1. Introduction

Industry has been worldwide forced to reduce to acceptable levels the contents of heavy metal in waters and industrial wastewaters. Compared with other typical methods such as precipitation and filtration, ion exchange provides numerous advantages. The conventional methods like precipitation, flocculation, and coagulation are unfavourable especially when dealing with large volumes of matter, which contain heavy metal ions in low concentrations. Typically, these ions are precipitated as hydrated metal oxides or hydroxides, sulfides or xanthiogenates using calcium oxide. Precipitation is accompanied by flocculation or coagulation, and one major problem is associated with the formation of large amounts of sediments containing heavy metal ions. For example, industrial wastewaters containing 0.1 g mL\(^{-1}\) of Cu(I), Cd(I) or Hg(II) compounds give 10-, 9- and 5-times larger amounts of sediments, respectively. 6 kg of sediments are obtained from one kilogram of chromates [1]. For effective precipitation suitable pH conditions and temperature as well as concentration of metal ions and controlled stirring intensity are required.

Instead of using ion exchange method either all of the ions can be removed from a solution or substances are separated. Therefore, selective removal of ionic contamination and complete deionization can be distinguished. The choice depends mainly on the composition of solution and on the extent of decontamination required. New types of ion exchangers achieve selectivity with specific affinity for definite metal ions or groups of metals. It should be emphasized that in most cases ion exchange method enables the replacement of the undesirable ion by another one, which is neutral in the environment [2].

Heavy metal ions such as nickel, cobalt, zinc, chromium, copper, lead, cadmium cause serious environmental problems for animals, plants, and humans because of their extreme toxicity [3]. Moreover, they can contaminate soil, potable water source, groundwater, and crops. Another disadvantage is the limited reuse of the contaminated water source [4].

Copper is one of the most important heavy metal.
It is characterized by high electrical and thermal conductivity, and has good malleability and ductility. It has been commonly used for the production of electronic components. Large amounts of copper bearing waste streams are formed during electronic processes as well as different processing steps, viz. electroplating, etching, rinsing, and chemical and mechanical polishing [5,6]. Due to their toxicity, copper ions, inhibit natural growth and development of plants and affect negatively self-purification of water and living organisms in the water environment [7]. For people, typical symptoms of a copper imbalance are headaches, skin rashes or learning disorders. The World Health Organization (WHO) suggests that 10-12 mg per day of copper may be the upper limit for safe consumption. In larger doses copper can cause abdominal pain and cramps, nausea, and can be a contributing factor in many medical conditions including schizophrenia, hypertension, stuttering, autism, muscle and joint pain, headaches, childhood hyperactivity [8].

Copper like nickel is released to the environment from the paint industry, metal finishing, mineral processing, silver refineries, hydrometallurgical industry, leather tanning, electroplating, zinc base casting, storage battery industries and steam-electric power plants [9]. Nickel is used in many industrial applications and consumer products including magnets, stainless steel, plating and special alloys (such as nickel steels, nickel cast irons, nickel brasses and bronzes). Nickel alloys with aluminium, lead, copper, silver, chromium, cobalt, and gold are also applied. It is also used for minting of coins and as a green tint in glass [10]. Nickel and their compounds cause various diseases and disorders including renal edema, skin dermatitis, pulmonary fibrosis and gastrointestinal distress are carcinogenic, non-biodegradable and tend to accumulate in living organisms. Divalent nickel especially causes cancer of lungs, nose and bones [11-14]. Because of these unfavorable symptoms, many government policies had put strict legislative acquiescence on the release concentration of heavy metals. For example, Food & Agricultural Organization (FAO) of the United Nation recommended the maximum level in irrigation water for nickel be 200 µg L⁻¹ [4].

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. As well, 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. In the group of risky substances identified in detergents four are chelating agents such as phosphonates, EDTA, NTA and polycarboxylates. The alternative for these substances in the areas where these products are required to be replaced by biodegradable complexing agents such as methylglycinediacetic acid (MGDA) [15-17]. As follows from the literature data, MGDA possesses good efficiency in chelating and removing metal ions [16]. MGDA chelating capacity was investigated by Tandy et al. [18] in soil washing and reported the following order of extraction efficiency to Zn(II): NTA > EDDS > EDTA > MGDA > IDS. MGDA demonstrated a far higher biodegradability with respect to EDTA. It was established that 89-100% of MGDA can be degraded in 14 days [19,20], while no EDTA was degraded in 30 days.

In the literature there is limited information about the removal of heavy metal ions in the presence of biodegradable complexing agents like MGDA on anion exchangers and sorbents 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 the sorption of heavy metal ions under different conditions on the microporous anion exchangers on the Lewatit group as well as on nitrolite and clinoptilolite. Microporous, monodisperse anion exchangers like Lewatit MonoPlus M 500 and Lewatit MonoPlus M 600 were obtained by the polymerization of monovinyl monomer with a basic group (styrrene) and divinyllic monomer (divinylbenzene). The quantity of divinylbenzene (DVB) added defines the degree of the cross-linking of the network. Typical microporous anion exchangers have about 8% DVB cross-linking that provides both mechanical strength and easy diffusion of exchangeable ions into contact with aqueous phase. Zeolites - clinoptilolite and nitrolite used are characterized by high stability towards dehydration, good thermal stability, very good sorbent properties for cations, notably ammonium and noncharged but polar organic compounds. Clinoptilolite is the most common natural zeolite. Its composition is 42.4% SiO₂, 15.3% Al₂O₃, 1.7% Fe₂O₃, 0.5% MgO, 2.01% CaO, 4.02% K₂O, 0.21% Na₂O and 0.12% TiO₂. The high aluminium concentration as well as the presence of the main exchangeable cations (Na, K) are directly related to the ion exchange capacity of clinoptilolite. Nitrolite is also a mineral from the group of zeolites. It is activated and classified in order to obtain a definite granulation of the product. According to the producer’s data, the content of pure clinoptilolite is 70%. In the paper by Inglezakis et al. [22], it was shown that clinoptilolite has a high selectivity for heavy metal ions such as Pb(II), Cr(III) and...
Fe(III). Finally, it should be mentioned that the benefit of a zeolites application compared to microporous anion exchangers is evident owing to their low cost and great effectiveness. They can be also used for extraction of toxic metals and after their exhaustion applied as raw material in constructions [21-25].

