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# Chelating Agents of a New Generation as an Alternative to Conventional Chelators for Heavy Metal Ions Removal from Different Waste Waters

Dorota Kołodyńska  
*Maria Curie-Skłodowska University,  
 Poland*

## 1. Introduction

In the aqueous media free metal ions catalyze many reactions disadvantageous for man. Therefore it is necessary to control accessibility and a number of metal ions both during technological processes and in their final products. This aim could be achieved owing to metal ions complexation by the compounds characterized by complex formation ability. Therefore, the chelating agents belonging predominantly to two different groups i.e. aminopolycarboxylates (APCAs) and polyphosphonates are commonly used (Nowack, 2007; Knepper, 2003). APCAs containing carboxylic groups connected to one or a few atoms of nitrogen are able to complex metal ions by formation around them one or a few stable heteroatom rings. This phenomenon is called chelating. Forming of stable complexes with metal ions is the base of their application for analytical and industrial purposes. The complexes formed due to chelation are dissolved in water and metal ions found in them do not exhibit such chemical activity as uncomplexed ions. Because of the importance of chelating agents they are produced and used in large quantities and their behaviour as well as their effect on the environment have received considerable attention.

## 2. Traditional chelating agents and their complexes with heavy metal ions

### 2.1 EDTA and NTA

The first synthesis of a compound from the group APCAs i.e. NTA (nitrilotriacetic acid) was described by Heintz in 1862 (Heintz, 1862). Much later in 1935 I.G. Farbenindustrie carried out the synthesis of EDTA (ethylenediaminetetraacetic acid) which consisted in the reaction of monochloroacetic acid with ethylenediamine in the presence of sodium hydroxide. Another way to obtain EDTA is the reaction of ethylenediamine with sodium cyanide and formaldehyde in the presence of sodium hydroxide. Depending on the amine used also other APCAs can be obtained using this method. Since that time, on a worldwide scale over 100,000 tons of aminopolycarboxylic acids have been produced annually. It was estimated that 65,000 tons of EDTA and DTPA would be used up a year by the pulp and paper industry in the USA (Tucker, et al. 1999). Its annual consumption in West Europe was about

30,000 tons in 1987. However, in 1998 this amount was doubled and reached 64,000 tons. In 1996 the amount of EDTA in Germany was 3,686 tons and in 1999 – 3,894 tons. The pulp and paper industry is a major user of EDTA. It was estimated that about 15,000-20,000 tons of EDTA are used in pulp processing each year (Jones & Williams, 2002). From the late 1960s, NTA generally replaced phosphates in commercial detergents due to the increasing surface water eutrophication and its disastrous effect on natural environment (Anderson, et al. 1985). The Environmental Protection Agency (EPA) estimated that 35,000 to 38,000 tons of NTA were produced in the United States, and 27,000 to 30,000 tons were exported. However, in March 2006, the Commission's Working Group on the Classification and Labelling of Dangerous Substances decided to classify NTA, trisodium salt as a Category 3 Carcinogen with an R40 label (limited evidence of a carcinogenic effect) with a specific concentration limit of 5%.

## 2.2 Phosphonates

As for the second group of chelating agents, according to (Nowack, 1998, 2003) in 1998 the worldwide consumption of phosphonates was 40,000 - 56,000 tons in the USA, 15,000 tons in Europe and less than 800 tons in Japan. The demand for phosphonates grows steadily at 3% annually. Besides DTPPH (diethylenetriaminepenta(methylenephosphonic acid)) and NTMP (nitrilotris(methylenephosphonic acid)), HEDP (1-hydroxyethane-1,1-diphosphonic acid) is the most important in this group. HEDP is widely used in a broad variety of applications, among others, as ingredients of detergents. Bonding Ca(II) ions, which deactivate the surfactants improves their cleaning process. Its ability to prevent precipitation of calcium salts (called the threshold effect) finds also wide application in water treatment for scale inhibition in circulating cool water system, oil field and low-pressure boilers in such fields as electric power, chemical industry, metallurgy, fertilizer production, etc.

## 2.3 Degradation of EDTA and NTA

Degradation of EDTA and NTA in natural conditions proceeds due to growth of specific bacteria from the subclass of *Proteobacteria*. Several bacteria strains such as the gram-negative strain BNC1 were also found to be able to degrade EDTA. It was found that M(II)-EDTA complexes with the stability constants below  $10^{12}$  such as Ba(II), Mg(II), Ca(II) and Mn(II) were degraded whereas chelates with higher stability constants such as Fe(III), Co(II), Cd(II), Pb(II), Ni(II) or Cu(II) (Table 1) were not metabolized (Nörtemann, 2005). The system of EDTA transport is based on its extracellular evolution with metal ions found in the solution and intracellular absorption and precipitation of metals combined with EDTA to form complexes (Witschel, 1999). It should be noticed that probably only the complexes of stability constants  $<10^{14}$  can be transported inside the cell. Contrary to EDTA, transport of NTA inside the bacterium cell has not been well recognized yet. It is assumed that it gets inside the cell through the active transport. As established the metabolic intermediates of EDTA biodegradation include ethylenediaminetriacetic acid (ED3A), N,N'-ethylenediaminediacetic acid (N,N'-EDDA), ethylenediaminemonoacetic acid (EDMA), ethylenediamine (ED) and glyoxylate. The metabolic intermediates of NTA biodegradation are iminodiacetic acid (IDA), glycine, and glyoxylate (Yuan & VanBriesen, 2008). EDTA and DTPA are also reported to be photodegradable in the form of Fe(III) complexes (Cokesa, et al. 2004a). The process is pH dependent. It was found that it is faster in acidic conditions.

M(II)	EDTA	NTA	DTPA	NTMP
Al(III)	16.5	11.4	18.6	—
Ba(II)	7.9	4.8	8.7	—
Ca(II)	10.7	6.4	10.8	5.75
Cd(II)	16.5	9.8	—	6.4
Co(II)	16.5	10.4	18.8	7.5
Cu(II)	18.8	12.9	21.2	10.7
Fe(II)	14.3	8.3	16.2	—
Fe(III)	25.1	15.9	28.0	—
Hg(II)	21.5	—	26.4	—
Mg(II)	8.8	5.5	9.3	4.3
Mn(II)	13.9	7.5	15.2	—
Ni(II)	18.4	11.5	20.1	7.1
Pb(II)	18.0	11.4	18.8	—
Zn(II)	16.5	10.6	18.2	8.2

Table 1. Comparison of the stability constants of M(II)-L=1:1 complexes with EDTA, NTA, DTPA and NTMP (Martell & Smith, 1982). (— data not available)

2.4 Application of APCAs

Aminopolycarboxylic acids are used as components or process chemicals in a wide variety of applications, however, according to Fig.1 only pulp and paper, cleaning, chemical processing, agriculture and water treatment constitute 80% of their consumption.

APCAs are used for:

- **pulp and paper production** - stabilization of ozone and hydrogen peroxide action on pulp by complexing with metal ions (especially Fe, Cu and Mn that catalyse their decomposition), prevention from brightness reversion and protection of bleach potency;
- **household and industrial cleaning** - removal of hard water scale, soap film and inorganic scales, for example to improve the bottle cleaning in the beverage industry; *detergents, soaps processing* - prevention from precipitation of calcium and magnesium salts (deliming action) and their deposition on clothes, prevention soaps from becoming rancid, intensification of the adhesion of dirty surface and the cohesion of dirt particles to each other due to complexing metal ions (to better soil removal during laundering), to prevent from decomposition of bleaching agents such as sodium perborate, inhibition of colour changes, stabilization of hydrogen peroxide in liquid detergents for special requirements; to enhance the antibacterial effect, *cosmetics industry* - stabilization of creams, lotions and emulsions, reduction of allergic reactions to nickel and chromium, hair preparations, shampoos and almost every type of personal care formulation, blue colour of the [Cu(edta)]<sup>2-</sup> complex is used in many shampoos;
- **agrochemicals** - full utilization of micronutrients by plants (complexing agents are used to complex the microelements, which are then gradually released to the relevant ionic

- form, the micronutrient chelates protect metal cations against reduction in soil and facilitate their uptake by leaves and roots);
- **water treatment** – to scale control; control water hardness and scale-forming calcium and magnesium ions;
  - **photographic industry** – prevention from precipitation of calcium and magnesium salts onto the photosensitive layer,  $[\text{NH}_4\text{Fe}(\text{edta})]$  complex is used as an oxidizing agent for Ag in bleach baths;
  - **textile industry** – to remove trace metal impurities in all phases of textile processing, particularly the scouring, dyeing and color stripping stages;
  - **consumer products** – *food industry* by complexing metal ions to prevent from oxidation processes leading to colour changes especially in the case of canned food, for example vegetables; *pharmaceuticals* – stabilize formulations, antioxidants and anticoagulants added to stored blood in blood banks ( $[\text{K}_2(\text{H}_2\text{edta})]$  to prevent clotting;  $[\text{NaFe}(\text{edta})]$  and  $[\text{Na}_2(\text{H}_2\text{edta})]$  added to typical iron fortification compounds in cereals increasing the adsorption of iron in adult humans, Gd(III) complex with DTPA is used as a contrast agent in diagnosis by nuclear magnetic resonance imaging;
  - **metalworking** – for surface preparation, metal cleaning, metal plating and in metalworking fluids;
  - **Others**  
*nuclear industry* – formation of water soluble complexes with radionuclides in the decontamination of reactors; *adhesives productions* – production of latex-based coating compounds; *dispersants* – prevention from scale build up in industrial water handling processes which results in reduced water flow through pipes, reduced heat transfer in boilers and condensers, causes pump failures; *dispersants in paints and coatings production* – to disperse solid pigments such as titanium dioxide, sunscreen pigments during the manufacture of chemical dyes; *fuel gas cleaning and oil production* – to stabilize  $\text{Na}_2\text{SO}_3$  solution used for adsorption of  $\text{SO}_2$ ; components of cleaners for platforms and scale inhibitors especially for platforms which are not too deep; in drilling, production, and recovery of oil; *biodiesel production* – it was found that the addition of APCAs to biodiesel

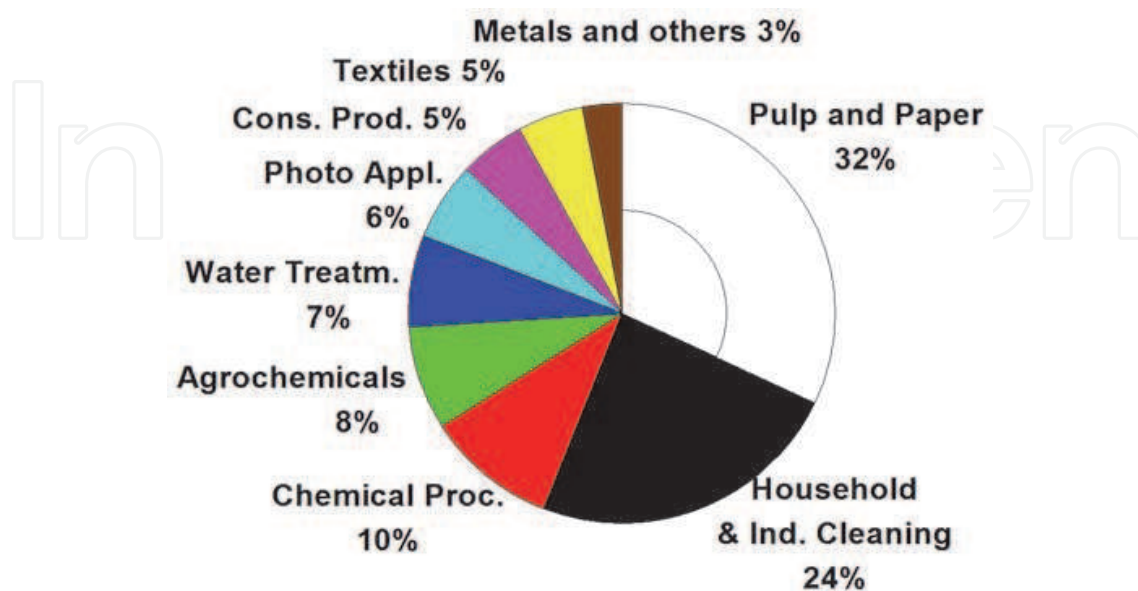


Fig. 1. The percentage contribution of different applications of APCAs.



reduces the humidity and kinematic viscosity; *polymerization* – for suspension, emulsion, and solution polymers, both in polymerization reactions and for finished polymer stabilization, *electroplating* – to control the level of Cu(II) ions and improve the quality of the Cu layer formed in copper plating, whereas in nickel and gold plating – to prevent from co-precipitation of other metals; *antiscalants* to prevent from scale formation. On the other hand, aminopolycarboxylates which act as dispersants are able to keep the scale particles suspended in the bulk fluid by imparting a negative charge to the particles, *soil remediation and chelant-enhanced phytoremediation* – chelates have been shown to significantly increase metal concentrations in soil solution, the enhancement of plant uptake varies greatly, depending on the specific metal, chelate, plant combination and on soil conditions.

