

Molecularly Imprinted Affinity Membrane: A Review

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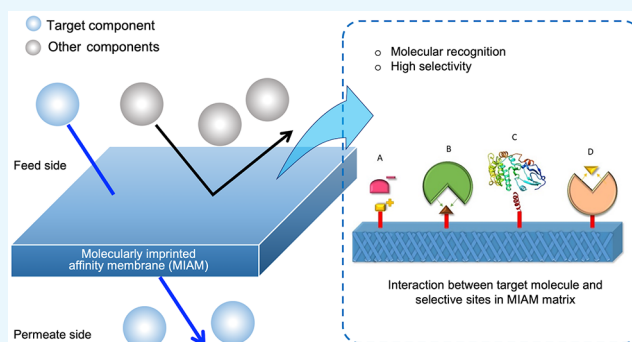
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ABSTRACT: A molecularly imprinted affinity membrane (MIAM) can perform separation with high selectivity due to its unique molecular recognition introduced from the molecular-imprinting technique. In this way, a MIAM is able to separate a specific or targeted molecule from a mixture. In addition, it is possible to achieve high selectivity while maintaining membrane permeability. Various methods have been developed to produce a MIAM with high selectivity and productivity, with their respective advantages and disadvantages. In this paper, the MIAM is reviewed comprehensively, from the fundamentals of the affinity membrane to its applications. First, the development of a MIAM and various preparation methods are presented. Then, applications of MIAMs in sensor, metal ion separation, and organic compound separation are discussed. The last part of the review discusses the outlook of MIAMs for future development.



1. INTRODUCTION

In chemical industries, the quality and cost of products are determined by the synthesis route and separation processes. The former can be economical by shortening the route or using a catalyst, while the latter can be problematic on a large scale. Purifying the product from leftover reactants, catalysts, impurities, and byproducts involves general separation processes such as distillation, extraction, absorption, crystallization, chromatography, and membrane. An ideal separation process should have minimal steps, with no or low amount of solvent and low energy consumption. Chromatography is convenient on a laboratory scale for different target molecules; however, they are not applicable in large scale in terms of cost and environmental impacts. Membrane has been considered as an interesting separation process because it is usually operated under mild conditions, with no phase change, and with relatively less energy consumption.^{1–4} In addition, membrane technology offers easy scalability and a lower footprint with high selectivity and productivity, which are preferable for large-scale applications.^{5–7}

Biologically active compounds, whether small organic chiral molecules or peptides, and proteins require even more robust methods in separation because a trace impurity of similar molecules could interfere with the functions and even be lethal if introduced to the human body. Hence, a special type of membrane that recognizes specific molecules, termed an affinity membrane, was developed.^{8–12} One way of introducing molecular recognition was by imprinting techniques, in which template molecules were introduced covalently or non-

covalently during membrane synthesis, followed by leaching of the templates, leaving specific pores in the membranes that have an affinity toward molecules resembling the templates. The aim is to achieve high permeability with maintained permselectivity. This is termed a molecularly imprinted affinity membrane (MIAM).

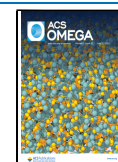
The unique features of a MIAM have resulted in it gained increasing attention from researchers and have driven more studies to explore the potential application of MIAMs. As shown in Figure 1 a, the number of publications has increased over the years. As mapped in Figure 1 b, a MIAM is mainly applied in the separation of a specific component because a MIAM can perform separation through selective recognition, where the separation of a target component or molecule is possible.^{13,14} Therefore, a highly selective separation is obtained. This feature is crucial, such as in the case of sensor applications.

Molecularly imprinted membranes have been reviewed in the literature, focusing on transport properties,¹⁵ separation mechanisms,¹⁶ molecularly imprinted nanofiber membranes,¹⁷ applications,¹⁸ and molecularly imprinted polymeric materials.¹⁹ In this paper, the MIAM is reviewed comprehensively,

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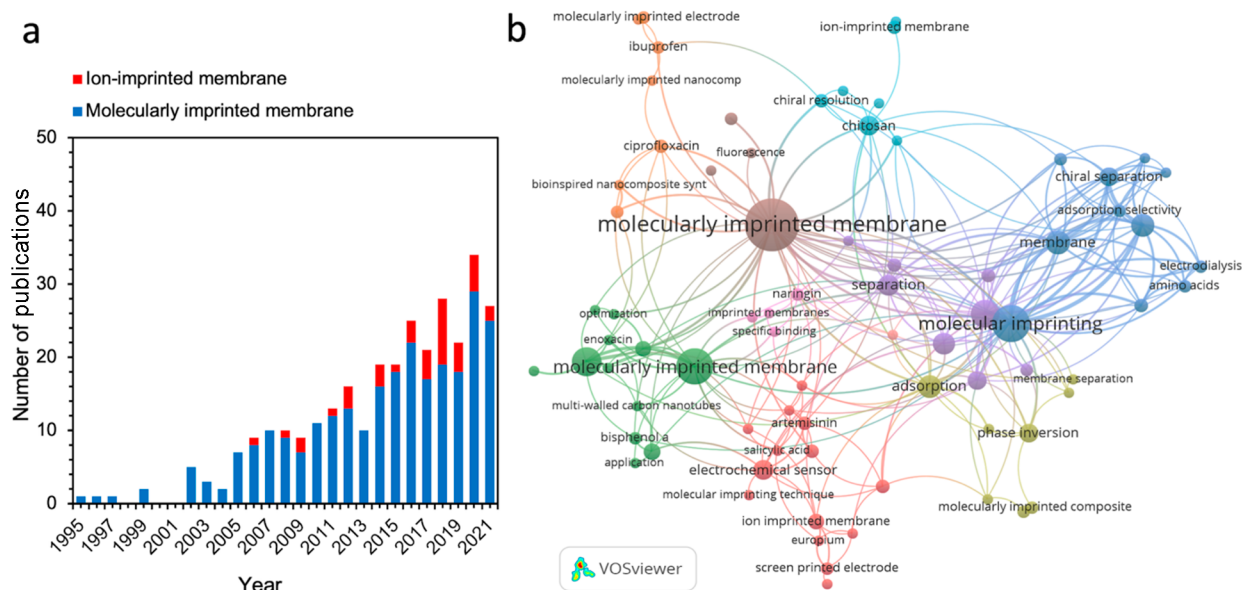


Figure 1. Number of publications related to a molecularly imprinted affinity membrane (MIAM). (a) Number of publication(s) per year. Data were obtained from SCOPUS with queries TITLE-ABS-KEY(terms). (b) Bibliometric analysis of keywords in MIAM-related publications constructed by using VOSviewer.

from the fundamental basis of an affinity membrane to MIAM applications. The development of a MIAM and various preparation methods are presented. Then, applications of MIAMs in sensors, metal ion separation, and organic compound separation are discussed. The last part of the review discusses the future outlook of MIAMs.

2. FUNDAMENTALS OF AN AFFINITY MEMBRANE

Affinity membranes are characterized by their capacity to specifically tie certain substances by utilizing an arrangement of carefully created intermolecular interactions between the film surface and the target molecules. The use of affinity membranes has been demonstrated across length scales, from capturing small cations and organic compounds to binding more complex macromolecules, such as proteins. Furthermore, specific membranes were even developed to trap viruses and bacteria. The selective binding is due to the affinity ligand attached to the membrane's surface, which could be tailored according to its intended purposes. Figure 2 depicts the illustration of four possible specific interactions between the surface-immobilized ligands and the target molecules, i.e.,

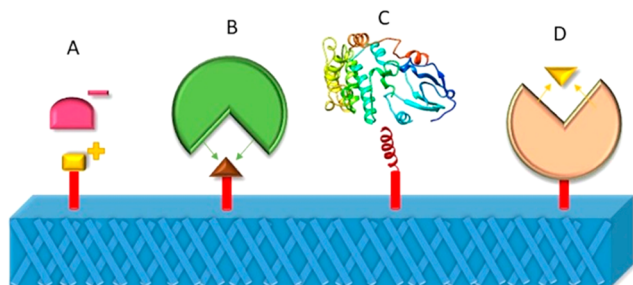


Figure 2. Interactions between affinity ligands and target molecules. (A) Electrostatic interaction, (B) coordination complex between surface-immobilized metal ion and a chelating target, (C) protein–ligand interaction, and (D) coordination complex between surface-immobilized chelating ligand and a metal ion as the target molecule.

electrostatic interaction, coordination complexes, and protein–ligand binding. In recent years, numerous endeavors have been undertaken to create affinity membranes with improved selectivity, tunability, and reusability.

