

The ecological impact of membrane-based extraction of phenolic compounds – a life cycle assessment study

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ABSTRACT

Many phenolic compounds show high boiling points, low molecular weights, moderate polarities or high toxicities. Therefore, conventional wastewater treatment is limited or expensive. Recycling of the separated compounds is often not possible. But, if liquid-liquid reactive extraction is linked to a non-porous membrane, some or all of the above mentioned limitations may be overcome. The key element is a composite membrane with a dense, hydrophobic top layer which avoids the mixing of the two aqueous fluid streams. The dilute phenol stream is one of them, the other is caustic soda as stripping solvent. Since the basics of this technology have been discussed before, the scope of this study is to facilitate process implementation and integration. To this end, a life cycle assessment framework is used to identify the optimal equipment size for the treatment of wastewater that may, for example, originate from the production of polycarbonate. Limiting for this application is not the environmental performance though, but most likely process economics.

Key words | industrial water treatment, liquid-liquid membrane contactor, recovery, recycling

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INTRODUCTION

Due to the inherent properties of many phenolic substances like high boiling points, low molecular weights, moderate polarities or high toxicities, the applicability of conventional wastewater treatment is limited or expensive. Further, with conventional treatment options a recycling of separated compounds is often not feasible. But, if liquid-liquid reactive extraction is linked to a non-porous membrane, some or all of the above mentioned limitations may be overcome. The key element is a composite membrane with a dense hydrophobic top layer which separates two aqueous fluid streams so that they do not mix. The dilute phenol stream is one of them, the other is caustic soda as stripping solvent. This technology is presented e.g. by Ferreira *et al.* (2005) covering the basic principles to a large extent. The scope of our study is therefore not about enhancing basic process knowledge, but about facilitating process implementation

and integration. To this end, a life cycle assessment study is performed based on the characteristics of the wastewater as it may originate from the production of polycarbonate.

SYSTEM INTEGRATION AND PROCESS DESIGN

The polycarbonate production process

Polycarbonate is formed in a continuous interfacial condensation reaction from bi-functional organics such as bisphenol A with phosgene. Bisphenol A is a weak organic acid only slightly soluble in water at neutral or acidic pH, but extremely well soluble under caustic conditions as bisphenolate ion (Kosky *et al.* 1991). Linking monomers and oligomers to polymeric chains finally yields long-chain polycarbonate. To intentionally abort the condensation

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reaction thus adjusting the length of the polymer chain and material properties, mono-functional substances like phenol are added as chain-terminators (Frunze *et al.* 1961). After the condensation reaction comes to an end, the aqueous phase is discharged for stripping the phase-transfer catalyst, neutralization and further treatment to eliminate mainly phenolic compounds.

Typical contaminant concentrations in the process water as given in Table 1 can be mainly found in the patent literature (e.g. Juptner (2004) and Verhoeven *et al.* (1995)) and were crosschecked with a process model relating known input data and process chemistry to obtain such output concentrations.

Membrane-based reactive extraction

The two aqueous streams are separated by a silicon-type dense membrane coating on top of a porous support. Phenols are weak acids and react rapidly with caustic soda, which is made available in the porous membrane support layer, to their anionic form, the phenolates (Figure 1). Membrane permeability data for phenol are made available by Daisley *et al.* (2006), who reports an overall transport coefficient of 5×10^{-7} m/s. Data for bisphenol A is unfortunately not available. However, bisphenol A tends to be better soluble in organics as indicated by its significantly larger octanol/water partition coefficient, which usually translates into improved membrane permeability according to the widely applied solution-diffusion transport model (Mulder 1991). But, the bisphenol molecule is significantly larger compared to phenol, which reduces its mobility in the polymeric phase. The transport coefficient is therefore estimated to 1×10^{-7} m/s until our own experimental data become available.

Assuming for this study a hollow-fiber membrane contactor operated with excess caustic soda as stripping

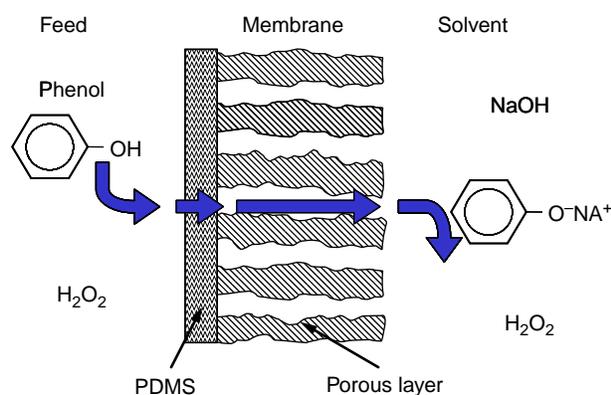


Figure 1 | Illustration of the membrane contactor principle of operation for wastewater treatment.

solvent, the stripping side concentration level of the (permeating) neutral phenolics renders negligible. Consequently, only the phenol concentration on the feed side affects the driving force. Feed fluid transport along the fiber can be described assuming pure convection coupled to a source term, which accounts for trans-membrane phenol transport. This yields with the inlet concentration c_α for the outlet concentration c_ω :

$$c_\omega = c_\alpha \exp - \left(\frac{4kL}{d} \frac{1}{v} \right)$$

where k is the transport coefficient of the membrane, d the inner diameter of the membrane and L its length. v accounts for the convective fluid velocity inside the fibers.

