Selective Removal of Heavy Metal Ions from Waters and Waste Waters Using Ion Exchange Methods

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Additional information is available at the end of the chapter

1. Introduction

Environmental pollution by toxic metals occurs globally through military, industrial, and agricultural processes and waste disposal (Duffus, 2002). Fuel and power industries generate 2.4 million tons of As, Cd, Cr, Cu, Hg, Ni, Pb, Se, V, and Zn annually The metal industry adds 0.39 million tons/yr of the same metals to the environment, while agriculture contributes 1.4 million tons/yr, manufacturing contributes 0.24 million tons/yr and waste disposal adds 0.72 million tons/yr. Metals, discharged or transported into the environment, may undergo transformations and can have a large environmental, public health, and economic impact (Brower et al. 1997; Nriagu & Pacyna, 1988; Gadd & White, 1993).

Among different techniques used for removal of high concentrations of heavy metals, precipitation-filtration, ion exchange, reverse osmosis, oxidation-reduction, solvent extraction, as well as membrane separation should be mentioned (Hubicki,et al. 1999; Dąbrowski et al. 2004). However, some of the wastes contain substances such as organics, complexing agents and alkaline earth metals that may decrease the metal removal and result in unacceptable concentrations of heavy metals in the effluents. The pollutants of concern include cadmium, lead, mercury, chromium, arsenic, zinc, cobalt and nickel as well as copper. They have a number of applications in basic engineering works, paper and pulp industries, leather tanning, petrochemicals, fertilizers, etc. Moreover, they have also negative impact on human health.

Cadmium is a metal of great toxicological concern. An important source of human exposure to cadmium is food and water, especially for the population living in the vicinity of industrial plants, from which cadmium is emitted to the air. In the case of exposure to occupational cadmium compounds, they are absorbed mainly by inhalation. Through the

gastrointestinal tract less than 10% cadmium is absorbed. An important source of human exposure to cadmium is food and water. In natural water its typical concentration lies below 0.001 mg/dm^3, whereas, the upper limit recommended by EPA (Environmental Protection Agency) is less than 0.003 mg/dm^3. The maximum limit in drinking water is 0.003 mg/dm^3.

Cadmium accumulates in kidneys, pancreas, intestines and glands altering the metabolism of the elements necessary for the body, such as zinc, copper, iron, magnesium, calcium and selenium. Damage to the respiratory tract and kidneys are the main adverse effects in humans exposed to cadmium compounds. In humans exposed to fumes and dusts chronic toxicity of cadmium compounds is usually found after a few years. The main symptom of emphysema is that it often develops without preceding bronchitis. The second basic symptom of chronic metal poisoning is kidney damage. It includes the loss and impairment of smell, pathological changes in the skeletal system (osteoporosis with spontaneous fractures and bone fractures), pain in the extremities and the spine, difficulty in walking, the formation of hypochromic anemia. The most known 'Itai-Itai' disease caused by cadmium exposure is mixed osteomalacia and osteoporosis. However, an important source of cadmium in soils are phosphate fertilizers. Large amounts of cadmium are also introduced to soil together with municipal waste. The high mobility of cadmium in all types of soils is the reason for its rapid integration into the food chain. Daily intake of cadmium from food in most countries of the world is 10-20 mg.

Lead is a toxic metal, which accumulates in the vital organs of men and animals and enters into the body through air, water and food. According to the WHO (World Health Organization) standards, its maximum limit in drinking water is 0.05 mg/dm^3 but the maximum discharge limit for lead in wastewater is 0.5 mg/dm^3. Its cumulative poisoning effects are serious haematological damage, anaemia, kidney malfunctioning, brain damage etc. Chronic exposure to lead causes severe lesions in kidney, liver, lungs and spleen.

Lead is used as industrial raw material in the manufacture of storage batteries, pigments, leaded glass, fuels, photographic materials, matches and explosives. Lead being one of very important pollutants comes from wastewaters from refinery, wastewaters from production of basic compounds containing lead, wastewaters with the remains of after production solvents and paints. Large toxicity of lead requires that its contents are reduced to the minimum (ppb level). To this end there are applied chelating ions with the functional phosphonic and aminophosphonic groups. Also weakly basic anion exchangers in the free base form can be used for selective removal of lead(II) chloride complexes from the solutions of pH in the range 4-6. Also a combined process of cation exchange and precipitation is often applied for lead(II) removal form wastewaters (Pramanik et al. 2009). The average collection of lead by an adult was estimated at 320-440 mg/day. Acute poisoning with inorganic lead compounds occurs rarely. In the case of acute poisoning in man, the symptoms are burning in the mouth, vomiting, abdominal cramps, diarrhea, constipation progressing to systolic, blood pressure and body temperature. At the same time there is hematuria, proteinuria, oliguria, central nervous system damage. Alkyl lead compounds are more toxic than inorganic lead connections. Tetraethyl lead toxicity

manifested primarily in lead damage of the nervous system. Toxic effects of lead on the central nervous system are observed more in children. In adults, the effects of lead toxicity occur in the peripheral nervous system. Symptoms of chronic poisoning may vary. The acute form of poisoning known as lead colic is the general state of various spastic internal organs and neurological damage in the peripheral organs. Long-term lead poisoning can lead to organic changes in the central and peripheral nervous systems. Characteristic symptoms include pale gray skin colour and the lead line on the gums (blue-black border).

In nature, natural circulation of **mercury** vapour has a significant influence on the content of the soil and water. Elemental mercury in the rain water creates compounds by oxidation to divalent mercury. Both the chemical reaction, and under the influence of biological factors, and especially the activity of bacteria in the sediments of water bodies methyl and dimethyl mercury compounds are formed. Mercury, a fixed component of the waste water treatment that may be used for soil fertilization is a major threat to the inclusion of the metal in nutritional products. Drinking water may contain up to 300 ng Hg/dm^3, in highly industrialized areas it can reach up to 700 ng/dm^3. Daily consumption of mercury from food in the general population is less than 20 $\mu g/day$. 80% of mercury absorbed by the respiratory system is retained in the body. In the case of ingestion of inorganic mercury salts, salivation, burning in the throat, vomiting, bloody diarrhea, necrosis of the intestinal mucosa and kidney damage, leading to anuria and uremii can occur. The concentration of mercury vapour over 1 mg/m^3 damages lung tissue and causes severe pneumonia. The classic symptoms of metallic mercury vapour poisoning are manifested by tremor, mental disorders, inflammation of the gums. Its maximum limit in drinking water is 0.0005 mg/dm^3.

Chromium, occurring as Cr(III) or Cr(VI) in natural environments, is an important material resource, an essential micronutrient or toxic contaminant. Cr(III) is required for normal development of human and animal organisms but Cr(VI) activates teratogenic processes, disturbs DNA synthesis and can give rise to mutagenous changes leading to malignant tumours (WHO, Report 1998). Natural sources of chromium include weathered rocks, volcanic exhalations and biogeochemical processes and, in the man-polluted environment, mainly wastes after processing and utilization of chromium compounds. Chromium is an important and widely applied element in industry. The hexavalent and trivalent chromium is often present in electroplating wastewater. Other sources of chromium pollution are leather tanning, textile, metal processing, paint and pigments, dyeing and steel fabrication. To remove toxic chromium compounds from sewages there are used such methods as: precipitation, coagulation, solvent extraction and various kinds of membrane processes, ion flotation, adsorption and ion exchange (Bajda, 2005). The maximum limit in drinking water is 0.05 mg/dm^3. The Polish drinking groundwater chromium content ranges on the average from 0.07 to 2 mg/dm^3. 0.02 mg/dm^3 is accepted as the permissible content of chromium in groundwater. The daily dose taken by the adult can be 50-200 mg/day (or 60-290 mg/day). Cr(III) cation predominates in most tissues except the liver. Chromium is associated with nucleic acids and is the subject to the concentration in liver cells. It plays an important role in the metabolism of glucose, certain proteins and fats, is part of enzymes and stimulates the activity of others. All compounds of chromium, with the exception of chromate, are rapidly

cleared from the blood. Chromium also accumulates in the liver and kidneys. High concentrations of chromium, observed in the lungs of people exposed to this metal, indicate that at least part of chromium is stored in this organ in the form of insoluble compounds. The binding of chromium with the elements of the blood and transport of chromium by the blood depends mainly on its valence. Hexavalent chromium readily crosses the membranes of red blood cells and after reduction to trivalent chromium is bound to hemoglobin. The reduction of hexavalent to trivalent chromium, occurring within cells, considered as the activation of the carcinogenic chromium, increases because the probability of interaction of trivalent chromium on the DNA. Clinical signs of acute toxicity of chromium compounds are characterized by severe abdominal pain, vomiting and bloody diarrhea, severe kidney damage with hematuria leading to anuria, observed gastrointestinal ulceration. Chromium compounds and chromic acid are especially dangerous and cause serious damage to internal organs. Chronic exposure leads to chronic disorders in the body.

Arsenic is present in over 160 minerals. It is readily bioaccumulative and therefore its concentration in polluted waters may reach 430 mg/dm^3 in plants and 2.5 mg/dm^3 in fish**.** The upper limit of arsenic recommended by US EPA, EU and WHO is 0.01 mg/dm^3. However, many countries have retained the earlier WHO guideline of 0.05 mg/dm^3 as their standard.

Arsenic accumulates in tissues rich in keratin, like hair, nails and skin. Arsenic and its inorganic compounds can cause not only cancer of the respiratory system and skin, but also neoplastic lesions in other organs. Arsenic compounds enter the body from the gastrointestinal tract and through skin and respiratory system. Arsenic compounds have affinity for many enzymes and can block their action, and above all disturb the Krebs cycle. Inorganic arsenic compounds are more harmful than organic and among them AsH_3 and As_2O_3 should be mentioned. 70-300 mg of As_2O_3 is considered to be the average lethal dose for humans. The dose of 10-50 ppb for 1 kg of body weight can cause circulatory problems, resulting in necrosis and gangrene of limbs. The dominant effects of arsenic in humans are changes in the skin and mucous membranes as well as peripheral nerve damage. There are xerosis soles and palms, skin inflammation with ulceration. In addition, there is perforation of the nasal septum. The values of the maximum allowable concentration (NDS) in Poland set for inorganic arsenic compounds are 0.3 mg/m^3 and 0.2 mg/m^3 for AsH_3.

In nature, **zinc** occurs in the form of minerals. An important source of zinc pollution is the burning of coal, petroleum and its products. Incineration of municipal solid waste can introduce about 75% zinc to urban air. Also, municipal wastewater generally contains significant amounts of zinc. The use of municipal and industrial waste in agriculture results in the accumulation of zinc in the surface layers of soil. Another source of this metal in soils are some preparations of plant protection products, as well as phosphatic fertilizers. The degree of toxicity of zinc is not big, but it depends on the ionic form, and changes under the influence of water hardness and pH. The daily average download of zinc by an adult is estimated at about 10-50 mg /day. The toxic dose is 150-600 mg. It is necessary for the proper functioning of living organisms and it is involved in the metabolism of proteins and carbohydrates. High doses of zinc cause damage to many biochemical processes followed by

its deposition in the kidneys, liver, gonads. Kidney play an important role in maintaining zinc homeostasis in the body. Zinc is relatively non-toxic to humans and animals. Hazard zinc mainly connected with secondary copper deficiency does not give specific symptoms.

Nickel is a moderately toxic element as compared to other transition metals. It is a natural element of the earth's crust; therefore its small amounts are found in food, water, soil, and air. Nickel occurs naturally in the environment at low levels. Nickel concentrations in the groundwater depend on the soil used, pH, and depth of sampling. The average concentration in the groundwater in the Netherlands ranges from 7.9 $\mu g/dm^3$ (urban areas) to 16.6 $\mu g/dm^3$ (rural areas). Acid rain increases the mobility of nickel in the soil and thus might increase nickel concentrations in the groundwater. In the groundwater with a pH below 6.2, nickel concentrations up to 0.98 mg/dm^3 have been measured, whereas the upper limit recommended by FAO (Food & Agricultural Organization of the United Nation) for nickel in water is 0.02 mg/dm^3. According to the Polish standards the maximum discharge limit for nickel in waste water is 2-3 mg/dm^3. The maximum limit in drinking water in Europe is 0.01 mg/dm^3. Although it has been suggested that nickel may be essential to plants and some animal species as well as in human nutrition, this metal causes damage to humans. Nickel occurs in seams of coal in the amount of 4-60 mg/kg. Crude oil contains about 50-350 mg/kg of the metal. The most dangerous is tetracarbonyl nickel occurring mostly in nickel refineries. The content of this metal in industrial and municipal wastewater ranges 20-3924 mg/kg. An important source of nickel pollution is its emissions to the air, the combustion of coal and liquid fuels, primarily by diesel engines. It is assumed that the concentration of nickel in the waters of the rivers should be about 1 $\mu g/dm^3$, while in most rivers of Europe it is as high as 75 $\mu g/dm^3$. Large amounts of nickel are given to surface waters from municipal wastewater in which the concentration exceeds 3000 ppm s.m. The permissible concentration should be 20 $\mu g/dm^3$. Nickel readily accumulatives particularly in phytoplankton or other aquatic plants. The daily absorption of nickel by humans ranges 0.3-0.5 mg. In humans, the absorption of nickel from the gastrointestinal tract is less than 10%. Nickel taken with food and water is poorly absorbed and rapidly excreted from the body. It accumulates mainly in bones, heart, skin and various glands. Nickel inhalation of atmospheric air is largely accumulated in the lungs. Practically fatal or acute poisoning with nickel or its salts is not found. The most toxic compound is carbonyl nickel. An excess of inhaled nickel causes damage to the mucous membranes. Moreover, its symptoms are allergic disorders (protein metabolism disorder in plasma, changes in the chromosomes and changes in bone marrow and cancer. It is known that inhalation of nickel and its compounds can lead to serious problems, including, among others, respiratory system cancer. Moreover, nickel can cause skin disorder which is a common occupational disease in workers who handle its large amounts. Also dermatitis is the most common effect of chronic dermal exposure to nickel. Chronic inhalation exposure to nickel in humans also results in detrimental respiratory effects.