Among intermolecular interactions commonly present at the surface, coordinate covalent bonds between metal ions and the chelating ligands (for example, amine compounds) are often used to obtain a selective capture. The systems are utilized for removing the metal ions from wastewater, e.g., removal of copper(II) ions using chitosan/poly(vinyl alcohol) electrospun nanofibrous affinity membranes (ENAM)²⁰ and removal of lead(II) ions using highly porous polyacrylonitrile (PAN) nanofibrous membranes aminated with diethylenetriamine.²¹ In that sense, the membranes maintain at least 90% binding capacity over six cycles of metal ions capture.²¹ Increasing the amine-binding sites was reported to improve the affinity to metallic ions, such as copper(II).²² A particular example of copper(II) capture was demonstrated using amine-grafted nanofibers (AGNFs) that exhibited a higher adsorption capacity than the conventional chitosan adsorbents. The high adsorption of copper ions and iron was achieved by using layered cellulose nanocomposite membranes functionalized with cellulose nanocrystals in a gelatin matrix.²³ In addition, membranes with chelating ligands are also used for binding metal nanoparticles. For instance, an electrospun polyacrylate membrane modified with amide, pyridine, and quaternary amine showed excellent performance in capturing gold nanoparticles (AuNPs).²⁴

Carbohydrate-based membranes, such as cellulose and chitosan, are versatile for ion capture due to the abundance of functional groups present at their surfaces. In comparison to cellulose, chitosan also contains amine groups, which can act as a chelating ligand as well as a favorable site for electrostatic interactions. The pK_a of amine groups is usually >9 , rendering the amine groups protonated at acidic, neutral, and slightly basic environments. The electrostatic interaction between protonated amine groups with anions can further enhance the binding selectivity. Moreover, it was exemplified in chromate

ion (CrO_4^{2-}) capture using chitosan membranes, in which the binding of chromate ion was highly preferred to those of copper(II), cadmium(II), and lead(II) ions.²⁵ Similar principles based on the electrostatic interactions can remove anionic dyes from wastewater. In addition, the protonated amines of chitosan/poly(vinyl alcohol) electrospun membranes were reported to effectively remove anionic Direct Red 80 dyes from colored wastewater.²⁶ A combination of chitosan/poly(vinyl alcohol) and montmorillonite (clay) was also investigated to capture dyes from colored wastewater.²⁷ Other membranes can be covalently modified into amine-bearing entities. For instance, an electrospun polyacrylonitrile (PAN) nanofiber matrix was functionalized with amine groups to further provide positively charged sites for electrostatic interactions with anions.²⁸ Such PAN nanofibers could remove anionic Congo Red dyes from aqueous media upon matrix modification with amine, amide, or ethylenediamine groups.²⁸ A higher amine density resulted in a better performance for the selective binding of anionic dyes.²⁸

Selective binding of noncharged organic compounds using affinity membranes has also been demonstrated in various reports. A study reported an improvement in carbon dioxide separation using amine-functionalized organosilica membranes.²⁹ The chosen affinity ligand was 4,6-bis(3-triethoxysilyl-1-propoxy)-1,3-pyrimidine (BTTP), which enabled an efficient CO_2 capture.²⁹ Notably, modification with BTTP molecules resulted in a mild-affinity membrane with intermediate-to-low CO_2 binding energy, which performed better in CO_2 separation compared to a strong-affinity membrane using (3-aminopropyl)triethoxysilane (APTES) ligands.²⁹ Selective adsorption of CO_2 was also investigated using metal-organic framework (MOF) membranes that featured high-density oxalate anions and hydrophobic methyl groups that attracted CO_2 from the mixture of humid gases.³⁰ Importantly, by using such platforms CO_2 was effectively separated from methane and nitrogen gases, particularly under elevated temperature and humid conditions.³⁰ A membrane-based on the MOF of copper ion and pyrazine-2,3-dicarboxylate (pzdc) ligand was designed to capture C_3H_6 over C_3H_8 selectively.³¹ MOF membranes intended for both CO_2 and C_3H_6 capture were reported to be thermoresponsive.^{30,31}

In addition to those for small molecules like CO_2 and simple hydrocarbons, several affinity membranes have also been developed to capture more complex organic compounds, such as pollutants. One of the most discussed organic pollutants is phenolic compounds. Ong et al. reported a colloidal suspension of fish scales and poly(vinyl alcohol) cast into a membrane coated with cellulose to capture phenol and quinone.³² The result shows that the pyrolyzed fish scale membrane possesses >90% retention of phenolic compounds in alcohol solutions. Another interesting strategy to capture pollutants is by applying host-guest chemistry. The membranes can be chemically modified with cyclodextrin, which acts as the host to capture phenolic compounds, such as bisphenol A.³³ Bisphenol A is a well-known toxin that disrupts the human endocrine system and is usually found as an intermediate in plastic production. A graphene oxide membrane modified with β -cyclodextrin resulted in stable binding and selective capture of bisphenol A.³³ A similar host-guest approach was employed to remove steroid pollutants, in which a polymethacrylate membrane was functionalized with β -cyclodextrin.³⁴

While the aforementioned systems were employed to solve environmental issues, e.g., wastewater treatment, the affinity membranes capable of capturing hormones and metabolites are particularly relevant for medical applications. Biocompatibility is often the requirement for affinity membranes used in medical settings. For example, an anticoagulant affinity membrane was investigated to capture bilirubin from human blood.³⁵ It is required in hemoperfusion treatment, in which the patient's blood is cleared from bilirubin using adsorbents. The key to selectively binding bilirubin is the incorporation of poly(L-arginine) into the surface of a porous nylon membrane coated with poly(pyrrole-3-carboxylic acid), enabling bilirubin clearance of up to 86.1%.³⁵ A similar blood-purification system was also developed to remove creatinine in kidney dialysis settings.³⁶ To this end, a bifunctional thin-film nanofibrous composite (TNFC) membrane made of poly(vinyl alcohol) hydrogel, polyacrylonitrile membrane, and carboxylated zirconium-based MOF nanoparticles was investigated.³⁶ The TNFC membrane showed a clearance of creatinine in blood samples of up to 62.8% while rejecting other blood components, such as the serum albumin (98%).³⁶

Furthermore, recent years have witnessed various affinity membranes specifically developed to target a particular protein. Protein-selective binding can be used to capture the tagged protein via a specific interaction.³⁷ For example, a His-tagged protein possessed chelating ligands in amine groups of histidine. This system has been widely applied in protein purification by using affinity chromatography, where nickel(II) ions are adhered to the membrane's surface. Apart from nickel(II) ions, cobalt(II) ions have also been used to bind several proteins, e.g., a scaffolding protein,¹⁰ and fused xylanase and bovine serum albumin.³⁸ A combination of ions can also be used to further enhance the selectivity to His-tagged proteins, e.g., the coimmobilization of nickel(II) and copper(II) ions to the surface of a cross-linked chitosan/poly(vinyl alcohol) membrane.³⁹

Chelating ligands, such as nitrilotriacetic acid (NTA), are ordinarily used to stabilize immobilized ions. The chelating ligands are incorporated into the membrane by covalent interaction. A few techniques have been detailed to effectively introduce NTA ligands into the membranes, such as through click chemistry to azido-containing cellulose acetate membranes.⁴⁰ Hydroxamic acid is another example of a chelating ligand that can stabilize copper(II) ions anchored onto the poly(methyl methacrylate)-grafted cellophane membranes.⁴¹ It was reported that there was no leakage of Cu^{2+} ions observed when the hydroxamic acid- Cu^{2+} system was eluted while eluting 88% of the absorbed His-tagged chitinase.⁴¹ Aside from nickel(II) and copper(II), ions like zirconium(IV) and iron(III) have emerged as an alternative to improve binding selectivity. A metal-affinity membrane with phosphate- Zr^{4+} moieties was shown to selectively capture phosphoproteins, such as casein and ovalbumin, in a mixture with non-phosphoproteins, such as albumin and lysozyme.⁴² Iron(III) ions stabilized by iminodiacetic acid chelating ligands were also proven to be effective in capturing lysozyme (i.e., the capacity of up to 0.365 g of lysozyme per 1 g of regenerated cellulose nanofibrous membranes) during an adsorption time of 4 h.⁴³

Organic molecules could also function as a selective affinity ligand for selectively capturing protein. For instance, macroporous membrane supports could be grafted with polymers bearing diethyl-4-aminobenzyl phosphonate, a specific ligand for lysozyme.⁴⁴ Another choice of ligand for selective lysozyme

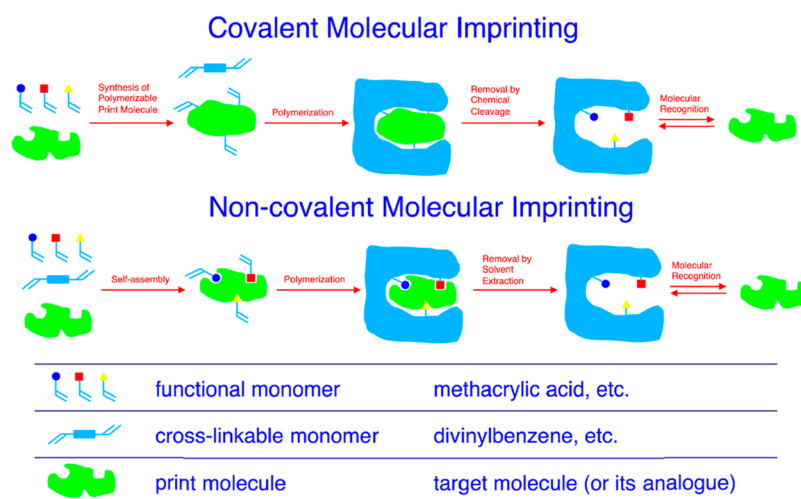


Figure 3. Covalent and noncovalent interactions in molecular imprinting techniques. Reprinted with permission from ref 17. Copyright 2016 American Chemical Society.

capture is tris(hydroxymethyl)aminomethane, which allowed for a 100-fold increase in purity when introduced onto a polyacrylonitrile nanofiber membrane.⁴⁵ Besides, lysozyme can bind dye ligands. Therefore, a membrane incorporated with dye ligands can be used to capture lysozyme selectively. For instance, cyclodextrin molecules were anchored into a membrane made of clickable ethylene vinyl alcohol (EVAL).⁴⁴ Via click chemistry, azide-bearing cyclodextrin was attached to the membrane surface and subsequently bound the dye ligands with lysozyme through host–guest interactions.⁴⁴

Blood proteins, such as albumin and antibodies (immunoglobulins), are typical examples of emerging targets of separation using an affinity membrane.³⁷ Albumin is selectively adsorbed onto cholic-acid-immobilized poly(2-hydroxyethyl methacrylate) brushes.⁴⁶ Polypeptides are also attractive options of affinity ligands for protein separation. For example, sericin, a silkworm polypeptide, can increase the adsorption capacity of a chitosan/sericin membrane (4:1 w/w) toward serum albumin up to 45% higher than the sole chitosan membrane.⁴⁷ Tryptamine is an alternative ligand that can be used to purify antibodies because it can bind the nucleotide-binding site on the Fab (fragment antigen binding) domain of the antibodies.⁴⁸ In this way, the purification of monoclonal and polyclonal antibodies from the cell culture media of ascites fluids is possible.⁴⁸ It was found that the length of the chemical spacer affects the selective capture of immunoglobulin G (IgG) by a cellulosic affinity membrane.⁴⁹ Another option of affinity ligand, which is also able to purify antibodies, is a completely folded complex protein chain, such as protein G. A cellulose membrane surface anchored with protein G can selectively bind the interleukin-6 (IL-6) antigen.⁵⁰ Another blood protein, which is also a target of selective separation, is the plasminogen. Regenerated cellulose membranes were functionalized with L-lysine as the affinity ligand to bind plasminogen.⁵¹

