RECOVERY OF OLIVE MILL WASTEWATER POLYPHENOLS THROUGH LIQUID-SOLID EXTRACTION

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INTRODUCTION

POSSIBLE INDUSTRIAL EXPLOITATION OF POLYPHENOLS

Food industry (conservation and dietary supplements) (1)

Cosmetic (2)

Human health (3)

- reduction of the oxidation of Low-Density Lipoprotein (LDL) (risk factor for arteriosclerosis);
- reduction of Leukotriene B4 production ⇨ decreasing of inflammation processes;
- reduction in DNA oxidation and in the growth of cancer masses.

1) De Leonardis et al. (2007) Food Chem. 100: 998-1004; Soni et al. (2006) Food and Chem. Toxicol. 44: 903-915.

2) Hepstein (2009) Clinics in dermatology 27: 475-478.

3) Léger et al. (2000) J. Agric. Food Chem. 48: 5061–5067; Kohyama et al. (1997) Biosci. Biotechnol. Biochem. 61: 347-350; Cicerale et al. (2009) Critical Rev. in Food Sci. and Nutrition. 49: 218–236; D'Angelo et al. (2005) Free Radical Biol. Med. 38: 908-919.

INTRODUCTION

PROPOSED TECHNOLOGIES FOR POLYPHENOL RECOVERY

1) Membrane processes [1]
2) Liquid-liquid extraction [2], eventually improved by the employment of surfactants [3]
3) Liquid-solid (LS) extraction

Objective: wastewater decontamination ⇨ low cost unselective solid phases (e.g.: olive pomaces [4]; granular activated carbon [5])

phenols recovery ⇨ selective adsorption process is needed [6]

1) Fiorentino et al. (2003) J. Agric. Food Chem. 51: 1005–1009
2) De Leonardis et al. (2008) Eur Food Res Technol, 226 653–659.
3) De Marco et al. (2007) Food Chem., 104: 858–867.
4) Stasinakis et al. (2008) J. Haz. Mat. 160: 408-413;
5) El-Shafey et al. (2005) Sep. Sci. Technol. 40: 2841-2869; Azzam et al. (2004) J. Env. Sci. Health Part A – 39: 269-280
6) Agalias et al. (2007) J. Agric. Food Chem. 55: 2671–2676

AIM OF THE RESEARCH

To define the adsorption and desorption features of resins having different physical properties towards:

1. **the whole phenolic fraction;**
2. **the single low-molecular weight phenols**

occurring in two OMWs collected from different Italian regions.

A special attention was devoted on the evaluation of the performances of the LS extraction process by employing a non-toxic solvent as the desorbing phase.

MATERIALS & METHODS

RESINS EMPLOYED:
Main physical properties

Resin	*Matrix*	*Particle diameter*	*Surface area* *($m^2\ g^{-1}$)*	*Average pore diameter* *(Å)*	*Polarity*
XAD7	acrylic ester	20-60 (mesh)	450	n.a.*	Weakly polar
XAD16	polystyrene	20-60 (mesh)	800	100	Non polar
IRA96	polystyrene-divinylbenzene (polyamine functional group)	16-50 (mesh)	n.a.*	n.a.*	Polar
ENV+	polystyrene-divinylbenzene	90 (μm)	1000	800	Non polar

n.a. = not available

MATERIALS & METHODS

RESINS EMPLOYED:

..why?

XAD16 (non-polar polystyrene-based resin) was already used in efficient processes dedicated to the recovery of polyphenols from synthetic solutions[(1)] and from an OMW[(2)]

XAD7 (weakly-polar acrylate-based resin) was used in parallel with XAD16 with lower performances[(2)]; however, it was successfully employed in the extraction of polyphenols from grape pomace[(3)]

IRA96 (polar styrene-divinylbenzene-based resin) contains polyamine groups responsible for its polarity;

ENV+ (non-polar hydroxylated polystyrene-divinylbenzene resin) was suggested for the adsorption from water phases of polar and weakly polar compounds, such as polyphenols are.

1) Bretag et al. (2009) Eur. Food Res. Technol. 228: 985-999; Kammerer et al. (2010) J Food Eng. 96: 544-554
2) Agalias et al. (2007) J. Agric. Food Chem. 55: 2671–2676
3) Gómez-Plazaet al. (2006) Food Chem. 97: 87-94.