### 2.5 Heavy metal complexes with EDTA and NTA

EDTA includes six donor atoms and acts as a hexadentate ligand whereas NTA includes four donor atoms so it is a tetradentate ligand. EDTA and NTA form the complexes with metal ions of the molar ratio  $M(II):L=1:1$ . The complexes possess the octahedral structure. In the case of EDTA octahedral coordination is possible only with small size cations. With large cations limitations in the EDTA structure do not allow for such ideal structure and the complexing metal ion can be accessible for other ligands such as water molecules. X-ray investigations show that the structures of most metal complexes are different from octahedral ones and the cations coordination numbers are often larger than six. On the other hand, in some complexes such as with Cu(II) or Ni(II), EDTA does not make full use of donor possibilities leaving one carboxyl group uncoordinated. To octahedral system is completed by a water molecule.

### 3. Characterization of chelating agents of a new generation and their complexes with heavy metal ions

Despite obvious advantages, the conventional complexing agents, due to some undesired features such as their persistence or slow transformation in the environment, remobilization of toxic metal ions mainly from sediments and soils as well as radionuclides from radioactive waste and their implication in eutrophication of natural water systems, are of great concern, therefore their replacement and the use of chelating agents with improved biodegradability is necessary (Reinecke, et al. 2000). It should be stressed that most of the APCAs (such as EDTA – ethylenediaminetetraacetic acid, IDA – iminodiacetic acid, DTPA – diethylenetriaminepentaacetic acid) are resistant to conventional biological and physicochemical methods of waste water treatment and purification of drinking water. During the last few years complexing agents of a new generation have appeared on market as a solution to this problem. Their biodegradability is an important focus because of the renewed attention towards environmental protection issues. They are also proposed as a response to the changes in terms of legislation i.e. BREF documents, (EU EDTA risk reduction strategy documents, 2004, IPPC Directive 96/61/EC, BAT - Best Available Techniques Reference documents or OSPAR documents). For example, in the case of Austrian waste water emission legislations for the pulp and paper industry, the use of chelating agents with biodegradation levels below 70% or 80% is forbidden using the 28-day EN ISO (International Standards Organization) 7827 test. Nowadays, DTPA and EDTA are widely used in modern, total chlorine-free washing (TCF) and bleaching steps of pulps

using hydrogen peroxide for complexing metals such as Mn(II) and Fe(III). As a result of their practical non-degradability, the attempts were made to find the alternative products (Matzinger, et al. 2007). New developed ligands to be used in practice should form strong complexes with the minimal content of nitrogen. The presented below biodegradable ligands of a new generation contain a basic nitrogen atom or two atoms (in the case of EDDS) with an electron pair capable of interacting with metal ions and acidic carboxylic groups capable of coordinating metal ions through the oxygen. The basic properties of the IDS (N-(1,2-dicarboxyethyl)-D,L-aspartic acid also known as iminodisuccinic acid), DS (polyaspartic acid), EDDS (ethylenediamine-N,N'-disuccinic acid), GLDA (N,N-bis(carboxymethyl)glutamic acid) and MGDA (methylglycinediacetic acid) and their complexes with heavy metal ions are described in detail in the next paragraphs.

### 3.1 IDS

Iminodisuccinic acid (N-1,2-dicarboxyethyl)-D,L-aspartate acid, (CAS No. 144538-83-0) also denoted as IDS has been commercialized since 1998 by the Lanxess (Germany, formerly Bayer AG) to the name Baypure CX 100. Its production is based on the reaction of maleic anhydride with ammonia and sodium hydroxide (Fig.2):

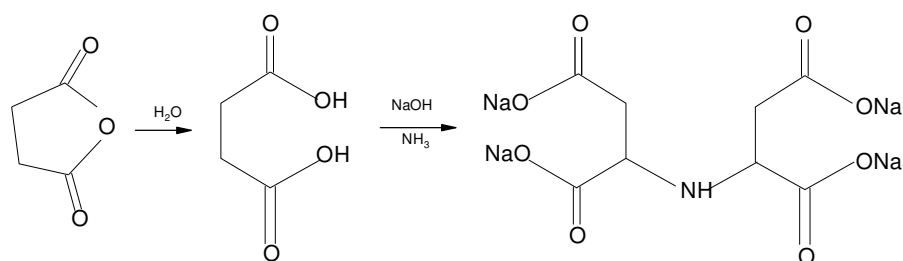


Fig. 2. Scheme of IDS production.

The process is extremely environment-friendly and does not generate any off-gases or effluents contaminating the environment. The sodium salts of iminodisuccinic acid (>32%), aspartic acid (<7%), fumaric acid (<3.5%), hydroxosuccinic acid (<0.9%), maleic acid (<0.9%) are the main ingredients of Baypure CX 100. It was also found that there are four possible stereoisomers of IDS: [R,R], [S,S], [R,S] and [S,R]. However, the two meso forms [R,S] and [S,R] are identical. The isomeric mixture of IDS consists of 25% [S,S], 25% [R,R] and 50% [R,S] forms (Fig. 3).

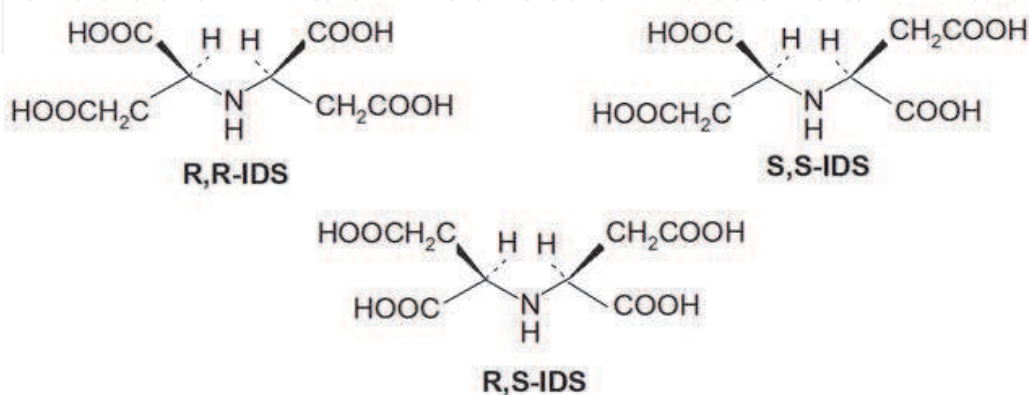
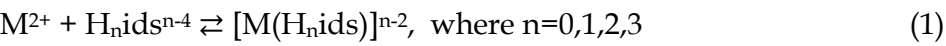


Fig. 3. The structural isomers of IDS.

IDS exhibits extremely rapid biodegradation, which equals approx. 80% after just 7 days. It is characterized by excellent calcium binding properties, stability in a wide pH, good complexation of heavy metal ions and low environmental impact due to low toxicity and good biodegradability according to the OECD (Organization of Economic Cooperation and Development) tests (OECD 301E i.e. modified OECD-screening test: > 78%, OECD 302 B i.e. Zahn-Wellens test: >89%). IDS undergoes lysed dependent degradation. The end product of transformation of [S,S]-IDS and [R,S]-IDS isomers by *Ralstonia sp. SLRS7* is fumaric acid. However, in the case of the [S,S]-IDS and [R,S]-IDS isomers as metabolites L-aspartic acid and D-aspartic acid were found. As further stages fumaric acid and ammonia are supposed (Cokesa, et al. 2004a). As for IDS the following pKs values were found: pK<sub>1</sub>=2.8, pK<sub>2</sub>=3.6, pK<sub>3</sub>=4.7 and pK<sub>4</sub>=10.2 the reaction of complexes formation with M(II) ions can be summarized as:



The comparison of the stability constants of metal complexes with IDS in the M(II):IDS=1:1 system is presented in Table 3 (Hyvönen & Aksela, 2010, Vasilev, et al. 1996, Vasilev, et al. 1998).

M(II)	IDS	DS	EDDS	GLDA	MGDA
Ag(I)	3.9	—	—	—	—
Al(III)	14.1	—	—	—	—
Ba(II)	2.1	—	3.0	3.5	<b>4.9</b>
Ca(II)	5.2	2.7	4.6	5.2	<b>7.0</b>
Cd(II)	<b>8.4</b>	<b>1.7</b>	<b>16.4</b>	<b>9.1</b>	—
Co(II)	10.5	—	13.6	10.0	—
Cr(III)	9.6	7.5	—	—	—
Cu(II)	<b>13.1</b>	<b>4.8</b>	<b>18.4</b>	<b>13.1</b>	13.9
Fe(II)	8.2	10.0	—	8.7	<b>8.1</b>
Fe(III)	15.2	18.5	22.0	11.7	<b>16.5</b>
Hg(II)	14.9	2.8	—	14.3	—
Mg(II)	6.1	2.0	6.0	6.1	<b>5.8</b>
Mn(II)	7.7	2.1	—	7.6	<b>8.4</b>
Ni(II)	12.2	—	16.7	10.9	<b>12.0</b>
Zn(II)	<b>10.8</b>	<b>2.2</b>	<b>13.4</b>	<b>10.0</b>	10.9
Pb(II)	<b>11.0</b>	—	<b>12.7</b>	<b>10.5</b>	—

Table 3. Comparison of the stability constants of M(II)-L=1:1 complexes with IDS, DS, EDDS, GLDA and MGDA (— data not available).

In the paper (Hyvönen, et al. 2003) it was found that in the dilute solutions of IDS more than 90% of metal ions are bound over a wide pH range. The percentage distribution of copper(II) complexes with IDS as a function of pH was presented in (Kołodzyńska, 2009b).



For Cu(II) ions the effective complexation region was at the pH values from 3 to 12, for Zn(II) from 5 to 11 and for Mn(II) from 7 to 11. According to (Cokesa, et al. 2004b) some metal complexes with IDS satisfy the criteria of ready biodegradability. In this group Ca(II)-IDS and Fe(II)-IDS were found. Mn(II)-IDS and Cu(II)-IDS complexes revealed only 55% and 40% biodegradation after 28 days, respectively.

In perspective IDS can be used in oxidative bleaching of cotton with  $H_2O_2$ , as a component of detergents – very good results were achieved for spinach and tea removal by detergents containing Baypure CX 100, for cleaning of membranes blocked by diesel oil, silicon fluid, floors and glass. Baypure CX 100 brings good results in cutlery cleaning (Brochure of Baypure CX 100). A new proposal for the use of IDS is its application for coating seeds to enhance the adherence of trace metals and nutrient salts (Aksela, et al. 2004). IDS can be also applied for production of fertilizers. In Poland the leader in the production of micronutrient fertilizers based on IDS is the Production-Consulting Firm 'ADOB'. It has been producing iminodisuccinic acid since 2005. They also proposed a new Fe(III) chelates with N,N'-bis(2-hydroxy-5-methylbenzyl)ethylenediamine-N,N'-diacetic acid (HJB) and N,N'-di(2-hydroxybenzyl)ethylenediamine-N,N'-diacetic acid (HBED) (Stegient-Nowicka & Michalek, 2010).

### 3.2 DS

Polyaspartic acid (CAS No. 181828-06-8) is accessible on a commercial scale as Baypure DS 100 (denoted as DS), the commercial product of Lanxess (Germany). However, the Donlar Corporation were the first to develop an economical way to produce polyaspartates in high yield and with little or no waste products from L-aspartic acid, a natural amino acid. The way of the synthesis is presented in Fig. 4 (Wheeler & Koskan, 1993). In the first reaction, polysuccinimide (poly(anhydroaspartate)) is synthesized by dry thermal polycondensation of powdered aspartic acid. Subsequently, the polyimide rings are hydrolyzed with stoichiometric quantities of base to form poly(aspartate). Typically, the resulting polyamide contains a racemic mixture of D- and L-aspartic acid and is a copolymer in which the amide bonds are formed from either the  $\alpha$ - or  $\beta$ -carboxyl groups (Mosig, et al. 2000).

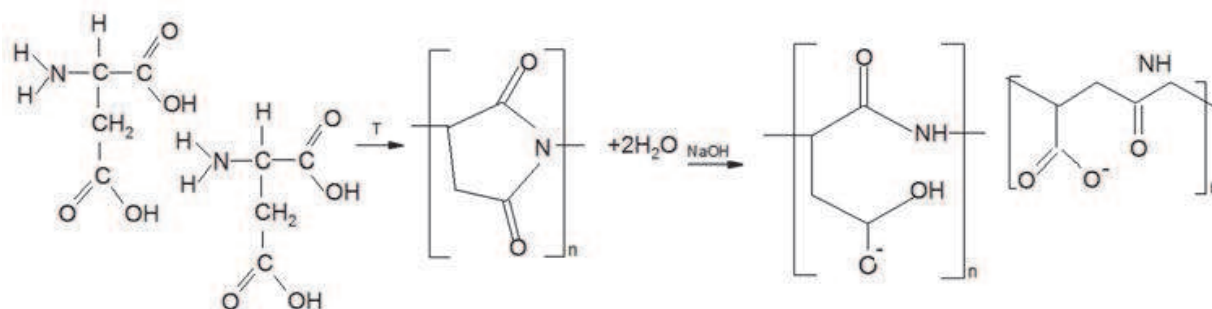


Fig. 4. Scheme of DS production.