2. Experimental Procedure

2.1. Materials

In the investigations the microporous, monodisperse, polystyrene anion exchangers strongly basic Lewatit MonoPlus M 500 and Lewatit MonoPlus M 600 were used. For comparison the weakly basic macroporous anion exchanger Lewatit MP 62 was also tested. They were produced by Lanxess (Germany). The physico chemical properties and short specification of these resins are presented in Table 1. Prior to use they were washed with 1M NaOH and 1M HCl (to remove organic and inorganic impurities) and then several times with distilled water. The resins were finally converted to the (Cl-) and hydrated amine (OH-) forms, respectively. Clinoptilolite was obtained from Radus (Poland) and nitrolite was obtained from Purolite International, Ltd. (United Kingdom). The samples of zeolites were washed prior to the experiments in order to remove the surface dust. Their physico chemical characteristics are also presented in Table 1.

Methylglycinediacetic acid (MGDA), patented by BASF (Germany) and marketed under the brand name, Trilon M, is strong, readily biodegradable and in compliance with the OECD (Organization for Economic Co-operation and Development) standards for a complexing agent. The physico chemical properties and short specification of this chelating agent are also presented in Table 1.

The stock solutions of Cu(II) and Ni(II) (1.0×10^{-3} mol L^{-1}) in the M(II):MGDA=1:1 system were prepared by dissolving CuCl_2•2H_2O or NiCl_2•6H_2O in a MGDA solution. 0.1 mol L^{-1} of hydrochloric acid and sodium hydroxide solutions were used for pH adjustment. All the reagents were of analytical grade obtained from POCh S.A. Gliwice (Poland) and the distilled water was used to prepare all the solutions.

2.2. Procedures

2.2.1. The batch studies

In batch operations, the anion exchangers and zeolites (0.2 g) were agitated in a 100 mL vessels with the solution treated (20 mL) at fixed concentrations on a laboratory shaker at 180 rpm with the desired pH and temperature. The solutions were then filtered and the concentration of Cu(II) and Ni(II) ions in the filtrate was determined using the AAS method.

In order to establish the effect of pH on the sorption, the experiments were performed at with a pH range between 1.0-12.0 and at a temperature of 25°C by agitating 0.2 g of sorbents with 20 mL (9.0×10^{-3} mol L^{-1}) Cu(II) and Ni(II) complexes with MGDA solution for 3 h at 180 rpm. The amount of the metal sorbed at equilibrium q_e (mg g^{-1}) was obtained using Eq. 1 [26,27]:

\[ q_e = \frac{(c_0 - c_e) V}{m} \]  

where \( c_0 \) is the initial concentration of M(II) solution (mg L^{-1}), \( c_e \) is the equilibrium concentration of M(II) (mg L^{-1}), \( m \) is the mass of the ion exchanger (g) and \( V \) is the volume of the solution (L).

The \( q_e \) was calculated in a similar manner. In the sorption studies the phase contact time was established to be 3 h to be sure that the changes between the successive sorption capacities values were almost constant (not greater than 5%).

The sorption isotherms were investigated in the M(II):MGDA=1:1 system using (0.2 g) of sorbents and (20 mL) of Cu(II) and Ni(II) complexes with MGDA at various concentrations (1.0×10^{-3} mol L^{-1}, 3.0×10^{-3} mol L^{-1}, 5.0×10^{-3} mol L^{-1}, 7.0×10^{-3} mol L^{-1}, 9.0×10^{-3} mol L^{-1}, and 1.5×10^{-2} mol L^{-1}). These mixtures were agitated for 3 h at 25°C. The concentration of Cu(II) and Ni(II) ions in the filtrate was determined using the AAS method. The Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) equations were employed to fit the experimental data [28,29]:

\[ q_e = \frac{q_0 K_L c_e}{1 + K_L c_e} \]  

where \( c_e \) is the equilibrium concentration of M(II) (mg L^{-1}), \( K_L \) is the Langmuir constant related to the free energy of the sorption (L mg^{-1}), \( q_e \) is the amount of M(II) sorbed at equilibrium (mg g^{-1}) and \( q_0 \) is the Langmuir monolayer sorption capacity (mg g^{-1}),

\[ q_e = K_F \frac{c_e^{1/n}}{1 + c_e} \]  

where \( K_F \) is the Freundlich sorption capacity (mg g^{-1}), \( 1/n \) is the Freundlich constant related to the surface heterogeneity,

\[ q_e = K_T \frac{c_e^2}{b_T + c_e} \]  

where \( K_T \) is the Temkin isotherm constant related to the heat of sorption (J mol^{-1}), \( K_T \) is the Temkin isotherm constant.
$Q_t = \frac{X_m}{1 + e^{RT}]}$  

where $X_m$ is the D-R sorption capacity (mg g\(^{-1}\)), $\beta$ is the constant related to the sorption energy (mol\(^2\) kJ\(^{-1}\)), $e$ is the Polanyi potential given by:

$$e = RT \ln\left(1 + \frac{1}{c_e}\right)$$

The sorption kinetics were studied using 0.2 g of sorbent and 20 mL of Cu(II) and Ni(II) complexes with MGDA at a pH of 9.0 (without adjustment), 25°C. The initial Cu(II) and Ni(II) complexes with MGDA concentrations were 9.0×10\(^{-3}\) mol L\(^{-1}\). At various time intervals, the sorbent was filtered and the concentrations of Cu(II) and Ni(II) ions in solutions were determined as previously described.

