Continuous flow adsorption of phenolic compounds from olive mill wastewater with resin XAD16N: life cycle assessment, cost-benefit analysis and process optimization

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SUPPORTING INFORMATION

Table S1
Procedure for the evaluation of the performance indicators obtained from the breakthrough tests.

1) PC and COD adsorption yield ($Y_{ads,i,}$) $Y_{ads,i,}$ was evaluated at a 0.20 PC breakpoint as $m_{i,sorbed,20\%}$ / $m_{i,fed,20\%}$, where: ➢ $m_{i,sorbed,20\%}$ indicates the PC or VS mass adsorbed until the attainment of a 20% outlet normalized PC concentration; ➢ $m_{i,fed,20\%}$ indicates the corresponding PC or COD mass fed to the adsorption column. $m_{i,sorbed,20\%}$ was estimated as $m_{i,fed,20\%} - m_{i,out,20\%}$, where $m_{i,out,20\%}$ indicates the mass lost in the outlet up to the 20% breakpoint. $m_{i,out,20\%}$ was calculated by integration of the experimental breakthrough curve until the selected 20% PC breakpoint: $m_{i,out,20\%} = Q \cdot \int_0^{t_{20\%}} C_{L,i,OUT} \cdot dt$, where Q indicates the OMW flow rate fed to the column.
2) PC desorption yield ($Y_{des,i,}$) $Y_{des,i,}$ was evaluated as $m_{PC,desorbed}$ / $m_{PC,sorbed}$. $m_{PC,\ desorbed}$ was calculated by integration of the experimental curve of PC concentration obtained at the column outlet during the desorption procedure: $m_{PC,\ desorbed} = Q_{des} \cdot \int_0^{t_{final}} C_{L,PC,OUT} \cdot dt$, where Q_{des} indicates the desorption solvent flow rate fed to the column.
3) Resin operating capacity (η_{resin}) η_{resin} was evaluated at a 0.20 PC breakpoint as $m_{PC,sorbed,20\%}$ / $m_{PC,sorbed,saturation}$. $m_{PC,sorbed,saturation}$ indicates the PC mass theoretically adsorbed by the resin upon saturation of the sorption capacity. $m_{PC,sorbed,saturation}$ was calculated by integration of the simulated breakthrough curve until the attainment of a 99% PC dimensionless concentration: $m_{PC,sorbed,saturation} = Q \cdot \int_0^{t_{99\%}} \left(C_{L,PC,IN} - C_{L,PC,OUT}\right) \cdot dt$, where Q indicates the OMW flow rate fed to the column.

Table S2
Procedure for the sensitivity analysis aimed at evaluating the sensitivity of the model to variations of the key parameters ($K_{eq,PC}$, k_La, $\alpha_{L,resin}$, $\varepsilon_{\text{resin}}$) and assessing the uncertainty in the estimate of the resin operating capacity.

Step	Description
a	As the intermediate conditions of superficial velocity and HRT resulted in the best process performances in terms of resin operating capacity and sorbed product purity, the average values of the model parameters obtained in the 4 repeated tests (T2 and T4-T6) conducted under these intermediate conditions were selected as the optimal ones for the process scale-up and for the sensitivity analysis: superficial velocity = 2.78±0.25 m/h; HRT in the resin = 0.56±0.04 h; $K_{eq,PC}$ = 131±21 L/kg$_{\text{dry resin}}$; k_La = 0.0030±0.0003 1/s; $\alpha_{L,resin}$ = 0.034±0.021 m; $\varepsilon_{\text{resin}}$ = 0.86±0.03.
b	The resin operating capacity η_{resin} – selected as key performance parameter – resulting from a process simulation conducted with these average parameter values and with the same resin bed height of the experimental plant (1.82 m) was evaluated (0.456).
c	Starting from the "baseline condition" simulated in step b), further simulations were conducted in which one model parameter was taken equal to the maximum or minimum value allowed by the 95% confidence interval reported in step a), whereas the other parameters were maintained equal to the average value reported in step b); these parameter variations were extended to $K_{eq,PC}$, k_La, $\alpha_{L,resin}$ and $\varepsilon_{\text{resin}}$, but not to superficial velocity and HRT, under the assumption that in a full-scale process the OMW flow rate, and therefore the velocity and – given the resin bed height and porosity – the HRT, is controlled in a very precise way; this approach therefore resulted in 8 additional simulations.
d	For each simulation included in step c), the relative variation in resin operating capacity in comparison with the baseline value calculated in step b) was determined.

Table S3
Design values and performance parameters of the full-scale plant of OMW filtration, PC adsorption / desorption and ethanol recovery.

Parameter	**Value**	**Unit**
Total OMW treated	10 000	m^3
OMW flow rate at the adsorption step	4.17	m^3/h
Ethanol flow rate at the desorption step	2.08	m^3/h
Duration of the adsorption / desorption cycle	14.7	h
Column diameter	1.38	m
Resin bed height	1.82	m
OMW superficial velocity in the adsorption step	2.78	m/h
HRT of the adsorption step	0.56	h
Bed volumes / hour of the adsorption step	1.53	BV/h
Adsorption yield	0.922	-
Desorption yield	0.704	-
Process yield	0.650	-
Resin operating capacity	0.456	-
Number of adsorption / desorption cycles performed with the same resin load	500	-

Table S4
Inventory for the LCA and CBA of the process.