Baypure DS 100 is characterized by excellent calcium(II) tolerance, corrosion inhibition properties, stability in a wide pH range as well as low environmental impact by low toxicity and good biodegradability (OECD 301E: > 60%, OECD 302 B: >75%). It is also an effective chelating agent of a new generation which can be applied for heavy metal ions removal (Freeman, et al. 1996). As follows from the structure, it consists of polymerized  $\alpha$ - and  $\beta$ -

aspartyl residues, each containing carboxylic functional groups that can combine with metal ions to form M(II)-DS complexes. In paper (Wu & Grant, 2002) it was found that aspartyl residues undergo protonation, deprotonation and complexation in solution. For sodium polyaspartate with a molecular weight of 10 000, 72 repeated units of aspartyl residues can be recognized as 18 independent hypothetical polyaspartic acid molecules (denoted as H<sub>4</sub>ds) for which the pKs of DS are equal to: pK<sub>1</sub>=2.27, pK<sub>2</sub>=3.60, pK<sub>3</sub>=4.09, pK<sub>4</sub>=5.17. At pH 1 about 100 % of DS occurs as H<sub>4</sub>ds, at pH 3 about 70 % occurs as H<sub>3</sub>ds<sup>-</sup>, at pH 4 about 48 % occurs as H<sub>2</sub>ds<sup>2-</sup>, at pH 4,8 about 65 % occurs as Hds<sup>3-</sup> and at pH above 7 100% occurs as ds<sup>4-</sup> (Burns, et al. 2003). The formation of metal complexes with DS can be summarized as:



The stability constants of M(II)-DS=1:1 complexes are presented in Table 3 (Brochure of Baypure DS 100). It should be also stressed that the theoretical capacity of polyaspartic acid for heavy metal ions is about 7.2 meq/g, whereas EDTA is only 6.0 meq/g. Although polyaspartic acid has also a quite high capacity, it shows poor efficiency at a low ion concentration (Sun, et al. 2005, Kołodyńska, et al. 2008a, 2008b).

Polyaspartates are used as corrosion and scale inhibitors, dispersing agents, waste water additives, superabsorbers, and also as agricultural polymers. It should be mentioned about polyaspartic resins obtained by modification of polyaspartic acid. They are characterized by high water absorbency and used as soil amendments, manufacturing of diapers, sanitary napkins, medicals, cosmetics, fabrics, metal absorbent materials and etc. (Zhao, et al. 2005). Among their other important properties super-absorption, fluid retention capacity and stability can be included (Zhao, et al. 2006). For example, AmiSorb® is the Donlar's brand name polymer used to enhance the growth and yield of corn, wheat, cotton, soybean and other crops. It contains polyaspartates which cause that mineral nutritions are more available and efficiently sorbed by plants. Recently it was proven that the overall yield change from the addition of AmiSorb® was equal to +1.75 bu/a for corn and +1.07 bu/a for wheat (Goos & Cattanaach, 1996).

In June 2001 Lanxess was awarded with the Presidential Green Chemistry Award by the US Environmental Protection Agency (US EPA) for the best product in the field of industrial environment protection promotion. The product awarded was the Baypure CX 100. In 2002 Baypure DS 100 was given a prestigious award by the German Industry Federation (BDI). The Baypure based Danish product Groen Linie Maskinvask Color/Ultra became the first laundry detergent in the world to receive the 'EU Flower' ecolabel.

### 3.3 EDDS

Ethylenediamine-N,N'-disuccinic acid (H<sub>4</sub>edds, EDDS) (CAS No. 144538-83-0) is a structural isomer of EDTA. On a commercial scale this complexing agent is produced, among others, by Innospec Inc., UK (formerly Octel) as Enviomet™. It forms four isomers: S,S- (25%), R,R- (25%), R,S- (50%), S,R- (50%). The S,S-isomer of EDDS, based on the naturally occurring amino acid i.e. L-aspartic acid, is readily biodegradable. According to the OECD 83% of S,S-EDDS convert to CO<sub>2</sub> within 20 days (Jaworska, 1999). However, the others are partly or completely non-biodegradable (Tandy, et al. 2006a). The chemical structure of EDDS isomers is presented in Fig.5.

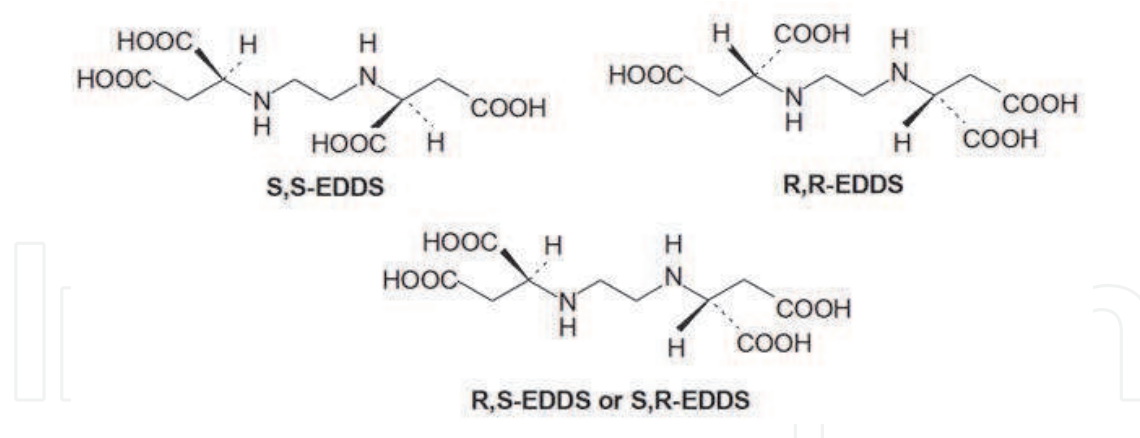


Fig. 5. The structural isomers of EDDS.

The *S,S*-EDDS isomer is produced by the actinomycete strain *Amycolatopsis orientalis* (Zwicker, et al. 1997). It can be also obtained in the reaction between 1,2-dibromoethane and L-aspartic acid (Fig.6).

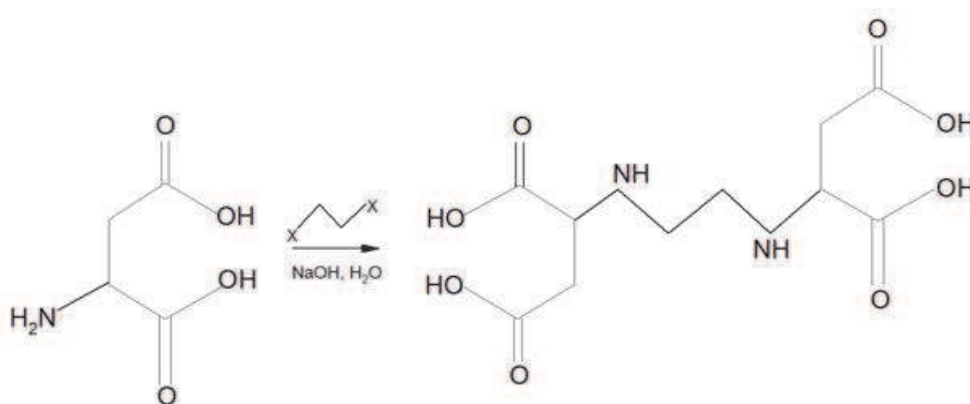
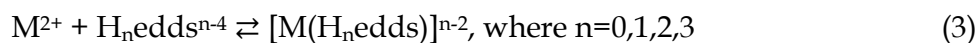


Fig. 6. Scheme of EDDS production.

The isomeric mixture of EDDS can be also synthesized from ethylenediamine and maleic anhydride. On the contrary to the other biodegradable complexing agents like NTA, gluconic acid or citric acid it is characterized by high capacity for complexing cations as well as low toxicity (to fish and daphnia  $EC_{50} > 1000$  mg/L).

As follows from the speciation diagram of EDDS at  $pH > 10$  the predominant form of  $H_4\text{edds}$  is  $\text{edds}^{4-}$  presented in 62% whereas the  $\text{Hedds}^{3-}$  form is present in 38% (Crouch, et al. 2001). The appropriate ligand protonation constants  $pK_s$  are as follows: 3.03, 3.92, 7.01, and 9.70 (Loonen, et al. 1999). They are very close to the data for EDTA. The process of heavy metal ions complexation by EDDS is characterized by the formation of stable 1:1 metal to ligand complexes as the major species according to the reaction:



Metal ions in the formed complexes were bound to two nitrogen atoms and one oxygen atom of each of the four carboxylate groups. For example, for  $\text{Cu(II)}$  ions there was assumed formation of the following complexes:  $[\text{Cu}(\text{H}_2\text{edds})]$ ,  $[\text{Cu}(\text{Hedds})]$ ,  $[\text{Cu}(\text{edds})]^{2-}$ ,  $[\text{Cu}(\text{OH})(\text{edds})]^{3-}$ ,  $[\text{Cu}(\text{H}_2\text{edds})_2]^{2-}$ ,  $[\text{Cu}(\text{H}_2\text{edds})(\text{Hedds})]^{3-}$ ,  $[\text{Cu}(\text{Hedds})_2]^{4-}$ ,  $[\text{Cu}(\text{Hedds})\text{edds}]^{5-}$  and  $[\text{Cu}_2\text{edds}]$  whereas for  $\text{Zn(II)}$  they are as follows:  $[\text{Zn}(\text{H}_2\text{edds})]$ ,

$[\text{Zn}(\text{Hedds})^-]$ ,  $[\text{Zn}(\text{edds})]^{2-}$ ,  $[\text{Zn}(\text{OH})(\text{edds})]^{3-}$  (Knepper, et al, 2005). It was shown that under some conditions of pH EDDS is more efficient than EDTA as far as chelation of metal ions is concerned. For example, in the case of Cs(I), Mg(II), Sr(II) they are not well complexed by EDDS at acidic and neutral pH and for them EDTA appears to be superior to EDDS (Jones & Williams, 2002), for Cr(III), Mn(II) their total amount is almost equal whereas in the case of Fe(III), Co(II), Ni(II) the complexation occurs in an identical manner. The obtained complexes are mostly not biodegradable (Loonen, et al. 1999; Vandevivere, et al. 2001). For example, Pb(II) and Zn(II) complexes with EDDS (Kos & Lëstan, 2003; Neal & Roshe, 1973) have practically the same stability constants but the Pb(II)-EDDS complex is much more readily biodegradable than Zn(II) one (Orama, et al. 2002). For M(II) complexes with EDDS the stability constants are presented in Table 3 (Vandevivere, et al. 2001) and compared to IDS, DS, GLDA and MGDA.

According to the literature data EDDS showed good chelation properties towards heavy metal ions. As mentioned earlier, it is also characterized by better extraction efficiency in the *ex situ* washing tests and phytoextraction process of heavy metals from contaminated soils than EDTA (Tandy, et al. 2004; Tandy, et al. 2006b). It can be also used as the  $\text{H}_2\text{O}_2$  stabilizer in the pulp and paper industry.

In 2002 EDDS production achieved 10,000 tons. Nowadays EDDS is a chelating reagent available in Europe on a large scale. The demand for ethylenediaminedisuccinic acid has been growing at the rate of 15 % per year. Also Innospec, the producer of EDDS was awarded by RoSPA (Royal Society for the Prevention of Accidents). Moreover, the Enviomet™ was the winner of the UK Green Chemical Technology Award in 2003 as a chemical product and then awarded by CRYSTAL Faraday Partnership (Institute of Chemical Engineers, Royal Society of Chemistry, Chemical Industry Association) (Brochure of Enviomet™).

### 3.4 GLDA

A novel readily biodegradable chelating agent, tetrasodium of N,N-bis(carboxymethyl) glutamic acid (also denoted as Dissolvine GL-38 or GLDA, CAS No. 51981-21-6) was also introduced on the commercial scale by AkzoNobel Functional Chemicals (The Netherlands). Its production process is based on the flavour enhancer monosodium glutamate (MSG) from the fermentation of readily available corn sugars and according to the following reaction (Fig.7) (Hauthal, 2009):

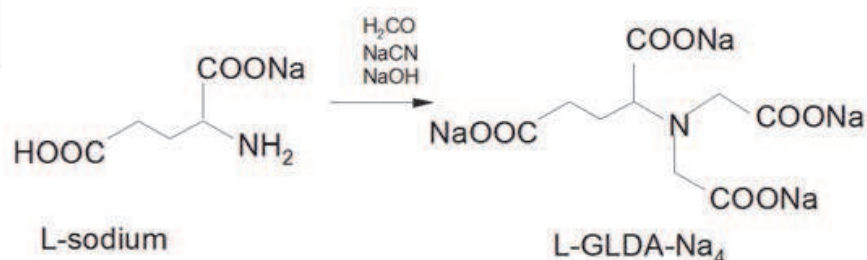


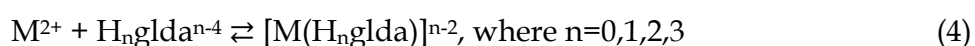
Fig. 7. Scheme of GLDA production.

