IMMOBILIZED MATERIALS FOR REMOVAL OF TOXIC METAL IONS FROM SURFACE/GROUNDWATERS AND AQUEOUS WASTE STREAMS

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Environmental impact

Toxic metal ions released from industrial activities pose a significant threat to the environment and public health. Immobilized materials (novel sorbents and membranes with doped ligands) provide a viable attractive remediation alternative for toxic metal ions removal from polluted streams due to their high efficiency, selectivity and rapid operation. The present review article explores all the aspects of separation processes using these materials. This manuscript covers the general characteristics of immobilized materials, understanding of the metal ions removal mechanisms, as well as the impacts of various parameters on removal efficiency. The authors expect this review will facilitate a current and objective evaluation of the potential of immobilized materials in existing and new applications and inform future research efforts to address pertinent engineering challenges.

IMMOBILIZED MATERIALS FOR REMOVAL OF TOXIC METAL IONS FROM SURFACE/GROUNDWATERS AND AQUEOUS WASTE STREAMS

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Abstract: Heavy metals from industrial processes are of special concern because they produce chronic poisoning in aquatic environment. More strict environmental regulations on the discharge of toxic metals require developing various technologies for their removal from polluted streams (i.e. industrial wastewater, mine waters, landfill leachate, groundwater). The separation of toxic metal ions using immobilized materials (novel sorbents and membranes with doped ligands), due to their high selectivity and removal efficiency, increased stability, and low energy requirements, is promising for applying to improve the environmental quality. This critical review is aimed at studying of immobilized materials as potential remediation agents for the elimination of numerous toxic metal (eg. Pb, Cd, Hg, As) ions from polluted streams. It includes general characteristics of immobilized materials and separation processes, understanding of the metal ions removal mechanisms, a review of the application of immobilized materials for the removal of toxic metal ions, as well as the impacts of various parameters on the removal efficiency. In addition, emerging trends and opportunities in the field of remediation technologies using these materials are addressed.

1. Hazards associated with toxic metals in the aquatic environment

Industrial development leads to the generation of effluents – polluted streams, which if untreated may result in water, sediment, groundwater and soil pollution. Industrial wastes and emissions contain toxic compounds, most of which are detrimental to humans. Among the various toxic pollutants, heavy metals represent an interesting group of elements due to their strong impact on the stability of aquatic ecosystems, bioaccumulation in living organisms and toxicity persistence.[1,2] Heavy metals are of special concern because they produce chronic poisoning in the terrestrial and/or aquatic environment. Generation of large quantities of toxic metals and their by-products due to the industrial and transport activities, overpopulation, improper hazardous waste storage, along with their persistence in the environment have continuously increased over last decades.[3] Understanding the impacts of contaminants on the environment (lakes, rivers, wetland estuaries, groundwater) and ecosystems (i.e. biota represented by fauna and flora) is a key issue.[4] If overall health of the ecosystem is to be properly evaluated and understood, the impact of chemicals on interactions among organisms, their physical and chemical environment, and climate conditions must be jointly assessed.[5]

There are 35 metals of environmental concern due to occupational or residential exposure - 23 of these are heavy metals. The term "heavy metals" comprises chemical elements with a specific gravity at least 5 times that of water, e.g.: arsenic (5.7), cadmium (8.65), lead (11.34), and mercury (13.546).[6] Arsenic (1), lead (2), mercury (3), and cadmium (7) are included in the Priority List, the so-called "Top 20 Hazardous Substances" List compiled by the US Agency for Toxic Substances and Disease Registry (ATSDR) in cooperation with US EPA.

The biota is often exposed to heavy metals released to the ecosystems (e.g. aquatic environment) from number of sources, including: municipal wastewater treatment plants, industries, mining, oil spills, rural (agricultural, cultivation and fertilization) and transportation. The industries pertaining toxic metals comprise: power generation, pulp and paper, petrochemicals, refineries, explosive manufacturing, electronic, automotive, coating, painting, storage batteries, alloy and steel production. As a result toxic metals may damage the environment and produce deleterious effects on the adjacent ecosystems.

The aqueous waste streams include mainly: industrial wastewaters, power generation liquid waste streams, acid mine drainage (AMD) and landfill leachates. Industrial wastewaters contain toxic heavy metals (e.g. Zn, Cu, Cr, Ni, Cd and Hg).[7] In liquid waste streams in coal-fired power plants a wide spectrum is found of trace elements (Cd, Cu, Pb, Zn, As, Se and Cr), most of which originate in the coal and remain in the fly or bottom ashes when the coal is burnt.[8] Moreover, trace contaminants from the sources other than the coal may be concentrated in cooling tower blowdown and other waste streams. Landfill leachate is the main environmental impact from controlled landfilling regarded often as an efficient, economical and technically sound system of disposal for solid waste.[9] Leachate constitution depends on: waste composition, site hydrology and geochemistry, moisture and oxygen contents, as well as on age, design and operation of a landfill,[10,11] i.e. reflects the type of landfill from which it originates.[12] The major sources of metals in municipal and industrial landfills are: incinerator ashes, mine wastes and household hazardous substances (e.g. batteries, paints, dyes, inks).[13-15] Heavy metals commonly found in high concentrations in landfill leachate which comprise: Mn, Zn, Cr, Pb, Cu and Cd, are a potential source of contamination of ground an surface waters and the adjacent ecosystems.[10,16-18] Mine wastes are considered the largest volume of materials handled in the world. AMD and acid rock drainage (ARD) are both strong acidic waste waters rich with dissolved metal sulphates. They are formed in a complex process, in which pyrite and other sulphide minerals (e.g. pyrrholite, marcasite, chalkosite, covellite, arsenopyrite, chalcopyrite etc.) oxidize in the presence of oxygen, water and acidophilic chemotrophic bacteria, to produce dissolved metals, sulphate, and acidity.[19-21] The release of water polluted by acid, iron, sulfur and aluminum is drained away from the mines and into streams. AMD is currently the main contamination source of surface water and aquatic life in many mining regions worldwide, thus one of the most serious water pollution and economic concern (e.g. corrosion of infrastructure). Although AMD is commonly associated with the extraction and processing of sulfide-bearing metalliferous ore deposits and sulfide-rich coal, it can occur wherever sulfide minerals are excavated and exposed to atmospheric oxygen.[22,23] AMD also contains elevated levels of potentially toxic metals, especially Ni and Cu, as well as: Pb, As, Al, and Mn. Tailings piles or ponds, mine waste rock dumps and coal spoils are also an important source of AMD.

Contamination of aquatic environments by AMD and associated toxic metals is a widespread problem in watersheds affected by hard-rock mining. Erosion and weathering can mobilize toxic metals from exposed mineral deposits and altered rock. This process can be accelerated by mining activities, which expose large amounts of sulfide minerals in mine tunnels, waste-rock piles and deposits of mine and mill tailings.[24] Adverse effects of acidity and associated toxic metals on aquatic ecosystems may extend far downstream from sources of acidic drainage. Fish are absent and invertebrate fauna is limited in highly acidic streams (pH 4.5), and adverse effects on aquatic communities are also severe in mixing zones of acidic and neutral-pH waters. Colloidal precipitates of iron and aluminum oxyhydroxides formed upon neutralization of acidic water are typically enriched with high concentrations of potentially toxic metals, and these precipitates may be transported on substantial distances downstream.[25] Metals may remain in bioavailable forms in water and sediments downstream of mixing zones, leading to metal bioaccumulation and toxic effects on fish and invertebrates.[26,27]

The aquatic environment makes up the major part of our environment and resources, therefore, its safety is directly related to human health. The excessive contamination of aquatic ecosystems is currently one of major environmental and health concerns worldwide[28] as the aquatic environment is the ultimate recipient of contaminants from natural and anthropogenic sources.[29] The agricultural runoff has cumulative negative impacts on the water quality, which is considered the main environmental factor controlling the state of health and disease in both cultured and wild fish.[30,31]

Certain heavy metals (e.g. Fe, Cu, Mn, Zn) are common in the natural environment in low concentrations, whereas some, like e.g.: V and Zn are considered nutritionally essential for good health. These elements, or some form of them, are commonly found naturally in food, fruits and vegetables, and in commercially available multivitamin products.[32] They are also present in diagnostic medical applications[33] and industrial use, such as, e.g.: production of pesticides, batteries, alloys, electroplated metal parts, textile dyes, steel.[32] Toxic metals may enter the human body via food, water, air, or absorption through the skin in agriculture, manufacturing, pharmaceutical, industrial, or residential settings. Industrial exposure is common for adults, while ingestion is the most common uptake route in the case of children.[33] Less common routes include; radiological procedures, inappropriate dosing or monitoring during intravenous (parenteral) nutrition, a broken thermometer.[34]

Heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissues. Their toxicity can result in damaged or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver and other vital organs. Long-term exposure may result in slowly progressing physical, muscular, and neurological degenerative processes, muscular dystrophy, and multiple sclerosis. Allergies, including auto-allergic diseases are also observed, while repeated long-term contact with some metals (or their compounds) may cause cancer. Acute poisoning is more likely to result from inhalation or contact with dust, fumes or vapors, or materials in the workplace. However, lower levels of contamination may occur in residential settings, particularly in older homes with e.g. lead paint or old plumbing.[32] Ecotoxicological effects (acute and/or chronic) of heavy metals occur from the molecular to ecosystem (both: terrestrial and aquatic) levels. A key issue when dealing with contaminated sites is the assessment and evaluation of the toxicity of contaminants to the environment, while the bioavailability is a key factor for predicting their ecotoxicological effects.[35]

Release of toxic substances and their spread in the environment can be hazardous for exposed populations, thus their elimination from aqueous solutions is important for the protection of public health.[36] However, these substances are more easily monitored and removed when they are generated than they have been dispersed. To describe and predict the fate of toxic metals in the natural environment requires a fundamental understanding of the mechanisms controlling the chemical reactions in which they participate. Hence, the success in minimizing the adverse impacts depends largely on the treatment processes that isolate and remove the contaminants at their source. Up to now various techniques, including: chemical precipitation, extraction, ion exchange, membrane separation and sorption have been developed for the effective removal of heavy metals from different aqueous solutions at various concentrations.[22,37-48]

2. Sorption and membrane separation processes using immobilized materials for remediation of hazardous waste streams – an overview

2.1. Adsorption processes

Methods on treatment of heavy metal-polluted wastewater can be divided into (1) physical and/or chemical reactions, such as: chemical precipitation, ion exchange, filtration, and (2) adsorption either by biomaterials, like microbial and plant derived biomasses,[49-51] or by non-biomaterials, e.g.: fly ash, carbon slurry, red mud, kaolinite, baggage fly ash, bentonite, electric furnace slag, and montmorillonite.[52-55] Physical and/or chemical reactions are not fast for the heavy metals removal processes but easy to commercialization and application. However, physical and/or chemical reactions-based methods have unacceptable defects, such as: high costs and energy consumption, secondary pollution, and/or production of large amounts of toxic chemical sludge which is difficult to treat. Relatively, adsorption methods have an advantage over physical and/or chemical methods because of low costs and energy demands, and particularly due to no secondary pollution.[56]

Adsorption processes are very important for the removal of toxic metals from aqueous solutions due to their high efficiency in a wide range of metal ion concentrations, as well as easy handling under working conditions; one should also point out the selectivity and rapidity of these methods.[57-59] However, the choice of an appropriate adsorbent is crucial for the achievement of full recovery of metal ions.[60] The commonly used adsorbents are: activated carbon, alumina, silica and ferric oxide, and they generally have high metal adsorption capacity. However, they are expensive and difficult to be separated from the wastewater after use.[15] Most of traditional sorbents do not lead to satisfactory treatment effectiveness with respect to their operational costs and binding capacities. Though they are easily available and inexpensive, the agricultural by-products usually have poor binding capacities and insufficient stability. Consequently, the development of real time applicable adsorbents for the effective removal of metal ions from aqueous environments is of particular concern.[57]

An adsorbent must have by definition high internal volume accessible to the components being removed from the solvent. Surface area, particularly the internal surface area, pore size distribution and the nature of the pores markedly influence the type of adsorption processes. It is also important that the adsorbent has good mechanical properties, such as strength and resistance to destruction, and that the adsorbent particles are of appropriate size and form. The chemical properties of the adsorbent, namely: degree of ionization at the surface, types of functional groups present, and the degree to which these properties change in contact with the solution, are important considerations in determining the adsorption capacity of a given material. The presence of active functional groups on the adsorbent surface allows chemical interactions to occur that usually produce effects different from and less reversible than physical adsorption.[61]

In the recent years, this has prompted a growing research interest into the modification and impregnation of a solid phase to increase the surface adsorption capacity and enhance the removal efficiency of the adsorbent.[60,62] One of the most common, easy, simple and even accessible routes for modification of solid sorbents is their surface impregnation by various chelating agents through a physical pathway.[63] One of these sorbents are novel types of resins incorporating macrocyclic ligands (Fig. 1), e.g. Amberlite XAD-4 impregnated with calixarene derivatives. Amberlite XAD-4 is a cross-linked polymer, which has excellent adsorptive properties for neutral small molecules onto its macroreticular structure and a higher surface area. These structures provide excellent chemical, physical and thermal stability.[64] The feasibility that it offers for surface modification has led to its wide ranging development as a selective sorbent. The modification of Amberlite XAD-4 with calixarenes results in the high capacity and selectivity of the impregnated resins. The extractant is retained in the micropores of an inert polymer without any chemical bonds onto the polymer matrix, and the properties of the impregnated extractant are responsible for adsorption of a novel resin.[65] The unique features of impregnated resins, such as high capacity and selectivity, are associated with metal ion properties including soft hardness, hydrated ionic radii, hydration energies, electronegativity, stability constants of metal-ion hydroxides and complexation constants.[46] The impregnated resin may be used to recover the particular targeted metal from the industrial effluents for reuse, but also to restore the original state of contaminated sites.

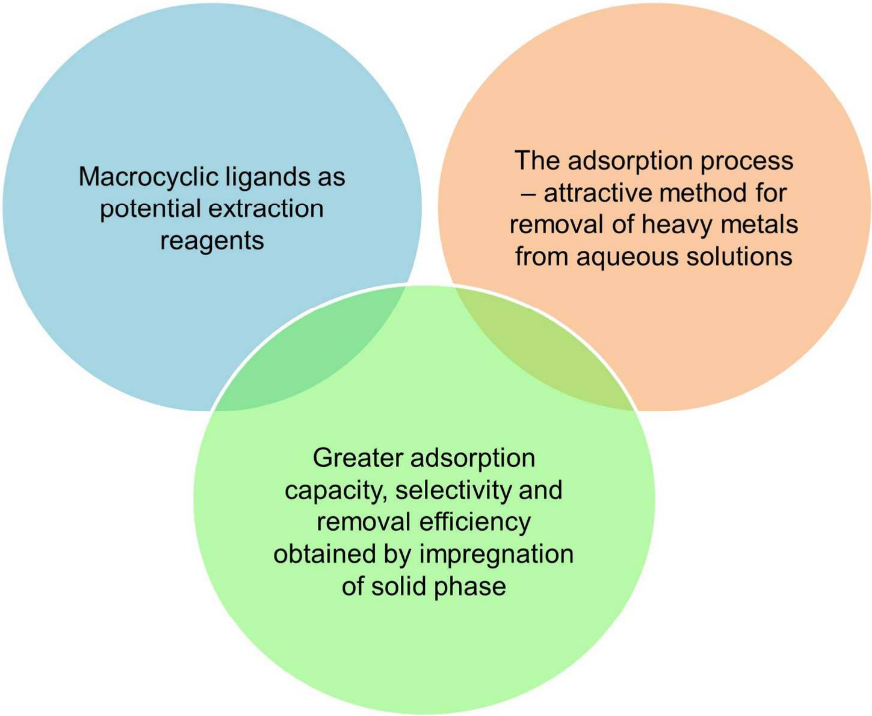

Fig. 1. The concept of novel sorbents - resins impregnated with macrocyclic ligands

Biosorption can be defined as the passive uptake of pollutants by dead or inactive biological materials through different physicochemical mechanisms.[66] Mechanisms of metal removal from waste streams usually include physical adsorption, ion exchange, chelation, complexation, and micro-precipitation.[67] Since biosorption involves a variety of metabolism-independent processes taking place essentially in the cell wall, the mechanisms responsible for the metal binding differ according to the biomass type. Biosorbents that are commonly used for the removal of metal ions from aquatic solutions include algae (fresh and marine), fungi, bacteria, industrial wastes, agricultural wastes and other polysaccharide materials. These biosorbents show good removal efficiency toward different metal ions: Pb, Cr, Ni, Zn, Cu, Hg and Cd.[68]