Copper is generally found in the earth's crust, usually in the form of sulphides. Municipal and industrial waste waters are an important source of pollution of rivers and water reservoirs. Copper accumulating plants may be the cause of poisoning. Copper is present in

all types of water, and its content is subject to large variations (Barceloux, 1999). The natural content of copper in the river water ranges 0.9-20 µg/dm^3 and for saline waters 0.02-0.3 µg/dm^3. Copper is an essential nutritional element being a vital part of several enzymes. It is one of the components of human blood. The estimated adult dietary intakes are between 2 and 4 mg/day. The demand for copper is increased in pregnant women, children and the elderly. Good dietary sources of copper include animal liver, shellfish, dried fruit, nuts and chocolate. In some cases drinking water may also provide significant levels of copper. Copper in the body is involved in oxidation-reduction processes, acts as a stimulant on the amount and activity of hemoglobin, in the process of hardening of collagen, hair keratinization, melanin synthesis as well as affects on lipid metabolism and properties of the myelin sheath of nerve fibers. In animal cells it is mainly concentrated in the mitochondria, DNA, RNA, and the nucleus. Copper readily forms a connection with various proteins, especially those of sulphur. Although copper is an essential metal, it can, in some circumstances, lead to toxic effects including liver damage and gastrointestinal disturbances. Such as Wilson's disease (also known as hepatolenticular degeneration), Indian Childhood Cirrhosis (ICC) which are characterised by an accumulation of copper-containing granules within liver cells. Ingestion of high levels of copper salts is known to cause gastrointestinal upsets. Additionally, absorption of copper compounds by inhalation causes congestion of the nasal mucosa, gastritis, diarrhea and toxic symptoms such as chronic lung damage. Copper compounds act on the intact skin, causing it to itch and inflammation. They can cause conjunctivitis, ulceration and corneal opacity, nasal congestion and as well as sore throat and nasal septum. The upper limit recommended by WHO for copper is less than 1.3 mg/dm^3. The maximum limit in drinking water is 0.05 mg/dm^3 (Fewtrell et al. 1996).

2. Ion exchange (IX)

Ion exchange may be defined as the exchange of ions between the substrate and surrounding medium. The most useful ion exchange reaction is reversible. When the reaction is reversible, the ion exchanger can be reused many times. Generally resins are manufactured in the spherical, stress and strain free form to resist physical degradation. They are stable at high temperatures and applicable over a wide pH range. Ion exchange resins, which are completely insoluble in most aqueous and organic solutions, consist of a cross linked polymer matrix to which charged functional groups are attached by covalent bonding (Sherrington, 1998). The ion exchangers which contain cations or anions as counter-ions are called cation exchangers or anion exchangers, respectively. The usual matrix is polystyrene cross linked for structural stability with 3 to 8 percent of divinylbenzene (3-8 % DVB) (Kunin, 1958; Helfferich, 1962). The resins of higher cross linking (12-16% DVB) are more costly, both to make and to operate and they are specially developed for heavy duty industrial applications. These products are more resistant to degradation by oxidizing agents such as chlorine, and withstand physical stresses that fracture lighter duty materials. Typical ion exchangers are produced with a particle size distribution in the range 20-50 mesh (for separation of anions from cations or of ionic species from nonionic ones). For more difficult separations, materials of smaller particle size or lower degrees of cross linking

are necessary. Moreover, when the separation depends solely upon small differences in the affinity of the ions, a particle size of 200-400 mesh is required and when the selectivity is increased by the use of complexing agents, the particle size in the 50-100 mesh is adequate. The ion exchangers finer than 100 mesh are employed for analytical purposes and for practical applications on the commercial scale the materials finer than 50 mesh are used.

Depending on the type of functional groups of exchanging certain ions, the ion exchangers with strongly acidic e.g., sulphonate -SO_3H, weakly acidic e.g., carboxylate -COOH, strongly basic e.g., quaternary ammonium -N^+R_3 and weakly basic e.g., tertiary and secondary amine -N^+R_2H and -N^+RH_2 should be mentioned. The strong acidic cation exchangers are well dissociated over a wide pH range and thus reaching its maximum sorption capacity. On the other hand, weak acidic cation exchangers containing, for example, carboxylic functional groups reach the maximum sorption capacity at pH> 7.0 as presented in Fig.1.
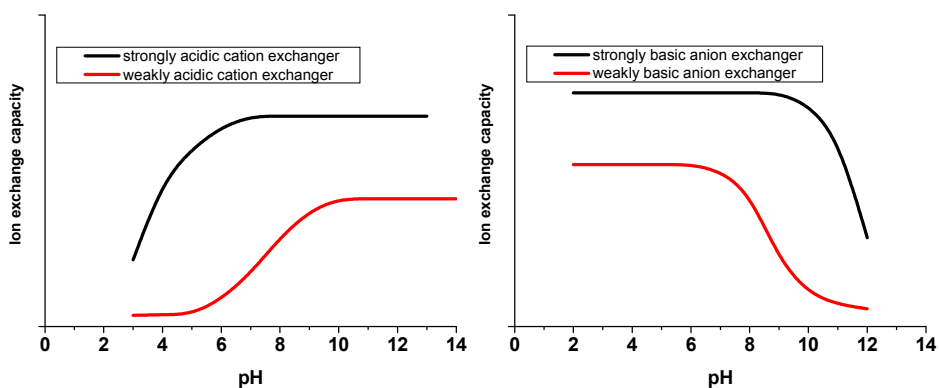

Figure 1. The sorption capacity of ion exchangers depending on pH.

Additionally, ion exchangers possess: the iminodiacetate functional groups (-N{CH_2COOH}$_2$), phenol (-C_6H_4OH), phosphonic (-PO_3H_2) and phosphine (-PO_2H) functional groups. These groups are acidic in nature and are dissociated with the exchange of H^+ or Na^+ ions for other cations from the solution. Negative charge of the functional groups is offset by an equivalent number of mobile cations so-called counter ions. Counter ions can be exchanged for other ions from the solution being in the contact with the resin phase.

There are also amphoteric exchangers, which depending on the pH of the solution may exchange either cations or anions. More recently these ion exchangers are called bipolar electrolyte exchange resins (BEE) or zwitterionic ion exchangers (Nesterenko & Haddad, 2000). The aminocarboxylic amphoteric ion exchangers AMF-1T, AMF-2T, AMF-2M, ANKB-35 as well as the carboxylic cation exchanger KB-2T were, for example used for recovery of Ni(II) from the Mn(NO_3)$_2$–H_2O system (Kononowa et al. 2000).

The individual ions present in the sample are retained in varying degrees depending on their different affinity for the resin phase. The consequence of this phenomenon is the

separation of analyte ions, such as metal ions, however, the nature and characteristics of the resin phase determine the effectiveness of this process (Fritz, 2005). The affinity series which for various types of ion exchangers are as follows:

2.1. Cation exchangers with the sulphonic functional groups

It is well known that the affinity of sulphonic acid resins for cations varies with the ionic size and charge of the cation. The affinity towards cation increases with the increasing cation charge:
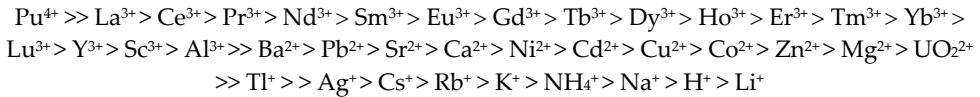
$$Na^+ < Ca^{2+} < Al^{3+} < Th^{4+},$$
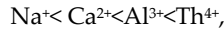
and in the case of different cations with the same charge the affinity increases with the increasing atomic number:

$$Li^+ < H^+ < Na^+ < NH_4^+ < K^+ < Rb^+ < Cs^+ < Ag^+ < Tl^+$$

$$Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$$

$$Al^{3+} < Fe^{3+}.$$
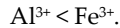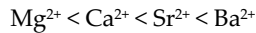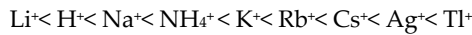
Generally, the affinity is greater for large ions with high valency.

For the strong acidic cation exchanger the affinity series can be as follows:

$$Pu^{4+} \gg La^{3+} > Ce^{3+} > Pr^{3+} > Nd^{3+} > Sm^{3+} > Eu^{3+} > Gd^{3+} > Tb^{3+} > Dy^{3+} > Ho^{3+} > Er^{3+} > Tm^{3+} > Yb^{3+} > Lu^{3+} > Y^{3+} > Sc^{3+} > Al^{3+} \gg Ba^{2+} > Pb^{2+} > Sr^{2+} > Ca^{2+} > Ni^{2+} > Cd^{2+} > Cu^{2+} > Co^{2+} > Zn^{2+} > Mg^{2+} > UO_2^{2+} \gg Tl^+ > > Ag^+ > Cs^+ > Rb^+ > K^+ > NH_4^+ > Na^+ > H^+ > Li^+$$

and for Lewatit SP-112 it is as: $Ba^{2+} > Pb^{2+} > Sr^{2+} > Ca^{2+} > Ni^{2+} > Cd^{2+} > Cu^{2+} > Co^{2+} > Zn^{2+} > Fe^{2+} > Mg^{2+} > K^+ > NH_4^+ > Na^+ > H^+$.
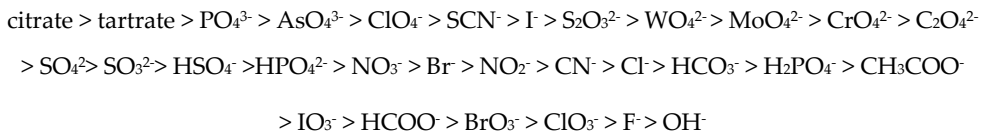
2.2. Cation exchangers with the carboxylic functional groups

Cation exchangers with the carboxylic functional groups show the opposite the affinity series for alkali and alkaline earth metal ions. Noteworthy is the fact that the cations exhibit a particularly high affinity for H^+. The affinity of this type of cation is therefore as follows:

$$H^+ > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+} > Li^+ > Na^+ > K^+ > Rb^+ > Cs^+.$$
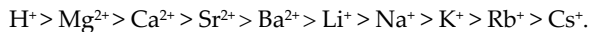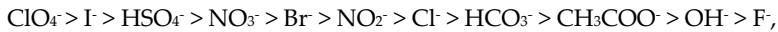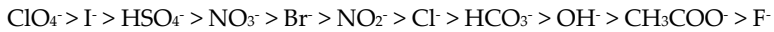
2.3. Anion exchangers with the quaternary ammonium functional groups

The charge of the anion affects its affinity for the anion exchanger in a similar way as for the cation exchangers:

$$citrate > tartrate > PO_4^{3-} > AsO_4^{3-} > ClO_4^- > SCN^- > I^- > S_2O_3^{2-} > WO_4^{2-} > MoO_4^{2-} > CrO_4^{2-} > C_2O_4^{2-}$$

$$> SO_4^{2-} > SO_3^{2-} > HSO_4^- > HPO_4^{2-} > NO_3^- > Br^- > NO_2^- > CN^- > Cl^- > HCO_3^- > H_2PO_4^- > CH_3COO^-$$

$$> IO_3^- > HCOO^- > BrO_3^- > ClO_3^- > F^- > OH^-$$

for *Dowex 1* (type 1):

$$ClO_4^- > I^- > HSO_4^- > NO_3^- > Br^- > NO_2^- > Cl^- > HCO_3^- > CH_3COO^- > OH^- > F^-,$$

for *Dowex 2* (type 2):

$$ClO_4^- > I^- > HSO_4^- > NO_3^- > Br^- > NO_2^- > Cl^- > HCO_3^- > OH^- > CH_3COO^- > F^-$$

2.4. Anion exchangers with the tertiary and secondary amine functional groups

Only with the exception of the OH- ion, the affinity of the anion exchangers with the tertiary and secondary functional groups is approximately the same as in the case of anion exchangers with the quaternary ammonium functional groups. These medium and weakly basic anion exchangers show very high affinity for OH^- ions.

Anion exchange materials are classified as either weak base or strong base depending on the type of exchange group. These are two general classes of strong base anion exchangers e.g. types 1 and 2 depending on chemical nature. The synthesis of the weak base anion exchangers with the tertiary amine groups is usually provided by the chloromethylation of PST-DVB followed by the amination by secondary amine (Drăgan & Grigoriu, 1992). Weak base resins act as acid adsorbers, efficiently removing strong acids such as sulphuric and hydrochloric ones. They are used in the systems where strong acids predominate, where silica reduction is not required, and where carbon dioxide is removed in degasifiers. Preceding strong base units in demineralizing processes, weak base resins give more economical removal of sulphates and chlorides. The selectivity for the bivalent ions such as SO_4^{2-} depends strongly on the basicity of the resin, the affinities of various functional groups following the order: primary > secondary > tertiary > quaternary. Therefore among the factors affecting the sorption equilibrium the most important are: first of all nature of functional groups and the concentration of the solution (Boari et al. 1974). At low concentration the resin prefers ions at higher valency and this tendency increases with solution diluting. It should be also mentioned that obtaining resins with the primary amine functional groups is difficult by chemical reactions on polystyrene-divinylbenzene copolymers. Weakly basic anion exchangers can be used, for example for zinc cyanide removal from the alkaline leach solutions in the Merrill Crowe process (Kurama & Çatlsarik, 2000).

2.5. Gel and macroporous resins

The development in polymerization technique has provided novel matrices for a series of new ion exchangers. They differ from the earlier corresponding copolymers that are characterized by being essentially cross linked gels of polyelectrolytes with pore structure defined as the distance between polymeric chains.

It is well known that the fouling of the resin by organic compounds and mechanical stress imposed by plant operating at high flow rates are the most important problems encountered in the use of the ion exchange resins (De Dardel & Arden, 2001). To overcome these

problems the ion exchangers with a high degree of cross linking containing artificial open pores in the form of channels with diameters up to 150 nm were introduced (Fig. 2).
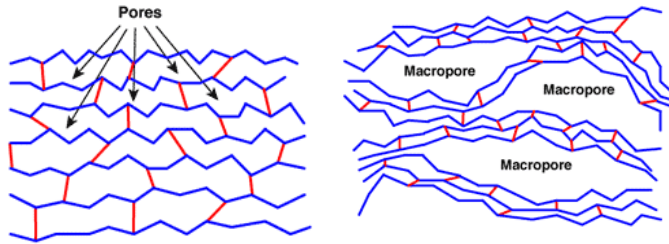

Figure 2. The structure of gel and macroporous ion exchangers (http://dardel.info/IX/index.html)

The first macroporous ion exchanger was a carboxylic resin made by Rohm and Haas, which covered a wide variety of acrylic compounds copolymerized with polyvinyl cross linking agents to make insoluble, infusible weakly acidic resins. By 1948 AmberliteTM IRC-50, made by the copolymerization of methacrylic acid and divinylbenzene was in production and possessed the 'sponge structure' (Abrams & Milk, 1997). According to the definition by Stamberg and Valter (1970) the macroporous resin should be characterised by measurable inner surface by any suitable method resulting from pores 5 nm, even in the completely dried state. In contrast, the gel materials did not show any porosity in the dry state. Then the term 'macroreticular' (sometimes abbreviated to MR) was selected to distinguish resins with a particular type of porosity obtained by application of precipitating diluents such as t-amyl alcohol. In 1979 Amber-Hi-Lites stated that 'macroreticular' resins are those made by a copolymerization technique which brings about precipitation during the polymerization, thus resulting in a product which has two phases, a gel phase in the form of microspheres formed during the phase separation and the pore phase surrounding the microspheres (Kunin, 1979). Later when quantitative porosity measurements were used it was shown that other methods of preparation gave products similar to those declared as 'macroreticular'. Therefore classification of resins should be based on their properties and function (Ion exchange resins and adsorbents, 2006).

