

**MGDA AS A NEW BIODEGRADABLE COMPLEXING AGENT FOR  
SORPTION OF HEAVY METAL IONS ON ANION EXCHANGER  
LEWATIT MONOPLUS M 600**

Dorota KOŁODYŃSKA, Justyna JACHUŁA, Zbigniew HUBICKI

*Department of Inorganic Chemistry, Faculty of Chemistry,  
Maria Curie-Skłodowska University, Maria Curie-Skłodowska Sq.2. 20-031  
Lublin, Poland, Tel.: +48 (81) 5375736; Fax: +48 (81) 533 33 48,  
e-mail: kolodyn@poczta.onet.pl*

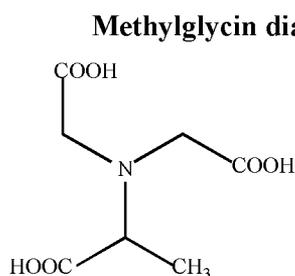
The use of the most known and popular chelating agent ethylenediaminetetraacetic acid (EDTA) is prohibited in some countries and is restricted in others in the European Union due to its slow biodegradability. Also nitrilotriacetic acid (NTA) is restricted and poses a risk for the detergent producers due to the re-classification and re-labelling. Therefore the Scientific Committee on Toxicity, Ecotoxicity and the Environment recommended that consideration should be given to the health and environmental risks associated with the co-builders added to detergents. Although considerable progress has been made in relation to surfactants, culminating in the recently implemented Detergents Regulation, there remains some concern over other chemicals with particular reference to organic compounds. In the group of risky substances identified in detergents four are chelating agents such as phosphonates, EDTA, NTA and polycarboxylates. The alternative for them in the areas where these products need to be replaced are biodegradable complexing agents such as methylglycindiactic acid (MGDA) [1].

The application of readily biodegradable complexing agents can be associated with phytoremediation in order to reduce the time required for remediation of heavy metal contaminated soils. As follows from literature data, for this aim the most common two easily biodegradable chelating agents EDDS and MGDA were used. Chelates were selected for their efficiency in removing metals and for their high biodegradability. Kos and Leštan [2] compared the effect of EDTA and EDDS addition on the chelate assisted phytoextraction process. Plant metal uptake increased 96.8 and 50.1 times over the control treatments using 10 mmol/kg of soil of EDTA and EDDS, respectively. MGDA chelating capacity was investigated by Tandy et al. [3] in soil washing and obtained the following order of extraction efficiency to Zn: NTA > EDDS > EDTA > MGDA > IDSA. MGDA and EDDS demonstrated a far higher biodegradability with respect to EDTA. It was established that 89-100% of MGDA can be degraded in 14 days (Data sheet, BASF), 90% of EDDS in 20 days while no EDTA was degraded in 30 days [2].

In the literature there is limited information about removal of heavy metal ions in the presence of biodegradable complexing agents like MGDA on ion exchangers of different types. Therefore, the aim of the present study is to verify the possibility of using the easily biodegradable chelating agent MGDA to enhance

sorption of heavy metal ions on the polystyrene strongly basic anion exchanger Lewatit MonoPlus M 600 and to investigate its influence on the efficiency of their removal under different conditions.

## EXPERIMENTAL



**Methylglycin diacetic (MGDA)**, patented by BASF and marketed under the brand name Trilon M, is a strong, readily biodegradable in compliance with OECD standards complexing agent. It is used for enhancing the cleaning efficiency of laundry and dishwashing detergents as well as industrial and all-purpose cleaners because of effective removal of residues while treating the surface with care and conserving the environment. The properties of MGDA make it an ideal substitute for phosphate in detergent and cleaner formulations. Phosphate free products based on Trilon M can even surpass the performance of their phosphate containing counterparts. It can be effortlessly added into neutral, alkaline as well as acidic formulations [4-7].

Table 1. Characteristics of MGDA

<b>Methylglycynediacetic acid</b>	
Appearance	clear, yellowish liquid
Molar mass	271 g/mol
Concentration of MGDA-Na <sub>3</sub>	40%
Chelation value	160 mg CaCO <sub>3</sub> /g
Water content	57 %
Specific gravity	1.31 g/mL
pH 1% water	11.0
Solubility	in all proportions

A major difference between MGDA and other alternative chelating agents is the superior ecological and toxicological profile. Unlike other products, MGDA does not require adapted bacteria for decomposition, but instead is degraded under the standard conditions. Furthermore, MGDA was thoroughly tested with respect to its toxicological properties. It is now the only alternative complexing agent

to have undergone the full regiment to toxicological tests. MGDA poses no risk to humans or the environment. Consequently, the EU does not require any safety or hazard labelling for MGDA. It is worth mentioning that in 2008, the producer of MGDA started the new production line, which can supply over 120 thousand ton of this complexing reagent after 2010. BASF manufactures its complexing agents at Ludwigshafen (Germany) as well as in Lima, Ohio (USA) and Guaratinguetá (Brazil).

The strongly basic polystyrene anion exchanger **Lewatit MonoPlus M 600** produced by the Lanxess, Germany was used in the investigations. Its brief characteristic is presented in Table 2 [8].

