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# Ion-imprinted polymers: synthesis, characterization and applications

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Ion-imprinted polymers (IIPs) are created based on enzyme phenomenon, where these polymers exhibit selective recognition of metal ions in the presence of matrix ions. For that reason IIPs find many applications in sensors, solid phase extraction and membrane separation of metal ions. This review focuses on the synthesis, characterization and application of IIPs.

**Keywords:** Ion-imprinted polymers, Imprinting, Selectivity, Template

## 1. INTRODUCTION

IIPs can be defined as a group of highly selective materials, which recognize selected ions in the presence of different competing ions from the same matrices. IIPs are similar to molecularly imprinted polymers (MIPs), which are based on the interaction of enzymes and antibodies. The difference between MIPs and IIPs lies in the type of recognition substance, which can be molecules or ions. The first MIPs were proposed by Wulff and Klotz in 1972 [1, 2] and the number of papers concerning MIPs are still increasing. IIPs have been introduced by Nishide et al. [3] by cross-linked of poly(4-vinylpyridine) with 1,4-dibromobutane in the presence of metal ions: Co(II), Cu(II), Fe(III), Hg(II), Ni(II) and Zn(II), as templates. The number of publications dealing with IIPs, originated in 1976, but has increased drastically over the last decade.

Ion imprinted polymers possess distinguished recognition capabilities. IIPs are characterized by high affinity, selectivity for the target ion, easy and low preparation costs, reusability, easy storage and long lifetime [4]. IIPs generally are prepared with a reaction mixture composed of a functional monomer, a crosslinker, an initiator and a template [5-7]. During polymerization, a complex creation occurs between the monomer and the template. In the next step the complex is surrounded by the crosslinker, forming a three-dimensional polymer network where the template ions are trapped. Subsequently, the template ions are leached to leave sites complementary to the template in shape, size and interaction. The schematic representation of an IIPs synthesis is given in Fig.1. IIPs can be divided according to approaches for elaboration, type of polymerization and kind of interaction between the binding sites and templates [8].

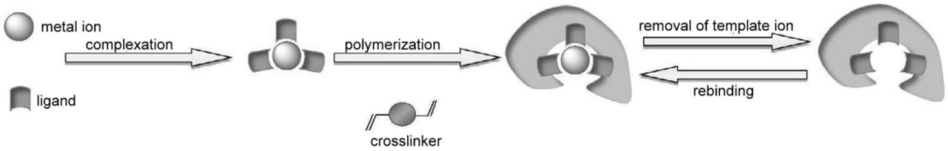


Fig.1. Scheme for the general synthesis of IIPs.

Many advantages of IIPs can be the grounds for their use in wide range of potential applications such as solid phase extraction [9], selective adsorption and separation [10, 11], environmental analysis [12], membranes and metal ion sensors [13].In this review different approaches for IIPs elaboration, polymerization techniques, characterization and applications will be described.

## 2. GENERAL STEPS IN THE IMPRINTING TECHNIQUE

The general procedure for IIPs synthesis consist in three steps [14]:

- complexation of the ion (template) to a polymerizable ligand,
- polymerization of this complex,
- removal of the template after polymerization.

In the first step the connection between template ions and functional monomers is achieved and it is the basis of the synthesis of this family of polymers. This step of the preparation IIPs determine the type of imprinting used, hence, the type of polymers to be produced. The template can interact with functional monomers in three ways, which will be described in the next chapter. In the next step of the preparation of IIPs an initiator and crosslinker are added and the template-functional monomer complex is polymerized. There are four main polymerization methods used in the imprinting technique: bulk polymerization, precipitation polymerization, suspension polymerization and surface (emulsion) polymerization, which will be studied later in this paper. In the final step of the preparation the IIPs template is removed from polymer network. After extraction of the templates, cavities or active binding sites are left behind which are morphologically similar to the target materials hence making these prepared polymers ion-specific and highly selective from this process.

## 3. IIPs ELABORATION

Crosslinking is the main step in the synthesis of IIPs, it can be accomplished in several ways. Rao et al. have classified of these different mechanisms into the following four groups [13]: (i) crosslinking of linear chain polymers carrying metal-binding groups; (ii) chemical immobilization by formation of binary complexes of vinylated ligands with metal ions and polymerization with monomers; (iii) surface imprinting conducted aqueous-organic interface; (iv) trapping of non-functionalized ligand inside the polymer network. These different approaches for IIPs elaboration process are summarized in Fig.2.