	Amount	Unit
Infrastructure		
Microfiltration unit	1	unit
Adsorption / desorption column (diameter 1.38 m, resin bed height 1.82 m)	1	unit
Desorption solvent evaporation / recovery unit (rotary dryer)	1	unit
Desorption solvent and OMW storage tanks	2	units
Gas Boiler (85 kW)	1	unit
Ethanol recovery condenser (3.4 m^2)	1	unit
Cooling Tower	1	unit
Pumps (2-4.2 m^3/h)	4	pumps
Operation		
Ethanol periodic re-integration	4.5	m^3/season
HCl periodic re-integration	27	kg/season
Resin XAD16N periodic disposal and re-integration	350	kg/season
Water periodic re-integration	405	m^3/season
Electricity for pumping	12 000	kWh/season
Heat for ethanol evaporation	990 500	MJ/season
PC mass produced	3.25 – 26[a]	t_{PC}/season
End of Life (EOL)		
Wastewater produced	10 000	m^3/season
Solid waste sent to anaerobic digestion	30 000	kg/season
Infrastructure	12	units

[a] In order to develop a CBA applicable to different OMW types, and not only to the specific OMW object of this work, the PC concentration in OMW was assumed to vary over the 0.5-4 g/L range.

Table S5. LCA of the PC recovery process: impact of each life cycle stage and component of the process on the different environmental compartments and aspects taken into consideration in the ILCD 2011 Midpoint+ V1.10 method. For each environmental compartments and aspect, the table reports the total impact of the process, and the % relative impact of each life cycle stage and component.

Impact category	Unit	Total LCA score	Infra-structure	Operation					End of life		
				Desorption solvent (ethanol + HCl)[a]	Water[a]	Resin XAD16N[a]	Electricity for pumps	Heat for ethanol evaporation	EOL – Diverse[b]	Wastewater treatment	Solid waste anaerobic digestion
Climate change	kg CO_2 eq	$6.42 \cdot 10^{0}$	3.9%	6.8%	< 0.1%	1.7%	9.4%	51.7%	0.2%	10.8%	15.6%
Ozone depletion	kg CFC-11 eq	$6.67 \cdot 10^{-7}$	1.8%	1.8%	< 0.1%	0.7%	9.0%	78.4%	0.1%	5.5%	2.7%
Human toxicity, non-cancer effects	CTUh	$3.66 \cdot 10^{-6}$	5.3%	1.6%	< 0.1%	0.7%	4.0%	2.8%	0.4%	82.0%	3.3%
Human toxicity, cancer effects	CTUh	$4.05 \cdot 10^{-7}$	31.8%	3.3%	< 0.1%	1.3%	9.4%	7.3%	0.4%	41.6%	4.8%
Particulate matter	kg PM2.5 eq	$2.22 \cdot 10^{-3}$	16.0%	10.3%	< 0.1%	3.7%	9.9%	18.5%	0.3%	20.2%	21.0%
Ionizing radiation HH	kBq U235 eq	$4.64 \cdot 10^{-1}$	3.4%	1.6%	< 0.1%	1.1%	58.4%	17.5%	0.1%	14.0%	4.0%
Ionizing radiation E (interim)	CTUe	$1.42 \cdot 10^{-6}$	4.2%	2.0%	< 0.1%	1.3%	48.8%	24.9%	0.1%	13.7%	5.0%
Photochemical ozone formation	kg NMVOC eq	$1.23 \cdot 10^{-2}$	7.1%	17.8%	< 0.1%	4.0%	9.6%	33.8%	0.3%	18.2%	9.2%
Acidification	mol H^+ eq	$2.40 \cdot 10^{-2}$	7.1%	8.1%	< 0.1%	2.4%	13.7%	24.0%	0.2%	24.3%	20.2%
Terrestrial eutrophication	mol N eq	$5.21 \cdot 10^{-2}$	5.2%	6.8%	< 0.1%	1.6%	8.1%	22.7%	0.3%	30.1%	25.2%
Freshwater eutrophication	kg P eq	$2.36 \cdot 10^{-3}$	5.8%	7.6%	< 0.1%	1.5%	21.5%	7.8%	0.2%	48.6%	7.0%
Marine eutrophication	kg N eq	$2.39 \cdot 10^{-2}$	1.1%	1.4%	< 0.1%	0.3%	2.0%	4.7%	0.1%	87.8%	2.6%
Freshwater ecotoxicity	CTUe	$3.30 \cdot 10^{1}$	18.7%	4.7%	< 0.1%	2.3%	15.0%	8.8%	4.0%	38.6%	8.0%
Land use	kg C deficit	$1.29 \cdot 10^{1}$	3.4%	1.7%	< 0.1%	0.6%	3.6%	17.1%	0.1%	34.1%	39.4%
Water resource depletion[c]	m^3 water eq	$-1.38 \cdot 10^{1}$	0.4%	< 0.1%	-4.7%	-0.1%	-2.7%	2.1%	< 0.1%	105.0%	< 0.1%
Mineral, fossil & ren. resource depletion	kg Sb eq	$1.05 \cdot 10^{-4}$	41.3%	11.9%	< 0.1%	7.7%	4.1%	4.9%	2.5%	20.8%	6.9%

[a] Periodic re-integration. [b] Infrastructure disposal + spent resin incineration. [c] The negative LCA score in terms of water resource depletion, indicating a positive environmental impact, is due to the wastewater treatment process, which increases the availability of high-quality water.

