Book Chapter

New Trends for Removal of Water Pollutants

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Abstract

In recent years, a wide range of treatment technologies have become more stringent, requiring an improved quality of treated water pollutants (wastewater). Many techniques can be employed for the treatment of wastewater laden with organic and inorganic contaminants. However, it is important to select the most suitable technique to optimize the removal of target contaminants compared to other technologies, in regard to environmental impact and economics issues such as the capital investment, operational costs, technical applicability, plant simplicity and selectivity. These are the key factors that play

major roles in the selection of the most suitable treatment system to optimize target pollutant removal. New procedure of alternative treatment techniques today is to design robust molecular recognition materials such as imprinted polymer (IP) technology, which are able to mimic natural recognition entities for the target compounds of interest. IP technology is today a viable synthetic approach to promote the future of bulk polymerization techniques through development of molecularly imprinted polymers (MIPs) or ion-IPs (IIPs) that are still a real challenge for a wide range of applications including selective pollutant recovery (*i.e.*, inorganic or organic compounds) from wastewater effluents and treatment as well. Therefore, this review aims to highlight the development of IPs (MIPs and IIPs) and the latest progress in the synthetic approaches of IPs-based composites as a new trend in wastewater treatment that could offer future success in the field of wastewater treatment and enhancement of molecular recovery. Primary attention is given to the developments of MIPs-based sorbent materials for quantitative determination and purification of contaminants in environmental wastewater resources.

Keywords

Molecularly Imprinted Polymers; Selective Removal;
Wastewater Treatment-Adsorption

List of Abbreviations

ACH- Aluminum Chlorohydrate; AIBN- Azoinitiator azobisisobutyronitrile; AMPS- 2-acrylamido-2-methyl-1-Propanesulfonic Acid; CA- Cellulose Acetate; 2,4-D- 2,4-dichlorophenol; DBT- Dibenzothiophene; DMIP- Dual Molecularly Imprinted Polymer; EDMA- Ethyleneglycoldimethacrylate; EGDMA- Ethylene Glycol Dimethacrylate; IPs- Imprinting Polymers; IIPs- Ion imprinting polymers; MF- Micro-filtration; MHAP- Magnetic Hydroxyapatite; MIPs- Molecular Imprinting Polymers; NIP- Non-imprinted Polymer; PACl- Polyaluminium Chloride; PEG- poly(ethylene glycol) (PEG; PFOS-Perfluorooctanesulfonate; PLA- Poly(lactic acid); PS- Polystyrene; RhB- Rhodamine B;

RO- Reverse Osmosis; RSM- Response Surface Methodology;
SLL- Stabilized Landfill Leachate; SPS- Sulfonated polysulfone;
TOC- Total Organic Carbon; UF- Ultra-Filtration; VP-4-
vinylpyridine

Introduction

Various pollutant exposures and poisoning in aqueous environment are considered as hazardous. Hence, precautions are required to prevent these toxins from entering our bodies. The traditional methods of wastewater treatment become increasingly challenged with the identification of more contaminants as shown in Figure (1), rapid population growth, increasing industrial activities, and ever shrinking fresh water sources. In **1903**, water softening was invented as a technique for water desalination. Cations were removed from water by exchanging them with sodium or other cations, in ion exchangers.

Eventually, starting in **1914**, standards were implemented for drinking water supplies in public traffic. However, it would take until the **1940** before such drinking water standards were applied to municipal drinking water. Starting in **1970**, public health concerns shifted from wastewater containing disease-causing microorganisms, to anthropogenic water pollution such as pesticide residues and industrial sludge and organic chemicals. In **1972**, the Clean Water Act was passed in the United States. In **1974**, the Safe Drinking Water Act (SDWA) was formulated. The general principle in the developed world now was that every person had the right to safe drinking water. Regulation now focused on industrial waste and industrial water contamination, and water treatment plants were adapted. Techniques such as aeration, flocculation, and active carbon adsorption were applied. In the **1980s**, membrane development for reverse osmosis was added to the list. Risk assessments were enabled after **1990**. Water treatment experimentation today mainly focuses on disinfection by-products [1].

Figure 1: Different water contaminants [1].

Conventional processes were adopted to remove many chemical and microbial contaminants from wastewater. However, the effectiveness of these processes has become limited over the last two decades because of new challenges related the removal of unknown hazardous pollutants and the increased knowledge about the consequences from water pollution and public demand for better quality water. Currently, the challenge in construction of wastewater treatment plants is to develop and implement new trends for effective wastewater reclamation technology with continuous ability to recover precious compounds (target organic or inorganic elements) efficiently from wastewater effluent for economic recycling. Various methods are available to remove pollutants from water as shown in Figure (2), including adsorption [2], microbial degradation [3], chemical oxidation [4,5], membrane separation [6], catalytic oxidation [7], and electrochemical treatment [8,9].

Conventional Treatment Techniques for Contaminated Wastewater

Conventional methods for removing metals are either becoming inadequate to meet current stringent regulatory effluent limits or are increasing in cost. As a result, alternative, cost effective technologies are in high demand. Conventional techniques for removing dissolved heavy metals include chemical precipitation, carbon adsorption, ion exchange, evaporations and membrane processes as shown in Figure (2) [10]. The selection of a particular treatment technique primarily depends on a variety of factors, e.g. waste type and concentration, effluent heterogeneity, required level of cleanup, as well as economic factors.

Figure 2: Conventional technologies for pollutant removal [10].

Chemical Treatment Methods

Chemical precipitation is most widely used for heavy metal removal from inorganic effluents. Lime and limestone are the most commonly employed precipitant agents due to their availability and low-cost in most countries [11].

Coagulation is the process in which colloidal particles in water are clumped together into larger particles, called flocs. Coagulants have been known since the early twentieth century and have been playing a vital role in the removal of many impurities from polluted waters. The aim of applying coagulation–flocculation treatment is generally to remove the colloidal matter present in the wastewater. Nutrients can also be removed during the process. There are various types of coagulants in the chemical market such as inorganic metal based-coagulants such as aluminum sulfate (alum), ferric chloride, and ferric sulfate. Alum has been used for water purification since ancient times [12]. Ahmed et al. [13] investigated application of the coagulation/flocculation process coupled with the Fenton reaction to remove organic matter from stabilized landfill leachate (SLL), using ferric chloride as the coagulant. The removal reached 71% at pH 6, then the pretreated SLL was subjected to the Fenton reaction that recorded 50% of total organic carbon (TOC) removal at pH 3, using a $\text{H}_2\text{O}_2:\text{Fe}^{+2}$ ratio of 20:1, H_2O_2 dosage of 240 mM and 1h of reaction time. By coupling the coagulation-flocculation with the Fenton reaction, the removal of TOC was 85%.

Physical Treatment Methods

Physical treatment processes include gravity separation, phase change system such as air stream stripping of volatile from liquid waste, adsorption, reverse osmosis, ion exchange, and electrodialysis. Some of the new technologies being used and introduced for wastewater treatment globally to reclaim the resources are discussed below.

Membrane Filtration

Membrane filtration has received considerable attention for the treatment of inorganic effluent, since it is capable of removing suspended solid and organic compounds. Depending on the size of the particle that can be retained, various types of membrane filtration such as ultrafiltration, nano-filtration and reverse osmosis can be employed for contaminant removal from wastewater.

Micro- and ultra-filtration (MF or UF) membranes provide excellent pretreatment to remove a wide range of dissolved contaminants. MFs and UFs are advanced treatment tools that utilize to separate heavy metals, micro-molecules and suspended solids from inorganic solution on the basis of the pore size (5–20 nm) and molecular weight of the separating compounds. Some significant findings were reported by Juang and Shiau [14], who studied the removal of Cu^{2+} and Zn^{2+} ions from synthetic wastewater using chitosan-enhanced membrane filtration. The Amicon[®]-generated cellulose YM10 was used as the ultra-filter. About 100% and 95% removal were achieved at pH ranging from 8.5 to 9.5 for Cu^{2+} and Zn^{2+} ions, respectively. The results indicated that chitosan significantly enhanced metals removal by 6–10 times compared to a simple membrane. This could be attributed to the major role played by the amino groups of the chitosan chain, which served as coordination site for metal-binding. In acidic conditions, the amino groups of chitosan are protonated after reacting with H^+ ions [15]. Recently, advanced membrane bioreactor filtration technology has been used for advanced wastewater treatment for reuse by industries. The complementary treatment processes which included a membrane bioreactor followed by reverse osmosis (RO) membrane and ultraviolet treatment is now poised to be implemented by many industrial processes to produce cleaned and disinfected non-potable water effluent that can be more easily reused in closed cycle for a save water environment at low operational costs.