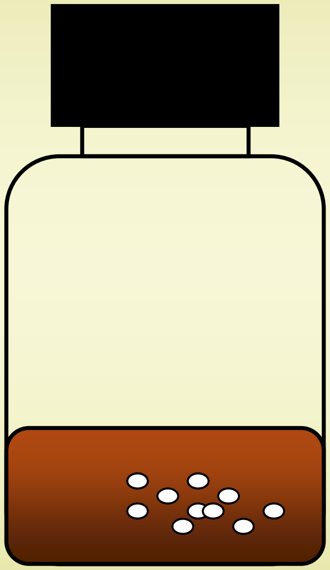
MATERIALS & METHODS

EXPERIMENTAL APPROACH: ADSORPTION

50 mL glass bottles

0.7 g (dry weight) of resin

10 ml of liquid phase (OMW or synthetic solution)



Adsorption conditions:

180 rpm

Room temperature

1 h

Adsorbtion ratio (A): $A = (C_0 - C_{eq})/C_0 * 100$

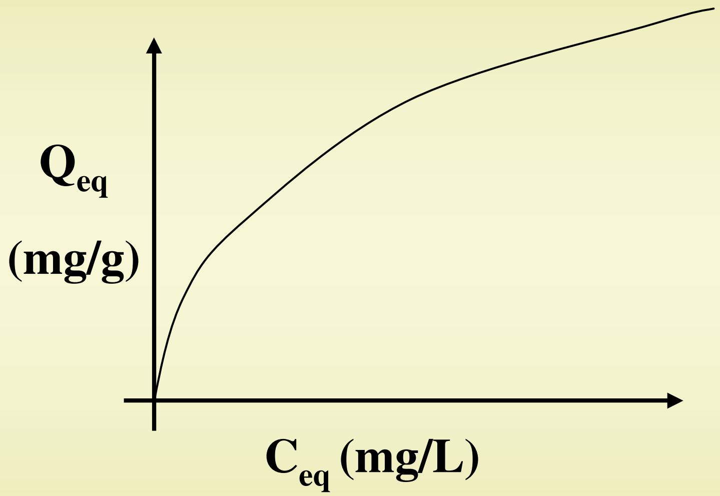
MATERIALS & METHODS

EXPERIMENTAL APPROACH: ADSORPTION ISOTHERMS

Q_{eq} = adsorbate in the solid phase at equilibrium

$(Q_{eq} = (C_0 - C_{eq})*V_0/W$

C_{eq}= concentration at equilibrium
W = resin dry weight



liquid phase dilutions: 100%, 50%, 20%, 10%, 5%

Langmuir model: $Q_{eq} = Q_{max}*C_{eq}/(1+KC_{eq})$
Freundlich model: $Q_{eq} = K*C_{eq}$^(1/n)

MATERIALS & METHODS

EXPERIMENTAL APPROACH: DESORPTION

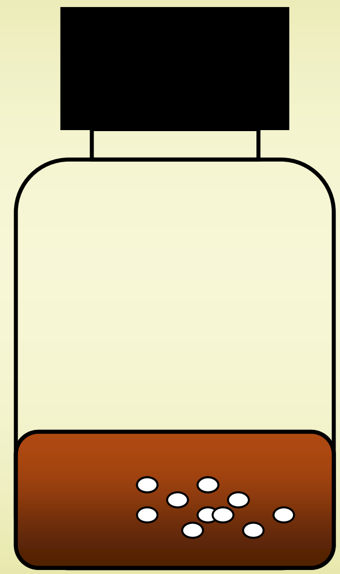
Solvents employed in the desorption experiments:

Water

Methanol

Ethanol

Acidified ethanol (0.5% HCl)



Desorption conditions:

180 rpm

Room temperature

1.5 h

Desorption ratio (D): $D = (C_d*V_d)/((C_0-C_{eq})*V_0)*100$

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MATERIALS & METHODS

EXPERIMENTAL APPROACH:OVERALL PRODUCTIVITY

$$P = A^* D_{ov}/100$$

MAIN RESEARCH EVIDENCES

The employment of liquid-solid extraction procedures appears a feasible option for the recovery of polyphenols from OMWs.

ENV+ resin gave rise to the best overall process productivities.

Acidified ethanol allowed higher desorption ratios of total polyphenols, while the solvent through which low-aromatic weight phenols were more efficiently desorbed depended on the nature of such compounds. In particular, higher amounts of more polar phenols (and among them of hydroxytyrosol) were generally recovered by using ethanol as the desorbing phase.

OMW itself appeared to be a parameter able to influence the whole process performances.

POSSIBLE FURTHER INVESTIGATIONS

Solid phase amount optimization

Antioxidant activity test

Resin/solvent regeneration