



# Advanced polymeric materials: Synthesis and analytical application of ion imprinted polymers as selective sorbents for solid phase extraction of metal ions



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## ABSTRACT

Over the past several decades, much progress has been made in the development of ion-imprinted polymers (IIPs) with the aid of novel types of tailored polymeric materials (e.g., nanomaterials and hybrid materials). Because of such efforts, IIPs are now widely employed as advanced analytical tools in a variety of sectors (e.g., as sorbents for solid phase extraction of metal ions). Recently, due to the advancement of polymeric materials (PMs), an increased number of studies have been made to expand the practical applicability of IIPs. In this review, the basic theories involved in the polymerization methods of IIPs are described along with their synthesis and diverse fields of applications (e.g., solid phase extraction (SPE), sensors, and membrane separators).

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**Abbreviations:** 1-VI, 1-Vinylimidazole; 2-MAH, 2-Methacryloylamidohistidine; 5-VHQ, 5-Vinyl-8-hydroxyquinoline; 8-AQ, 8-Acryloyloxyquinoline; 8-HQ, 8-Hydroxyquinoline (oxine); 5-Br-PADAP, 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol; AA, Acrylamide; AAA, Allyl acetoacetate; AAPT3, 3-(2-Aminoethylamino) propyltrimethoxysilane; AAS, Atomic absorption spectrometer; AC, Acetonitrile; ACAC, Acetylacetone; AcTSn, Acetaldehyde thiosemicarbazone; AcTSn, Acetaldehyde thiosemicarbazone; AIBN, Azobisisobutyronitrile; AMP, 2,20-Azobis(2-methylpropionamide) dihydrochloride; APDC, Ammonium pyrrolidine dithiocarbamate; APS, Ammonium persulfate; 2-ABN, 2-Aminobenzonitrile; APTS, 3-Aminopropyltrimethoxysilane; AQ, 8-Amino quinolone; BAEBE, (2Z)-N,N9-bis(2-aminoethyl)but-2-enediamide; BnTSn, Aenzaldehyde thiosemicarbazone; BP, Benzoyl peroxide; BPHA, N-benzoyl-N-phenyl hydroxyl amine; caaH, 2-Chloroacrylic acid; CRM, Certified reference material; CS, Chitosan-succinate; CVAAS, Cold vapor atomic absorption spectrometry; DAAB, Diazoaminobenzene; DBDA15C4, 5,6,14,15-Dibenzo-1,4-dioxo-8,12-diazacyclopentadecane-5,14-diene; DC18C6, dicyclohexyl 18C6; DCM, Dichloromethane; DCQ, 5,7-Dichloroquinoline-8-ol; DBQ, 5,7-Dibromoquinoline-8-ol; DIQ, 5,7-Diiodoquinoline-8-ol; DDDPA, 1,12-Dodecanediol-O,O'-diphenyl-phosphonic acid; DEM, 2-(Diethylamino) ethyl methacrylate; DEM, 2-(Diethylamino) ethyl methacrylate; DET, Diethylthiourea; DMF, Dimethylformamide; DMG, Dimethylglyoxime; DMSO, Dimethylsulfoxide; DOLPA, Dioleoyl phosphate; DTPA, Diethylenetriamine pentaacetic acid; DVB, Divinylbenzene; EDMA, Ethylene dimethacrylate; EDTA, Ethylenediaminetetraacetic acid; EGDMA, Ethylene glycol dimethacrylate; ETAAS, Electrothermal atomic absorption spectrometry; EtOH, Ethanol; FI, Flow injection; Fm, Formaldehyde; GTA, Graphite tube atomizer; HAc, Acetic acid; HAQ, 1-Hydroxy-2-(prop-2-enyl)-9,10-anthraquinone; HEMA, Hydroxyethyl methacrylate; HEMA, Hydroxyethyl methacrylate; HPEA, 1-Hydroxy-4-(prop-2-enyloxy)-9,10-anthraquinone; HQ, 8-Hydroxy quinoline (oxine); LIX 622, Commercial liquid ion exchanger containing 5-dodecylsalicylaldehyde; MAA, Methacrylic acid; MAC, N-methacryloyl-(L)-cysteine (methyl ester); MAGA, N-Methacryloyl-L-glutamic acid; MAH, Methacryloylhistidinedihydrate; MBAA, N,N'-methylenebisacrylamide; MBAAm, Methylenebis(acrylamide); MCOS, Mercaptosilane; MeOH, Methanol; MMA, Methyl methacrylate; Morin, 3,5,7,20,40-pentahydroxyflavone; MQ, 8-Mercapto quinolone; MTMAAm, 5-Methyl-2-thiozymethacrylamide; NIPA, N-Isopropylacrylamide; N-MAH, N-Methacryloyl-L-histidine; NNAE, (2Z)-N,N-bis(2-aminoethyl)but-2-enediamide; EBAm, N,N-ethylene bisacrylamide; NVP, N-vinyl-2-pyrrolidone; PAN, 1-(2-Pyridylazo)-2-naphthol; pyr2en, N,N'-ethylenebis(pyridoxylideneiminato); PAR, 4-(2-Pyridylazo) resorcinol; PETRA, Pentaerythritol triacrylate; ph, Phenol; Phe, Phenanthroline; 2,9-D-1,10-Phe, 2,9-Dimethyl-1,10-phenanthroline; Pir, Piroxicam; PP, Potassium persulfate; Q, Quinoline-8-ol; quinizarin; QZ, 1,4-Dihydroxy-9,10-anthraquinone; salen-OME, 2,2'-[Ethane-1,2-diylbis(nitrilo(E)methylidene)] bis(6-allyl-methoxyphenol); SALO, Salicylaldehyde; SPANDS, 2-(P-Sulphophenylazo)-1,8-dihydroxy-3,6-naphthalene disulphonic acid trisodium salt; STY, Styrene; T, Theoretical; TAN, 1-(2-Thiazolylazo)-2-naphthol; TAR, 4-(2-Thiazolylazo) resorcinol; TCPTS, 3-Thiocyanatopropyltriethoxysilane; TEMED, Tetramethylene diamine; TEOS, Tetraethoxysilane; TMA, 2-Thiozymethacrylamide; TMPTA, Trimethylpropane trimethacrylate; TMPTM, Trimethylolpropane trimethacrylate; TRIM, Trimethylolpropane trimethacrylate; TSd, Thiosemicarbazide; Vb, Vinylbenzoic; VbIDA, Vinyl benzyl iminodiacetate; VGAAAS, Vapor generation accessory-atomic absorption spectrometer; VP, Vinyl pyridine.

