Role of Chelating Agents of a New Generation in Sorption of Metal Ions

D. Kołodyńska[1], M. Siek[2], M. Gęca[3], Z. Hubicki[4]

Department of Inorganic Chemistry, Faculty of Chemistry, Maria Curie Skłodowska University, Maria Curie Skłodowska Sq.2, 20-031 Lublin, POLAND,
[1]**kolodyn@poczta.onet.pl**, [2]**maciek.siek@wp.pl**,
[3]**marzena.geca@poczta.umcs.lublin.pl**, [4]**zbigniew.hubicki@poczta.umcs.lublin.pl**

Abstract

The comparison of Cu^{2+}, Zn^{2+}, Ni^{2+} and Cd^{2+} sorption in the presence of MGDA on the strongly basic anion exchanger Amberjet 4400 was studied. As previously stated the complexones of new generation such as IDS N-(1,2-dicarboxyethylene)-D,L-asparagine acid, EDDS ethylenediaminedisuccinic acid, GLDA N,N-bis(carboxylmethyl)-L-glutamic acid and MGDA methylglycinediacetic acid influence on the effectiveness of sorption of heavy metal ions on different ion exchangers. Determination the effect of different chemical conditions on the ion exchange capacity and on the kinetics of Cu^{2+}, Zn^{2+}, Ni^{2+} and Cd^{2+} permitted for optimalization of heavy metal ions removal. Among others, the effects of the phase contact time, pH, concentration of the solutions and temperature were studied. The most representative isotherm model to describe complexes sorption and the mathematical models describing kinetics of sorption were proposed.

Key words: Heavy metals, chelating agents, ion exchange, biodegradation, methylglycinediacetic acid

Introduction

Large quantities of heavy metals released into the natural environment have resulted in a number of environmental problems. Such pollutants are not biodegradable, accumulate in nature and in specific limits cause various diseases and disorders (Friberg, 2009; Hubicki et al. 1999). Classical techniques of heavy metal removal from solutions include such processes like precipitation, electrolytic methods, ion exchange, evaporation and adsorption. Among these methods ion exchange receives considerable interest with high efficiency and low operational costs. The main advantages of ion exchange over chemical precipitation are recovery of metal value, selectivity, less sludge volume produced and meeting of strict discharge specifications. Among the materials used in ion exchange processes, synthetic resins are commonly preferred as they are effective and inexpensive. In literature, there have been various investigations about removal of heavy metals by ion exchange resins. However, the presence of the complexing agents in waste solutions enhances the difficulty of removing heavy metals, such as copper, zinc, cobalt, nickel, cadmium and lead. Therefore, it is of importance taking into account the growth in the use of the chelating agents in different branches of industry and agriculture. It should be stressed that the complex forma-tion capacity of chelating agents plays an important role in the distribution of transition metals in the aquatic environment and in their remobilizing from the sediments. Moreover, the negative side of the chelating agents such as EDTA (ethylenediaminetetraacetic acid), DTPA (diethylenetriaminepentaacetic acid), or HEDTA ((hydroxyethyl)ethylenediaminetri- acetic acid) is their low biodegradability. Chelates have also been implicated in eutrophication in natural systems (Sykora et al. 2001; Fuerhacker, 2003; Munn et al. 2004).

Lately more attention has been paid to the complexing agents of new generation characterized by much better biodegradability (Knepper, 2003). In this group a great attention is paid to:

