ION Imprinted Polymers: General Characteristics and Applications

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Abstract

A recent multidisciplinary topic called "molecular imprinting" that falls under the category of "host-guest chemistry" is important in the development of molecular recognition sites in the polymer matrix. Ion imprinted polymers are widely used in a variety of industries. We provide a thorough overview of the fundamental characteristics of ion imprinted polymers and their applications in this review paper.

Keywords: Recognition, Polymers, Ionimprinting

INTRODUCTION

Designing synthetic materials that can imitate the natural processes of recognition has grown to be a significant and active topic of study. Today, a practical synthetic method for designing strong molecular recognition materials that may replicate natural recognition entities, such as antibodies and biological receptors, is known as molecular imprinting technology (MIT). MIT is regarded as a flexible and promising method that can identify both biological and chemical compounds, including proteins and amino acids, toxins, medicines, and food. Separation sciences and purification, chemical sensors, catalysis16, drug administration, and biological antibodies and receptor systems are more application fields.

The foundation of molecular imprinting technology is the creation of a complex between a functional monomer and an analyte (template). A three-dimensional polymer network is created when there is an excessive amount of the crosslinking agent present. Following the polymerization process, the template is taken out of the polymer, leaving behind particular recognition sites that are similar to molecules in terms of size, shape, and chemical activity. The molecular recognition phenomenon is often driven by intermolecular interactions such as hydrogen bonds, dipole-dipole interactions, and ionic interactions between the template molecule and functional groups present in the polymer matrix. As a consequence, only the molecules from the template are recognised by and bound by the resulting polymer.

For a broad variety of applications in analytical chemistry, the selective identification of metal ions presents a significant problem. Ion-imprinted polymers (IIPs), which work on the same principle as molecularly imprinted polymers, have been developed more and more during the last few years to achieve this goal. Because of metal ions' high toxicity, endurance, and potentially carcinogenic impact, metal ion extraction in the aquatic environment continues to be a significant problem. It is crucial to remove metal ions from various water sources. The most popular liquid-liquid extraction and solid-liquid extraction techniques, also known as solid-phase extraction (SPE), as well as chemical precipitation, membrane filtration, flotation, electrochemical, and biofiltration techniques, may all be used to remove metal ions.

For metal ion separation, solid phase extraction using ion exchange or chelating materials has various benefits since it streamlines the separation process, lowers disposal costs, and utilises and exposes less solvents. Numerous synthetic polymers with different chelating properties have been investigated. They may be created through direct copolymerization of a functional monomer with a crosslinker, impregnation, grafting of commercial sorbents or home-made copolymers, or copolymerization of a functional monomer with a crosslinker.

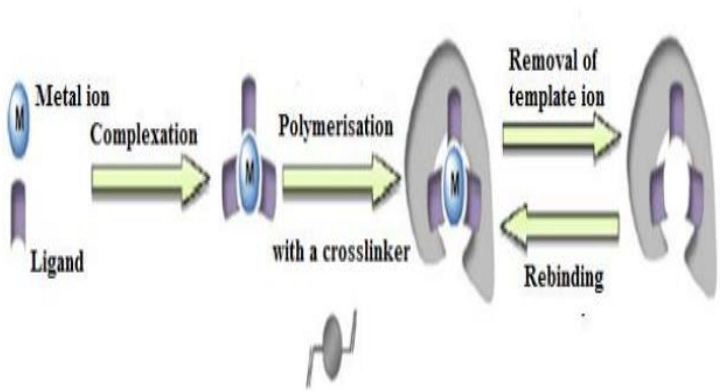

Fig.1. Schematic representation of synthesis of metal ion imprinted interpenetrating polymer networks

Nishide et al. first developed ion-imprinted polymers (IIPs) by crosslinking poly(4-vinyl pyridine) with 1,4-dibromobutane when a metal ion was present. By converting the template molecule into a metal ion, this idea resembles that of the MIPs (Fig. II. 1). IIPs, on the other hand, may use coordination chemistry, while MIPs often interact with template molecules through conventional functional monomers via hydrogen bonds or van der Waals interactions. In order to provide selective binding sites following metal leaching, a ligand must typically form a complex with the metal ion during the manufacture of IIPs. Not long after Wulff and Klotz created the first molecularly imprinted polymeric materials in 1972, Nishide et al. disclosed the first IIPs in 1976.

