REVIEW ARTICLE

Imprinted membranes for sustainable separation processes

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Abstract The rapid industrial growth and the necessity of recovering and recycling raw materials increased the interest in the production of highly selective and efficient separation tools. In this perspective, a relevant input was given by the membrane-based technology and the production of imprinted membranes, which possess specific recognition properties at molecular and ionic level, offers the possibility of developing sustainable and green processes. Furthermore, the integration of imprinted membranes with traditional or membrane-based approaches is a promising strategy in the logic of process intensification, which means the combination of different operations in a single apparatus. This work discusses the concept and separation mechanisms of imprinted membranes. Furthermore, it presents an overview of their application in organic solvent nanofiltration, for the removal of toxic agents and recovery solvent, as well as valuable compounds. The recent advances in water treatment, such as pesticide removal and recovery of metal ions, are also discussed. Finally, potential applications of imprinted membranes in hybrid processes are highlighted, and a look into the future of membrane separations for water treatment and recovery of critical raw materials is offered.

Keywords sustainable processes, membrane separation, molecular recognition, imprinted membranes, water treatment

1 Introduction

Nowadays, it is well recognized the necessity to minimize costs and environmental impact of traditional separation processes for realizing a sustainable industrial growth, in the logic of reducing manufacturing costs and environmental impact, in terms of energy preservation, waste minimization and resources recycle, as well as health safety. In this view, Membrane Technology had a significant influence in many sectors and membrane operations as separation and purification tools in promoting process intensification are viewed [1–4]. Membrane operations are easily achievable and scalable; they exhibit high selectivity and permeability, do not involve any phase change and are stable in a wide pH range. Furthermore, they do not require the addition of chemicals (additives) to achieve the required separations or, in some cases, require only a minimal part of it. They have low energy consumption, low environmental impact and can operate in integrated continuous processes, as well as in hybrid processes that combine membrane technology with other operations [5–7]. Until now, many sectors exploited the potential of membrane processes. For example membranes were used in water treatment [8–10], food processing [11,12], solvent recovery together with pharmaceutical purifications [13,14] and much more [15–20].

In parallel to the development of the membrane science have been also strongly demanded highly selective materials and the production of imprinted membranes (IMs) is a challenge increasingly pursued by the scientific community in the last years. Imprinted membranes have specific recognition properties at molecular and ionic level. Therefore, miming the interaction strategy employed by living systems they are able to selectively separate target ions or molecules of particular interest from a mixture containing other substances or similar compounds. The idea to introduce specific recognition properties into a membrane had significant evolution in the development of bio-mimetic smart membranes exhibiting high stability, sensitivity and specificity. This approach leads to overcome the problem of achieving the real separation of structural homologues or ions having the same radii

observed with traditional membrane separation technologies.

Imprinted membranes were prepared in both, flat-sheet and hollow fibre configurations exploiting different strategies. The capacity of IMs to promote the selective retention or transport of the targeted compounds has rendered them good candidates for the development of highly innovative membrane processes. Imprinted membranes were applied in different fields, such as recovery of bioactive compounds from raw sources, water treatment, sensors, recovery of valuable ions from seawater, organic solvent nanofiltration, enantiomeric separations and so on [21–27]. However, these examples mostly concern academic applications, while the acceptance of IMs at industrial level needs to be much more encouraged, also taking into account the rational use of available resources, as required by current times. Hindering industrial implementation of imprinted membranes are various factors. Among them, a certain increasing of membrane cost, membranes stability, reproducibility and life time. All these points might be easily overcome with the increasing of the visibility and industrial testing of these membrane systems. In the logic of developing sustainable processes, the integration of imprinted membranes with other membrane-based separation units, such as membrane distillation (MD) and membrane crystallization (MC), as well as nanofiltration, offers the possibility to implementing the separation efficiency, allowing also the better exploitation of raw materials, balancing the economic, environmental and social aspects. These strategies can really facilitate a future industrial application of imprinted membranes. Recently it was discussed about the sustainable aspect of molecular imprinting in terms of used solvents, functional monomers, operating conditions, energy efficiency, waste generation and so on [28].

This review deals with the introduction to the basic concept of membrane-based separation technology, as well as the separation mechanism of imprinted membranes. Furthermore, it presents an overview concerning the more recent application of IMs in the field of organic solvent nanofiltration, water treatment (i.e., removal of pesticides) and recovery of valuable compounds (i.e., ions and rare earth metals) from water and raw matrices. Finally, it highlights the potential advantages of integrating advanced imprinted membranes with other membrane-based operations contributing to the future development of sustainable processes. It is expected that this work will have a great impact on the research in this field.

2 Membrane-based separation technology and molecularly imprinted membranes

The term "membrane separation processes" means all the technologies in which the separation and concentration of one or more substances is achieved using membranes. The separation of the compounds of interest is possible owing to their different permeability under an appropriate driving force (pressure gradient, concentration gradient, etc.) through a membrane, which may have a dense or porous structure, depending on its application field. Today it is well demonstrated that membrane separation processes represent more and more systems that can replace traditional separation techniques (or can be integrated with them) for obtaining high purification grade of products of interest from raw materials in conditions of eco-sustainability. In addition, membrane separations represent innovative technologies that allow exploiting and recycling industrial waste substances and promoting the development of products with high value [2–4,7,29–32].

In general, the processes employing membranes as separation units are defined membrane operations and differ according to the size and physical state of the substances to be processed. Membrane operations are easy to realize, do not need the use of additives (or only in minimal part), can be applied in mild conditions, wide pH range, as well as in water and organic medium. Furthermore, they do not involve any phase change, have low energy consumption and can work in continuous processes [5–7,18,30,32].

In the last decades membrane processes found application in different fields, such as water treatment [8–10], solvent recovery and pharmaceutical purifications [13,14] food processing and biotechnological applications [11,12,32,33], and much more [15–20].

The first membrane separations of industrial interest were realized for the desalination of water by reverse osmosis. From then on, numerous membrane operations were developed. In this perspective, some of the most common membrane operations that employ also imprinted membranes are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (OI), membrane distillation (DM), electrodialysis (ED), pervaporation (PVP), etc. [7,8,18,22,30–33].

Moving from microfiltration to reverse osmosis, separations are achieved by applying a pressure gradient as driving force and the dimensions of the molecules (or particles) that must be separated become smaller and smaller. At the same time, the pore size of the membranes also decreases and this leads to an increase in the resistance to the transport of solutes and solvent (mass transport) by the membrane itself. This means that to obtain the desired separation it is necessary to increase the applied pressure. Pervaporation allows the movement of volatile organic compounds from a liquid phase to a vapour phase, through the solubility-diffusion mechanism. The process uses both a pressure gradient and a temperature gradient as the driving force. The electrodialysis permits the removal of ions from the solutions of interest by using an electric potential in the presence of a charged membrane (anionic or cationic). The separation is obtained thanks to the ability

of the membrane to let itself be crossed by ions of opposite charge (counter-ions) with respect to those present on its surface and retain those of the same charge [7,8,18,22,30–33].

The advent of molecularly imprinted membranes (MIMs) signed a new pathway for the detection and separation of targeted compounds. MIMs are special type of membranes that contain the molecular memory of the substance to be recognized (which is called template) and are capable to separate it from other similar compounds, also including structural homologues. In comparison with a traditional membrane, MIMs display improved sensitivity and selective separation properties. They can exercise a selective retention or transport of the target molecules and are promising tools for the development of advanced membrane processes. Figure 1 shows an example of an imprinted flat-sheet membrane able to bind selectively the template. As it can be seen, owing to the existing complementarity between the recognition sites of the membrane and the template, the latter is retained by the membrane and separated from the other molecules, which are collected in the permeate volume. After the recognition process, filtrations with appropriate solvents let to recovery the template. A substantial feature that must be taken into account is the fact that the preparation of any kind of imprinted membrane requires the presence of the template molecule, for promoting the formation of its complementary specific recognition sites into the membrane matrix. Also in this case, after the membrane formation the template must be removed from the membrane matrix.
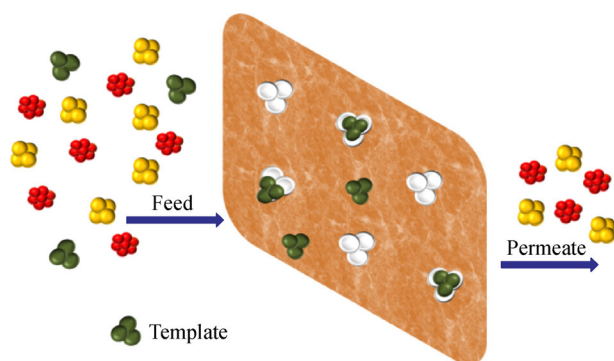

Fig. 1 Representation of an imprinted flat-sheet membrane able to bind selectively the template molecules.