Maintaining structural integrity and activity during adsorption and elution is the major challenge in the development of affinity membranes for protein separation. Affinity membranes created by metal ion immobilization show high reusability and do not change the bound enzyme activity, even after several adsorption–elution cycles.^{10,52} The introduction of specific ligands on the membrane surface also shows an insignificant

effect on the enzyme activity. For instance, a cellulose membrane incorporated by Cibacron Blue F3G-A dye can selectively bind amylase and shows improved starch hydrolysis on the surface.⁵³ Binding one protein from a mixture of diverse proteins, such as in blood plasma, is another challenge in the use of an affinity membrane for protein separation. To address this issue, the surface properties and the affinity ligands should have specific interactions, with minimal nonspecific interactions. For instance, when nonspecific adsorption is reduced significantly, a nylon membrane with alginate dialdehyde layers can achieve high selectivity of human IgG over human serum albumin.⁵⁴ Another example is the introduction of peptides on membrane surfaces to obtain high selectivity toward monoclonal antibodies, such as immunofibers.⁵⁵

Affinity membranes have also been investigated regarding virus and bacteria capture. A sulfated cellulose membrane was employed to bind the influenza virus, resulting in a 75% viral-particle capture while reducing protein and DNA contamination to <25%.⁵⁶ On the other hand, selective capture of cells was achieved by attaching cell affinity peptides on block copolymer brushes made of poly(2-hydroxyethyl methacrylate [HEMA]-*co*-propargyl acrylate) and poly(*N*-isopropylacrylamide-*co*-HEMA).⁵⁷ In addition to polymer brushes, electrospun nylon nanofibrous membranes were also shown to selectively capture bacteria and yeast, such as *Idobacter fluviatilis* and *Saccharomyces cerevisiae*.⁵⁸ Poly(vinylidene fluoride) membranes could concentrate bacteria from seawater for environmental assessment.⁵⁹ In later studies,^{47,58} the selectivity of bacteria capture was also attributed to the size factor, apart from interactions between the cell surface and the membranes.

3. DEVELOPMENT OF A MOLECULARLY IMPRINTED AFFINITY MEMBRANE

The initial development of affinity membranes was a modification of common microporous membranes such as polyethylene (PE), polypropylene (PPr), polycarbonate (PC), polysulfone (PS), and other hydrocarbon polymers.⁶⁰ Biobased membranes, such as cellulose²³ and chitosan,⁴⁷ were also popular choices for affinity membrane applications by modifying the membrane surface to recognize specific target molecules ranging from metal ions to peptides and proteins,

Table 1. Summary of the Advantages and Disadvantages of MIAM Synthetic Methods

type of synthesis method	advantages	disadvantages
in situ polymerization	high satisfactory adhesion good convenience side reactions may occur	thicker membrane more compact structure lower sensitivity
electrochemical polymerization	high sensitivity could control the film thickness	polymerization potential window is high during the polymerization method
post-polymerization	possibly for tuning the polymers with varying properties that could not be obtained from the same starting polymer or incompatible with the polymerization process results in a smaller microparticle size	kinetics are highly sensitive to the difference between the reaction temperature and the melting temperature
click chemistry	very mild condition tolerance to a variety of solvents and functional groups high yield	poor solubility of the final product difficulty of removing the catalyst upon polymerization
electrospray deposition	usually produces a strongly adhered film could coat the complex shape	possibility to damage the molecule
chemical vapor deposition	eliminates the need for dissolving the molecules coating components could conform to the geometry of the underlying substrate	involves a complex mechanism that includes highly active species

thus widening the potential application. Candidate polymers should have resistance toward solvent, and even a small amount of swelling could compromise selectivity toward the target molecule. In addition, it should be in a glassy state to retain a rigid three-dimensional structure.⁶¹

The early development of MIAMs involved covalent interactions within highly cross-linked polymers that cannot be dissolved in most solvents, limiting their renderability. In this case, a given molecularly imprinted material with molecular-recognition sites prepared to recognize a specific target molecule cannot be applied to recognize other molecules. Hence, its application is intended for only a particularly selected print molecule. The noncovalent technique has advantages of easy synthetic procedure and template removal, which is performed through a simple continuous extraction; thus, various functionalities can be incorporated into binding sites.⁶² Fan et al. reported that the preparation of a novel mix of noncovalent and semicovalent molecularly imprinted membranes with hierarchical pores could be performed via cryopolymerization methods.⁶³ The hierarchical pore structure of the molecularly imprinted polymers was confirmed by scanning electron microscopy (SEM) and nitrogen adsorption–desorption isotherm analysis. Noncovalent interactions include hydrogen bonding, van der Waals forces, and hydrophobic interactions. Electrostatic interactions, as mentioned previously, are also considered noncovalent interactions.

Figure 3 shows a comparison of covalent and noncovalent interactions in the preparation of imprinted materials for membrane separation.¹⁷ In covalent molecular imprinting, the functional monomers are functionalized with template molecules to make a polymerizable print molecule, which upon addition of a cross-linker forms polymers. Removal of the template molecule is commonly done by chemical cleavage due to strong covalent interactions between the template and the polymers. Upon leaching, the polymer with molecular recognition is obtained. On the other hand, in the preparation of noncovalent molecular imprinted materials, functional monomers, a cross-linker, and a template molecule are mixed to form self-assembly materials with weak interactions. Upon polymerization, the template molecule can be removed by

simple extractions to yield polymers with similar structural integrities while being more flexible for molecule recognition of different analogues.

In addition to polymeric membranes, covalent organic frameworks (COFs) are gaining popularity as membrane materials with molecular affinity. COFs possess inherent porosity and structural periodicity, which offer superior properties to conventional polymeric membranes. Moreover, COFs display low density, high thermal stability, and high surface area, which are essential properties in affinity membrane development. An efficient synthesis of molecularly imprinted COFs has been reported with specific recognition, such as toward cyano pyrethroids.⁶⁴ In this report, COFs are prepared by Schiff base reactions (amine–aldehyde condensations) at room temperature in the presence of scandium(III) trifluoromethanesulfonate ($\text{Sc}(\text{OTf})_3$) as the catalyst. The prepared materials are demonstrated to have selectivity toward cyano pyrethroids, which are common active materials in insecticides and increasingly found in plant samples.

4. MIAM PREPARATION METHODS

This section includes the preparation of affinity membranes designed for specific purposes mainly achieved by molecularly imprinted polymerization methods. The ligand is incorporated into the polymers through a covalent or noncovalent interaction. The introduction of template molecules in membrane preparation can be carried out by either postpolymerization or in situ polymerization, producing different membrane morphologies. The former results in a smaller microparticle size, while the latter offers a more compact structure. It has been demonstrated that membranes prepared from these two techniques showed different adsorptions toward D-phenylalanine, in which postimplanted templates showed better performances.⁶⁵ In addition to conventional polymerization methods, utilization of click chemistry, electrospray deposition, and chemical vapor deposition are among emerging methods in recent years that offer efficient fabrication of affinity membranes. Table 1 summarizes the advantages and disadvantages of each synthetic method.

4.1. In Situ Polymerization. In situ polymerization of templates, monomers, and cross-linkers in the fabrication of affinity membranes has evolved since its initial development, following the needs of its application. For example, arginine-rich proteins are potentials for delivering chemotherapeutics into cancer cells. These proteins can be separated from other proteins by an affinity membrane prepared from diethyl 4-aminobenzylphosphonate (D4ABP) via graft polymerization onto a macroporous membrane support.⁴⁴ The membrane was then characterized by infrared and energy-dispersive spectroscopy. Furthermore, this membrane has been applied in membrane chromatography to replace bead matrixes that offer convective protein transport to the binding site due to its open pore structure.⁶⁶

A membrane with a hierarchical structure can also be prepared by in situ polymerizations, imitating core–shell-based synergistic interactions.⁶⁷ This is in agreement with Wu et al., which reported the double-layer-based molecularly imprinted membranes (DLMIMs) synthesized based on a polydopamine (PDA) imprinting process on the surfaces of SiO₂ and activated carbon nanoparticles (ACNPs) to obtain the first PDA-based tetracycline (TC)-imprinted layers.⁶⁷ The first step is the preparation of silica nanoparticles based on the Stöber method, followed by the synthesis of PDA-based imprinted ACNPs/SiO₂ nanoparticles. The phase inversion process was carried out using poly(vinylidene fluoride) (PVDF) powder with a *N*-methylpyrrolidone (NMP)/acetonitrile mixture with the addition of polyvinylpyrrolidone (PVP) as a pore-foaming agent during the whole membrane synthesis. After a phase inversion, a sol–gel polymerization procedure was performed for preparing second TC-imprinted layers. The performance of this membrane was tested for solutions containing different substrates, after which concentrations were measured using high-performance liquid chromatography (HPLC). A large rebinding capacity (115.5 mg g⁻¹), fast adsorption kinetics, and high permselectivity coefficients (>6.5) toward TC were successfully achieved.⁶⁷

Inspired by biomimetic polydopamine (PDA), the synthesis of molecularly imprinted nanocomposite membranes (MINCMs) was developed via polymerization.⁶⁸ The two-faced nanocomposite was obtained using PDA nanospheres as the supports modified by gold (Au) nanoparticles grown on the surface. This membrane was applied for the separation of tetracycline (TC), a broad-spectrum antibiotic. Unlike the typical procedure of growing molecular imprinted polymers (MIPs) on the membrane surface, MINCMs were prepared via directly infiltrated Janus nanostructures into the casting solution during the phase inversion process.⁶⁸ The first step was typical polydopamine (PDA) nanoparticle synthesis followed by Au⁺ reduction on the surface of nanostructures. The resulting nanocomposite was further treated with KH570 to introduce the polymerizable double bonds for the TC-imprinted polymerization process. The imprinting process utilized methylenbisacrylamide (MBAA) and acrylamide (AM) as monomers, TC as a template, and azobisisobutyronitrile (AIBN) as a radical initiator.⁶⁸ Among others, the advantages of this method were that it needed low temperature and ordinary pressure and was energy-efficient and environmentally friendly for large-scale applications.