IDS N-(1,2-dicarboxyethylene)-D,L-asparagine acid, EDDS ethylenediaminedisuccinic acid, GLDA N,N-bis(carboxylmethyl)-L-glutamic acid and MGDA methylglycinediacetic acid (Kołodyńska, 2010). Their structural formulae are presented below:
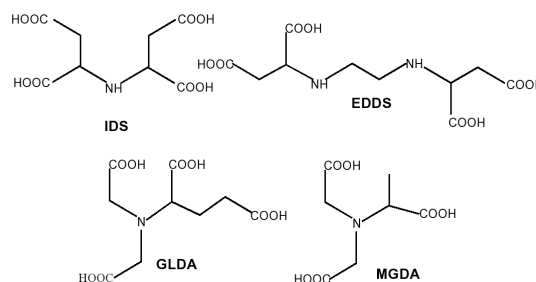
So far the influence of the above-mentioned complexones on the effectiveness of heavy metal ion sorption was tested for the strongly, weakly and medium basic polystyrene anion exchangers as well as the chelating ion exchangers (Kołodyńska et al. 2008; Kołodyńska, 2009a; Kołodyńska, 2009b; Kołodyńska 2010). It was found that the sorption depends on the type of chelating agent used, the kind of ion exchanger as well as on the external conditions such as concentration, pH, time of the treatment, interfering ion presence. In the case of anion exchanger the sorption mechanism is ion exchange whereas for chelating ion exchangers both ion exchange and chelation of metal ions take place.

In the presented paper the evaluation of the effects of the phase contact time, pH, temperature, concentration of the solutions, and regenerating agent on the ion exchange capacity and the kinetics of Cu^{2+}, Zn^{2+}, Ni^{2+} and Cd^{2+} in the presence of MGDA on Amberjet 4400 were studied.

Materials and Methods

The strongly basic anion exchanger Amberjet 4400 (Rohm and Haas, France) proposed for many water treatment applications, the total anion exchange capacity of 1.40 meq/mL, the particle size of 0.58 +/- 0.05 mm, the thermal stability up to 333 K was used. $CuCl_2 \cdot 2H_2O$, $ZnCl_2$, $NiCl_2 \cdot 6H_2O$, $Cd(NO_3)_2$ were used as sources of Cu^{2+}, Zn^{2+}, Ni^{2+} and Cd^{2+}. MGDA (BASF, Germany) was used to react with appropriate solutions of these metal ions at pH without adjustment. The stock solution was further diluted to the required experimental concentration. The other chemicals used were of analytical grade. The adsorption performance of metal ions on a selected anion exchanger was investigated by batch and column tests. 250 mg of resins were suspended in 25 mL solution in flasks, which were placed in the thermostatic shaker. At a desired temperature, the flasks were shaken for 2 h, which proved to be enough to reach sorption equilibrium. The solutions were filtrated, and the concentrations of metal ions in the filtrate were determined by the AAS method. The sorption capacity was calculated by the following equation:

$$q=(c_0-c_e)V/m \qquad (1),$$

where: q is the adsorption capacity [mg/g], c_0 is the initial concentration of solution (mg/L), c_e is the concentration after sorption (mg/L), V is the volume of the solution used for sorption (L), and m is the mass of the dry resin (g).

The breakthrough curves were determined using 10 mL of the swollen anion exchanger. The prepared solutions of complexed metal ions were passed continuously downwards through the resin beds keeping the flow rate at 0.6 mL/cm^{2}min. The effluent was collected in fractions to determine the M^{2+} content by the AAS method.

Results and Discussion

The heavy metal complexes

The removal of Cu^{2+}, Zn^{2+}, Ni^{2+} and Cd^{2+} in the presence of organic ligands occurs mainly due to formation of negative complexes between the ligand and the metal ion, which interact with the ionized functional groups of the ion exchanger. In the case of the chelating ion exchangers such as Purolite S 920, Purolite S 930, Lewatit TP 208, Diphonix or Dowex M 4195 sorption of simple metal ions takes place. Therefore, the main parameter which affects their sorption is the value of the stability constant of the appropriate complexes.

The complexation of IDS, DS, EDDS, GLDA and MGDA is characterized by the formation of stable 1:1 metal to ligand complexes as the major species according to the reaction:

$$M^{m+} + L^{4-} = [ML]^{(4-m)-} \qquad (2),$$
where L=iDS, EDDS and GLDA,
$$M^{m+} + L^{3-} = [ML]^{(3-m)-} \qquad (3),$$
where L=MGDA.