All microbial biomasses require immobilization to be employed in continuous biosorption applications. Microbial biomasses are basically small particles, with low density, poor mechanical strength and little rigidity. Even though these biosorbents possess high biosorption capacity, rapid equilibrium attainment, good particle mass transfer, they often suffer from various drawbacks, such as: biomass swelling, solid-liquid separation problems, difficulty to regenerate/reuse and development of high pressure drop when used in the column mode.[66,68] To overcome these defects, immobilization techniques for microbial biomasses have been developed.[68] Most researches on immobilization techniques-based metal removal from the solutions that have been conducted were based on the use of granulized microbial adsorbents packed in columns.[69] This approach seems to be inapplicable to metal removal by free cells because the resulting bed is easily plugged.[56] Therefore, when microbial biomass is immobilized in a polymeric matrix as a bio-carrier, its presence confers high resistance to chemical environments and also provides additional advantages, such as efficient regeneration and easy separation from solution.[70,71] The selection of an optimal immobilization matrix in a biocarrier is vital to the environmental application of immobilized biomass as bio-sorbent because the polymeric matrix determines the mechanical strength, rigidity and porosity characteristics of the bio-carrier.[72] By now, numbers of immobilization matrices have been developed and used, such as: sodium or calcium alginate, polysulfone, polyacrylamide, polyurethane and silica.[66] Even so, immobilization techniques specific to bacterial species are required not only because of bacterial species diversity[73] but also owing to difference in the nature of immobilization matrices.[56] Various polymeric materials, such as: polysulfone, alginate, polyacrylamide and polyvinyl alcohol, have been used as immobilized matrixes for bio-sorption.[68]

2.2. Membrane separation processes

Membrane processes provide a viable alternative for heavy metal removal, as they can achieve high permeate fluxes and high rejection coefficients at low energy costs and under mild conditions.[45] Renou *et al*.[48] reported that the use of membrane technologies in leachate treatment plants has shown to be an indispensable means to achieve purification. This technology can be used either as a main step in the landfill leachate treatment plant, or as a single post-treatment step. Moreover, the use of membrane technology separation can be carried out continuously, and membrane processes can easily be combined with other separation processes (hybrid processing).[45]

Liquid membranes (LMs) play an important role in science and technology, and many efforts are being made for development of these kind of membranes. They include: bulk liquid membranes (BLMs), emulsion liquid membranes (ELMs) and supported liquid membranes (SLMs)[74] (Fig. 2). Polymer inclusion membranes (PIMs) are being developed as an alternative of SLMs. In recent years membrane based processes have gained much attention in separation science. The chemical and physical properties of membrane polymers can be tailor made for specific applications. It is difficult to obtain membranes which serve well for the particular purpose, hence, for specific chemical sensors they have to be synthesized according to the requirements of the researcher. Two routes for the preparation of the membranes inlude physical and covalent immobilization of required components in the polymer matrix.[75]

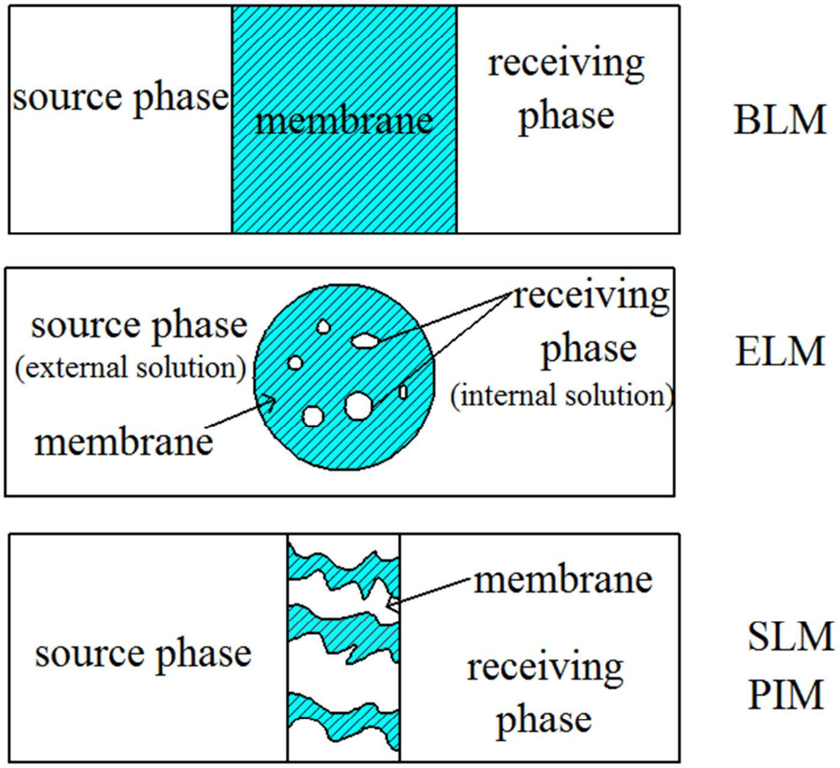

Fig. 2. The types of liquid membranes

PIMs are a class of liquid membranes used on a large scale as chemical sensors. These membranes are easy to prepare and have reasonably good optical and electrical properties. They are prepared by the physical immobilization of a receptor and an indicator in the plasticized polymer matrix. The stability of these membranes depends on their hydrophobicity. The composition of these membranes does not require any synthetic chemistry and, therefore they can be varied according to the requirements. PIMs are prepared by casting a solution containing an extractant, a plasticizer and a base polymer, such as: casting cellulose triacetate (CTA) or polyvinyl chloride (PVC) to form a thin flexible and stable film. The resulting self-supporting film can be used to selectively separate the solutes of interest in a similar way to that of SLMs. The PIMs have most of the advantages of the SLMs while exhibiting good stability and versatility. In contrast to a SLM, it is possible to prepare a PIM with a negligible carrier loss during the membrane extraction process. The amount of the carrier extractant can be greatly reduced allowing the use of more expensive materials.[76,77]

The base polymer plays a crucial role in providing mechanical strength to the membranes and enhances the membrane stability, and at the same time it creates minimum hindrance to the transport of metal ions and small organic compounds within the membrane. Polymers that make up the skeleton of the membrane are thermoplastic. They consist of linear polymer strands and because there is no crosslinking connection between these strands, they can be dissolved in a suitable organic solvent, where the polymer strands get separated. PVC and CTA are such base polymers used for most of the PIMs preparations. Also the feasibility of several cellulose derivatives, like cellulose acetate propionate (CAP) and cellulose tributyrate (CTB) as base polymers in PIMs have been recently studied.[78] PVC and CTA can be used to prepare a thin film with a relatively simple procedure based on its dissolution in an organic solvent. CTA is a polar polymer with a number of hydroxyl and acetyl groups that are capable of forming a highly oriented hydrogen bonding. PVC is an amorphous polymer with a small degree of crystallinity whereas CTA is often highly crystalline. CTA can be slightly hydrated while PVC cannot. The hydration characteristics of CTA and other cellulose derivatives make them able to hydrolysis in an acidic medium. The bulk properties of base polymers govern the metal ion transport through a membrane.[77,79]

The glass transition temperature (Tg) of an amorphous polymer and the melting point of a crystalline polymer (Tm) are used to characterize the inherent polymer flexibility and to investigate its micro structural characteristics. Both amorphous and crystalline domains exist in any thermoplastic polymer. Below the glass transition temperature (Tg) the polymer is rigid and glassy and individual polymer strands are unable to change their conformations. Since this condition is unfavourable for metal ion transport in the membranes, plasticizers are often added to the polymer to lower its Tg value and create more flexible and less brittle membranes.[79]

The individual molecular chains in a PIM are held together by a combination of various types of attractive forces. Amongst them, Van der Waals forces are abundant but are weak and non-specific, while polar interactions are much stronger but can only occur at polar centers of the molecules.[80] The polar interactions result in a rigid non-flexible thin film with a 3-D structure within its polymeric matrix. This 3-D structural rigidity is unfavorable for a diffusive flux of material within the polymer matrix. Consequently, plasticizers are used to increase the metal species flux as well as membrane softness and flexibility. The role of a plasticizer is to penetrate between polymer molecules and neutralize the polar group of the polymer with its own polar groups, or merely to increase the distance between the polar molecules and to reduce the strength of the intermolecular forces. Some of the commonly used plasticizers in PIMs are: di-octylphthalane (DOP), 2-nitrophenyl- octyl ether (2-NPOPE), di-octyl terephthalate (DOT), di-octyl phthalate (DOP), tris-(2-ethylhexyl)phosphate (T2EHP).[81] Plasticizers are generally organic compounds containing a hydrophobic background with one or several highly solvating polar groups. The former governs the compatibility of the plasticizer with the membrane, while the latter interacts with the polar groups of the base polymers and neutralizes them. The essential properties required for a good plasticizer are: good compatibility with the base polymer, low volatility, low viscosity, high dielectric constant, good resistance to migration from the base polymer, and low costs and toxicity.[81,82]