4.2. Post-polymerization. Affinity membranes prepared by post-polymerization could originate from naturally occurring resources as well as from synthetic polymers. An example of the former category is adsorbers prepared from alginate

dialdehyde as an intermediate layer on nylon membranes that can recognize histidine, peptide, and metals, among others, to fractionate an IgG/HSA (human serum albumin) mixture.⁵⁴ Alginate dialdehyde was prepared from naturally occurring sodium alginate via treatment with ethylene glycol. The resulting powder was used to activate nylon membranes to produce constructing cation exchange (CEX), His-Affinity, Me-Affinity, and pep-affinity accordingly. Another example of molecularly imprinted membranes based on sodium alginate as a polymer is introducing 3-aminopropyltriethoxysilane (APTES) as a precursor.⁶⁹ The hybrid membrane was prepared in an aqueous environment using *D*-phenylalanine (*D*-Phe) as imprinting templates. The silica phase was introduced in the alginate matrix by the sol–gel process of APTES. It was demonstrated that the percentage of APTES determined the selectivity of the molecularly imprinted membrane.⁶⁹ At a concentration of <30% (w), the loose and excessive flexible structure led to selectivity loss. In contrast, at a concentration of 40% (w) and above, the MIP had less ability to create template–polymer interactions. These molecularly imprinted SA–APTES hybrid membranes showed chiral separation ability toward the *D,L*-Phe isomers with a maximum selectivity ($\alpha_{D/L}$) of 1.8 at 40% (w) APTES content.⁶⁹

Mujahid et al. reported the development of dibenzothiophene-imprinted poly(methyl methacrylate) (PMMA)–nickel sulfide hybrid membranes (MIP-NiS) for desulfurization of crude oil by removing dibenzothiophene to produce cleaner transportation fuels via an adsorption mechanism.⁷⁰ Nickel sulfide (NiS) nanoparticles are incorporated into the membranes to enhance the desulfurization capability. The dispersion of nanoparticles in the membrane was analyzed by atomic force spectroscopy, and the membrane was shown to have effective (97%) recognition toward dibenzothiophene and its removal of up to 1 ppmw, which was superior to that with the nonimprinted membrane (NIP) or imprinted membrane without nanoparticles (MIP).⁷⁰ The method used was postpolymerization imprinting of commercial PMMA due to the solubility of the matrix.

Bidirectional MIP for the separation of pyrimethamine (PMIMs), a veterinary antibiotic, was also developed by Wu and co-workers inspired by a semipermeable membrane in biological systems.⁷¹ The common membrane is usually one-way, and cleaning was carried out by backwashing. On the other hand, double-faced loading of carbon nanotubes (CNTs) on the support membranes could be a game changer due to stable adhesion between the support membrane and the CNTs network. The membrane was synthesized by a carbon nanotube double-faced loading strategy, incorporating photo-initiation click chemistry to offer advantages of rapid rates, high yield, and mild conditions. The synthesis was initiated by modifications of cellulose membrane by polydopamine followed by loading double-faced CNTs. The surface of the resulting membranes (CNT@DRCMs) was modified by introducing template molecules. Chemical constitutions and bond cooperation were analyzed by X-ray photoelectron spectroscopy (XPS), element analyzer, and Fourier transform infrared spectroscopy (FTIR). Interactions of the template and the functional monomers were measured using ultraviolet–visible spectroscopy (UV–vis) and ¹H NMR (nuclear magnetic resonance) spectroscopy. The results show the membrane permselectivity and generation rates of 3.99, 4.03, 4.21, and >90%, respectively. Incorporating quantum dots (QDs) into MIMs expands the application toward sensors/

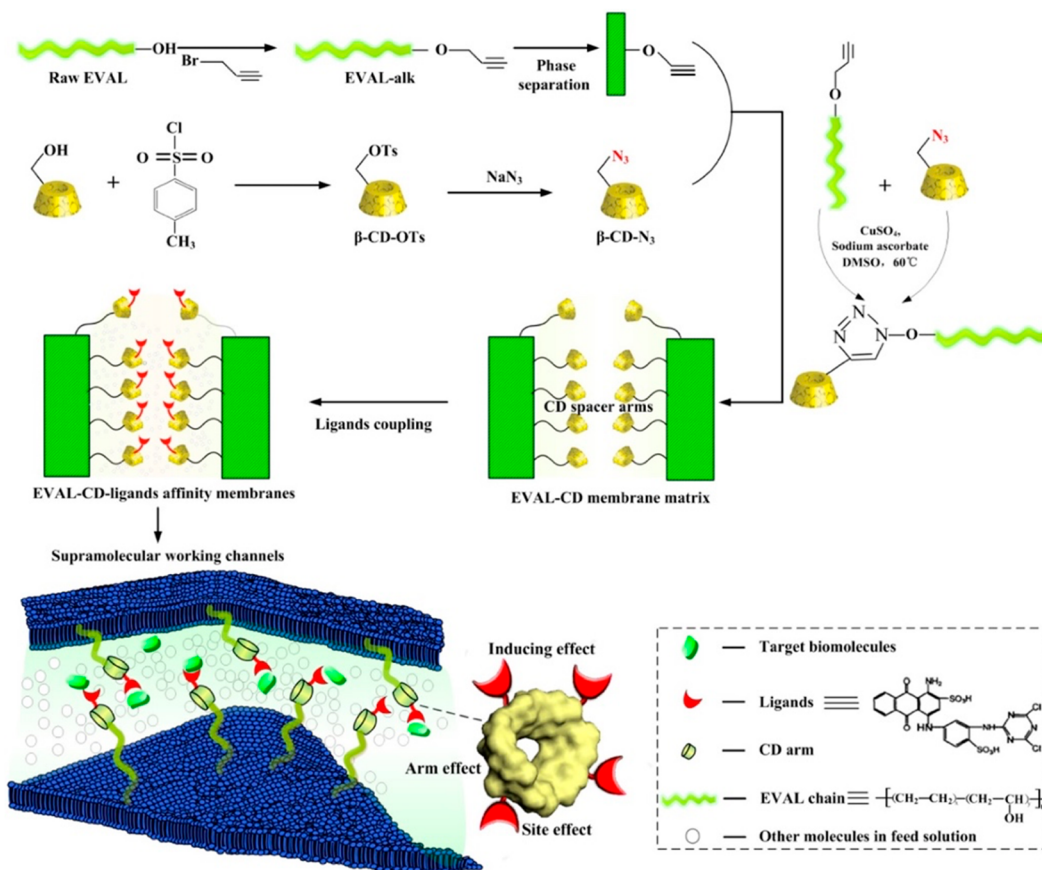


Figure 4. Formation strategy of affinity membranes with macrocyclic spacer arms via click chemistry. Reprinted with permission from ref 75. Copyright 2017 Elsevier.

biosensors.⁷² The key point of this approach is that the fluorescent QDs engrafted into MIMs enable the optical readout characteristic and high selectivity within the membrane. When the fluorescent MIMs selectively capture the target protein, the electron transfer between the QDs and the target protein will result in fluorescence quenching of the membrane. The quenched fluorescence emission intensity was proportional to the concentration of the analytes.⁷² For this purpose, QD-embedded MIM was synthesized on a glass surface using acrylamide monomer and lysozyme as the template molecule, followed by the addition of *L*-cysteine-capped Mn²⁺-doped QDs. The lysozyme template was then eluted by incubating the membrane in the mixture of sodium dodecyl sulfate (10%, w/v) and acetic acid (10%, v/v).⁷²

4.3. Click Chemistry. In recent years, significant trends in MIMs synthesis have been dominated by the utilization of click chemistry. Liang and co-workers reported that molecularly imprinted polymers can be prepared based on thiol-ene click chemistry, using pentaerythritol tetra(3-mercaptopropionate) and dipentaerythritol pentaacrylate as binary cross-linkers, pyrimethamine as a template, and methacrylic acid as a functional monomer.⁷³ It was demonstrated that the synthesized MIPs have a higher extraction capacity than the corresponding nonimprinted polymers (NIPs). Other researchers have also reported the fabrication of an aquaporin-based biomimetic water purification membrane utilizing click chemistry. A propargyl-functionalized β -sheet peptide (FBP1) was clicked onto a polysulfone-based membrane using a circulating system. The successful immobilization was verified

by surface chemical composition analysis and surface morphology analysis.⁷⁴ Furthermore, click chemistry has been successfully utilized to develop a membrane with affinity sites toward lysozymes, the azide-alkyne click reaction (Figure 4).⁷⁵ In this report, Lin et al. prepared an affinity membrane via the azide-alkyne click reaction to yield a porous membrane matrix with an efficient working channel. The EVAL-membrane matrix was functionalized with alkyne parallel, while the cyclodextrin (CD) spacer was functionalized with azide. The click reaction of these entities yields an EVAL-CD membrane matrix, which upon the ligand-coupling process results in affinity membranes that can be modified further to have multiple working channels. This membrane demonstrated efficient lysozyme binding, which suggested that macrocyclic spacer arms and supramolecular working channels could be potential factors in developing MIAMs with better performance.⁷⁵

Another example in the utilization of click chemistry for the synthesis of MIAMs was demonstrated in the preparation of bisphenol A molecularly imprinted membranes (BPA-MIMs).⁷⁶ The hierarchical microporous substrate membranes were prepared by imprinting the BPA template via photo-induced thiol-ene click chemistry followed by modification using ZnO and Ag nanoparticles. The first step of the synthesis was the preparation of hierarchical microporous PVDF membranes by treating commercial PVDF membranes with sodium chloride. Subsequently, a hydrophilicity modification was carried out by adding ZnO seeds, followed by improving the antibacterial activity through the addition of

AgNO₃ to form a Ag/ZnO@PVDF membrane.⁷⁶ After ethylene modification, the photoinduced sulfhydryl–vinyl click chemistry furnished the BPA-MIMs for applications in water-purification technology.