Nanotechnology

The emergence of nanotechnology and the incorporation of living microorganisms in bio-microelectronic devices have revolutionized the treatment process. The advantage of nanotechnology is that it can easily merge with other technologies and modify, endorse and clarify any existing concept. Nanotechnology uses materials of sizes smaller than 100nm in at least one dimension, i.e. at the level of atoms and molecules [16]. At this scale, materials possessing novel and significantly changed physical, chemical, and biological properties mainly due to their structure, higher surface area-to-volume ratio, high reactivity and strong sorption capability, are explored for application in water/wastewater treatment based on their functions in unit operations [16]. Nanotechnology concepts are being investigated for higher performing membranes for decomposition of toxic compounds during the treatment. It will also provide effective segregation of metals, bimetallic nano particles, mixed oxides, zeolites and carbon compounds from the wastewater resources. With improved membranes and configurations, more efficient pumping and energy recovery systems will be possible.

Inorganic Nanoparticles: Green Approach for Construction and Applications:

The biological synthesis of nanoparticles (NPs) is a challenging concept known as “green synthesis”. Biosynthesis of nanoparticles could be an alternative to traditional chemical methods to produce metallic nano-materials in a clean, nontoxic and ecologically sound manner. Green synthesis of nanoparticle is cost effective, easily available, eco-friendly, non-toxic, large scale production can be done easily and acts as reducing and capping agent when compared to chemical methods which are very costly and may emit dangerous by-products which can have some deleterious effects on the environment. Synthesis of nanoparticles using plants provides more biocompatible nanoparticles than chemical synthesis, whereas chemical synthesis may lead to the presence of some toxic chemical by-products on the surface of nanoparticles that may have unwanted effects in biomedical

applications. Plant-mediated biological synthesis of nanoparticles has acquired prominence only in recent years. Phum ying et al. [17] reported the synthesis Fe_3O_4 nanoparticles using Aloe Vera plant extract the high purity of which was confirmed with XRD. The intermediate particle size calculated from XRD increased with an increase in temperature and time. Based on the coercivity, it was deduced that the nanoparticles were superparamagnetic in nature. Chen et al. [18] reported the synthesis of face-centered cubic NiNPs by reducing an aqueous solution of $\text{Ni}(\text{NO}_3)_2$ with an aqueous extract of *Medicago sativa* (alfalfa). The typical synthetic method of Ni NPs involved the vigorous stirring of precursor solution with alfalfa solution at 60°C for 4 hours. The reaction was carried out at 60°C because at room temperature it is difficult to reduce Ni^{2+} to Ni^0 . Subsequently, the NP solution was freeze-dried for 24 h to obtain Ni NPs powder. Pandian and coworkers [19] formed Ni nanoparticles by using an aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as precursor and leaf extract of *Ocimum sanctum* as reducing as well as stabilizing agent. These reduced Ni^0 atoms then aggregate and Ni NPs were formed as confirmed by UV/Vis spectroscopy and XRD. Saad et al., [20] prepared zinc oxide nanoparticles using *Corriandrum sativum* leaf extract and zinc acetate dehydrate, Figure (3). It was utilized as a photocatalyst for the degradation of anthracene. Optimum photocatalytic degradation of $100 \mu\text{g L}^{-1}$ anthracene is $1000 \mu\text{g L}^{-1}$ ZnO NP's, at ambient temperature (25°C), pH 7 and ultraviolet irradiation for 240 min. Under these conditions the percentage decomposition of anthracene is 96%.

Figure 3: Green synthesis of ZnO nanoparticles using *Corriandrum sativum* leaf extract [20].

Hybrid Organic/Inorganic Nanoparticles (Metal-Organic Frameworks):

Metal-organic frameworks (MOFs) are virtually infinite crystalline structures composed of metal clusters bound via coordination to organic ligands. These structures are highly porous and flexible owing to their structural and chemical tunability. Adsorption on porous materials has become one of the most promising approaches for water purification during the past decades [21]. With their exposed high surface area (inner as well as outer surface), porous materials such as zeolites, activated carbon, silica, polymeric materials and hybrid materials have drawn much interest among scientists, because they were found to be good candidates to overcome several obstacles such a slow capacity, weak interaction and difficulty in regeneration that affect contaminant removal in water purification. Therefore, superior adsorbents with large numbers of active sites and higher surface areas are desirable to obtain better access to qualified water in a reliable, efficient, convenient and low cost way. Known as a class of crystalline porous materials possessing ordered structures, high surface area, adjustable functional groups and numerous active metal sites, metal-organic frameworks (MOFs) could be promising candidates in pollutant removal. During the past decades, their applications for water purifications have been widely investigated. In this review, we will systematically present the performances of MOFs for contaminants (*i.e.* heavy metal ions, non-metal inorganics, organic dyes and pharmaceuticals).

Water Treatment by Natural Adsorbents

Natural water treatment is a complementary process that works simultaneously with other conventional treatment techniques to remove a range of contaminants and is effective for water reclamation. To date, natural treatment systems are increasingly being used to capture, retain and treat wastewater. Hence, they are waste management processes aimed to converting natural waste products into a valuable product by enhancing the cleaning of water environments and reducing the toxicity generated by

chemical technologies and a variety of physical processes as shown in Figure (4).

Figure 4: Some conventional methods for metal removal [34].

Adsorption on Modified Zeolite Materials:

Natural zeolites gained significant interest, mainly due to their valuable properties such as ion exchange capability. Among the most frequently studied natural zeolites, clinoptilolite was shown to have high selectivity for certain heavy metal ions such as Pb^{2+} , Cd^{2+} , Zn^{2+} and Cu^{2+} . It was demonstrated that the cation-exchange capability of clinoptilolite depends on the pre-treatment method and that conditioning improves its ion exchange ability and removal efficiency [22]. The ability of different types of synthetic zeolite to remove heavy metals was recently investigated. The role of pH is very important for the selective adsorption of different heavy metal ions [22]. Barakat [23] used 4A zeolite, synthesized by dehydroxylation of low-grade kaolin, and reported that Cu^{2+} and Zn^{2+} were adsorbed at neutral and alkaline pH, Cr^{6+} was adsorbed at acidic pH while

the adsorption of Mn^{4+} was achieved at high alkaline pH values. Nah et al. [24] prepared synthetic zeolite magnetically modified with iron oxide (MMZ). MMZ showed high adsorption capacities for Pb^{2+} ions and good chemical resistance in a wide pH range of 5–11. The natural clay minerals can be modified with a polymeric material in a manner that significantly improves their capability to remove heavy metals from aqueous solutions. These kinds of adsorbent are called clay–polymer composites [25]. Different phosphates such as calcined phosphate at 900 °C, activated phosphate (with nitric acid), and zirconium phosphate have been employed as new adsorbents for removal of heavy metals from aqueous solution [26].

Adsorption on Industrial By-Products:

Industrial by-products such as fly ash, waste iron, iron slags, or hydrous titanium oxide can be chemically modified to enhance their removal performance for organic and inorganic contaminants from wastewater. Lee et al. [27] studied green sands, another by-product from the iron foundry industry, for Zn^{2+} removal. Feng et al. [28] investigated Cu^{2+} and Pb^{2+} removal using iron slag at a pH of 3.5-8.5 and 5.2-8.5, respectively. Fly ashes were also investigated as adsorbents for removal of toxic metals. Alinnor [29] used fly ash from coal-burning for removal of Cu(II) and Pb(II) ions. Sawdust treated with 1,5-disodium hydrogen phosphate was used for adsorption of Cr(VI) at pH 2[30]. Iron based sorbents such as Ferro Sorp[®] Plus[31] and synthetic nanocrystalline akaganeite[32] were recently used for simultaneous removal of heavy metals.

Adsorption on Modified Agricultural and Biological Wastes:

Recently, much research interest in removal of pollutants from industrial effluent has been focused on the use of agricultural by-products as adsorbents. The use of agricultural by-products in bioremediation of heavy metal ions, is known as bio-sorption. This utilizes inactive (non-living) microbial biomass to bind and concentrate heavy metals from waste streams by purely physicochemical pathways (mainly chelation and adsorption) of uptake [33]. New resources such as hazelnut shells, rice husks,

pecan shells, jackfruit, maize cobs or husks can be used as adsorbents for heavy metal uptake after chemical modification or by heating to form activated carbon. Ajmal et al. [34] employed orange peels for Ni^{2+} removal from simulated wastewater. They found that the maximum metal removal occurred at pH 6.0. Cu^{2+} and Zn^{2+} removal from real wastewater were studied using pecan shells-activated carbon [35-36] and potato peels charcoal [37].