During last decades the great progress was made by the development of the macroporous ion exchange resins. It should be mentioned that macroporous resins can also perform as adsorbents because of their pore structure. For organic ion exchange resins based on cross linked polystyrene the porosity was originally selected by the degree of cross linkage. These gel type resins are able to sorb organic substances from water according to their degree of porosity and the molecular weight of the adsorbate. They not only allow for large molecules or ions to enter the sponge like structure but also to be eluted during the regeneration. Therefore they perform two functions: ion exchange by means of the functional groups and the reversible adsorption and elution due to the macroporous structure. They are also resistant against organic fouling which results in a longer resin life compared with the conventional gel type ion exchangers as well as the quality of the treated water is much better because of the adsorption of organic species by the macroporous structure. The SEM scan of the macroporous anion exchanger Lewatit MonoPlus MP 500 is presented in Fig. 3.
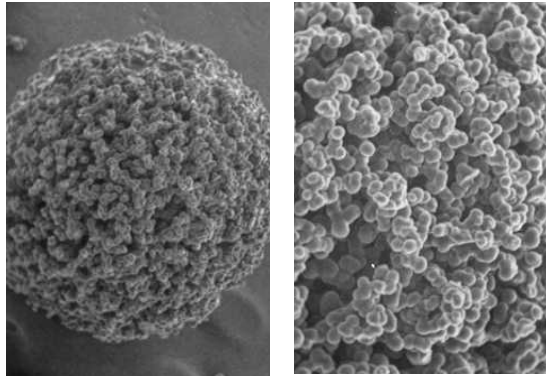
Figure 3. SEM scans of macroporous resins.

Ion exchange applications can be performed by either column (flow continuous) and batch technique. In column operations the ion exchange resin is placed in the vertical column to form a bed. Once the application is completed, the resin can be regenerated to use in another cycle. In batch operations the resin is shacked in a vessel with the solution to be treated. After the application is completed, the resin can be regenerated in place or transferred to a column for regeneration.

While the main aims in the production of conventional ion exchangers were focused on obtaining a high ion exchange capacity and improved chemical resistance and thermal and mechanical strength, in the case of monodisperse ion exchange resins, these efforts directed towards improvement of kinetic parameters. Heterodisperse ion exchangers are usually characterized by a standard grain size of 0.3-1.2 mm and uniformity coefficient (UC) within the limits of 1.5-1.9. In the case of monodisperse ion exchange resins during the manufacturing process the grain size from 0.6 mm and uniformity coefficient within the limits 1.1-1.2 is usually achieved. In addition, monodisperse ion exchangers, due to the uniform packing of the column, show more than 12% higher ion exchange capacity, faster kinetics of exchange and a much higher mechanical strength, which is extremely important from the economical point of view. As the particle size of the ion exchanger material and its uniformity are the most important parameters influencing the hydraulics and kinetics of the ion exchange therefore the monodisperse ion exchangers provided better flow characteristics in column applications in comparison to the conventional heterodisperse ion exchangers (the flow rate decreases with the decreasing particle size, however, smaller particles have larger outer surface, but cause larger head loss in the column processes) (Scheffler, 1996; Krongauz & Kocher, 1997). The visualization of the monodisperse and hetrodisperse ion exchangers is presented in Fig. 4a-b.

For example the research carried out by Zainol & Nicol (2009a) shows that in the the sorption process of Ni(II) and other metal ions the monodisperse resin (Lewatit MonoPlus TP 207) proved to be superior to the conventional heterodisperse ones in terms of loading capacity for Ni(II) and also the kinetics of adsorption. This makes it a preferred choice for different applications.
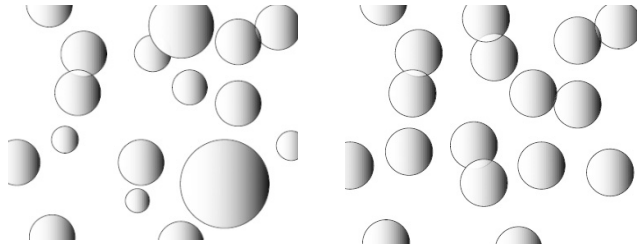
Figure 4. The monodisperse and hetrodisperse ion exchangers.

The influence of temperature on the equilibrium properties of ion exchange resins was studied extensively. The decrease of the capacity of the cation exchange resins based on the polystyrene matrix due to the operation temperature is not a significant problem. However, the relatively slight decomposition gives enough decomposition products to cause significant problems elsewhere. This may be decomposition of the bone polystyrene matrix, resulting in styrene sulphonic acid derivatives or as a substitution of the sulphonic group giving sulphate. Further decomposition of styrene sulphonic acid derivatives will also result in sulphate as one of the end products (desulphonation). The amount of sulphate produced is sometimes high. The information on the stability of the ion exchange resins mainly deals with the anion exchange resins. The mechanism of the degradation of quaternary ammonium salts and tertiary anions is well-known (Reynolds, 1982; Fernandez-Prini, 1982; Fisher, 2002). The effect of temperature on the properties of chelating ion exchangers was also described in the paper by Ivanov (1996).

3. Application of ion exchangers for heavy metal ions removal

Ion exchange technique can remove traces of ion impurities from water and process streams and give a product of desired quality. Ion exchangers are widely used in analytical chemistry, hydrometallurgy, antibiotics, purification and separation of radioisotopes and find large application in water treatment and pollution control (Clifford, 1999; Luca et al. 2009). The list of metals which are recovered and purified on an industrial scale by means of ion exchange include: uranium, thorium, rare earth elements (REEs), gold, silver, platinum metals (PGM), chromium, copper, zinc, nickel, cobalt and tungsten.

In some of these cases, the scale of operations is relatively small, for instance in the rare earth elements or noble metals, but the values of recovered metals are very high. Ion exchange process is particularly suitable for purification of metal ions with a high value and low processing. The alternative is also a process of large-scale recovery of trace amounts of metals from waste streams, such as cadmium and mercury, chromium, or copper and zinc. The use of ion exchange processes in hydrometallurgy is high and every year continues to grow. It is associated mainly with the progress of what is observed in the synthesis of new selective chelating ion exchangers containing complexing ligands (Minczewski, et al. 1982;

4. Chelating and special ion exchangers

Typical disadvantage of lack a of the selectivity towards heavy metal ions and alkali and alkaline earth metal ions of most widely used functionalized ion exchangers such as Chelex 100 is overcome by introducing chelating ligands capable of removing selective metal ions. It exhibits high affinity for heavy metal ions: $Cu^{2+} > Hg^{2+} > Pb^{2+} > Ni^{2+} > Zn^{2+} > Cd^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+} > Ca^{2+} > Mg^{2+} > Sr^{2+} > Ba^{2+} >>>$ **alkali ions $> H^+$,** whereas for sulphonic ones the analogous affinity series can be as presented earlier (for Lewatit SP 112).

Generally, the functional group atoms capable of forming chelate rings usually include oxygen, nitrogen and sulphur. Nitrogen can be present in a primary, secondary or tertiary amine, nitro, nitroso, azo, diazo, nitrile, amide and other groups. Oxygen is usually in the form of phenolic, carbonyl, carboxylic, hydroxyl, ether, phosphoryl and some other groups. Sulphur is in the form of thiol, thioether, thiocarbamate, disulphide groups etc. These groups can be introduced into the polymer surface by copolymerization of suitable monomers, immobilization of preformed ligands, chemical modification of groups originally present on the polymer surface. However, the last two are most often used (Warshawsky, 1987). Chelating resins with such type of ligands are commonly used in analysis and they can be classified according to Fig.1. (Kantipuly et al. 1990). The choice of an effective chelating resin is dictated by the physicochemical properties of the resin materials. These are the acid-base properties of the metal species and the resin materials, the polarizability, selectivity, sorptive capacity, kinetic and stability characteristics of the resin. The sorption capacity of chelating ion exchangers depends mainly on the nature of functional groups and their content as well as solution pH as for their selectivity it depends on the relative position of functional groups, their spatial configuration, steric effects, and sometimes their distance from the matrix and to a lesser extent on the properties of the matrix. Their use allows the recovery of valuable metals from ores and sludge, sea water and industrial effluents. They are used as flotation agents, depressants, flocculants and collectors.

It is worth emphasizing that these resins are invaluable wherever it is necessary to concentrate or remove elements present in very low concentrations.

With a range of well known chelating ion exchangers only a few types are produced on an industrial scale. Among the most important ones these with the functional groups: amidoxime, dithiocarbamate, 8-hydroxychinoline, iminodiacetate, aminophosphonic, bispicolylamine, diphosphonic, sulphonic and carboxylic acid groups, thiol, thiourea as well as isothiourea should be selected (Sahni & Reedijk, 1984; Busche et al. 2009). Among them the chelating ion exchangers possessing methylglucoamine, bis(2pirydylmethyl)amine also known as bispikolilamine, thiol etc. are used for special applications such as removal of precious metal ions, heavy metal ions from the acidic medium, boron and special oxoanions removal. A separate group are ion exchangers of solvent doped type used for In, Zn, Sn, Bi, etc. separation. The advantages of ion exchangers from these groups include good selectivity, preconcentration factor, binding energy and mechanical stability, easy regeneration for multiple sorption-desorption cycles and good reproducibility in the sorption characteristics.

5. Chelating ion exchangers with the hydroxamic and amidoxime functional groups

The choice of hydroxamic acids is based on their application in mineral processing as collectors in flotation of haematite, pyrolusite or bastnaesite ores. The copolymer of malonic acid dihydroximate with styrene-divinylbenzene was used for uranium(VI) removal from sea water (Park & Suh, 1996). In the paper by Ahuja (1996) it was found that glycin hydroximate resin shows maximum adsorption for Fe(III), Cu(II) and Zn(II) at pH 5.5; for W(VI), U(VI), Co(II) and Ni(II) at pH 6.0 as well as for Cd(II) at pH 6.5. It can be recommended for separation of Cu(II) from Co(II) and Ni(II) at pH 5.5. However, the iminodiacetic– dihydroximate resin can be applied for U(VI), Fe(II), Cu(II) separation according to the affinity series: **UO_2^{2+} > Fe^{3+} > Cu^{2+} > Zn^{2+} > Co^{2+} > Cd^{2+} > Ni^{2+} > Zn^{2+}.** Hydroxamic acids exist in the two tautomeric forms:
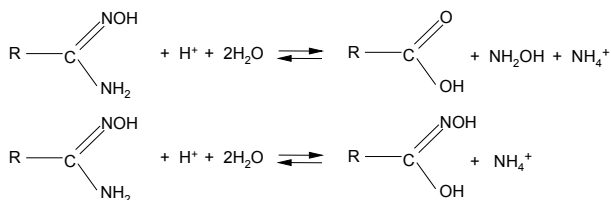

(a)   **(b)**
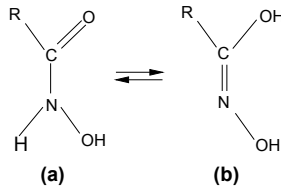
and metal ions are coordianated by the hydroxamide functional group (a).

Chelating resins with the amidoxime functional groups such as Duolite ES-346, and Chelite N can be applied for the concentration of solutions containing Ag(I), Al(III), Cd(II), Co(II), Cr(III), Cu(II), Fe(III), Hg(II), Mn(II), Ni(II), Mo(VI), Pb(II), Ti(IV), U(VI), V(V) and Zn(II) in the presence of alkali and alkaline earth metal ions (Samczyński & Dybczyński, 1997; Dybczyński et al. 1988). Alkali and alkaline earth metal ions are poorly retained by these resins. Duolite ES-346 is commonly used to extract uranium(VI) from seawater and As(III) from aqueous solutions. It can be also applied for Pd(II) removal (Chajduk-Maleszewska & Dybczyński, 2004). It is characterized by high selectivity towards Cu(II) ions due to the presence of amidoxime groups and small quantities of hydroxamic acid (RCONHOH):
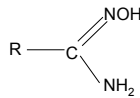

where: R is the resin matrix.

It was found that for the amidoxime resins the selectivity series can be as follows: **Cu(II) > Fe(III) > As(III) > Zn(II) > Ni(II) > Cd(II) > Co(II) > Cr(III) > Pb(II).** Interesting results were obtained by observing the impact of acidity on the behaviour of this ion exchanger. At low pH values (<3) there was a decrease in the chelating ability of Duolite ES 346 for heavy metal ions as well as degradation of its functional groups according to the reactions (Ferriera et al. 1998):

$$R-C{\overset{NOH}{\underset{NH_2}{}}} + H^+ + 2H_2O \rightleftharpoons R-C{\overset{O}{\underset{OH}{}}} + NH_2OH + NH_4^+$$

$$R-C{\overset{NOH}{\underset{NH_2}{}}} + H^+ + 2H_2O \rightleftharpoons R-C{\overset{NOH}{\underset{OH}{}}} + NH_4^+$$

However, the second reaction is the representative of the degradation of amidoxime groups under less acidic conditions (pH < 3.0). The increase in pH causes the weakening of the hydrogen ions competition for active sides resulting in an increase in the complexation of metal ions such as Cu(II). The fact that the degradation of the functional groups of Duolite ES-346 occurs under the influence of strong mineral acids is a serious problem which can significantly reduce the chelating capacity of the resin. However, this effect was made use of the recovery of adsorbed ions on the resin ion exchange. Corella et al. (1984) demonstrated that poly(acrylamidoxime) can be successfully used for the preconcentration of trace metals from aqueous solutions.