In contrast to the manufacture of EDTA whose carbon content is fossil based, the carbon source of GLDA is primarily biobased. Therefore, GLDA is the only chelating agent with 'green' carbon atoms. The biodegradation of GLDA is initiated by mono-oxygenases



catalysing the removal of carboxymethyl groups. According to the Swedish Society for Nature Conservation GLDA is 86% based on natural, raw materials. It also possesses good solubility at both low and high pH. Greater than 60% of L-GLDA degrades within 28 days. Dissolvine GL-38 consists only of the L-form. This is significant, because the D-form is not biodegradable. The thermal stability of GLDA is surprisingly high. When tested at temperatures above 573 K it showed no significant decomposition. This property has been used to develop water treatment systems for operating boilers to reduce the effect of hard water. Tests have also shown up to 10 times higher solubility of GLDA in 25% NaOH sodium hydroxide solution compared to EDTA and NTA. It is also characterized by excellent solubility at low pH (Seetz, 2007; Seetz & Stanitzek, 2008).

GLDA possesses complexing properties comparable to EDTA and NTA. In the case of GLDA 1:1 metal to ligand complexes are formed according to the reaction:



The stability constants for this type of complexes are presented in Table 3 (Brochure of Dissolvine GL-38). Therefore, it can be an alternative to EDTA and NTA. The benefit of GLDA in such formulations is its broad effective pH range for the chelation of calcium and magnesium ions equal to 4-12.

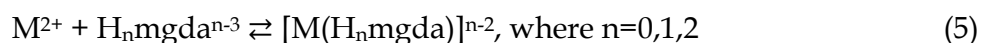
GLDA is directly used in all ordinary industrial cleaning applications. It has further potential uses in the production of micronutrient fertilizers (Borowiec & Hoffmann, 2005; Borowiec, et al. 2007).

### 3.5 MGDA

Methylglycinediacetic acid (MGDA) also known as glycine-N,N-diacetic acid is manufactured by BASF the Chemical Company as a brand name Trilon<sup>®</sup> M. MGDA and its derivatives are prepared by reacting glycine with formaldehyde and alkali metal cyanide in the aqueous alkaline medium (Schneider, et al. 1999).

The BASF started the new production line in 2008, which can supply over 120,000 tons of this complexing agent after 2010.

MGDA is readily biodegradable >68% and does not require adapted bacteria for decomposition, but instead is degraded under the standard conditions. Consequently, the EU does not require any safety or hazard labelling for MGDA. In the case of MGDA high stability throughout the entire pH range and even at elevated temperatures is found (Table 3). This sets Trilon M apart from the chemicals like EDDS or IDS which show much lower stability. Furthermore, the metal complexing power of MGDA is stronger than that of citrates. The complexes formed by it are characterized by high stability over a wide range of both pH and temperature. In the case of MGDA the reaction of complexes formation can be as follows:



MGDA can be applied as an excellent ingredient of products used for lime scale removing and for CIP (cleaning in place) cleaning processes (due to its dissolving power for fatty acids containing stains) (Brochure of Trilon M<sup>®</sup>; Jachula, et al. 2011).

Owing to its properties it can be a perfect substitute for phosphates (STPP) in detergents and cleaners as well as complexing agent used in phytoremediation (Cao, et al. 2007, Jachula, et al. 2011).



The properties of the above-described chelating agents are summarised in Table 3.

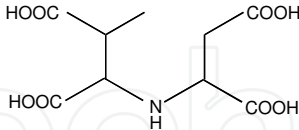
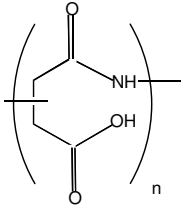
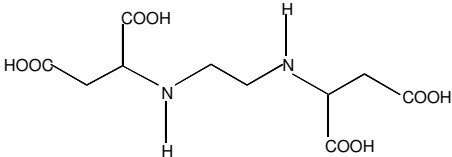
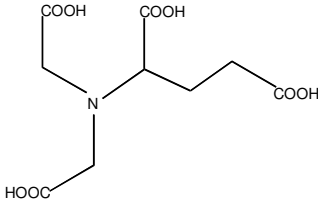
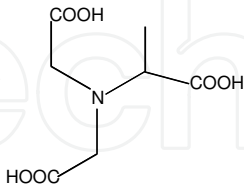
Name	Schematic structure	Physicochemical characteristic
<b>IDS</b> N-(1,2-dicarboxyethylene)-D,L-asparagine acid		<b>molecular weight:</b> 337.1 <b>appearance:</b> colourless to light yellow <b>pH:</b> 10.3-11.4 <b>density:</b> 1.32-1.35 g/mL <b>solubility in H<sub>2</sub>O:</b> in any ratio <b>biodegradability:</b> > 80%
<b>DS</b> polyaspartic acid		<b>molecular weight:</b> [C <sub>4</sub> H <sub>4</sub> NO <sub>3</sub> Na] <sub>x</sub> <b>appearance:</b> clear reddish <b>pH:</b> 9.5-10.5 <b>density:</b> 1.3 g/mL <b>solubility in H<sub>2</sub>O:</b> in any ratio <b>biodegradability:</b> > 60%
<b>EDDS</b> ethylenediamine-disuccinic acid		<b>molecular weight:</b> 358.1 <b>appearance:</b> colourless to yellowish <b>pH:</b> 9.2 <b>density:</b> 1.26 g/mL <b>solubility in H<sub>2</sub>O:</b> in any ratio <b>biodegradability:</b> > 60%
<b>GLDA</b> N,N-bis(carboxymethyl)-L-glutamic acid		<b>molecular weight:</b> 351.1 <b>appearance:</b> colourless to yellowish <b>pH:</b> 13.5 <b>density:</b> 1.38 g/mL <b>solubility in H<sub>2</sub>O:</b> in any ratio <b>biodegradability:</b> > 83%
<b>MGDA</b> methylglycine-diacetic acid		<b>molecular weight:</b> 271.0 <b>appearance:</b> clear yellowish <b>pH:</b> 11.0 <b>density:</b> 1.31 g/mL <b>solubility in H<sub>2</sub>O:</b> in any ratio <b>biodegradability:</b> > 68%

Table 3. Physicochemical properties of IDS, DS, EDDS, GLDA and MGDA.

4. Determination of aminopolycarboxylic acids

It should be mentioned that speciation determination of the above presented chelating agents can be done by the gas chromatographic method using the international standard ISO 16588:2002. According to this norm the EDTA, NTA, DTPA, β-ADA (β-alaninediacetic acid) and 1,3-PDTA (1,3-propylenedinitrilotetraacetic acid) as well as MGDA can be determined in drinking, ground, surface and waste water samples. In waste waters and

especially in pulp and paper wastes EDTA and DTPA can be determined by the liquid chromatography method in the form of Fe(III) complexes. The high performance liquid chromatography and electrophoresis methods can be used to determine Fe(III)-IDS complexes in cosmetic products (Sillanpää, et al. 1995; Katata, et al. 2006). The rapid UV-Vis method of determination of IDS was described in (Reinecke, et al. 2000). The samples containing IDS should be contacted with an appropriate amount of  $\text{CuSO}_4$  in order to form blue  $[\text{Cu}(\text{ids})]^{2-}$  complexes. Their absorption was measured at 305 nm and 710 nm. The found absorption coefficients were equal to 327.7 and 67.5 for IDS concentrations in the range from 2 mM to 16 mM. It was also stated that the absorption of the  $[\text{Cu}(\text{ids})]^{2-}$  complexes was almost constant at pH values between 4 and 9. The modification of this method was also proposed and pH of the samples was adjusted at 1.3 by phosphoric acid to avoid  $\text{Cu}(\text{OH})_2$  precipitation. The obtained detection limit was 0.075 mM. The IDS can be also analysed by the ion chromatography (IC) method with isocratic elution (methanol in formate buffer) on the Purospher RP18 column. The method allows separation of [R,S]-IDS from [R,R]- and [S,S]-IDS isomers. In the paper by (Knepper, et al. 2005) the determination of EDTA and DTPA in aqueous solutions by the IC-MS method using the A Supp5 anion exchange column was described. The advantages of the method are: simple sample preparation, analysis without derivatization and possibility of determination of chelating agents in complex matrices (with high salt content). Quantification to a concentration down to the level of 1  $\mu\text{g/L}$  was achieved by applying the  $^{13}\text{C}$  marked internal standards.

## 5. Sorption of heavy metal ions in the presence of IDS, EDDS and GLDA

### 5.1 Experimental

In the presented paper the results of the sorption of heavy metal ions such as, Cd(II), Pb(II), Cu(II), Zn(II) as well as Cr(VI) and As(V) in the presence of the above-mentioned complexing agents on commercially available anion exchangers and chelating ion exchangers are presented. It provides overview of the information obtained using batch and column studies and descriptions of various sorption mechanisms. The obtained sorption results were fitted using the Langmuir, Freundlich, Dubinin-Radushkevich (D-R) or Temkin sorption isotherm models, whereas the kinetic data were analysed using the sorption kinetic Lagergren, Ho and McKay, Elovich, Weber and Morris (W-B) as well as Boyd models. It should be stressed that the choice of a particular chelating agent is dependent on several factors, including the pH and temperature range of the system in which they are used, which metal ions are to be controlled and the overall economy of the system. Therefore, the studies were carried out considering the effects of some important parameters such as phase contact time, initial concentration, pH and temperature. The aim of the presented studies was to compare sorption of heavy metal ions in the presence of the biodegradable chelating agents IDS, EDDS and GLDA. After comparison the most suitable treatment ways of waste waters containing heavy metal ions and the complexing agents of a new generation will be discussed. The literature lacks the data concerning sorption of heavy metal ions in the presence of biodegradable complexing agents of a new generation on ion exchangers.

In the investigations the following strongly basic anion exchangers were used: Amberlite IRA 900, Amberlite IRA 910, Amberjet 4200, Amberjet 4400, Amberjet 4600 and Purolite A520 E. In the chapter they were also denoted as: IRA 900, IRA 910, 4200, 4400, 4600 and A520E. For comparison the anion exchangers of Lewatite group: Lewatit MonoPlus M 500, Lewatit MonoPlus M 600 and Lewatit MonoPlus MP 500 as well as the chelating ion

exchangers: Dowex M 4195 and Diphonix® were also used (denoted as M 500, M 600, MP 500, M 4195 and Diphonix, respectively). The physicochemical properties of ion exchangers used are summarized in Table 4.

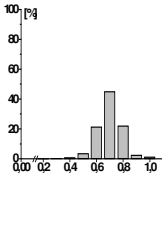
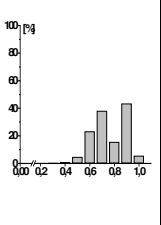
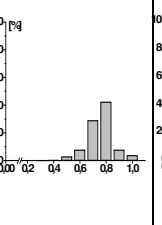
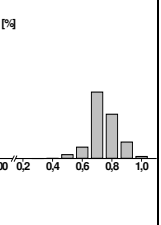
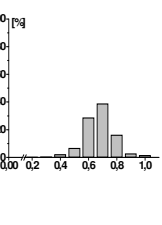
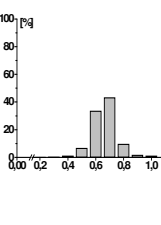
Anion exchanger	Amberlite IRA 900	Amberlite IRA 910	Amberjet 4200	Amberjet 4400	Amberjet 4600	Purolite A520E
Manufacturer	Rohm and Haas, France	Rohm and Haas, France	Rohm and Haas, France	Rohm and Haas, France	Rohm and Haas, France	Purolite International, Ltd., UK
Functional groups	$\text{—N}^+(\text{CH}_3)_3$	$\text{—N}^+(\text{CH}_3)_2\text{C}$ $\text{H}_2\text{CH}_2\text{OH}$	$\text{—N}^+(\text{CH}_3)_3$	$\text{—N}^+(\text{CH}_3)_3$	$\text{—N}^+(\text{CH}_3)_2\text{C}$ $\text{H}_2\text{CH}_2\text{OH}$	$\text{—N}^+(\text{CH}_3)_3$
Matrix	PS-DVB	PS-DVB	PS-DVB	PS-DVB	PS-DVB	PS-DVB
Structure	macroporous	macroporous	gel	gel	gel	macroporous
Capacity [eq/L]	1.0	1.0	1.3	1.4	1.25	0.9
Bead size [μm]	650-800	530-800	600-800	530-630	600-800	300-1200
Zingg classification						
pH range	0-14	0-14	0-14	0-14	0-14	0-14
Max.temp.range [K]	350	350	350	350	350	350
BET surface area [m²/g]	36.00	39.25	5.27	1.96	1.47	23.52
Aver. pore diameter [nm]	15.45	16.02	9.03	6.14	17.53	16.37

Table 4. Physicochemical properties of used anion exchangers.