Adsorption on Modified Biopolymers and Hydrogels:

Biopolymers are industrially attractive because they are capable of lowering transition metal ion concentrations to sub-part per billion concentrations, are widely available, and environmentally safe. Another attractive feature of biopolymers is that they possess a number of different functional groups, such as hydroxyl and amine groups, which increase the efficiency of metal ion uptake and the maximum chemical loading capacity. New polysaccharide-based-materials were described as modified biopolymer adsorbents (derived from chitin, chitosan, and starch) for the removal of heavy metals from wastewater. There are two main ways to prepare sorbents containing polysaccharides: (a) crosslinking reactions, a reaction between the hydroxyl or amino groups of the chains with a coupling agent to form water-insoluble cross-linked networks (gels); (b) immobilization of polysaccharides on insoluble supports by coupling or grafting reactions in order to obtain hybrid or composite materials [38]. Chitin is a naturally abundant mucopolysaccharide extracted from crustacean shells, which are waste products of seafood processing industries. Chitosan, which can be formed by deacetylation of chitin, is the most important derivative of chitin. Chitosan in partially converted crab shell waste is a powerful chelating agent and interacts very efficiently with transition metal ions [39], other modified chitosan beads were proposed for diffusion of metal ions through cross-linked chitosan membranes [40]. The excellent saturation sorption capacity for Cu^{2+} of cross-linked chitosan beads was achieved at pH 5. Liu et al. [41] prepared new hybrid materials that adsorb transition metal ions by immobilizing chitosan on the surface of non-porous glass beads. Column chromatography on the resulting coated glass beads revealed that they have strong

affinities for Cu^{2+} , Fe^{3+} and Cd^{2+} . Hydrogels, which are cross-linked hydrophilic polymers, are capable of expanding their volumes in water due to their high swelling ability. Accordingly, they are widely used in purification of wastewater. Various hydrogels were synthesized and their adsorption behavior for heavy metals was investigated. Kesenci et al. [42] investigated the sorption capacity of poly(ethyleneglycol dimethacrylate-co-acrylamide) hydrogel beads for metal ions in the order $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Hg}^{2+}$. Essawy and Ibrahim [43] prepared poly(vinylpyrrolidone-co-methylacrylate) hydrogel with $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+}$ while Barakat and Sahiner [44] prepared poly(3-acrylamidopropyl)trimethyl ammonium chloride hydrogels for As^{5+} removal. The removal is basically governed by the water diffusion into the hydrogel, carrying the heavy metal ions inside especially in the absence of strongly binding sites. Maximum binding capacity increases with pH increase to >6 . Table (1) summarizes the main advantages and disadvantages of the various chemical, physical and biological treatments presented in this review.

Table 1: Advantages and disadvantages of the various physico-chemical treatments.

Treatment methods	Advantages	Disadvantages	References
Chemical process	<ul style="list-style-type: none"> • Rapid and efficient process • Removes all pollutants types, produce a high-quality treated effluent • No loss of sorbent on regeneration and effective 	<ul style="list-style-type: none"> • Expensive, and although the pollutants are removed, accumulation of concentrated sludge creates a disposal problem • High energy cost, chemicals required. 	Abdel-Raouf and Abdul-Raheim[15]
Physical process	<ul style="list-style-type: none"> • The most effective adsorbent, great, capacity, produce a high-quality treated effluent • No sludge production, little or no consumption of chemicals. 	<ul style="list-style-type: none"> • Economically unfeasible, formation of by-products, technical constraints 	Zunaira and Zhi [45]; Neeta et al. [46]
Biological process	<ul style="list-style-type: none"> • Economically attractive, publicly acceptable treatment 	<ul style="list-style-type: none"> • Slow process, necessary to create an optimal favorable environment, maintenance and nutrition requirements 	Rajender et al.[47]

Biological Treatment (Bioremediation)

Bioremediation is a technology that explores the metabolic potential of microorganisms to clean up the contaminated sites, *i.e.* wastewater, ground or surface waters, soils, sediments, and air [48]. The process of bioremediation includes detoxification and mineralization that convert waste into inorganic compounds such as carbon dioxide, water and methane. The term bioremediation encompasses both microbial remediation and phytoremediation. Microbial remediation in turn, includes the employment of bacteria, fungi and algae for remediation purposes, thereby involving multiple steps of various enzymatic reactions. In recent years, phytoremediation has evolved as one of the best sustainable way to remove the harmful compounds present in the environment. The main advantage of the photoautotrophic cultivation of algae is the CO₂ sequestration during cell growth. The nutrients present in the wastewater, rather of being waste, become feed for the algae that are utilized and accumulated effectively. Phytoremediation of wastewater is an emerging low-cost technique for removal of hazardous metal ions from industrial wastewater and is still in an experimental stage. Heavy metals such as cadmium and lead are not easily absorbed by microorganisms. In such case, phytoremediation proves a better treatment tool for bio-treatment because natural plants or transgenic plants are able to bio-accumulate these toxins [49]. Aquatic plants have excellent capacity to reduce the level of toxic metals, biochemical oxygen demand (BOD) and total solids from the wastewater. Billore et al. [50] treated industrial effluent with *Typhalatifolia* and *Phragmitiskarka* plants. This treatment eventually led to COD, BOD, total solids and phosphorus content reduction

Catalytic Treatment (Photocatalysis and Ozonation) Processes

To treat wastewater containing trace amounts of recalcitrant organic compounds, such as organo-halogens, organic pesticides, surfactants, and dye matters, environmental engineers are now required to develop more advanced and fast treatment processes including advanced oxidation technologies using photocatalysis

and ozonation. Advanced oxidation processes (AOPs) were developed to generate hydroxyl free radicals using different oxidants under different combinations and these radicals were found to destroy components that are not destroyed during conventional oxidation. The main advantage of AOPs over other treatment processes is their pronounced destructive nature which results in the mineralization of organic contaminants present in wastewater [51-52]. AOPs are considered as low or non-waste generation technologies, which destroys the complex structures using short-lived chemical species with a high oxidation power. The hydroxyl radical ($\text{OH}^\bullet$) is the main oxidative power of AOPs [53]. The $\text{OH}^\bullet$ radicals can be generated by chemical, electrical, mechanical or radiation energy. Therefore, AOPs are classified under chemical, catalytic, photochemical, photocatalytic, mechanical and electrical processes. However, certain organic compounds can hardly be degraded by ozonation or photolysis alone and the treated wastewater may be more dangerous as a result of ozonation. So, a combination of several treatment methods, such as O_3/VUV (ozone/vacuum ultraviolet), $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$ (ozone/hydrogen peroxide/ultraviolet), and $\text{UV}/\text{H}_2\text{O}_2$ (ultraviolet/hydrogen peroxide) followed by natural treatment or biological systems can safely improve the removal of pollutants from the wastewater [53]. The basic principle of semiconductor-based photocatalysis is depicted in Figure (5).

Figure 5: Basic principles of semiconductor-based photocatalysis [58].

AOPs show several advantages unparalleled in the field of water treatment: It could effectively eliminate organic compounds in aqueous phase, rather than collecting or transferring pollutants into another phases. Due to the remarkable reactivity of $\text{OH}^\bullet$, it virtually reacts with almost every aqueous pollutant without much discrimination. AOPs could therefore be applicable in many, if not all, scenarios where many organic contaminants are expected to be removed at the same time. Some heavy metals could also be removed in forms of precipitated $\text{M}(\text{OH})_x$. In some AOPs designs, disinfection could also be achieved, leading AOPs to an integrated solution to some of the water quality problems. Since the complete reduction product of $\text{OH}^\bullet$ is H_2O , AOPs theoretically do not introduce any new hazardous substances into the water. It should also be aware that AOPs are not perfect and have several disadvantages. Most prominently, costs of AOPs are too high, since a continuous input of expensive chemical reagents is required to maintain the operation of most AOPs systems. Some techniques require pre-treatment of wastewater to ensure reliable performance, which could be potentially costly and technically demanding. For instance, the presence of bicarbonate ion (HCO_3^-) can appreciably reduce the concentration of $\text{OH}^\bullet$ due to scavenging processes that yield H_2O and a much less reactive species, $\text{CO}_3^{\bullet-}$. As a result, bicarbonate must be wiped out of the system or AOPs are compromised otherwise. Given the potential costs, AOPs may not individually handle a large amount of wastewater. Instead, AOPs should be deployed in the final stage after primary and secondary treatment, for the purpose of successful removal of a large proportion of contaminants. A novel photocatalyst, titanium dioxide (TiO_2) doped with neodymium (Nd), was prepared by the sol-gel method and used for the photocatalytic reduction of Cr^{6+} under UV illumination [54]. The results indicated that the presence of Nd^{3+} in TiO_2 catalysts substantially enhances the photocatalytic reduction of Cr^{6+} . The neodymium ions deposited on the TiO_2 surface behave as sites at which electrons accumulate. The improved separation of electrons and holes on the modified TiO_2 surface allows more efficient channeling of the charge carriers into useful reduction and oxidation reactions rather than recombination reactions. The

presence of sacrificial electron donors such as formic acid enhances the photocatalytic reduction. The Cr^{6+} adsorbed on the surface of the TiO_2 particles was observed to be almost completely photoreduced to Cr^{3+} . To overcome the limitation of powdery TiO_2 , a novel technique of immobilization based on anodization was applied and investigated [55]. Immobilized TiO_2 electrode was applied to reduce toxic Cr^{6+} to less-toxic Cr^{3+} in aqueous solution under UV irradiation. The anodization was performed with 0.5% hydrofluoric acid, and then the anodized samples were annealed under oxygen stream in the range 450–850 °C. The photocatalytic Cr^{6+} reduction was favored in acidic conditions, with 98% of the Cr^{6+} being reduced within 2 h at pH 3.