4.4. Electro spray Deposition. Electro spray deposition is also suitable for obtaining MIMs with large surface areas. Higher flux and permselectivity can be obtained in a separation consisting of polymeric nanofibers, in which its diameter range could be controlled from nanometers to micrometers.^{77,78} Typically, a polymer solution is pumped through a thin nozzle that simultaneously serves as an electrode connected to a high-voltage source. The applied voltage causes a cone-shaped deformation of the drop of polymer solution, the solvent evaporates, and solid fibers are precipitated with high velocities on the counter electrode.

Electrode-surface polymerization is among the most attractive techniques for preparing self-supported membranes. One such report used a gold (Au) electrode surface, modified with allylmercaptan and 1-butanethiol and coated with a polymerization mixture containing the print molecule.⁷⁸

Zhu et al. reported that the surface molecularly imprinted electrospun affinity membranes with multimodal pore structures efficiently separated proteins.⁶⁹ Bovine serum albumin (BSA) and hemoglobin from bovine blood (bHb) were chosen as template molecules. Polyvinylpyrrolidone (PVP), 3-aminopropyltrimethoxysilane (APTES), and tetraethoxysilane (TEOS) were used to build the polymer matrixes, and subsequently, the membrane was prepared by the electrospun method.

Integration of both unique properties of molecular imprinting and electrospinning techniques to produce affinity nanofibrous membranes is emerging as an important and promising development of nanostructured MIP materials and has drawn increased attention. Researchers have demonstrated such methods using polyethylene terephthalate (PET) as the supporting nanofiber matrix to encapsulate theophylline and 17 β -estradiol-imprinted nanoparticles.⁷⁹

4.5. Chemical Vapor Deposition. Covalent organic frameworks (COFs) are potential membranes materials that can also be developed by chemical vapor deposition. It has been demonstrated that the COF-TpPa1 affinity membranes could be prepared by simultaneous evaporation of *p*-phenylenediamine (PDA) and 2,4,6-trihydroxybenzene-1,3,5-tricarbaldehyde (TFP) onto a poly(1,1-difluoroethylene) membrane. The membranes showed excellent water permeance with high rejection (>90%) for different dyes and low rejection (<8.2%) for salts, rendering potential applications for the separation of dyes.⁸⁰

Song et al. investigated an anticoagulant affinity membrane (AAM) to clear bilirubin from human blood in a pore-flow-through way.³⁵ First, a nylon net membrane with a regularly arranged pore as the matrix was coated with polypyrrole-3-carboxylic acid via the chemical vapor deposition (CVD) method. Polymerization of pyrrole-3-carboxylic acid on the membrane surface allowed the membrane to keep its porous structure, albeit slightly thicker. The water contact angle (WCA) of the nylon membrane was 62.8° as compared to 46.3° of the AAM membrane, which indicated improved hydrophilicity of the membrane. In the next step, poly(L-arginine) (PLA), as a highly specific ligand of bilirubin, was immobilized onto the surface of the composited membrane after the modification of heparin. Characterization of the membrane was carried out using XPS, which exhibited a NH-

C-(NH₂)²⁺ peak at 400.9 eV, confirming PLA's successful immobilization. This research reported that AAM has enormous potential in blood-purification therapy for enhancing hemocompatibility and bilirubin removal.

It is common to find a combination of the methods discussed earlier in the preparation of specific affinity membranes. For example, post-polymerization modifications of thin-film composite (TFC) membranes by chemical vapor deposition of acrylic acid (AA) and 2-hydroxyethyl methacrylate (HEMA) were reported.⁷² Rapid progress in instrumentation also contributes to various preparation methods of molecularly imprinted affinity membranes, which would accelerate commercial applications of MIAMs in many areas of separation and purification.

5. SENSOR-BASED MIAM

The inevitable improvement of MIAMs is the capability to recognize components due to the presence of a selective cavity from imprinted molecules. This unique property of MIAMs is crucial for the separation of a specific or targeted molecule such as in sensor applications. High selectivity toward target molecules can realize the fabrication of a sensor with high accuracy. Gao et al. successfully prepared a sensor based on an MIAM to detect curcumin (CUR).⁸¹ The sensor was fabricated using *in situ* bulk polymerization using 4-pentenyl-alanyl-chitosan oligosaccharide (PACO) accompanied by surface electrochemical polymerization. The results showed that the sensor presented good selectivity, sensitivity, and reproducibility in detecting curcumin compounds. This result is in accordance with the use of PACO in the membrane, which generates remarkable sensing properties, including excellent target recognition and good permeability. The excellent target recognition is a result of a strong interaction between CUR and functional polymers in the membrane. Besides, the increase of membrane thickness can cause the permeability of the membrane to reduce slightly. Furthermore, after being stored in a coated capsule at room temperature for 30 days, the electrode still presented >90% of the initial test value. Therefore, the MIM-based sensors possess high storage stability and can be used repeatedly.

An electrochemical sensor based on MIAM for the detection of simazine (SMZ) herbicide has been successfully prepared.⁸² The results revealed that the attachment of AuNPs in the device could enhance the electrode's effective surface area and facilitate the transfer of electrons. Moreover, the addition of nanoparticles in the MIAM material can expand attainable complementary cavities toward target molecules. MIAM exhibited excellent selectivity to SMZ due to the dimension and composition of the cavities matching with SMZ in the films.

Bai et al. reported a sensor based on MIAM for the detection of artemisinin (ART).⁸³ A glassy carbon electrode (GCE) was modified with graphene (G) via the *in situ* polymerization method using acrylamide (AM) as the functional monomer. The cycle voltammetry analysis shows that the peak current of GCE modified with graphene showed a substantial increment. This result is possibly associated with a high surface area-to-volume ratio and excellent electrical conductivity of graphene nanosheets. After removing the template from the membrane, the imprinted cavities were formed; thus, the diffusion process and redox reaction of [Fe(CN)₆]³⁻/[Fe(CN)₆]⁴⁻ could occur on the sensor surface.

An electrochemical sensor based on MIP modified with metal–organic frameworks and graphene (MOFs@G) has been prepared for the detection of ketamine (KT), one type of drug that could cause severe damages to organ systems in the long term.⁸⁴ The MOFs@G has a large surface area that gives more space for the imprinted film and effectively improves the binding cavity for identifying the target. The sensor exhibited good sensitivity, selectivity, and long-term stability with a detection limit of 0.04 nM. Moreover, Wang et al. fabricated an electrochemical sensor based on MIP membranes by electropolymerization using *p*-aminothiophenol (*p*-ATP) and propionamide (PAM) as template molecules for the determination of acrylamide (AM).⁸⁵ The adsorption of PAM toward the membrane surface through hydrogen bonding could increase the number of imprinted sites on the electrode surface. In addition, the doped nanoparticles could enhance the sensitivity of the electrodes. The sensor demonstrated sensitive, fast, and real-time detection of AM, with recoveries >95% and with a detection limit of 0.0005 nM.

A conductometric probe of a portable sensor based on an MIAM has been prepared through in situ photopolymerization methods for the determination of salbutamol.⁸⁶ The MIAM-based sensor exhibited excellent sensitivity and selectivity for salbutamol with a detection limit of 13.5 nM.⁸⁶ The interaction between the template molecule and the specific cavities can be assumed to result in the conformational reorganization polymer structure; therefore, the diffusion of the target is disturbed during the adsorption process on the MIM.⁸⁶

Kong et al. reported the fabrication of a colorimetric sensor based on molecularly imprinted polymer membranes to determine bisphenol A (BPA).⁸⁷ Specifically, magnetic nanoparticles (MNPs) of ZnFe₂O₄ and cellulose fibers were covered by MIP membranes (ZnFe₂O₄@MIP membranes). The results indicated that the MIAM exhibited remarkable selectivity for BPA over other compounds such as *tert*-butylhydroquinone (TBHQ), diethylstilbestrol (DES), hydroquinone (1,4-DHB), and phenolphthalein (PP). The surface of the MIAM contains recognition sites. When the BPA molecule is absent, the adsorption of H₂O₂ can occur on the surface to produce ·OH, and then ·OH oxidizes tetramethylbenzidine (TMB) to produce a blue-colored product that makes a noticeable color change. On the other hand, when BPA is attached to the MIAM membrane surface, H₂O₂ cannot interact with ZnFe₂O₄ MNPs and ·OH is not produced, indicating that the sensor can detect BPA-based on the MIP membrane.

Su et al. fabricated a sensor based on a magnetic surface MIAM with Fe₃O₄@SiO₂ nanoparticles (NPs) for the detection of acetaminophen (AP).⁸⁸ The MIAM was introduced to the magnetic electrode (MCPE) by magnetic attraction in the preparation technique. The sensor accurately detected AP using differential pulse voltammetry (DPV) with a detection limit of 17 nM. The satisfying performance of the sensor is due to a larger specific surface area, excellent response, and ability to convert signals immediately between the imprinted hole and the target molecules/ions.

Furthermore, Sergeyeva et al. have successfully decorated optical biomimetic sensors based on MIAM via in situ molecular imprinting combined with semi-interpenetrating polymer networks (semi-IPNs).⁸⁹ The sensor was employed to determine aflatoxin B, one of the toxic compounds found in fodder. The sensor exhibited excellent selectivity with a detection limit of 20 nM compared with the analogue structures of aflatoxin G2 and ochratoxin A.⁸⁹ The monomers

were varied, and two functional monomers, namely, 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA) and acrylamide (AA), were found to generate high fluorescent sensor responses and high selectivity.