Table 2. Characteristic of Lewatit MonoPlus M 600

<b>Lewatit MonoPlus M 600</b>	
Matrix	PS-DVB
Structure	gel
Commercial form	Cl <sup>-</sup>
Appearance	beige, opaque
Total capacity (Cl <sup>-</sup> form)	1.3 eq/L
Bead size	0.62 mm ±0.05
Max temp. range	60 °C
Operating pH range	0 – 12

Prior to the use it was washed with 1 M NaOH and 1M HCl to remove organic and inorganic impurities and then washed several times with deionized water. In order to determine sorption capacity of resins towards copper(II), cobalt(II) and nickel(II), in the presence of MGDA, it was reacted with appropriate solutions of these metals at pH without adjustment.

The stock solution was further diluted to the required experimental concentration. The other chemicals used were of analytical grade.

The sorption of Cu(II), Co(II) and Ni(II) complexes with MGDA on Lewatit MonoPlus M 600 was investigated by batch operation as a function of contact time and concentration. Batch experiments were performed to determine the concentration of analyzed metals at the equilibrium ( $q_e$ ) and at the specific time ( $q_t$ ) [6]. The appropriate amounts of anion exchanger and a solution of known metal ion concentration were shaken in a mechanical shaker (ELPINE type 357) at the constant temperature of 25°C. The experiments were conducted in the two parallel series. The reproducibility of the measurements was within 5%. The concentrations of metals were measured by the AAS method.

## RESULTS AND DISCUSSION

Table 3. The stability constants of M(II)-L=1:1 complexes with MGDA [4]

<b>M(II)</b>	<b>MGDA</b>
Ba(II)	4.8
Ca(II)	7.0
Cd(II)	na
Co(II)	na
Cu(II)	13.9
Fe(III)	16.5
Mg(II)	5.8
Ni(II)	12.0
Zn(II)	11.0
Pb(II)	na

na – data not available

The aqueous complexation of MGDA is characterized by the formation of stable 1:1 metal to ligand complexes, weak complexes with alkaline earth metals and the stable transition metal monocomplexes. The stability constants of M(II)-L=1:1, (L=mgda) complexes is presented in Table 3. MGDA is a much stronger chelating agent than citrate and can replace citrate in substoichiometric quantities. High stability throughout the entire pH range and even at

elevated temperatures. This sets MGDA apart from chemicals like EDDS or IDS, which show much lower stability.

In the studies the effect of initial concentration of metal ions and complexing agent and the phase contact times on the percentage uptake was investigated in the batch experiments. In Fig. 1 the contact time curves for sorption of Cu(II), Co(II) and Ni(II) complexes with MGDA on Lewatit MonoPlus M 600 are presented. The sorption equilibrium was reached after 120 min, depending on the initial metal ion concentration.

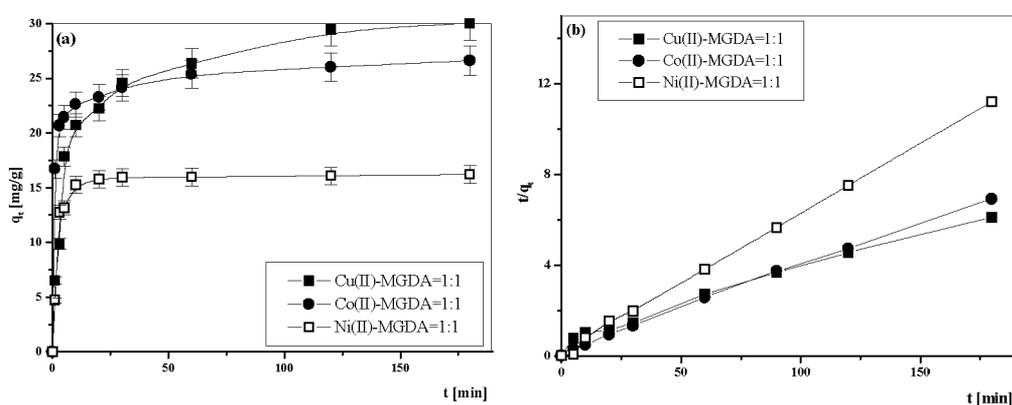


Fig. 1. Comparison of the sorption capacities (a) and the pseudo second order linear equations (b) for the Cu(II), Co(II) and Ni(II) complexes with MGDA on Lewatit MonoPlus M 600 depending on the phase contact time

The rate of sorption was assumed to be proportional to the difference between the capacity at equilibrium and the capacity at any time. As follows from the data presented in Table 4, the  $R^2$  values for the pseudo second order kinetic model were closer than the pseudo first order kinetic model indicating better agreement. The  $R^2$  for the pseudo second order model were 0.9850 for Cu(II)-MGDA, 0.9982 for Co(II)-MGDA, 0.9969 for Ni(II)-MGDA complexes. The obtained results show that the pseudo first order model did not adequately describe the sorption.