Transport in PIMs is done by a carrier that is essentially a complexing agent or an ion exchanger. The complex or ion pair formed between the metal ion and the carrier is stabilized in the membrane and facilitates the metal ion transport across the membrane. When the carrier used in the membrane phase is in an uncharged form, the transported ionic substance can be extracted only as an ion pair, which is formed by adding to the feed phase a counterion or chelating agent. The carrier reacts with such a neutral ion pair giving a complex which is transported through the membrane. The concentration gradient of cotransported compound is the driving force in this type of transport. The ionic substances and their co-unterions are transported in the same directions and their fluxes are stoichiometrically coupled (Fig. 3 a). Many permanently charged compounds, especially metal ions can also be efficiently transported through PIM membranes by ionic carriers. In these cases, a gradient of counterions from the strip (receiving) phase to the feed (source) phase provides the driving force for the transport. Therefore, the metal carrier complex is transported through the membrane from the feed to the strip phase, and the counterions are transported in the opposite direction (Fig. 3 b).[83]

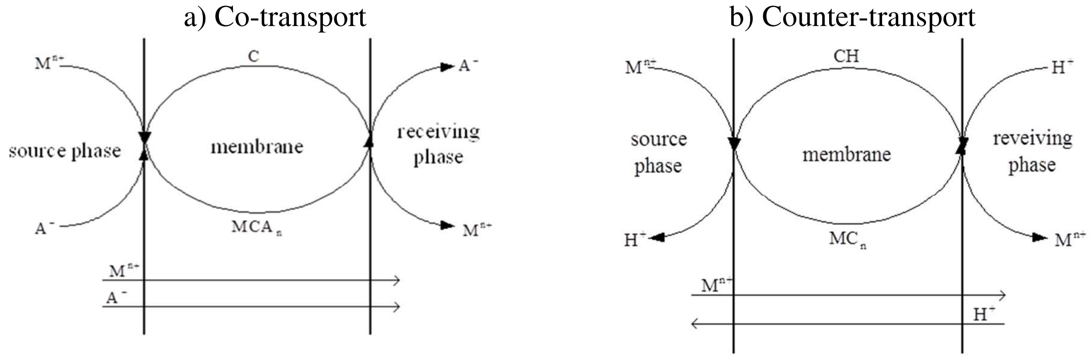
a) Co-transport
b) Counter-transport

Fig. 3. Transport mechanisms through PIMs

Various solvent extraction agents, namely: acidic, basic, chelating, neutral or solvating, macrocyclic and macromolecular have been used in PIMs[75] (Table 1). Some of the examples of carriers are: quaternary amines like Aliquat 336, tertiary amines, pyridine and their derivatives, acidic and chelating agents like hydroxyoximes, hydroxyquinoline, β-diketones, alkyl phosphoric acids and carboxylic acids. Different types of carriers exhibit considerably different transport efficiencies because of differences in their complexation mechanism. The molecular structure of the carrier and the chemistry involved in the complexation and transport processes are the most important factors governing the membrane selectivity. It has been shown that the carrier molecular structure can be tailored to achieve a specific selectivity.[84,85]

Table 1. Examples of PIM carriers reported in the literature for transport of various metal ions

Type of carriers	**Examples**	**Target metal ions**	**References**
Basic			
Quaternary amines	Aliquat 336	Au(III), Cd(II)	86,87
Tertiary amines	TOA, other tri-alkyl-amines	Cr(VI), Zn(II), Cd(II)	88,80
Pyridine and derivatives	TDPNO	Cr(VI), Zn(II), Cd(II)	89
Acidic and chelating			
Hydroxyoximes	LIX 84	Cu(II)	90
Hydroxyquinoline	Kelex 100	Cd(II)	91
B-Diketones	Benzolyacetone	Sc(III), Y(III)	92
Alkyl phosphoric acids	D2EHPA, D2EHDTPA	Hg(II), Ag(I)	93

Neutral solvating Phosphoric acid esters	DBBP	As(III)	94
Macrocyclic	Calix[4]azacrown ethers Diazadibenzocrown ethers B-cyclodextrin polymers	Ag(I) Pb(II) Cu(II)	95 96 97

The membrane is prepared by the optimization of analyte specific components, i.e. the polymer matrix, the extractant and the plasticizer with a desirable texture and thickness. The optimized membrane is then equilibrated with the solution of the target analyte for an experimentally determined equilibration time. The prepared membrane is used to separate source and receiving aqueous phases, but it does not contain an organic solvent to facilitate the transport of ions or molecules through PIMs.[98]

The PIM separation processes can be an attractive alternative for the removal of metal ions from waste streams with a very high efficiency. In these membrane systems the driving force are extraction and re-extraction processes which occur simultaneously in both interfaces of membranes.[75] PIMs combine the advantages of higher selectivity with increased stability, because the ion carrier is immobilized in the solid polymer matrix which is responsible for membrane stability, while the addition of plasticizer significantly facilitates the permeation of metal ions.[77] Moreover, mechanical properties of PIMs are quite similar to those of filtration membranes, thus enable PIM-based systems to exhibit many advantages, such as: the ease of operation, minimum use of hazardous chemicals and flexibility in membrane composition, to achieve the desired selectivity and separation efficiency.[74,76]

3. Current status of application of immobilized materials for the removal of toxic metal ions from waste streams and impacts of various process parameters on the removal efficiency

There are diverse immobilized materials for the removal of toxic metal ions (Pb, As, Cd and Hg) from surface/groundwaters and aqueous waste streams, which include: impregnated resins and other solid phases, biomass immobilized in a matrix as bio-carriers and immobilized membranes (Fig. 4).

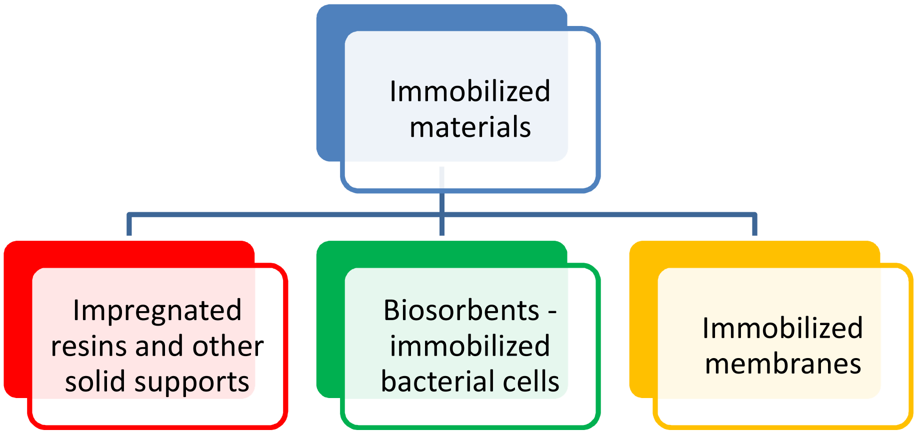

Fig. 4. Immobilized materials used for the removal of toxic metal ions from aqueous solutions

Surface modification of Amberlite XAD resin is an easy and economical choice for the separation of toxic metal ions from aqueous solutions (Fig. 5).[63] Calixarenes and their derivatives are a new generation of highly selective carriers for heavy metal and transition ions. Calixarenes are important macrocyclic compounds with high thermal stability and are known as interesting building blocks for the recognition of metal ions. An immense interest of researchers in these macrocyclic compounds is because of their easy synthesis, high yield, and functionalization of their aromatic core (narrow or wide rim) with different functional groups.[99]

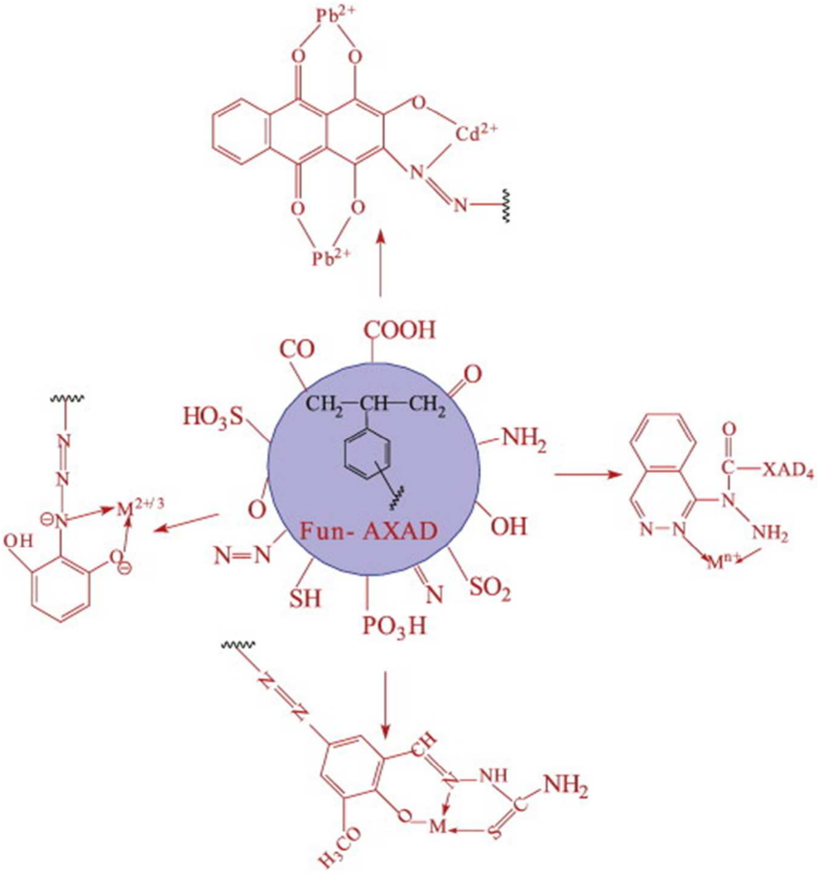

Fig. 5. Co-ordination of heavy metals with the functionalized Amberlite XAD resin. Reprinted from ref. 63 with permission from Elsevier.