Additionally, the sorption percent ($S\%$) as well as the distribution coefficient $K_d$ (L g\(^{-1}\)) were calculated using the following relations:

$$S\%(\%) = \frac{c_0 - c_t}{c_0} \times 100$$  

$$K_d = \frac{c_0 - c_t}{c_t} \times \frac{V}{m}$$

where $c_t$ is the concentration of M(II) in the aqueous phase at time $t$ (mg L\(^{-1}\)).

The desorption process was carried out using different regenerating agents. 0.2 g of the sorbents loaded with Cu(II) complexes with MGDA were agitated with 1 mol L\(^{-1}\) solutions of HCl, HNO\(_3\), H\(_2\)SO\(_4\) and NaCl for 3 h at 25°C. This experiment was made in three cycles.

### 2.2.2. The column studies

Ion exchange applications were also performed using a column technique. In the column operations the swollen ion exchangers (10 mL) were placed in a vertical glass column of 10 mm diameter with a glass wool stopper forming a bed. The prepared solutions of Cu(II) complexes with MGDA in the M(II):MGDA=1:1 system were passed continuously downwards through the resin bed at a constant flow rate of 0.6 mL min\(^{-1}\). The effluent was collected in fractions and the metal content was determined by the AAS method. From the determined breakthrough curves the mass ($D_g$) and the volume ($D_v$) distribution coefficients as well as the working ion exchange capacities were calculated according to Eqs. 8-10 [30]:

$$D_g = \frac{\bar{V} - (V_0 + V_f)}{m}$$  

$$D_v = \frac{\bar{V} - (V_0 + V_f)}{V_j}$$  

$$C_w = \frac{V_s c_0}{V_j}$$

### Table 1. Characteristics of anion exchangers and sorbents.

| Ion exchanger/sorbent | Lewatit MonoPlus M 500 | Lewatit MonoPlus M 600 | Lewatit MP 62 | Nitrolite | Clinoptilolite |
|-----------------------|------------------------|------------------------|--------------|-----------|---------------|
| Matrix/composition    | PS-DVB                 | PS-DVB                 | PS-DVB       | (K,Na,1/2Ca)\(_2\)\text{SiO}_2\text{O}_8\text{H}_2\text{O} | Na\(_8\)Al\(_{10}\)Si\(_{2}\)O\(_{4}\)\text{H}_2\text{O} |
| Structure             | microporous            | microporous            | macroporous  | —         | —             |
| Functional groups     | quaternary ammonium type I | quaternary ammonium type II | tertiary amine | —         | —             |
|                        | $-N^+(CH_3)_2$         | $-N^+(CH_2)_2$         | $-N(CH_2)_2$ | —         | —             |
| Commercial form        | Cl                     | Cl                     | OH           | —         | —             |
| Total capacity         | 1.3 eq L\(^{-1}\)      | 1.3 eq L\(^{-1}\)      | 1.7 eq L\(^{-1}\) | 0.7 eq L\(^{-1}\) (NH\(_4^+\) ions) | 1.2 eq g\(^{-1}\) (NH\(_4^+\) ions) |
| Bead size              | 0.62 mm ±0.05          | 0.62 mm ±0.05          | 0.47 mm      | 0.63 – 1.4 mm | 0.5 – 1.5 mm |
| BET surface area       | 13.49 m\(^2\) g\(^{-1}\) | 15.67 m\(^2\) g\(^{-1}\) | —           | —         | 31.12 m\(^2\) g\(^{-1}\) |
| Max temp. range        | 333 K                  | 333 K                  | 313 K        | 1023 K    | 1023 K        |
| Operating pH range     | 0 – 12                 | 0 – 12                 | 0 – 8        | 6 – 8     | 6 – 8         |

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Not available
Sorption of Cu(II) and Ni(II) ions in the presence of the methylglycinediacetic acid by microporous ion exchangers and sorbents from aqueous solutions

Table 2. Characteristics of MGDA [19].

| Appearance                  | clear, yellowish liquid or solid |
|----------------------------|----------------------------------|
| Molar mass                 | 271 g mol⁻¹                      |
| Concentration of MGDA-Na₃ | 40% (solution)                   |
| Chelation value            | 160 mg CaCO₃ g⁻¹                 |
| Water content              | 57%                              |
| Specific gravity           | 13.1 (g mL⁻¹)                    |
| pH 1% water                | 11.0                             |
| Solubility                 | in all proportions               |

where \( m_i \) is the dry ion exchanger mass (g), \( V_e \) is the effluent volume to the break point (L), \( V_i \) is the void (interparticle) ion exchanger bed volume which amounts to ca. 0.4 of the bed volume (mL), \( V_j \) is the bed volume (mL), \( V_d \) is the dead volume in the column (liquid volume in the column between the bottom edge of ion exchanger bed and the outlet) (mL), \( V \) is the volume of effluent at \( c = c_0 / 2 \) (determined graphically) (mL).

