Sorption of Zn(II) ions in the presence of methylglycinediacetic acid (MGDA) on the anion exchangers of various basicity degree

Justyna JACHUŁA, Zbigniew HUBICKI – Department of Inorganic Chemistry Maria Curie-Skłodowska University, Lublin

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Introduction

Heavy metals are some of the most common chemical contaminations of the environment. They get to waters with industrial waste waters, wastes, flows from fields and metallurgical dumps. They can cumulate in bottom sediments. They are toxic for living organisms including man. They can cause diseases, permanent and irreversible damages of various organs e.g. liver, kidney and brain.

There have been worked out many technologies of waste Walters purification from heavy metals of which sorption processes play significant role owning to their great effectiveness and simplicity as well as possibility of using a wide range of ion exchange resins. Very good results are achieved in the heavy metal ions sorption using sulfonic cation exchangers e.g. Amberlite IR 120, Lewatit SP 112 or Purolite C 100 [1÷3]. Also ion exchangers with functional carboxilic groups e.g. Lewatit CNP 80 are applied [4].

At present also anion exchangers are used in the heavy metal ions sorption. This is possible due to applying chelating agents such us methylglycinediacetic acid (MGDA), iminodisuccinic acid (IDS) or ethylenediaminodisuccinic acid (EDDS) forming anion complexes with metal ions (Fig. 1).

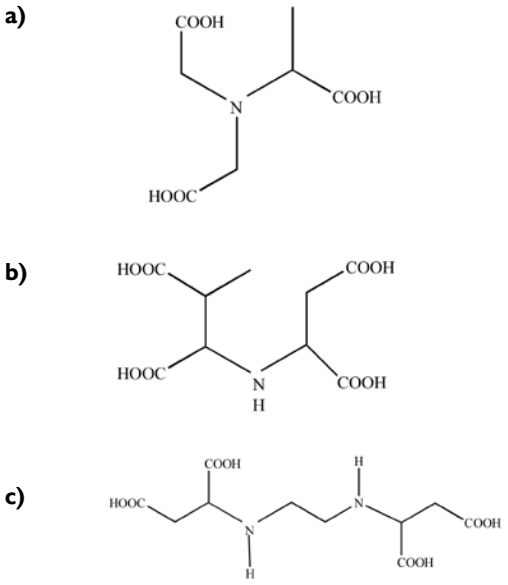

Fig. 1. Structural formulae of the chelating agents a) MGDA, b) IDS, c) EDDS

These complexones are characterized by good biodegrability so they can replace traditional chealting agents, among others, EDTA or DTPA. Kos and Lestan state that 89-100% of MGDA undergo biodegradation within 14 days, 90% EDDS within 20 days whereas EDTA does not decompose even after 30 days [5]. Moreover, the chelating agents in question are not toxic and do not provide additional hazard for the environment.

In very scarce literature on this subject the studies of heavy metal ions in the presence of chelating agents on the polyacrylate anion exchangers of various basicity degree: Amberlite IRA 458, Amberlite IRA 958, Amberlite IRA 67 should be mentioned [6].

Experimental

Materials and methods

The paper presents the studies of mechanism of Zn(II) ions sorption from aqueous solutions in the presence of methylglycinediacetic acid. This is a triproton acid. It dissociates in Tyree stages. It is characterized by great stability in whole pH range and at high temperatures which distinguishes it from other complexing agents. It is a stronger chelating agent than citric acid. It is capable of forming soluble complexes with metal ions (calcium, magnesium, copper, lead, zinc, cadmium, mercury, manganese and iron) in water in the pH range 2-13.

In the studies there was used sodium salt of methylglycinediacetic acid (Trilon M), which is the commercial product of the firm BASF. This is a dense, clear liquid of pH=11. It is soluble in water in all proportions. The chelating strength of Trilon M is 160 mg $CaCO_3$/g. It is commonly employed as the detergent additive in order to improve its cleaning properties. This is also a component of agents used for cleaning and polishing of various kinds of surfaces [7].