Non-Conventional Treatment (Molecular Imprinting) Techniques

Numerous adsorbent materials have been tested for removal of toxic ions for example, Pb^{2+} from aqueous solutions over the last two decades. It is noteworthy that ion imprinted polymer represent a potential source of abundant low-cost adsorbents. The values of maximum adsorption capacity of the adsorbents for the removal of lead are given in Table (2).

Table 2: Comparison of maximum adsorption capacity of Pb (II) using different materials.

Adsorbent	Capacity (mg/g)	Reference
Amino-functionalized MNPs	4.10	Hao et al.[56]
Magnetic nanoadsorbents	36	Nassar [57]
Magnetic nanocomposite beads chitosan	63.33	Tran et al. [58]
Hydroxyapatite	1429	Yan et al. [59]
Biochar-alginate capsule	263.15	Do and Lee [60]
Chitosan/Fe-hydroxyapatite	596.7	Saber-Samandari et al.[61]
Redwood bark	6.8	Belete [62]
Dry desulfurization slag	130.2	Wu et al. [63]
Mof-5	658.5	Rivera et al[64]
Pb^{2+} ion-imprinted polymers	29.67	Xianglong and Hongzhi [65]

The advanced new technical methods are being introduced to overcome the conventional methods of waste water treatment [66], Molecular imprinting technique (MIT) is considered to have advantages superior over the conventional methods for example:

- It does not result in the generation of oxidation or degradation by-products that can potentially be more harmful than the parent compound.
- It has strong affinity for target chemicals and thus, may be ideal for industrial wastewater treatment where high concentrations of specific compounds used in manufacturing need to be removed from waste water.
- The particles would need to be removed after their application and this can be achieved through physical, chemical or magnetic techniques, in addition it is inexpensive to manufacture.
- Materials can be produced in large quantities, have high surface area, are reusable and can be stored for years at room temperature.

Imprinting techniques employ new kinds of smart material with promising selective molecular recognition abilities. Molecular imprinting technique is a burgeoning field that can mimic the specificity of molecular recognition ability. It plays a decisive role in biological activity by creation of an imprinted material with carefully shaped pores that become artificial receptors. The relationship between the template and the imprinted cavity corresponds to a theory originating in biochemistry, which is called the “lock-and-key” mechanism proposed by Nobel Laureate Emil Fischer to explain enzyme-substrate interaction about 100 years ago [66].

History of Molecular Imprinting

The history of molecular imprinting technology appears to be somewhat complicated. The first appearance of molecularly imprinted technique (MIT) dates back to the early 1930s. Polyakov [67] and Erkut et al. [68] performed a series of investigations on silica for use in chromatography. It was

observed that when silica gels were prepared in the presence of a solvent additive the resulting silica demonstrated preferential binding capacity for that solvent. The mechanism proposed by Polykov was largely overlooked by the scientific community. In 1931 the group of Polyakov, reported some unusual adsorption properties in silica particles prepared using a novel synthesis procedure. Sodium silicate had been polymerized in water using ammonium carbonate as the chelating agent. After two weeks, additives (benzene, toluene or xylene) were added. The silica was subsequently allowed to dry for 20-30 days, after which the additive was removed by extensive washing in hot water. Subsequent adsorption studies revealed a higher capacity for uptake of the additive by the silica than for structurally related ligands, i.e. some kind of memory for the additive was apparent, at least in the cases of benzene and toluene. Attempts were subsequently made to apply the principles of the instructional theory in an inorganic system, silica. In the 1940s, Pauling [69] first put forward the idea of molecular imprinting, which involved a protein antibody self-assembly with an antigen acting as a template. However, no significant advances in molecular imprinting have been made in the following 20 years. It was not until 1972 that Wulff and Sarhan [70] laid the foundation for the current field with the first report of organic polymers prepared by reversible chemical bonds. Vlatakis et al. [71] have successfully prepared MIPs by using non-covalent molecular imprinting technology. Based on these pioneering studies, molecular imprinting technology started to grow rapidly [72].

The Concept of Imprinting

In this technique, functional monomers and cross-linkers are copolymerized in the presence of a template molecule. Later on, the template molecule is removed forming a molecularly imprinted polymer (MIP) with imprinted recognition sites and cavities complementary to the shape, size and functionality of the template. On the one hand, the polymers should be rather rigid to preserve the structure of the cavity after splitting off the template. On the other hand, a high flexibility of the polymers should be present to reach a fast equilibrium between release and reuptake of the template in the cavity. Since these two properties are

contradictory to each, other careful optimization is necessary that occurs in three steps as follows: (i) complexation of the metal ion to a polymerizable ligand, (ii) polymerization of this complex, and (iii) removal of the template ion after polymerization (Figure (6)).

Figure 6: Principle of preparation of MIPs [68].

Factors Affecting the Imprinting Process

The rational design of MIPs is very complicated owing to a number of experimental variables including the type of template, functional monomer(s), ratio of functional monomer(s) to template, cross-linker(s), ratio of functional monomer(s) to cross-linker(s), pre-polymerization interactions, solvent(s), initiator, temperature, pressure and polymerization parameters. Binding site orientation, stability and accessibility are governed by the structural characteristics of the polymeric matrix and are essential to recognition of the polymers formed. For these reasons, investigating and optimizing various parameters are essential in order to make progress in maximizing recognition effects.

Template: The template is of central importance as it directs organization of the functional groups dependent to the functional monomers in all molecular imprinting processes. In terms of

compatibility with free radical polymerization, templates should ideally be chemically inert under the polymerization conditions, thus alternative imprinting strategies may have to be sought if the template can participate in radical reactions or is for any other reason unstable under the polymerization conditions. The shape, size and chemical functionality of the template species has significant bearing on the imprinting approach utilized. At present, imprints of several hundred template species have been accomplished, including a vast range of molecular sizes, shapes and functionality. Generally, with regard to choice of template, factors should be considered such as: solubility in organic solvents, possession of electrostatic functionalities, being chemically inert under polymerization conditions to be compatible with free radical polymerization. For larger molecules, imprinting can be difficult to achieve.

Ligand: The polymerizable ligands are often called bi-functional reagents: one functionality coming from their chelating ability and the other one from the vinyl function. A simpler method to prepare ion imprinting polymers (IIPs) consists in using non-polymerizable ligands in which the ligand is embedded inside the polymer matrix through some trapping process. The role of the ligand is the basic criterion since ion chelation is involved in the process of recognition. Since the template in ion imprinted polymers is an ion, reacting via its unfilled orbitals of the outer sphere, the major interactions with the polymer matrix will occur with some electron donating heteroatom. The general trend is to use a ligand bearing one or more chelating groups. Typical functionalized ligands used in the chemical immobilization approach are shown in Figure (7)

Figure 7: Typical functionalized ligands used in the chemical immobilization approach [68].