Table S6. LCA of the PC recovery process: impact of each life cycle stage and component of the process on the different environmental compartments and aspects taken into consideration in the Ecological Scarcity 2013 method. For each environmental compartments and aspect, the table reports the total impact of the process, and the % relative impact of each life cycle stage and component.

Impact category	Total LCA score (kPt)	Infra-structure	Operation					End of life		
			Desorption solvent (ethanol + HCl)[a]	Water[a]	Resin XAD16N[a]	Electricity for pumps	Heat for ethanol evaporation	EOL - Diverse[b]	Wastewater treatment	Solid waste anaerobic digestion
Total	$8.67 \cdot 10^{0}$	5.9%	5.8%	0.1%	1.8%	6.6%	25.6%	0.3%	43.8%	10.0%
Water resources[c]	$-2.82 \cdot 10^{-1}$	0.3%	-0.1%	-1.9%	< 0.1%	-0.5%	0.3%	< 0.1%	101.9%	0.1%
Energy resources	$3.60 \cdot 10^{-1}$	3.5%	15.6%	< 0.1%	2.7%	11.4%	56.3%	0.1%	6.0%	4.5%
Mineral resources	$1.74 \cdot 10^{-1}$	46.9%	3.9%	< 0.1%	2.0%	1.4%	5.9%	0.7%	36.2%	2.9%
Land use	$4.93 \cdot 10^{-2}$	3.9%	2.1%	< 0.1%	0.7%	6.6%	2.7%	0.1%	18.1%	65.8%
Global warming	$2.92 \cdot 10^{0}$	4.0%	6.9%	< 0.1%	1.7%	9.4%	52.5%	0.1%	7.9%	17.5%
Ozone layer depletion	$4.19 \cdot 10^{-3}$	2.5%	2.5%	< 0.1%	1.2%	11.1%	60.7%	0.1%	8.8%	13.1%
Main air pollutants and PM	$1.08 \cdot 10^{0}$	14.6%	8.5%	< 0.1%	3.2%	10.3%	24.9%	0.3%	22.7%	15.6%
Carcinogenic substances into air	$2.64 \cdot 10^{-1}$	13.5%	2.7%	< 0.1%	15.7%	4.0%	12.3%	0.3%	36.4%	15.2%
Heavy metals into air	$2.11 \cdot 10^{-1}$	28.2%	8.8%	< 0.1%	3.0%	7.7%	13.0%	1.3%	25.7%	12.4%
Water pollutants	$2.35 \cdot 10^{0}$	0.1%	4.8%	< 0.1%	0.3%	0.2%	1.1%	< 0.1%	91.8%	1.8%
POP into water	$1.27 \cdot 10^{-2}$	9.1%	7.5%	< 0.1%	2.5%	8.5%	35.4%	0.8%	22.0%	14.2%
Heavy metals into water	$7.28 \cdot 10^{-1}$	4.3%	0.9%	< 0.1%	0.2%	0.9%	12.7%	0.1%	80.2%	0.7%
Pesticides into soil	$2.10 \cdot 10^{-2}$	0.1%	< 0.1%	< 0.1%	< 0.1%	0.3%	0.1%	< 0.1%	68.0%	31.5%
Heavy metals into soil	$5.60 \cdot 10^{-1}$	0.1%	0.1%	< 0.1%	< 0.1%	0.4%	0.1%	< 0.1%	98.3%	0.9%
Radioactive substances into air	$3.70 \cdot 10^{-8}$	3.4%	1.6%	< 0.1%	1.1%	58.4%	17.5%	0.1%	14.0%	4.0%
Radioactive substances into water	$1.77 \cdot 10^{-3}$	4.0%	1.5%	< 0.1%	1.2%	62.3%	12.4%	0.0%	14.3%	4.2%
Non radioactive waste to deposit	$5.46 \cdot 10^{-2}$	5.8%	1.2%	< 0.1%	1.1%	0.7%	3.4%	30.4%	56.3%	1.1%
Radioactive waste to deposit	$1.60 \cdot 10^{-1}$	4.0%	1.5%	< 0.1%	1.2%	62.3%	12.4%	0.0%	14.3%	4.2%

[a] Periodic re-integration. [b] Infrastructure disposal + spent resin incineration. [c] The negative LCA score in terms of water resource depletion, indicating a positive environmental impact, is due to the wastewater treatment process, which increases the availability of high-quality water