Table 4. Kinetic parameters for Cu(II), Co(II) and Ni(II) with MGDA on Lewatit MonoPlus M 600 for different kinetic models

Model	Linear form	Parameters				
Pseudo I-order	$\log(q_e - q) = \log(q_e) - \frac{k_1 t}{2.303}$	M(II):L=1:1	$q_e$ [mg/g]	$k_1$ [1/min]	$R^2$	
		Cu(II)	21.483	0.017	0.9140	
		Co(II)	10.376	0.022	0.8247	
		Ni(II)	5.465	0.038	0.7855	
Pseudo II-order	$\frac{t}{q} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2}$	M(II):L=1:1	$q_e$ [mg/g]	$k_2$ [g/mg min]	$h$ [mg/g min]	$R^2$
		Cu(II)	30.581	0.021	1.975	0.9850
		Co(II)	26.109	0.010	7.062	0.9982
		Ni(II)	16.556	0.013	3.758	0.9969
Intraparticle	$q = k_i t^{0.5}$	M(II):L=1:1	$k_i$ [mg/gmin <sup>0.5</sup> ]		$R^2$	
		Cu(II)	0.2145		0.8991	
		Co(II)	1.4112		0.6000	
		Ni(II)	1.058		0.6380	

Sorption equilibrium is usually described by an isotherm equation whose parameters express the surface properties and affinity of the ion exchanger. Equilibrium models have been developed to describe the sorption isotherm relationships (equations often used are developed by Langmuir, Freundlich and Dubinin-Radushkevich etc.). For the solid-liquid systems the linear form of these isotherms can be expressed as follows:

The Langmuir isotherm model:  $\frac{c_e}{q_e} = \frac{1}{q_o b} + \frac{c_e}{q_o}$

The Freundlich isotherm model:  $\log q_e = b_F \log c_e + \log K_F$

The plots of  $c_e/q_e$  versus  $c_e$  and  $\log q_e$  versus  $\log c_e$  give straight lines. The values  $q_o$  and  $b$  as well as  $K_F$  and  $b_F$  ( $b_F = 1/n$ ) were calculated from the slopes and intercepts of the linear forms of these plots. The isotherm constants obtained from the linearized plots of the Langmuir and Freundlich equations as well as the values of correlation coefficients ( $R^2$ ) for the Cu(II), Co(II) and Ni(II) complexes with MGDA on Lewatit MonoPlus M 600 are presented in Table 5. The obtained values of  $R^2$  suggest that the Langmuir isotherm provides a good model of the sorption system.

Table 5. Isotherm parameter values for the removal of Cu(II), Co(II) and Ni(II) in the presence of MGDA on Lewatit MonoPlus M 600

System		Langmuir constants	
	$q_0$	$b$	$R^2$
Cu(II)-MGDA=1:1	23.256	0.012	0.9740
Co(II)-MGDA=1:1	22.550	0.007	0.8880
Ni(II)-MGDA=1:1	20.907	0.0315	0.9920
Freundlich constants			
System	$K_F$	$n$	$R^2$
Cu(II)-MGDA=1:1	3.147	3.558	0.9493
Co(II)-MGDA=1:1	2.157	2.984	0.8630
Ni(II)-MGDA=1:1	0.885	1.338	0.4000

The sorption capacity for Cu(II)-MGDA is higher than those for Co(II)-MGDA and Ni(II)-MGDA, The experimental sorption capacities were 24.79 mg/g of Cu(II)-MGDA, 26.02 mg of Co(II)-MGDA and 16.08 for Ni(II)-MGDA, respectively and they are with agreement with the obtained capacities. The sorption capacity order has been found for the M(II)-MGDA = 1:1 complexes sorption on Lewatit MonoPlus M 600 as: Cu(II) > Co(II) > Ni(II).

The obtained results demonstrate the possibility of simultaneous one-step removal of heavy metal ions in the presence of MGDA on Lewatit MonoPlus M 600. The efficiency of the sorption process was studied as a function of contact time and concentration of metal solutions. The batch equilibrium was relatively fast and reached equilibrium after about 120 min of the contact. The sorption of studied metal ions in the presence of MGDA on Lewatit MonoPlus M 600 followed the pseudo second order reversible kinetics The experimental data have been better fitted using the Langmuir than Freundlich isotherm model.

#### REFERENCES

1. *Non-surfactant organic ingredients and zeolite-based detergents*, Final Report, June 2006 European Commission, Risk & Policy Analysts Limited (RPA)
2. B. Kos, D. Leštan, *Plant Soil*, 253(2003)403
3. S. Tandy, K. Bossart, R. Mueller, J. Ritschel, L. Hauser, R. Schulin, B. Nowack, *Environ. Sci. Technol.*, 38(2004)937
4. *Trilon M liquid chelating agent*, Technical Bulletin. BASF Corporation, 2003
5. A. Cao, A. Carucci, T. Lai, P. L. Colla, E. Tamburini, *Eur. J. Soil Biol.*, 43(2007)200
6. *Low-alkaline MGDA-containing dishwasher rinsing agent*, WO/1997/049792
7. Binding agent for solidification matrix comprising MGDA, *United States Patent 7442679*
8. *Lewatit MonoPlus M 600*, Technical Bulletin. Lanxess, 2007