



Removal of heavy metal ions in the presence of the biodegradable complexing agent of EDDS from waters



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HIGHLIGHTS

- ▶ Ion exchangers with different basicity of functional groups were used in removal of heavy metals from solutions.
- ▶ The different factors affecting the metal ions loading onto Lewatit MonoPlus M 800.
- ▶ The pH, contact time and system composition were studied.

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ABSTRACT

In the investigations three polystyrene divinylbenzene ion exchangers with different degrees of basicity of the functional groups for removal of heavy metal ions from aqueous solutions were used. The experiments were conducted in the multicomponent systems in the presence of the complexing agent – ethylenediaminedisuccinic acid (EDDS) and the accompanying ions (Cl^- , NO_3^- and SO_4^{2-}). Their related absorption behaviors such as thermodynamic equilibrium, pH effect and the Langmuir and Freundlich models to evaluate the experimental data are discussed in this paper. As shown for the ion exchanger Lewatit MonoPlus M 800 the values of monolayer capacity in the multicomponent system including Cr(VI), Cu(II), Zn(II) and EDDS are 111.11 mg/g, 120.48 mg/g and 116.28 mg/g for Cr(VI), Cu(II) and Zn(II) ions, respectively. With respect to the parameters K_L and q_0 the studied elements can be ordered $\text{Cu(II)} > \text{Zn(II)} > \text{Cr(VI)}$. According to the results, this resin can be a promising reagent for disposal of industrial wastes.

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1. Introduction

Heavy metals is not a precise term used to describe more than a dozen elements that are metals or elements having both metal and nonmetal characteristics so called metalloids. However, regardless of the definition and the fact that they cannot be degraded or destroyed, heavy metals are persistent in all parts of the environment. Human activity affects natural geological and biological redistribution of heavy metals through pollution of air, water and soil. The primary anthropogenic sources of heavy metals are the single sources such as mines, foundries, smelters, and coal burning power plants, as well as diffuse sources such as combustion by products and vehicle emissions [1–3]. It is also well known that the main threats to human health from heavy metals are associated with exposure to lead, cadmium, mercury and arsenic. They are highly toxic at low concentrations and can accumulate in living organisms causing several disorders and diseases. Due to their

chemical transformations they have impact not only on human health but also environment and economy [4–6].

Conventional methods for the removal of heavy metal ions from waste water streams include chemical coagulation and precipitation. Metal precipitation is primarily dependent upon the concentration of the metal and the pH of the solution. Heavy metals are usually present in waste waters in dilute quantities ($1\text{--}100\text{ mg/dm}^3$) and at acidic pH values (<7.0). Therefore large doses of alkaline chemicals are necessary to increase and maintain pH values of 4.0 to above 7.0 for optimal metal removal. Furthermore, this produces secondary wastes in the form of metal hydroxide sludges. Among other processes used for toxic metal ions removal membrane filtration, ion exchange and adsorption should be mentioned. However, it is undeniable that the adsorption and ion exchange methods are the most frequently used. They are also the most effective and economical (due to regeneration of adsorbent in the reversible sorption). It is also connected with considerable progress in the synthesis of ion exchangers with various functional groups [7–17]. The properties of the ion exchange synthesis resins are affected by their chemical structure and kinds of functional groups. The ion exchangers with great variability of their chemical structures based on polystyrene,

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polyacrylic and other matrices, monofunctional (sulfonic, carboxylic, phosphonic, phenolic etc.), bifunctional (hydroxamic and amidoxime) and polyfunctional (diphosphonic, sulfonic and carboxylic acid groups) were applied. Such ion exchangers are characterized by large ion exchange capacity, good chemical, thermal and mechanical resistances [18–20]. Among them, strong cation exchangers are the most frequently employed in industrial operations for cations separation from an aqueous stream. Moreover, the enhancement of kinetic capability of ion exchangers was achieved by production of monodisperse ion exchangers. Additional improvement of ion exchange selectivity is aimed at overcoming limitation of ion exchange capacity of cation exchangers. This was attained by synthesis of some selective ion exchangers characterized by different affinity for particular ions. It should be stressed that of several scores of types of selective ion exchangers known at present, only a few are produced on the commercial scale [21]. In this group these with amidoxime, dithiocarbamate, 8-hydroxyquinoline, iminodiacetate, aminophosphonic, bispicolylamine, diphosphonic, sulfonic and carboxylic acid groups, thiol, thiourea as well as isothiourea functional groups are the most popular. Chelating resins possessing specific ligands are commonly applied in analytical studies. On the commercial scale they are used to recover precious metals from ores and sludges as well as waters and waste waters. They are indispensable for separation, concentration and recovery of trace elements. Recently, instead of using commercial ion exchangers some inexpensive materials, such as chitosan, zeolites and other adsorbents are also proposed [22–26]. They can be obtained from by-products and waste materials, however, rarely reused.