Process integration

The membrane contactor is introduced to recover the phenolics and to recycle an aqueous stream at alkaline pH loaded with phenol and bisphenol A to the PC synthesis. The cleaned wastewater is to be discharged without further treatment (Figure 2).

The geometrical characteristics of the contactor device and its mode of operation are chosen in a way that minimizes the total environmental burden. The environmental burden (ecological impact) is defined as the sum of normalized emissions and normalized resource usage, even though both impact groups are hardly comparable.

Table 1 | Typical contaminant concentrations for process water originating from the production of polycarbonate

	Content
Sodium chloride (wt.-%)	2–4
Bisphenol A (mg/L)	10–100
Phenol (mg/L)	100–200

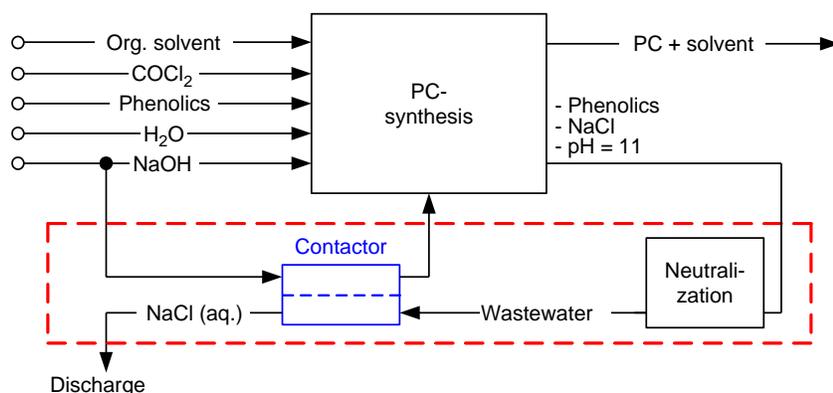


Figure 2 | Schematic flow-sheet of the polycarbonate synthesis process with the membrane contactor for wastewater treatment (dashed line: system boundary).

LIFE CYCLE ASSESSMENT

Methodology

The environmental assessment is based on the EDIP97 Life Cycle Assessment (LCA) method (Wenzel *et al.* 1997), which is in agreement with the ISO 14040 framework. The system under investigation is defined so that all data on process inputs and outputs are taken into account that either induce or avoid environmental impacts.

The reference case for judging the environmental effect of the (additional) contactor treatment is the discharge of the (not-additionally treated) process water, i.e. all remaining phenolic compounds are discharged. The material flows are

compiled and the sizing of the device is performed with Matlab 7. The impacts are assessed with GaBi 4.2 based on the commercial databases ProfDB and Ecoinvent. The databases are complemented with literature data if required. Further, most membrane processes scale linearly in costs and technical properties, so that the functional unit as a specified volume of wastewater to be treated can be arbitrarily chosen. However, its value is not of significance for this study, because total environmental burdens are compared. The impact categories are normalized (Table 2) with the impact of the yearly background load on the environment from an average person in a given year, which yields as common unit *person equivalents years* (pe yrs; according to EDIP97).

Table 2 | Normalization factors

Impact categories	Normalization factor* (10 ⁻⁶ pe yrs/unit)	Reference year	Reference region
Nutrient enrichment potential (kg NO ₃ ⁻ equiv.)	2,410 [†]	2007	EU-25
Oxygen consumption (kg COD)	541 ^{†,‡}	2007	EU-25
Ecotoxicity potential, acute (m ³ water)	38	2004	EU-15
Ecotoxicity potential, chronic (m ³ water)	3.5	2004	EU-15
Global warming potential, 100 years (kg CO ₂ equiv.)	126	2004	World
Acidifying potential (kg SO ₂ equiv.)	17,600	2004	EU-15
Photochemical oxidant potential, high NO _x (kg ethylene equiv.)	52,000	2004	EU-15
Fossil energy resources, including feedstock (MJ)	51.8	2004	World
Nuclear energy, uranium resource (MJ)	317	2002	World
Renewable energy resources (MJ)	0 [§]	–	–

*If not stated otherwise, the data presented by Stranddorf *et al.* (2005) are used;