A quartz crystal microbalance (QCM) sensor based on MIAM via electropolymerizing *o*-aminothiophenol on Au nanoparticles@mesoporous carbon CMK-3 for the detection of citrinin has also been prepared.⁹⁰ The sensor shows remarkable selective recognition, high stability, anti-interference ability, and reproducibility with a detection limit of 1.8 nM. These occurrences could be due to several factors, such as that the AuNPs promote the electron-transfer reaction of the redox probe by facilitating an effective electron conductive pathway. In addition, a rougher surface due to the 3D porous support structure of AuNPs@CMK-3 enhances the specific surface area of the electrode.

D'Agostino et al. reported an MIAM synthesized using methacrylic acid as the functional monomer.⁹¹ The sensor was applied for detecting atrazine with excellent selectivity and a detection limit of 2×10^4 nM. The MIAMs have specific molecular interaction sites that make them selective for the targeting molecules. In addition, the pH of the solution can affect the sensor's performance, in which atrazine is adsorbed more strongly at low pH because the carboxylate groups in the polymer membrane are already protonated. Suedee et al. fabricated a conductometric sensor based on the MIAM using two methods, bulk polymerization (BP) and multistep swelling polymerization (MSP), for haloacetic acid (HAA) screening in drinking water.⁹² The prepared sensors showed a better selective response to HAA than those prepared using BP method due to the MIAM having the possibility of providing binding sites with specific shapes, sizes, functions and possessing group orientation to identify the target molecules. In addition, the MIAM shows good selectivity toward HAA, where the electrostatic interaction through hydrogen bonding is the driving force for the binding of HAA to MIAM.⁹²

Furthermore, Yuan et al. prepared MIAMs using the nylon-66 (NY-66) membranes with two functional monomers, methacrylate (MA) and 1-vinylimidazole (1-VM), for the identification of enrofloxacin (ENR) and ciprofloxacin (CIP) in egg samples.⁹³ The sensor shows high sensitivity results, good recovery, and a low detection limit. The results were related to the characteristics of MIAMs possessing a rough surface with a large surface area and specific sites to distinguish the target molecule. Moreover, a sensor based on MIAM using methylacrylic acid (MAA) to detect chloramphenicol succinate (CAP-SC) using the photopolymerization method on screen-printed electrodes has also been fabricated.⁹⁴ The sensor exhibited excellent sensitivity and specificity to the target CAP-SC with a detection limit of 2 nM. The MIAM has a thickness of ~80–100 nm, and the recognition capacity is based on the interaction of the dominant group and the whole molecule characteristics.

On the other hand, amperometric sensors based on screen-printed electrodes modified with multiwalled carbon nanotubes (MWCNTs) and MIAM using MAA as a functional polymer have been fabricated.⁹⁵ As a result, the sensor was able to determine ractopamine in pig urine with a detection limit of 6 nM. Furthermore, the modified MWCNT-MIAM has a pore that selectively facilitates a channel for ractopamine diffusion and electron-transfer reactions, leading to an additional current increase. Besides, MWCNTs have the ability to enhance the electron-transfer area on the surface electrode. A summary of

Table 2. Applications of Sensor-Based MIAMs^a

name of sensor-based MIAM	synthesis method	target molecule	functional monomer/oligomer	performances				ref										
				in situ bulk polymerization accompanied by surface electrochemical polymerization	in situ photo polymerization	in situ polymerization	UV-induced polymerization		electropolymerization	self-assembly and electrodeposition	bulk polymerization	electropolymerization	electrodeposition	plasticizer-free MIP-based potentiometric sensor using a novel copolymer				
				in situ bulk polymerization accompanied by surface electrochemical polymerization	in situ photo polymerization	in situ polymerization	UV-induced polymerization	electropolymerization	self-assembly and electrodeposition	bulk polymerization	electropolymerization	electrodeposition	plasticizer-free MIP-based potentiometric sensor using a novel copolymer	linearity	LOD	selectivity	stability	
CUR-MIM/GCE	in situ bulk polymerization accompanied by surface electrochemical polymerization	curcumin	PACO		10 nm–2.0 μm	5.0 nm	THC, FA, CRT, and QCT	30 days	81									
screen-printed carbon electrode coated with MIMs	in situ photo polymerization	salbutamol	MAA		50–280 nm	13.5 nm	ractopamine and clenbuterol	4 months	86									
ART-MIM/G/GCE	in situ polymerization	artemisinin	acrylamide		10 nm–40 μm	2.0 nm	DHA, ARM, and ARTS	80 times, 60 days	83									
MOFs@graphene	UV-induced polymerization	ketamine	MAA		0.1 nm–40 μm	0.04 nm	MDMA, MA, DA, and ascorbic acid	60 times, 2 months	84									
p-ATP–AuNP/AuNP/GCE	electropolymerization	acrylamide	p-ATP and PAM		0.001 nm–0.1 μm	0.005 nm	AA, methacrylamide, MAA, and PAM	30 days	85									
ATP@AuNPs-modified gold electrode	self-assembly and electrodeposition	herbicide simazine	ATP		0.03–1.40 μm	0.013 μm	acetochlor, terbutylazine, picloram	30 days	82									
ZnFe ₂ O ₄ @MIP membranes	bulk polymerization	BPA	acrylamide		10–1000 nm	6.18 nm	TBHQ, DES, (1,4-DHB), and PP		87									
MMP with Fe ₃ O ₄ @SiO ₂ NPs	bulk polymerization	AP	(4-VP) and MAA		60 nm–40 μm	17.3 nm	PAP and AAA	30 days	88									
QCM sensor based on MIP membrane on AuNPs@CMK-3	electropolymerization	citrinin	ATP		6.0 nm–0.2 μm	1.8 nm	DON, OTA, and ZEN	2 weeks	89									
molecularly imprinted QCM on Au electrode surface	electrodeposition	ractopamine			2.50 μm–0.115 nm	1.17 μm	ISOP, TER, and ISOX	2 weeks	96									
plasticizer-free MIP-based potentiometric sensor using a novel copolymer	electrodeposition	neutral phenol (bisphenol A)	methyl methacrylate			32 nm	phenol, catechol, and 3-nitrophenol	1 month	97									

^aCUR-MIM/GCE, molecularly imprinted membrane of curcumin on glassy carbon electrode; ART-MIM/G/GCE, artemisinin-imprinted membranes on the surface of graphene-modified glassy carbon electrode; ATP@AuNPs, *o*-aminothiophenol-functionalized Au nanoparticles; MMIP, molecularly imprinted membrane; QCM, quartz crystal microbalance; PACO, 4-pentenyl-alanyl-chitosan oligosaccharide; MAA, methacrylic acid; 4-VP, vinylpyridine; p-ATP, *p*-aminothiophenol; DHA, dihydroartemisinin; ARM, artemether; ARTS, artesunate; MDMA, methylenedioxymethamphetamine; MA, methylamphetamine; DA, dopamine; AA, acrylic acid; PAM, propionamide; TBHQ, *tert*-butylhydroquinone; DES, diethylstilbestrol; 1,4-DHB, hydroquinone; PP, phenolphthalein; PAP, *para*-aminophenol; AAA, acetamide; DON, deoxynivalenol; OTA, ochratoxin A; ZEN, zearalenone; ISOP, isoproterenol; TER, terbutaline; ISOX, isosuxprine.

the performances of sensor-based MIAMs is tabulated in Table 2.

6. MIAMS FOR SEPARATION OF TARGET IONS

MIAMs can perform separation by combining membrane and ion-exchange processes. This combined process can be used to remove ions by ion-selective recognition, resulting in high selectivity toward ions, such as heavy metal ions.⁹⁸ Unlike an ion-exchange membrane, which usually separates ions based on the charge difference (cations and anions), an MIAM is able to discriminate ions with the same charge. Therefore, target ions can be separated from a mixture of various ions having the same charge, such as Cr(VI)/Cr(III),⁹⁹ Na⁺/Li⁺, and K⁺/Li⁺.¹⁰⁰ This ability is important, for example, in drinking water decontamination, wastewater treatment, or removal of low-concentration metal ions.

For instance, a molecularly imprinted polymer, which is the key of an MIAM, can absorb chromium(III) or Cr(III) through a polymerization process.⁹⁹ A Cr(III)-imprinting polymer, i.e., Cr(III) ion-imprinted ethylene glycol dimethacrylate–methacryloylhistidine, has selective cavities that only fit with Cr(III) ion geometry.⁹⁹ The selective cavities improve membrane selectivity toward Cr(III) during the separation process. The adsorption capacity of the molecularly imprinted polymer can reach 338.73 mg of Cr(III)/g of polymer, as determined by the functional monomer.¹⁰¹ In the study,¹⁰¹ 4-vinylpyridine is the functional monomer that can achieve the highest adsorption capacity, where the synthesized molecularly imprinted polymer shows excellent selectivity. The selectivities of the molecularly imprinted polymer were 189.1 and 96.6 for Cr(VI)/Cu(II) and Cr(VI)/Cr(III), respectively. The high selectivity was due to the high adsorption capacity of the ion-imprinted polymer toward Cr(III). It was provided by electrostatic interaction between Cr(III) and the protonated N atoms of the functional pyridine groups.

Another example is Hg ion separation. In Hg ion removal, the mechanism can be a chelation process, as occurred in a molecularly imprinted polymer containing a dithizone chelation agent.¹⁰² The molecularly imprinted polymer exhibited a selectivity of 33 for Hg²⁺/Zn²⁺ and displayed high reusability. Moreover, the molecularly imprinted polymer can discriminate between Hg²⁺ and organic mercury, thanks to the dithizone–Hg²⁺ chelate template.¹⁰² The result of 10 cycles of the adsorption–desorption process revealed that the adsorption capacity loss was within 5%. High reusability was also demonstrated in the adsorption of Cu(II) by using a prepared molecularly imprinted polymer containing functional polymers of gelatin, 8-hydroxyquinoline, and chitosan.¹⁰³ The adsorption capacity was retained at 90% after 10 cycles of adsorption–desorption processes.