### *3.1.Crosslinking of bifunctional reagent with linear chain polymers*

The crosslinking of linear chain polymers carrying metal-binding groups was the first method used to prepare IIPs. Nishide et al. used ion imprinted technique in the formation of chelating polymers in1976 [3]. They copolymerized poly(4-vinylpirydyne) with 1,4-dibromobutane in presence of metal ions as templates. The resins better adsorb the metal ion, which had been used as the template. Kabanova et al. crosslinked a copolymer of diethyl vinyl phosphonate and acrylic acid with N,N'-methylene diacrylamide in the presence of metal ions [15]. Ohga et al. crosslinked chitosan with epichlorohydrin to form an imprinted resin [16].

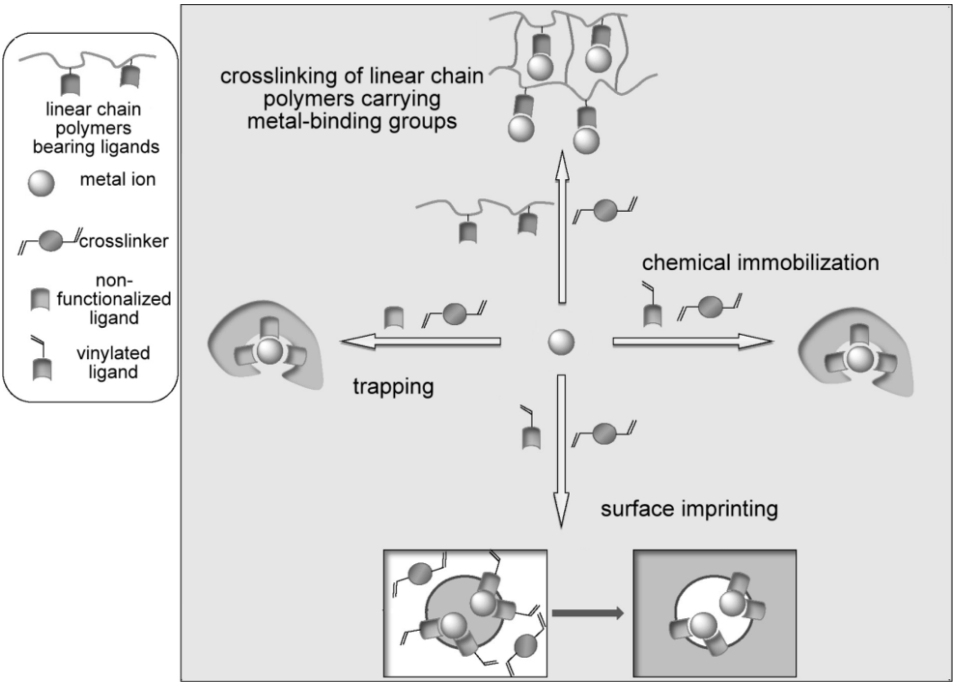


Fig.2. Different approaches for IIPs elaboration.

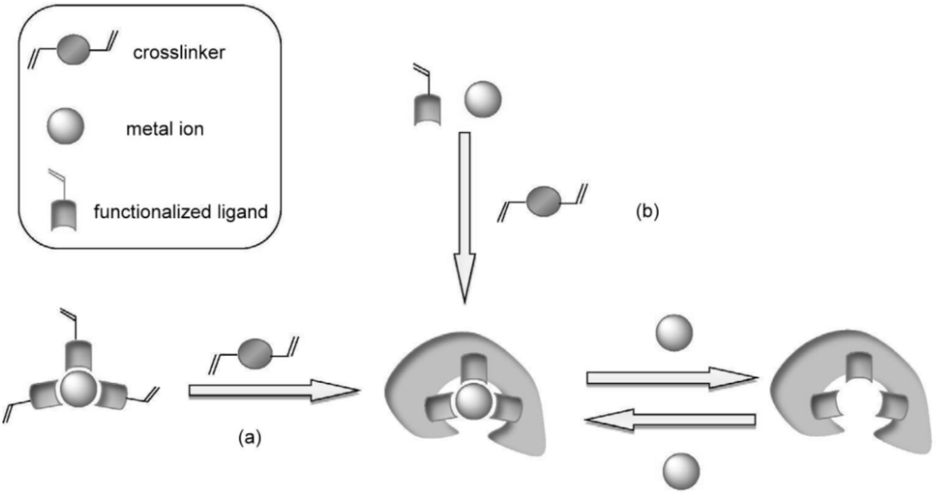
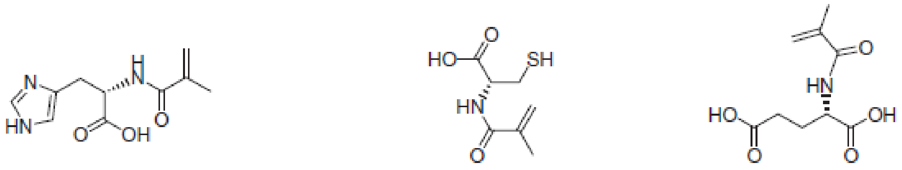


Fig. 3. Elaboration of IIPs by the two step (a) and one step (b) chemical immobilization approaches.