Functional Monomer: A functional monomer is based on its ability to bind with a template through weak and reversible interactions. The most efficient and specific non-covalent imprinting is achieved through hydrogen bonding [73]. This kind of bonding is always exploited when a template molecule has a functional group able to accept or donate protons: $-\text{COOH}$, $-\text{COO}^-$, $-\text{CN}$, $-\text{NO}_2$, $-\text{N}=\text{}$, $-\text{Cl}$, $-\text{NH}_2$, $-\text{OH}$, $-\text{SH}$ [74] as shown in Figure(8). Considering the effects of changing the template to functional monomer ratio is unnecessary because the template dictates the number of functional monomers that can be covalently attached. Furthermore, the functional monomers are attached in a stoichiometric manner essential in the trapping approach to form a ternary complex with the metal ion. However, even when a functionalized ligand is used in the chemical approach, some other monomers may be introduced in the polymerization mixture. Kai and Guohua [75] have prepared a cross-linked starch xanthate by graft copolymerization of acrylamide and sodium acrylate onto starch xanthate using potassium persulfate and sodium hydrogen sulfite initiating system and $\text{N,N}'$ -methylenebisacrylamide as a cross-linker. As this kind of cross-linked potato starch xanthate can effectively absorb heavy metal ions, it was dispersed in an aqueous

solutions of divalent heavy metal ions (Pb^{2+} and Cd^{2+}) to investigate their absorbency by the polymer. The study of the effect of the weight ratio of starch xanthate to monomers (ranging from 1 : 5 to 1 : 14) revealed that the absorbency increased with increasing ratio of matrix to monomers and reached a maximum. Subsequently, it slowly decreased with further increasing of the amount of monomers. The maximal adsorption amount of Pb^{2+} was 47.02mg/g when the weight ratio of starch xanthate to monomers reached 1 : 12, and the absorbency of Cd^{2+} was 36.33mg/g when the ratio reached 1 : 11. This can be explained as follows. On the one hand, as the weight ratio of matrix to monomers increased, more and more functional groups such as $-\text{COONa}$, $-\text{CONH}_2$, and $-\text{CONH}$ were grafted onto the starch xanthate that enhanced the capacity of the cross-linked starch xanthate chelated with metal ions and the chemical adsorption improved. On the other hand, when the grafted rate increased the branch chain grafted in starch became long, which was conducive to the formation of the ideal network structure and the grafted products formed appropriate holes so that the physical adsorption improved. The acrylic acid self-polymerization enhanced with increasing amount of monomers. Although the polyacrylic acid has many carboxyl groups, these groups are packed inside the polyacrylic acid and thus, are difficult to chelate with metal ions. When the compactness of the cross-linked starch xanthate increased, the polymeric network became denser [76] and thus, the absorbency decreased. Nitu et al. [77] synthesized polymers by changing the functional monomer. The binding capacity of itaconic acid and acrylamide MIPs is 4.2 and 1.8, respectively. The imprinting factor of itaconic acid MIPs is 2, which is higher than that of acrylamide (0.32). Using itaconic acid as functional monomer shows excellent binding ability because the hydrogen binding interaction between the functional groups of quercetin and itaconic acid and its imprinting factor are high and hence, they are selected as the best MIPs on the basis of their high imprinting factor of 8. Imprinting factor is a measure of the strength of interaction of the imprinted polymer towards the template molecule.

Figure 8: Common functional monomers used in non-covalent molecular imprinting procedures [68].

Cross-linkers: A cross-linker constitutes the framework of a polymer network, which carries binding sites. The role of the cross-linker is to fix functional groups of monomers around imprinted molecules, and thereby to form a highly cross-linked rigid polymer. The cross-linker plays a major role in the ion imprinted polymers elaboration since it enables the generation of binding sites. After removal of templates, the holes left should completely complement to target molecules in shape and functional groups. Types and amounts of cross-linkers have profound influences on selectivity and binding capacity of molecularly imprinted polymers. Together with a solvent, a cross-linker determines the morphology of a polymer network. The higher the content of cross-linker in a MIP pre-polymerization mixture and the higher its functionality number, the more cross-linked and rigid polymer network will be formed. Although a cross-linker does not often bear any specific functional groups such as functional monomers, it can still cause

non-specific binding to a template by hydrophobic interactions [76]. When the dosage of cross-linkers is too low, molecularly imprinted polymers cannot maintain stable cavity configurations because of the low cross-linking degree. However, excess amounts of cross-linkers will reduce the number of recognition sites per unit mass of molecularly imprinted polymers. Commonly used cross-linkers involve ethylene glycol dimethacrylate (EGDMA), trimethylolpropanetrimethacrylate, divinylbenzene (DVB), etc. Their structures are displayed in Figure (9). Kai and Guohua [75] study the effect of the amount of N,N'-methylenebisacrylamide as a cross-linker on the removal efficiency of Pb^{2+} and Cd^{2+} . When the amount of cross-linker was, respectively below 12 and 13mg/g(?), the absorbency of Pb^{2+} and Cd^{2+} increased with the amount of cross-linker rising. However, the maximal absorbency of Pb^{2+} and Cd^{2+} was up to 46.95mg/g and 36.05mg/g when the dosage of cross-linker was 12 and 13mg/g(?), respectively. According to Flory's theory, increasing cross-linker addition increases the number of nodes of the network and the cross-linker density, which favorably increased the absorbing capacity of cross-linked starch xanthate. Since low concentration of the cross-linker led to low degree of cross-linking and impeded a network structure to form, the absorbency of metal ions was low [77].

Figure 9: Chemical structure of common cross-linkers used in non-covalent molecular imprinting [68].

Porogenic solvents: A solvent is introduced during the synthesis of ion imprinted polymers in order to generate a porous structure. A solvent must be able to dissolve MIP components, for example, 4-vinylpyridine and ethylene glycol dimethacrylate(EGDMA) are not soluble in each other, but their mixture in methanol/water is homogeneous. Another reason to use a solvent is to render porosity to the final polymer network. Otherwise, without a solvent, the polymer network would be dense, having low permeability to water or other solvents. Because of its role in creating the porosity of the final polymer, the solvent is also called the “porogen” [78]. Bhagyashree and Reddithota [79] studied the interaction energy between benzo[a]pyrene and the functional monomer methacrylic acid in different solvents. They stated that using chloroform exhibited a low adsorption capacity while the MIP prepared in the presence of acetonitrile displayed the best, since acetonitrile has the smallest ΔE value that results in only weak influence of the solvent on the interaction between benzo[a]pyrene and methacrylic acid. Normally, this implies that a polar, non-protic solvents, e.g. toluene, are preferred as such solvents stabilize hydrogen bonds. However, if hydrophobic forces are being used to drive the complexation then water could well be the solvent of choice. Table (3) lists most commonly used porogens.

Table 3: Most commonly used porogens [80].

Solvent	MW (g mol ⁻¹)	Boiling point (°C)	Density (g ml ⁻¹)	Polarity index	Dielectric constant*	H-bond strength
Acetone	58.8	56.2	0.786	21.0	20.7 (25)	7.0
Acetonitrile	41.05	81.6	0.786	5.8	37.5	6.1
Carbon tetrachloride	153.82	76.7	1.587 (liquid)	1.6	-	-
Chloroform	119.38	61.7	0.795	4.1	4.81	5.7
Dichloromet hane	84.93	39.8	1.326	3.1	9.08	7.1
Dimethylfor mamide	73.09	189	0.944	6.4	36.7	11.3
DMSO- acetonitrile	-	-	-	-	-	-
Ethanol	46.07	78.5	0.789	5.2	24.6	19.4
Ethanol- water	-	-	-	-	-	-
Methanol	32.04	64.6	0.791	5.1	32.6 (25)	22.3

Methanol-water	-	-	-	-	-	-
2-Methoxy ethanol	76.09	125.0	0.965	-	16.9	-
Tetrahydrofuran	72.11	66.0	0.886	4.0	7.6	8.0
Toluene	92.14	110.6	0.867	2.4	2.38 (25)	2.0

* T= 20°C, unless specified

Initiators: The role of the initiator in radical polymerization is crucial as it is responsible for the creation of monomer radicals in order to propagate the polymer formation. The initiator is cleaved by thermal decomposition, photolysis or ionizing radiation. For example, the azoinitiator azobisisobutyronitrile (AIBN) can be conveniently decomposed by photolysis (UV) or thermolysis to give stabilized, carbon-centered radicals capable of initiating the growth of a number of vinyl monomers. As an illustrative example of the use of AIBN, or indeed other initiators, to polymerize vinyl monomers, AIBN can polymerize methylmethacrylate under thermal or photochemical conditions to obtain poly(methyl methacrylate). Oxygen gas retards free radical polymerizations, thus in order to maximize the rates of monomer propagation, and to ensure good batch-to-batch reproducibility of polymerizations, removal of the dissolved oxygen from monomer solutions immediately prior to proliferation is advisable. Removal of dissolved oxygen can be achieved simply by ultrasonication of the monomer solution by an inert gas, e.g. nitrogen or argon (Figure (10)).

Figure 10: Chemical structure of common initiators used in non-covalent molecular imprinting [58].

Kai and Guohua[75]studied also the effect of potassium per sulfate as initiator and found that the maximum absorbencies of Pb^{2+} and Cd^{2+} were 47.11mg/g and 36.55mg/g when the dosages of potassium per sulfate were 70 mg and 80mg, respectively. This was related to the relationship between average chain length and concentration of the initiator in the copolymerization [80]. More graft copolymerization occurred between the monomers and the starch xanthate leading to the formation of more stable network structures, which was helpful to increase the absorbency. On the one hand, when the concentration of the initiator was too high, there would be a strong reaction with the starch molecules, resulting in the decrease of the main chain length [81-82]. On the other hand, with the increase of $K_2S_2O_8$, the copolymerization rate became so fast that the polymeric heat could not transfer in time, leading to higher temperature of the system, and consequently enhanced the chance of chain transfer and chain cessation. Hence, the absorbency of the polymer decreased [83].