In general, the removal of the template from an imprinted material (polymer or membrane) after its preparation is a factor of a relevant importance. In fact, some traces of the template can be hard to remove, even after washing the membrane for a long time. This means that the presence of residual template into the imprinted material reduces the number of the available recognition sites for rebinding with it and thus the recognition

performance [34]. In addition, the residual template may be released during the recognition step, thus negatively affecting the analytical results. Finally, large volumes of organic solvents saturated with organic compounds are used [34,35] in conventional template removal via exhaustive washing with them. Considering these aspect, the possibility of achieving total template removal was investigated using different strategies, also including green template removal. Some examples are the microwave-assisted extraction and the ultrasound assisted extraction [23,36]. Supercritical CO_2 and pressurized hot water extraction are other two extraction strategies aiming in alternative to organic solvent [35,36]. Lorenzo and co-authors deeply discussed the mechanism of these template removal strategies [34].

Two different interactions in the preparation of an imprinted membrane can be exploited: covalent and non-covalent binding. The first one, pioneered by Wulff and Sarhan [37,38], is based on the establishment of covalent bonds between the template and the functional groups of the membrane forming material and in the subsequent recognition process. The second type of interaction, firstly applied by Mosbach and Sellergren [39], is characterized by the presence of non-covalent chemical bonds. Even though the covalent binding allows creating into the membrane recognition sites that are more homogeneous (thanks to the possibility of monitoring the stoichiometry of the process), the non-covalent strategy is the most widely applied. This is because the covalent imprinted materials present a restricted number of functional groups to interact with the template and display slow binding kinetics. On the other hand, in the non-covalent imprinting the weak interactions (i.e., ionic bond, hydrogen bond, hydrophobic interactions, van der Waals forces, etc.) permit the easier recovery of the template after the imprinting procedure and the recognition process [39–42]. Furthermore, the non-covalent binding is the recognition mechanism adopted by living systems. In some cases, a combination of the two methods is also realized.

Molecularly imprinted membranes exhibit two different mechanisms for the separation of the template molecules: retarded permeation and facilitated permeation. In the first case, the membrane works as an adsorber system and retains the template, retarding or avoiding its permeation with respect to other analytes. This behaviour is due to the binding affinity between the template and the complementary recognition sites of the membrane. In the second case, the formation of a preferential pathway for the template molecules via binding to and dissociating from neighboured recognition sites in the membrane promote their more rapid permeation with respect to the other solutes that pass slowly through the membrane [43,44]. MIMs are prepared with numerous materials in both, flat-sheet and hollow fibre configurations by exploiting different strategies. Flat-sheet membranes are thin films, which can have a dense or a porous structure, while hollow-fibers have a

spaghetti-like tubular configuration and a macroporous structure that supports a dense selective layer. The main applied preparation methods are: 1) the surface imprinting of a pre-existing membrane; 2) the contemporary formation of membrane structure and recognition sites of a self-supported membrane; 3) the hybridization of a polymer forming membrane with a pre-synthesised imprinted polymer (MIP) [22,23,25,44–49].

The surface imprinting strategy involves the formation of recognition sites on the surface of a pre-existing support membrane, for example *via* thermal of photo co-polymerization with a thin layer of an imprinted polymer that covers entirely the membrane surface and preserves its pore structure. The method allows obtaining composite membranes, by combining the selective properties of the polymer layer with the mechanical integrity of the support membrane (Fig. 2(a)). In the second case, the simultaneous formation of membrane structure and recognition sites is obtained by means of two different ways: the *in situ* cross-linking polymerization and the alternative molecular imprinting. In the first case, a mixture solution containing the template, a functional monomer, a cross-linker, an initiator and a plasticizer is polymerized *via* thermal or ultraviolet initiated polymerization method, for obtaining a flexible membrane. The alternative molecular imprinting is one of the most used approaches for preparing imprinted membranes. According to this method, a polymer, having chemical functions complementary to the template, is used
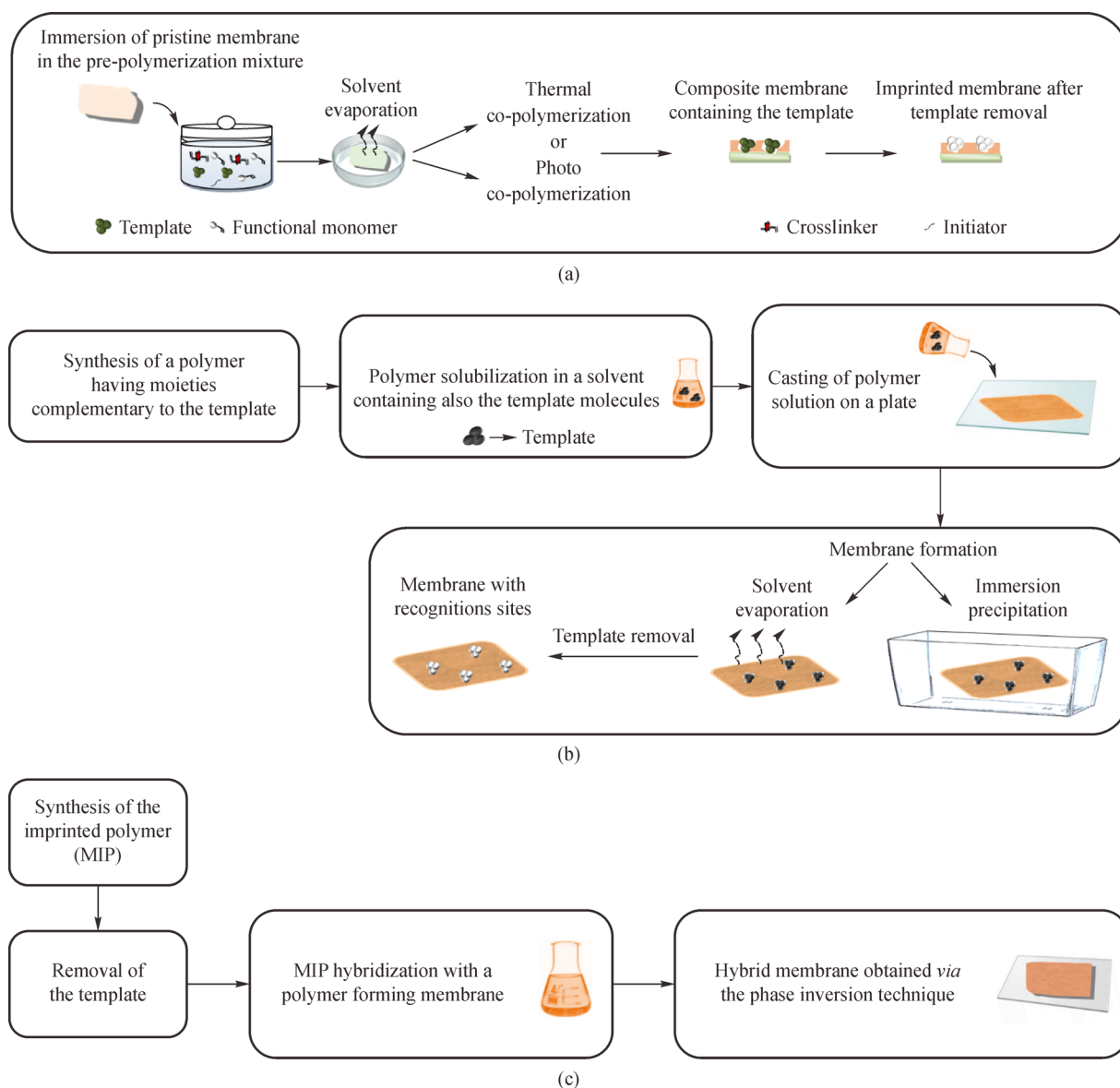