Also salicylic acid is a ligand which can selectively complex with Zn(II), Pb(II), Fe(III). Using the salicylic acid loaded resin for preconcentration of Zn(II) and Pb(II), it was proved that the preconcentration factors are much higher than those for bis(2-hydroxyethyl)dithiocarbamate (Saxena et al. 1995). However, the phenol-formaldehyde resin with the salicylaldoxime and salicylaldehyde functional chelating groups shows high selectivity for Cu(II) ions (Ebraheem & Hamdi, 1997).
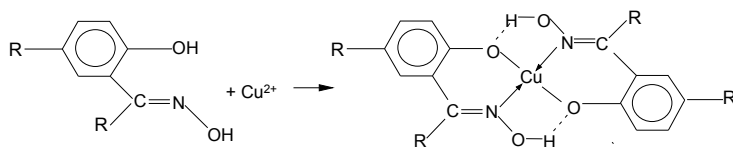
The affinity order of metal complexes of salicylaldoxime is as follows: $Fe^{3+} > Cu^{2+} > Ni^{2+} > Zn^{2+} > Co^{2+}$.

6. Chelating ion exchangers with the dithiocarbamate functional groups

The high affinity for transition metal ions is also exhibited by the classes of ion exchangers with the dithiocarbamate functional groups (including commercially available Nisso ALM 125), in which sulphur is the donor atom. Ion exchangers of this type have high affinity for the Hg(II), Pb(II), Cd(II) ions as well as precious metal ions, however, they do not adsorb alkali and alkaline earth metals. It was shown that dithiocarbamates obtained with the share of primary amines are less stable than those obtained with the share of secondary amines, and the binding of metal ions to the functional group of the donor atom increases in the number of $Fe^{2+} < Ni^{2+} < Cu^{2+}$. The sorption efficiency is dependent on the presence of ions in the solution such as SCN^-. In the paper by McClain and Hsieh (2004) the selective removal of Hg(II), Cd(II) and Pb(II) was presented. This resin is also effective for separation and
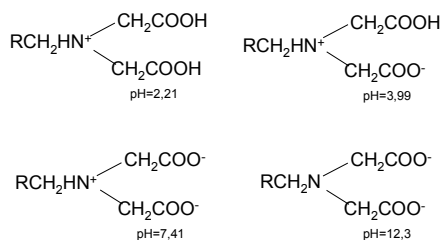
concentration of Mn(II), Pb(II), Cd(II), Cu(II) , Fe(III) and Zn(II) from complex matrices (Yebra-Biurrun et al. 1992). The copolymer of poly(iminoethylo)dithiocarbamate was used for sorption of VO^{2+}, Fe(II), Fe(III), Co(II), Ni(II) and Cu(II) (Kantipuly et al. 1990)

7. Chelating ion exchangers with the 8-hydroxyquinoline functional groups

A simple method for immobilization of 8-hydroxyquinoline in a silica matrix is described by Lührmann (1985). The sorbent was used in the sorption of Cu(II), Ni(II), Co(II), Fe(III), Cr(III) , Mn(II), Zn(II), Cd(II), Pb(II) and Hg(II) at pH from 4 to 6. It was shown that the sorption capacity varies in the range from 0.2 to 0.7 mM /g, and the partition coefficients from 1×10^3 to 9×10^4. Ryan and Weber showed (1985) that this type of sorbent has better sorption properties with respect to Cu(II) than Chelex 100 with the iminodiacetate functional groups. Th sorbents based on 8-hydroxyquinoline can be used, e.g. for concentration of the trace metal ions Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pb(II) and Cr(III) from sea water (Pyell & Stork, 1992).

## 8. Chelating ion exchangers with the iminodiacetic functional groups

Recently the attention has been paid to the ion exchangers with the amino- or iminoacids groups. The presence of two carboxyl groups and the tertiary nitrogen atom provides strong preference for chromium(III) and copper(II) (Marhol & Cheng, 1974). Therefore, for the commercial chelating ion exchangers such as Chelex 100, Dowex A 1, CR-20, Lewatit TP 207, Lewatit TP 208, Purolite S 930, Amberlite IRC 748 (formely Amberlite IRC 718) or Wofatit MC-50 the sorption process of metal ions proceeds according to the order: $\mathbf{Cr^{3+} > Cu^{2+} > Ni^{2+} > Zn^{2+} > Co^{2+} > Cd^{2+} > Fe^{2+} > Mn^{2+} > Ca^{2+} \gg Na^+}$. This type of ion exchangers also exhibis high affinity for Hg(II) and Sb(V) ions. It should be noted that depending on the pH value they may occur in the following forms (Zainol & Nicol. 2009a):

$$
\begin{array}{cc}
\text{RCH}_2\text{HN}^+ \begin{array}{l} \text{CH}_2\text{COOH} \\ \text{CH}_2\text{COOH} \end{array} & \text{RCH}_2\text{HN}^+ \begin{array}{l} \text{CH}_2\text{COOH} \\ \text{CH}_2\text{COO}^- \end{array} \\
\text{pH=2,21} & \text{pH=3,99} \\[2mm]
\text{RCH}_2\text{HN}^+ \begin{array}{l} \text{CH}_2\text{COO}^- \\ \text{CH}_2\text{COO}^- \end{array} & \text{RCH}_2\text{N} \begin{array}{l} \text{CH}_2\text{COO}^- \\ \text{CH}_2\text{COO}^- \end{array} \\
\text{pH=7,41} & \text{pH=12,3}
\end{array}
$$

At pH <2.0 the nitrogen atom and the two carboxylic groups are protonated. In this case the chelating ion exchanger with the iminodiacetic functional groups behaves as a weakly basic anion exchanger. At pH ~ 12, the nitrogen atom and the two carboxylic groups undergo deprotonation – the ion exchanger behaves as a typical weakly acidic cation exchanger. For pH medium values, the iminodiacetic resin behaves as an amphoteric ion exchanger. The iminodiacetate groups provide electron pairs so that the binding force for the alkaline earth

metals is 5000 times as large as that for alkali metals like Ca(II), which react with divalent metals to form a stable coordination covalent bond. Therefore, the affinity series determined for the iminodiacetic ion exchanger can be presented in the order: $Hg^{2+} > UO_2^{2+} > Cu^{2+} > Pb^{2+} > Ni^{2+} > Cd^{2+} > Zn^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+} > Ca^{2+} > Mg^{2+} > Ba^{2+} > Sr^{2+} \gg Li^+ > Na^+ > K^+.$

Amberlite IRC 748 in the K(I) form was also used for removal of Ca(II), Mg(II) from the potassium chromate solution (Yua et al. 2009). The optimum pH obtained for Ca(II) and Mg(II) adsorption onto Amberlite IRC 748 from the potassium chromate solution is 9.8 and 9.5, respectively. It was also noted that an increase of temperature and resin dosage resulted in their higher adsorption and the equilibrium conditions were attained within 480 min. The experimental data were relatively well interpreted by the Langmuir isotherm and the monolayer adsorption capacities of Ca(II) and Mg(II) were equal to 47.21 mg/g and 27.70 mg/g, respectively. This is of great importance because manufacturing of chromium trioxide by electrolyzing chromate salts, as a green process with the zero emission of waste, is studied widely now (Li et. al 2006). It should be also pointed out that separation factors between Mg(II) and Ca(II) and other divalent metal ions on an iminodiacetate resin are much smaller than those expected from the stability constants of their IDA complexes in solutions. Such phenomena were qualitatively described as the 'polymer effect' or operation of ion exchange as well as complexation reactions. Pesavento et al. (1993) gave a quantitative explanation for these anomalies on the basis of the Gibbs-Donnan model. Ca(II) and Mg(II) ions are adsorbed forming the $R(Hida)_2M$ complexes in acidic media and R(ida)M in neutral and alkaline systems whereas Ni(II) or Cu(II) etc. forms the R(ida)M complexes:
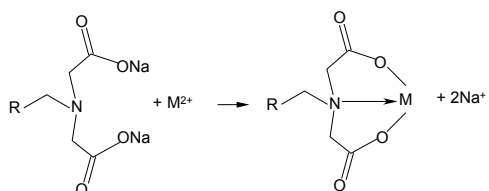
Commercially available chelating resins with the iminodiacetate functional group (Amberlite IRC 748, Lewatit TP 207, Lewatit TP 208, Purolite S 930, Lewatit MonoPlus TP 207) have been evaluated for their suitability for the adsorption of Ni(II) and other metal ions (Al(III), Ca(II), Co(II), Cr(III), Cu(II), Fe(II/III), Mg(II), Mn(II) and Zn(II)) from the tailings of a pressure acid leach process for nickel laterites. The Amberlite IRC 748 and TP MonoPlus 207 resins were found to be the most suitable in terms of loading capacity for nickel and kinetics of adsorption. Although all the five resins studied have the same functional groups their performance is not identical. The observed differences are possibly caused by variations in the synthesis procedure which results in variations in the structure of the matrix, degree of cross linking, density of functional groups, proportion of iminodiacetate groups and also the particle size (Zainol & Nicol, 2009a)

Additionally, the research carried out by Biesuz et al. (1998) shows that in the case of Ni(II) and Cd(II) sorption the structure of formed complexes is different. Ni(II) forms complexes of

R(ida)M type, whereas Cd(II) R(idaH)₂M. However, in the paper by Zagorodni & Muhammed (1999) it was stated that the complexes R(Hida)₂M should be extremely weak or even impossible. The adsorption equilibrium of Ni(II), Co(II), Mn(II) and Mg(II) on Amberlite IRC 748 has been discussed in (Zainol & Nicol, 2009b). The resin proves to have high selectivity for Ni(II) and Co(II) which suggests that these metals can be easily separated from Mg(II) and Mn(II) at pH 4 and 5. The following order of selectivity of the resin was also found: Ni(II) > Co(II) > Mn(II) > Mg(II).

The kinetics of Cd(II) sorption from separate solutions and from the mixtures with the nonionic surfactant Lutensol AO-10 (oxyethylated alkohols) in the hydrogen form of chelating iminodiacetic ion exchanger has also been investigated (Kaušpėdienė et al. 2003). It was stated that the sorption of Cd(II) from separate solutions and from the mixture with AO-10 is controlled by the intraparticle diffusion in acidic (pH 5) and alkaline media (pH 7.6). The presence of AO-10 leads to a decrease in the rate of intraparticle diffusion. The iminodiacetate resin has a large collective adsorption with Cr(III) ion. The Cr(III) form bearing waste water can be removed at any pH in the range 3-6 at 2h of the phase contact time. Therefore for treatment of leather tanning, electroplating, textile and dyeing waste water the application of this resin is economical (Gode & Pehlivan, 2003)

Adsorption of trivalent metal ions on iminodiacetate resins was not studied as extensively as that of divalent metal ions. The known selectivity order of trivalent metal ions on an iminodiacetate resin can be presented as: $Sc^{3+} > Ga^{3+} > In^{3+} > Fe^{3+} > Y^{3+} > La^{3+} > Al^{3+}$ (Yuchi et al. 1997).

Also since the end of the 1960s fibrous adsorbents with the iminodiacetic acid groups have been studied. For example, the capacity of a commercially available iminodiacetic acid fiber named Ionex IDA-Na was established to be 0.9-1.1 mmol/g for Cu(II). The fibrous materials containing iminodiacetate groups were developed by the group of Jyo et al. (2004) . Although the metal ion selectivity of the present fiber was close to that of iminodiacetic acid resins, the metal adsorption rate of chloromethylstyrene-grafted polyethylene coated polypropylene filamentary fiber is much higher than that of commercially available granular exchangers of this type having cross-linked polystyrene matrices. In the column mode adsorption of Cu(II), breakthrough capacities of Cu(II) were independent of the flow rates of feeds up to 200-300/h. The main reasons for the extremely fast adsorption rate of sorbent can be ascribed to the diameter of the fiber being much less than those of the resins as well as to the fact that the functional groups were introduced onto non cross linked grafted polymer chains. Their chemical and physical stabilities are comparable to those of commercially available iminodiacetic acid resins.

9. Chelating ion exchangers with the phosphonic and aminophosphonic functional groups

Among various types of ion exchangers with the acidic ligands, those having phosphonate functionality are of particular interest since they are selective towards heavy metal cations.

Development of this type of ion exchangers started in the late 1940s with phosphorylation of poly(vinyl alcohol) using various phosphorylating agents (Trochimczuk & Streat, 1999; Trochimczuk 2000). Besides phosphate, phosphinic and phosphonic resins, containing –$OPO(OH)_2$, –$PO(OH)$ and -$PO(OH)_2$ functional groups, respectively, they also contain methylenediphosphonate, ethylenediphosphonate and carboxyethyl phosphonate ones (Marhol et al. 1974;

Kabay, 1998a; Ogata et al. 2006). In all cases they display good selectivity towards metal ions even at very low pH (except for ethylenediphosphonate and carboxyl containing resins, being less acidic, more selective at the pH value from 1 to 2).