The total ion exchange capacities \( (C_r) \) were calculated by integrating the curve.

After the sorption process, the FT-IR spectra of the samples of anion exchangers were obtained in the range of 4000-400 cm⁻¹ with a resolution of 2 cm⁻¹ using a FT-IR spectrometer. The surface morphology of anion exchanger Lewatit MonoPlus M 500 can be written as:

\[
R-N^+(CH_3)_3Cl^- + [Cu(mgda)] ⇄ [R-N^+(CH_3)_3][Cu(mgda)]^+ + Cl^- \quad (12)
\]

for Lewatit MonoPlus M 600:

\[
R-N^+(CH_3)_2(C_2H_5OH)Cl^- + [Cu(mgda)] ⇄ [R-N^+(CH_3)_2(C_2H_5OH)][Cu(mgda)]^+ + Cl^- \quad (13)
\]

for Lewatit MP 62:

\[
R-N^+(CH_3)_2OH + [Cu(mgda)] ⇄ [R-N^+(CH_3)_2][Cu(mgda)]^- + OH^- \quad (14)
\]

where \( R \) is the anion exchanger skeleton (PS-DVB).

2.3. Apparatus

The laboratory shaker Elpin type 357, (Elpin-Plus, Poland) was used for agitation. The pH values were measured with a PHM 84 pH meter (Radiometer, Denmark) with the glass REF 451 and calomel pHG 201-8 electrodes. The concentrations of the heavy metals were measured with an AAS spectrometer Varian AA (Varian, USA). The FT-IR spectrometer, type ALPHA including a Platinum ATR sampling module with a single bounce diamond crystal and a deuterated triglycine sulphate (DTGS) detector (Bruker Optik GmbH, Germany) was used to record the FT-IR spectra. The surface morphology of the anion exchanger was studied by means of atomic force microscopy (AFM) using a NanoScope III (Digital Instruments, USA).

3. Results and Discussion

3.1. Complexes with MGDA

\( H_3mgda \) is a tribasic acid that dissociates in three steps. The acid dissociation constants \( (pK_a) \) are as follows: for \( H_3mgda \) \( pK_{a1} = 1.6 \), for \( H_2mgda \) \( pK_{a2} = 2.5 \), and \( Hmgda^2- \) \( pK_{a3} = 10.5 \). The formation of chelates reduces the concentration of the free metal ions \([M^{n+}]\)

to the extent that the solubility products of many of the sparingly soluble metal salts are no longer exceeded. The result is that the salts no longer precipitate or may even redissolve. The aqueous complexation of MGDA is characterized by the formation of 1:1 metal to ligand complexes \([Cu(mgda)]^-\) and \([Ni(mgda)]^-\) over a wide pH range of 2 to 13.5. Therefore, in the present paper, the reaction of the complex formation:

\[
M^{n+} + L^{2-} \rightleftharpoons [ML]^{(3-m)-} \quad (11)
\]

was taken into account, where \( L = mgda \) [19].

Assuming that the Cu(II) and Ni(II) complexes are formed in a ratio of 1 to 1, the anion exchange reactions for Lewatit MonoPlus M 500 can be written as:

for Lewatit MonoPlus M 600:

In this study, the microporous anion exchangers Lewatit MonoPlus M 500 of type I and Lewatit MonoPlus M 600 of type II, were used, respectively. They possess two different functional groups which are shown in Figs. 1a,1b.

Type I contains a trimethylamine group and type II a dimethylhydroxyethylamine group. Type I is more strongly basic than type II, but more difficult to regenerate. Type II has a higher thermal stability, but is more sensitive to oxidants. For comparison, the macroporous anion exchanger Lewatit MP 62 was also tested (Fig. 1c). These anion exchangers are characterized by a strong affinity for heavy metal ions and can be successfully used in their sorption from wastewaters.

3.3. The effect of the phase contact time and kinetic studies.

A series of contact time experiments for the sorption of Cu(II) and Ni(II) in the presence of MGDA were carried
out at an initial concentration \((9.0 \times 10^{-3}\, \text{mol L}^{-1})\) on Lewatit MonoPlus M 500, Lewatit MonoPlus M 600, Lewatit MP 62 as well as with clinoptilolite and nitrolite. It was found that the amount of sorbed \(\text{Cu(II)}\) and \(\text{Ni(II)}\) ions in the presence of MGDA on the studied anion exchangers increases with time and achieved the constant value after about 60 min. Generally, the sorption capacities \((q_t)\) for \(\text{Cu(II)}\) complexes were higher than for \(\text{Ni(II)}\) ones. The obtained values were equal to: 31.75 mg g\(^{-1}\) for \(\text{Cu(II)}\) on Lewatit MonoPlus M 500, 29.46 mg g\(^{-1}\) for \(\text{Cu(II)}\), 9.46 mg g\(^{-1}\) for \(\text{Ni(II)}\) on Lewatit MonoPlus M 600 and 14.00 mg g\(^{-1}\) for \(\text{Cu(II)}\), 7.99 mg g\(^{-1}\) for \(\text{Ni(II)}\) on Lewatit MP 62, respectively. The lowest values were obtained in the case of clinoptilolite and nitrolite (data not shown). The sorption capacities \((q_t)\) for \(\text{Cu(II)}\) and \(\text{Ni(II)}\) complexes sorbed on clinoptilolite after 60 min were 3.07 mg g\(^{-1}\) and 1.67 mg g\(^{-1}\), respectively. The \(q_t\) values for the metal ions sorption on nitrolite were equal: 2.34 mg g\(^{-1}\) for \(\text{Cu(II)}\) and 1.56 mg g\(^{-1}\) for \(\text{Ni(II)}\). These results were in agreement with the values obtained by Nagy and Kónya \([31,32]\). They found that \(\text{Pb(II)}\) and \(\text{Co(II)}\) ions do not sorb on the calcium-montmorillonite in the presence of EDTA, DTPA (diethylenetriaminepentaacetic acid), tartaric and citric acids. The formation of negative complexes with the chelating agent MGDA by \(\text{Cu(II)}\) and \(\text{Ni(II)}\) ions also excludes the use of these zeolites. Therefore they will not be considered in further studies.