Different Interactions in the Preparation of Imprinted Polymers

Covalent Interactions

Covalent imprinting [84] is distinguished by the use of templates which are covalently bound to one or more polymerizable groups. After polymerization, the template is cleaved and the functionality left at the binding site is capable of binding the target molecule by re-establishment of the covalent bond. The advantage of this approach is that the functional groups are only associated with the template site. However, only a limited number of compounds (alcohols, aldehydes, ketones, amines and carboxylic acids) can be imprinted with this covalent approach [85,86].A schematic representation of such a reaction is shown in Figure (11).

Figure 11: Schematic illustration of the covalent imprinting of 4-nitrophenyl- α -D- mannopyranose

using 4-vinylphenylboronic acid as functional monomer [85]. Jie et al. [85] postulated that two molecules of 4-vinylphenylboronic acid bonded covalently to the hydroxyl groups of the sugar molecule by an ester linkage which formed two cyclic boronate ester groups. Subsequently, this template-monomeric complex was incorporated into a polymer matrix by the polymerization of the vinyl function of the monomer with a high proportion of cross-linking monomer. Later hydrolysis of the ester linkages resulted in the formation of a cavity within the polymer structure, which is able to covalently rebind the template molecule.

Non-Covalent Interactions

In non-covalent imprinting the interactions between functional monomer and template during polymerization are the same as those between polymer and template in the rebinding step. These are based on non-covalent forces such as H-bonding, ion-pairing and dipole-dipole interactions as shown in Figure (12). This method was first introduced in organic polymers by Arshady and Mosbach [87] who reported that methacrylic acid is the most

common functional monomer. Due to its simplicity this method is the most widely used to create imprinted polymers.

Figure 12: Examples of interactions found in non-covalent imprinting. A; electrostatic: dipole-dipole, B; hydrogen bonding, C; π - π stacking, D; van der Waals, E; coordination bond, F; electrostatic ion-ion [87].

The Semi-Covalent Approach

A semi-covalent approach aims to unite the advantages of the covalent and non-covalent approach, the functionality is recovered after cleavage of the templates found at the binding site, and rebinding takes place via non-covalent interactions. As the template is covalently bound to a polymerizable group, the functionality which is recovered after cleavage of the template should only be found at the binding site. This results in a more uniform distribution in binding site affinities [88]. The rebinding taking place via non-covalent interactions has no kinetic restrictions except diffusion. Two variations in the semi-covalent approach can be distinguished in Figure (13).

- (i) The template and the monomer are connected directly
- (ii) The template and the monomer are connected using a spacer group.

The first true semi-covalent approach was reported by Sellergren and Andersson [88] for the imprinting of *p*-aminophenylalanine ethyl ester and was used in combination with the (reversible) covalent approach [99]. The semi-covalent imprinting of the template cholesterol was the first example of the use of the sacrificial spacer approach and is shown in Figure(13). As cholesterol has limited functionality, it was a difficult molecule to imprint through conventional routes. Cholesterol was attached via a carbonyl spacer 4-vinylphenol, resulting in cholesteryl 4-vinylphenyl carbonate as the template monomer. Following polymerization, the cholesterol was cleaved from the polymer by base hydrolysis. A phenolic hydroxyl group is left in the binding site which is able to interact with cholesterol through hydrogen bond formation. Adequate space between functional groups remained in order to establish hydrogen bonding and creation of an imprinted site displaying a recognition site matching that of the cholesterol molecule as shown in Figure (13).

Figure 13: Schematic illustration of the sacrificial spacer approach to the molecular imprinting of cholesterol [90].

IPs Polymerization Conditions

Several studies have shown that polymerization of MIP at lower temperatures forms polymers with greater selectivity compared to polymers made at elevated temperatures. Usually, 60°C is the preferred polymerization temperature. However, the initiation of the polymerization reaction is very fast and therefore hard to control at this temperature and results in low reproducibility of the molecular imprinted polymer. Furthermore, the relatively high temperatures have a negative impact on the complex stability, which reduces the reproducibility of the monolithic stationary phases and produces high column pressure drops. Thus, relatively low temperatures with a prolonged reaction time are selected to obtain more reproducible polymerization. When complexation is driven by hydrogen bonding, lower polymerization temperatures are preferred, and under such circumstances photochemically active initiators may well be preferred as these can operate efficiently at low temperature. For example, Kempe and Mosbach [90] presented a study on enantioselectivity of 1-PheNHPh imprinted polymers, one polymer being thermally polymerized at 60°C, the other photochemically polymerized at 0°C. The results showed that better selectivity is obtained at the lower temperature compared to the identical polymers thermally polymerized. The reason for this has again been postulated on the basis of Le Chatelier's principle, which predicts that lower temperatures will drive the pre-polymer complex toward complex formation, thus increasing the number and, possibly, the quality of the binding sites formed. Moreover, Krupadam et al. [91] made a cost comparison of MIP and activated carbon showing that 1 g of MIP can purify 3,810 l of contaminated water with the cost of 1.2 USD, while 1 g of activated carbon can purify only 190 l at the cost of 0.9 USD.

Effect of Water Characteristics on IPs Performance

Effect of pH: Changing the pH of the solution can lead to ionization of the adsorbate or changes in the surface charge of the MIP. Therefore, the effect of pH is specific to the MIP used and must be studied separately for each case [92]. Several MIP researchers have studied the effects of varying pH on MIP

performance and these studies can provide clues about the performance of other MIPs in the future. Yu et al. [93] suggested that the significant effect of pH on a selected MIP indicated that the adsorption was predominately due to electrostatic attractions because only electrostatic attractions are sensitive to pH. Li et al. [94] recorded a maximum removal of 83.2 % at pH 7 on using 2,4-dichlorophenol (2,4-D) imprinted MIP. They noted that since the main binding force was hydrogen bonding, minimizing the concentrations of H^+ and OH^- ions in solution would maximize the removal efficiency.

Effect of Ionic Strength: Adding ions to the solution can lead either to increased adsorption by decreasing the solubility of the adsorbate in solution or to decreased adsorption by acting like a shield that decreased the electrostatic attraction between the MIP and the template [94]

Effect of Competing Micropollutants: Although MIP is designed with one template molecule, similar molecules are also capable of binding into the specific cavity, and the template experiences some competition from these similar compounds. Both MIP and NIP also exhibit some degree of nonspecific adsorption, which is not compound specific. Yu et al. [93] prepared a solution of PFOS with an equal concentration of phenol, sodium dodecyl benzene sulfonate, or pentachlorophenol. They observed a decrease in the adsorption of PFOS, but the adsorption decreased less for MIP than NIP. Li et al. [94] studied adsorption with 2,4-D imprinted MIP in the presence of methylbenzene and aniline which have structures similar to 2,4-D. Adsorption decreased from 83.2 % to approximately 72 %, but adsorption of the competitors was below 40 %, indicating good selectivity.

Dual/Multiple Components Imprinting Strategies

Although IPs are suitable to separate and remove metal ions and organic compound, improvement of the selectivity is still urgently required. Besides the novel, self-synthetic monomers, the strategies of dual/multiple functional monomers and dual/multiple template ions have gradually aroused increasing

attention. Dual template imprinting can have several advantages over the conventional technique involving single template analytes present in a single sample, as it has memory sites complementary to the targeted single analyte. Dual molecularly imprinted polymers (DMIPs) can be used for a group of analytes in a single sample and can therefore be cost effective, offer short analysis time and also simultaneous removal of multiple ions, in contrast to conventional MIP.

Application of IPs in Wastewater Treatment

Development of molecular and ionic imprinted polymers with separation of organic or inorganic compounds in general prior to analysis are considered smart materials.

Ion Imprinted Polymers (IIPs)

IIPs are 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, either molecules or ions. Fan et al. [95] prepared a Pb^{2+} -imprinted silica sorbent functionalized with chelating N-donor atoms for the selective removal of Pb^{2+} ion from aqueous solution by hydrothermal-assisted surface imprinting technique. The results revealed that the Pb^{2+} -imprinted silica sorbent had high adsorption capacity (61.9 mg/g), fast adsorption equilibrium rate within 30 min, wide pH range (3.5 to 6.5) for constant adsorption capacity, high selectivity and good regeneration performance. The whole preparation process of the Pb^{2+} -imprinted silica is shown in Figure. (14).

Figure 14: Preparation Procedure of Pb(II)-Imprinted Silica Sorbent.