2. Polymers with ion imprints:

The production of a ligand-metal complex, followed by copolymerization with a cross-linker to produce three-dimensional recognition cavities within the polymer networks, is the standard method for IIP elaboration. This procedure is broken down into the following three parts by Denizli et al. Metal ion complexation to a polymerizable ligand, polymerization of this complex, and removal of the template ion following polymerization are the first three steps. The polymerizable ligands are sometimes referred to as bi-functional reagents since they possess both chelating and vinyl functions. Utilising a non-polymerizable ligand that is trapped within the polymer matrix during the preparation of IIPs is a more straightforward procedure. The interactions between the polymer framework and the complexed ion, regardless of the method used to introduce the ligand, are based on coordinative bonds formed by certain electron-donating heteroatoms to the open orbitals of the metal ions' outer sphere.

Because of their strong selectivity towards the target ion and a memory effect brought on by their fabrication procedure, ion-imprinted polymers have unique features. High selectivity is primarily caused by two factors: the ligand's affinity for the imprinted metal ion and the size and shape of the produced cavities35. This configuration allows the binding sites to match the charge, size, and coordination number of the ion since recognition sites are produced via the self-assembly of some ligand(s) around the template ion and subsequent crosslinking. Additionally, the crosslinking and leaching processes may retain the complicated geometry, creating a favourable environment for the template ion rebinding. Ion-mediated biological self-assembly processes like intercellular junctions may be used to compare the workings of IIP. The recognition in such ion-mediated biological self-assembling processes is mediated by calcium ions. IIPs are strong polymers that may be reused repeatedly without losing their functionality because of their high crosslink density.

3. Molecular imprinting reagents

Many variables, including the kind of monomer, crosslinker, initiator, temperature and duration of polymerization, the presence or absence of a magnetic field, and the volume of the polymerization mixture, may influence the polymerization reaction, which is known to be a highly complicated process. Numerous aspects need to be optimised in order to have the perfect imprinted polymer. As a result, creating imprinted polymers requires a lot of time. Numerous efforts have been undertaken to examine such influences on the recognition characteristics of the polymeric materials39 in order to manufacture imprinted polymer with optimal qualities.A key stage in the molecular imprinting process is choosing the proper reagents. The kind of template, ligand, functional monomer, crosslinkers, solvent, and initiator employed all affect how well an imprinted polymer works.

3.1 Templates

In analytical procedures, target substances are often template molecules. The next three criteria should be met by a perfect template molecule. First, it shouldn't have any groups that promote or hinder polymerization. Second, it must demonstrate outstanding chemical stability during the polymerization process. Last but not least, it must have functional groups that are well suited to assembling with functional monomers.

The majority of templates used in molecular imprinting are sourced from common environmental contaminants, which may be divided into three major groups, including medicines, hazardous metal ions, and endocrine disrupting chemicals (EDC)41. Endocrine disruptive substances have received a lot of attention when discussing issues with the environment on a global scale since they may affect both humans and other animals' key regulating processes. Even worse, certain endocrine disrupting substances have been linked to infant development retardation or human infertility. Hormone medications, 40 triazine insecticides, bisphenol A, and other endocrine disrupting chemicals are the most commonly regarded pollutants employed in the production of imprinted polymers. Due to their ongoing discharge into the environment, pharmaceuticals have attracted more and more interest in recent years. The area of molecular imprinting technology has advanced significantly with the invention of water-compatible imprinted polymers.

3.2 Ligand

Since ion chelation plays a part in the recognition process, the function of the ligand is the fundamental criteria.

The main interactions with the polymer matrix will take place with some electron-donating heteroatom since the template in ion imprinted polymers is an ion, responding through its empty orbitals of the outer sphere. Utilising ligands with one or more chelating groups is the prevalent tendency. Fig. 2 lists a few of the functionalized ligands employed in the chemical immobilisation method.