The introduction of a molecularly imprinted ion membrane allows ion separation with high selectivity. The functional groups of the molecularly imprinted polymer act as carriers that facilitate ion transfer through the membrane. This mechanism is also referred to as facilitated transport. The high adsorption capacity introduced by the functional groups or selective cavities of the molecularly imprinted polymer can improve the separation of ions or selectivities. For instance, the adsorption ability introduced by the molecularly imprinted polymer facilitates the separation of heavy metals by ultrafiltration, which cannot be achieved by the conventional or regular ultrafiltration membrane.¹⁰⁴ This is because the conventional ultrafiltration membrane relies solely on a sieving

mechanism. Because the membrane pores or ultrafiltration are generally larger than the ions, separation of ions cannot take place. Therefore, by adding an adsorption process, heavy metal ion removal by membrane ultrafiltration becomes possible.^{105–107}

The separation of uranyl ions using MIAM has also been clearly demonstrated.¹⁰⁸ The membrane was made of uranyl vinylbenzoate (UO₂(VBA)₂), styrene, and divinylbenzene. The flux of uranyl ion UO₂²⁺ was 2.74 nmol cm⁻² h⁻¹, superior to those of other ions. The membrane showed good selectivity toward uranyl ions, ranging from 100 to 150. The membrane was also reusable with a retained capacity.¹⁰⁸ The highly selective transport of uranyl ions across the membrane was associated with the presence of an ion-imprinting complex, UO₂(VBA)₂. The UO₂(VBA)₂ created selective binding of uranyl ions, forming a selective path along the membrane.

Thermodynamic modeling of a nickel ion-imprinted membrane was conducted to investigate the adsorption behavior of an MIAM.¹⁰⁹ The MIAM contained a poly(vinylidene fluoride) microfiltration membrane as the support, methacrylic acid as the functional monomer, and Ni–dithizone complex as the complexing agent. The adsorption process of the synthesized membrane was performed for Ni(II) and Co(II) ions. The thermodynamic analysis confirms the spontaneous adsorption of these ions. From the adsorption and kinetic analysis, the MIAM shows that the adsorption and permeation rate of nickel ions are higher than those of the cobalt ion. The improved adsorption and permeation rate result in higher membrane selectivity toward nickel ion served by the Ni–dithizone complex.

An MIAM with high selectivity toward lithium ions has also been fabricated by Lu et al.¹⁰⁰ The active site of the MIAM was formed by introducing 12-crown-4 (12C4). The MIAM was prepared from poly(ether sulfone) as the substrate, polydopamine as an interfacial layer, silica nanoparticles as the hydrophilic agent, and Li-imprinted polymer as the active separation layer. Then, the prepared MIAM was used to separate lithium ions, and the flux of lithium ions was compared to those of other monovalent ions, i.e., sodium and potassium. Lithium, sodium, and potassium ions have similar hydration radii, and hence, the mixture of these ions would be challenging to separate. The results showed that the MIAM could achieve high permselectivity for Na⁺/Li⁺ and K⁺/Li⁺. The high selectivity was obtained by restricting the permeation of lithium ion through the membrane due to the presence of selective adsorption toward lithium provided by the Li-imprinted polymer. Selective sites that only fit to the Li⁺ ion structure inhibit the transport of Na⁺ and K⁺ ions through the MIAM.

Zeng et al.¹¹⁰ reported the preparation and characterization of MIAM used to separate anions, i.e., molybdate anions, from water solution.¹¹⁰ The membrane comprises a ceramic membrane support and an ion-imprinted polymer created by combining graft polymerization and surface-printing methods. In a binary solution adsorption experiment, the membrane exhibited an adsorption capacity of 0.69 nmol/g for Mo(VI) and a selectivity of 7.48 for Mo(VI)/W(VI). Similar to previously mentioned results, the imprinted cavities of Mo(VI) increase MIAM selectivity for Mo(VI). Another anion-selective MIAM was also synthesized on a ceramic support.¹¹¹ This later membrane is selective to tungstate ion with selectivities of 15.5 and 19.7 for W(VI)/Mo(VI) and W(VI)/Cr(VI), respectively. The membrane restricts tungstate ion permeation by binding

Table 3. Applications of MIAMs for Ion Separation^a

name of MIAM	synthesis method	target ions	functional monomer	performances			ref
				maximum adsorption capacity (mg/g)	selectivity coefficient	sorption time equilibrium	
poly(EGMA-MAH/Cr(III))	dispersion polymerization technique	Cr(III)	MAH	69.28	6.35 for Cr(III)/Co(II), 8.88 for Cr(III)/Ni(II), and 5.66 for Cr(III)/Cr(VI)	30 min	99
Cr(VI)-IIP	bulk polymerization	Cr(IV)	4-VP	338.73	189.05 for Cr(VI)/Cu(II) and 96.56 for Cr(VI)/Cr(III)	3 min	101
G-HQ-C IIPs	dimple chemical cross-linking method	Cu(II)	gelatin (G), HQ, and chitosan (C)	111.81	18.7	180 min	103
high-selectivity multilayered Li-IIMs	two-step modification strategy	Li(II)	MAA		1.85 for Li ⁺ /Na ⁺ and 2.07 for Li ⁺ /K ⁺	60 min	100

^apoly(EGMA-MAH/Cr(III)), Cr(III) ion-imprinted ethylene glycol dimethacrylate–methacryloyl histidine; Cr(VI)-IIP, Cr(VI) ion-imprinted polymer; G-HQ-C IIPs, green ion-imprinted polymers; Li-IIMs, Li⁺-imprinted membranes; 4-VP, 4-vinylpyridine; HQ, 8-hydroxyquinoline; MAA, methacrylic acid.

Table 4. Applications of MIAM for Organic Compounds Separation^a

name of MIAM	synthesis method	target compound	functional monomer	performances			ref
				maximum adsorption capacity	permselectivity factor	sorption time equilibrium	
AMINMs	imprinting polymerization	atrazine	MAA	5.857 mg/g	2.34	90 min	112
MINCMs	vacuum-assisted filtration process and photo of the suction filter device	norfloxacin	dopamine	25.35 mg/g	>15.2	60 min	118
GT-MIMs	two-step temperature imprinting process	propranolol	AM and MAA	55.12 mg/g	>11.35	30 min	114
molecularly imprinted membrane (MIM)	infiltration of prepolymerization solution	synephrine	MAA and 2-HEA	158.23 (μmol/g)	2.13		115

^aAMINMs, atrazine-based molecularly imprinted nanocomposite membranes; MINCMs, molecularly imprinted nanocomposite membranes; GT-MIMs, GO/TiO₂-based molecularly imprinted nanocomposite membranes; MIMs, molecularly imprinted membranes; 2-HEA, 2-hydroxyethyl acrylate.

the ion while allowing other ions and water to pass through. Polyethylenimine in the membrane contributes to tungstate ion adsorption by electrostatic interaction. The membrane also shows remarkable water flux above 3000 L m⁻² h⁻¹ at 0.2 bar pressure difference.

A summary of MIAM performances for metal ion separation is provided in Table 3. Even though MIAMs show remarkable separation, especially toward targeted ions, the performance relies on its adsorption capacity, so regeneration is crucial. Regeneration has been performed in several studies to examine the reusability of MIAMs. However, it still needs a long-term performance test to evaluate MIAM reusability, especially at a larger scale. In addition, effective and efficient regeneration protocols of MIAMs are rarely reported.

7. MIAMS FOR ORGANIC COMPOUNDS SEPARATION

Separation of organic compounds with similar molecular weights is challenging in membrane separation. By employing molecular recognition, MIAMs can have a high separation performance in organic compounds separation. Table 4 provides a summary of MIAM performances for organic compounds separation.

Janus nanocomposite-incorporated molecularly imprinted membranes (MINCMs) for selective adsorption and separation of tetracycline (TC) molecules are presented in Figure 5a. A two-step strategy was used to fabricate the MINCMs; first, polydopamine (pDA) nanospheres were prepared by oxidative polymerizing dopamine molecules. Second, pDA@Au was used for the synthesis of Janus-nanostructure membranes. In

addition, the selectivity of MINCMs toward TC compounds was investigated with comparative molecules, such as cefalexin (CEX) and sulfamethazine (SMZ).⁶⁸ The MINCMs have a rougher surface, and the imprinting process causes a decrease of the pore size. TC compounds are linked by molecular affinity imprinting sites, while other molecules (CEX and SMZ) will pass through MINCMs without any interaction. On the basis of affinity binding, there are two suggested mechanisms for selective permeation of MINCMs, namely, facilitated permeation, which is the slower movement of other solutes, and retarded permeation, which is the faster movement of other solutes.¹⁶ In the permeation and separation of TC, the retarded-permeation mechanism is more dominant. The TC molecules surround the MINCM surface, followed by its adsorption through the rebinding hole. Affinity imprinting sites preferentially bind the TC molecule, and other nonspecific molecules (CEX and SMZ) will transport immediately through the MINCM without any restraint.⁶⁸

Xing et al. prepared inorganic MINCMs using methacrylic acid (MAA) as a functional monomer to separate atrazine compounds (AMINM).¹¹² The results of the permselectivity of AMINMs toward atrazine compared to amethrin revealed that the atrazine concentration in the solution is lower than that of amethrin. This result relates to steric imprinting cavities in AMINMs that can gain objective molecules by preventing transport from the interference of identifying sites. As shown in Figure 5b, atrazine molecules can be prevented by cavity imprinting when they cross the imprinted membrane of AMINMs due to the interaction between template molecules