Chelating ion exchangers with the phosphonic functional groups are characterized by extremely high selectivity towards Th(IV) and U(IV,VI) as well as Cu(II), Cd(II), Zn(II), Ni(II), Ag(I), Au(III) and Fe(III) ions. Commercially available resins containing the phosphonic groups are Diaion CRP200 and Diphonix® Resin. In the case of Diphonix® Resin besides the diphosphonic functional groups in the structure of the ion exchanger, there are also carboxylic and sulphonic functional groups whose presence determines better hydrophilic properties. Diphonix® Resin as well as Diphonix A with the functional phopshonic and ammonium (type 1) or pyridyne (type 2) groups have been of significant interest lately (Chiarizia et al. 1993; Horwitz et al. 1993; Chiarizia et al. 1994; Chiarizia et al. 1996, Alexandratos, 2009). Diphonix® Resin was developed by the Argonne National Laboratory and University of Tennessee. It is synthesized by a patented process involving copolymerization of tetraalkylvinylidene diphosphonate with styrene, divinylbenzene, and acrylonitrile followed by sulphonation with concentrated sulphuric acid. Finding a method for effective copolymerization of vinylidene-1,1-diphosphonate (VDPA) ester was a major achievement because of the steric hindrance imposed on the vinylidene group by the diphosphonate group. This difficulty was overcome by using another relatively small monomer, acrylonitrile, as a carrier to induce polymerization of vinylidene-1,1-diphosphonate (Horwitz et al. 1994; Horwitz, et al. 1995). The protonation constants of Diphonix Resin® which are pK_1 and $pK_2 < 2.5$ $pK_3=7.24$ and $pK_4=10.46$ appear almost equal to the protonation constants of the starting material VDPA which are $pK_1=1.27$, $pK_2 = 2.41$, $pK_3=6.67$ and $pK_4=10.04$ (Nash et al. 1994).
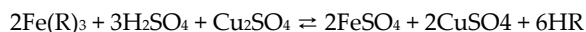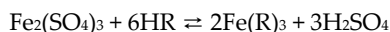
In the past few years there were many publications on the separation of lanthanides and actinides on the chelating resins with the phosphonic groups. Lanthanides in minerals occur in small amounts, usually in the form of mixtures, often isomorphic, so that their extraction and separation create many problems. To this end also Diphonix® Resin can be used especially at low pH. It is characterized by high affinity for U(VI), Pu(IV), Np(IV), Th(IV), Am(III) and Eu(III). It was found that from 1 M HNO_3 solutions the distribution coefficient of Diphonix® Resin for U(VI) ions is 70,000 compared to 900 for sulphinic acid resin (Alexandratos, 2007) and the recovery coefficient for Eu(III) under the same conditions is 98.3, whereas for the sulphonic acid resin 44.9 (Ripperger & Alexandratos, 1999). In the paper by Phillips et al. it was demonstrated that Diphonix Resin® can be successfully used for removal of uranium from the solutions of pH > 5 including high concentration of NO_3^- ions as it is less sensitive to interference by such ions as carbonates, nitrates(V),

sulphates(VI), Fe(III), Ca(II) and Na(I) (Philips et al. 2008). It can be also used for removal of V(V), Cr(III), Mn(II), Co(II), Ni(II), Zn(II), Cd(II), Hg(II) and Pb(II) form waters and waste waters; V(V), Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and Pb(II) from drinking water; Mn(II), Co(II) and Ni(II) from waste waters of the oil industry; Cr(III) from acidic solutions, Fe(III) from the solutions containing complexing agents in the process of removing scale and radionuclides from radioactive waste waters. Smolik et al. (2009) investigated separation of zirconium(IV) from hafnium(IV) sulphuric acid solutions on Diphonix Resin®. It was found that the best medium for separation of hafnium(IV) and zirconium(IV) is 0.5 M sulphuric acid. A decrease in temperature lowers the degree of metals separation, while lower flow rates through the column increases zirconium(IV) from hafnium(IV) separation. Recent studies have shown that Diphonix Resin® can also be used for removal of Cd(II) and Cr(III) from the phosphoric acid solutions through column tests. Kabay et al. (1998b) found that the acid concentration strongly determines the resin behaviour with respect to the sorption/elution of Cd(II) and Cr(III). In the paper by Cavaco et al. it was pointed but that Diphonix Resin® has strong affinity for Cr(III) ions and high selectivity towards Fe(III) and Ni(II) (Cavaco et al. 2009). The mechanism of sorption on Diphonix Resin® can be written as (Hajiev et al. 1989):

$$R–(PO_3H_2)_2{}^{2-} + M^{2+} \rightleftarrows R–(PO_3H_2)^{2-}\text{--}M^{2+}$$
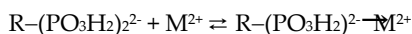
where: R is the resin matrix.

However, according to the literature, Diphonix Resin® has the best selectivity for transition metals such as Fe(III), Cu(II) and Ni(II) over Cr(III). High affinity of Diphonix Resin® for Fe(III) compared to the mono- and divalent ions e.g. Ca(II) was reported in several papers. Owing to its very good separation capability, Diphonix Resin® was also applied in the project FENIX Iron Control System to remove iron from the spent copper electrolyte in Western Metals Copper Ltd. (Queensland, Australia). In this plant, copper(I) sulphate(VI) was used as a reducing agent at the reaction temperature of 85 °C to increase the elution of Fe(III):

$$Fe_2(SO_4)_3 + 6HR \rightleftarrows 2Fe(R)_3 + 3H_2SO_4$$

$$CuSO_4 + Cu \rightleftarrows Cu_2SO_4$$

$$2Fe(R)_3 + 3H_2SO_4 + Cu_2SO_4 \rightleftarrows 2FeSO_4 + 2CuSO4 + 6HR$$

where: R is the resin matrix.

In the paper by Lee & Nicol (2007) it was proved that sorption capacities of Diphonix Resin® for Fe(III) and Co(II) ions in the sulphate(VI) system at pH 2 are equal to 130 mg/g and 90 mg/g, respectively.

The obvious disadvantage of this ion exchanger is therefore the fact that it is difficult to remove Fe(III) ions. To this end 1-hydroxyethane-1,1-diphosphonic acid (HEDP) is used. In the case of Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), Sn(II) and Pb(II) ions 2M H_2SO_4 can be also applied.

In the group of chelating ion exchangers containing phosphonic and aminophosphonic functionalities the resins with aminoalkylphosphonic functional groups, such as Duolite C-467, Duolite ES-467, Lewatit OC 1060, Purolite S 940, Purolite S 950 and Chelite P occupy a significant position. In the sorption of heavy metal ions on this kind of chelating ion exchangers the following affinity series is obtained: $Pb^{2+} > Cu^{2+} > UO_2^{2+}$, Zn^{2+}, $Al^{3+} > Mg^{2+} > Sr^{2+} > Ca^{2+} > Cd^{2+} > Ni^{2+} > Co^{2+} > Na^+ > Ba^{2+}$. These ion exchangers as well as the previously mentioned phosphonic ones exhibit poor affinity for Ca(II) and Mg(II). The effectiveness of sorption of the above mentioned metal ions, however, decreases with the decreasing pH. It is worth mentioning that depending on pH value, the aminoalkylphosphonic groups may occur in the following forms:
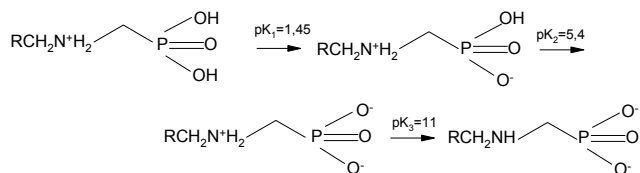

and therefore the selectivity of metal ions sorption depends on the degree of ionization of phosphonic groups. In the case of acidic solutions due to protonation of the nitrogen atom of aminophosphonic group there are formed combinations with the following structure:
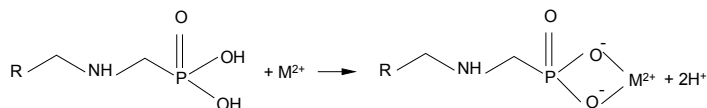

One of the most favourable modes of chelation of the phosphonic acid group is the formation of a four-membered ring through determination of two P-OH groups.

Additionally, in the case of the aminoalkylphosphonic groups, due to the fact that between the aromatic ring of the matrix and the nitrogen atom there is also presented the alkyl group, the increase of the electron density on the nitrogen atom of the amino group is expected. It affects the growth of its protonation. Therefore, this preferred zwitterion form can be as follows:
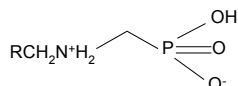
However, the possibility of coordination of the secondary nitrogen atom at lower pH seems to be impossible with respect to its protonated nature and also for steric reasons. Therefore the only potential donor and binding sites of Duolite ES-467 are the oxygen atoms of the phosphonic groups at lower pH values. The chelating, aminomethylphosphonic functional group is also potentially a tridentate ligand having two bonding sites at a phosphonic acid groups and one coordination site at the secondary nitrogen atom (Kertman, 1997; Nesterenko et al. 1999). Formation of a four membered ring through bonding of one of the

OH groups and coordination of the oxygen atom has also been reported. These structures are presented below:
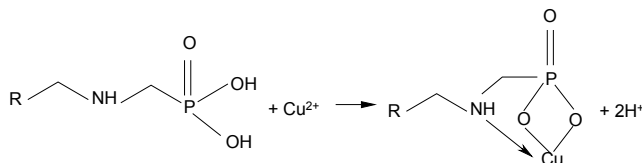

Chelating ion exchangers with the aminoalkylphosphonic functional groups, like picolylamine resins - Dowex M 4195 exhibits moderate selectivity for Cu(II) over Fe(III) in the acidic sulphate(VI) solutions compared to the iminodiacetic acid resins which show no or limited selectivity depending on pH. The stability constants for divalent metal ions with aminomethylphosphonic acid have been found in the order: $Ca^{2+} < Mg^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$ (Sahni et al. 1985). In the paper by Milling and West (1984), it was found that Duolite ES-467 possesses a higher capacity for copper(II) ions compared to nickel(II) and iron(III) and that the capacity decreases with the decreasing pH and metal ion concentration in the solution.

Besides Duolite ES-467, Purolite S 950 has been proved to have a high affinity for various heavy metal ions and it is successfully applied in metallurgical and wastewater treatment processes. In the paper by Koivula et al. (2000) Purolite S-950 was used for purification of effluents from metal plating industry containing Zn(II), Ni(II), Cu(II) and Cd(II) ions. Among others, it was stated that Purolite S-950 showed lower sorption capacity equal to 1.2 eq/dm^3 for zinc chloride compared to zinc solutions containing KCl and NH$_4$Cl (1.3 eq/dm^3). Under analogous conditions the sorption capacity for Cd(II) was 1.1 eq/dm^3. Recovery of Ni(II) and Co(II) from organic acid complexes using Purolite S 950 was also studied by Deepatana & Valix (2006). They found that sorption capacities for nickel sulphate(VI) for Dowex M4195 (94.51 mg/g), Amberlite IRC 748 (125.03 mg/g) and Ionac SR-5 (79.26 mg/g) are much higher than those for Purolite S-950 in the case of sorption of Ni(II) complexes with citric acid (18.42 mg/g), malic acid (14.45 mg/g) and lactic acid (19.42 mg/g) mainly due to the steric hindrance. For Co(II) ions analogous results were obtained (citric 5.39 mg/g for citric acid; 7.54 mg/g for malic acid and 10.48 mg/g for lactic acid). The elution efficiencies of these complexes from Purolite S-950 resins were high (82–98%) therefore it would appear that the adsorption process involves weak interactions. However, in the case of the sorption of Cu(II) and Zn(II) ions from the sulphate solutions at pH 1.9 on the aminomethylphosphonic resin Lewatit R 252K and the iminodiacetic resin Lewatit TP 207 it was found that separation factors were much lower for Lewatit R 252K (83.0 at 10 ºC and 30.0 at 80 ºC) than for Lewatit TP 207 (1.67 at 10 ºC and 1.4 at 80 ºC) (Muraviev et al. 1995).

10. Chelating ion exchangers with the methylglucamine functional groups

Selective ion exchange resins also include chelating ion exchangers containing N-methyl (polyhydroxohexyl)amine functional groups also called methylglucamine. Commercially available ion exchangers of this type are: Amberlite IRA 743, Duolite ES-371, Diaion CRB 02, Dowex BSR 1, Purolite S 108 and Purolite S110.

These ion exchangers show high selectivity for boron (in the form of trioxyboric acid H_3BO_3) (Alexandratos, 2007; Alexandratos, 2009). The boron sorption process proceeds according to the scheme:
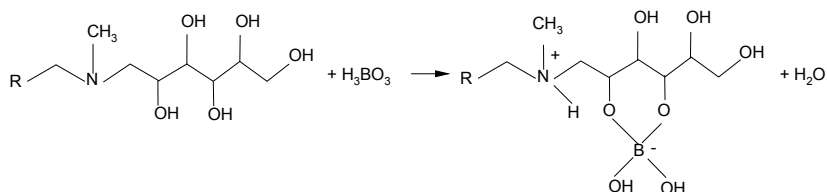
Besides boron the following components of waste water should be also taken into account: Na(I), K(I), Ca(II), Mg(II), Cl^-, SO_4^{2-}, HCO_3^-, CO_3^{2-} and effects should be also considered. Ion exchangers of this type can be used in the removal of Cr(VI) and As(V) (Dambies et al. 2004; Gandhi et al. 2010) although the mechanism of sorption of chromate ions(VI) involves both electrostatic interactions with the protonate amino group and the reduction of Cr(Vl) to Cr(III):
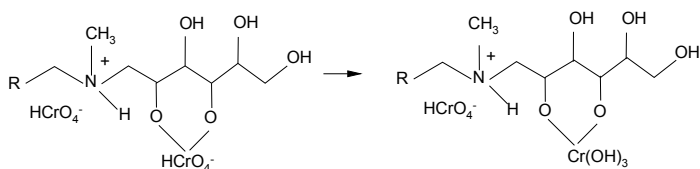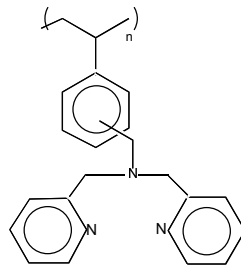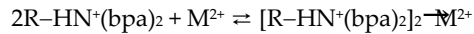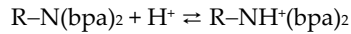

As for arsenate removal the process should be conducted from aqueous solutions at neutral pH. The percent removal of arsenate from the aqueous solution of 100 mg/ dm^3 arsenate and 560 mg/dm^3 sulphate on NMDG resin is 99% and the reaction is unaffected by the presence of phosphate ions and the solution pH above 9.0, indicating that it can be regenerated with the alkaline solution. It was determined that the key variable in its selectivity is that the resin has to be protonated prior to contact with the aqueous solution (Alexandratos, 2007).

11. Chelating ion exchangers with the bis(2-pyridylmethyl)amine functional groups

The ion exchange resins with the bis(2-pyridylmethyl)amine (bpa) functional groups also known as bispicolylamine are capable of selective sorption of transition metals, particularly Cu(II) ions due to the presence of donor atoms (nitrogen atoms) which are capable of coordination reaction with Cu(II). Due to this fact, such chelating ion exchange resins can combine ion exchange and complexing reactions and then exhibit high selectivity for metal ions. Dowex M 4195 possessing such functional groups is commercially available. It was synthesized in the early 1970s by Dow Chemical Co. and formerly known as Dowex XFS-4195 or DOW 3N. Also two others: Dowex M4196 (formerly Dowex XFS-4196) N-(2-hydroxyethyl)picolylamine or Dowex XFS-43084 (DOW 2N) with N-(2-hydroxypropyl)picolylamine were recognized (Jones & Pyper, 1979; Grinstead, 1984).