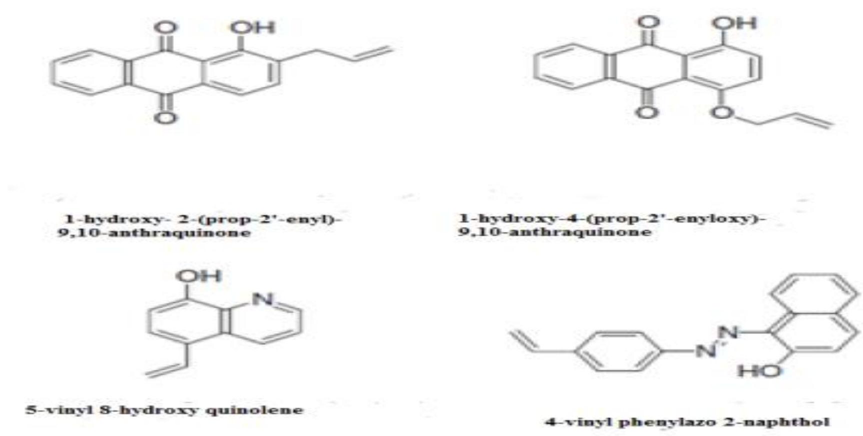

Fig.2. Functionalized ligands used in the synthesis of IIP

3.3 Functional monomer

The job of the monomer is to give functional groups that may engage either covalently or non-covalently with the template to generate a complex. The trapping strategy to build a ternary complex with the metal ion has shown to be dependent on the usage of a mono vinylated monomer, such as 4-vinylpyridine. However, different monomers could be added to the polymerization mixture even when a functionalized ligand is utilised in the chemical method. Methacrylic acid (MAA), acrylic acid (AA), 2- or 4-vinylpyridine (2- or 4-VP), acrylamide, trifluoromethacrylic acid, and 2-hydroxyethyl methacrylate (HEMA) are among the monomers often employed for molecular imprinting. Due to its distinctive properties, including its ability to operate as a hydrogen-bond donor and acceptor and demonstrating high compatibility for ionic interactions, methacrylic acid has been employed as a "universal" functional monomer.

3.4 Crosslinkers

In order to create a stiff, highly crosslinked polymer, the crosslinker's job is to fix the functional groups of functional monomers around imprinted molecules. Since it initiates the formation of the binding sites, the crosslinker is crucial to the development of the ion imprinted polymers. After the templates have been removed, the holes that have been created should perfectly match the shape and functional groups of the target molecules. The crosslinker types and quantities have a significant impact on the selectivity and binding ability of molecularly imprinted polymers. Molecularly imprinted polymers struggle to maintain stable cavity topologies when the dose of crosslinkers is too low due to the low crosslinking level. However, excessive crosslinker use will result in fewer recognition sites per molecularly imprinted polymer mass.

Ethylene glycol dimethacrylate (EGDMA), trimethylolpropane trimethacrylate, divinylbenzene (DVB), and others are frequently used crosslinkers.

3.5 Solvent

To create the porosity structure, solvent is used during the manufacturing of ion imprinted polymers. For the analytes to have access to a large number of binding sites, this porosity is crucial. The "porogen" features of this kind of solvent, which are often referred to as "porogen" properties, rely on the difference between its solubility parameter and that of the monomers and polymer chains41. As monomers are used up throughout the polymerization process, the medium's solvating power will change. Each component of the polymerization process must dissolve in the porogen. This pertains to the ion template in either free form or trapped inside a complex during the IIP preparation process, in addition to the monomers and initiator. The porogenic solvent is crucial to the polymerization process. Additionally, it affects the shape and properties of polymers, particularly in non-covalent interaction systems, as well as the strength of the bonds between functional monomers and templates. In order to achieve excellent imprinting efficiency, aprotic and low polar organic solvents including toluene, acetonitrile, and chloroform are often utilised in non-covalent polymerization methods. Due to the ''solvent memory,'' it is noteworthy that imprinted polymers made in organic solvents perform poorly in aqueous media.

3.6 Initiators

The initiator plays a well-known function in radical polymerization because it generates radicals from monomers to help the polymerization process progress. Thermal decay, photolysis, or ionising radiation all homolytically cleave the initiator. Rarely are these latter two methods utilised to make ion imprinted polymers. In the presence of the template, free radical polymerization may be started using any of the initiation techniques. Initiators that can be activated photochemically or thermally, respectively, would not be desirable if the template is photochemically or thermally unstable. Lower polymerization temperatures are desired and photochemically active initiators are favoured in situations where complexation is driven by H-bonding. The kind and concentration of the initiator have an impact on the rate of radical polymerization. The most effective initiators are potassium persulate and 2, 2'-azo-bis-isobutyronitrile (AIBN). The choice of the initiator relies on the type of the template.

4. Polymerization techniques

While organic ion imprinted polymers are mostly made using free radical polymerization, ion imprinted polymers are often made through polycondensation. The polymerization procedure may affect the forms of these ion imprinted polymers. Bulk polymerization will result in monolithic materials, while heterogeneous (suspension or emulsion) or homogeneous (dispersion or precipitation) polymerization may yield well-defined particles.

5. Different stages in the preparation of imprinted polymers

5.1 Preorganization stage

A preorganized method that makes advantage of covalent reversible bonds produces a population of binding sites that is rather homogenous while minimising the number of non-specific sites. However, the covalent connections must be broken in order to extract the template from the polymer matrix. The behaviour of the resultant molecular imprinted polymer may be deduced from the structure and stability of this combination.