The distribution coefficient, \(K_d\), is defined as the ratio of metal ion concentration on the resin to that in the aqueous solution and can be used as a valuable tool to study metal cation mobility. High values of the distribution coefficient, \(K_d\), indicate that the metal has been retained by the solid phase through the sorption reactions, whereas low values of \(K_d\) indicate that a large fraction of the metal remains in solution. According to Eq. 8, after a phase contact time of 60 minutes, the \(K_d\) values for the sorption of \(\text{Cu(II)}\) complexes with MGDA on Lewatit M 500 are equal to 0.12 L g\(^{-1}\), 0.09 L g\(^{-1}\) for the sorption on Lewatit M 600 and 0.03 L g\(^{-1}\) for the sorption on Lewatit MP 62. The \(K_d\) values for the sorption of \(\text{Ni(II)}\) complexes with MGDA on the same anion exchangers were as follows: 0.022 L g\(^{-1}\), 0.021 L g\(^{-1}\) and 0.017 L g\(^{-1}\), respectively.

The obtained sorption percent \(S(\%)\) was 55.5\% for \(\text{Cu(II)}\) ions sorbed on Lewatit MonoPlus M 500, 51.5\% on Lewatit MonoPlus M 600 and 24.5\% on macroporous Lewatit MP 62. The sorption percent \(S(\%)\) was 81.2\% for \(\text{Ni(II)}\) ions sorbed on Lewatit MonoPlus M 500, 80.0\% on Lewatit MonoPlus M 600 and 59.6\% on Lewatit MP 62.

It is necessary to predict the sorption kinetics to design an industrial sorption column. The most commonly used kinetic expressions to explain the solid-liquid sorption processes known in literature are pseudo first order kinetic and pseudo second order kinetic models according to the Eqs. 15 and 16 \([33]\):

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

(15)

\[
\frac{t}{q_t} = \frac{1}{k_1 q_e} + \frac{1}{q_e}
\]

(16)

where \(k_1\) is the equilibrium rate constant \((1 \text{ min}^{-1})\), \(k_2\) is the equilibrium rate constant \((\text{g mg}^{-1} \text{ min}^{-1})\).

The intraparticle diffusion model was also used to predict the sorption kinetics.
where \( k_i \) is the diffusion coefficient (mg g\(^{-1}\) min\(^{-0.5}\)).

In the presented studies Cu(II) and Ni(II) complexes with MGDA were used for evaluation. The obtained data are presented in Figs. 2a-2d and Table 3. Figs. 2c and 2d show the plots of the linearized form of the pseudo second order model. The \( R^2 \) values for the pseudo second order kinetic model (0.993-0.999) were closer to that than the pseudo first order kinetic model indicating better agreement. The calculated equilibrium capacities (\( q_{e,cal} \)) according to the pseudo first order rate expression were in disagreement with the values of experimental capacities (\( q_{e,exp} \)) for solutions with an initial concentration of \( 9.0 \times 10^{-3} \) mol L\(^{-1}\).

### 3.4. The effect of the pH values

It is well known that solution pH is an important factor for controlling the surface charge of the sorbent and the degree of ionization of the sorbate in aqueous solution [33]. The effect of pH on the sorption of Cu(II) and Ni(II) ions was tested with different pH values (1.0-12.0) at an initial concentration \( 9.0 \times 10^{-3} \) mol L\(^{-1}\). The results, shown in Fig. 3a, indicated that the maximum uptake of Cu(II) ions in the presence of MGDA on strongly basic Lewatit MonoPlus M 500 and Lewatit MonoPlus M 600 occurred when the initial pH was between 11 to 12. The sorption capacity increased with the increasing pH of the aqueous solution and achieved a maximum value of 35.03 mg g\(^{-1}\) and 36.19 mg g\(^{-1}\) for these anion exchangers. For the weakly macroporous basic anion exchanger Lewatit MP 62 the sorption capacity increased in the pH range from 1 to 6 and achieved the maximum value 26.92 mg g\(^{-1}\). Furthermore, the sorption of Ni(II) complexes with MGDA increases insignificantly with the increasing pH in the case of above mentioned basic anion exchangers (Fig. 3b). The maximum values of the sorption capacity were 10.50 mg g\(^{-1}\) for Lewatit MonoPlus M 500, 9.84 mg g\(^{-1}\) for Lewatit MonoPlus M 600 and 8.85 mg g\(^{-1}\) for Lewatit MP 62.