In the sorption process there were applied polystyrene-divinylbenzene anion exchangers produced by Lanxess, Germany of various basicity degrees: strongly basic Lewatit MonoPlus M 500, medium basic Lewatit MonoPlus MP 64 and weakly basic Lewatit MP 62. Table 1 presents some physicochemical properties of the ion exchangers in question.

Table 1

Some physicochemical properties of studied anion exchangers

Anion exchanger	Lewatit M 500	Lewatit MP 64	Lewatit MP 62
Type	strongly basic	medium basic	weakly basic
Functional group	-CH_2 - $N(CH_3)_3Cl$	-CH_2 - $N(CH_3)_2OH$/ -CH_2 - $N(CH_3)_3Cl$	-CH_2 - $N(CH_3)_2OH$
Structure	gel	macroporous	
Effective size of grain, mm	0.62-0.67	0.59-0.64	0.47-0.52
Total ione-xchange capacity, val/dm3	1.3	1.3	1.1

Studies of Zn(II) sorption with MGDA were carried out by the static method. The complexed Zn(II)-MGDA solutions were

prepared mixing suitable amounts of Zn(II) chloride and a complexing agent. The initial pH of the complex solution of the concentration 0.001 mol/dm^3 was 9.8. The static studies were performed in 100 cm^3 cone flasks tightly sealed with a silicon stopper. The flasks containing 20 cm^3 of the initial aqueous phase and 0.2 g of weighted ion exchanger were put into the mechanical shaker ELPHINE 357 and their content was stirred at a defined temperature and fixed time. When shaking was over, the raffinate was determined by means of the atomic absorption (AAS) method using a spectrometer SpectrAA 240 FZ produced by the firm Varian. The sorption capacity of the ion exchangers towards Zn(II) (mg/g of dry ion exchanger) was calculated from the dependence:

$$q_t = (c_0 - c_t) \cdot \frac{V}{m} \qquad (1)$$

where: c_0 - the initial concentration M(II) in the aqueous phase [g/dm^3], c_t - the concentration M(II) in the aqueous phase after time t [g/dm^3], V - the volume of solution [dm^3], m - the mass of ion exchanger [g].

From the obtained results there were determined kinetic parameters of Zn(II)-MGDA sorption on the ion exchangers based on the dependences [8]:

$$log(q_1 - q_t) = log(q_1) - \frac{k_1}{2.303} t \qquad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{1}{q_2} t \qquad (3)$$

where: q_t - the mass of adsorbed complexes M(II)-MGDA at time t [mg/g], q_1 and q_2 - the mass of adsorbed complexes M(II)-MGDA at equilibrium for the first and second order reactions [mg/g] respectively, k_1 and k_2 - the rate constants of the first order [1/min] and the second order [g/mg min] reactions.

The maximal sorption capacities q_o, mg/g and the Langmuir constant b, dm^3/mg were determined from the linear dependence of the Langmuir isotherm:

$$\frac{c_e}{q_e} = \frac{1}{q_o b} + \frac{c_e}{q_o} \qquad (4)$$

where: q_e - the mass of adsorbed ions [mg/g], c_e - the concentration at equilibrium [mg/dm^3].

Using the Freundlich isotherm there was calculated the constant n related to the affinity of sorbate for the sorbent:

$$q_e = K_F c_e^{1/n} \qquad (5)$$

where: K_F - the Freundlich isotherm constant connected with the sorption capacity [mg/g] [9].

Results and discussion

Based on the analysis of kinetics of Zn(II) ions sorption in the presence of MGDA on the anion exchangers' Lewatit M 500, Lewatit MP 64 and Lewatit MP 62 it was found out that the sorption capacity of ion exchangers increase with the phase contact time for different initial concentrations. The equilibrium was reached after phase contact time about 15-20 minutes. After 180 minutes maximal sorption capacities of anion exchangers are 5.15 mg/g, 5.52 mg/g and 4.65 mg/g for Lewatit M 500, Lewatit MP 64 and Lewatit MP 62 respectively (for the initial concentration of the complex solution 0.001 mol/dm^3).