The stability constants for the formation of metal complexes can be defined as:

$$Kn=[MH_{n-1}L][H^+]/[M][H_nL] \qquad (4),$$

where M is the metal concentration; L is the acid ligand concentration and MHn-1L is the metal organic complex concentration. The stability constants are as follows: for Cu^{2+}, Zn^{2+}, Ni^{2+} and Cd^{2+} complexes with IDS: 13.1; 10.8; 12.2; 8.4, respectively. For EDDS 13.1; 13.4; 16.7; 16.4, GLDA 13.1; 10.0; 10.9; 9.1 and MGDA 13.9; 11.0; 12.0, not available, respectively.

The effect of the phase contact time

Fig. 1 shows the example of the studies concerning the effect of the phase contact time on the sorption capacity of Amberjet 4400 towards Cu^{2+}, Zn^{2+}, Ni^{2+} and Cd^{2+} in the presence of MGDA. The sorption capacities of metal complexes increase by increasing the phase contact time during the first 1 h, and then they are on the whole

constant. In general, the three main steps involved in metal ions removal on a selected anion exchanger can be distinguished: the transport of the complexes from the solution to the anion exchanger surface; sorption on the surface and transport within the anion exchanger. Because the sorption is a chemical process, the second step is fast. Also the transport within the anion exchange matrix is rapid, which indicates that the metal complexes interact with functional groups of the anion exchangers. The maximum sorption capacities were found for Cd^{2+} and the minimum was for Ni^{2+}. The sorption values depend on the metal ion in questions and follow the order: $Cd^{2+}>Cu^{2+}>Zn^{2+}>Ni^{2+}$. This observation is in agreement with the stability constants presented above. As follows from the kinetic analysis the sorption can be reported as the pseudo second order kinetic process. Therefore the following ion exchange reaction can be proposed:
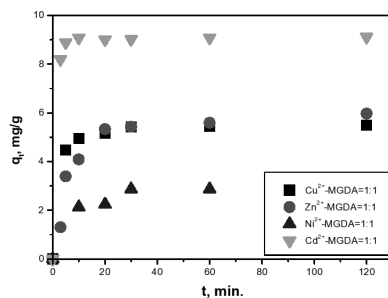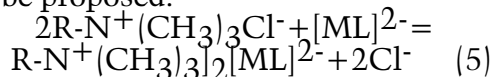
$$2R\text{-}N^+(CH_3)_3Cl^- + [ML]^{2-} = R\text{-}N^+(CH_3)_3]_2[ML]^{2-} + 2Cl^- \quad (5)$$

Figure 1. The effect of the phase contact time on sorption of Cu^{2+}, Zn^{2+}, Ni^{2+} and Cd^{2+} in the presence of MGDA on Amberjet 4400.

The effect of concentration

Fig. 2 presents the effect of different metal ion concentrations on the sorption capacity. It was shown that in the range from 1 min. to 2 h the sorption capacity increases with the increasing concentration of copper complexes with MGDA from 1×10^{-3} M to 7×10^{-3} M. The similar effect was observed in the case of other complexes.

The sorption parameters $(q_{e,cal})$ obtained from the Langmuir equation for the studied complexes of copper, zinc, nickel and cadmium are equal to: 26.3 mg/g, 21.9 mg/g, 18.6 mg/g and 94.3 mg/g, respectively. These values are almost in agreement with the experimental sorption capacities $(q_{e,exp})$.
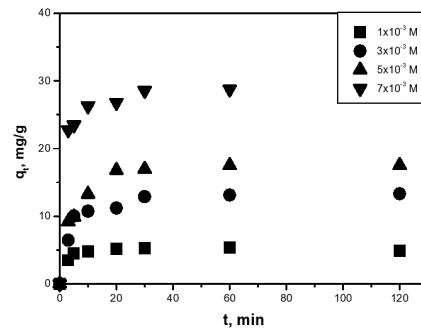

Figure 2. The effect of concentration on sorption of Cu^{2+} in the presence of MGDA on Amberjet 4400.