Incorporation of calixarene based ionophores onto synthetic resins offers promising solution to the sorption technology. It is an emerging area of research, which involves impregnation or immobilization through physical adsorption or covalent linkage of calixarene derivatives onto the framework of resin. These polymeric materials act as efficient adsorbents for toxic metals. Calixarenes appended resins are highly selective, thermally stable and have of regeneration ability.[99,100] Adhikari *et al.*[58] reported high Pb(II) loading capacity of the polyvinylcalix[4]arenetetraacetic acid resin due to high content of calixarene units per weight of the resin. Moreover, they observed that the resin was regenerated with no physical/chemical damage making it industrially useful in routine operations for the adsorptive removal of trace amounts of Pb(II). The calix[6]arene-based cation exchange resin was highly efficient for the selective and quantitative removal of Pb from aqueous environments.[57] In turn, the p-tert-butylcalix[8]areneoctamide impregnated Amberlite XAD-4 resin exhibited excellent sorption properties toward Cr(VI)[64] and As(V).[101] It was highly effective for the removal of As(V) from aqueous solutions at a wide range of pH, i.e. from pH 4 to pH 8, and attained a maximum value, i.e. 99% at pH 4. Application of this resin to real (environmental) samples indicated only a slight decrease (5-7%) in As(V) removal efficiency, so even high concentration of total dissolved salts (TDS) did not affect the performance of this sorbent.[101] The calix[4]arene appended resins have also an ability to sorb As(III) directly (up to 97%) without transformation to As(V), and are capable of removing up to 95% of As(V). Another important feature is that resins are regenerable with only 2 to 3% loss in sorption capacity; this property makes the sorption process more economical in term of costs, as well as material and energy demands.[102]

Zawierucha *et al.*[103] noted that the carboxypheny[l]resorcinarene impregnated resin had remarkable efficiency for the sorption of Pb(II) from aqueous solutions; it was optimal at pH 6.5, at contact time of 60 min., and at initial Pb(II) concentration equal to 10 mg L^{-1}. The sorption capacity for Pb(II) in the batch system was of 107.6 mg g^{-1}, i.e. 99.7%.of the initial concentration in the solution. Application of sorption models to the experimental data revealed that physisorption was the mechanism of adsorption of metal ions onto resorcinarene impregnated resin. The column test confirmed these results and showed that the total uptake of Pb(II) was of 104.4 mg g^{-1}. The carboxypheny[l]resorcinarene derivative impregnated resin was efficient and easily regenerative, thus can be used several times. Higher selectivity towards the target ion due to size-match complementarity effect and high metal uptake capacity of the resin immobilized with macrocyclic ligand make it easier to separate Pb(II) ions from wastewater than traditional sorbents.[57] The uptake of Pb(II) ions with resorcinarene derivative in the resin is facilitated by the participation of hydroxyl groups towards metal binding, coupled with inclusion complexation via macrocyclic ring.[99] Therefore, the resins impregnated with calixarenes derivatives hold a tremendous promise for processing of toxic metal ions bearing effluents and cleansing of contaminated groundwater.

The adsorption capacities of the thiacalix[4]arene-loaded resin toward Cu(II), Pb(II) and Cd(II) ions were investigated by Hu *et al.*[104] They found that the selective adsorption capacities of the thiacalix[4]arene-loaded resin were mainly attributed to the complex of the loaded thiacalix[4]arene with heavy metal ions. The pH value of the aqueous solution was the most important variable governing the adsorption capacity of adsorbent for heavy metal ions. The removal efficiency of three heavy metal ions increased sharply along with the increase of the solution pH from 2 to 7, and reached 94% at $pH \geq 6$. This indicates that the heavy metal ions adsorption capacity of the thiacalix[4]arene-loaded resin in weak acidic or neutral solutions is better than in strong acidic solutions.

The complementary system for the removal of toxic metal ions from industrial landfill leachate using immobilized materials was proposed by Zawierucha *et al.*[105] They observed that in the first step, toxic metal ions were effectively removed by transport through PIMs with the alkyl(aliphatic) resorcinarene derivative 1 as an ionic carrier into 0.1 M HNO_3 as a receiving phase. The optimal PIMs content was of: 25, 15 and 60% wt. of cellulose triacetate as the support, resorcinarene 1 as the ionic carrier and o-nitrophenylpentyl ether as the plasticizer, respectively. The Pb(II) concentration was reduced in the source aqueous phase from 11.2 to 1.2 mg L^{-1} by transport across the PIM after 3 hours of the process. Competitive transport of Pb(II), Cd(II) and Zn(II) from the leachate through PIMs with resorcinarene 1 was efficient for Pb(II), with the recovery factor of 89% at the source/receiving phase volume ratio of 10: 1. In the second step, the use of resin impregnated with resorcinarene 1 allowed for further decline of metal ions concentrations in the leachate. Passing of pre-treated landfill leachate through the column filled with the impregnated resin reduced concentrations of Pb(II), Cd(II) and Zn(II) ions by 95, 75 and 40%, respectively. The authors postulated that resorcinarene 1 was effective in sorption of Pb(II) from landfill leachate due to the larger surface area provided by the framework of the Amberlite resin to the ligand for interaction with Pb(II) ions. Moreover, they noted that the impregnated resin was regenerable and could be used several times. The reported overall removal efficiency of heavy metals from the landfill leachate by the system based on immobilized materials was of 99%, 88 and 55% for Pb(II), Cd(II) and Zn(II) ions, respectively. Moreover, the contents of metal ions in the leachate after treatment was below the permissible limits in wastewater according to the Polish Standards.[105]

Immobilizing Cyphos® IL-101 in Amberlite XAD-7 allowed preparing the resin that was very efficient for Cd(II) binding in acidic solutions.[106] In this case it was observed that the presence of metal cations affected Cd(II) sorption only when the competitor metal formed anionic species that can compete with chloroanionic cadmium species. Moreover, it was noted that Cd(II) desorption and resin recycling can be performed using nitric acid (0.1 M) with sorption and desorption performances maintained for at least five cycles.

The removal of Pb(II) from aqueous solutions using a novel extractant-impregnated resin (EIR) - gallocyanine-impregnated XAD-16 (GCN/XAD-16) - was studied by Hosseini-Bandegharaei *et al.*[107] They noted that the removal process was highly pH dependent and best results were obtained at narrow pH range of 7–7.5. The equilibrium between the Pb(II) ion in the solution and on the EIR surface was practically achieved within 65 minutes. The maximum adsorption capacity of GCN/XAD-16 for the removal of Pb(II) from aqueous solutions was of 367.92 mg g^{-1} at 25°C. Adsorption of Pb(II) onto the EIR was favorably influenced by an increase of temperature during the process. The adsorbent has a very good reusability and thus the EIR could be successfully recycled for several consecutive cycles without significant loss in its adsorption capacity.

Another extractant-impregnated resin, 1-(2-thiazolylazo)-2-naphtol (TAN) impregnated Amberlite XAD-4 resin, was studied by Hosseini-Bandegharaei *et al.*[108] for the removal of Hg(II) from aqueous solutions. The influences of various experimental parameters (pH, initial concentration, EIR dosage, contact time and temperature) were evaluated. Optimum conditions for the Hg(II) removal were: pH range of 5–6, EIR dosage: 0.5 g L^{-1} and equilibrium time of 55 minutes. The maximum sorption capacity of the EIR for Hg(II) ions in terms of monolayer sorption was of 450.45 mg g^{-1} at 25°C. The removal process was highly pH dependent and best results were obtained at a narrow pH range of 5–6. An increase in mass of adsorbent led to higher Hg(II) ion sorption due to the increased number of chelating ion exchange sites. The complete removal of Hg(II) from aqueous solutions (initial concentration of 100 mg L^{-1}) was achieved by using a minimum of 0.5 g L^{-1} of the EIR and at the contact time of 55 minutes. Higher temperature also increased the sorption of Hg(II). Moreover, the resin could be successfully recycled for several consecutive cycles without any significant loss in its sorption capacity. The maximum sorption capacity of TAN/XAD-4 for the removal of Hg(II) from aqueous solution was of 450.45 mg g^{-1}.

