Le-Cocq, *Chem. Eng. Process.*, 2017, **113**, 20.
14. N. Joshi, A. Keshav and A. K. Poonia, *J. Chem. Eng. Data*, 2019, **64(6)**, 2826.
15. A. I. Galaction, M. Camarut and D. Cascaval, *Environ. Eng. Manag. J.,* 2008, **7(2)**, 89.
16. A. S. Kertes and C. J. King, *Biotechnol. Bioeng.*, 1986, **28(2)**, 269.
17. B. S. De, K. L. Wasewar and V. Dhongde, *Chem. Data Coll.*, 2018, **15**, 244.