The detailed characteristics of Lewatit MonoPlus M 500, Lewatit MonoPlus M 600 and Lewatit MonoPlus MP 500 as well as Dowex M4195 and Diphonix were presented in (Kołodyska, 2009a, 2010b, 2011b). The metals chosen for the evaluation were Cu(II), Zn(II), Pb(II), Cd(II) as well as Cr(VI) and As(V) due to their occurrence and abundance in waste water streams. The sorption tests included: evaluation of the rate and extent of complexes sorption on ion exchangers (%S), single vs. multi-component sorption, pH and temperature effects, interfering ions influence as well as exposition to UV light. The rate of metal complexes sorption was measured under the batch and the column conditions.

The objectives of the isotherm studies were to describe and quantify the partition of metals between the liquid phase and the ion exchanger phases with varying concentrations, and to determine the equilibrium capacity of the ion exchangers for the metal complexes. In order to compare the surface morphologies of the studied ion exchangers before and after the sorption process AFM (Atomic Force Microscopy) scans were made. The infrared spectroscopy was used to identify the changes after the sorption process. The details for the experimental procedures were presented in (Kołodyska, et al. 2009; Kołodyska, 2009ab; 2010a-c; 2011a-d).

## 5.2 Sorption of heavy metal complexes with IDS, EDDS and GLDA – the batch studies

### 5.2.1 pH effect

The chelating ability of IDS, EDDS and GLDA depends on the pH value, however, in the case of the use of anion exchangers as potential materials for heavy metal ions removal only complexes with more negative charge will be sorbed effectively. As has already been shown, IDS, EDDS and GLDA form 1:1 complexes with M(II). The effective regions for forming this type of complexes are above 4. As sorption of anionic complexes onto the selected ion exchangers depends on the acidity of the medium, pH of the metal complexes solution must be rigorously controlled. Therefore, to determine the optimum working conditions for sorption of the  $[ML]^{2-}$  and  $[ML]^{-}$  complexes by Lewatit MonoPlus M 500, Lewatit MonoPlus M 600, Lewatit MonoPlus MP 500, Amberlite IRA 900, Amberlite IRA 910, Amberjet 4200, Amberjet 4400, Amberjet 4600 and Purolite A520E, the effect of acidity was studied. The exemplary results for the Cu(II), Zn(II), Cd(II) and Pb(II) complexes with IDS and EDDS sorption on Amberlite IRA 900 (anion exchanger of type 1) and Amberlite IRA 910 (anion exchanger of type 2) are presented in Fig.8a-d.

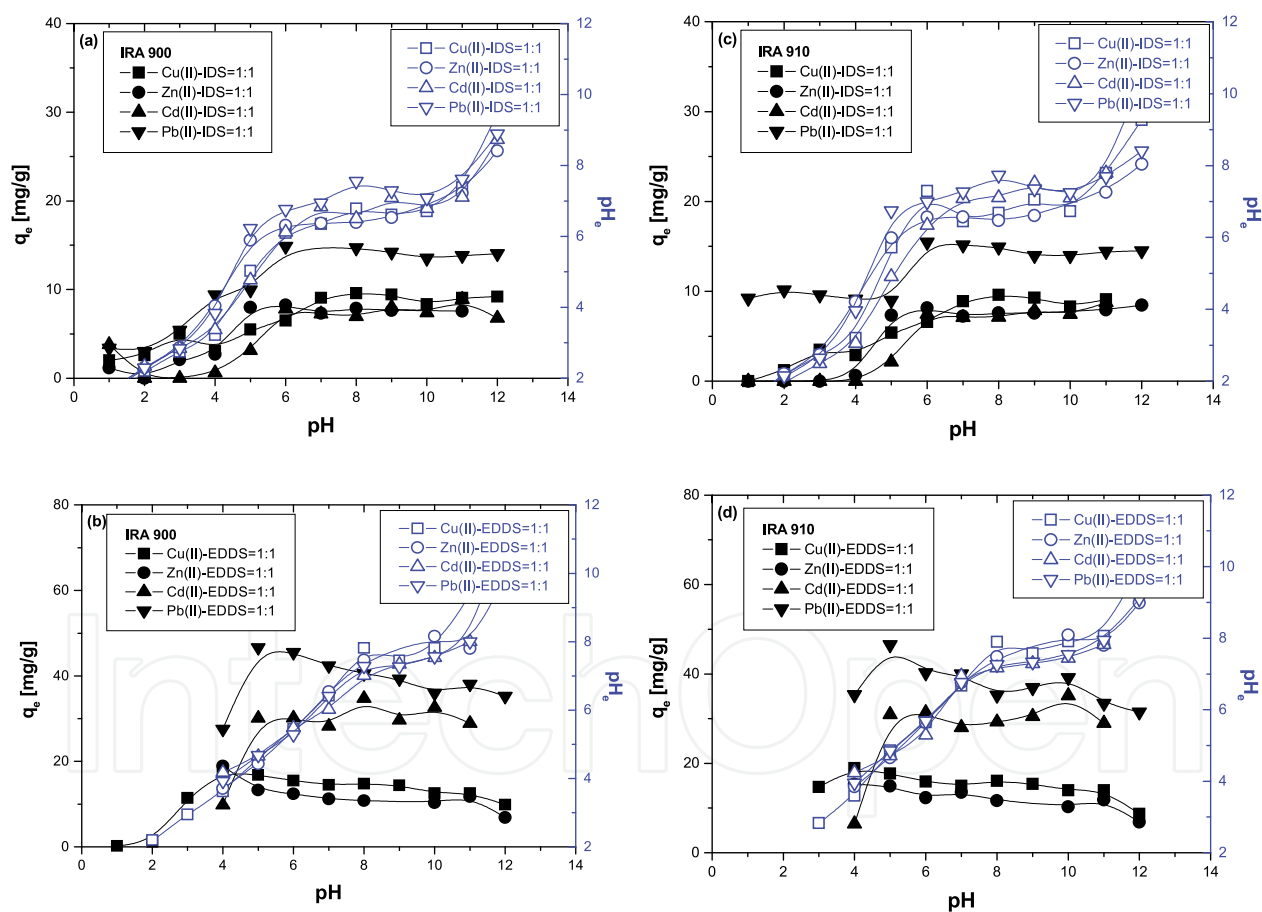


Fig. 8. a-d Effect of pH on the sorption capacities of Cu(II), Zn(II), Cd(II) and Pb(II) complexes with IDS and EDDS on the Amberlite IRA 900 (a, b) and Amberlite IRA 910 (c, d) ( $c_0 1 \times 10^{-3}$  mol/L for IDS and  $c_0 2 \times 10^{-3}$  mol/L for EDDS complexes, shaking time 180 min, shaking speed 180 rpm, room temperature).

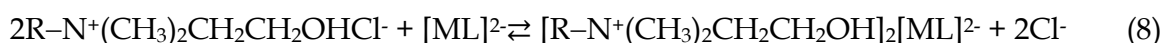
It was found that the sorption capacity increased in the pH range from 4.0 to 9.0 for IDS and GLDA (not presented) complexes and achieved the maximum values at pH >6.0. For EDDS

complexes the sorption effectiveness slightly decreases with the increasing pH and the optimal sorption conditions were at pH >4.0. The pHs of the metal complex solutions were also measured during the sorption process. For the initial pH values from 4 to 12 the decrease in the equilibrium pH was observed due to the release of the Cl<sup>-</sup> ions from the resin. Therefore, for the studied strongly basic anion exchangers from the Lewatite, Amberjet and Amberlite groups the following reactions of the process can be written:

the anion exchangers of type 1:



the anion exchangers of type 2:



where R is the resin matrix.

The highest values of the pH decrease were found for the initial pH equal to 11-12 and for the IDS complexes. For these values the decrease of the complexes removal was also observed. In the system containing, for example Cu(II) ions without the presence of complexing agents, their precipitation in the form of Cu(OH)<sub>2</sub> should be observed at pH > 6.5. However, in the presence of complexing agents the hydrolysis accompanied by precipitation of metal hydroxides does not occur. It is obviously connected with the stability constants of formed complexes (Table 3), which are the lowest for IDS. For Lewatit MonoPlus M 500, Lewatit MonoPlus M 600, Lewatit MonoPlus MP 500, Amberlite IRA 900 and Amberlite IRA 910 the obtained results were almost analogous to those for Amberjet 4200, Amberjet 4400, Amberjet 4600 and Purolite A520E anion exchangers and presented in (Kołodziejńska, et al. 2009, Kołodziejńska, 2011d). However, in the case of the chelating ion exchangers Dowex M 4195 and Diphonix a slight decrease of the sorption effectiveness with the increasing pH values was observed. Additionally, it was also found that at lower initial concentrations the amount of the sorbed complexes decreases while the pH increases. At higher concentrations, the sorbed amount does not increase (up to 2 × 10<sup>-2</sup> mol/L) due to the low concentration of free functional groups near the saturation stage. On the other hand, the increase of the concentration of the solution is accompanied by further pH decreasing. Since Cl<sup>-</sup> ions are less competitive with respect to the metal complexes with IDS, EDDS and GLDA in the ion exchange process, the ion exchange increases or stays constant in spite of pH lowering.

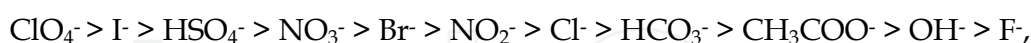
### 5.2.2 Effect of interfering ions

Besides the effect of pH, the sorption of Cu(II), Zn(II), Cd(II) and Pb(II) complexes with IDS, GLDA and EDDS is strongly affected by the interfering ions presence. In the case of the system without interfering ions, strongly basic anion exchangers have high affinity for anionic complexes of [ML]<sup>2-</sup> or [MHL]<sup>-</sup> types. At the initial concentration of 1 × 10<sup>-3</sup> M, almost 100 % of the sorption percentage (%S) of Cu(II), Zn(II), Cd(II) and Pb(II) in the presence of IDS was observed for the studied anion exchangers. However, only 55-60% removal was found in the presence of SO<sub>4</sub><sup>2-</sup> ions, while sorption in the presence of Cl<sup>-</sup> ions was reduced minimally which confirms the results obtained for pH changes. In the presence of NO<sub>3</sub><sup>-</sup> interfering ions S%



changes in the range of 81-92% depending on the anion exchanger used. The described results for the IDS complexes presented in Fig.9, show the general trend which is consistent with those obtained for other complexing agents. The %S values are also in agreement with the affinity of the anion exchangers for anions (Helfferrich, 1962; Minczewski et al. 1982):

the anion exchangers of type 1:



the anion exchangers of type 2:

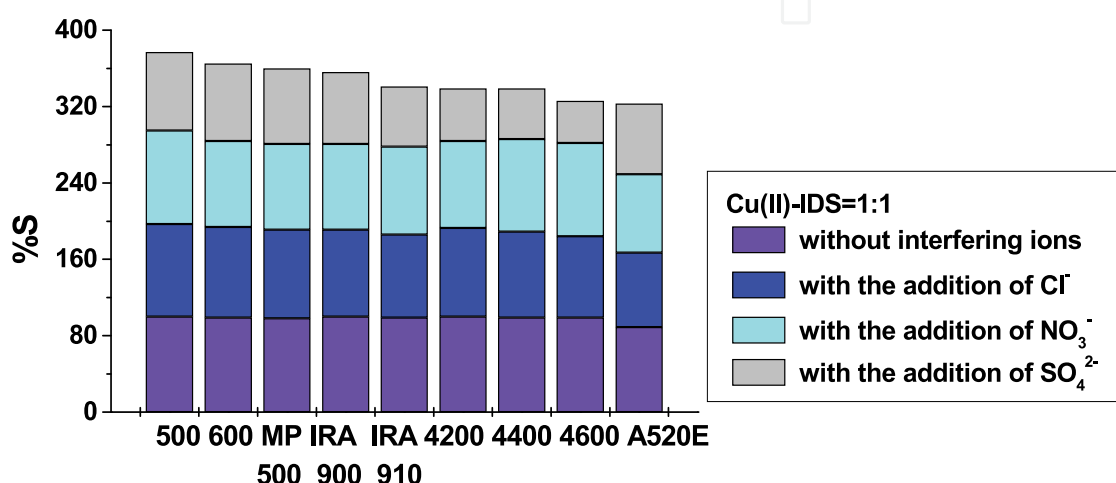
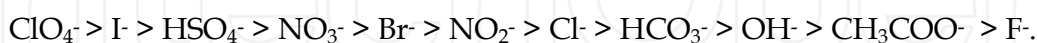


Fig. 9. Effect of interfering ions on the sorption percentage (%S) of Cu(II) complexes with IDS on the Lewatit MonoPlus M 500, Lewatit MonoPlus M 600, Lewatit MonoPlus MP 500, Amberlite IRA 900, Amberlite IRA 910, Amberjet 4200, Amberjet 4400, Amberjet 4600 and Purolite A520E ( $c_0 \times 10^{-3}$  mol/L for IDS complexes, shaking time 180 min, shaking speed 180 rpm, room temperature).