Bis(2-pyridylmethyl)amine (bpa) is an uncharged tridentate ligand having the ability to form charged complexes with most divalent metals. The 1:1 complexes with the metal ions of $[M(bpa)]^{2+}$ type are stable (Hirayama & Umehara, 1996). Based on the pK_a values of bis(2-pyridylmethyl)amine (pK_1=0.5, pK_2=2.2, pK_3=3.4), it can be stated that at low pH values three nitrogen atoms would be protonated, while in the middle range of pH only one. For instance, Cu(II) ions (the coordination number is equal to 4) with the bis(2-pyridylmethyl)amine group and water molecule coordinate to it giving a square planar structure. In the next stage the H_2O molecule can be replaced by the anion, which is able to coordinate Cu(II) by a ligand exchange reaction:

$$R\text{–}N(bpa)_2 + H^+ \rightleftharpoons R\text{–}NH^+(bpa)_2$$

$$2R\text{–}HN^+(bpa)_2 + M^{2+} \rightleftharpoons [R\text{–}HN^+(bpa)_2]_2\text{–}M^{2+}$$


The complexes formed in the resin phase possess the following structure:
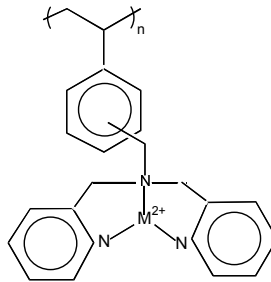
The obtained complex ion exchanger provides a new mode for the recognition of ions in the chromatographic analysis. Dowex M-4195 is a weak base ion exchanger and 1 M H_2SO_4 is in the protonated form (pKa = 3.2). It is also resistant to osmotic shock. Diniz et al. (2000, 2002, 2005) showed that the affinity series of metal ions determined in the one-component system for Dowex M 4195 is as follows: Cu(II) > Ni(II) > Co(II) > Pb(II) > Fe(III) > Mn(II) and it is slightly different from that in the multicomponent system: Cu(II) > Ni(II) > Pb(II) > Fe(III) > Co(II) > Mn(II). The affinity of the transition metal cations for Dowex M 4195 in most cases was in agreement with the Irving-Williams order (Irving and Williams, 1953): Fe(II) < Co(II) < Fe(III) < Ni(II) < Cu(II) > Zn(II). It can be used for purification of chloride solutions after leaching of Mn(II) containing trace amounts of Co(II), Pb(II), Ni(II) and Cu(II). It can be also used for gold recovery (Tuzen, 2008).

On a commercial scale Dowex M 4195 has been used, among others, for separation of Ni(II) ions in the presence of Co(II) at INCO's Port Colborne refinery in Canada and Zambia Chambishi Cobalt Plant (Diniz et al. 2005) for purifying cobalt electrolytes. The efficiency of sorption of both ions is affected not only by pH, but by also by the concentration of sulphate(VI) ions and temperature. It is worth mentioning that separation of the twin pair Co(II)-Ni(II) is one of the most difficult tasks in inorganic chemistry. Contrary to Lewatit TP 207 and Amberlite IRC 718 with the iminodiacetate functional groups, Dowex M-4195 is characterized by the maximum sorption capacity towards Cu(II) ions in the pH range 1-4 (Melling and West, 1984). The sorption process can be presented in the following reaction:
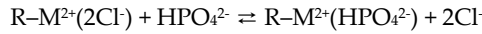
$$RH_n + Cu^{2+} \rightleftarrows R–Cu^{2+} + nH^+$$
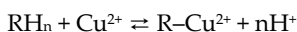
where: R is the resin matrix, n is the stoichiometric ratio, for $n \neq 2$ the SO_4^{2-} ions sorption occurs.

Partial washing out of copper(II) ions proceeds by means of 4M H_2SO_4, whereas the total one by means of $NH_3 \cdot H_2O$. In the case of sorption of Cu(II) ions sorption in the presence of Fe(III) ions, the ion exchange mechanism must be assumed. Sorption of both ions is affected not only by pH, but also by concentration of sulphate(VI) ions and temperature. Fe(III) ions sorption increases significantly with the temperature rise from 293 K to 303 K, whereas it does not change for Cu(II) ions.

The ion exchangers with the picolylamine functional groups can be the basis for obtaining the polymeric ligand exchanger (PLE) with the structure presented above (Zhao et al. 1998; Kołodyńska 2009c):
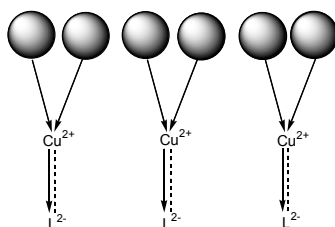
Such kind of ion exchanger consists of the cross linked polystyrene-divinylbenzene matrix, covalently attached bispicolylamine functional groups and Lewis acid cations (such as Cu^{2+}, Ni^{2+}, Fe^{3+}, Co^{2+} according to the series: $Cu^{2+} > Ni^{2+} > Fe^{3+} > Co^{2+}$) coordinated to the functional groups and without neutralization of their positive charge so that the anion exchanger is obtained. It is expected to show high affinity not only for phosphates(V) HPO_4^{2-}, arsenate(V) $HAsO_4^{2-}$ and chromate(VI) CrO_4^{2-} ions but also oxalates ox^{2-}, perchlorates ClO_4^-, tartaric acid as well as simultaneous and selective removal of heavy metal and chromate ions (contrary to other ion exchangers) (Saygi et al. 2008; Dimick, 2008; Du et al. 2008). It was found that for phosphates(V) HPO_4^{2-} removal, the sorption efficiency is much higher than that for the strongly basic macroporous anion exchanger Amberlite IRA 958 and proceeds according to the reaction:

$$R–M^{2+}(2Cl^-) + HPO_4^{2-} \rightleftarrows R–M^{2+}(HPO_4^{2-}) + 2Cl^-$$

The desorption process can be written as follows:

$$R–M^{2+}(HPO_4^{2-}) + 2Cl^- + H^+ \rightleftarrows R–M^{2+}(2Cl^-) + H_2PO_4^-$$

$$R–M^{2+}(HPO_4^{2-}) + 2Cl^- \rightleftarrows R–M^{2+}(2Cl^-) + HPO_4^{2-}$$
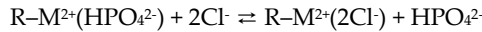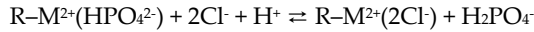
Four chelating ion exchange polymeric resins were tested to remove Ni(II) and Co(II) from synthetic solutions on the commercially available ion exchangers Dowex M4195, Amberlite IRC 748, Ionac SR-5 and Purolite S930. Among the selected resins, Dowex M4195 showed the best results for Ni(II) and Co(II) selective sorption from acid liquors in the whole pH range and with small influence of other elements. Even at pH 1 Dowex M4195 was the most effective (Mendes & Martins, 2004).

12. Chelating ion exchangers with the thiol, thiourea and isothiourea functional groups

In the group of ion exchangers with the thiol functional groups (Chelite S, Duolite ES-465, Imac GT 73) Imac TMR resin is very important. It is the macroporous ion exchanger with the PS-DVB matrix, which besides the thiol ones, also possesses the sulphone groups. Imac TMR is used for selective sorption of Hg(II) ions from the process solutions as well as Ag(I), Au(III), Pt(IV) and Pd(II). The sorption process of Hg(II) with the saline solution proceeds according to the reaction:

$$R–SH + Hg^{2+} \longrightarrow (R–S)_2Hg^{2+} + 2H^+$$

$$R–SH + HgCl^+ \longrightarrow R–SHgCl + H^+$$
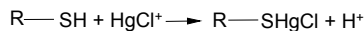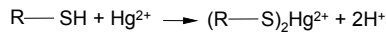
Also ion exchangers with the isothiourea functional groups (Ionac SR 3, Lewatit TP 214, Purolite S 920, Srafion NMRR) exhibit high affinity for Hg(II) ions. They are also selective for noble metal ions. Depending on the pH, the isothiourea groups occur in the following forms:
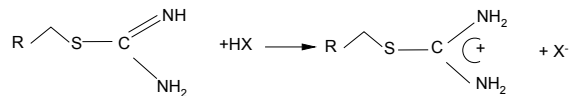
For the first form, coordination bond formation is possible, whereas for the second one the sorption process proceeds in accordance with the anion exchange mechanism:
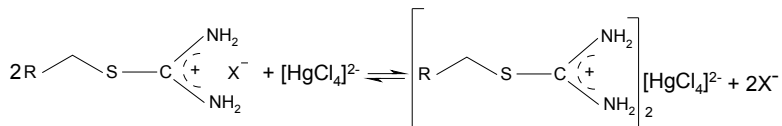
13. Retardion 11A8

Dowex Retardion 11A8 is an example of a very interesting ion exchanger of the type 'snake in a cage' with the quaternary ammonium and carboxylic functional groups (amphoteric resin) (Dybczyński, 1987). It is produced by polymerizing acrylic acid monomer inside an anion exchange resin. Polyacrylic chains are (snake) alternate with the PS-DVB matrix (cage) and therefore they are trapped inside the cross linked ion exchange resin and cannot diffuse out. As a result, cationic and anionic sites are so closely associated that they partially neutralize their electric charges. Mobile ions, such as chlorides, nitrates(V) are attracted and retained on these unique sites until they are eluted with hot water.

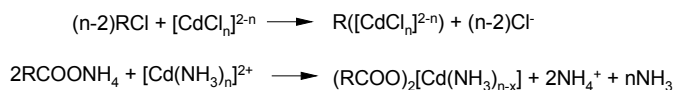Dowex Retardion 11A8 can be used for selective separation of Cd(II) ions in the presence of other heavy metal ions (Samczyński & Dybczyński, 2002). Cd(II) ions are sorbed from 2 M HCl and 2 M NH$_4$OH with 0.1 M NH$_4$Cl systems according to the reactions:

$$(n-2)RCl + [CdCl_n]^{2-n} \longrightarrow R([CdCl_n]^{2-n}) + (n-2)Cl^-$$

$$2RCOONH_4 + [Cd(NH_3)_n]^{2+} \longrightarrow (RCOO)_2[Cd(NH_3)_{n-x}] + 2NH_4^+ + nNH_3$$

In the case of separation of Ga(III), In(III), Tl(III), Pt(II), Pd(II) and Na(I), Ni(II), Cu(II) and Zn(II) mixtures in acidic media the resin acts mainly as an anion exchanger. For the elements that can exist as both cations and anions in solution (e.g., Ni, Co, Cu and Zn), the amphoteric properties of Retardion11A8 permit more specific isolation of certain elements from complex mixtures than would be possible with the use of monofunctional ion exchangers (Dybczyński & Sterlińska, 1974).

14. Impregnated ion exchangers

The impregnated resins obtained by physically loaded organic reagents on a solid inert support material such as Amberlite XAD resins are an attractive material for separation and preconcentration of heavy metal ions (Prabhakaran & Subramanian, 2003). They are characterized by good porosity, uniform pore size distribution, high surface area as a chemical homogeneous, non-ionic structure. For instance, it was found that Amberlite XAD-2 functionalized with dithiocarbamate ligand, 1,8-dihydroxynaphthalene-3,6-disulphonic acid (chromotropic acid), 2(2-thiazolylazo)-*p*-cresol, l-(2-pyridylazo)-2-naphthol, calmagite, xylenol orange (Abollino et al. 1998; Ferreira & Brito, 1999, Ferreira et al. 1999; Ferreira et al. 2000a; Ferreira et al. 2000b; Tewari & Singh, 1999; Tewari & Singh, 2000; Tewari & Singh, 2001; Tewari & Singh, 2002) can be used for selective sorption and preconcentration of heavy metal ions. Amberlite XAD-4 loaded with sodium diethyl dithiocarbamate; 2,3-dihydroxy benzoic acid (DHBA), ammonium pyrrolidine dithiocarbamate (APDC) and piperidine dithiocarbamate (pipDTC) were used for preconcentration and determination of metal ions in various matrices (Uzun et al. 2001; Hosseini et al. 2006; Ramesh et al. 2002). However, the most promising polymeric support with a larger surface area is Amberlite XAD 16. Amberlite XAD-16 loaded with quercitin (Sharma & Pant, 2009) is characterized by good adsorbent properties for large amounts of uncharged compounds (Tokalıoğlu et al. 2010). The solid phase extraction

(SPE) process with the application of such materials is characterized by important advantages such simplicity, flexibility, economical, rapid, higher enrichment factors, absence of emulsion and low cost because of lower consumption of reagents.

In general, sorption selectivity of a resin can be affected by both sorbate-sorbent and sorbate-solvent interactions. It has been well recognized that resin matrix and functional groups can strongly affect ion exchange capacity and selectivity. Therefore in the presented paper the chelating ion exchangers Diphonix Resin® containing diphosphonic, sulphonic and carboxylic acid groups and Dowex M 4195 with the bis(2-pyridylmethyl) amine functional group were used for the sorption of Cu(II), Zn(II), Co(II), Pb(II) complexes with Baypure CX 100 (IDS) and Cu(II), Zn(II), Cd(II), Pb(II) complexes with Trilon M (MGDA). The presence of the sulphonic functional groups determines better hydrophilic properties of Diphonix Resin® compared to the traditional monofunctional ion exchangers.

15. Experimental

In the paper the results of the sorption of heavy metal ions such as Cu(II), Zn(II), Cd(II) and Pb(II) in the presence of the complexing agents of a new generation Baypure CX 100 (IDS) and Trilon M (MGDA) on commercially available chelating ion exchangers are presented.

The essential physicochemical properties of these chelating agents are given in Table 1.

16. Characteristics of the chelating ion exchange resins

The chelating ion exchange resins Dowex M 4195 and Diphonix Resin® were tested. Their short characteristics are presented in Table 2.
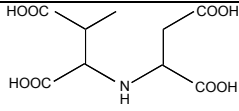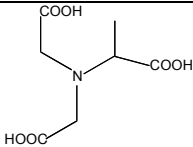
Properties	IDS	MGDA
Structure		
Form supplied	liquid	liquid
Molecular weight	337.1	271.0
Appearance	colourless to light yellow	clear yellowish
pH	10.3-11.4	11.0
Density [g mL^{-1}]	1.32-1.35 g/mL	1.31 g/mL
Solubility in H$_2$O	in any ratio	in any ratio
Solubility in NaOH	in any ratio	in any ratio
Biodegradability [%]	> 80%	> 68%
Termal stability	in any range	in any range

Table 1. Physicochemical properties of IDA and MGDA.

Properties	Dowex M 4195	Diphonix Resin®
Matrix	PS-DVB	PS-DVB
Structure	macroporous	gel
Functional groups	bis(2-pyridylmethyl) amine bis-picolylamine	diphosphonic sulphonic carboxylic
Commercial form	weak base, partially H_2SO_4 salt	H^+
Appearance	brown to green, opaque	beige, opaque
Total capacity	1.3 [eq/dm³]	5,6 [mol/kg]
Moisture content	40-60 %	58.3 %
Bead size	0.300-1.200 [mm]	0.074-0.150 [mm]
Density	0.67 [g/cm³]	1.05-1.11 [g/cm³]
Max temp. range	353 K	313 K
Operating pH range	2 – 6	0 – 12

Table 2. Physicochemical properties of Dowex M 4195 and Diphonix Resin®.