### *3.2. Chemical immobilization*

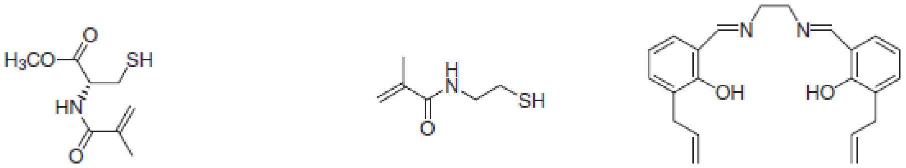
In this procedure the ligand is chemically immobilizied in the polymer matrix. This process can be carried out in two ways. According to the first technique in the first step, the binary complex of metal ions with ligands having vinyl groups is prepared and then polymerized with matrix-forming monomers (Fig. 3a).The advantage of this procedure is the control of the structure and amount of particular polymer components [17].The first example of this synthesis was proposed by Nishide and co-workers in 1981 [18]. They polymerized a metal complex of 1-viny-imidazole with 1-vinyl-2-pyrollidone and divinyl benzene. The binary complex was copolymerized and crosslinked with 1-vinyl-2-pyrollidone by γ-irradiation and the template metal ion was removed. Alizadeh et al. used this procedure with Pb(II) and MMA (methacrylic acid) [19]. Kim et al. applied this process with Cu(II) and MMA [20–22]. The most important functionalized ligands used for two-step chemical immobilization approach are shown in Fig. 4.



N-methacryloyl-(L)-histidine

N-methacryloyl-(L)-cysteine

N-methacryloyl-(L)-glutamic acid



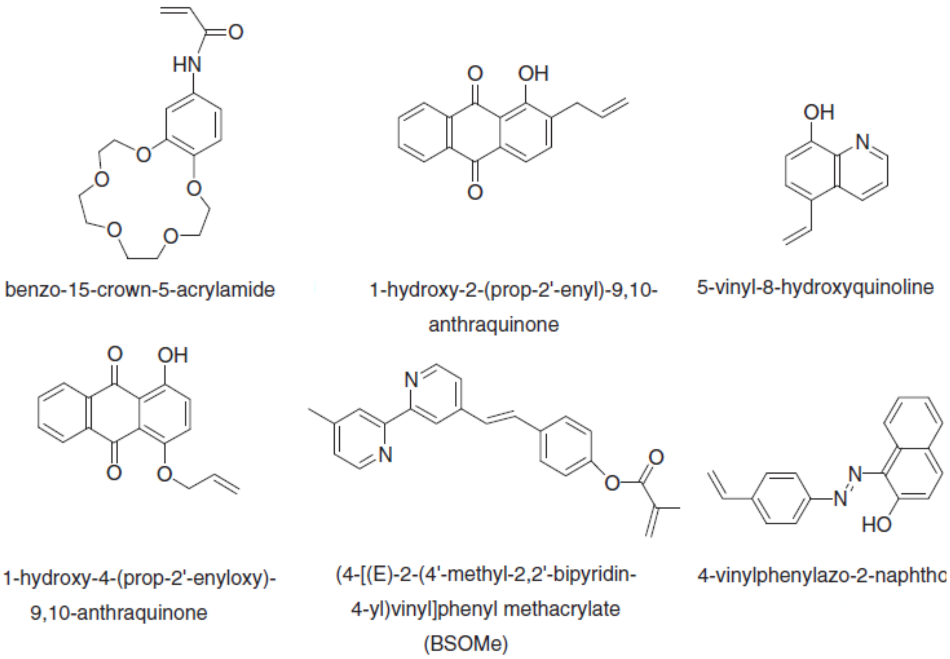
N-methacryloyl-(L)-cysteine methyl ester

N-methacryloyl-2-mercaptoethylamine

Salen

Fig. 4. The most important functionalized ligands used for two-step chemical immobilization approach.

