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Combining the European chemicals regulation and an (eco) toxicological screening for a safer membrane development

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A B S T R A C T

Membranes are permeable or semi-permeable barriers used to separate a wide range of particulate and dissolved compounds in liquid or gas. Polymeric membranes for water applications are arousing great interest as potentially cost-effective answers to a growing range of separation needs in different sectors. Although the polymeric membrane is not considered as toxic, the raw materials and additives used during the membrane manufacturing could be hazardous for human health and the environment. The aim of the present study was to evaluate the toxicity and ecotoxicity of chemicals used for phase inversion manufacturing of polyvinylidene difluoride (PVDF) and polyethersulfone (PES) membrane, and the REACH compliance analysis of these chemicals and membrane. The results show that 2 of 9 substances, the N,N-Dimethylacetamide (DMA) and 1-Methyl-2-pyrrolidone (NMP) solvents used for, or potentially present in, membrane are identified under REACH either as a substance of very high concern (SVHC). However, the identification of DMA and NMP as SVHC does not encompass any use restrictions. Among raw materials, the tetrahydrofuran (THF) showed evidence of carcinogenic potential, while the toluene of possible reproductive toxicant. Washing and drying procedures are usually applied by manufacturer to remove solvents to the extent possible. However, how residual solvents may be released during the life cycle of membrane and affect membrane toxicology profile are still open issues. In summary, we argue that to improve sustainable of phase inversion membrane, it is necessary to minimize the input of hazardous solvents, and to simultaneously stimulate the search for alternative eco-friendly solvents.

1. Introduction

Today, water treatment is one of the cornerstones of environmental technologies in Europe. The increased occurrence and awareness of a whole range of pollutants originating from many sources (e.g. agriculture, industry, households) is a predominant trend in the water treatment industry which will continue to gain importance in the future (European Environment Agency, 2012). During the years a lot of efforts were made to seek new technological solutions for water treatment which are suitable for scale up of plants with simple operational and maintenance procedures and which guarantee efficiency (European Commission; EC, 2010). Process separation with synthetic membrane may be used to satisfy these requirements. Membrane processes are currently utilized in a diverse range of applications and each year more and more effective uses for membrane technologies are developed and marketed (Watanabe and Kimura, 2011). Reverse osmosis, nanofiltration, ultrafiltration, and microfiltration membranes have achieved widespread use in many countries to provide adequate supplies of water

Abbreviations and acronyms: CLP, Classification, Labelling and Packaging; CMR, carcinogenic, mutagenic and toxic for reproduction; DMA, N,N-Dimethylacetamide; DMSO, dimethyl sulfoxide; ECHA, European chemical agency; ESIS, European chemical Substances Information System; GESTIS, Gefahr SToff Informations System (i.e. German Social Accident Insurance); IARC, International Agency for Research on Cancer; IRIS, Integrated Risk Information System; ISS, Istituto Superiore di Sanità (Italy's National Health Institute); IUCLID, International Uniform Chemical Information Database; LC50, Lethal (Effective) concentration 50; LD50, Lethal (Effective) dose 50; MSDS, Material Safety Data Sheet; NMP, 1-Methyl-2-pyrrolidone; NOEC, no observed effect concentration; OECD, Organisation for Economic Co-operation and Development; PBT, Persistent, Bioaccumulative and Toxic; PES, polyethersulfone; PROP, Propan-2-ol; PVDF, polyvinylidene difluoride; PVP, polyvinylpyrrolidone; REACH, Registration, Evaluation, Authorisation and restriction of Chemicals; SID, Screening Information Dataset; SVHC, Substances of Very High Concern; TOL, toluene; TOXNET, Toxicology Data Network; TS, Technical Sheet; UF, ultrafiltration; vPvB, very Persistent, very Bioaccumulative.

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for food and beverage processing, semiconductor and electronics manufacturing, pharmaceuticals and biopharmaceuticals production, as well as for separations in the chemical and petrochemical industries (EC, 2010). The market for membrane filtration is expected to reach $2.64 billion in 2018, after increasing at a five-year compound annual growth rate of 10% (BBC Research, 2013).

Although filtration with membrane is a mature market, there are a number of technical challenges that require further research and development. For example, much effort is currently being devoted to improve the performance of the existing membranes in terms of anti-fouling properties, high mechanical strength and good chemical resistance (Liu et al., 2011). The need to increase membrane lifetime and selectivity has also received great attention in the recent years (Jeazet et al., 2013). These developments are also motivated by the needs in the industrial sectors to reduce the overall operational costs and to enlarge the membrane applications (Liu et al., 2011). A good understanding of the materials features and transport mechanisms, as well as the realization of innovative functional materials with enhanced properties, are key issues for the development of new membrane, which require an intensive research activity (Chung et al., 2007).