Before the experiments, the resins were washed with hydrochloric acid (0.1 M) or sulphuric acid (0.5 M) to remove impurities from their synthesis. After pre-treatment they were washed with deionised water.

The solutions of Cu(II), Zn(II), Cd(II) and Pb(II) complexes with Baypure CX 100 and Trilon M with the desirable concentrations were prepared by mixing appropriate metal chlorides or nitrates with the complexing agents solutions, respectively. For the studies the obtained solutions were used without pH adjustment. The pH values of the solutions of Cu(II), Zn(II), Cd(II) and Pb(II) complexes with IDS were as follows: 6.7, 6.5, 69 and 7.3, respectively. For the Cu(II), Zn(II), Cd(II) and Pb(II) complexes with MGDA these values were equal to 8.3, 9.8, 10.5 and 10.4. The other chemicals used were of analytical grade.

In batch experiments, 50 cm³ of sample solution and ion exchanger (0.5 g) were put into a conical flask and shaken at different time intervals using the laboratory shaker Elpin type 357, (Elpin-Plus, Poland). After the pH of solutions was stabilized and equilibrated, the ion exchangers were filtered. The experiments were conducted in three parallel series. The reproducibility of the measurements was within 5%. Adsorption isotherms were obtained with different initial concentrations varying from 1×10^{-3} M to 2.5×10^{-2} M of metal ions and ligands while keeping the constant amount of resins at room temperature (295 K). The equilibrium between the solid and liquid phases was modelled by the Langmuir and Freundlich equations as presented earlier (Kołodyńska, 2010a; Kołodyńska 2010b; Kołodyńska 2010c). Kinetic studies were carried out at different time intervals varying from 1 to 120 min keeping the constant amount of resins at room temperature (295 K). The shaking speed was 180 rpm to maintain resin particles in suspension.

The amount of heavy metal complexes sorbed onto the resins was calculated by the difference between the amounts added and already present in the solution and that left in the solution after equilibrium.

The pH values were measured with a PHM 84 pH meter (Radiometer, Copenhagen) with the glass REF 451 and calomel pHG 201-8 electrodes. The concentrations of heavy metals were measured with the AAS spectrometer Spectra 240 FS (Varian, Australia).

17. Results

As for the removal of toxic metal ions many different methods are available. Among them, the most commonly used are ion exchange, adsorption, reduction and precipitation. In many cases, the environmentally most compatible and cost-effective solutions include combination of two or more of these processes. From different waste waters those containing heavy metal ions and complexing agents require special attention.

18. Complexing agents

For over fifty years synthetic chelating agents from the group of aminopolycarboxylic acids (APCAs) have been the basis in many technological processes. Ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA) and diethylenetriaminepentaacetic acid (DTPA) are the best known traditional complexing agents. They are commonly applied in many branches of industry forming stable, water soluble complexes with various metal cations or as a masking agent. Nowadays there are a number of alternative products on the market which claim to be as effective as EDTA and NTA. Among them, IDS and MGDA should be listed.

Iminodisuccinic acid (IDS) also known as Baypure CX 100 is a medium-strong chelator consisting of: iminodisuccinic acid sodium salt > 32%, aspartic acid sodium salt < 7%, fumaric acid sodium salt < 3.5 %, hydroxysuccinic acid < 0.9 %, maleic acid sodium salt < 0.9 % (IDS Na-salz, 1998; Vasilev et al. 1996; Vasilev et al. 1998; Reinecke et al. 2000, Kołodyńska et al. 2009; Kołodyńska, 2009a). Iminodisuccinic acid sodium salt can form quintuple-bonded complexes with metal ions. In this case, complexing occurs via the nitrogen and all four carboxyl groups. As a result of the octahedric structure of the complete complex, a water molecule is required for the sixth coordination point (Kołodyńska, 2009b). In the paper by Hyvönen it was found that for low pH conditions (less than 3), the tendency for M(II)/M(III) ions to form complexes with IDS may be assumed as: Cu(II)>Fe(III)>Zn(II)>Mn(II), whereas for pH >7 it can be as follows: Cu(II)>Zn(II)>Mn(II)>Fe(III) (Hyvönen et al. 2003; Hyvönen & Aksela, 2010). IDS is able to replace EDTA when rather moderate chelating agents are sufficient for masking alkaline earth or heavy metal ions. As a substitute for EDTA it is used in a variety of applications, including detergent formulations, corrosion inhibitors, production of pulp and paper, textiles, ceramics, photochemical processes, and as trace nutrient fertilizers in agriculture.

Methylglycinediacetic acid (MGDA) was patented by BASF and marketed under the brand name Trilon M. The active ingredient contained in Trilon M is the trisodium salt of methylglycinediacetic acid. The acid dissociation constants pK_a of MGDA are as follows: pK_1=1.6, pK_2=2.5 pK_3=10.5 (Jachuła et al. 2011; Jachuła et al. 2012). The most important property of Trilon M is the ability to form complexes (MGDA is a tetradentate chelating

ligand where chelation involves three carboxylate groups and nitrogen atom) with metal ions, soluble in water in the large pH range 2-13. These complexes remain stable, especially in alkaline media and even at temperatures of up to 373 K. It is worth mentioning that MGDA chelating capacity was investigated by Tandy et al. (2004) in soil washing. It was found that 89-100% of MGDA can be degraded in 14 days, 90% of EDDS in 20 days while no EDTA was degraded in 30 days.

Fig. 5a-b shows the comparison of the logarithmic stability constants (log K) for the complexes of IDS and MGDA and selected metal ions with the stability constants for EDTA.
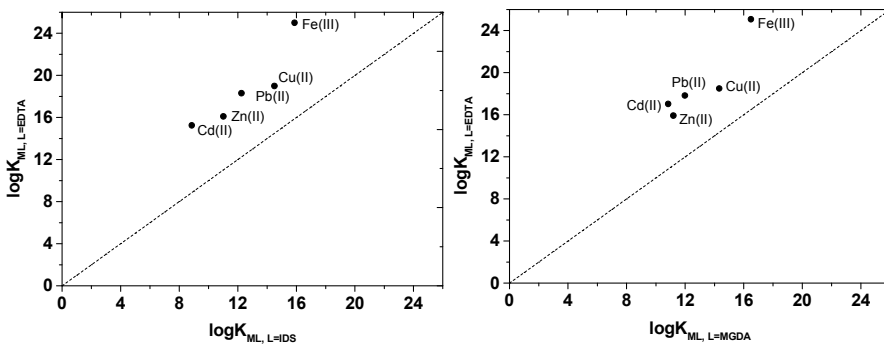

Figure 5. a-b. Comparison of conditional stability constants values of some complexes of metals with EDTA and IDS (a) as well as EDTA and MGDA (b).
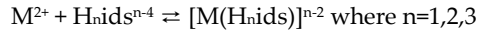
A high or moderately high value for log K of Cu(II), Zn(II), Cd(II) and Pb(II) and first of all Fe(III) with IDS and MGDA indicates that these chelating agents have a high affinity for particular metal ions and they provide a preliminary indication of whether the chelating agent is suitable for the specific application.

As these complexing agents are widely applied, removal of their complexes with heavy metals is essential, especially when typical chemical precipitation methods are ineffective, even if solutions with high metal concentrations are treated. Therefore, more advanced techniques are required for cleaning up such contaminants and retardation of heavy metal ions mobility. Among these, the ion exchange with application of selective resins appears to be a more promising method for the treatment of such solutions.

Generally, chelating properties and selectivity of ion exchangers have been enhanced by: (i) immobilization of ligands with multiple coordinating sites such as bifunctional polymers or polyfunctional polymers possessing different functional groups, (ii) immobilization of low molecular weight complexing agents, (iii) by preparation of ion imprinted polymers (IIP), (iv) preparation of reactive ion exchangers (RIEX), (vi) immobilization of specific donor groups through application of Pearson's hard soft acid base theory, (vii) immobilization of macrocycles e.g. crown ethers, calixarenes, resorcinarenes etc. These approaches correspond to both chelating ion exchangers Dowex M 4195 and Diphonix Resin®. Additionally, their

sorption selectivity can be affected by sorbate-sorbent and sorbate-solvent interactions. It has been well recognized that the resin matrix and the functional groups can strongly affect ion exchange capacity and selectivity (Clifford & Weber, 1983; Barron & Fritz, 1984; Li et al. 1998). Therefore, in the case of chelating ion exchangers, where the formation of coordination bonds is the basis of the sorption process, besides the parameters related to physicochemical properties of the resins, the effect of the presence of complexing agents should be also taken into account.

In the presence of the complexing agents, IDS and MGDA, there are formed:

$$M^{2+} + H_n ids^{n-4} \rightleftharpoons [M(H_n ids)]^{n-2} \text{ where n=1,2,3}$$

and

$$M^{2+} + H_n mgda^{n-3} \rightleftharpoons [M(H_n mgda)]^{n-2}, \text{ where n=1,2.}$$
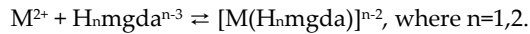
Therefore using selective chelating ion exchangers the sorption effectiveness will be dependent on the decomposition of neutral or anionic species of [MH$_2$L], [MHL]$^-$ and [ML]$^{2-}$ type, where L=ids^{4-}, mgda^{3-}. Additionally, the 'sieve effect' is also important (Kołodyńska, 2010b; Kołodyńska 2010c; Kołodyńska 2011). In the case of the chelating resin Dowex M 4195 possessing the bis(2-pyridylmethyl)amine (bpa) functional groups, depending on the pH value the mechanism of sorption can be as presented earlier. Additionally, the ionic interaction mechanism between the protonated amines and the anionic complexes of the [ML]$^{2-}$ and [ML]$^-$ is also possible (Kołodyńska 2011). Therefore, appropriate reactions can be as follows:

$$2R-HN^+(bpa)_2 Cl^- + [ML]^{2-} \rightleftharpoons [R-HN^+(bpa)_2]_2[ML]^{2-} + 2Cl^-$$

$$R-HN^+(bpa)_2 Cl^- + [MHL]^- \rightleftharpoons [R-HN^+(bpa)_2][MHL]^- + Cl^-$$

or

$$R-HN^+(bpa)_2 Cl^- + [ML]^- \rightleftharpoons [R-HN^+(bpa)_2][ML]^- + Cl^-$$
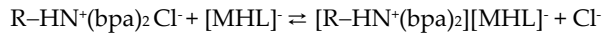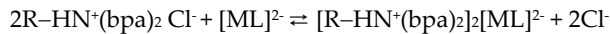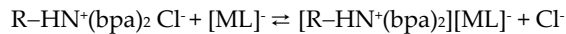
where: R is the Dowex M 4195 skeleton (PS-DVB), L is the ids^{4-} or mgda^{3-} ligand.

The analogous mechanism of sorption in the case of Diphonix chelating ion exchanger should be considered.

Kinetic studies

For the kinetic data, a simple kinetic analysis was performed using the pseudo first order and the pseudo second order equations:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303}$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2}$$

where: q_e is the amount of metal complexes sorbed at equilibrium (for the pseudo first order model also denoted as q_1 and q_2 for the pseudo second order model) (mg/g), q_t is the amount of metal complexes sorbed at time t (mg/g), k_1, k_2 are the equilibrium rate constants (1/min), respectively.

The sorption of Cu(II), Zn(II), Cd(II) and Pb(II) complexes with IDS on Dowex M 4195 in the M(II)-L=1:1 system is presented in Fig.6a. The analogous data for the Cu(II), Zn(II), Cd(II) and Pb(II) complexes with MGDA sorption on Dowex M 4195 are presented in Fig.6b and for Diphonix Resin® in Figs.6c and 6d.
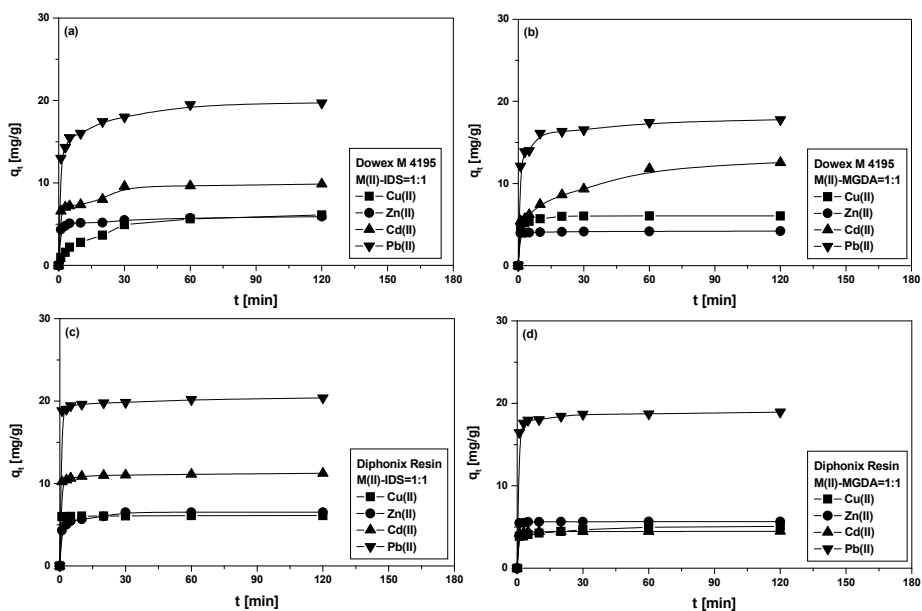
Figure 6. a-b. The effect of the phase contact time on the sorption capacities of Cu(II), Zn(II), Cd(II) and Pb(II) complexes with IDS on Dowex M 4195 (a) and Diphonix Resin® (c) as well as the Cu(II), Zn(II), Cd(II) and Pb(II) complexes with MGDA on Dowex M 4195 (b) and Diphonix Resin® (d) (c_0 1×10^{-3} mol/dm^3, shaking speed 180 rpm, shaking time 1-120 min, room temperature).

The straight lines of t/q_t vs. t suggest the applicability of the pseudo second kinetic model to determine the q_e, k_2 and h parameters (from the intercept and the slope of the plots). These kinetic parameters are presented in Tables 3 and 4.