The multi-component studies of sorption of metal complexes on the selected anion exchangers are also very important for assessing the degree of interferences in waste waters treatment. In the case of the binary (Cu(II)-Zn(II)) and quaternary (Cu(II)-Zn(II)-Cd(II)-Pb(II)) sorption studies of Cu(II), Zn(II), Cd(II) and Pb(II) complexes with IDS, EDDS and GLDA, their co-sorption induces a decrease in equilibrium sorption capacity. However, the percentage of decrease depends on co-metal ion present in the system. Other authors also presented such competitive sorption in the multi-component systems. This can be connected with the structure of the sorbed complexes and the ease with which they are formed. It should be stated that the ionic radius of Pb(II) equal to 1.12 Å is greater than that for Cd(II) 0.97 Å, Zn(II) 0.83 Å and Cu(II) 0.72 Å. Pb(II) has also the maximum hydrated radius and molecular weight in comparison to Cd(II), Zn(II) and Cu(II). Therefore, its connection with such ligands as EDDS or DS may be difficult taking into account the spatial reasons. This is evidenced, among others by large values of the maximum sorption capacity of the chelating ion exchanger Diphonix towards Pb(II) ions (357 mg/g) in the presence of EDDS compare to those obtained for Amberjet 4200 (216 mg/g), Amberjet 4400 (159 mg/g), Amberjet 4600 (164 mg/g) and much higher to the Lewatit MonoPlus M 500 (128 mg/g), Lewatit MonoPlus M 600 (139 mg/g) and Lewatit MonoPlus MP 500 (120 mg/g).

### 5.2.3 Anion exchanger properties - particle size, cross-linking, type of functional groups

The size of the polymer droplets formed during polymerisation and thus the size of the beads depend on the polymerisation technique, the suspension medium and the monomer concentration. Several producers now offer ion exchange resins with a very uniform size distribution. The example of this type of resins are Amberjets (Rohm and Haas) or Lewatit MonoPlus manufactured by Lanxess. Standard ion exchange resins have the mean particle sizes of 500-800  $\mu\text{m}$ . In the presented studies the used anion exchangers possess the following bead sizes: 650-800  $\mu\text{m}$  - Amberlite IRA 900, 530-800  $\mu\text{m}$  - Amberlite IRA 910, 600-800  $\mu\text{m}$  - Amberjet 4200, 530-630  $\mu\text{m}$  - Amberjet 4400, 600-800  $\mu\text{m}$  - Amberjet 4600 and 300-1200  $\mu\text{m}$  - Purolite A520E. The scans of the Amberjet 4200 and Amberjet 4400 anion exchangers with the uniform size are presented in Fig.10a-b.

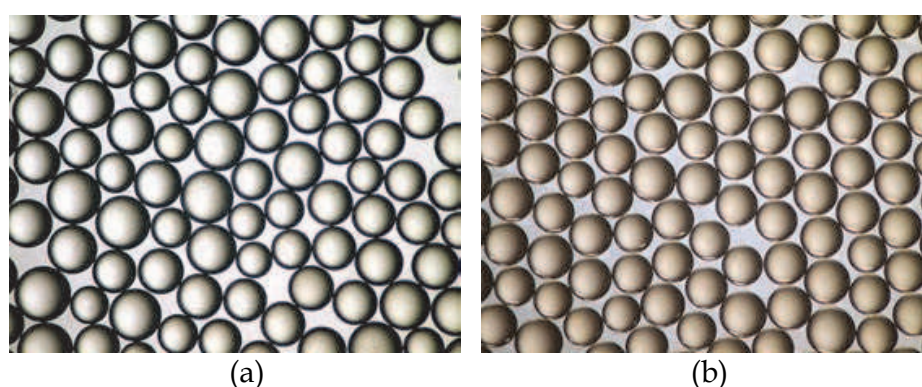


Fig. 10. The scans of the Amberjet 4200 (a) and Amberjet 4400 (b) anion exchangers (<http://dardel.info/IX/>).

Using AWK 3D Analyser (Kamika Instruments, Poland) for determining size and shape of particles based on the Zingg classification the granulometric analysis was performed (Zingg, 1935). The Zingg classification is based on the proportions between three dimensions of ion exchanger beads  $a$  - the longest,  $b$  - mean and  $c$  - the shortest. However, the following assumptions should be made: (i) beads with the proportions  $b/a > 0.67$  and  $c/b > 0.67$  are similar to spheres, (ii) for  $b/a = c/b = 1$  beads are spheres (iii) for  $b/a > 0.67$  and  $c/b < 0.67$  beads are similar to discs, (iv) for  $b/a < 0.67$  and  $c/b > 0.67$  beads are similar to cylinders, and (v) for  $b/a < 0.67$  and  $c/b < 0.67$  beads are similar to blades. Volume fractions of beads for  $b/a = 1$  were shown in the figures in Table 4 (in these figures  $x$  axis presents  $c/b$ ). As follows from the obtained results the bead size of the ion exchangers used has an approximately the Gaussian distribution. It was found that with the increase of beads dimensions, the volume fractions of disc-similar beads decrease and the beads are more spherical. For example, for Amberlite IRA 900 it is 45% at  $c/b=0.6-0.7$ ; for Amberlite IRA 910 38%, for Amberjet 4200 36,5% and 40% at  $c/b=0.7-0.8$ ; for Amberjet 4400 48% and 32% at  $c/b=0.7-0.8$ ; for Amberjet 4600 38,8% and 28.6 at  $c/b=0.5-0.6$ ; for Purolite A520E 47% and 27.5% at  $c/b=0.5-0.6$ . Moreover, for chelating ion exchangers these values are as follows: for Dowex M4195 43% at  $c/b=0.6-0.7$  and 33% at  $c/b=0.5-0.6$ ; for Diphonix 44% at  $c/b=0.6-0.7$ . The ideal spheres do not occur.

The particle size of the ion exchanger material and its uniformity are the most important parameters influencing on hydraulics and kinetics of the ion exchange process especially in the column mode technique. It is also obvious that 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. In the investigations the influence of size and shape of the used anion exchangers on sorption effectiveness was compared based on the results of sorption of Cu(II), Zn(II), Cd(II) and Pb(II) complexes with IDS. To this aim, Amberjet 4200 and Amberjet 4400 strongly basic anion exchangers of type 1 were used. The obtained results are presented in Fig. 11a-b and for the complexes with GLDA in Fig.12.

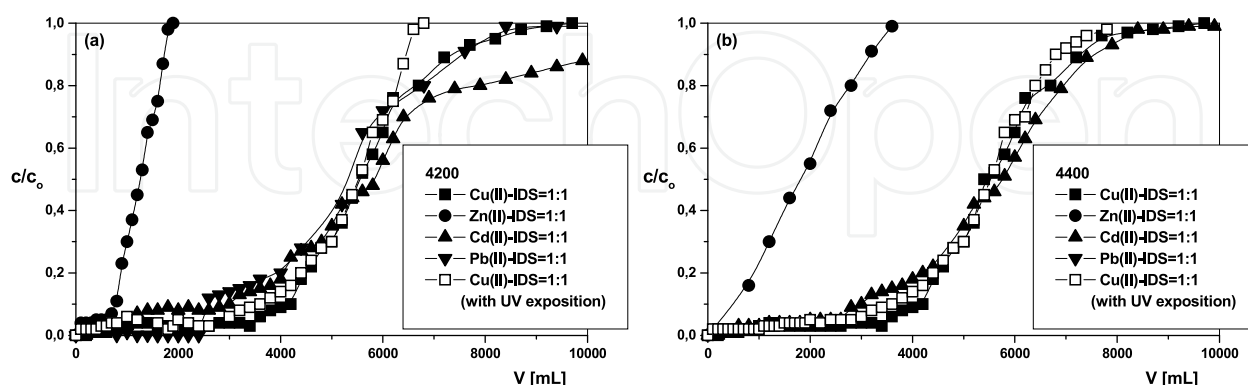


Fig. 11. a-b Breakthrough curves of Cu(II), Zn(II), Cd(II) and Pb(II) complexes with IDS on the Amberjet 4200 (a) and Amberjet 4400 (b) anion exchangers ( $c_0 1 \times 10^{-3}$  mol/L for IDS complexes, bed volume 10 mL, flow rate 0.6 mL/min)

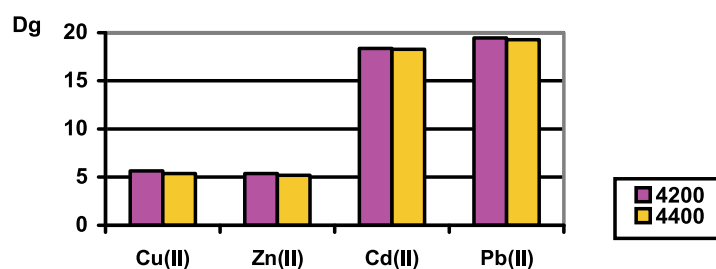


Fig. 12. Comparison of the mass distribution coefficients ( $D_g$ ) for sorption of Cu(II), Zn(II), Cd(II) and Pb(II) complexes with GLDA on the Amberjet 4200 and Amberjet 4400 anion exchangers.

It was found that the anion exchanger with a large size of beads and moreover, high percentage of spherical beads is characterized by better sorption properties toward the GLDA complexes with Cu(II), Zn(II), Cd(II) and Pb(II). Both anion exchangers exhibit higher affinity for the Cu(II) complexes with IDS than for the corresponding Zn(II) one (Fig.11a-b). These breakthrough curves indicate also that their affinity for the Cu(II) complexes is higher in the case of Amberjet 4200 ( $c/c_0=0,5$ ;  $V$ = about 5560 mL) than Amberjet 4400 ( $c/c_0=0,5$ ;  $V$ = about 5400 mL). The affinities for the complexes with GLDA are arranged in a similar order which is confirmed by the mass distribution coefficients ( $D_g$ ) (Fig.12). The obtained breakthrough curves have typical S-shape. As follows from Fig.11a-b the UV exposition does not have a significant effect on the decomposition of the complexes in the resin phase.

In the waste water treatment polystyrene ion exchangers usually have a DVB (divinylbenzene) concentration of ca. 8 %. Ion exchangers with a higher degree of cross-linking (10-12%) are used to obtain water of very high purity, and with a lower degree of cross-linking (5-7%) for softening. In the presented studies the anion exchangers have probably the same %DVB (this parameter is not given by the manufacturers) and therefore it is difficult to estimate.

Among the factors, which strongly affect selectivity of anion exchangers are type of functional groups, active site spacing and hydrophobic or hydrophilic nature of the resin matrix. The resins with the quaternary ammonium groups  $-N^+(CH_3)_3$  are strongly basic (Lewatit MonoPlus M 500, Lewatit MonoPlus MP 500, Amberlite IRA 900, Amberjet 4200, Amberjet 4400, Purolite A520E). These are also known as type 1. The strongly basic anion exchangers possessing  $-N^+(CH_3)_2CH_2CH_2OH$  groups (Lewatit MonoPlus M 600, Amberlite IRA 910, Amberjet 4600,) are denoted as type 2. The behaviour of the above-mentioned groups depends mainly on the acidity of the solution. The anion exchangers of type 1 are more strongly basic compared to type 2 and have the greatest affinity for weak acids. However, the efficiency of their regeneration to the hydroxide form is lower. Taking this parameter into account the effect of this type of functional groups was compared for Cu(II), Zn(II), Cd(II) and Pb(II) complexes(II) with IDS, EDDS and GLDA. As expected, under these conditions the most effective results were obtained for the anion exchangers of type 1. For example, the amount of Cu(II), Zn(II), Cd(II) and Pb(II) complexes with IDS sorbed on Amberlite IRA 900 was 4.32 mg/g; 3.25 mg/g; 18.51 mg/g and 24.35 mg/g whereas only 4.26 mg/g; 3.68 mg/g; 17.96 mg/g and 21.35 mg/g on Amberlite IRA 910. The analogous results were obtained in the case of EDDS and GLDA complexes. Comparing the strongly basic anion exchangers supplied by different manufacturers, it was found that only in some cases Amberlite anion exchangers are slightly less effective than Amberjet anion exchangers (4.32 mg/g and 5.17 mg/g for Amberlite IRA 900 and Amberjet 4200 in the case of Cu(II)-IDS sorption, respectively). However, the strongly basic anion exchangers from Lewatit group are characterized by the highest sorption capacities for these complexes. For example, for Cu(II)-EDDS complexes at the initial concentration  $2 \times 10^{-3}$  M the obtained sorption capacities for Lewatit MonoPlus M 500, Lewatit MonoPlus M 600, Lewatit MonoPlus MP 500 and Amberjet 4200, Amberjet 4400, Amberjet 4600 are as follows: 12.66 mg/g; 12.58 mg/g; 12.72 mg/g and 12.14 mg/g; 11.85 mg/g; 11.43 mg/g, respectively. On the other hand, taking into account the matrix of the used anion exchangers (gel or macroporous) such as for Lewatit MonoPlus M 500 and Lewatit MonoPlus MP 500, the anion exchangers of macroporous type are slightly more effective than the gel ones.