Fig. 2 (a) Scheme of the preparation of an imprinted membrane *via* the surface imprinting method; (b) Scheme of the preparation of an imprinted membrane *via* the alternative molecular imprinting; (c) Scheme of the preparation of a hybrid imprinted membrane using the phase inversion technique.

for preparing the membrane in the presence of the template *via* the phase inversion technique. During the membrane formation, the polymer chains are organized around the template molecules. Afterwards, the template is extracted from the membrane, leading the formation of its complementary recognition sites into the polymeric matrix (Fig. 2(b)). The phase inversion technique is employed also for hybridizing a polymer forming membrane with a pre-synthesised imprinted polymer. In particular, the process entails the dispersion of MIP in a polymer commonly used for preparing membranes, and the subsequent membrane formation *via* the phase inversion (Fig. 2(c)). This method permits to obtain high selective composite membranes (also called hybrid imprinted membranes).

In addition to these basic and consolidated methods, imprinted membranes are prepared exploiting other approaches. For example, Silvestri et al. used imprinted particles for modifying the surface of poly (acrylic acid-co-methylmethacrylate) membranes by simple deposition [50]. Furthermore, imprinted nanofibers with a simultaneous application of the phase inversion technique and the electrospray deposition were produced for application in enantiomeric separation [51,52]. Imprinted nanofibers were also prepared *via* electrospinning and other methods [53–58]. Thin imprinted polymer films on Teflon filters, inorganic microporous glass-fiber membranes and multi-walled carbon nanotubes *via* surface sol–gel process were also produced [59–61]. Supported liquid membranes-protected molecularly imprinted beads [62,63], (hydro)/(cryo)gel [64,65] MIMs as well as submicrosized imprinted microfiltration membranes using the "two-dimensional" molecular imprinting method were also prepared [66]. These cases are only few examples of MIMs development approaches summarized by some reviews in the last decade and showed in Table 1.

However, for implementing the great potential of MIMs in sustainable growth this topic needs to be explored much more. In this perspective, the present review focuses the attention to the application of MIMs in the recovery of valuable compounds from raw matrices and in the removal of toxic agents from both water and organic media in the

last years. Finally, it looks to the future perspectives in the combination of MIMs with other emerging membrane-based operations (as for example membrane distillation and membrane crystallization) in sustainable processes.

3 Imprinted membranes and organic solvent nanofiltration

Organic solvent nanofiltration (OSNF) is a pressure driven membrane process that permits the separation of molecules present in organic media according to their size (from 100 Da to 2000 Da) [69–71]. The organic solvent recovery in OSNF is a relevant aspect for making sustainable the separation at nanoscale. However, traditional OSNF membranes are not able to retain compounds having molecular weight less than 200 Da and impurities accumulate in the used solvent during the process. The idea to combine OSNF and the imprinting technology allowed developing molecularly imprinted-organic solvent nanofiltration membranes (MI-OSNFMs) that can help to solve this problem. MI-OSNMs are high selective membranes that in comparison with the traditional ones have the advantage of acting both as size exclusion systems and shape-specific adsorbing membranes. Therefore, it is important to make an effort for employing imprinted membranes in OSNF and other membrane-based processes in organic environment, as for example ultra-filtration. In fact, up to now, MIMs were widely used in water phase but there are only few studies on their application in organic media, also considering the solvent consumption, which is a problem of pharmaceutical field. For example, MI-OSNFMs were prepared *via* the phase inversion technique using the genotoxic compound 2-aminopyrimidine (2AP) as template molecule. For the first time, polybenzimidazole, which possess excellent chemical and solvent stability, was employed as functional polymer [72]. Membranes were used in a hybrid process, combining molecular imprinting with nanofiltration for separating the antibiotic roxythromycin (Roxy) from both the template and the catalyst 4-dimethylaminopyridine (DMAP). The adopted strategy allowed to adsorb the

Table 1 A summary of more recently published reviews on molecularly imprinted membranes

Title	Publication year	Ref.
Molecularly imprinted polymer membranes and thin films for the separation and sensing of biomacromolecules	2017	[67]
Molecularly imprinted membranes: past, present, and future	2016	[22]
The recognizing mechanism and selectivity of the molecularly imprinting membrane, molecularly imprinted catalysts	2016	[45]
Bio-mimetic sensors based on molecularly imprinted membranes	2014	[23]
Emerging tools for recognition and/or removal of dyes from polluted sites: molecularly imprinted membranes	2014	[24]
Molecular imprinting science and technology: a survey of the literature for the years 2004–2011	2014	[47]
Molecularly imprinted membranes	2012	[25]
Molecularly imprinted nanofiber membranes	2011	[68]

genotoxin on the membrane (owing to the molecular interactions with the membrane recognition sites) and to permeate the solvent and the catalyst. In addition, the membrane easily rejected roxythromycin. Figure 3 shows the hybrid proposed strategy with the 2AP-imprinted nanofiltration membrane.

The effect of dope solution concentration and applied pressure on the molecular recognition behaviour of the prepared membranes was investigated. Experimental results evidenced that an increase of the polybenzimidazole concentration in dope solution (from 18 to 24 wt-%) lead to obtain more homogeneous recognition site distribution into the membrane matrix and high solute rejection values. On the opposites, the permeate flux decreased. Furthermore, increasing the transmembrane pressure from 1.0 to 15 bar, the molecular recognition capacity irreversibly decreased. This behaviour was probably because when increasing the pressure the recognition sites of the membrane were subject to an irreversible deformation [72].

In another work, authors proposed a different hybrid process for the removal of the genotoxic 1,3-diisosopropylurea (IPU) from active pharmaceutical ingredients (APIs) post reaction streams [73]. The molecular weight of IPU is 144 Da and therefore OSNFMs only partially retain it. For overcoming this problem, an IPU-imprinted polymer [74] binding unit and an organic nanofiltration system were combined strategically. The process underway with a nanofiltration step that permitted to recovery the large fraction of IPU in the permeate stream, while the residual IPU in the retentate containing APIs was removed with the imprinted polymer. The recovery of IPU with methanol allowed regenerating and recycling the imprinted material. Below 100 mg·L^{-1} of initial IPU concentration, in one single passage was achieved an IPU removal of 83%. Furthermore, the combination of the NF with a diafiltration permitted to reduce the IPU contamination from 100 mg IPU/g API to 2 mg IPU/g API. The API loss during the NF step was only about 3% [73].

More recently hybrid processes were also developed for selectively recognizing bioactive compounds. In particular, Didaskalou et al. proposed a continuous adsorftion process with *in situ* solvent recovery and continuous purification of the bioactive compound oleuropein from olive three leaves [6]. Authors coupled the adsorption of oleuropein performed with an imprinted polymer with a nanofiltration-based solvent recovery step in the logic of a process intensification. Figure 4 shows the scheme of the process.