According to the pH changes, the behaviours of the studied anion exchangers towards Cu(II) and Ni(II) complexes with MGDA were different. As mentioned earlier, negative complexes take part in the sorption process on anion exchangers. Their structure, charge as well as concentration affect the sorption process. Occurrences of individual, negative forms of metal complexes and free ligands depend on the pH value of the solution. Thus the determination of pH ranges in which heavy metals occur in the form of anion complexes allows for preliminary determination of a sorption system in which the removal of heavy metal complexes can take
place. Additionally, the pH of a solution determines the degree of ionization of the functional groups especially in the case of weakly basic anion exchangers. In the case of Lewatit MonoPlus M 500 and Lewatit MonoPlus M 600 the sorption increases with the increasing pH, reaching the highest value around a pH of 11.0. At all studied pH values, the above mentioned ion exchangers exhibit largest sorption values for Cu(II) complexes compared to those of Ni(II) in the presence of MGDA. At low pH values only weakly basic Lewatit MP 62 possesses a higher sorption capacity for these species which is in agreement with the nature of the anion exchanger.

3.5. Effect of temperature

For the Cu(II) complexes with MGDA, at an initial concentration 9.0×10⁻³ mol L⁻¹, the effect of temperature on the sorption effectiveness on Lewatit MonoPlus M 500, Lewatit MonoPlus M 600 and Lewatit MP 62 was investigated. A slight increase in the Cu(II)-MGDA complexes with the increasing reaction temperature was observed. Based on the obtained results the thermodynamics parameters for the sorption of Cu(II)-MGDA complexes such as Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were determined using Eqs. 18 and 19 [34]:

\[
\log \frac{q_e}{c_e} = -\frac{\Delta H^o}{2.303RT} + \frac{\Delta S^o}{2.303R}
\]

\[
\Delta G^o = \Delta H^o - T\Delta S^o
\]
where $\Delta G^o$ is the Gibbs free energy (kJ mol$^{-1}$), $\Delta H^o$ is the enthalpy (kJ mol$^{-1}$), $\Delta S^o$ is the entropy (J mol$^{-1}$ K$^{-1}$).

The values of $\Delta H^o$ and $\Delta S^o$ were obtained from the slope and intercept of the plots of $\log q_e/ce$ versus $1/T$ (Fig. 4). The overall free energy change during the sorption process was positive in the range of temperatures (Table 4), corresponding to a nonspontaneous process of Cu(II)-MGDA sorption on the above mentioned ion exchangers. The positive values of $\Delta S^o$ for Lewatit M 500 (56.21 J mol$^{-1}$ K$^{-1}$), Lewatit M 600 (40.24 J mol$^{-1}$ K$^{-1}$) and Lewatit MP 62 (6.05 J mol$^{-1}$ K$^{-1}$) indicate that there is an increase in the degree of randomness during the sorption process. The $\Delta H^o$ values were found to be 21.23 kJ mol$^{-1}$ for the Lewatit MonoPlus M 500, 16.16 kJ mol$^{-1}$ for Lewatit MonoPlus M 500 and Lewatit MP 62 which indicates the endothermic character of the sorption process.

3.6. Sorption isotherm studies

The established sorption pH values and the equilibrium data, commonly known as sorption isotherms, are basic requirements for the design of a sorption system required to remove a unit mass of pollutant under system conditions. This data provides information about the capacity of the sorbent or amount [35]. In this paper the Langmuir isotherm model was chosen first to investigate the estimation of maximum sorption capacity corresponding to complete monolayer coverage on the resin surface.

The studies were carried out at a constant concentration of ion exchanger and with various initial concentrations of Cu(II) and Ni(II). As follows from the
kinetic studies for the initial concentration $1 \times 10^{-3}$ mol L$^{-1}$, equilibrium is reached after a phase contact time equals less than 3 h. However, in the sorption studies the phase contact time was established to be 3 h to be sure that the changes between the successive sorption capacities values were almost constant (not greater than 5%). The results indicated that the increases in the initial metal ion concentration resulted in the metal sorption increase (Figs. 5a, 5b). It was found that Cu(II) sorption in the presence of MGDA was well represented by the Langmuir isotherm model described by Eq. 2 (Figs. 6c, 6d). The correlation coefficient ($R^2$) ranged from 0.991 to 0.996 for Lewatit MonoPlus M 500, Lewatit MonoPlus M 600 and Lewatit MP 62. The correlation coefficient for the sorption of Ni(II) in the presence of MGDA on Lewatit MonoPlus M 600, Lewatit MonoPlus M 500 and Lewatit MP 62 were 0.993, 0.990 and 0.990, respectively. These values for the sorption of Cu(II) and Ni(II) complexes on microporous and macroporous anion exchangers are shown in Table 5.

The Freundlich sorption isotherm (Eq. 3), one of the most widely used mathematical descriptions, tends to fit the experimental data over a wide range of concentrations. The isotherm gives an expression encompassing the surface heterogeneity and the exponential distribution of the active sites and their energies. Table 5 shows that the sorption of Ni(II) complexes in presence of MGDA on the discussed anion exchangers was well represented by the Freundlich isotherm model. This was also true with the Cu(II)-MGDA complexes.

To describe the equilibrium characteristics of the sorption metal ions in the presence of MGDA Temkin and Dubinin-Radushkevich (D-R) isotherm Eqs. 4 and 5 have been also used. The Temkin isotherm assume that the heat of sorption of all the molecules in the layer decreases linearly with the coverage due to the sorbent-sorbate interactions and that the sorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. The constant $\beta$ from D-R equation gives the mean free energy of sorption ($E$) of sorption per molecule of sorbate when it is transferred to the surface of the solid from infinity in the solution. The mean free energy of sorption was calculated using the relation [28]:

$$E = 1/(2\beta)^{-1/2}$$

(20)

where $E$ is the free energy of sorption per molecule of sorbate (kJ mol$^{-1}$).