The range of materials used as solid supports for impregnation/immobilization for treating water contaminated with toxic metals ions has been truly limitless. Besides Amberlite XAD resins, the other materials discussed below have been reported as good solids for preparing novel surface modified adsorbents.

Wang *et al.*[109] investigated magnetic nanoparticles impregnated chitosan beads (MICB) for the uptake capacity of arsenic in batch studies. The maximum capacity of the MICB was calculated as 35.7 and 35.3 mg g^{-1} for As(V) and As(III), respectively at pH 6.8, which was reasonably good compared with other granular adsorbents. A distinct advantage of this adsorbent was that it could readily be isolated from solutions by application of an external magnetic field. The study of adsorption mechanism indicated that the hydroxyl groups on the adsorbent surface were involved in arsenic adsorption. The MICB could retain about 88.2 and 76.02% of the original adsorption capacity for As(V) and As(III), respectively, after 5 cycles of reuse. Moreover, the adsorbent showed an excellent arsenic removal performance for real groundwater (i.e. the natural water samples from Tuoketuo County in Inner Mongolia of China). A field application of this adsorbent demonstrated that the initial As concentration in groundwater of 0.103 mg L^{-1} could be decreased to below 0.05 mg L^{-1} without any pre-treatment within 60 minutes and, reduced further to less than 0.01 mg L^{-1} after 5 hours using the adsorbent dose of 1 g L^{-1}. As a result, over 96% of As was removed, and the effluent quality met the guideline limit in drinking water regulated by the WHO.

Mondal *et al.*[110] explored the possibility of the ferric chloride impregnated granular activated carbon (GAC-Fe) to remove As species in presence of iron and manganese ions which are available frequently in groundwater. They observed that using GAC-Fe (8 g L^{-1}) the As concentration in the treated water was reduced below 10 and 50 μg L^{-1} from the maximum initial value of 200 and 520 μg L^{-1}, respectively. The capacity of GAC-Fe for the removal of As(III) and As(V) from the treated water is approximately seven and four times higher than that of GAC, respectively. Moreover, they observed that the effect of adsorbent particle size on the removal of As and Fe was negligible while for Mn it was significant, which may indicate the dominating role of physical adsorption over the electrostatic attraction (chemical adsorption) in the case of Mn removal.

The nano-sized-iron oxide-immobilized-sand (INS) was obtained by Lee *et al.*[111] and employed for the low level removal of Cu(II), Cd(II) and Pb(II) from wastewater. The authors observed that an increase of pH, increased the uptake of these ions, whereas an increase of the concentrations (1–20 mg L^{-1} for Cu(II) and Cd(II), and 1–50 mg L^{-1} for Pb(II)) caused a drop of the uptake of these metal cations. Moreover, a 1000 times increase of the background electrolyte concentration (from 0.001 to 1 mol L^{-1} $NaNO_3$) resulted in a significant decrease of the Cd(II) and Pb(II) removal, whereas Cu(II) was almost unaffected with this increase. These results implied that the sorption of copper follows the 'ion-exchange' along with the inner-sphere surface complexation, while Cd(II) and Pb(II) sorption is presumably proceeded with ion-exchange along with the electrostatic attraction by the solid surface. The INS sorption capacity in a batch mode was of 1.2649, 0.5282 and 2.0877 mg g^{-1} for Cu(II), Cd(II) and Pb(II), respectively. In turn, this capacity in a column was of 5.81, 7.13 and 11.30 mg g^{-1} for Cu(II), Cd(II) and Pb(II), respectively. It was shown that the INS could be considered as one of the efficient material of potential application in the remediation of wastewater contaminated with heavy metal toxic ions, like Cu(II), Cd(II) and Pb(II).

Papain has been immobilized on activated charcoal through a physical adsorption process by Dutta *et al.*[112] and used for the removal of Hg from wastewater. To assess the removal efficiency of the charcoal-immobilized papain (CIP), the simulated solution of mercuric chloride were contacted with the CIP in a batch mode of operation. They achieved the highest removal efficiency of about 99.4% at the initial Hg concentration of 20.0 mg L^{-1}, mass of the CIP 0.03 g and pH 7 within 2 minutes. They also noted that with same amount (0.0014 g) of raw activated charcoal and CIP at initial concentration of mercury = 15 mg L^{-1} and pH= 7), the Hg removal by the CIP is much higher (72.0%) compared to that removed by raw activated charcoal (30.3%). This confirms the chemical binding of Hg with papain immobilized on activated charcoal in the case of CIP while physical adsorption is the sole characteristics of raw activated charcoal. Thus, it can be stated that papain, having the characteristics of metal binding due to presence of four sulfhydryl groups in its active sites, can be used to modify the free matter space of activated charcoal, a micro-porous solid matrix, and thereby increasing the number of active sites of charcoal for the removal of Hg from industrial wastewater streams.

Within the current decade, many research works have focused on the development of biological based materials – biosorbents, including immobilized systems of bacterial cells that are discussed below.

Podder and Majumder[113] investigated the removal of arsenic (As(III) or As(V)) from industrial wastewaters using *Bacillus arsenicus* MTCC 4380 immobilized on a sawdust/$MnFe_2O_4$ composite bed in a bio-column reactor. They noted that a longer bed column extended its life span with a maximum capacity of 87.573 and 88.990 mg g^{-1} for the As(III) and As(V), respectively. The total removal efficiency of As(III) and As(V) also increased with the increase of the biosorbent bed height. For the following process parameters: flow rate of 251.2 mL h^{-1}; the As(III)/As(V) initial concentration of 2000 mg L^{-1}; particle size of 1.18 mm; pH of 7.0; temperature of 30°C, they reported the removal efficiency of 66.3% (As(III)) and 67.4% (As(V)) In turn, the breakthrough time and the exhaustion time were reduced by 9% and 14%, respectively, in the case of presence of co-existing ions (Cu(II), Zn(II), SO_4(II), Fe(III), Cd(II), Bi(III), Pb(II), Co(II), Ni(II) and Cr(VI)) through biosorption of As.

Sorption of heavy metals ions by the immobilized *Trichoderma viride* biomass in a packed-bed column was also studied by Kumar *et al.*[114] The fungal biomass was immobilized to Ca-alginate and used for the removal of Cr(VI), Ni(II) and Zn(II) ions from synthetic solutions and electroplating effluents. The sorption capacity of Cr(VI), Ni(II) and Zn(II) ions increased with the increasing flow rate, bed height and initial metal ions concentrations. Moreover, any significant alteration in the sorption capacity was observed after five sorption-desorption cycles.

Ahmad *et al.*[115] investigated immobilized *Bacillus subtilis* beads (IBSB) for the removal of Cd(II) ions from the aqueous solution. They observed the equilibrium biosorption capacity of IBSB of 251.91 mg g^{-1} at the optimum pH of 5.91, temperature of 45°C and equilibrium time of 3 hours for an initial Cd(II) concentration of 496.23 mg L^{-1}. Moreover, successful regeneration of IBSB for five times were achieved using 0.1 M HCl that indicates the potential of this biosorbent for industrial use.

The potential of a novel biosorbent (silicon dioxide nanopowder-combined-heat inactivated *Aspergillus ustus*) to remove Cd(II) from tap and sea water samples was examined by Mahmoud *et al.*[116] The identified extraction of Cd(II) from the tap water sample was of 97.7% based on twice passages through micro-columns in multi-step treatment system. The same procedure was also followed for the sea water sample leading to the removal of 97.0%. In addition, Cd sorption capacity of this biosorbent significantly increased with the pH increase, and relatively decreased in presence of interfering ions.

Batch, column and pilot scale feasibility experiments for a biosorption process using dead *Bacillus drentensis* sp. immobilized in polysulfone polymer were performed by Kim *et* *al.*[72] to remove heavy metals (Pb(II) and Cu(II)) from groundwater originating from AMD. For batch experiments, more than 92% reduction of the initial Pb(II) and Cu(II) concentrations (10 mg/L at pH=3) was observed when 2 g of bio-carrier containing 5% of biomass were used. For a continuous experiment with a column (L = 1 m; D = 0.02 m) packed with this biosorbent, more than 98% of Pb(II) removal efficiency was maintained for the 36 pore volumes exchange; and 1.553 g of Pb(II) per g of biosorbent was removed. In total, 80 tons of groundwater (pH < 4) were successfully treated during the pilot-scale feasibility test (Fig. 6) within 40 working days with the removal efficiencies of Cu(II), Cd(II), Zn(II), and Fe(III) maintained above 93%, indicating that under field conditions one kg of the biosorbent can clean up at least 1098 L of contaminated groundwater.