Firstly, the olive leaf extract was collected to two chromatographic columns containing oleuropein-imprinted polymer that adsorbed the template on its complementary recognition sites. Simultaneously, for desorbing the oleuropein from the imprinted polymer, ethyl acetate was also recirculated along the columns. Next, polybenzimidazole-based nanofiltration membranes were used for recovering the ethyl acetate in the permeate stream and concentrating the oleuropein in the retentate. The continuous hybrid process allowed recovering and recycling the 97.5% of ethyl acetate. Furthermore, was achieved an oleuropein purity of the 99.7% (at a rate of 1.75 g product per kg of adsorbent per hour). The possibility of recycling the solvent reduced the environmental impact and the proposed strategy can be applicable for the purification of other compounds from complex mixtures. For example, in 2019, Voros and co-workers proposed a similar continuous process for the simultaneous isolation and fractionation of oleuropein, luteolin, and pinoresinol from agricultural waste based on temperature-swing adsorption. In this case two sets of three columns (two for each compound) containing the imprinted polymers were integrated with the NF units. The process allowed to reduce the solvent consumption of the 97.5%
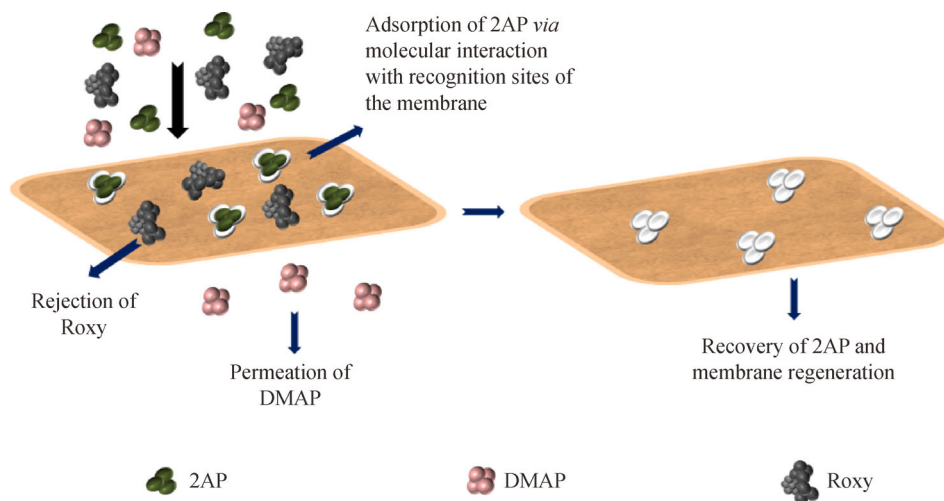

Fig. 3 Hybrid process for the molecular recognition of 2AP, rejection of Roxy and permeation of DMAP with the 2AP-imprinted nanofiltration membrane.
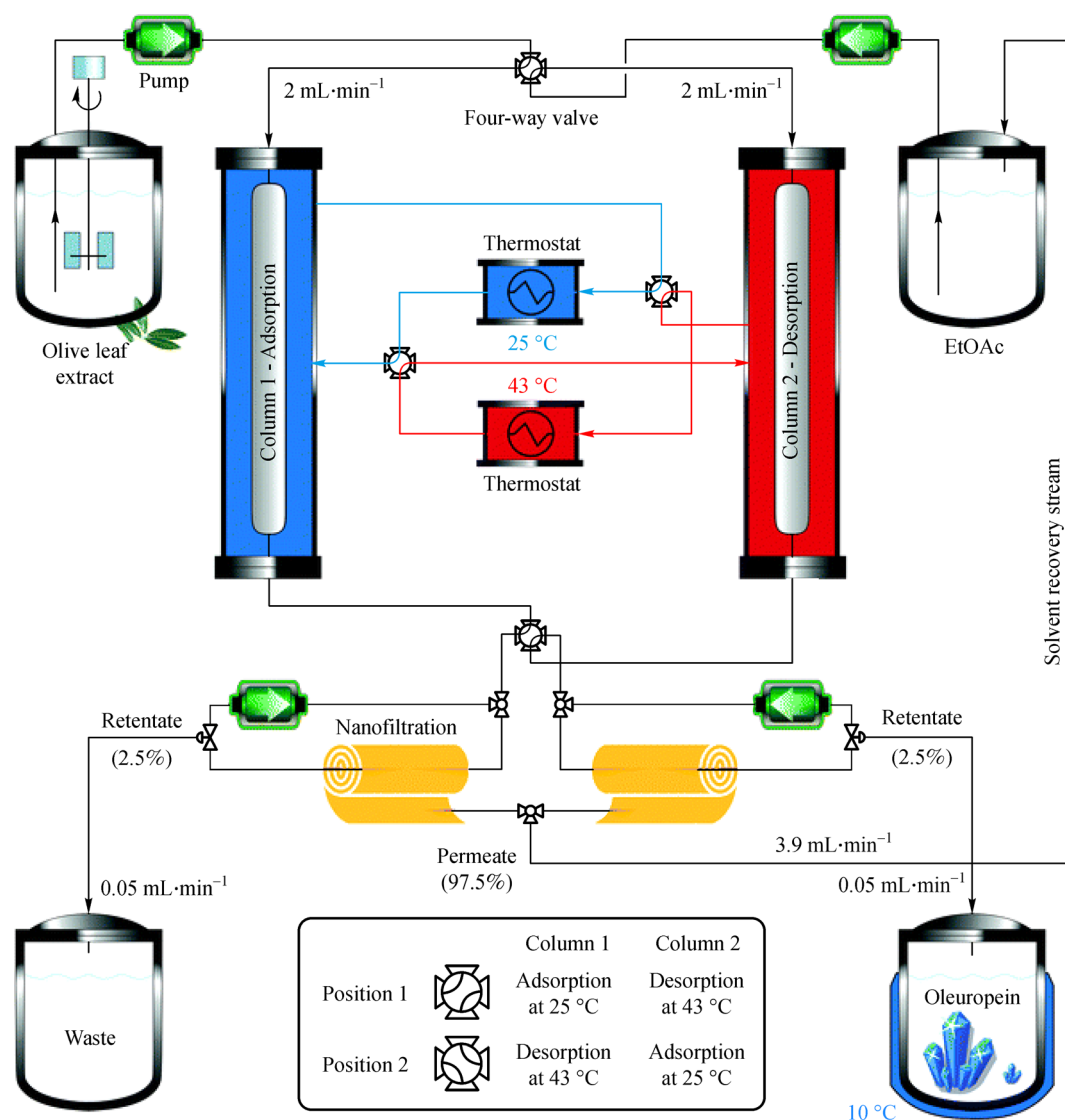
Fig. 4 Scheme of the continuous hybrid for the purification of oleuropein from olive three leaves and ethyl acetate recovery. Reproduced from ref. [6] with permission, copyright 2017 The Royal Society of Chemistry.

and to achieve the selective scavenging of the target compounds with 95%–99% purity at a rate of 1.75, 3.42, and 0.12 g of product per kilogram of scavenger per hour for oleuropein, luteolin, and pinoresinol, respectively [75].

The phase inversion technique was also applied for developing diosgenin-molecularly imprinted membranes made of poly(acrylonitrile-co-acrylic acid) [76]. Diosgenin is a bioactive compounds (which can be extracted from *Dioscorea*) capable of reducing cholesterol level in the blood [76]. Adsorption tests carried out in ethanol showed that the imprinted membranes efficiently bounded the template molecules with respect to the corresponding non-imprinted ones (NIMs) that exhibited poor non-specific binding only. In addition, the imprinted membranes were able of discriminating diosgenin from the similar compound stigmasterol [77].

Others used the atom transfer radical polymerization for

imprinting the surface of polyvinylidene fluoride (PVDF) membranes modified with dopamine. The anti-malaria drug artemisinin was chosen as template molecule [78]. The recognition performance of the produced artemisinin-imprinted nanocomposite membranes were evaluated in ethanol. Results of adsorption tests showed that in the case of imprinted membranes the permeation of template molecules was much higher than the values observed for the non-imprinted membranes. This was due to the presence of template-recognition sites of the surface of imprinted membranes. The adsorption kinetic followed the pseudo-second order model. The adsorption equilibrium was reached after 200 min.