5.2 Covalent interactions

The use of templates that are covalently attached to one or more polymerizable groups distinguishes covalent imprinting from other imprinting techniques. After polymerization, the template is broken up, and the functionality that is left at the binding site may re-establish the covalent link and bind the target molecule. With this strategy, the functional groups are only linked to the template site, which is advantageous. However, this method can only imprint a small subset of molecules (alcohols, aldehydes, ketones, amines, and carboxylic acids).

5.3 Non-covalent interactions

The interactions between the functional monomer and template during polymerization in non-covalent imprinting are the same as those between the polymer and template during the rebinding stage. These rely on non-covalent forces such H-bonding, ion pairing, and interactions between dipoles. For the first time, this technique was used with organic polymers. This technique is the one most often used to make imprinted polymers since it is so straightforward. Methacrylic acid, which has been modified for the imprinting of 2,4-D, hydroquinidine, hormones, nucleotides, and cyclic peptides, is now the most widely used functional monomer.

6. Advantages of molecular imprinted polymers

High selectivity and affinity for the target molecule utilised in the imprinting process are the key benefits of molecularly imprinted polymers. Imprinted polymers exhibit superior physical robustness, strength, tolerance to high temperatures and pressures, and inertness towards acids, bases, metal ions, and organic solvents as compared to biological systems like proteins and nucleic acids. They also cost less to produce because of how long the polymers can be stored at ambient temperature without losing their ability to recognise molecules.

7 Applications of molecular imprinted polymers

MIPs are a particularly intriguing tool for a variety of application domains, including separation sciences and purification, sensors and biosensors, catalysis, and drug delivery, because to their unusual features.

One of the most explored uses of MIPs, which are excellent for chromatographic separation, chiral separations, solid phase extraction, antibody and receptor mimicking, enzyme mimetic catalysis, chemical synthesis, and drug administration, is molecular imprinting chromatography.

7.1 MIPs in separation techniques

One of the oldest uses of molecularly imprinted polymers, particularly for liquid chromatography, is molecular imprinted chromatography. Imprinted polymers are typically produced by bulk polymerization, mechanically ground and sieved, and then packed into a chromatographic column. A packing of irreproducible quality results from the mechanical processing, which creates irregular particles with a generally wide size dispersion. Due to this, monolithic molecular imprinting columns have recently been created within capillary or stainless steel columns. According to experimental evidence, imprinted particles that aren't always uniform may nonetheless perform better in chromatography. It has been observed that the porosity of the beads has a significant impact on the chromatographic performance of these systems. For example, precipitation polymerization was used to prepare spherical beads, but with a total pore volume that was still lower than that of the irregular particles obtained by bulk polymerization. Due to the selective interactions that are shown, imprinted polymer sorbents retain the analyte more effectively than non-imprinted polymer materials. In high performance liquid chromatography, imprinted polymers are commonly employed as chiral stationary phases to provide enantiomeric resolution of racemic mixtures, such as amino acid derivatives and pharmaceuticals.

Recently developed capillary electro chromatography (CEC) micro-columns for the separation of various substances are MIP based. Another significant area of use for imprinted polymers in analytical chemistry is solid phase extraction (SPE). Multiple chemicals were extracted using Molecular Imprinted Solid Phase Extraction (MISPE) from a variety of sample matrices, including biological, environmental, and dietary samples. In 1994, Sellergren achieved a selective extraction of pentamidine, a medication used to treat illnesses connected to acquired immune deficiency syndrome, in urine samples. This was the first use of MISPE.

7.2 As chemical sensors and biosensors

Modern analytical chemistry has recently seen an increase in interest in chemical sensors and biosensors. This is a result of the new requirements that are emerging, notably in food analysis, environmental analysis, and clinical diagnostics. A sensor is defined by two key components that interact with an analyte in a certain way and translate that interaction into a measuring effect. Artificial receptors that can bind a target analyte with similar affinities and selectivities to natural antibodies or enzymes have recently been synthesised. Due to their long-term stability, chemical inertness, and insolubility in water and organic solvents, imprinted technology may also be utilised to create materials that resemble antibodies and have great selectivity and sensitivity. In example, in situ polymerization, utilising a photochemical or thermal initiator, or surface grafting with chemical or UV initiation may be used to realise the integration of imprinted polymers with sensors.Imprinted polymers were synthesised as monoliths for the first generation of imprinted polymer sensors. The developed imprinted polymer sensor was effectively used to assess atropine levels in human serum and urine. Imprinted polymers were often used as sensors for the separation of various substances' enantiomers. The creation of very sensitive imprinted polymer sensors for cells and viruses was an intriguing field of study. The potential uses of molecularly imprinted polymer technology in sensing have been thoroughly investigated.