It was shown that the equilibrium was reached very quickly. More than 90% of metal ions were bound to Dowex M 4195 and Diphonix Resin® within 10-20 min of the phase contact time and therefore a slight increase until a plateau was reached after about 2 h was observed. The values of the theoretical q_e for the studied resins were in good agreement with those obtained experimentally ($q_{e,exp}$). On Dowex M 4195 about 95 %, 100 %, 99 % and

System	$q_{e.exp}$ [mg/g]	q_2 [mg/g]	k_2	h	R^2
Cu(II)-IDS=1:1	5.63	5.61	1.012	5.789	0.9987
Zn(II)-IDS=1:1	5.91	5.88	1.007	4.897	0.9988
Cd(II)-IDS=1:1	9.81	9.89	0.987	12.456	0.9999
Pb(II)-IDS=1:1	19.10	19.00	0.845	16.789	0.9992
Cu(II)-MGDA=1:1	6.05	5.98	2.335	9.237	0.9999
Zn(II)-MGDA=1:1	4.17	4.03	1.017	16.783	0.9996
Cd(II)-MGDA=1:1	12.55	12.23	0.924	10.123	0.9999
Pb(II)-MGDA=1:1	17.77	17.46	0.688	7.525	0.9999

Table 3. The pseudo second order kinetic parameters for the sorption of Cu(II), Zn(II), Cd(II) and Pb(II) complexes with IDS and MGDA on Dowex M 4195.

System	$q_{e.exp}$ [mg/g]	q_2 [mg/g]	k_2	h	R^2
Cu(II)-IDS=1:1	6.12	6.21	2.211	10.207	0.9999
Zn(II)-IDS=1:1	6.01	6.09	1.345	7.123	0.9991
Cd(II)-IDS=1:1	10.21	10.11	0.988	23.434	0.9999
Pb(II)-IDS=1:1	20.39	20.26	0.876	37.551	0.9998
Cu(II)-MGDA=1:1	5.66	5.61	3.469	11.111	0.9999
Zn(II)-MGDA=1:1	4.48	4.48	2.395	48.077	0.9999
Cd(II)-MGDA=1:1	10.23	10.24	0.024	2.475	0.9999
Pb(II)-MGDA=1:1	18.94	18.93	0.188	67.568	0.9999

Table 4. The pseudo second order kinetic parameters for the sorption of Cu(II), Zn(II), Cd(II) and Pb(II) complexes with IDS and MGDA on Diphonix Resin®.

97.5 % of the Cu(II), Zn(II), Cd(II) and Pb(II) complexes with IDS and 94 %, 98 %, 96 % and 95 % complexes with MGDA are sorbed at this time, respectively. On Diphonix Resin® for the Cu(II), Zn(II), Cd(II) and Pb(II) complexes with IDS and MGDA the adequate values are as follows: 94 %, 89 %, 97 % and 98 % as well as 97 %, 86 %, 99 % and 96 %. These results indicate that the sorption process of metal ions in the presence of IDS and MGDA on Dowex M 4195 and Diphonix Resin® followed a pseudo second order kinetics, which meant that both the external mass transfer and intraparticle diffusion together were involved in the sorption process. The correlation coefficients (R^2) obtained for the pseudo second order kinetic model are in the range 0.9991 -1.000 for all metal complexes. The pseudo first order parameters were not shown because the correlation coefficients for this model are low (0.7438-0.8745 for the IDS complexes and 0.919-0.986 for the MGDA complexes on Diphonix Resin®.

The breakthrough curves for Cu(II) ions in the presence of MGDA on Dowex M4195 from single metal ion solutions of a concentration 1×10^{-3} M are shown in Fig. 7. Typical 'S' shaped curves were obtained in the experiments. Analogous results were obtained on Diphonix Resin®. It should be mentioned the UV exposition does not have a significant effect on the decomposition of the complexes in the resin phase.
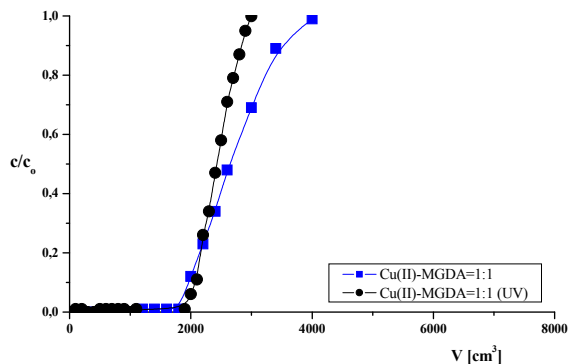
Figure 7. The breakthrough curves of Cu(II) complexes with MGDA on Dowex M 4195 without and with UV exposition (c_0 1×10^{-3} mol/dm^3, bed volume 10 cm^3, flow rate 0.6 cm^3/min)

It is well known that the particle size of ion exchange resins influences the time required to establish equilibrium conditions and two types of diffusion must be considered in an ion exchange equilibrium e.g. the film diffusion (the movement of ions from a surrounding solution to the surface of an ion exchange particle) and the internal diffusion (the movement of ions from the surface to the interior of an ion exchange particle). Film diffusion is usually the controlling reaction in dilute solutions whereas the internal diffusion is controlling in more concentrated solutions. The particle size of an ion exchange resin affects both the film diffusion and the internal diffusion (Kołodyńska, 2011).

According to the manufacturer data the particle size of Dowex M 4195 is 0.300-1.200 mm. However, Diphonix Resin® available on the commercial scale is in the range 0.30-0.85 mm, 0.15-0.30 mm and 0.075-0.15 mm.

In the presented paper Diphonix Resin® with the particle size 0.075-0.150 mm was used to study the sorption process of Cu(II), Zn(II), CdII) and Pb(II) in the presence of IDS and MGDA. In the paper by Cavaco et al. (2009) it was found that for the range 0.15-0.30 mm, 50 % of the particles have diameters less than 0.223 mm. As follows from the obtained results, the bead size of the used chelating ion exchangers has also approximately the Gaussian distribution (Fig. 8 a-b). It was found that with the increase of bead dimensions, the volume fractions of disc-similar beads decrease and the beads are more spherical (Kołodyńska, 2011).

A decrease in the particle size thus shortens the time required for equilibration of particle size and pore characteristics have an effect on equilibrium concentration and influence sorption kinetics. Therefore this factor is essential, especially when the sorption of metal complexes, not metal ions is taken into account. In the case of large complexes the sieve effect is observed.

Kinetic sorption experiments were also carried out with the increased complexes concentrations from 1×10^{-3} mol/dm^3 to 2×10^{-2} mol/dm^3 and these results were presented in
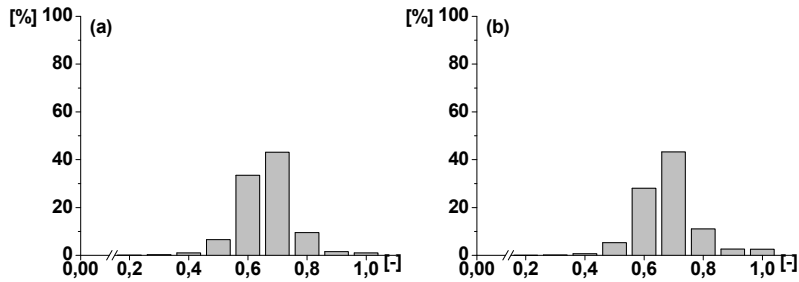
Figure 8. a-b. Comparison of the distribution of the bead size of Dowex M 4195 (a) and Diphonix Resin® (b) based on the Zingg classification.

(Kołodyńska, 2011). It was found that with an increase of metal complexes concentrations a continuous increase in the amount adsorbed per unit mass of ion exchanger was observed till the equilibrium was achieved. For the pseudo second order kinetic model, the rate k_2 values decrease with the increasing initial concentrations, while h increases.

19. pH effects

The effect of pH was studied for the Cu(II), Zn(II), Cd(II) and Pb(II) in the M(II)-IDS=1:1 and M(II)-MGDA=1:1 systems at the pH varied from 2 to 12. The optimal sorption range of the Cu(II), Zn(II), Cd(II) and Pb(II) complexes with IDS practically does not change in the pH range from 4 to 10 both on Dowex M 4195 and Diphonix Resin® whereas, at high pH values, decrease in removal efficiency is observed. In the case of the Cu(II), Zn(II), Cd(II) and Pb(II) complexes with MGDA a slight decrease in sorption efficiency with the increasing pH was also shown.

20. Adsorption studies

The Langmuir equation was applicable to the homogeneous adsorption system, while the Freundlich equation was the non-empirical one employed to describe the heterogeneous systems and was not restricted to the formation of the monolayer. The well-known Langmuir equation was represented as:

$$\frac{1}{q_e} = \frac{1}{bq_0c_e} + \frac{1}{q_0}$$

where: q_e is the equilibrium M(II) ions concentration on the ion exchanger, (mg/g), c_e is the equilibrium M(II) ions concentration in solution (mg/dm³), q_0 is the monolayer capacity of ion exchanger (mg/g), b is the Langmuir adsorption constant (L/g) related to the free energy of adsorption.

The values of q_0 and b were calculated from the slope and the intercept of the linear plots c_e/q_e vs. c_e. On the other hand, the Freundlich equation was represented as:

$$q_e = K_F c_e^{bF}$$

where: KF and 1/n are the Freundlich constants corresponding to the adsorption capacity and the adsorption intensity.

The plot of ln q_e vs. ln c_e was employed to generate the intercept KF and the slope 1/n.

The exemplary results presented in Fig.9a-b indicate that for the studied range of concentration of Cu(II) complexes with MGDA (1×10^{-3} M - 2×10^{-2} M) the sorption capacity of Dowex 4195 and Diphonix Resin® increases.
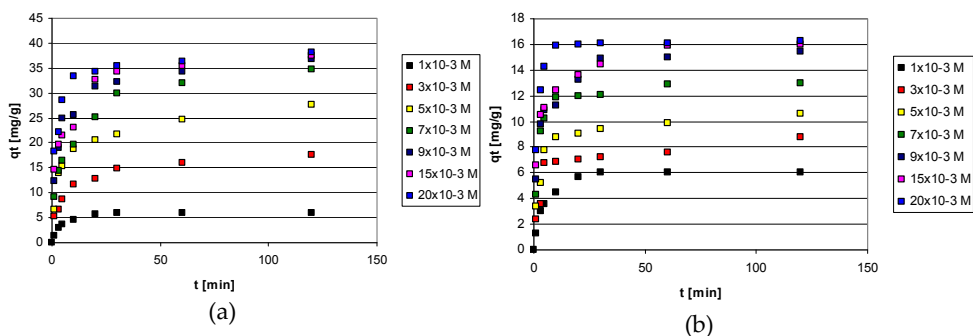

Figure 9. a-b. The effect of the concentration on the sorption capacities of Cu(II) complexes with MGDA on Dowex M 4195 (a) and Diphonix (b) (c_0 1×10^{-3} -20×10^{-3} mol/dm³, shaking speed 180 rpm, shaking time 1-120 min, room temperature).

The experimental data obtained for the sorption of Cu(II), Zn(II), Cd(II) and Pb(II) in the presence of IDS and MGDA on Dowex M 4195 and Diphonix Resin® were well represented by the Langmuir isotherm model (Table 5). The correlation coefficients of the linear plot of c_e/q_e vs. c_e obtained from them were high, ranging from 0.9512 to 0.9999 (Kołodyńska, 2011). The highest values of the Langmuir parameter q_0 were obtained in the case of Pb(II)

System	Langmuir				Freundlich		
	$q_{e, exp}$	q_0	K_L	R^2	K_F	n	R^2
Cu(II)-IDS=1:1	38.23	37.56	0.023	0.9876	9.54	3.21	0.9865
Zn(II)-IDS=1:1	21.07	20.87	0.046	0.9923	6.23	2.45	0.9456
Cd(II)-IDS=1:1	88.00	87.65	0.008	0.9998	4.23	4.58	0.9687
Pb(II)-IDS=1:1	122.37	121.58	0.012	0.9989	1.23	5.69	0.9623
Cu(II)-MGDA=1:1	37.99	38.05	0.026	0.9932	12.48	4.23	0.9758
Zn(II)-MGDA=1:1	16.78	17.01	0.052	0.9983	7.56	3.69	0.9823
Cd(II)-MGDA=1:1	65.78	63.21	0.061	0.9996	6.23	6.11	0.9877
Pb(II)-MGDA=1:1	98.78	97.64	0.042	0.9999	2.48	9.25	0.9837

Table 5. The Langmuir and Freundlich isotherm parameter values for the sorption of Cu(II), Zn(II), Cd(II) and Pb(II) ions in the presence of IDS and MGDA on Dowex M4195.

complexes with IDS and MGDA on Dowex M 4195 and Diphonix Resin®. They are equal to 121.58 mg/g and 97.64 mg/g on Dowex M 4195 and 112.37 mg/g and 100.20 mg/g on Diphonix Resin®, respectively.

For the studied systems regeneration tests were conducted using HCl, HNO$_3$, H$_2$SO$_4$ and NaCl at 1M and 2M concentrations. Based on the series of five experiments using known amounts of Cu(II) complexes with IDS and MGDA sorbed, it was established that the overall recoveries of Cu(II) eluted from Dowex M 4195 and Diphonix Resin® by 2M HCl and H$_2$SO$_4$ were above 98 %, suggesting that the recovery is quantitative.

21. Conclusions

The presence of biodegradable complexing agents of a new generation that is IDS and MGDA affects the sorption process of Cu(II), Zn(II), Cd(II) and Pb(II) ions on Dowex M4195 and Diphonix Resin®. The effectiveness of sorption depends on the type of complexes and their stability that facilitates their decomposition in the resin phase. The batch equilibrium was relatively fast and reached equilibrium after about 10-20 min of the contact. The experimental data have been analyzed using the Langmuir and Freundlich models. The sorption of studied metal ions in the presence of IDS and MGDA Dowex M 4195 and Diphonix Resin® followed the pseudo second order kinetics. As follows from the experiment pH does not have a significant effect on the sorption of Cu(II), Zn(II), Cd(II) and Pb(II) ions in the presence of IDS and MGDA on the chelating ion exchanger under consideration. The affinity of the above analyzed heavy metal complexes with IDS and MGDA Dowex M 4195 and Diphonix Resin® were found to be as follows: Pb(II) > Cd(II) > Cu(II) > Zn(II) for IDS and MGDA. The studied complexing agents can be proposed as alternative chelating agents to EDTA or NTA for the removal of heavy metal ions from waters and wastewaters.

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