The maximum adsorption capacity of MIMs was 158.85 $mg \cdot g_{memb}^{-1}$, while that one of NIMs was 37.35 $mg \cdot g_{memb}^{-1}$. The imprinting factor was 4.25. In addition, in selective permeability experiments (carried out

with a diffusion cell) artemisinin permeated much more with respect to its structural analogue artemether. As it is shown in Fig. 5, The concentration of artemisinin in the receptor compartment increased in the time, while the concentration of arthemeter was almost constant.
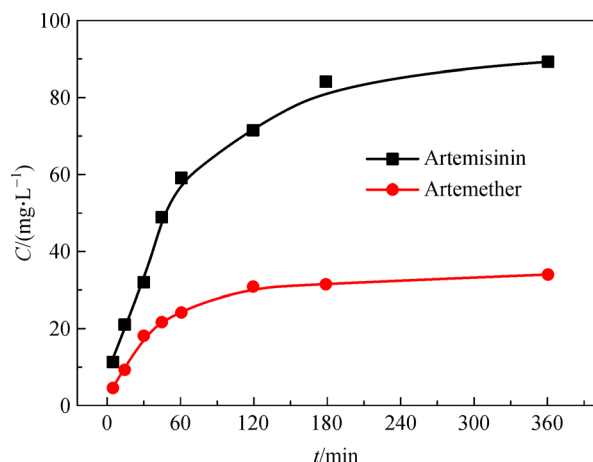

Fig. 5 Permeation behaviour of Artemisinin-imprinted membrane *vs* artemisinin and its competitor artthemeter. Reprinted from ref. [78] with permission, copyright 2016 John Wiley and Sons.

A selective facilitated permeation of the template was observed also with composite imprinted membranes produced *via* surface functionalization of commercial PVDF microfiltration membranes. In this case the selective removal of the herbicide podophyllotoxin from methanol was achieved [79].

3.1 Case study: development of 4,4-methylendianiline-imprinted membranes

As above discussed, the possibility of solvent cleaning and recovery in pharmaceutical and other industrial fields, is a challenge in process intensification and imprinted membranes have great potential in contributing to achieve this objective. Among the few investigated cases, authors have carried out some studies in the framework of the NEMOPUR Project, sponsored by the European Community. In particular, solvent resistant molecularly imprinted membranes with controlled specificity for the aromatic 4,4-methylendianiline (MDA), which is a member of the big family of primary amines, were developed [80,81]. The International Agency for the Research on Cancer consider the aromatic amines as potential carcinogens [82]. Because some of them are used as intermediate reagents in different synthesis, and owing possible in-complete reaction they might be present at low concentration in solvents. Membranes were prepared *via* the phase inversion technique according to the alternative molecular imprinting using poly(acrylonitrile) and some its copolymers: poly (acrylonitrile-co-acrylic acid) (P(AN-co-AA)), poly(acrylonitrile-co-itaconic acid) (P(AN-co-IA)) and poly(acrylo-

nitrile-co-methacrylic acid) (P(AN-co-MA)). For comparison, non-imprinted membranes were also prepared. Binding experiments showed that the membranes recognized the template in different extent. The better performance was exhibited by P(AN-co-AA)-imprinted membranes. Figure 6 shows the binding capacity *vs* the initial concentration of MDA in feed solution.
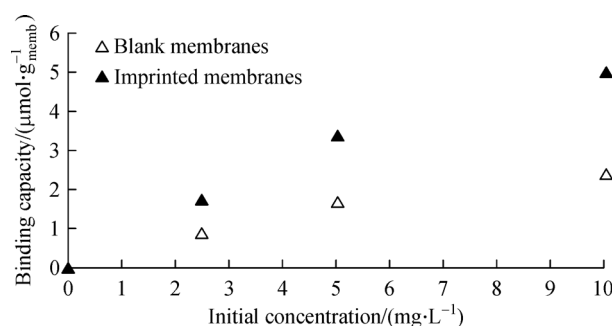

Fig. 6 Binding capacity of 4,4-methylendianiline-imprinted membranes and of the corresponding non-imprinted membranes in isopropanol *vs* the initial MDA concentration. Reprinted from ref. [80] with permission, copyright 2012 from Elsevier.

It is evident that increasing the initial MDA concentration also increased the binding capacity and the difference between the imprinted and non-imprinted membrane. This behaviour was because increasing the concentration also increased the number of template molecules available for interacting with the complementary recognition sites of the imprinted membrane. The molecular interaction occurred owing to the formation of hydrogen bonds between the hydroxyl group of acrylic acid and the amine group of DMA (Fig. 7).

At the initial MDA concentration of 10 mg·L^{-1} the binding capacity of the imprinted membrane was 5.0 μmol·g$_{memb}^{-1}$ while that one of the corresponding non-imprinted membrane was 2.4 μmol·g$_{memb}^{-1}$. In this condition, the specific binding capacity was 2.6 μmol·g$_{memb}^{-1}$. Furthermore, these membranes displayed selective properties towards the structural analogue 4,4-ethylendianiline (EDA) (see Fig. 8). The selectivity factor MDA/EDA was 1.6.

This study demonstrated the possibility of using P(AN-co-AA)-imprinted membranes in OSNF for the specific recognition of the genotoxic MDA. In the framework of NEMOPUR project authors produced also hybrid organic solvent resistant membranes [83]. In particular, polymer particles imprinted with MDA were dispersed in PVDF matrix for preparing the membranes *via* the phase inversion technique. Different samples were prepared varying the amount on the imprinted polymer added to the dope solution (or non-imprinted polymer). The permeability of these membranes was in the ultrafiltration range. After binding tests performed at an initial MDA
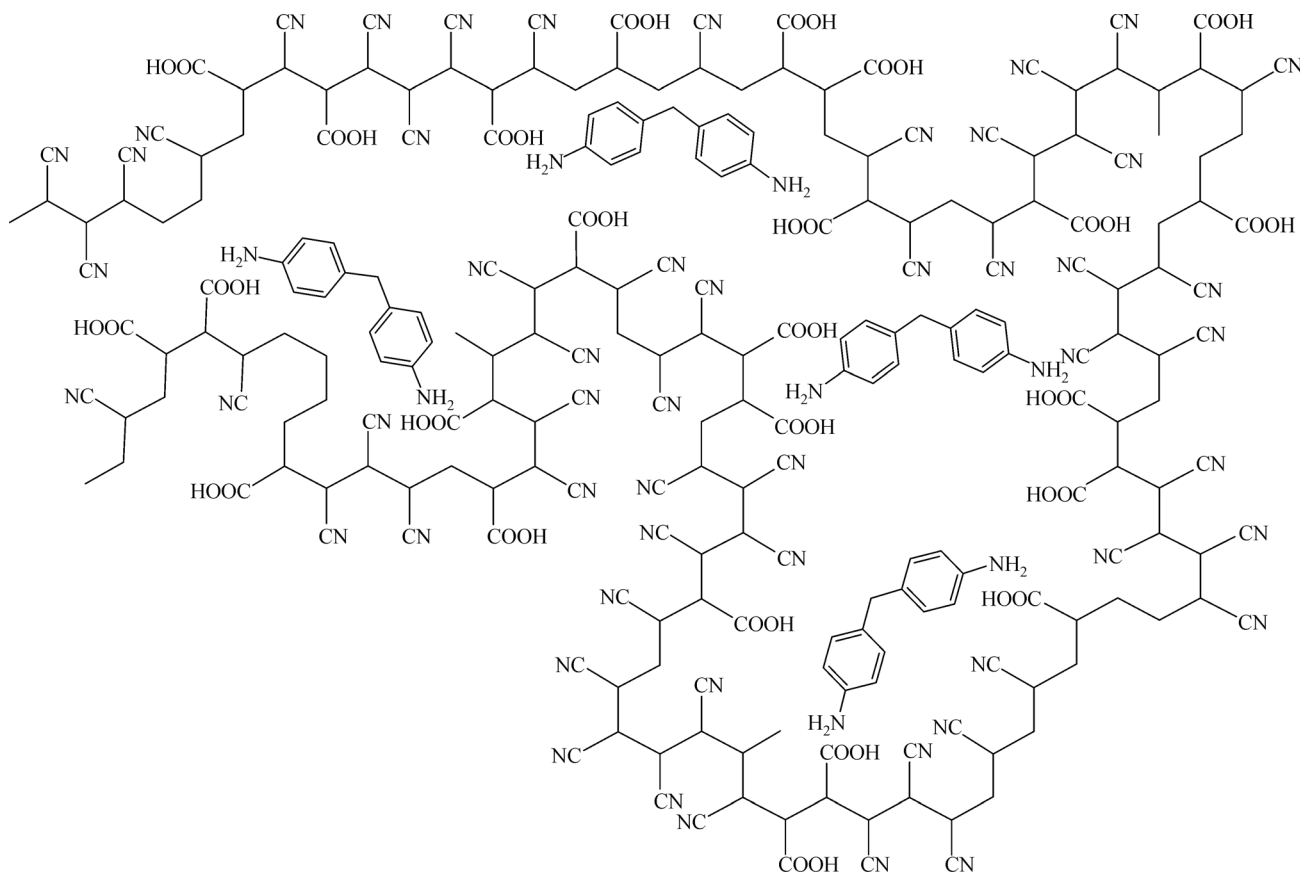
Fig. 7 Molecular interaction between the amine groups of MDA and the acrylic residues of P(AN-co-AA)-based membrane. Reprinted from ref. [80] with permission, copyright 2012 Elsevier.
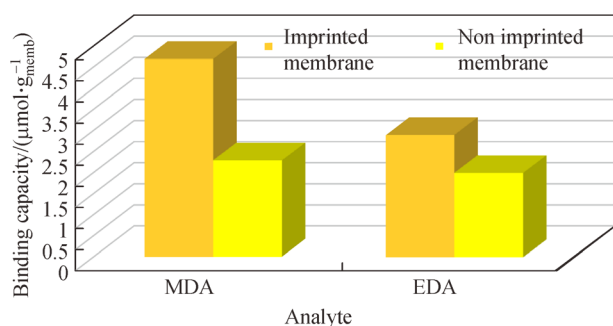