Second technique is easier and consists of one step synthesis by mixing the metal ions, the chelating monomers and the crosslinker before copolymerization (Fig. 3b). This method is widely used because of its simplicity. Fasihi et al. used this procedure with the vinylated form of 1-hydroxy-9,10-anthraquinone with EDMA (ethylene glycol dimethacrylate) in presence of uranyl ions [23]. Shamsipur et al. used1-hydroxy-4-(prop-2'-enyloxy)-9,10-anthraquinone with copper ions [24]. Wu et al. copolymerized a benzo-15-rown-5 crown ether with an acrylamide in presence of potassium ions [25]. Sellengren et al. compared two described synthesis method for the formation of Co(II) imprinted polymers [26]. The most important functionalized ligands used for one-step chemical immobilization approach are show in Fig. 5.



benzo-15-crown-5-acrylamide

1-hydroxy-2-(prop-2'-enyl)-9,10-anthraquinone

5-vinyl-8-hydroxyquinoline

1-hydroxy-4-(prop-2'-enyloxy)-9,10-anthraquinone

(4-[(E)-2-(4'-methyl-2,2'-bipyridin-4-yl)vinyl]phenyl methacrylate (BSOMe)

4-vinylphenylazo-2-naphthc

Fig. 5. The most important functionalized ligands used for one-step chemical immobilization approach.

### 3.3.Surface imprinting

The surface imprinting procedure, first proposed by Takagi et al. in 1992 involves emulsion polymerization[27]. An amphiphilic monomer forms a complex with the template at the interface of an emulsion. After polymerization the template is removed and binding sites remain on the surface of the material. In this procedure, binding sites are created near or on the surface of the imprinted polymers, meaning the complete removal of templates is facilitated and low mass-transfer is achieved [28]. Maeda et al. applied surface imprinting in an oil-water emulsion giving ion imprinted polymers for Cu(II), Zn(II) and Cd(II) ions [29]. Uezu et al.

proposed surface imprinting in an water-in-oil emulsion using diolephosphoric acid to obtain zinc ion-imprinted resins [30]. The surface imprinting process has developed in recent years. It is now mainly used for modification of small sized core-shell type particles. Kim et al. synthesized organic core-shell materials, by copolymerizing EDMA and the $Cu(MAA)_2$ complex on the surface of a polystyrene core [31-32]. In most cases, modified core-shell particles are inorganic, for example silica gel particles which have chemical and mechanical stability and ease of functionalization and preparation [33].

### *3.4.Trapping*

In the trapping process a vinylated and a non-vinylated chelating agent are used. The vinylated ligand is polymerized, while the non-vinylated ligand is trapped in a polymer network. The non-vinylated ligand is not chemically bound to the polymer network therefore, it is necessary to determine that it is correctly distributed in the polymer network and not leached out during the removal of the ion template.

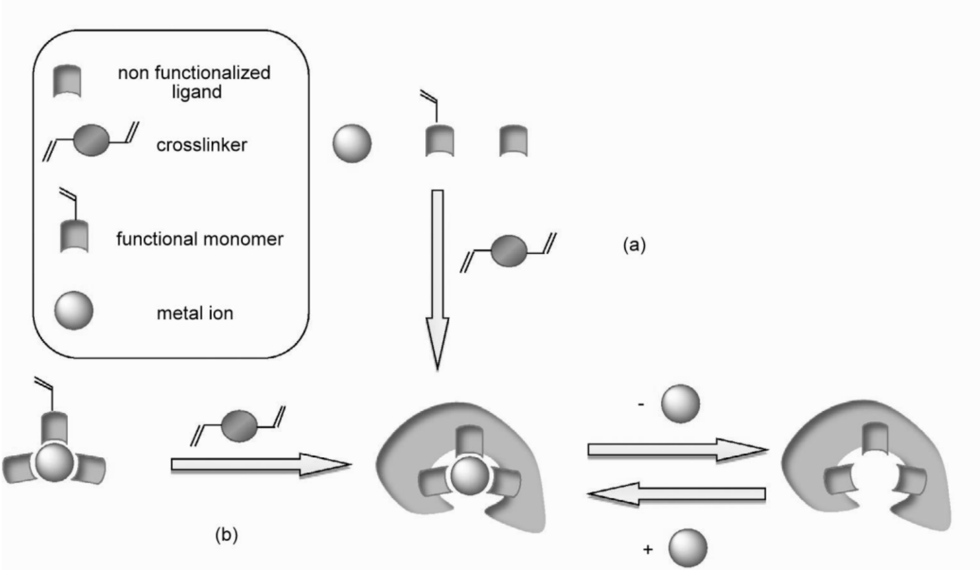


Fig. 6. Elaboration of IIPs trapping approach without (a) and with (b) prior formation of the complex between the template ion and ligand.