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## 1. Introduction

Various polymeric materials have been developed and implemented in everyday life. In order to expedite the practical applications of such materials and to ensure that they perform adequately, consideration of a material's molecular structure and synthesis is crucial. One such example is the successful application of ion imprinted polymers (IIPs) in different areas of science. The versatile applications of imprinted polymers, including selective extraction, separation, and sensing of metal ions in different media (such as water, wastewater, soil, and food samples), have opened a new frontier of research, enabling the investigation of many new scientific challenges. As shown in Fig. 1, both advantages and disadvantages in the IIP applications have been recognized. Imprinted polymers have many advantages such as specific sites for targets, good stability in different media, easy synthesis, and specificity of natural system; however, they also have some disadvantages such as poor processibility (after synthesis), diversity of sites, and complicated nature of sorption/desorption.

Industrial processes use large quantities of ionic species, especially metal ions in manufacturing processes. In light of the large quantity of industrial wastes containing metal ions, there is still inadequate control and regulation on their discharge which can adversely affect ecological systems [1]. The presence and accumulation of highly toxic metal ions in ecosystems poses a threat to

humans and other living organisms and can cause various chronic/acute diseases such as cancer and skin, cardiovascular, and blood disorders. Therefore, proper control of anthropogenic metal ion emissions is essential. In the past, various techniques have been proposed by researchers and implemented in this field. In this respect, ion imprinted polymers (IIPs) based on molecular imprinted polymers (MIPs) have been recognized as a feasible option for the amelioration of ion-related environmental concerns with a focus on ions [2].

The first IIPs were made through bulk polymerization process using a mixture of monomer, initiator, crosslinker, and template. The resulting polymeric mass was ground and sieved to obtain particles with suitable size for diverse analytical applications [1,2]. Basically, polymerization can be defined as the tailored reaction between bifunctional or polyfunctional compounds (e.g., olefins, diolefins, and other related compounds). Polymerization can be achieved without the formation of ring or cyclic structures. The functional groups utilized in polymerization strategies are comparatively diverse: reactive hydrogen ( $-H$ ), hydroxyl group ( $-OH$ ), halogen atom ( $-Cl$ ,  $-Br$ ), carboxyl group ( $-COOH$ ), amino group ( $-NH_2$ ), isocyanate group ( $-NCO$ ), aldehyde group ( $-CHO$ ), and double bond ( $C=C$ ) [2].

Ion imprinting is a procedure that can enhance selectivity by synthesizing polymers with tailored binding sites based on specific ligand structures around an ion template. This may be initiated by the proper choice of monomers, crosslinkers, and ligands to promote

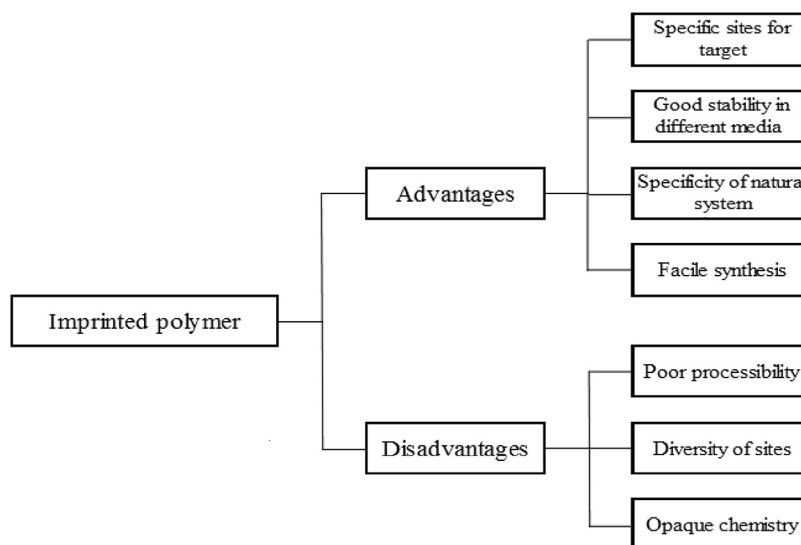


Fig. 1. Advantages and disadvantages of imprinted polymers.

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