It is defined as the free energy change when a mol of ion is transferred to the surface of a solid from infinity in a solution. The value of $E$ is very useful in predicting the type of sorption and if the value is less than 8 kJ mol$^{-1}$, then the sorption is physical in nature and if it is in between 8 kJ mol$^{-1}$ and 16 kJ mol$^{-1}$, then the sorption is due to exchange of ions.

According to Eqs. 4 and 5, the calculated Temkin, Dubinin-Radushkevich (D-R) isotherm constants are given in Table 6. It was found that the Temkin isotherm represented the sorption equilibrium in case of the sorption of Cu(II) complexes with MGDA on Lewatit MonoPlus M 600. The correlation coefficient ($R^2$) was equal 0.993. In the case of the sorption of Ni(II) complexes with MGDA, the Temkin isotherm also represented the sorption equilibrium for Lewatit MP 62. The correlation coefficient was equal to 0.988. The D-R equation was only a good fit for the sorption of Cu(II)-MGDA and
Ni(II)-MGDA complexes on Lewatit MonoPlus M 500. The highest value of free energy (E) was in the case of Cu(II)-MGDA complexes sorption on Lewatit MP 62 (15.81 kJ mol⁻¹).

### 3.7. Desorption studies

The desorption process was carried out using different regenerating agents. 0.2 g of the sorbents loaded with the maximum amount of Cu(II) complexes with MGDA were agitated with 1 mol L⁻¹ solutions of HCl, HNO₃, H₂SO₄, and NaCl for 3 h at 25°C. Tables 7 and 8 show the sorption-desorption data of these complexes after three cycles of the sorption and desorption procedures using HCl and H₂SO₄ as regenerating agents. It was shown that Lewatit MonoPlus M 500 and Lewatit MonoPlus M 600 can be used without significant loss of their capacities.

### 3.8. Sorption of Cu(II) in the presence of MGDA – column studies

The obtained data were confirmed by the results from the dynamic method. The breakthrough curves of Cu(II)-MGDA complexes on Lewatit MonoPlus M 500, Lewatit MonoPlus M 600 and Lewatit MP 62 are presented in Fig. 6. The breakthrough curves of Cu(II) complexes with...
MGDA obtained for strongly basic anion exchangers are apparently similar to the classical breakthrough curves (S-shape). High selectivity towards Cu(II) ions exhibited by Lewatit MonoPlus M 500 and Lewatit MonoPlus M 600 were evident. Cu(II) complexes appear in the effluent after ca. 500 mL volume. It was found that the weakly basic anion exchanger Lewatit MP 62 is of low effectiveness for the sorption of the mentioned complexes. As follows from the data presented in Table 9, in the case of Cu(II)-MGDA complexes the mass distribution coefficient was higher for Lewatit M 500 (Dg= 636.34) than Lewatit MonoPlus M 600 (Dg= 606.22). Similar values of volume (Dv) distribution coefficients were obtained for microporous Lewatit MonoPlus M 500 and Lewatit MonoPlus M 600. The smallest values of Dg and Dv as well as the sorption capacities (C) were achieved with Lewatit MP 62. Working (C) ion exchange capacities were parallel for all anion exchangers investigated.

### 3.9. FT-IR and AFM studies

The FT-IR spectra of the investigated ion exchangers recorded in the presence of MGDA before and after the sorption of Cu(II) complexes are presented in Figs. 7a-7c. According to the literature data [36,37] the bands of various intensity occurring at 3023 cm⁻¹, 2929 cm⁻¹ and 2858 cm⁻¹ are associated with valence vibrations of a C-H bond in an aromatic ring and the methylene group (–CH₂) in the polystyrene chain (3023 cm⁻¹ ν\text{as}(C-H); 2929 cm⁻¹ ν\text{as}(-CH₂); 2858 cm⁻¹ ν(-CH₂)). The bands at about 1636 cm⁻¹ are connected with the deformation vibrations of an O-H bond in the plane δ(O-H) and indicate the presence of water in the ion exchanger. However, the bands at about 1485 cm⁻¹, 1460 cm⁻¹, 1420 cm⁻¹ as well as 1380 cm⁻¹ correspond to the skeleton vibrations of the bonds C=C in the ring plane and the scissoring vibrations of the methylene group in the polystyrene chain δ\text{as}(-CH₂). For the frequencies at about 975 cm⁻¹ and 885 cm⁻¹ occur as a result of deformation vibrations of the 1.4 substituted benzene ring (ST with DVB). After the sorption of Cu(II) complexes with MGDA on the studied anion exchangers the bands characteristic of vibrations of the -COO⁻ group at 1610 cm⁻¹ and 1410 cm⁻¹ v\text{as}(COO⁻) and v\text{s}(COO⁻) appear. As well, the band connected with the presence of Cu(II) complex with MGDA can be seen at about 1614 cm⁻¹. As follows from the comparison of FT-IR spectra of the anion exchangers before and after the sorption frequencies of asymmetric and symmetric absorption bands of stretching vibrations of carboxylate groups are not shifted and occur in similar frequency ranges. Therefore one can assume that in the sorption of anionic complexes with Cu(II) with MGDA of [Cu(mgda)]²⁻ type, besides the counterion and exchanging ion interactions, no interactions of different...
4. Conclusions

The important results are summarized as follows:

1. MGDA is a tribasic acid with complexing properties. It forms chelates with many metal ions. The reaction between the metal ion and the anion of MGDA is reversible and occurs with the ratio 1:1. The sorption of Cu(II) and Ni(II) complexes with MGDA on Lewatit MonoPlus M 500, Lewatit MonoPlus M 600 an Lewatit MP 62 has anion exchange character.