Hongxing et al. [96] prepared Ni²⁺ ion-imprinted sulfonate-functionalized silica gel polymer with the surface imprinting technique by using Ni²⁺ as the template ion, grafted silica gel as the support, and 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) and ethylene glycol dimethacrylate (EGDMA) as the functional monomer and cross-linker, respectively. The Ni²⁺ ion-imprinted silica gel polymer (Ni²⁺-IIP) exhibited a higher adsorption capacity and selectivity for Ni²⁺ compared to the non-imprinted silica gel polymer (Ni²⁺-NIP). The maximum adsorption capacities of Ni²⁺-IIP and Ni²⁺-NIP were 20.30 and 4.87 mg g⁻¹, respectively. The relative selectivity coefficients of the adsorbent for Ni²⁺ in the presence of Co²⁺, Cu²⁺, Zn²⁺ and Pb²⁺ were 4.09, 3.62, 5.78 and 5.86, respectively. The procedure is described in Figure (15).

Figure 15: Scheme for preparation of Ni(II) ion-imprinted polymer.

Mostafa and Esmael [97] prepared ion-imprinted polymer for Mn^{2+} removal by formation of binary (1-(2-pyridylazo)-2-naphthol) complex in methanol (porogen), following copolymerization with 4-vinylpyridine (VP), ethyleneglycoldimethacrylate (EDMA), and 2,2'-azobisisobutyronitrile (AIBN) as a functional monomer, cross-linking agent, and initiator, respectively. The standardized effects of the independent variables and their interactions were also investigated using a Pareto chart. Results of the two-level fractional factorial design (2^{4-1}) based on analysis of variance demonstrated that solution pH, amount of polymer, and adsorption time were seen to be statistically significant. To optimize manganese removal from aqueous solution by manganese-imprinted polymer (Mn-IP), a three-factor, three level Box-Behnken statistical experimental design was used with 15 experimental data obtained in a batch study. The significance of independent variables and their interactions were tested by the analysis of variance (ANOVA) with 95% confidence limits. The optimum conditions were $\text{pH}=9.7$, 44.4 mg polymer, and 19.1 min adsorption time. Vusumzi et al [98] prepared a ternary complex of Ni^{2+} ions with acrylamide and 1-vinylimidazole as co-monomers in porogenic methanol. Polymerization was effected by addition of ethylene glycol dimethacrylate as a cross-

linker and 1,1azobis(cyclohexanecarbonitrile) as initiator. Optimum rebinding time was achieved after 10 min with good accessibility (pores on the surface of the polymer as discussed by SEM). The shorter contact times can also be explained by a known high affinity of Ni^{2+} ions for amino donors on acrylamide and vinylimidazole functional monomers. Xiaoyan et al. [99] synthesized a Cd magnetic ion-imprinted polymer (MIIP) via surface imprinting, using methacrylic acid and acrylamide as dual functional monomers, vinyltrimethoxysilane as ligand, $\text{Fe}_3\text{O}_4@\text{SiO}_2$ as support, azodiisobutyronitrile as initiator, and ethylene glycol dimethacrylate as cross-linker. The maximum adsorption capacities of the MIIP and magnetic non-imprinted polymer for Cd^{2+} were 46.8 and 14.7 $\text{mg}\cdot\text{g}^{-1}$, respectively. The selectivity factors of Pb^{2+} , Cu^{2+} , and Ni^{2+} were 3.17, 2.97, and 2.57, respectively. The adsorption behavior of Cd^{2+} followed the Freundlich isotherm and a pseudo second-order model. The MIIP was successfully used for the selective extraction and determination of trace Cd^{2+} in representative rice samples. The limit of detection and recovery of the method was 0.05 $\mu\text{g}\cdot\text{l}^{-1}$ and 80–103%, respectively, with a relative standard deviation less than 4.8%. A schematic diagram of the preparation of magnetic ion-imprinted polymer (MIIP) is shown in Figure (16).

Figure 16: Schematic diagram for the preparation of magnetic ion-imprinted polymer (MIIP).

Molecular Imprinted Polymers (MIPs)

The applications of MIPs to remedy contaminated water can be divided into four aspects:

- Technologies using MIPs as selective tools for determination of pollutants in wastewater.
- Technologies using MIPs as a kind of effective sorbent for purification of pollutants.
- Technologies using MIPs to improve the efficiency of catalytic removal for organic matters.
- Application of MIP-based fluorescence sensor to recognize and directly quantify target analytes.

Due to their advantageously high selectivity and strong affinity, MIPs became efficient materials for selective recognition, separation, determination, and purification of pollutants in wastewater.

According to previous research, mechanisms of contaminant adsorption in aqueous phase by MIPs can be classified into two types: *nonspecific adsorption and specific adsorption*.

Nonspecific adsorption results from hydrogen bonding, hydrophobic interaction, or van der Waals force, while **specific adsorption** comes from the selectivity recognition cavities which were introduced during the imprinting process. Saliza et al. [100] studied the preparation of a molecularly imprinted polymer for the removal of methylene blue dye from aqueous media. The methylene blue-molecularly imprinted polymer was prepared using bulk polymerization *via* radical polymerization containing methylene blue as a template, methacrylic acid, as a monomer, ethylene glycol dimethacrylate as a cross-linker, benzoylperoxide as an initiator and tetrahydrofuran as a solvent (porogen) in ratios of 0.117 mmol, 0.930 mmol, 4.650 mmol, 10.000 mg and 30.000 ml, respectively. The block polymer obtained was ground and sieved using a 90 μm sieve and the methylene blue template was removed from the methylene blue-molecularly imprinted polymer by extracting it with methanol/acetic acid/water (8:1:1) mixture. The non-molecularly imprinted polymer was synthesized as a reference. The methylene blue-molecularly imprinted polymer was characterized by using Fourier-transform infrared spectroscopy, scanning electron microscopy, a particle size analyzer and N_2 -adsorption/desorption techniques. The effect of different

parameters such as pH, time and concentration of methylene blue, selectivity and reusability of the methylene blue-molecularly imprinted polymer were evaluated. Maximum sorption of methylene blue occurred at pH 5 within 30 s. The sorption followed a pseudo second-order kinetic model. The adsorption isotherm of methylene blue followed the Freundlich isotherm model. The selectivity study had proved that the methylene blue-molecularly imprinted polymer was highly selective to the methylene blue analyte. Hager et al. [101] studied the preparation of a molecularly imprinted polymer (MIP) deposited on the surface of magnetic hydroxyapatite (MHAP) which was used as a sorbent for dibenzothiophene (DBT) removal. The MIP/MHAP and NIP/MHAP were synthesized by grafting polymerization and surface molecular imprinting using DBT as the template molecule, styrene as the functional monomer, and ethylene glycol dimethacrylate as the cross-linker. The experimental data exhibits excellent adsorption capacity for DBT that reaches 247 mg/g within 60min. The route of preparation and the mechanism of the desulfurization process are shown in Figure (17).

Figure 17: Schematic illustration of the prepared route.

Hager [102] used photo-coupling of $\text{Ag}_3\text{PO}_4\text{-Ag}_2\text{CO}_3$ with molecularly imprinted polymer using the Taguchi method for enhanced photocatalytic removal of phenol under sunlight exposure. The results indicate that the optimum dosage of the catalyst was 1.5 g/l, pH = 9, phenol concentration = 50 mg/l, and irradiation time = 120 min, and the phenol removal efficiency reached up to 73.9 % at these optimal conditions. MIPs have been used in recent studies for the selective removal of single pollutants or groups of pollutants from complex water samples. For example, a MIP was used for the selective removal of single contaminants, such as 17 β -estradiol at trace concentration [103], 2,4-dichlorophenol from contaminated water [104], cephadrine from water [105] and phenol from aqueous solution [106].

In addition, magnetic particles (Fe_3O_4) have drawn considerable attention because of the fundamental scientific interest and the promising application in separation, catalysis, and biological and environmental remediation. Moreover, Fe_3O_4 shows advantages such as low toxicity, low cost, and eco-friendliness. More recently, there has been an increasing interest in combining magnetic particles with molecular imprinting technique for the comprehensive benefits in selectivity and sensitivity. It is expected that the presence of the magnetic particles and MIPs will provide a new approach toward separation application and broaden the use of MIPs in wastewater treatment. When magnetic particles are encapsulated inside of imprinted polymers, the resulting MMIPs cannot only selectively recognize the target analytes, but also can be quickly isolated from the complex matrix with an external magnetic field.