The effect of pH

Due to the protonation and deprotonation of the functional groups of the ion exchangers the sorption behaviour for metal ions is influenced by the pH values. For strongly basic anion exchangers the sorption efficiency is almost constant, whereas for medium and weakly basic ones is higher at low pH. In the case of chelating ion exchangers the effect of pH is neglectable. Therefore, in the case of Amberjet 4400 the test was limited to the pH range from 1.0 to 12.0 (Fig. 3). The sorption capacities of metal complexes in question increase by increasing pH values within the studied range. At pH 1 only in the case of Ni^{2+} complexes sorption capacity reached the maximum value. At pH 2.0-6.0 for all metal complexes sorption capacities reached different values depending on the nature of metal ion used and the sorption follows the order: $Cd^{2+}>Zn^{2+}>Ni^{2+}>Cu^{2+}$.
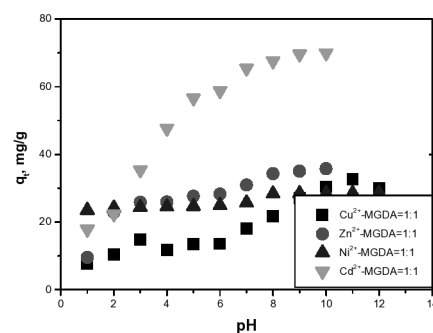

Figure 3. The effect of pH on sorption of Cu^{2+}, Zn^{2+}, Ni^{2+} and Cd^{2+} in the presence of MGDA on Amberjet 4400.

The effect of temperature

As follows from Fig. 4 the sorption of metal complexes decreases by increasing the temperature from 293 K to 333 K at the optimum treatment time 2 h. This can be

explained in terms of higher stability of formed chelates at lower temperatures as generally observed for low molecular weight complexes.
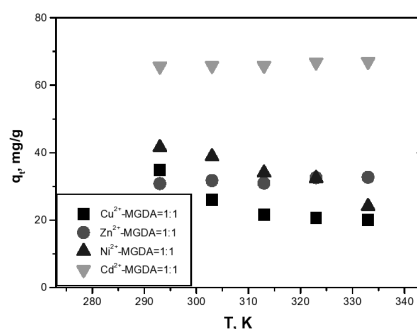

Figure 4. The effect of temperature on sorption of Cu^{2+}, Zn^{2+}, Ni^{2+} and Cd^{2+} in the presence of MGDA on Amberjet 4400.

<u>The column studies</u>
Based on the calculated values of the mass (Dg) and volume (DV) distribution coefficients as well as the working (Cw) ion exchange capacities it was found that the affinity order of the studied complexes towards Amberjet 4400 is as follows: $Cd^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+}$.

The obtained results are in agreement with those obtained from the batch studies. The breakthrough curves of Cu^{2+}, Zn^{2+}, Ni^{2+} and Cd^{2+} complexes with MGDA on Amberjet 4400 are presented in Fig. 5.
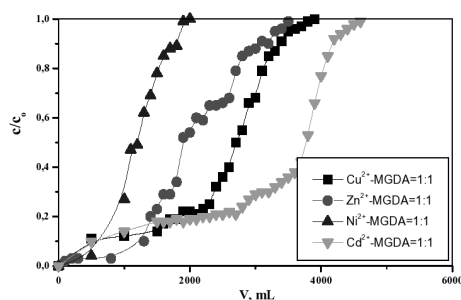

Figure 5. The breakthrough curves of Cu^{2+}, Zn^{2+}, Ni^{2+} and Cd^{2+} in the presence of MGDA on Amberjet 4400.

Conclusions
The sorption behaviour of Amberjet 4400 towards heavy metal complexes with MGDA was investigated under different conditions including metal ion concentration, pH, treatment time and temperature. It was found that this is effective for the removal of different heavy metal ions from aqueous solutions and the affinity series follows the order: $Cd^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+}$. It would be interesting to use for the economic treatment of effluent containing the above-mentioned metal ions. The obtained affinity for Amberjet 4400 can be explained in terms of the differences between the metal ions in questions with respect to relative atomic size, metal ions charge density and reactivity as well as the ability for metal complexes to interact with the quaternary ammonium functional groups of the anion exchanger connected with the stability constant of these complexes.

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