Fig. 8 Binding capacity of 4,4-MDA-imprinted membranes and of the corresponding non-imprinted membranes in isopropanol *vs* MDA and the structural analogue EDA (data from [80]).

concentration of 10 mg·L^{-1}, the highest specific binding for MDA (3.1 μmol·g$_{memb}$$^{-1}$) was observed in the case of a membrane containing the 33 wt-% of imprinted polymer with respect to the PVDF matrix [83]. For this membrane, the selectivity factor MDA/EDA was 1.82.

The membranes helped to maintain stable the recognition properties of the imprinted polymer and contemporary exploited the typical features of membrane-based processes. Industrial sectors are the main responsible of the greenhouse emission and environment contamination and innovative strategies for the economical and chemical sustainability of the production processes are today well accepted. In this scenario, the possibility of integrating the imprinting technology with membrane-based operations in organic phase can help to reduce the environmental impact by lowering the amount of solvent discarded and therefore of the fresh solvent consumption.

4 MIMs for the selective recognition of pesticides in water

Pesticides are a wide number of compounds used in agriculture, which can contaminate the surface and the ground water. They are involved in the origin of different maladies such as birth defects, developmental disorders, impaired reproductive abilities, etc. Owing to their ecological and human health impact, their removal from water and wastewater today is a priority. Here, some of the most recent papers concerning the production of MIMs for the specific recognition of pesticides are discussed. For example, Donato et al., developed molecularly imprinted membranes with affinity properties for the dimethoate, an

organophosphorus pesticide largely used for its insecticide and acaricide activity. It is highly soluble in water and adsorbs very weakly to soil particles and can causes oncogenicity, mutagenicity, fetotoxicity and reproductive defects [84]. Imprinted membranes, prepared *via* the phase inversion technique using poly(acrylonitrile-co-methacrylic acid) and poly(acrylonitrile-co-acrylamide) exhibited good recognition performance in comparison with their corresponding blank membranes and poly (acrylonitrile) homopolymer. However, the highest overall (10 mmol·g_{memb}^{-1}) and specific (7.5 mmol·g_{memb}^{-1}) binding capacity was showed by the AN-co-MAA dimethoate-imprinted membrane. This means that the carboxyl groups of methacrylic acid were more effective in the interaction with the template. In selectivity studies, the selectivity factor dimethoate/trichlorphon was 2.3 [84].

More recently, methacrylic acid as functional monomer for preparing nanopore imprinted membranes for the selective removal of the herbicide 2,4-dichlorophenoxya-cetic acid from water was used by Kashani et al. [85]. 2,4-Dichlorophenoxyacetic acid is classified as a possible carcinogen and mutagen by the International Agency for Research on Cancer [86]. Imprinted polymer particles made of poly(methacrylic acid) have been dispersed in a polysulfone dope solution and membranes were prepared *via* phase inversion. Different membranes were prepared by changing the amount of imprinted particles added to the system. Permeation tests showed that the template transport mechanism was based on the facilitated permea-tion, while the template's structural analogue 2,4-dichlor-ophennoxyacetic acid was subjected to a retarted permeation [85]. For inducing bergenin crystallization in supercritical CO_2 were also produced molecularly imprinted composite membranes [87]. Supercritical CO_2 is used as processing medium in crystal growth, solvent precipitation, etc. In particular, owing to its high diffusivity and low viscosity its employment is interesting in the crystallization of compounds difficult to be separate. Varying the ratio template/functional monomer authors prepared different imprinted membranes by means of ultraviolet photo-copolymerization of polysulfone support with acrylamide functional monomer. Then, the mem-branes were used for inducing bergenin crystallization in a supercritical fluid extraction system. Results of this study showed that the use of the imprinted membrane prepared at bergenin/acrylamide ratio of 1:4 improved both the crystallization rate and the crystal purity with respect to the non-imprinted membrane. In Fig. 9 it is evident that in the case of MIM the crystallization rate of bergenin reached the 44.7% and its purity was 98.1%.

This approach exploited the property of the imprinted membrane to withstand high pressure. In addition, the presence of the complementary sites with the template on the membrane surface promoted a more rapid formation of the crystal nucleus and consequently their growth rate [87]. In another work, composite membranes were imprinted
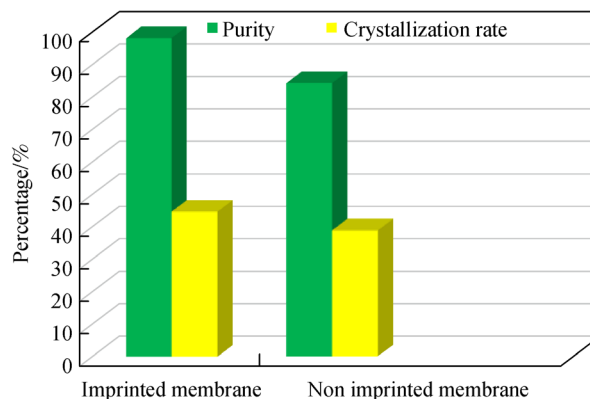

Fig. 9 Purity and crystallization rate of bergenin inducing crystallization in supercritical CO_2 with bergenin-imprinted membrane and its corresponding non-imprinted membrane (data from [87]).

with the herbicide nicosulfuron, which established hydro-gen bonds with the carbonyl groups of P(MAA) photo-copolymerized with microporous filter paper as membrane support [88]. Membranes were able to remove selectively the template from water samples by means of competitive binding with respect to similar analytes. Zhang et al. [89] produced molecularly imprinted composite membranes sensor, based on zinc porphyrin for the detection of dimethyl methylphosphonate. The membranes exhibited high selective recognition capacity and allowed to achieve high template-recovery rate from river water (ranging from 95% to 108.1%) and tap water (ranging from 96.5% to 106.2%). The detection limit was 0.1 μmol·L^{-1} [89]. Imprinted membranes for the selective extraction of triazine herbicides from water were also prepared using different methods [90–93]. Apart the examples discussed above, other MIMs were produced for the selective detection and separation of isoproturon [94], 2,4-dinitro-phenol [95], amitrol [96], chlorpyrifos [97] and recently the carbamate insecticide primicarb [98] as well as others pesticides as discussed elsewhere [22,23,99,100].