Mechanism of Zn(II) complexes sorption at the molar ratio Zn(II)-MGDA=1:1 on the anion exchanger Lewatit MonoPlus M 500 proceeds according to anion exchange mechanism as show by the equation below:

$$R\text{-}N^+(CH_3)_3Cl^- + [M(mgda)]^- = [R\text{-}N^+(CH_3)_3]\,[M(mgda)]^- + Cl^-$$

where R is the grain ion exchanger.

It can be assumed that the sorption process includes the following stages: outer diffusion of complex molecules towards the surface of the liquid surrounding the anion exchanger molecules, inner diffusion of the complex molecules on the surface and inside pores and specific sorption. The slowest stage is decisive for the rate of the whole process. Therefore the pseudo second order Lagergren models should be used for description of the sorption process.

Table 2

Kinetic parameters of sorption of Zn(II) ions with methylglycinediacetic acid on the anion exchangers Lewatit M 500, Lewatit MP 64 and Lewatit MP 62

	Zn(II)-MGDA=1:1		
Ion exchanger	**Lewatit M 500**	**Lewatit MP 64**	**Lewatit MP 62**
Pseudo first order model			
q1, mg/g	4.389	4.734	3.873
k1, 1/min	0.059	0.054	0.034
R^2	0.987	0.984	0.975
Pseudo second order model			
q2, mg/g	5.302	5.705	4.926
k2, g/g min	0.020	0.016	0.013
h, mg/min	0.554	0.517	0.308
R2	0.997	0.993	0.989

Table 2 presents the kinetic parameters calculated from equations 2, 3. The correlation coefficient values in the range 0.989-0.997 indicate that the systems under investigation can be described by means of the pseudo second order kinetic equation and the calculated sorption capacities are in agreement with the experimental data (Fig. 2).

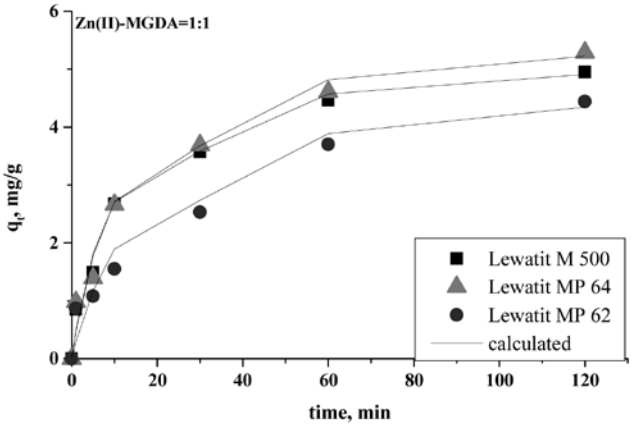

Fig. 2. Comparison of the amounts of the sorbed complex Zn(II)-MGDA on the anion exchangers Lewatit M 500, Lewatit MP 64 and Lewatit MP 62 obtained experimentally and the values calculated by means of the pseudo second order kinetic model (initial concentration of the complex solution is 0.001 mol/dm^3)

The dependence between the amount of Zn(II)-MGDA adsorbed on the anion exchangers Lewatit M 500, Lewatit MP 62 and Lewatit MP 64 and the equilibrium concentration of the complex is called the sorption isotherm. The data in Figure 3 made it possible to fit the Langmuir and Freundlich isotherm to the models and to determine maximal sorption capacities (Tab. 3).