Microanalysis, FTIR (Fourier Transform Infrared Spectroscopy)and energy dispersive X-ray spectroscopy analysis can confirm these properties of the material [34-35]. This process can be carried out in two ways. As in the chemical immobilization process, the complex can be prepared *in situ* or isolated before introducing it into the polymerization medium (Fig. 6). Guo et al. proposed a second way for preparing IIPs for Nd(III). They copolymerized 5,7-dichloroquinolne-8-ol and 4-VP (4-vinylpyridine) [36]. Gawin et al. in first step prepared complex of cadmium(II)bis(2-formylphenolate) with ethylenediamine and in the next step the complex was mixed with 4-VP in DMSO (dimethylsulfoxide) [37]. The most important functionalized ligands used for one-step (a) and two-step(b) trapping approach are shown in Fig. 7.

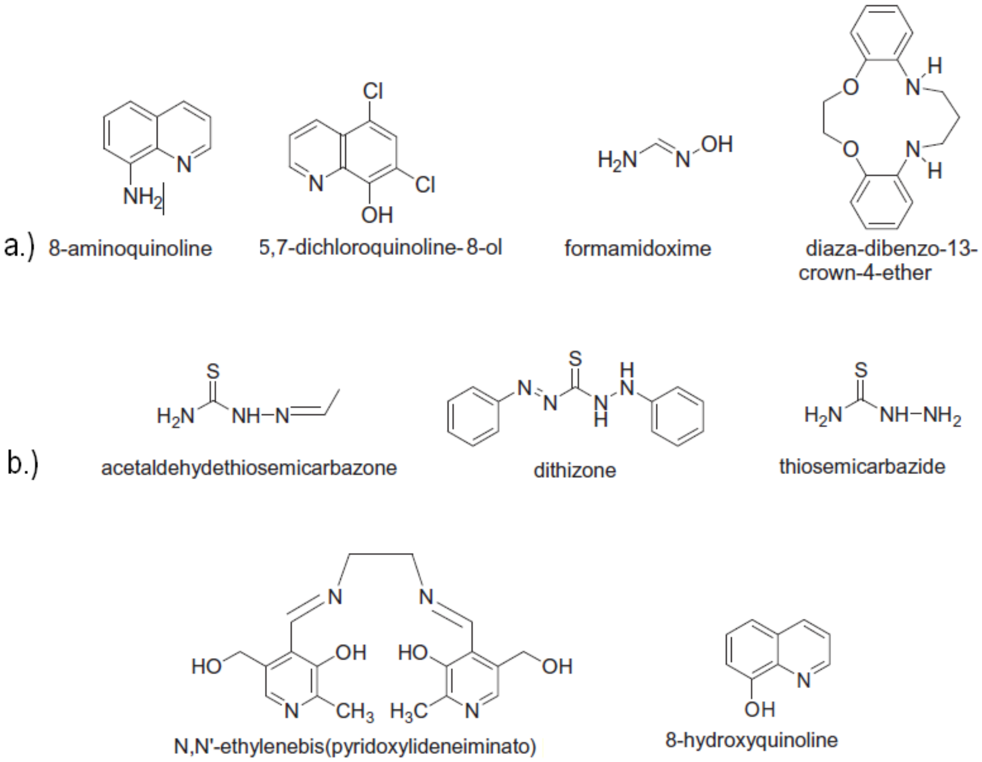


Fig. 7. Non-vinylated ligands used for the trapping approach without (a) and with (b) prior formation of the complex between the template ion and ligand.

## 4. IIPs COMPONENTS

Synthesis of IIPs includes the choice of proper components for the polymerization process: ligand, monomers, crosslinker, solvent and initiator. The quantity and nature of these components determine the properties of the ion-imprinted polymer.

### *4.1. Ligand*

Since the ion recognition process includes ion chelation, the role of the ligand is very important. The most popular ligands have one or more chelating groups, which can interact with the polymer matrix and the templates by heteroatoms. Figs. 4, 5 and 7 present the ligands used in the chemical immobilization and trapping procedures [38].