5   Ion imprinted membranes (IIMs)

IIMs are a particular type of non-covalent imprinted membranes endowed with selective recognition properties *vs* ions instead of molecules. In particular, thanks to electrostatic interactions they are selective for anions and cations. These kind of imprinted membranes are able to realize detection, separation and purification processes at ionic scale. For example, they have great potential for the detection of ion contaminants present in various matrices as well as for the selective recovery of high added-value metals. They may have a great impact in water treatment, rare earth metals recovery, battery preparation, pollution control, etc. [21,101,102]. Beside the high selective

detection and separation properties of IIMs, up to now, the number of publications dealing with their preparation and application is low and it needs to be implemented. Following will be discussed some important examples of more recent literature. Other and more detailed information can be found in a recent review published by Lu et al. [21] that summarized the number of publications per year on IIMs until December 2018 (see Fig. 10). Authors evidenced that the number of publications on IIMs is very low in comparison with the number of publications dealing with other ion selective membranes.

5.1 IIMs in the recovery of rare earth metals

Rare earth metal (REMs) are 17 special elements of the periodic table including lanthanides (La–Lu), yttrium (Y) and scandium (Sc). Owing to their electrical, magnetic and optical properties, they play an important role in the development of the clean energy, petrochemical engineering, high-tech manufacturing, etc. In the last years, the increased demand of REMs at industrial level determined also an increase of their price and of the water pollution. Therefore, they become critical raw materials, with high supply risk for the future years and great environmental impact. Consequently, the development of efficient techniques for their removal and recovery from water, wastewaters and other resources is a pursued challenge of the entire scientific and industrial community [103–106]. However, REMs have chemical similarity and it is rather difficult to separate them from each other. Among the different investigated separation approaches, the employment of IIMs membranes in the recovery of rare earth metals is a promising strategy also at low concentration level, owing to their high selectivity and low energy consumption. REMs-imprinted membranes were prepared with different methods. For example, IIMs for selectively recognize some member of the family of lanthanides were produced by many authors. Lanthanides, are largely

employed in many fields such as agricultural, catalysts, etc., are increasingly present in environment and food chain. Liu et al. used the immersion-precipitation evaporation method for preparing a chitosan membrane with 3D macroporus structure imprinted with dysprosium, one of the REMs that the European Community included in the list of the critical raw materials [107]. Adsorption experiments demonstrated that at pH 7 the imprinted membrane exhibited the highest imprinting factor (28). Furthermore, the binding capacity of the 3D imprinted membrane was higher not only with respect to that one showed by the corresponding non-imprinted membrane but also with respect to that one of the imprinted membrane prepared without the macroporous structure. This means that the adsorption of dysprosium was based on both the coordination bonds (between the NH_2 groups of the membrane with dysprosium) and the spatial structure. Finally, the membrane was able to separate Dy^{3+} from other REMs having the same valence, such as neodium Nd^{3+}, Pr^{3+}, Tb^{3+} and Fe^+, which coexist in untreated water solution [107]. In a more recent work ionic-imprinted bilayer films prepared according the dual-template docking oriented ionic imprinting were able to simultaneously adsorb and separate neodium Nd(III) and dysprosium Dy(III), used both as template ions [108]. At acidic conditions (pH 4) the adsorption capacity was 17.50 mg·g^{-1} for Dy (III) and 12.15 mg·g^{-1} for Nd(III). These new membranes are promising tools for the selective recovery of these two rare earth elements from sintered neodymium magnets (NdFeB) where they are present as components [109]. Previously, neodium-imprinted films were prepared by exploiting this approach [110]. Apart the above cases, only other few papers were devoted to the production of rare earth metals-imprinted membranes. For example, Zheng and co-workers developed three-dimensionally interconnected macroporous chitosan films imprinted with gadolinium Gd (III) [111]. Imprinted membranes exhibited high adsorption capacity with
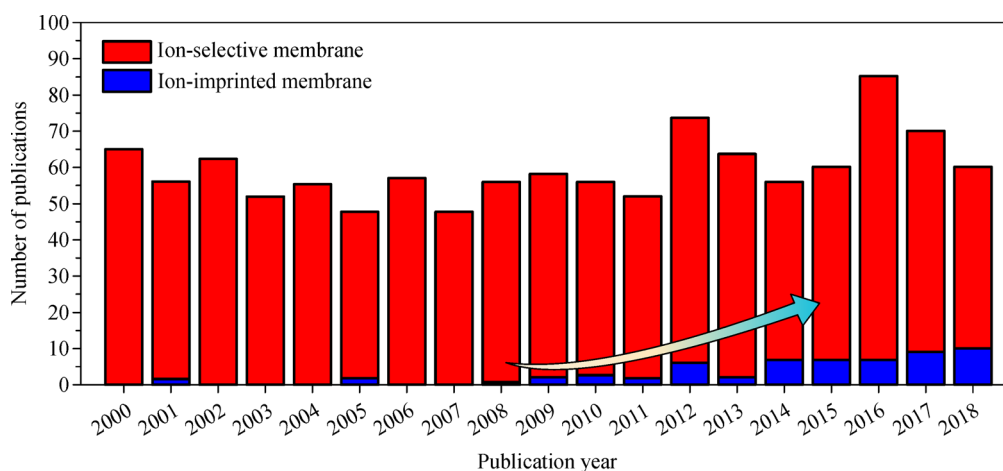

Fig. 10   Number of pubblications per year on IIMs until December 2018. Reproduced from ref. [21] with permission, copyright 2019 The Royal Society of Chemistry.

respect to the non-imprinted ones, indicating the high affinity between gadolinium owing to the coordination interactions occurred between the carboxyl groups ($-COO^-$) of Gd (III) and the amino groups ($-NH_2$) of the imprinted membrane. The maximum adsorption capacity at pH 7 and 298 K was 51.36 mg·g^{-1}. Recently, efficient free standing gadolinium-imprinted mesoporous carboxymethyl chitosan films were developed by other authors [112]. Anti-fouling and thermosensitive ion-imprinted nanocomposite membranes based on graphene oxide and silicon dioxide were also developed for the selective separation of europium (Eu^{3+}) from its analogues [113]. In adsorption tests, performed in water phase (pH 7, 25 °C), the binding capacity (Q) of these membranes vs Eu^{3+} was higher than the value observed with NIMs also prepared in this work and other adsorbent materials reported in literature [113]. In addition, high Eu^{3+} adsorption was observed in comparison with its similar REMs (La^{3+}, Gd^{3+} and Sm^{3+}). The binding capacity of both Eu-IIMs and NIMs for each tested ion, as well as the imprinting factor are reported in Table 2. For imprinted membranes, the maximum binding capacity (101.14 mg·g$_{memb}^{-1}$) was observed for Eu^{3+}, while the value measured for other ions and those detected in the case of NIMs were lower one order of magnitude. The highest imprinting factor was 5.17. Studies on the separation mechanism of these membranes evidenced a retarded permeation of the targeted Eu^{3+} with respect to its similar ions. In fact, the template ions were captured by the recognition sites present in the imprinted membrane, while the competitive ions (La^{3+}, Gd^{3+} and Sm^{3+}) permeated without problems. No difference in ions transport was observed in the case of NIMs [113].

5.2   IIMs in the recovery of metal ions

In the framework of IIMs production for the selective recognition of metals, the attention was focused mainly on the alkali metal ions and the transition metal ions. Alkali metal ions are the elements of the first group (IA) of the periodic table and form cations with $+1$ charge. The transition metal ions are typical of different groups (from IIIB to VIII). They have a large radius with respect to alkali metals and tend to form coordination complexes with suitable ligands. On the other hand, owing to their small radius, the imprinting of alkali metal ions requires the use

of complexing agents like crown-ethers and cup-like calixarene, which are compatible with their hydration radius [21].

This paragraph deals with the discussion of some papers concerning the development of IIMs for metal ions recovery. One on the most imprinted alkali ions is lithium. It is widely used in pharmaceutical industry, metallurgy, in lithium ion battery industry and aluminium production. Therefore, there is a growing demand and consequently great interest in developing innovative technologies for achieving high selectivity and efficiency in recovering this metal ion from wastewaters, lake water and seawater. An important aspect is the possibility of separating it from other elements present in abundance in the same matrices, such as magnesium [114,115]. For example, high-hydrophilic and stable mutilayered Li-IIMs were prepared exploiting the synergistic effect of 12-crown-4 and polysulfone. During permeation tests performed with mix solutions of Li$^+$, Na$^+$ and K$^+$ these Li-IIMs also exhibited low lithium permeation rate in comparison with the competitive ions. In particular, the order of permeability rate was Na$^+$ > K$^+$ > Li$^+$ and the permeability coefficient were 9.0625, 2.884 and 1.1791, respectively [116]. A schematic representation of the recognition site and of the interaction between Li^{1+} and CE is shown in Fig. 11.