[†]Normalization reference calculated from CML2001-Dec 07 and the Eurostat population statistics (EU-25 in 2007); results in kg PO₄³⁻ equivalents/person/year, which is recalculated to NO₃⁻ equivalents from the Redfield ratio;

[‡]1 kg COD recalculated to 0.2247 kg NO₃⁻ equivalents from the Redfield ratio;

[§]If usage and replenishment are in balance, the supply horizon is indefinite and the weighted normalized value is zero;

Table 3 | Phenol properties and effect data

Phenol properties	Value	Unit	Source
Biodegradability	Yes (OECD)	–	CSTEE (2003)
$PNEC_{w,c}$	7.7×10^{-6}	g/L	ECB (2006, p. 44)
$EF_{w,a}^{*,\ddagger}$	13,000	m^3/kg	–
$EF_{w,c}^{\ddagger,\ddagger}$	26,000	m^3/kg	–

*The biodegradation factor used for calculating the EF value was chosen to be one for acute effects, since biodegradation generally occurs on a much longer time scale to be of relevance.

†Since the OECD criterion is fulfilled, phenol is considered readily biodegradable, which gives a biodegradation factor of 0.2.

‡Phenol is considered non-volatile and it partitions preferably into the aqueous phase yielding a distribution factor of one (ECB 2006, p. 15).

Fate and toxicity

The phenolic compounds not recovered are discharged to a water course, i.e. a river. Therein they impose toxic effects and are eventually fully degraded to CO_2 , thereby consuming oxygen and contributing to global warming. The NOEC (No Effect Concentration) and the PNEC value (Predicted No Effect Concentration, 10% of NOEC) are used to calculate the equivalence factors (EF) for aqueous acute (index w,a) and chronic (index w,c) toxicity, respectively, according to the EDIP97 procedure. The Equivalence Factors represent the amount of water required to dissolve a given amount of harmful material such that no adverse effects can be observed. The key assumptions and nominal data are summarized in Tables 3 and 4.

Table 4 | Bisphenol A properties and effect data

Bisphenol A properties	Value	Unit	Source
Biodegradability	Yes (OECD)	–	ECB (2003, p. 47)
$PNEC_{w,c}$	1.6×10^{-6}	g/L	ECB (2003, p. 84)
$EF_{w,a}^{*,\ddagger}$	62,500	m^3/kg	–
$EF_{w,c}^{\ddagger,\ddagger}$	125,000	m^3/kg	–

*The biodegradation factor was chosen as one.

†The OECD criterion is met; bisphenol A can thus be considered readily biodegradable, which gives a biodegradation factor of 0.2.

‡A model calculation (ECB 2003, p. 48f) yields a distribution of 74% of BPA to the water and 26% to the soil and sediment compartment. However, the uncertainty regarding the partitioning under real conditions is significant. If the solutes were discharged into the aqueous phase and the transport via the gas phase is negligible, which can be safely assumed in this case, the EDIP97 procedure proposes the allocation of all solute to the aqueous compartment. Hence, the distribution factor is chosen to be one.

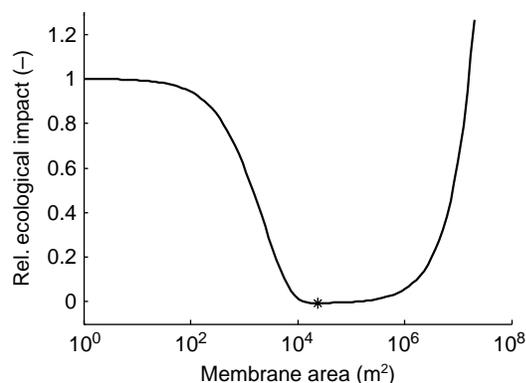


Figure 3 | Ordinate: relative ecological impact calculated as induced impacts + residual impacts – avoided impacts due to avoided production of phenols divided by the impact of process water without additional treatment; abscissa: membrane area in use for continuous treatment of $1 m^3/h$ of wastewater with phenol and bisphenol A concentrations of 100 mg/L each (* indicates the minimum ecological impact, approximately at $24,000 m^2$).