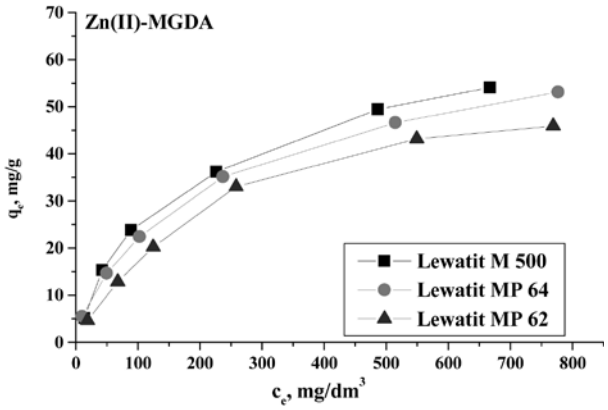

Fig. 3. Langmuir isotherm of Zn(II) ions sorption in the presence of MGDA on the anion exchangers Lewatit M 500, Lewatit MP 64 and Lewatit MP 62

Table 3

Isotherms of Zn(II)-MGDA complexes sorption on the anion exchangers Lewatit M 500, Lewatit MP 64 and Lewatit MP 62

Ion exchanger	$q_{e,exp}$	Langmuir constants			Freundlich constants		
		q_0, mg/g	b, dm^3/mg	R^2	K_F, mg/g	n	R^2
M 500	64.08	64.10	0.007	0.994	5.33	2.45	0.992
MP 64	53.10	55.50	0.006	0.990	1.61	1.80	0.992
MP 62	53.89	55.29	0.004	0.996	1.42	1.48	0.983

The effect of other anions present in the solution on sorption of Zn(II)-MGDA on Lewatit M 500, Lewatit MP 64 and Lewatit MP 62 was also studied. 0.1 mol/dm^3 solutions of NaCl, Na_2SO_4 and $NaNO_3$ were used. As follows from Figure 4 the addition of salt does not decrease sorption capacities of ion exchangers for the zinc complexes in question.

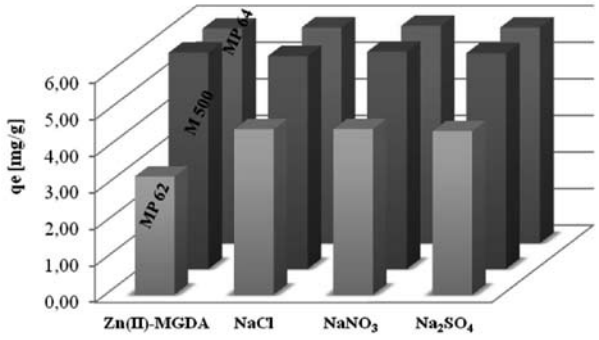

Fig. 4. Effect of the salt addition on the sorption of the Zn(II)-MGDA complexes on the anion exchangers Lewatit M 500, Lewatit MP 64 and Lewatit MP 62

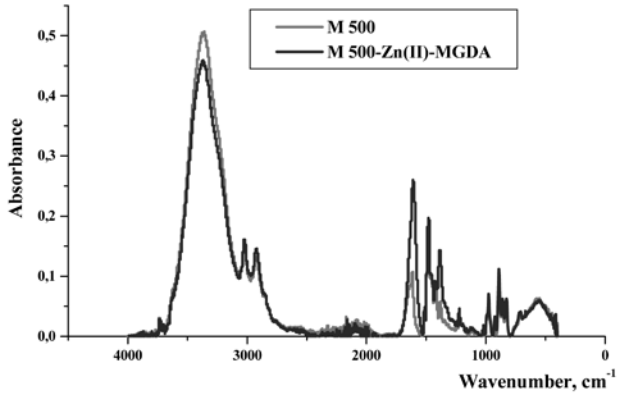

Fig. 5. FT-IR spectra of Lewatit M 500 before and after the sorption of the Zn(II)-MGDA complexes

The FT-IR spectrum (Fig. 5) show characteristic bands for stretching vibrations of the groups $-COO^-$ at about 1611cm^{-1} and 1401cm^{-1} ($\nu_{as}(COO^-)$ and $\nu_s(COO^-)$) after the sorption of Zn(II)-MGDA complexes on the anion exchanger Lewatit M 500. The carboxylate groups are connected with the presence of the anion complex $Zn(mgda)^-$ on the studied anion exchanger.