Selective Separation/Recovery Based-Imprinted Membranes

Investigation of MIP membranes has increased during the last few years. Work has been published on the preparation of MIP membranes, showing specific permeability and separation for template/ligands such as cholesterol, nucleotides, and various drugs. Recently, MIP membranes prepared by photo-initiated surface modification of microfiltration membranes in the presence of template molecules have attracted much research interest due to the ability to change their diffusive permeability automatically by responding to the template molecules [107]. The

vision of a tailored and truly molecule selective separation for a wide range of target molecules is the strongest motivation for the development of imprinted membranes. Molecular imprinted membranes for chiral separations may be the first examples for practical applications. In comparison with chromatography, the up scaling of a membrane separation should be much easier. Such success could serve as a “door opener” for other imprinted membranes. Molecular imprinted membranes with a microporous barrier enabling facilitated trans-membrane transport using imprinted sites would enable continuous separation. “Gate imprinted membranes” could be developed towards environment sensitive or switchable membranes. All technical areas with pure or purified special target molecules as products will in the future benefit from such novel imprinted membranes separation. Alternatively, imprinted membrane absorbers will be used mainly for isolation and removal of small molecular fractions, especially from a large volume. Such imprinted membranes will be applied instead of conventional absorbers or in combination with other membrane separation steps, especially in water treatment, and in food and pharmaceutical industries.

The MIP membranes have shown selective adsorption of target molecules [108]. Casting mixtures of polymers and templates for the preparation of MIP membranes has been used only in a few studies [109]. For such conventional MIP membranes, the limited accessibility of MIP binding sites due to a random distribution inside and on the surface of the bulk polymer remains one of the main unsolved problems. A functional polymer, sulfonated polysulfone (SPS) with a degree of substitution of 0.10, was prepared and then blended with cellulose diacetate (CA) as the matrix polymer for the preparation of molecularly imprinted polymer (MIP) membranes via phase inversion from a casting solution containing a template. Polyethylene glycol was found to be compatible with these polymers and was subsequently used as pore forming agent. Optimization studies with the aim to enhance the membrane permeability were carried out with respect to solvent, polymer blend composition and total polymer concentration. The effects onto pore structure were also studied by membrane water

uptake and specific surface area measurements. In conclusion from these investigations, dimethyl sulfoxide was chosen as the solvent, the CA/SPS composition was maintained at 90/10 (w/w) to minimize non-specific template binding and the total polymer concentration was set at 13 wt%. MIP membranes based on CA/SPS blends with rhodamine B (RhB) as template were prepared using the optimized conditions. Results for re-binding of RhB during filtration through MIP as well as blank membranes, prepared without RhB, provide evidence for surface imprinting of the porous membranes, Nor et al.[110] studied the removal of 2,4- dinitrophenol using MIP membrane, prepared by hybridization of MIP particles with cellulose acetate (CA) and polystyrene (PS) after being ground and sieved using bulk polymerization in acetonitrile using 2,4-dinitrophenol, acrylamide, ethylene glycol dimethacrylate, and benzoyl peroxide, as the template, functional monomer, cross-linker, and initiator, respectively. The sorption capacity of the other sorbent, PS-MIP, is lower than that of CA-MIP. For CA-MIP, as the pH value of the solution increased, the adsorption efficiency gradually increased and attained a maximum value at pH 7 and then decreased in the basic pH range. This may be because the main binding forces between CA-MIP and the 2,4-DNP molecule are both an ionic interaction and a hydrogen bond. Soheil et al. [111] prepared Cu^{2+} -ion-imprinted membrane adsorbents via cross-linking of blended chitosan/poly(vinyl alcohol) using glutaraldehyde as cross-linker and copper ions as template. The ability of IIMs to adsorb copper ions from aqueous solutions was assessed using a batch of experiments under different conditions by changing cross-linking density (0.05 mass %, 0.1 mass %, and 0.2 mass %), template content (0.2 mass %, 0.5 mass %, and 0.9 mass %), initial analyte concentration (50 mg l^{-1} , 100 mg l^{-1} , and 150 mg l^{-1}), and adsorbent concentration (0.5 g l^{-1} , 1.0 g l^{-1} , and 2.0 g l^{-1}). The Taguchi method was used to plan a minimum number of experiments. The following optimal levels were thus determined for the four factors: cross-linking density: 0.1 mass %; template content: 0.5 mass %; initial analyte concentration: 150 mg l^{-1} ; and adsorbent concentration: 0.3 g l^{-1} .

Due to the biological and environmental impact of metal ions, the development of new methods for selective separation, purification and determination of these compounds are of continuing interest. A new approach was proposed for preparing a metal ion-imprinted polymer membrane through *in situ* polymerization using the Zn^{2+} -(2,2'-bipyridyl) complex as the template, and 4-vinylpyridine as the monomer [112]. The imprinted membranes revealed higher selective adsorption and permeation for the template than for the control non-imprinted membranes. Selective permeation of Zn^{2+} over Cu^{2+} was observed. Imprinting with Ag^+ overcame this problem. Competitive removal of $\text{Ag}^+/\text{Cu}^{2+}$ and $\text{Ag}^+/\text{Ni}^{2+}$ from mixtures were also studied. The non-imprinted membranes are selective for Cu^{2+} and Ni^{2+} . Chitosan-imprinted membranes showed relative selectivity coefficients for $\text{Ag}^+/\text{Cu}^{2+}$ and $\text{Ag}^+/\text{Ni}^{2+}$ 9 and 10.7 times higher than the non-imprinted membrane, respectively. In this way, the imprinted membranes are good for selective silver removal in a solution containing interfering ions such as Cu^{2+} and Ni^{2+} .

Molecularly Imprinted Biodegradable Polymers

In the last few years, there has been a world-wide research effort to develop biodegradable polymers as an environmental waste-management option. Biodegradable polymers have attracted considerable interest for applications to drug delivery, owing to their biocompatibility and control of drug release [113]. Indeed, biodegradation of polymeric components may prevent accumulation of the nanoparticles in organs and tissues, thus improving the safety profile of the material, while enabling fine control of release kinetics. Hyeon-Kyeong and Beom [114] studied novel biodegradable MIPs based on poly(lactic acid)(PLA) and poly(ethylene glycol) (PEG) which can be potentially utilized as biomedical and environmentally degradable materials with molecular recognition properties. A biodegradable cross-linker, diacrylated PLA-PEG-PLA triblock copolymer was synthesized through ring-opening polymerization of D,L-lactide using hydrophilic PEG as a macroinitiator, followed by diacrylation of the end groups for the introduction of the polymerizable vinyl groups. These macromers were used to

prepare biodegradable molecularly imprinted polymers (MIPs) by photopolymerization with methacrylic acid (functional monomer) and theophylline (model template). Various polymers were prepared by changing the ratio of functional monomer to the cross-linking agent and the macromer concentration to obtain optimum conditions for MIP synthesis. The highest binding amount and distribution coefficient were obtained with a molar ratio of functional monomer to cross-linker of 1:1 and 40% (w/v) of macromer concentration. The theophylline-imprinted polymer demonstrated higher rebinding capacity to theophylline than its corresponding non-imprinted polymer (NIP) and selectivity for theophylline over caffeine (similar structure molecule), suggesting that these polymer networks can potentially be used as biodegradable materials with specific molecular recognition properties. Meng et al. [115] regenerated MIP with methanol/acetic acid (9/1, v/v) and were able to reuse the particles for five cycles without a loss in efficiency. Lin et al. [116] showed that the regenerated particles could be used for 30 cycles with no loss in efficiency. However, these researchers did not continue testing the regeneration of the particles until they observed a decrease in performance so it is unknown how many times their particles could actually be regenerated.

Conclusion and Outlook

Water pollution causes critical environmental problems for individual organisms and the population as a whole. Water used in domestic, industrial, and agricultural sectors is usually returned to rivers, lakes, estuaries, or oceans. However, industrial effluent is usually polluted by organic compounds and their derivatives being the most common. Thus, there is a need for an economically feasible technology for efficient removal and recovery of pollutant from aqueous solutions. The process of imprinting technique has many attractive features including the easily selective removal and recovery of pollutant with low capital and operational costs. The understanding of the mechanisms of interaction between the template molecules (i.e., organic molecules and/or metal ions) and the polymer matrix is a fundamental challenge in molecular imprinting method (MIPs or IIPs). Therefore, it could be a useful tool to design of selective

IPs sorbents for the simultaneous removal and recovery of hazardous metals from aqueous environment, especially precious elements like gold and silver, which is the focus of IPs. Future work should be done to investigate the use of new, more sensitive ligands for

- Enhancing the selectivity towards multiple molecules
- Exploring thin film membrane approaches for faster recovery response
- Developing “cocktail” approaches for multi-component recovery (organic and inorganic)
- Enhancing on-line regeneration of IPs.

To date, these are still challenges and could be resolved by increased focusing on the influence of other chemicals on the existing preparation technologies and selectivity to attain high scale production of ion imprinted polymers (IIPs). During the batch production, it should be kept in mind that cost-saving is almost always the primary requirement, but selectivity is the main goal to produce large amounts of IPs and biodegradable IPs polymer for successful commercialization.

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