2. The microporous anion exchangers Lewatit MonoPlus M 500 and Lewatit MonoPlus M 600 are capable of sorbing the Cu(II) and Ni(II) complexes with MGDA from an aqueous solution. At the initial concentration $9.0 \times 10^{-3}\text{ mol L}^{-1}$, the Cu(II) complexes reveal larger affinity than the Ni(II) ones.

3. The sorption capacity increases with an increase in the phase contact time. The sorption process is relatively quick and very efficient, especially for the solutions containing low concentrations of Cu(II) and Ni(II) complexes. The equilibrium was achieved very quickly at a time 60 min. The process is also pH and temperature dependent. The optimum pH values for sorption was found to be in the range from 10-12 and an increase in temperature from 293 to 333 K enhances the complex sorption because of the endothermic nature of the process.

4. The kinetics of Cu(II) and Ni(II) sorption was tested using different kinetic models. All results indicate that in the case of M(II)-MGDA=1:1 system it can not be described with pseudo first order kinetic model equation, but rather with pseudo second order kinetic equation extensively used to describe the sorption of toxic metal ions, dyes etc. onto sorbents.

5. The experimental data has been analyzed using the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models. Equilibrium sorption data for Cu(II) and Ni(II) ions in the presence of MGDA on discussed ion exchangers were best represented by the Langmuir isotherm. As follows from the sorption studies, the Temkin and Dubinin-Radushkevich sorption models fit the experimental data obtained from the sorption of Cu(II)-MGDA complexes on Lewatit MonoPlus M 500 and Lewatit MonoPlus M 600. The sorption of Ni(II) in presence of MGDA on Lewatit MP 62 was well described by the Temkin and Dubinin-Radushkevich sorption models.

6. The results from the static experiments were confirmed by the dynamic method.

7. Conversely, the maximum loaded studied anion exchangers can be efficiently regenerated by 1 M HCl and 1 M H$_2$SO$_4$ solutions.

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Table 7. Sorption-desorption behaviour of Lewatit MonoPlus M 600, Lewatit MonoPlus M 500 and Lewatit MP 62 for Cu(II)-MGDA complexes in presence of regenerating agent HCl.

| Cycle No. | Sorption (mg g$^{-1}$) | Desorption (%) |
|-----------|------------------------|---------------|
| Lewatit MonoPlus M 600 | 5.44 | 99.8 |
| 2 | 5.31 | 97.4 |
| 3 | 5.28 | 96.8 |
| Lewatit MonoPlus M 500 | 5.26 | 100 |
| 2 | 5.20 | 98.9 |
| 3 | 5.13 | 97.6 |
| Lewatit MP 62 | 4.39 | 74.1 |
| 2 | 4.38 | 74.0 |
| 3 | 4.32 | 72.8 |

Table 8. Sorption-desorption behaviour of Lewatit MonoPlus M 600, Lewatit MonoPlus M 500 and Lewatit MP 62 for Cu(II)-MGDA complexes in presence of regenerating agent H$_2$SO$_4$.

| Cycle No. | Sorption (mg g$^{-1}$) | Desorption (%) |
|-----------|------------------------|---------------|
| Lewatit MonoPlus M 600 | 5.45 | 100 |
| 2 | 5.39 | 98.9 |
| 3 | 5.31 | 97.5 |
| Lewatit MonoPlus M 500 | 5.12 | 97.3 |
| 2 | 5.09 | 96.7 |
| 3 | 5.09 | 96.7 |
| Lewatit MP 62 | 5.88 | 99.2 |
| 2 | 5.94 | 98.4 |
| 3 | 5.75 | 97.0 |

Table 9. Mass ($D_g$) and volume ($D_v$) distribution coefficients as well as working ($C_w$) and total ($C_r$) ion exchange capacities for the Cu(II)-MGDA complexes on Lewatit MonoPlus M 600, Lewatit MonoPlus M 500 and Lewatit MP 60.

| Anion exchanger | Cu(II):MGDA=1:1 | $D_g$ (mg L$^{-1}$) | $D_v$ (mg L$^{-1}$) | $C_w$ (mg L$^{-1}$) | $C_r$ (mg L$^{-1}$) |
|----------------|----------------|---------------------|---------------------|---------------------|---------------------|
| M 600 | 606.22 | 201.69 | 0.003 | 0.007 |
| M 500 | 636.34 | 211.43 | 0.003 | 0.008 |
| MP 62 | 219.23 | 62.93 | 0.002 | 0.004 |

The results obtained by the FT-IR method were confirmed by the AFM investigations. The surface morphology of the Lewatit MonoPlus M 500 before and after the sorption process of Cu(II)-MGDA complexes is presented in Figs. 8a, 8b. It could be seen that the surfaces of the Lewatit MonoPlus M 500 before the sorption process is more smooth with small number of aggregates. It is noticed that after the sorption process its surface changed. It was rougher, shown more waves with an increased number of visible aggregates.
8. The mechanism of the sorption process onto microporous Lewatit MonoPlus M 500 and Lewatit MonoPlus M 600 is anion exchanging. In the case of the studied zeolites (clinoptilolite and nitrolite) due to formation of the negative complexes between the heavy metal ions and the MgDA of M(mgda)²⁻ type the sorption proceeds to a small extent.

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