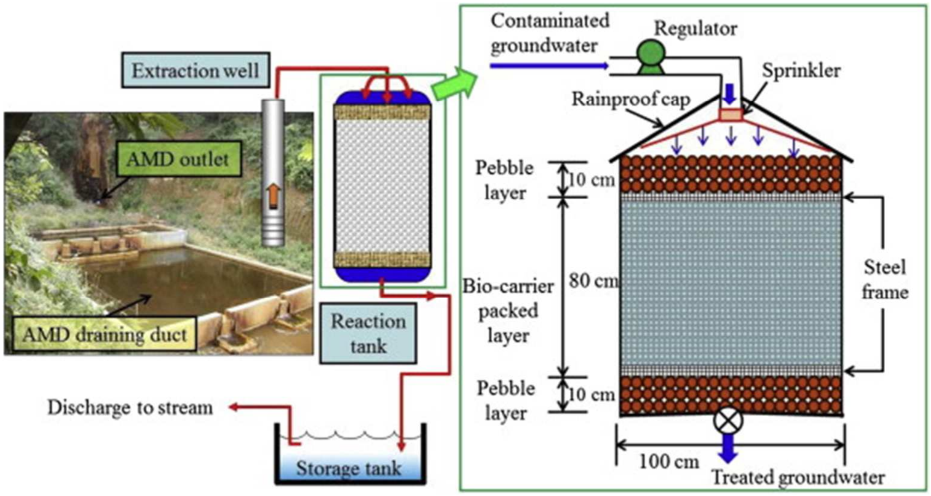

Fig. 6. Schematic of the pilot scale feasibility study. Reprinted from ref. 72 with permission from Elsevier.

In metal ions removal processes, desorption/regeneration of adsorbents is one of the essential aspects as it controls the economy of water treatment technology.[117] For effective regeneration of adsorbents and metal recovery, acids (such as: HCl, H_2SO_4, HNO_3, HCOOH and CH_3COOH), alkalis (NaOH, $NaHCO_3$, Na_2CO_3, KOH and K_2CO_3), salts (NaCl, KCl, $(NH_4)_2SO_4$, $CaCl_2 \cdot 2H_2O$, NH_4NO_3, KNO_3 and $C_6H_5Na_3O_7 \cdot 2H_2O$), deionized water, chelating agents and buffer solutions (such as: bicarbonate, phosphate and tris) were used in various studies.[118] Table 2 presents desorption of studied toxic metal ions (Pb, As, Cd and Hg) from immobilized sorbents.

Table 2. Recovery of metal ions from metal-loaded immobilized sorbents

Metal	**Sorbent**	**Eluent (desorbing/ regenerating agent)**	**Number of sorption/desorption cycles**	**Recovery (%)**	**References**
Pb	gallocyanine-impregnated XAD-16	0.5M HCl	25	98	107
Pb	the polyvinyl-calix[4]arenetetraacetic acid resin	1M HNO_3	5	100	58
Pb	methylene crosslinked calix[6]arene hexacaarboxylic acid resin	2M HCl	5	> 90	57
Pb	alkyl(aliphatic) resorcinarene impregnated resin	1 M HCl	15	>98	105
Hg	TAN impregnated Amberlite XAD-4 resin	0.5 M HCl	25	>99	108
As	magnetic nanoparticles impregnated chitosan beads	0.1 M NaOH	5	>80%	109
As	*Bacillus arsenicus* MTCC 4380 immobilized on a sawdust/$MnFe_2O_4$	0.05 M NaOH	3	>51%	113
Cd	Cyphos IL 101 impregnated Amberlite XAD-7 resin	0.1 M HNO_3	5	>99	106
Cd	immobilized *Bacillus subtilis* beads	0.1 M HCl	5	98	115

Desorption of toxic metal ions in acidic media (HCl and HNO_3 solution) appeared to be rapid and higher than in basic media.[119] However, the alkaline solution (NaOH) is recommended as the best desorbent for arsenic removal.[118] Zhou and Haynes[120] reported the possible mechanisms and conditions of desorption by acids: (i) low pH favors desorption and/or dissolution of metal cations, (ii) strong competition between H^+ ions and metal cations for adsorption sites causes displacement of cations into the acid solution, (iii) acidic condition favors dissolution of Fe and Al oxide/silicate adsorption surfaces and thus the release of adsorbed/surface-precipitated metals, and (iv) acid reacts with residual alkalinity and lowers adsorption capacity.

Desorption of the adsorbed metals with a suitable acid or base results in the regeneration of sorbents and the recovery of metals. When regeneration is economically not feasible, the adsorbent needs to be discharged after a single use.[121]

Adsorbents spent for oxyanion forming elements and heavy metals are classified as hazardous materials. The main disposal strategies for spent adsorbents are either incineration or landfilling.[122] Incineration is mainly used for carbonaceous adsorbents, so landfilling is the preferred option for most adsorbents. The toxic characteristics of metal ions require solidification/stabilization of the adsorbent before landfilling. The other valuable alternative is mixing adsorbents loaded with heavy metals with industrial sludge for the production of ceramic materials.[121]

In the case of arsenic-bearing wastes current disposal options include: landfilling, stabilization/solidification, cow dung mixing, passive aeration, pond disposal, and soil disposal. Portland cement/lime mixes are expected to be the most appropriate for wastes from sorptive filters. Portland cement can immobilise soluble arsenites, and it has been successfully used to stabilise As-rich sludges.[123,124]

Immobilized membranes are another type of immobilized materials used for the removal of toxic metal ions from waste stream. There are various ion carriers immobilized in a solid polymer matrix that are involved in the complexation and transport processes of metal ions through membranes.

The modified calixarenes have acceptable complexation-decomplexation dynamics coupled with the possibility of 3-D cation encapsulation by the calixarenes unit and the side arm. In order to achieve an effective transfer of the metal ion in a separation process, the system must have a counter anion that is soluble in both the aqueous and organic phases. However, the distribution coefficients of complexes formed with common anions, such as: chlorides, sulfates or nitrates, between aqueous and organic phases are too low to be useful. Attaching a proton-ionizable sidearm to the calixarene can eliminate the need to transfer aqueous phase anions into the organic phase. Another advantage of proton-ionizable calixarenes as ion carriers in liquid membranes transport processes is coupling of metal ions transport from the aqueous source phase into the aqueous receiving phase with back-transport of a proton. Thus, a pH gradient provides the potential for metal ions transport. A variety of proton ionizablecalixarenes have been synthesized and studied by Sgarlata *et al.*[125] Alpoguz *et al.*[126] studied a co-transport of metal ions (Hg(II), Pb(II), Na(I)) from an aqueous solution into an aqueous receiving phase through the bulk liquid membrane containing calix[4]arene nitrile derivatives as ion carriers. The transport rates showed that both nitrile derivatives were efficient and selective for Hg(II) ions with respect to Na(I) and Pb(II) ions, and the dinitrile derivative was a better carrier than the tetranitrile derivative.

Recently, competitive transports of a mixture of Zn(II), Cd(II) and Pb(II) cations from an aqueous source phase across PIMs with calix[4]crown-6 derivatives as ion carriers, were examined by Ulewicz *et al.*[127] The maximum Pb(II) removal efficiency increased in the following order of R groups attached to the compounds: -OH < $-OCH_3$ < $-OCH_2COOH$ < $OCH_2COOC_2H_5$ < $OCH_2CONHOCH_2C_5H_6$. The thiacalix[4]arene and p-t-butylthiacalix[4]arene were found to be effective ion carriers for transport of Cd(II) and Pb(II) ions across bulk and supported liquid membranes.[128,129]

The transport of Pb(II) has been studied by Aguilar *et al.*[96] who synthesized a series of diazadibenzocrown ethers and found that two of them possessed a high selectivity for Pb(II) over Cd(II) and Zn(II), when using a CTA/2-NPOE membrane. Hydrophilic diazadibenzocrown ethers were reported to have a higher selectivity for Pb(II) over Zn(II) and Cd(II) than the more hydrophobic derivatives. Also, the transport of Pb(II) ions was investigated by Nazarenko and Lamb.[130] They reported high transport fluxes of Pb(II) from nitric solutions across PIMs containing a mixture of dialkylnaphtalenesulfonic acid and bis-tert-butylcyclohexano-18-crown-6 or DC-18-crown-6. Moreover, Lamb and Christenson[131] showed that the permeability for Pb(II) across a membrane containing tBuDC18C6 was constant over a period of 20 days, and that Pb(II)was selectively transported over Na(I).