RESULTS

The relative ecological impact of the contactor operation is shown in Figure 3. Very small unit sizes do not significantly reduce the environmental load, because it is assumed that hydrochloric acid needs to be added to the wastewater for neutralization. Often the wastewater can be neutralized instead by mixing with other streams on site. This is not considered technically feasible for the membrane contactor

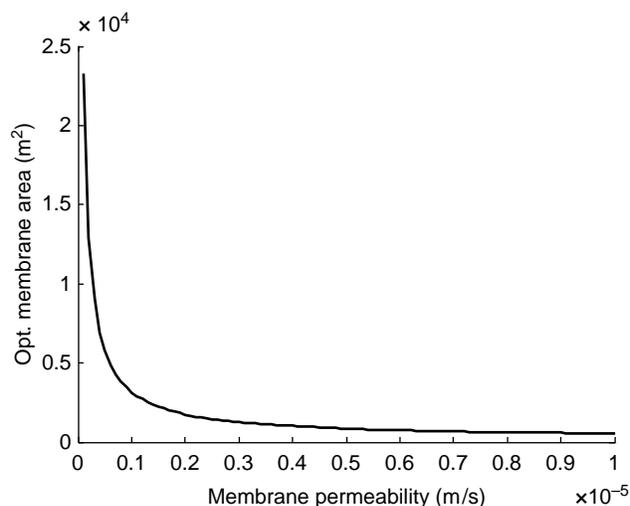


Figure 4 | Ordinate: membrane area considered optimal in environmental terms for continuous treatment of $1 m^3/h$ of wastewater; abscissa: membrane permeability of bisphenol A (ratio of permeabilities of phenol and bisphenol A are kept constant/as above).

system though, if the stripping solvent is to be reused in the PC synthesis process. Including the neutralizing acid in the assessment thus imposes an additional environmental burden. The effective impact is minimal (even negative) at approximately 24,000 m². The negative environmental impact results from the avoided production of phenolic compounds. At much larger membrane areas, the marginal separation efficiency is low due to the low remaining phenol (~0 mg/L at 24,000 m²) and bisphenol A content (~0.0175 mg/L at 24,000 m²). As a consequence, the environmental burden increases with increasing membrane area. This is due to the construction material, which becomes the main contributor to ecological impact.

The equipment efficiency (Figure 4) as indicated by the membrane permeability is decisive for the optimal equipment size. At a bisphenol A permeability of 10⁻⁶ m/s, the lowest environmental impact is reached at approximately 3,000 m², even though a very positive effect can be expected at much smaller equipment sizes.

SUMMARY AND CONCLUSIONS

This LCA study aimed at quantifying the ecological efficiency of a membrane contactor system applied to the polycarbonate process water for reuse of dissolved phenolic compounds. Very small as well as very large contactor systems do not yield significant improvements. At intermediate equipment sizes an optimum point of operation could be identified with virtually zero ecological impact. However, the optimal membrane area in terms of environmental burden appears to be large compared to the wastewater stream treated. Hence, applications are preferred which can be either operated more efficiently and/or which offer greater ecological benefit.

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REFERENCES

- CSTEE 2003 Scientific Committee on Toxicity, Ecotoxicity and the Environment: Opinion on the results of the risk assessment of phenol, Report: C2/VR/csteop/Phenol/06022003 D(03).
- Daisley, G. R., Dastgir, M. G., Ferreira, F. C., Peeva, L. G. & Livingston, A. G. 2006 Application of thin film composite membranes to the membrane aromatic recovery system. *J. Memb. Sci.* **286**, 20–36.
- ECB 2003 *European Union Risk Assessment Report—Bisphenol A*, (Vol. 37) European Chemicals Bureau, JRC Ispra, Italy.
- ECB 2006 *European Union Risk Assessment Report—Phenol*, (Vol. 64) European Chemicals Bureau, JRC Ispra, Italy.
- Ferreira, F. C., Peeva, L. G. & Livingston, A. 2005 Mass transfer enhancement in the membrane aromatic recovery system (MARS): experimental results and comparison with theory. *Chem. Eng. Sci.* **60**, 1029–1042.
- Frunze, T. M., Kurashev, V. V. & Kozlov, L. V. 1961 Advances in interfacial polycondensation. *Russ. Chem. Rev.* **30**, 252–270.
- Juptner, G. A. 2004 Method for Purifying Wastewater. *US 2006/0226078*.
- Kosky, P. G., Silva, J. M. & Guggenheim, E. A. 1991 The aqueous phase in the interfacial synthesis of polycarbonates. 1. Ionic equilibria and experimental solubilities in the BPA-NaOH-H₂O System. *Ind. Eng. Chem. Res.* **30**, 462–467.
- Mulder, M. 1991 *Basic Principles of Membrane Technology*. Kluwer, Boston, New York.
- Stranddorf, H. K., Hoffmann, L. & Schmidt, A. 2005 Impact categories, normalisation and weighting in LCA. *Environ. News*, 78.
- Verhoeven, W., Sluyts, D., Denecker, G., van Osselaer, T., Hinz, J., Vaes, J., van Herck, W. & De Vos, S. 1995 Verfahren zur Reinigung von phenolhaltigem Prozessabwasser (Treatment method for phenol containing process wastewater). *DE 19510063*.
- Wenzel, H., Hauschild, M. Z. & Alting, L. 1997 *Environmental Assessment of Products. Methodology, Tools, Techniques and Case Studies*, (Vol. 1). Chapman & Hall, London.