Conclusions

Zn(II) ions sorption in the presence of MGDA on anion exchangers Lewatit M 500, Lewatit MP 64 and Lewatit MP 62 is affected by many parameters, among others, phase contact time, initial concentration of the complex solution, pH, temperature and ions present in the solution. The presented results indicate that the studied ion exchangers can be used for effective, economical and easy removal of heavy metal ions in the presence of MGDA from aqueous solutions. The process equilibrium is reached after 15-20 minutes. Sorption of Zn(II)-MGDA complexes on the studied anion exchangers can be described by means of the second order kinetic model. The equilibrium data were used to analyze the Langmuir and Freundlich sorption isotherms. The values of Langmuir constant b connected with the anion exchangers' affinity for the studied complexes are 0.007, 0.006 and 0.004 dm^3/mg for Lewatit M 500, Lewatit MP 64 and Lewatit MP 62 respectively. The parameter K_F from the Freundlich isotherm which refers to the sorption density reaches the highest value for the ion exchanger Lewatit M 500 which is 5.33 mg/g.

English translation by the Author

Literature

1. Demirbas A., Pehlivan E., Goge F., Altun T., Arslan G.: *Adsorption of Cu(II), Zn(II), Ni(II), Pb(II) and Cd(II) from aqueous solution on Amberlite IR-120 synthetic resin.* Journal of Colloid and Interface Science 2005, **282**, 20-25.
2. Dizge N., Keskinler B., Barlas H.: *Sorption of Ni(II) ions from aqueous solution by Lewatit cation-exchange resin.* Journal of Hazardous Materials 2009, **167**, 915-926.
3. Abo-Farha S.A., Abdel-Aal A.Y., Ashourb L.A., Garamon S.E.: *Removal of some heavy metal cations by synthetic resin purolite C100.* Journal of Hazardous Materials 2009, **169**, 190-194.
4. Pehlivan E., Altun T.: *Ion-exchange of Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Ni^{2+} from aqueous solution by Lewatit CNP 80.* Journal of Hazardous Materials 2007, **140**, 299-307.
5. Kos B., Leštan D.: *Influence of biodegradable ([S,S]-EDDS) and nondegradable (EDTA) chelate and hydrogel modified soil water sorption capacity on Pb phytoextraction and leaching.* Plant Soil 2003, **253**, 403-411.
6. Kołodyńska D.: *Polyacrylate anion exchangers in sorption of heavy metal ions with the biodegradable complexing agent.* Chemical Engineering Journal 2009, **150**, 280-288.
7. Broszura informacyjna firmy BASF 2003.
8. Blanchard G., Maunayue M., Martin G.: *Removal of heavy metals from waters by means of natural zeolites.* Water Research 1984, **18**, 1501-1507.
9. Inoue K., Yoshizuka K., Ohto K. *Adsorption separation of some metal ions by complexing agent types of chemically modified chitosan.* Analytica Chimica Acta 1999, **388**, 209-218.

Justyna JACHUŁA - M.Sc., graduated from the Faculty of Chemistry, Maria Curie-Skłodowska University in Lublin in 2008. Since 2010 she has been a student of the doctoral course in the Department of Inorganic Chemistry, Maria Curie-Skłodowska University. Her scientific interests: sorption, chelating agents. She is the author of 2 chapters of monographs, 4 papers and several posters presented at national and international conferences.

e-mail: justyna.drabko@wp.pl, tel. 667 996 717

Zbigniew HUBICKI – Professor (Sc.D.), graduated from the Faculty of Chemistry, Maria Curie-Skłodowska University in 1969. Scientific interests: hydrometallurgy, chemistry and technology of save elements, methods of inorganic elements separation and environment protection. He is the author of a few chapters in monographs, over 200 scientific papers as well numerous presentations and posters at national and international conferences.

e-mail: zbigniew.hubicki@poczta.umcs.lublin.pl, tel.(81) 537 55 11