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RECOVERY OF PHENOLS
FROM OLIVE-OIL WASTEWATER

The purpose of this work was to verify the application of adsorption process in removing phenols' compounds from wastewater produced by olive-crushers.

The removal of phenols was important in order to assure good performances of the RO Membranes in the last stage of the treatment system based on the crossflow ultrafiltration of the wastewater followed by the reverse osmosis of the sorption effluent.

1. INTRODUCTION

In studying a method of disposal of wastewater produced by olive crushers, we adopted a separation system employing ultrafiltration (UF) and reverse osmosis (RO) membranes designed to recover valuable materials contained in water. It was essential to remove phenolic compounds in order to assure proper performance of the RO membranes in the last stage of pollution reduction [1]–[2].

The process is based on the following operations: (i) crossflow UF of the wastewater, (ii) sorption of the UF permeate on porous polymers, (iii) crossflow reverse osmosis of the sorption effluent.

The different methods of removing phenols from the wastewater produced by the food and agricultural industries can be roughly classified into two groups: (i) destruction methods and (ii) removal and recovery methods. Methods of the first group include microbiological degradation, oxidation with ozone, chlorine, and sodium hypochlorite, electrolytic oxidation and catalytic oxidation in the aqueous phase [3]–[6]. To non-destructive methods belong dialysis-based ones, extraction

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with solvent, and polymer or non-polymer based adsorption [7]–[9]. The use of exchange/adsorption resins has proved to be a promising method in the case of strong-base and weak-base anion exchange resins, macroporous styrene-divinyl-benzene copolymers without functionality, vinyl-pyridine-divinyl-benzene copolymer and polybenzimidazole [10]–[12]

We envisioned the recovery of phenols from the olives and their possible use as natural antioxidants in the food processing industry [13], [14]. Our choice of sorption polymers was oriented towards foodgrade safe resins and, in particular, styrene-DVB copolymers ensuring levels of monomers release within the standards [15].

Having previously studied the equilibrium and the adsorption equilibrium isotherms of different porous polymers with regard to plant-derived phenolic substances, and olives in particular [16], [17], we conducted dynamic adsorption tests designed to determine parameters of semi-industrial pilot columns.

2. EXPERIMENTAL

Comparative tests carried out in four columns each having 160 mm diameter and operational bed volume of 14 dm^3, have been performed using commercially available polymeric materials of properties listed in tab. 1. The influent stream was passed through parallelly operating columns at a constant rate of 70 dm^3/h. The effluent from each individual column was collected up to its breakthrough point, which was arbitrarily taken as 120 ppm leakage. The presence of sorbate in the effluent was checked colorimetrically, whereas the analytical determinations of the influent and effluents were done according to methods reported in [18]. Table 2 presents composition of the water before and after percolation; however, as mentioned above, the wastewater we treated was the permeate of UF membranes with an MWCO of 20,000.

Table 1

Typical properties of porous polymers

Properties	Polymers			
	A	B	C	D
Specific surface (m^2/g)	40	67	400	850
Pore size distribution				
mode (Å)	680	350	70	120
range (Å)	80÷700	90÷500	25÷110	20÷145
Apparent density (g/cm^3)	0.67	0.96	0.82	0.47

Table 2

Influent and effluent composition

Parameters	Influent	Effluent
Density 20°	1.01442	1.00135
Total solids (g/dm^3)	32.91	27.55
Ash (g/dm^3)	5.85	4.66
Total acids (meq/dm^3)	16.77	8.12
pH	4.96	4.10
Total phenols (g/dm^3)	2.26	0.12
Monomer phenols (g/dm^3)	1.35	0.07
Red polymer phenols (g/dm^3)	0.45	0.02
Dark polymer phenols (g/dm^3)	0.46	0.03
Total sugars (g/dm^3)	11.32	10.04
Viscosity 20°C	0.53	0.32
COD (g/dm^3)	41.6	14.8

For an adsorption process we have studied the following form of Hammett's equation [19]:

$$\log(P) = \delta\pi$$

where $P = V/m$ is the distribution coefficient of the substituted compound, V denotes the volume of the effluent collected up to the breakthrough point, m expresses the mass of sorbent, δ means a constant that depends on the type of reaction, π is a parameter that characterizes the chemical nature of the substituted and nonsubstituted compounds. In particular, π can be taken as the sum of the inputs of the substituting compounds to solubility, polarizability, ease of formation of hydrogen bonds and the importance of van der Waals interactions between the sorbate molecules [19]. In its simplified form, the above equation results in a straight line passing through the origin.