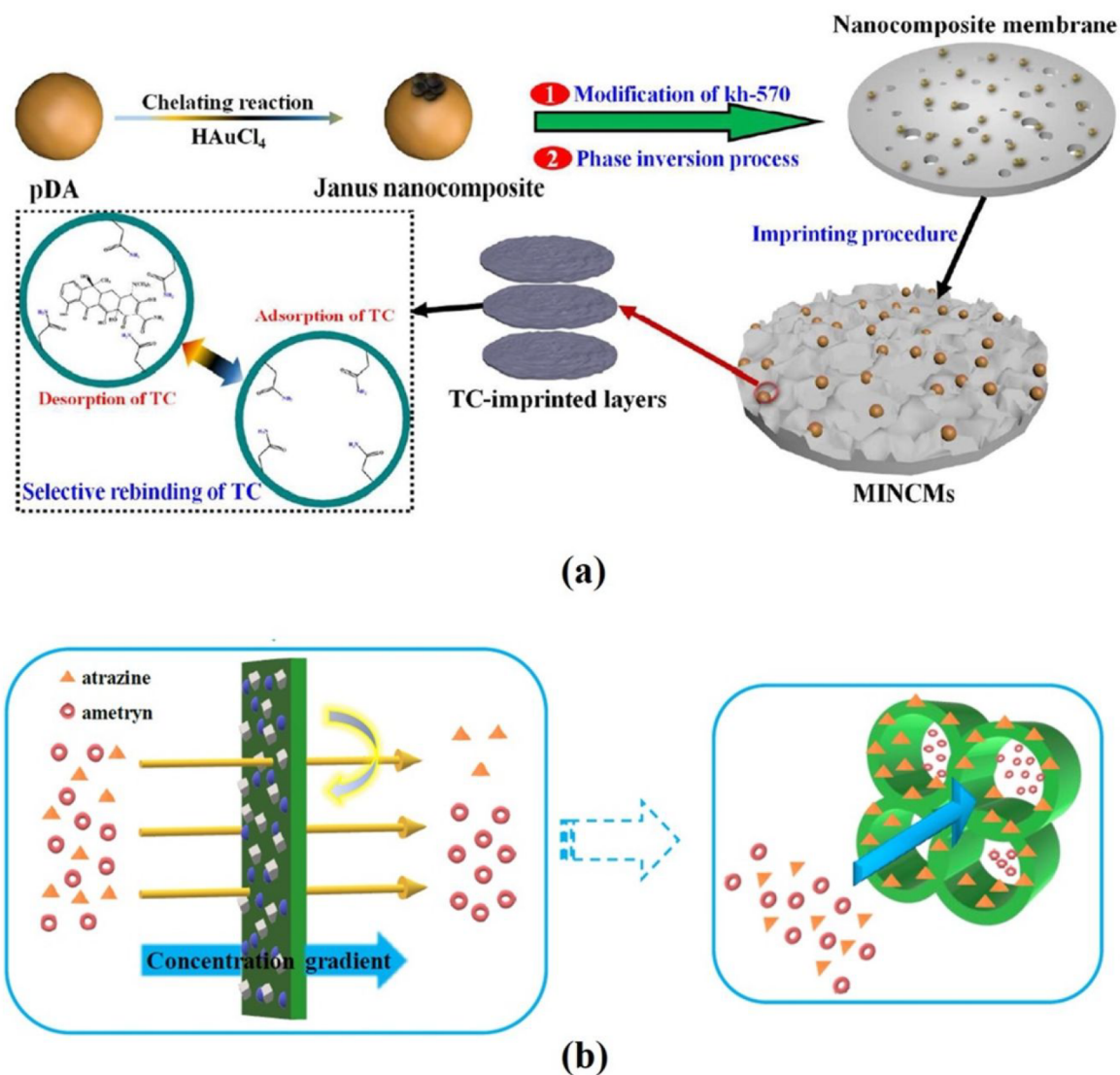


Figure 5. Schematic illustrations of (a) fabrication of molecularly imprinted nanocomposite membranes (MINCMs) for the selective separation of tetracycline (TC) and (b) mechanism of the permselectivity using atrazine-based molecularly imprinted nanocomposite membranes (AMINMs). (a) Adapted with permission from ref 68. Copyright 2018 American Chemical Society. (b) Adapted with permission from ref 112. Copyright 2020 American Chemical Society.

and molding cavities. Therefore, molecular recognition can be achieved due to the presence of imprinting cavities with a particular size and shape.¹¹³

A double-layer-based molecularly imprinted nanocomposite membrane (DLMIM) has also been fabricated.⁶⁷ In general, DLMIMs were prepared by a two-step imprinted process using polydopamine (pDA)-assisted inorganic film formation (PIFF). The first layer consisted of a PDA-based imprinted TC, while the second layer comprised a sol-gel TC-imprinted site assembled on DLMIMs. The essential characteristic for the selective identification and separation of target molecules or ions is the specific identification capability of MIAM. The selective identification mechanism of the membrane has a high affinity and specific selectivity resulting from the two-stage imprinting process. The selectivity was examined by employing a mixture of analogue components, such as cefalexin (CEX), oxytetracycline (OTC), and sulfamethazine (SMZ). The results revealed that DLMIMs have a higher rebinding capacity toward TC molecules than to CEX, OTC, and SMZ. Double-

layer-based printing generates an increment in the number of sites of a DLMIM. In addition, DLMIMs have excellent structural stability by retaining high rebinding performance after reuse several times. The first structure layer serves a crucial function in the rebinding capacity and specific identification capability of DLMIMs.

The GO (graphene oxide)/TiO₂-based molecularly imprinted nanocomposite membranes (GT-MIMs) could be used for the selective separation of propranolol molecules.¹¹⁴ The GT-MIM selective rebinding site mainly controls the propranolol separation process. Initially, the propranolol molecule moves toward the surface of the GT-MIMs and is adsorbed by the rebinding cavity. Hence, the imprinting site affinity preferentially binds the propranolol molecules. In addition, the selectivity of the GT-MIM toward propranolol using a mixture of *o*-pivaloylpropranolol (Opl) and *o*-acetylpropranolol (Oal) gained a maximum adsorption capacity of the GT-MIM on propranolol of 55.12 mg g⁻¹, which confirmed the remarkable selectivity of the GT-MIM.

Lu et al. prepared an MIAM using MAA as a functional monomer with double-faced loaded CNTs by photoinitiated polymerization and for selective recognition and separation of pyrimethamine (PMIM).⁷¹ The imprinted site designed on PMIM facilitates catching the target molecules and retarded permeation.^{115–117} Moreover, the PMIM shows a higher permselectivity coefficient. This result indicates that retarded permeation of the target molecule can provide stable selectivity in the long run. Therefore, the selective separation based on PMIM toward pyrimethamine (PMM) can be accomplished efficiently, quickly, and stably.

The molecularly imprinted nanocomposite membranes (MINCMs) using a vacuum-assisted filtration process for selective separation of norfloxacin as antibiotic pollutants in water have also been successfully fabricated.¹¹⁸ Norfloxacin was employed as the template, while dopamine was employed as both the functional monomer and cross-linker. The adsorption or desorption to the recognition site in the MICM inhibits norfloxacin molecules' transport. At the same time, other compounds are directly transported through the MINCM with less resistance because of no specific interaction with the imprinted cavities. In the retarded permeation mechanism, norfloxacin transport would be delayed by rebinding or desorption at the affinity site in MICM. Conversely, in facilitated permeation, the process would be driven through slower affinity-binding transport on the RCM structure. Other analogs are taken through the MINCM directly because they do not interact with the cavities in the MINCM.

Dong et al. prepared lincomycin molecularly imprinted membranes (LINMIMs) for selective separation of lincomycin (LIN) using dopamine (DA) and polyethylenimine (PEI) as functional monomers.¹¹⁹ The MIM showed high adsorptive selectivity and permselectivity. This result is related to the combination of PEI and DA that increases the hydrophilicity of the pure membrane and produces a specific recognition site.

8. FUTURE OUTLOOKS

An MIAM is a type of membrane that is able to bind a specific molecule by using molecular recognition sites selectively. The recognition sites are introduced by the molecular imprinting technique. As a result, an MIAM displays a highly selective separation toward the target component. The high selectivity is generally due to the formation of coordinate covalent bonds between metal ions and the chelating ligands.

MIAMs are usually developed by covalent and noncovalent interactions, where the latter is easy to fabricate, and the template could be simply removed. Several MIAM preparation methods are available, including in situ polymerization, post-polymerization, click chemistry, electrospray deposition, and chemical vapor deposition, with their respective advantages and disadvantages. Recently, click chemistry has dominated the trend of MIAM preparation because it requires a short fabrication time, results in a high yield, and is operated at mild conditions.⁷¹

MIAMs show remarkable performance in various applications, such as sensor, metal ion separation, and organic compounds separation, including proteins and antibiotics. The selective recognition mechanism improves membrane selectivity toward specific molecules, which is preferable for the separation process. In some cases, the molecular recognition sites bind the target molecules, so the mobility of the target molecule is restricted while allowing the permeation of others.

In another case, the recognition sites attract the target component and simultaneously allow its diffusion through the membrane. The first case relies on the adsorption capacity of the membrane, which requires chemical regeneration after being saturated by the target molecules. In addition, more studies are needed to create effective and efficient regeneration protocols of MIAMs. Affinity and mobility are involved in the separation process for the second case.¹⁹ These parameters should be optimized to obtain a highly selective membrane with a maintained permeation rate.

All efforts to realize an effective MIAM strictly require the appropriate combination of binding sites and target molecules. Hence, the cross-linked polymers, functional groups, and template molecules must be thoroughly selected to form an MIAM that selectively captures and strongly interacts with the target molecules. In this sense, the utilization of computational study (DFT-based calculation, molecular mechanics, and/or molecular dynamics) and machine learning could be essential to predict, predesign, and specify the crucial aspects of an MIAM–target molecule pair and, ultimately, accelerate the invention of a more efficient MIAM and its regeneration for a particular application. Moreover, alternative strategies such as fine-tuning the application conditions or incorporating the inorganic fillers might be adopted to improve the MIAM performance. For example, a solution could be rendered acidic to create a protonated MIAM with an enhanced binding selectivity toward anionic species for metal ion separation. Alternatively, the addition of inorganic nanomaterials, such as carbon nanotubes, might provide a selective pore channel that facilitates a better diffusion for the target molecules, leading to a better performance of MIAMs as sensing materials. Most MIAM preparations and applications are achieved at the laboratory scale; nevertheless, large-scale realization has been the final goal. Hence, extensive research is needed to fulfill this goal, and there is still plenty of room for improvement that is worthy of exploration.

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Notes

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