Shamsipur *et al.*[132] observed that transport of Hg(II) ions into 0.05 M ethylenediaminetetraacetic acid (EDTA) receiving phase at pH 6.0 through a chloroform-tetrathia-12-crown-4 bulk liquid membrane ran with the efficiency of 98%. They also revealed that among a wide variety of tested cations, only Ag(I) ions affect slightly the transport of Hg(II) ions from the mixture of Hg(II), Cd(II), and Ag(I) ions.

The competitive transport of Zn(II), Cd(II) and Pb(II) ions from dilute aqueous solutions across PIMs containing imidazole azacrown ether derivative and ionizable crown ether was extensively studied by Ulewicz *et al*.[133-136] The kind of carriers had an influence on the rate of constant transport of Pb(II), as well as Zn(II) and Cd(II). The selectivity order of metal ion fluxes for azacrown ether and ionizable lariat ether was: Pb(II) > Cd(II) > Zn(II). Using azocrown ethers in the presence of other metal ions, the highest initial fluxes were obtained for Pb(II) ions. Moreover, the acidity of the feed phase and the HCl concentration in the source phase had an influence on the selectivity coefficient value. Pyrrole azacrown ethers in an ordinary bulk membrane system were also found to preferentially transport Pb(II) from an equimolar mixture of Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Ag(I) and Pb(II) ions.[137]

To date a considerable number of studies on PIMs used polyethers. The sizes of the polyether cavities and of the inserted ions are fundamental parameters that make polyethers effective in the selective transport of metal ions across a liquid membrane. A series of polyesters were examined for the transport abilities toward the mixture of Pb(II), Cu(II), Cd(II), Zn(II), and Ni(II) ions by Hayashi *et al.*[138]. They used ionizable polyesters with different alkyl chain lengths (from $-C_7H_{15}$ to $-C_{16}H_{33}$) and found that one of them had a high selectivity for Pb(II). The metal ions were transported across the PIMs in the following sequence: Pb(II)> Cu(II)> Cd(II)> Zn(II)> Ni(II). On the other hand, Lee *et al.*,[139] using lipophilic acyclic polyether dicarboxylic acid, studied the transport of Pb(II), Cu(II), Co(II), Zn(II), and Ni(II) ions across PIMs and BLM. This PIM system exhibited a selective transport of Pb(II)over other transition metal ions.

The PIM systems possess several important advantages concerning the separation aspects, i.e. easy setup, high selectivity and durability. Although the use of macrocyclic compounds is expensive, their application as ion carriers in liquid membranes is more feasible in comparison to liquid extraction, since the smaller amount of reagent is required, and it can be used in repeated transport experiments.[75]

Lead is the most popular toxic metal which is involved in immobilized membrane separation processes. Different carriers were used in the extraction of Pb(II) with various PIMs (Table 3). Lee and Nam[140] were among the first reporting the extraction of Pb(II) by using bis-(2-ethylhexyl)-phosphoric acid (D2EHPA) and dithizone as carriers. In turn Gumi *et al.*[141] studied the extraction of Pb(II) with an activated composite membrane (ACM) containing D2EHPA as a carrier. D2EHPA, although used mainly as a carrier, also has a high potential to act as a plasticizer against a PVC matrix.[74,142] Currently, PVC-based PIMs are considered as more stable under acidic conditions[74] and more long-lasting than CTA-based PIMs.[143]

Table 3. The comparison of immobilized membranes used for extraction of Pb(II) from waste streams

Pb(II) initial concentration (mmol L^{-1})	Membrane composition (PIM)	Pb(II) initial flux (µmol s^{-1} m^{-2})	Ref.
2.50	CTA/calix[4]arene/2-NPOE	0.16	125
0.10	CTA/D2EHPA/TBEP	3.5	144
1.00	CTA/D2EHPA/o-NPPE	9.1	145
1.00	CTA/Cyanex 301/o-NPPE	6.1	76
1.00	CTA/azocrown ethers/o-NPPE	1.8	134
1.00	CTA/PNP-16-crown-6 derivatives/o-NPPE	2.24	146
1.00	CTA/calix[4]crown-6 derivatives/o-NPPE	5.56	147
1.00	CTA/_-CD polymer/o-NPPE	1.25	77
0.54	PVC/D2EHPA	7.19	148

4. Concluding remarks and future prospects

Over the past two decades environmental regulations have become more strict, requiring an improved quality of treated aqueous effluents. In recent years, a wide range of treatment technologies, such as: chemical precipitation, adsorption, membrane filtration, have been developed for toxic metal ions removal from contaminated water and wastewater. It is evident from the presented literature overview that novel sorbents and membranes are more frequently studied and widely applied for the treatment of the toxic metal-contaminated effluents; immobilized materials are the basis of promising innovative techniques to be developed for the efficient treatment due to their selectivity and rapid operation.

From the large number of recent works reviewed here, it is observed that the removal efficiency of metal ions using immobilized materials depend mainly on the chemical nature of the materials and the solution conditions like ion concentration, pH of the medium and presence of competing ions. Different types of forces and interactions, such as: hydrogen bonding, electrostatic interaction, surface complexation and van der Waal forces, ion exchange, and so forth, are responsible for the removal of toxic metal ions from waste streams using immobilized materials. The carboxylic and phenolic are the major groups that participate in the removal of metal ions by the proton exchange. Based on the electron donating nature of the oxygen containing groups in novel materials and the electron accepting nature of metal ions, the ion exchange mechanism could be preferentially considered.

The ability of immobilized materials to remove specific metal ions is controlled in part by the type of functional groups used for binding metal ions. Extractant molecules containing functional groups with a known affinity for specific metal ions can be physically impregnated onto adequate polymeric supports in order to create effective novel sorbents and membranes. The impregnation technique is the most convenient method of preparing immobilized materials, since it is exceedingly easy to perform, merely requiring agitation of the extractant solution and the polymeric support. Subsequently, impregnation methods have been more developed in the last decades, because the impregnation methods are free from difficulties encountered in chemically linking a chelating reagent to a polymeric matrix.

Although many techniques can be employed for the treatment of water/wastewater contaminated with toxic metals, it is important to note that the selection of the most suitable treatment depends on some basic parameters such as pH, initial metal concentration, the overall treatment performance compared to other technologies, environmental impact as well as economics parameter such as the capital investment and operational costs. Technical applicability, plant simplicity and cost-effectiveness are the key factors that play major roles in the selection of the most suitable treatment system for polluted effluents. All the factors mentioned above should be taken into consideration in selecting the most effective and inexpensive treatment in order to protect the environment.

The cleanup technologies using immobilized materials are on the rise. It is not only a viable option, but often a smart one when considering plant upgrades and capacity expansion. It seems to be quite realistic to use immobilized materials for the efficient removal of given ionic specimen and/or a group of such species. The potential of such separation systems using them is anticipated in their wide application in water processing operations accompanying the industrial activities, remediation of contaminated groundwater, as well as leachate from industrial landfills to fulfill very low toxic metal ions limits.

Positive results in separation of metal ions, achieved in processes using immobilized materials, along with their removal efficiency and reusability, are promising for wider use of these techniques in remediation of polluted water and industrial effluents. The further research will also focus on the stability of novel sorbents, mainly biocarriers, and easy of their regeneration. In turn parameterization of the immobilized membrane system by selection of a proper support, plasticizers and ion carriers, together with determination of the kinetic constants of transport (flux, permeability) will be developed to achieve the high effectiveness of separation process.

Comprehensive fundamental understanding of the key concepts affecting the performance of immobilized materials, including mechanisms of toxic metal ions removal involved with different types of materials, the relative influence of different experimental parameters affecting removal process, modes of operation and other related phenomena has already been given. With this knowledge, further advances are needed to transform these highly effective materials into practical applications. Although novel sorbents and immobilized membranes are used successfully for removal of toxic metal ions from water/wastewater, it still remains several problems; water/wastewater treatment on a large scale is the essential one. In particular, scale-up of removal processes using immobilized materials to various types of water/wastewater in a continuous large-scale operation is on the horizon. Immobilized materials can find potential applications in areas where toxic metals need to be removed from relatively concentrated solutions such as industrial effluents, mining effluents or from dilute solutions such as urban runoffs and groundwater. Thus, more research should be focused on commercialization of novel materials in various fields. Specifically, cross-disciplinary inputs from environmental researchers, wastewater treatment professionals, materials engineers and industrial communities will enhance the scope of ongoing research efforts on novel materials and will lead to development of the next generation treatment technologies in a cost-effective manner toward commercialization.

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