### *4.2. Monomers*

In the trapping procedure, a monovinylated monomer is necessary to create ternary complex with the metal ions. In the chemical approaches other monomers maybe introduced in the polymerization mixture. Denizili et al. combined the ligand-metal complex with HEMA (monovinylated monomer) and EDMA (crosslinker) [39-41]. Styrene [42], MAA [43], allyl alcohol [44], DEM(2-(diethylamino) ethyl methacrylate)[45] and 4-VP [17] are also used as monomers.

Crosslinkers play a major role in ion-imprited polymers synthesis. Crosslinkers determine orientation of functional monomers and template in polymerization network. The most commonly used crosslinker is EDMA. Some other crosslinkers have also been utilized such as DVB (divinylbenzene) [46], MBA (N,N’-methylene-bis(acrylamide)) [47], PETRA (pentaerythritoltriacrylate) [48] and TRIM (trimethylolpropane-trimethacrylate) [49]. The crosslinker should be used in the proper ratio with functional monomers.

### *4.3. Initiator*

The initiator of polymerization is responsible for initiating the reaction, and it can be achieved by thermal decomposition, photolysis or ionizing radiation. The first technique is the most common used in synthesis of ion imprinted polymers. The most popular applied initiators are BPO (benzoylperoxide) [20, 50] and AIBN (2,2’-azobisisobutyronitrile) [41, 51].

### *4.4. Solvents*

Good solvent should dissolve all the components used in the synthesis: monomers, crosslinker, initiator and ion template. Important properties of the solvent are dielectric constant, hydrogen bond characteristic, solubility and polarity, because they influence the durability of the polymer [14]. The commonly used solvents are toluene [42], chloroform [40], acetonitrile [44], DMSO [56], methanol [46] and many others.

## 5. POLYMERIZATION METHODS

There are four main methods used in the ion imprinted polymers preparation: bulk polymerization, precipitation polymerization, suspension polymerization and emulsion polymerization. These methods can be divided into two groups: 2D and 3D. In the first group binding sides are localized only on the surface of the polymer (emulsion polymerization). In 3D group active sites are located in whole polymer network (bulk and suspension polymerization) [52].

### *5.1. Bulk polymerization*

Bulk polymerization is most widely used in preparation of IIPs. It is an easy and simple method, complicated apparatus is not required. Preparation of IIPs involves mixing monomers, crosslinker, initiator and template in a reaction vessel. The resulting material has an irregular particle size therefore it must be ground and sieved to obtain the desired dimension. It is a time-consuming stage and it can destroy binding sites or contaminate the polymer [53].

### *5.2. Precipitation polymerization*

Precipitation polymerization is classified as homogenous polymerization, all components are dissolved in the solvent and the polymerization is started in a homogenous solution. This method is very similar to bulk polymerization, except that the amount of solvent used is much higher. Precipitation polymerization is the second most frequently used after bulk polymerization to prepare the IIPs. The shape and size of the synthesized particles are strictly defined by the ratio of monomers to the solvent. Usually this technique gives particles at the 0.3-10 μm range. Shamsipur et al. gave advantages of this method: the obtained IIPs are in the form of particles; all the synthesis materials are in usable form; removal of metal ions is easy and this technique gives particles in nano, submicron and micro size range [54].

### *5.3. Suspension polymerization*

Suspension polymerization is classified as a heterogeneous polymerization method with two immiscible phases. The first is a continuous phase, typically water, and the other is a dispersed phase that contains the monomers, the crosslinker, the initiator and the template ion. Droplets of the dispersed phase are suspended in the continuous phase, in the presence of a stabilizer (typically gelatine, hydroxyethyl cellulose or polyvinylalcohol), then polymerized. This technique produces micro-beads at the 0.5-10 µm range. Suspension polymerization is a fast method for preparing IIPs where control of the size and shape of the particles is possible [55].

### *5.4. Emulsion polymerization*

Emulsion polymerization is a heterogeneous polymerization method. Droplets of monomers with surfactants are emulsified in a continuous phase, which contains an initiator, then polymerized. In this method complete leaching of template ion is easy, adsorption and desorption kinetics are very fast and production of polymers of high molecular weight is possible. Advantages of this polymerization type may be applied to online SPE. The main drawback of this method is the low yield [56].

## 6. CHARACTERIZATION

Characterization of IIPs is a very important stage of their synthesis. This step involves checking if the ligand is properly distributed in the polymer network, the template has been completely removed and studying the properties such as shape, size and porosity of the particles. The first step can be achieved by elemental analysis comparing experimental and theoretical values. Commonly used is also FTIR spectroscopy, which detects and identifies the functional groups in the sample. The sample is exposed to infrared radiation and specific arrangements of atoms in functional groups absorb characteristic value of infrared energy. Comparison of FTIR spectra of the ion-imprinted polymer and the non ion-imprinted polymer (NIP) provides information about the incorporated ligand in polymer network [57].Singh and Mishra used FTIR to compare IIPs and NIP and show, that both polymers have a similar backbone [58].