Commercially applied membrane materials are mostly polymers, both flat sheet or hollow fiber membranes (Jeazet et al., 2013). Polyamides, polyether sulphones, polyolefins and fluoropolymers are widely used for the manufacture of polymeric membrane. These materials differ in their performance characteristics including mechanical strength, fouling resistance, hydrophobicity, hydrophilicity, and chemical stability. The surface of membrane may be changed to improve its surface properties (Rana and Matsuura, 2010), e.g. by grafting polymer branches (Ulbricht, 2006; Kumar and Ulbricht, 2013), or by immobilization of photocatalysts, e.g. titanium dioxide (TiO_2) (Liu, 2014). Alumina (Al_2O_3), silica (SiO_2), silver (Ag) nanoparticles, as well as carbon nanotubes may also be incorporated into membrane structure for better flux enhancement and fouling resistance (Kim and der Bruggen, 2010). In any polymeric product, however, non-polymeric components such as residual monomers, oligomers, solvents and a wide range of additives can be present (Crompton, 2007). All these non-polymeric components are usually of low molecular weight, may migrate from the plastic product to water and be toxics (Lithner et al., 2009, 2011).

In recent years increased attention has been given to the chemicals which are contained in marketed products. This growing awareness and concern of real or potential safety issues related to chemicals in products, has been driven by numerous factors, particularly: an increased knowledge of the hazards associated with chemicals used in products, development of new chemical regulations which established requirements for disclosure on those products containing chemicals onto markets, and consumers' desire for greater product safety (United Nations Environment Program, 2011). Harmonising chemical regulations with the aim of protecting human health and the environment has been important to Europe's chemical regulation development (Commission of the European Communities, 2001). REACH is the European Regulation (EC) No 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) adopted in 2006 (EC, 2006). REACH is based on the idea that the chemicals manufactured or imported in EU market by industry do not adversely affect human health or the environment (Askham et al., 2012). This implies that industry has certain knowledge of the properties of its chemicals and manages potential risks. The majority of the rules set forth by REACH apply to chemicals and mixtures produced or imported in more than 1 t per year and to manufacturer, importer and downstream user (EC, 2006).

This work presents and discusses the toxicological and ecotoxicological screening of chemicals used for the manufacturing of UF polymeric membrane and the REACH compliance analysis of these chemicals and membrane. Among various membranes that have found commercial application, flat sheet polymeric membrane are widely used in Europe (EC, 2010) The analysis focused on ultrafiltration (UF) polyvinylidene difluoride (PVDF) and polyethersulfone (PES) membranes manufactured by phase inversion processes, within the EU funded NANOPUR project (Development of functionalized nanostructured polymeric membranes and related manufacturing processes for water purification; FP7, Grant Agreement n° 280595) The polymers, block-copolymers, solvents and additives used in these processes were then analyzed.

2. Materials and methods

The methodological approach applied in this work is shown in Fig. 1. It includes a stepwise methodology with three main building elements: *identification of raw materials* (step 0), *(eco)toxicological assessment* (step 1 and 2), and *REACH compliance analysis* (from step A to step E). The raw materials identified for the membrane production (step 0) was then evaluated to focus which chemicals are hazardous and for which endpoint there is concern (from step 1 to step 2). While the production process and the final products were considered to identify to which REACH obligations the membranes manufacturer could be subjected (from step A to step E).

2.1. Identification of raw materials

With regard to the manufacture of PVDF and PES UF membrane, the dry-wet phase inversion process of GVS company was considered (GVS Group, Italy). In this process, a polymer solution is prepared by mixing polymer and solvent. The solution is then filtered and casted onto the non-woven support. After a partial evaporation of the solvent, the cast film is immersed in a nonsolvent medium, called coagulation bath. Due to exchange of solvent and nonsolvent between polymer solution and coagulation bath, the composition in the film is changed and phase separation is induced, with the solidification of the polymer film. During the first step of desolvation by solvent evaporation, a thin skin layer of solid polymer is formed instantly at the top of the cast film due to the loss of solvent. In the solvent–nonsolvent exchange process that follows, the nonsolvent diffuses into the polymer solution film through the thin solid layer while the solvent diffuses out. Afterwards the membrane is washed and then lightly dried in an oven. The raw materials used in phase inversion process were identified through a visit to membrane manufacturer, by collecting the Material Safety Data Sheets (MSDS) of the chemicals used, as well as information about the uses, functions and amounts. Other suitable data and information were collected from supplier, project partner, and literature.

A special attention was posed on impurities or residual undesired contaminants (free monomers) in polymers supplied, additives and solvents used and on their presence as residual contaminants in membranes, and on the use of other polymers/copolymers, in addition to those provided by polymers supplier.

2.2. (Eco)toxicological assessment of raw materials

A desk-based (eco)toxicological evaluation was performed in order to identify the hazard profile of polymers, copolymers, polymeric additives and solvents used for the development of UF membrane. The evaluation was based on literature review and expert judgment.