Table 3 reports the values of distribution coefficient P for the four resins. Elution steps, concerning the solution of 65% ethanol, 4% ammonia, 2% caustic soda, are shown in tab. 4; for our comparative basic scope, the collected volume V' comprises the percolated stripping solution and the rinse water, hence gives P' value.

3. RESULTS AND DISCUSSION

If we assume that adsorption depends on the surface of the sorbent, which in our case is a substance adsorbed by an aqueous solution on a non-specific sorbent like the copolymer styrene-DVB, then the distribution coefficient proves that, as we found, the surface area is not the only characterizing parameter. The morphology of the sorbent, and in particular the pore-size distribution, is also of fundamental

Table 3

Distribution coefficients for sorption of total phenols

Parameters	Polymers			
	A	B	C	D
Sorbent volume (cm³)	14,000	14,000	14,000	14,000
Sorbent mass m (g)	9,380	13,440	11,480	6,580
Effluent collected V (cm³)	74,650	95,600	81,850	78,580
$P = V/m$ (cm³/g)	7.958	7.113	7.130	11.942
log P	0.900	0.852	0.853	1.077
Effluent bed volumes	5.33	6.83	5.84	5.61
Sorbate (g/dm³ polymer)	11.4	14.6	12.5	12.0

Table 4

Stripping solvents and rinse water elutions

Characteristics of polymers	Stripping solvents		
	C_2H_6O	NH_4OH	NaOH
Polymer A			
Effluent bed volumes	6.8 —	12. —	16. —
Effluent collected V' (cm³)	95,200	168,000	224,000
$P' = V'/m$ (cm³/g)	10.149	17.910	23.880
log P'	1.006	1.253	1.378
Polymer B			
Effluent bed volumes	6.6	10. —	14. —
V'	92,400	140,000	196,000
P'	6.875	10.416	14.627
log P'	0.837	1.018	1.165
Polymer C			
Effluent bed volumes	4.4	8. —	12. —
V'	61,600	112,000	168,000
P'	5.366	9.756	14.634
log P'	0.729	0.989	1.165
Polymer D			
Effluent bed volumes	3.5	6.8	10.6
V'	49,000	95,200	148,400
P'	7.447	14.468	22.553
log P'	0.872	1.160	1.353

importance. As shown in tables 1 and 3, large surface areas are most likely associated with pores which, because of their size, are apparently more accessible to the sorbate molecules. The sorption binding energy can be indirectly revealed by the trends of the elution steps.

Comparative performances (fig. 1) prove that for the sorption, the optimal decreasing order of distribution coefficients was obtained in the case of resin D, followed by resins A, B and C, while for the stripping and rinse, the increase in values of P' coefficients occurs when resins C, followed by B, D and A, were applied. The cumulative performances, as algebraic sum of log (P'/P), are indicated in fig. 2.
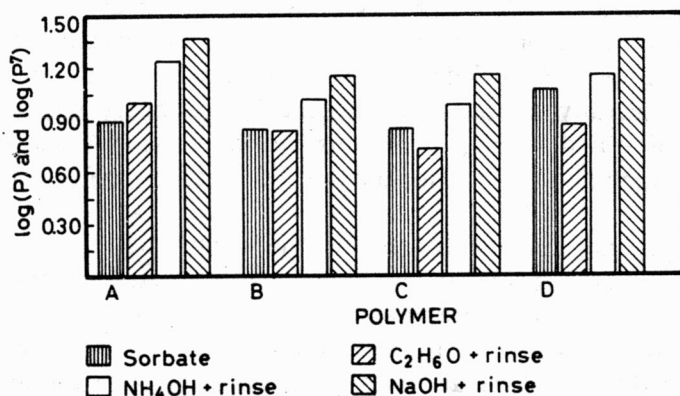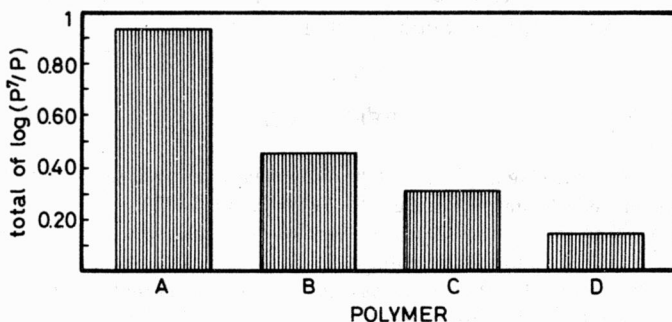
Fig. 1. Comparative performances