In another work, high selective Li-IMs with crown ether were produced using PVDF (modified with a thin layer of polydopamine) as membrane forming material [117]. During the imprinting process, crown ether formed a stable complex with Li$^+$ and therefore promoting the formation of Li-complementary recognition sites on the IIM surface. Binding tests showed high adsorption capacity of Li$^+$ in the presence of Mg^{2+}. The maximum selectivity factor (4.42) was observed at high initial ions concentration. In addition, permeation tests in a diffusion cell evidenced low lithium permeation, confirming that the absence of specific interaction between the Li-imprinted membrane and Mg^{2+} promoted its fast permeation. Membranes were regenerated six times without losing their performance. Nanocomposite [118], hybrid [119,120] and zwitterion [121] Li-IIMs have been also produced. Recently, Wang and co-workers used the cup-like oligomer calixarene as ligand for preparing dual-imprinted mesoporous films applied in the simultaneous separation of lithium and rubidium from other mono and divalent cations. The separation mechanism was based on the

Table 2   Binding capacity (Q) of Eu-IIMs and NIMs towards Eu^{3+} and its competitive ions and imprinting factor. Reprinted from ref. [113] with permission, copyright 2018 Elsevier

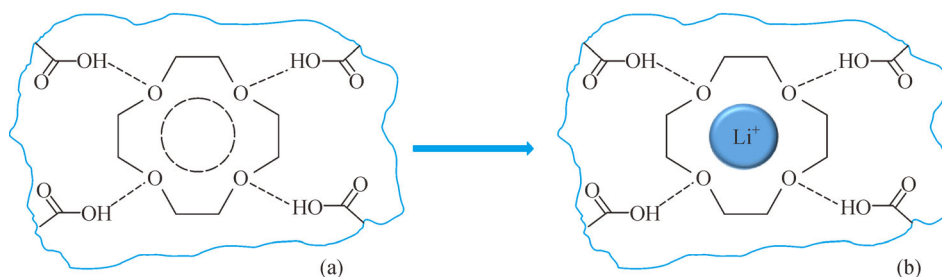| Ion	Eu-MIMs		Eu-NIMs		Imprinting factor
	Q(mg·g^{-1})	α	Q(mg·g^{-1})	α	
Eu^{3+}	101.14	–	19.58	–	5.17
La^{3+}	55.65	1.82	21.28	0.92	2.62
Gd^{3+}	64.36	1.57	19.39	1.01	3.32
Sm^{3+}	69.87	1.45	20.21	0.97	3.46

Fig. 11 (a) Recognition site complementary to Li^+ and (b) interaction of CE with Li^+ during the recognition process.

selective adsorption of the two template ions [122]. This work demonstrated that it is possible to realize the selective separation of different ions simply changing the internal size of the oligomer. In the last years, IIMs for the selective recognition of transition metals have been also produced by using different strategies. In 2014, Du and co-workers prepared composite film made of ferricyanide embedded conductive polypyrrole for the selective electrochemical removal of nickel (II) from wastewater [123]. Nickel is a heavy metal ion that owing to its human toxicity needs to be removed from the environment. Composite membranes exhibited a Ni^{2+} adsorption equilibrium time less than 50 s. The maximum ion exchange capacity for the uptake/release Ni^{2+} removal from water samples was 1.298 $mmol \cdot g^{-1}$. Separation factors Ni^{2+}/Ca^{2+}, Ni^{2+}/K^+, and Ni^{2+}/Na^+ were of 6.3, 5.6, and 6.2, respectively. Previously, Ni^{2+}-IIMs were also produced by copolymerization of methacrylic acid as functional monomer and dithizone as ligand on the surface of PVDF membranes [124]. In this case, IIMs showed a specific perm-selectivity of the targeted ion, separating it from water solution also containing the competitive cobalt ion (Co^{2+}). The separation factor Ni^{2+}/Co^{2+} was 2.6. Recently, Zeng et al. [125] proposed an advanced strategy in preparing Ni-imprinted membranes. Authors synthesized an ion imprinted polymer using silica gels. Subsequently, this polymer was used to create a dynamic membrane on the surface of a ceramic membrane. Imprinted dynamic membranes resulted more stable than original ceramic membranes. Furthermore, they had a higher permeate flux and Ni^{2+} rejection, allowing its efficient removal from water [125]. Another example of imprinted transition metal is Cupper Cu^{2+}. This element is largely present in the industrial wastewater and can be present in excess in drinking water. It is toxic for liver and stomach and can causes intestinal and other health problems. Therefore, it is important to remove it from these matrices because the copper is non-biodegradable and can accumulate in the food chain [126]. In 2018, ion imprinted membranes for the removal and recovery of Cu^{2+} from water were prepared by applying an advanced immobilization method entailing the preparation of polymerizable chelating monomer divinylbenzyl triethylenetetramine, the formation of complex Cu-functional

monomer, the subsequent polymerization/cross-linking of the complex within the pores of a PVDF-based membrane [127]. The recognition performance of the membranes were evaluated by performing adsorption and permeation tests as well as selectivity studies with mix solutions of Cu^{2+} and Ni^{2+}. The maximum copper adsorption (64.4 $mg \cdot g_{memb}^{-1}$) was observed at pH 6.0. At this pH, the amount of the cation adsorbed by the IIM was about of 4 times greater that the valued measured for the corresponding non-imprinted membrane. In addition, the permeation amount of Cu^{2+} through the imprinted membranes was higher than that of Ni^{2+}. This study demonstrated the possibility of separating Cu^{2+} from industrial wastewater containing Ni^{2+} [128]. Cu-imprinted membranes were also prepared via surface imprinting [128–131]. IIMs have been also prepared for the selective recognition of other metals ions such as Rh^{3+}, $Pt(IV)$, Pb^{2+}, Hg^{2+}, Cd^{2+}, Ag^{2+}, etc. The related literature reports detailed information [132–139].

6 Conclusions and future and perspectives

The rapid development of material engineering and nanoscience and the increased demand of designing functional materials with high separation efficiency have led to use membrane operations in larger industrial plants, especially for what concern water treatment. A contribution to the development of sustainable separations for recovering specific compounds from raw materials is coming from the integration of imprinted membranes with others membrane-based or traditional separation strategies. Up to now, despite the high specificity and selectivity of imprinted membranes and the optimal separation performance obtained at lab scale in different field, their application on a large scale is still a topic in infancy. However, the hypothesis of using them more than has hitherto been becoming a reality. This is due to the growing interest in membrane processes and to an increasingly high demand of their selectivity. In the perspective of developing sustainable processes, today it is possible to think to the integration of imprinting technology with other emerging membrane-based processes by means of the development

on novel porous imprinted membranes. Another aspect to consider is that up to date have been mostly produced MIMs exhibiting hydrophilic properties. Therefore, a field to explore is the preparation of hydrophobic MIMs. This will led to the development of new and more efficient integrated membrane operations, as it is the case of agricultural field and water treatment. For example, the integration of membrane crystallization or membrane distillation with novel hydrophobic imprinted membranes for recovering critical raw materials represent a very interesting topic to be investigated. High selectivity and recovery efficiency of critical raw materials from brine streams of nanofiltration and reverse osmosis desalination plants could be achieved by applying an integrated membrane process. In this context, the employment of new hydrophobic IIMs in MD/MC units can improve their performance in the recovery of trace elements like Li, Co or Ba, which are present in the final streams. Concluding, innovative selective separation strategies entailing the use of imprinted membranes render them good candidates for application at large scale and we think this is their future, their new investment in research, development and technological transfer.

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