Correct leaching of the template outside of the IIPs network is the most important step in the synthesis of these materials. Monitoring of this step can be achieved by many techniques: elemental analysis, FTIR spectroscopy, thermogravimetric analysis (TGA), X-ray diffraction (XRD) and dispersive X-ray (EDX) spectroscopy analysis. These methods allow comparison of the behaviour of IIPs with or without template ions and NIP and checking the presence or the absence of template ions in a polymer network. Daniel et al. used XRD analysis to check the presence of palladium ions in the IIPs before and after removal of the template [52]. Hoai et al. used FTIR to identify the chemical structure of the polymers synthesized before and after extraction of the copper ions [59].

Study of the properties of IIPs such as shape, size and porosity of the materials can be achieved by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and nitrogen adsorption/ desorption experiments. The first technique provides information about the surface of materials. SEM is able to show binding sites, cavities after imprinting, difference in the surface before and after the removal of template ions and give some information about the particle shape and porosity of the material [60].Nitrogen adsorption/desorption analysis gives more information about the porous structure. The pore volume, the surface area and an average pore diameter can be determined by using the BET (Brunauer, Emmett and Teller) method and the BJH (Barrett, Joyner and Halenda) model. Su et al. compared the surface area of IIPs and NIPs using BET analysis and demonstrated that the ion imprinting process significantly increases this value [61].Pan et al. used TEM to compare specific surface area, pore volume and mean diameter of IIPs and NIPs. In IIPs materials parameters like surface area and pore volume was higher than in NIP, this causes better adsorption efficiencies and selectivity [62].

## 7. APPLICATION

### *7.1. Solid phase extraction*

Solid phase extraction (SPE) is preferable to liquid-liquid extraction (LLE), due to many advantages like absence of emulsion, higher enrichment factors, low consumption of reagents and large choice of sorbents (Fig. 8.). IIPs are used in SPE due to their higher selectivity and better adsorption efficiencies than common solid sorbents such as silica gel, actived carbon or functionalized polymer [63-64].Ion-imprinted materials have affinity and selectivity similar to antibodies, IIPs are also easy to synthesise, stable in harsh environment and inexpensive to produce. The main application of ion-imprinted polymers is SPE preconcentration of trace amounts of ions and their separation from complex matrices and interferents.

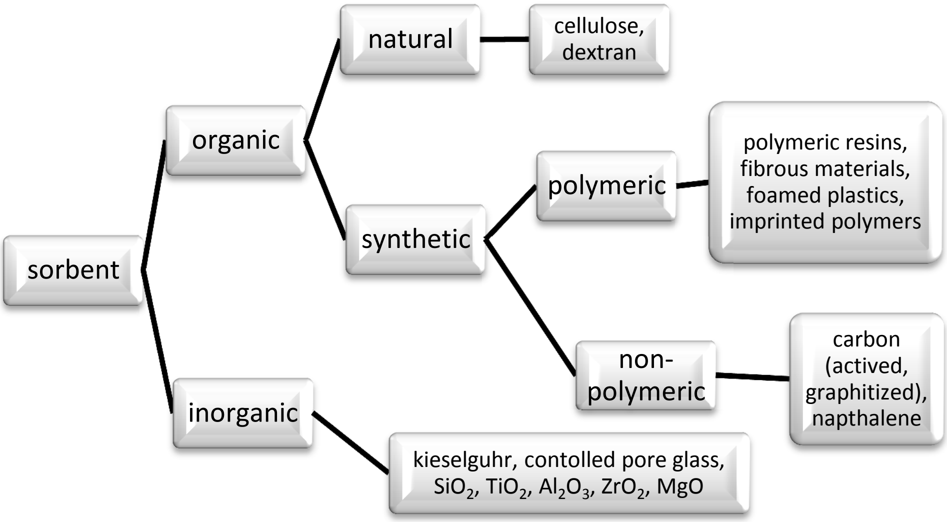


Fig.8. Sorbents used in SPE.