### 5.3 Kinetic evaluation

From the industrial point of view, where a solution flows through the ion exchanger the equilibrium is not necessarily reached and the results are influenced by kinetic consideration. Therefore, the experimental data for the M(II)-L=1:1 complexes sorption on the anion exchangers were fitted with the pseudo first-order (PF-order), pseudo second-order (PS-order) models proposed by Lagergren and Ho and McKay according (Blanchard, et al. 1984; Lagergren, 1898) as well as the intraparticle Webber and Morris (W-B) model (Weber & Morris, 1963). The kinetic parameters can be obtained by both linear and non-linear regression analysis. Linear regression is frequently used to determine the best fitting kinetic model, and the method of least squares is used for finding the parameters of the kinetic models. In the case of PS-order kinetic constant,  $q_e$  and  $k_2$ , they were calculated from the following plots:  $t/q_t$  vs.  $t$  (PS-order of type 1),  $1/q_t$  vs.  $1/t$  (PS-order of type 2),  $q_t$  vs.  $q_t/t$  (PS-order of type 3),  $q_t/t$  vs.  $q_t$  (PS-order of type 4), respectively. However, as was stated taking into account the sum of the squares of errors (SSE), except for the PS-order equation of type 1, no other model provided a better fit to the experimental kinetic data. In these cases the SSE values were for the PS-order model lower than for the PF-order one. Moreover, in the case of the intraparticle kinetic model of Weber and Morris, the linear part of the plot of  $q_t$  vs.  $t^{1/2}$  does not pass through the origin.



On the plots three different regions: before the equilibrium, the intraparticle diffusion and the stage to the final equilibrium can be distinguished. Therefore, it could be stated that the intraparticle diffusion is not the only rate controlling step. Similar results were obtained applying the Boyd model (Boyd, et al. 1947; Reichenberg, 1953). Based on it, two rate limiting steps for ion exchange kinetics – intradiffusion of counter-ions within the ion exchanger and interdiffusion of counter-ions in the adherent films can be distinguished. In this case the calculated diffusion rate constants  $B_t$ , which are related to the internal diffusion process plotted vs.  $t$ , do not give the lines which pass through the origin. This indicates that the rate limiting process is connected with film diffusion. It is well known that the film diffusion is a rate controlling step for the value of film diffusion coefficient  $D_f$  in the range  $10^{-6}$ – $10^{-8}$  cm<sup>2</sup>/s. On the other hand, the pore diffusion is rate controlling, the pore diffusion coefficient  $D_p$  is in the range  $10^{-11}$ – $10^{-13}$  cm<sup>2</sup>/s. For sorption processes of Cu(II), Zn(II), Cd(II) and Pb(II) complexes with IDS, EDDS and GLDA, the values of film  $D_f$  and pore  $D_p$  diffusion coefficients were found to be in the range  $10^{-6}$ – $10^{-7}$  cm<sup>2</sup>/s and  $10^{-8}$ – $10^{-9}$  cm<sup>2</sup>/s, respectively which indicates the film diffusion has some influence in the rate determining step. In order to establish affinity of anion exchangers for the above-mentioned complexes, the  $q_2$  values for the PS-order model of type 1 were compared and presented in Fig.13a-c.

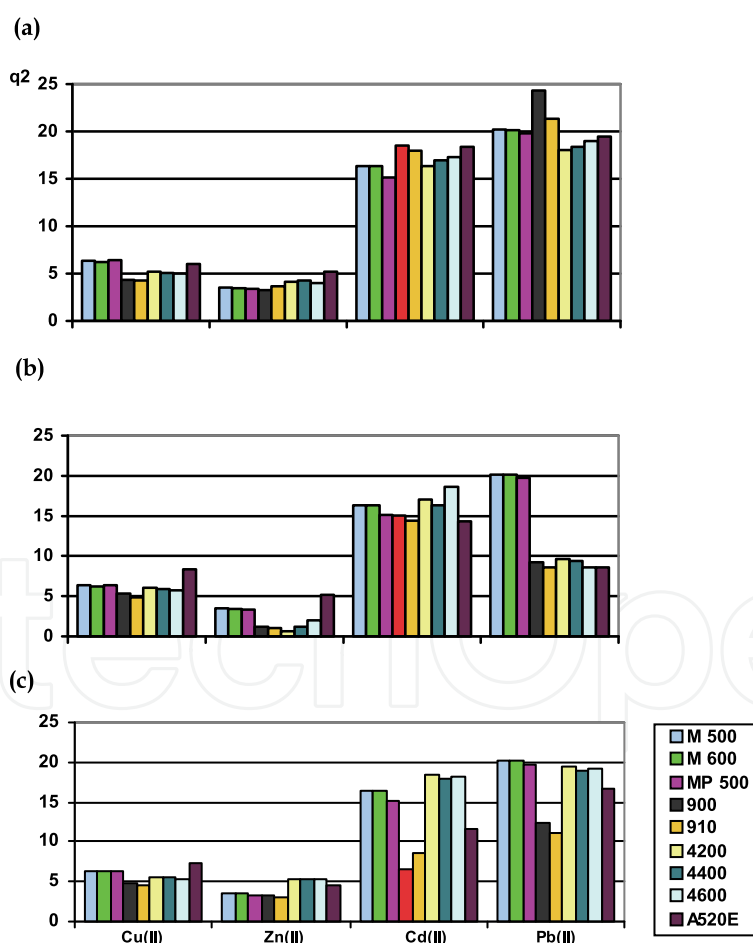


Fig. 13. a-c Comparison of sorption capacities  $q_2$  (mg/g) of Cu(II), Zn(II), Cd(II) and Pb(II) complexes with IDS (a), EDDS (b) and GLDA (c) on the studied anion exchangers ( $c_0$   $1 \times 10^{-3}$  mol/L for IDS and GLDA complexes as well as  $c_0$   $2 \times 10^{-3}$  mol/L for EDDS complexes, shaking speed 180 rpm, shaking time 1-60 min, room temperature).



Kinetic sorption experiments were also carried out with the increased complexes concentrations from  $1 \times 10^{-3}$  mol/L to  $2 \times 10^{-2}$  mol/L, with the ion exchanger amount of 10 g/L, time 120 min, pH without adjustment, at room temperature. 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. The amount of Cu(II)-IDS complexes sorbed on Dowex M4195 and Diphonix at different initial concentrations is shown in Fig.14a-b.

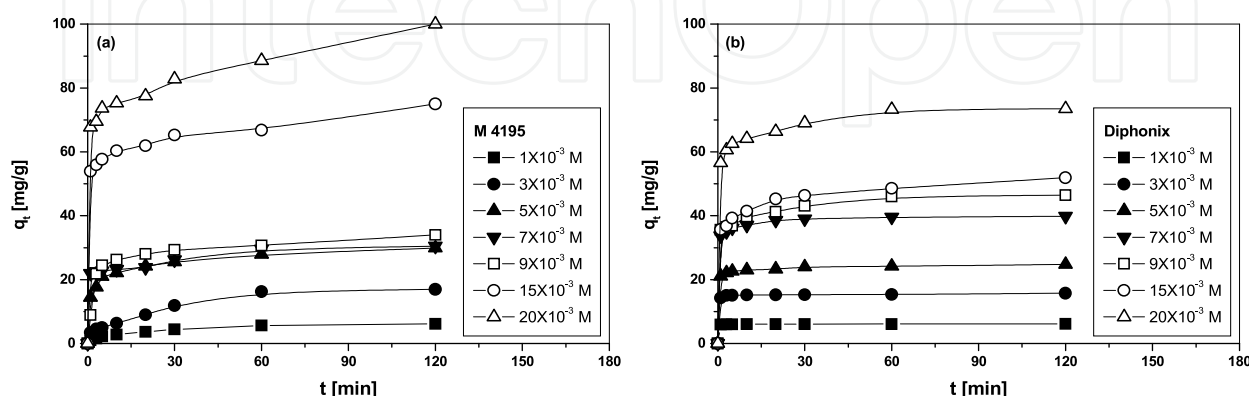


Fig. 14. a-b Effect of the phase contact time on the sorption capacities of Cu(II)-IDS complexes at different initial concentrations on the Dowex M 4195 (a) and Diphonix (b) ( $c_0$   $1 \times 10^{-3}$  mol/L- $2 \times 10^{-2}$  mol/L, shaking speed 180 rpm, shaking time 1-120 min, room temperature).

The sorption kinetics data of these complexes at different initial concentrations fitted to different kinetic models are presented in Fig. 15a-f. As follows from the obtained results for the most suitable kinetic model, the rate  $k_2$  values decrease with the increasing initial concentrations, while  $h$  increases.

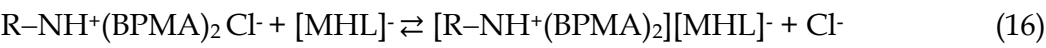
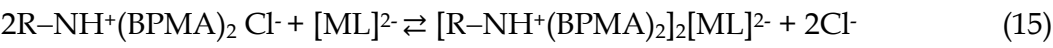
In the case of the chelating resin Dowex M 4195 possessing the bis(2-pyridylmethyl)amine (BPMA) functional groups, depending on the pH value, nitrogen atoms are capable of coordinating metal ions. Based on the  $pK_a$  values of bis(2-pyridylmethyl)amine ( $pK_1=0.5$ ,  $pK_2=2.2$ ,  $pK_3=3.4$ ), it can be stated that at low pH values three nitrogen atoms would be protonated, while in the middle range of pH only one:



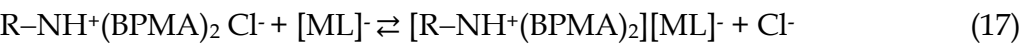
Therefore, in the presence of complexing agents decomposition of the complexes should be taken into account:



The ionic interaction mechanism between the protonated amines and the anionic complexes of the  $[ML]^{2-}$ ,  $[MHL]^-$  and  $[ML]^-$  is also possible. The appropriate reaction can be as follows:



or



The analogous mechanism of sorption is in the case of Diphonix chelating ion exchanger:

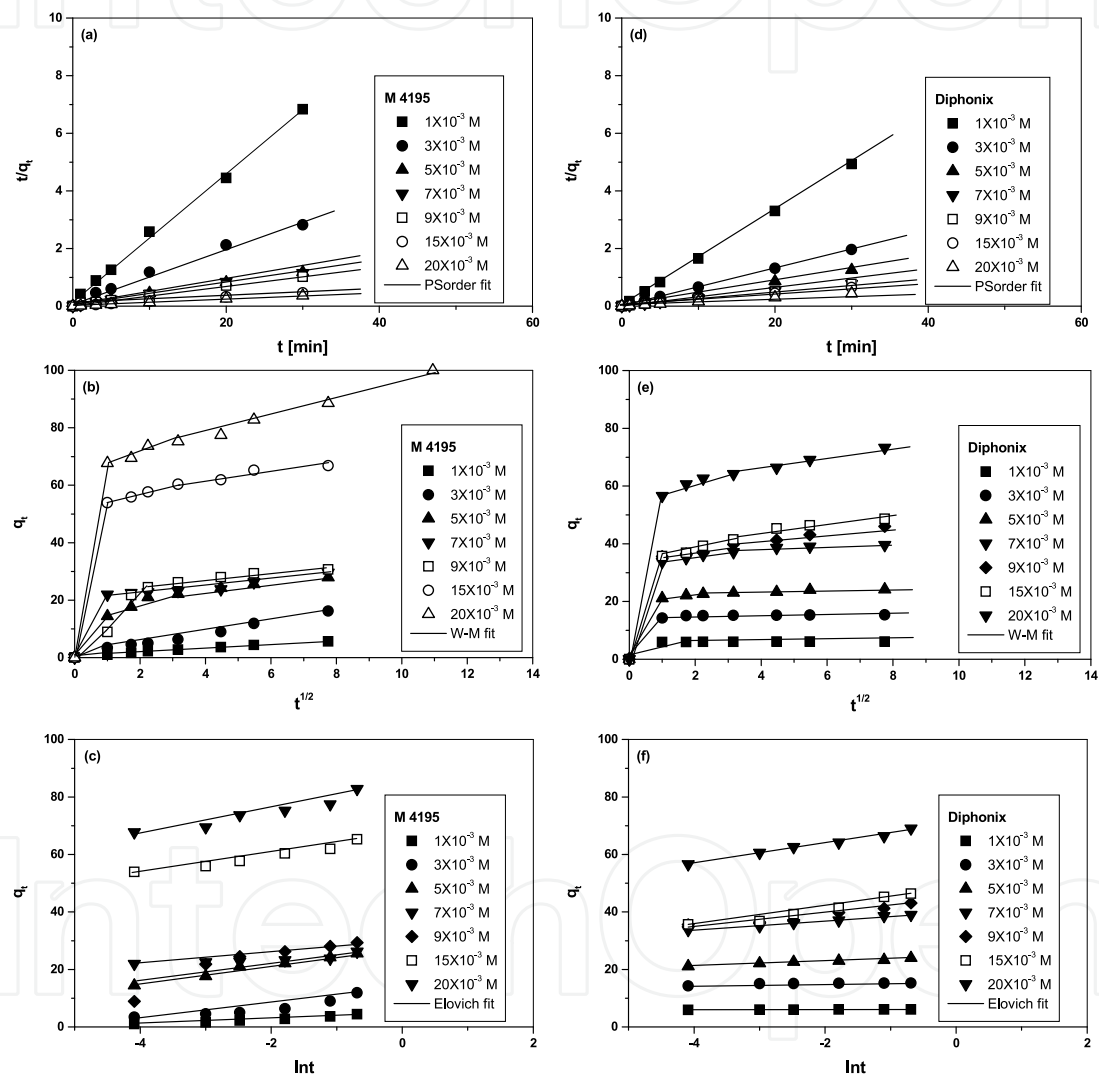
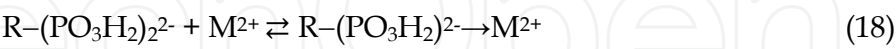


Fig. 15. a-f The comparison of the PS-order, Weber and Morris as well as Elovich kinetic models for the sorption of Cu(II)-IDS complexes at different initial concentrations on the Dowex M 4195 (a-c) and Diphonix (d-f) ( $C_0$   $1 \times 10^{-3}$  mol/L- $2 \times 10^{-2}$  mol/L, shaking speed 180 rpm, room temperature).