7.3 Catalysis

A lot of work has gone into researching how imprinted polymer may be used in catalytic applications. These polymers may be employed at high temperatures and pressures, in the presence of several organic solvents, as well as under acidic and basic reaction conditions due to their excellent selectivity and strength. Because they are less susceptible to specific circumstances than biomolecules like enzymes and naturally occurring catalytic antibodies, MIPs may be used in their place. Utilising substances that imitate the complicated interaction between the substrate and the matrix is part of the technique employing substrate analogues as a template. When the actual substrate is present, the catalytic groups will be inserted into the polymer's cavities in the proper places so that they may work as a catalyst. Finally, in order to comprehend molecular imprinting and its specificity, thermodynamic and kinetic investigations were also conducted on MIPs catalytic systems. Therefore, in logic, the particular identification and catalysis may be caused by the growing rate and the greater induction.

7.4 Drug delivery

Therapeutic drugs have recently posed a significant challenge for molecular imprinting technology. To construct drug delivery systems, several imprinted polymers have been exploited as novel synthetic polymeric carriers. Recently, molecularly designed methacrylate-based architectures including poly(ethylene glycol) in moderately and strongly cross-linked networks were used to create molecularly imprinted hydrogels for the identification of cholesterol. Given their physical capabilities to shield the medication from enzyme breakdown during systemic trafficking in the body, MIPs have received a lot of attention from researchers in recent years. Norell and colleagues have given the first report on imprinted polymers utilised as sustained release devices.

7.5 Selective removal of metal ions

The selective concentration of metal ions is a significant use of the polymer imprinted with metal ions. IIP is being used more and more often to selectively concentrate metal ions from aqueous solutions. The exact way that ligands interact with metal ions, the coordination number and shape of the metal ion, the charge on the metal ion, and, to some degree, the size of the metal ion all affect selectivity. Conventional chelating ligands have, however, run into issues including poor binding selectivity, sluggish rebinding kinetics, and selectivity loss with time.

In contrast, the metal ion-imprinted polymers show quick and typically robust complexation with the metal ion, leading to great selectivity for the imprinted ion. The functional groups in the imprinted holes in the polymers match the layout of the imprinted molecule. The selectivity for the optical separation of racemates, various configurational isomers, diastereo isomers, and metal ions are all rather high. With the substrate bonded within the cavities, stereoselective reactions are also conceivable. The selectivity was always further increased with metal ion imprinted polymers over ordinary chelating polymers, and the imprinted binding sites should be able to stabilise the expanding polymer chain in a predetermined topology. It should be able to rebind the imprinted molecule once the imprinted molecule has been removed. The macromolecular properties and the polymer matrix's structure are always of utmost significance for specificity and selectivity.

Water from taps, rivers, lakes, and wells is often treated with or analysed using ion imprinted polymers. Their use may be broadened to include complicated matrices like seawater and industrial waste water.

IIPs may be used to extract metal ions from solid samples including food, soil and mine tailing samples, and human hair after sample treatment. IIP particles may also be used in chromatographic columns as separation materials. The uses of IIP are rapidly expanding to include sensors. So, to create an ion-selective electrode, IIP particles may be combined with some carbon paste or added to a polyvinyl chloride membrane. IIPs and quartz crystal microbalances have recently been used to construct sensor devices.

8. Conclusion

Heavy metal exposures and poisoning are regarded as dangerous situations that call for the greatest vigilance and safety measures to prevent these poisons from entering our systems. Ion imprinting technique provides an effective method for removing and recovering metals from aqueous solutions while being economically viable. The method offers a number of appealing characteristics, including as the selective removal of metal ions across a wide pH and temperature range, its quick sorption and desorption kinetics, and its inexpensive capital and operating costs. The ion imprinted polymers may be readily made using low-cost growth medium or acquired as a byproduct from a particular sector. The commercial ion exchange polymers that have traditionally been utilised to remove metal ions may be outperformed by the wise selection of ion imprinted polymers. Ion imprinting technology will likely evolve in the future as SPE sorbents or as sensing components in biomimetic sensors as a result of the rising need for sample treatments and quality control. A key difficulty in the ion imprinting approach is comprehending the mechanics of interaction between the template metal ion and the polymer matrix. It could be helpful for designing polymers with ion imprints that can remove dangerous metals from aquatic environments.

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