The paper presents possible applications of anion exchangers with functional groups of different basicity and chelating ion exchangers used in the heavy metal ions removal from waters and waste waters. Particularly Ionac SR7, Lewatit MonoPlus M 800 and Lewatit MK51 were used in the paper. Detailed knowledge of the speciation, mechanism of sorption and kinetics is essential for full understanding of heavy metal ions removal by the ion exchangers. The optimization of many industrial chemical processes in hydrometallurgy, waste water treatment as well as in pulp and paper processing etc. consist in detailed understanding of such processes in multicomponent and multiphase systems.

2. Experimental

2.1. Materials and chemicals

In the investigations the three polystyrene divinylbenzene anion exchangers with different degree of basicity of the functional groups were used: Ionac SR7 (manufactured by Sybron Chemicals Inc.), Lewatit MonoPlus M 800 and Lewatit MK51 (manufactured by Lanxess, Germany). They are proposed for heavy metal ions removal from waters and waste waters. Their physicochemical properties are collected in Table 1.

Table 1
Physicochemical properties of Ionac SR7, Lewatit MonoPlus M 800 and Lewatit MK51.

Ion exchanger	Ionac SR7	Lewatit MonoPlus M 800	Lewatit MK51
Matrix	PS-DVB	PS-DVB	PS-DVB
Structure	Macroporous	Gel	Macroporous
Functional groups	Quaternary ammonium (type III)	Quaternary ammonium (type I)	Glucamine
Commercial form	Cl ⁻	Cl ⁻	OH ⁻ /Cl ⁻
Physical form	Yellow, white opaque	Yellow, white, half-transparent	White, opaque
Capacity (eq/dm ³)	0.65	1.4	1.1
Bead size (mm)	0.43–0.58 (±0.06)	0.59 (±0.05)	0.48–0.58
Max. temp. range (K)	353	343	303
pH range	0–14	0–12	0–14
Application	Removal of heavy metal ions, water demineralisation		

Multicomponent solutions in the model waste water form of the fixed pH 4.5 of the solution containing Na₂Cr₂O₇·H₂O, CuCl₂·2H₂O, ZnCl₂, Cd(NO₃)₂·4H₂O i Pb(NO₃)₂ were prepared for the experiments. In order to determine the effects of accompanying ions on the heavy metal ions there were prepared solutions containing 40 mg/dm³ of Cl⁻ and 20 mg/dm³ of NO₃⁻ and SO₄²⁻ ions. The starting salts were NaCl, NaNO₃ and Na₂SO₄. To study the effect of the complexing agent on sorption there was applied EDDS (produced by Innospec Speciality Chemicals, UK). The physicochemical properties of EDDS with its structure are presented in Table 2. Sorption kinetics was studied at the concentrations 1 × 10⁻³–5 × 10⁻³ M and for determination of the adsorption parameters at the concentrations 1 × 10⁻³–2.5 × 10⁻² M and the appropriate amount of EDDS were added. All used chemicals were used at analytical purity and purchased (if otherwise not mentioned) from POCh, Poland.

2.2. Sorption and kinetic tests

Sorption was carried out by the static method – with different phase contact times, concentrations and temperature of solutions. 2 g of ion exchanger and 100 cm³ of a suitable multicomponent solution containing Cr(VI), Cu(II), Zn(II), Cd(II) and Pb(II) ions and also the same systems with the addition of accompanying ions i.e. Cl⁻, NO₃⁻ and SO₄²⁻ were put into 250 cm³ conical flasks tightly closed with a silicone stopper. The systems with Cr(VI), Cu(II) and Zn(II) as well as Cd(II) and Pb(II) ions were analyzed in the presence of ethylenediaminedisuccinic acid (EDDS). The same systems but with the accompanying ions Cl⁻, NO₃⁻ and SO₄²⁻ were also studied. Then they were placed in a mechanical shaker for a definite time with the constant shaking rate and vibration amplitude. The laboratory shaker Elpin type 357 (Elpin-Plus, Poland) of constant vibration amplitude (180 rpm) was applied in the studies. During shaking after fixed time (1, 3, 5, 10, 15, 20, 30, 60, 120, 180 min.) the fractions of determined volume were taken. The anion exchanger phase was separated by filtration. The Cr(VI) ions content in the raffinate was determined by means of the spectrophotometric method from 0.2% solution of 1,5-diphenylcarbazide using the Pflaum and Howick method at λ_{max} = 545 nm using the spectrophotometer Specord M42 (Carl Zeiss-Jena, Germany). However, Cu(II), Zn(II), Cd(II) and Pb(II) ions were determined by the atomic absorption spectrometry method using a spectrometer Varian SpectraAA-240FS (Varian, Australia).

The sorption percent (%S) and the distribution coefficient (K_d, cm³/g) as well as the sorption capacities q_t (mg/g) were calculated using the following relationship:

$$\%S = \frac{(c_0 - c_t)}{c_t} \times 100 \quad (1)$$

$$K_d = \frac{(c_0 - c_t)}{c_t} \times \frac{V}{m} \quad (2)$$

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