A lot of IIPs for toxic metals, such as nickel, cadmium, arsenic, cobalt, lead, mercury and selenium, have been studied. Wang et al. prepared Pb-IIPs particles using surface molecular imprinting technique and sol-gel process with Pb(II) ion as the template, silica gel as the carrier, chitosan as the functional monomer and KH-560 as the cross-linking agent [65]. Sing and Mishra synthesized Cd-IIPs for selective solid phase extraction from aqueous solutions. It was prepared by the copolymerization of phenol and formaldehyde in the presence of Cd(II)-SPANDS complex in acidic medium [7]. Liu et al. employed the surface-grafting ion-imprinting technology to prepare Co-imprinted polymer for selective removal of Co(II) from aqueous solutions [66]. Otero-Romani et al. applied the precipitation polymerization technique to synthesise Ni-IIPs using Ni(II) ion as the template, 4-VP as the monomer and 8-hydroxyqunoinone as a non-vinylated chelating agent [45]. In all cases ion-imprinted polymers exhibited higher selectivity and better adsorption capacity than non ion-imprinted materials.

In the last decade, ion-imprinted polymers have found increased applications as efficient sorbents for noble metals. These include ruthenium, platinum, palladium and gold. Yang and Dukjoon applied the bulk polymerization technique to synthesize Pt(IV)-IIPs particles, using Pt-DMG complexes, 4-VP as functional monomer, AIBN as an initiator and DVB as crosslinker [11]. Daniel et al. employed the precipitation and suspension polymerization methods using a ternary complex of palladium(II) ions with 8-aminoquinoline, 4-VP as monomer, HEMA as a functional monomer, ethylene glycoldimethacrylate (EGDMA) as a crosslinker, AIBN as a initiator and 2-methoxy ethanol as a porogen [67].

### *7.2. Sensors*

Sensors have many potential applications in food analysis, environmental analysis, clinical diagnostic, pollution monitoring, detection of drugs and chemical warfare agents. The main part of a sensor is a recognition element, which is responsible for recognition and binding of the target analyte in complex samples. Ion-imprinted polymers make it possible to create selective chemical sensors with good thermal, mechanical and chemical properties at low cost. Two main methods, based on spectroscopic or electrochemical properties, are used for signal transduction in ion-imprinted sensors. The fusion of imprinting and transduction selectivities can give sensors that extremely well recognize the target ions without the interferences [68]. The first imprinted polymer fluorooptrode was described by Murray et al. The template used was Pb(II)-methyl-3,5-divinyl benzoate (DVMB) complex. This complex was binding in in-situ copolymerization on a vinylized optical fibre surface [69]. James et al. described an optrode for the detection and quantification of uranium. The ion imprinted polymer material was prepared by thermal polymerization via covalent immobilization of the newly synthesised ligand 4-vinyl phenylazo-2-naphthol [17]. Mosbach et al. has described for the first time an imprinted polymer potentioselectrode for calcium and magnesium using a neutral ionophore N,N'-dimethyl-N,N'-bis(4-vinylphenyl)-3-oxapentadiamine as the monomer [70]. Sensors for lead(II), uranyl, copper(II) and dysprosium(III) ions have also been described [69, 71–73].

### *7.3. IIPs membrane separation*

The ion-imprinted membrane showed higher adsorption affinity and permeation selectivity towards the template ions than the non imprinted membrane. Araki et al. prepared Zn(II) ion-selective membrane using surface molecular imprinting technique by water-in-oil emulsion polymerization. The polymerization was conducted in the presence of acetonitrile-butadiene rubber so that obtained membrane was flexible and mechanically stable [74]. Kimaro et al. described the synthesis of an uranyl ion permselective membrane using polymerization of uranyl vinyl benzoate and styrene/DBV after addition of 2-nitrooctylphenyl ether and polyester. Ion-imprinted membranes showed higher selectivity for uranyl ion over other bivalent transition metal ions [75].

## 8. CONCLUSION

The number of published papers on IIPs has been drastically increasing over the last few years. Due to their very interesting properties such as easy and low costs preparation, easy storage, reusability and long lifetime, IIPs have application as highly selective sorbents for SPE. Ion-imprinted polymers could also be applied in sensors and membrane separations.

IIPs may be prepared in different ways, but the most popular is bulk polymerizationdue to its simplicity. Very common methods are also precipitation and suspension polymerization. In these methods the shape and size of the synthesized particles are strictly defined. A promising method of polymerization is surface imprinting, especially in the generation of ion-imprinted hybrid materials.

Increased knowledge about processes of interaction between the polymer matrix and the template ion is a fundamental challenge. It could be employed in industrial scale for waste water treatment, drinking water treatment, drug delivery, portable biomimetic sensors and recycling of expensive and rare metals.

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