Fig. 2. Cumulative performances

On the other hand, if the slope of Hammett's equation is taken as a measure of the effect of polar groups of the sorbate on the adsorption process and, therefore, as a measure of its selectivity, we find that this quantity does not depend on the physical structure of the sorbent but rather on the polarity of its surface. It is also confirmed that excessively large pores, as in the case of resin A, can cause restrictions in adsorption forces, and, consequently, poor utilization of the kinetic requirements.

The specific sorbate and relevant non-destructive recovery show the typical composition of vegetable-origin species of phenols. Anthocyans are present in the form of heterosides, and chemical or physical factors can combine to condensate these flavonoids in forms that are more or less polymerized but still coloured; the different fractions responsible for their colouration are monomer dyes of average m.w. of 280, red polymers, dimers of an average m.w. of 560 and brown or dark polymers, having polymerization degree 2 and average m.w. above 560. Many kinds food containing fats have a limited storage life due to fat oxidation, and natural-origin antioxidants (e.g., vegetal phenols) are potential substitute for BHT/BHA (butylated hydroxytoluene/butylated hydroxyanisol) of a chemical origin.

An antioxidant used for practical purposes must meet certain subsidiary requirements depending upon its particular use, i.e., (i) sufficient solubility in the product, (ii) relatively low volatility, (iii) lack of stripping by water vapour, (iv) resistance to non-discolouration and staining, (v) it must be odourless and tasteless, (vi) it must not be toxic or irritating to the skin, and, last but not least, (vii) it must not cost too much.

The term *vegetable tannin* covers all those substances, present in vegetable materials, which are capable of combining with a pelt and converting it into a leather. Vegetable tannins are characterized by astringency, i.e., the ability to abstract water from the pelt or to neutralize forces whereby the collagen micelles hold water. Vegetable tannins are usually classified into two groups: (i) pyrogallol and (ii) catechol.

The above mentioned potential uses indicate that non-destructive recovery of phenols from olive-oil wastewater seems to be promising in utilization, including its refining in order to obtain specific products.

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ODZYSK FENOLI ZE ŚCIEKÓW POCHODZĄCYCH Z PRODUKCJI OLEJU OLIWKOWEGO

Określono przydatność procesu adsorpcji do usuwania fenoli ze ścieków powstających w czasie rozdrabniania oliwek. Usuwanie fenoli ma istotne znaczenie, gdyż zapewnia efektywną pracę membran do odwróconej osmozy w ostatnim stopniu oczyszczania składającym się z następujących procesów jednostkowych: ultrafiltracji ścieków, sorpcji otrzymanego permeatu i odwróconej osmozy cieczy oczyszczonej w procesie sorpcji.

РЕГЕНЕРИРОВАНИЕ ФЕНОЛОВ ИЗ СТОЧНЫХ ВОД, ОБРАЗУЮЩИХСЯ В ПРОЦЕССЕ ПРОИЗВОДСТВА ОЛИВКОВОГО МАСЛА

Целью работы было определить пригодность процесса адсорбции для удаления фенолов из сточных вод, образующихся во время дробления маслин.

Удаление фенолов имеет существенное значение из-за обеспечения эффективной работы мембран для обратного осмоза в последней стадии очистки, состоящей из следующих отдельных процессов: ультрафильтрация сточных вод, сорбция получаемого пермеата и обратный осмоз жидкости, очищенной в процессе сорбции.