As for sorption of As(V) ions, the obtained results reveal that rapid sorption of As(V) on strongly basic anion exchangers, similarly to the Cr(VI) sorption, is attributed to the surface sites initially available and is very large compare to the concentration of sorbed ions. However, the effect of the complexing agent added is neglectable (the obtained results are not presented).

### 5.4 Adsorption isotherm

To investigate the sorption capacity, various concentrations of Cu(II), Zn(II), Cd(II) and Pb(II) complexes with IDS, EDDS and GLDA were contacted with the studied ion exchangers. For interpretation the Langmuir, Freundlich, Dubinin-Radushkevich (D-R) and Temkin sorption isotherm models were used. The sorption data were drawn as the plots of  $q_e/q_e$  vs.  $c_e$  (Langmuir model);  $\log q_e$  vs.  $\log c_e$  (Freundlich model);  $\ln q_e$  vs.  $\varepsilon^2$  (D-R model) and  $q_e$  vs.  $\ln c_e$  (Temkin model). The exemplary results for the Cu(II)-IDS, EDDS or GLDA systems for Amberjet 4200 and Lewatit MonoPlus M 600 anion exchangers are presented in Fig. 16a-c and e-f, respectively.

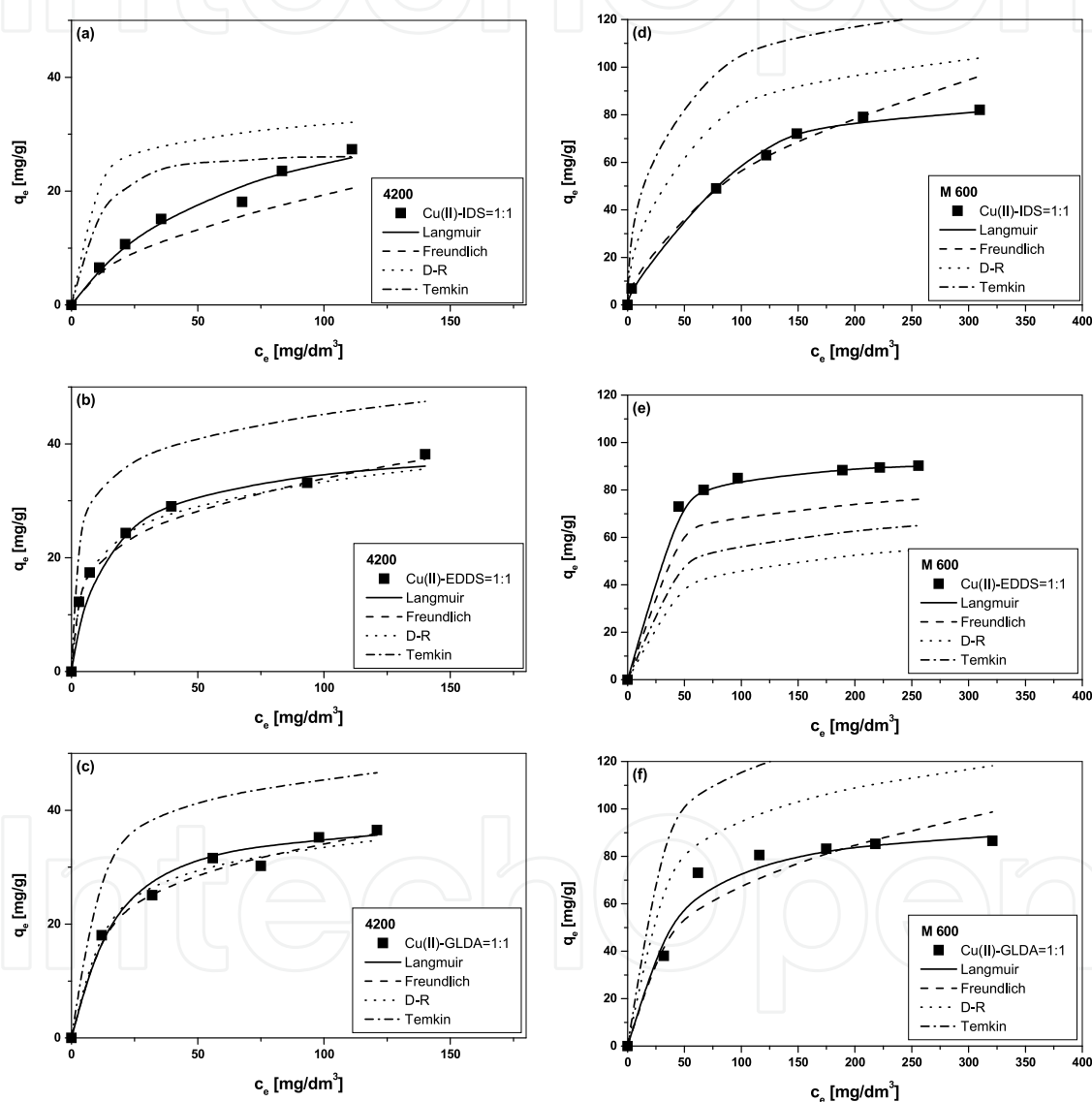


Fig. 16. a-f The isotherm of Cu(II)-IDS, EDDS and GLDA complexes sorption on Amberjet 4200 (a-c) and Lewatit MonoPlus M 600 (d-f) fitted by the Langmuir, Freundlich, D-R and Temkin models ( $c_0$   $1 \times 10^{-3}$  M– $2 \times 10^{-2}$  M, shaking speed 180 rpm, shaking time 120 min, room temperature).

As follows from the obtained results the Langmuir equation better fit the experimental data than the Freundlich, D-R or Temkin equations. However, to the removal of the heavy metal

ions in the presence of IDS, EDDS or GLDA under industrial condition fitting of the obtained results by D-R equation should be also taken into account.

### 5.5 Effect of temperature

Anion exchangers are temperature sensitive. When heated, the Hofmann degradation occurs transforming quaternary ammonium functional groups into tertiary amines or even destroying the functional groups completely. The strongly basic anion exchangers of type 1 such as Lewatit MonoPlus M 500, Lewatit MonoPlus MP 500, Amberlite IRA 900, Amberjet 4200, Amberjet 4400 or Purolite A520E are the most stable. However, for the strongly basic anion exchangers of type 2 such as Lewatit MonoPlus M 600, Amberlite IRA 910 and Amberjet 4600 the degradation undergoes more readily. Therefore, in the presented paper the effect of the temperature was studied in the range from 293 K to 333 K. The evaluated mean free energy value ( $\Delta G^\circ$ ) indicated that the sorption of Cu(II), Zn(II), Cd(II) and Pb(II) complexes with IDS, EDDS and GLDA onto Lewatit MonoPlus M 500, Lewatit MonoPlus M 600, Lewatit MonoPlus MP 500, Amberlite IRA 900, Amberlite IRA 910, Amberjet 4200, Amberjet 4400, Amberjet 4600 and Purolite A520E proceeded by anion exchange. The calculated thermodynamic parameters,  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  showed that the sorption was favourable, spontaneous and endothermic under the examined conditions.

## 6. Conclusions

Heavy metal complexes of Cu(II), Zn(II), Cd(II) and Pb(II) with IDS, EDDS and GLDA were removed from aqueous solution using the commercially available strongly basic anion exchangers Lewatit MonoPlus M 500, Lewatit MonoPlus M 600, Lewatit MonoPlus MP 500, Amberlite IRA 900, Amberlite IRA 910, Amberjet 4200, Amberjet 4400, Amberjet 4600 and Purolite A520E as well as chelating ion exchangers Dowex M 4195 and Diphonix. The influence of phase contact time (1-180 min), anion exchanger dosage (0.25-1.0g), solution pH (1-12), initial concentration ( $1 \times 10^{-3}$  mol/L- $2 \times 10^{-2}$  mol/L), temperature (293-333K) and interfering ions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ) in the single and multi-component systems was studied by the batch method. Additionally, the obtained results were compared with those for the column studies. The amounts of complexes sorbed at equilibrium using the strongly basic anion exchangers were differentiated and the following affinity series were found:

in the M(II)-IDS=1:1 system:

**Cu(II):**MP500>M500>M600>M4195>IRA910>IRA900>A520E≈4200>4400>Diphonix≈4600,

**Zn(II):**IRA900>IRA910>M500>M600>MP500>M4195>4200≈4400≈4600>A520E>Diphonix,

**Cd(II):**M500>MP500>M600>IRA900>Diphonix>IRA910>M4195>4200>4400>4600>A520E,

**Pb(II):**Diphonix>M600>M500>MP500>M4195>4200>IRA910≈4400>IRA900≈4600>A520E;

in the M(II)-EDDS=1:1 system:

**Cu(II):**M4195≈M500>M600>MP500>A520E>Diphonix>IRA900>IRA910>4200>4600>4400,

**Zn(II):**Diphonix>M4195>MP500>M500>M600>A520E>IRA900>IRA910>4400>4600≈4200,

**Cd(II):**Diphonix>MP500>4200>M500>M600>4400>IRA900>IRA910>4600>M4195>A520E,

**Pb(II):Diphonix>4200>A520E>4600>4400>M600>M500>MP500>IRA900>IRA910>M4195;**  
in the M(II)-GLDA=1:1 system:

**Cu(II):MP500>M500>M600>Diphonix>IRA900>IRA910>M4195>4200>A520E>4400>4600,**

**Zn(II):M600≈MP500≈M500>Diphonix>4200>M4195≈4400≈IRA910≈4600>IRA900>A520E,**

**Cd(II):M500>M600>Diphonix>4200>4400>4600>A520E>MP500>IRA900>IRA910>M4195,**

**Pb(II):M500≈M600>MP500>Diphonix>4200≈4400≈M4195≈4600≈A520E>IRA900≈IRA910.**

Comparing the types of the used anion exchangers, the strongly basic ones of type 1 were found to offer much greater capacities for the sorbed complexes than the anion exchangers of type 2. Also anion exchangers of macroporous type are slightly better than gel ones. For them the anion exchange process occurs. However, for Dowex M 4195 and Diphonix the decomposition of the M(II)-IDS, EDDS and GLDA complexes should be taken into account. It was also found that the equilibrium sorption capacity increased when the temperature of solutions increased from 293 to 333 K. The Langmuir, Freundlich, Temkin and Dubinin-Radushevish (D-R) models of adsorption were used for analysis of the experimental data. The Langmuir isotherm model was found to be the most appropriate. The kinetic data were fitted using the PF-order, PS-order, W-M as well as Boyd equations. The experimental data were well described by the PS-order kinetic model.

The anion exchangers can be regenerated very efficiently using 1 M HCl. They can be used in multiple cycles of operation without loss in capacity.

## 7. Acknowledgments

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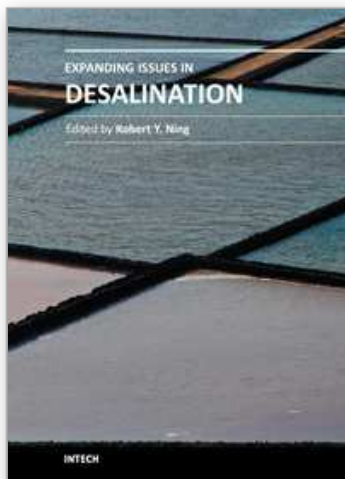
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## **Expanding Issues in Desalination**

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For this book, the term “desalination” is used in the broadest sense of the removal of dissolved, suspended, visible and invisible impurities in seawater, brackish water and wastewater, to make them drinkable, or pure enough for industrial applications like in the processes for the production of steam, power, pharmaceuticals and microelectronics, or simply for discharge back into the environment. This book is a companion volume to “Desalination, Trends and Technologies”, INTECH, 2011, expanding on the extension of seawater desalination to brackish and wastewater desalination applications, and associated technical issues. For students and workers in the field of desalination, this book provides a summary of key concepts and keywords with which detailed information may be gathered through internet search engines. Papers and reviews collected in this volume covers the spectrum of topics on the desalination of water, too broad to delve into in depth. The literature citations in these papers serve to fill in gaps in the coverage of this book. Contributions to the knowledge-base of desalination is expected to continue to grow exponentially in the coming years.

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Phone: +86-21-62489820  
Fax: +86-21-62489821

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