

Removal of Ni(II) ion in the presence of DS form waters and waste waters

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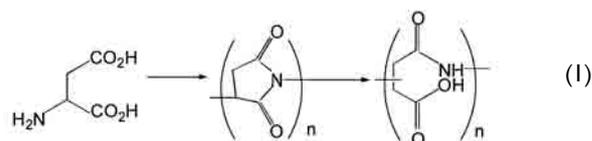
Introduction

Occurrence of heavy metals in waters and waste waters poses a serious threat for health of people. Nickel is one of such elements. Its content in industrial and municipal waste waters ranges 20-4000 mg/kg. The significant source of environmental contamination with nickel is its emission to the atmospheric air due to combustion of coal and liquid fuel. Large amounts of nickel get into surface waters with municipal sewages in which concentration of this element is 3000 mg/dm³.

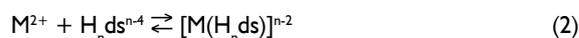
Physical and chemical features point to the fact if the substance is dangerous for human health and natural environment and the results depend on the dose and time of action. Nickel toxicity results from its great mobility in both soil and plants. Nickel availability in plants increases if the soil contains mobile forms and if soil pH decreases below 6. This element readily undergoes bioaccumulation mainly in seeds and grains. In the case of people exposed to longer contacts with this element or its compounds in large concentrations, they can develop lung cancer (compounds of low solubility i.e. metallic powder of nickel, sulphide and oxide of nickel deposit in lungs). Solution of nickel sulphate(VI), classified as a carcinogenic compound deposited on the human skin absorbs in 55-75% after 24h. Whereas nickel consumed by the alimentary track cumulates mainly in bones, flesh organs, heart muscle, skin and various glands. Nickel carbonyl, which gets into the organism mainly by respiratory track and partially by skin is the most toxic nickel compound. One should remember that nickel compounds cause skin diseases of allergic character.

Taking into account a negative effect of nickel ions on living organisms, purification of waste waters containing these ions is a vital task in the environmental protection. The processes connected with nickel(II) recovery from various systems are a subject of numerous papers. These results, among others, from the common use of this metal for preparation of protective coatings. There are many methods which can be applied to reach this goal. These are chemical precipitation, ion exchange, adsorption, membrane filtration and electrochemical technologies. Among the above adsorption based on the ion exchange is one of main techniques used for removal of heavy metals from waters or waste waters. This technique provides great possibilities of designing and exploitation as well as high effectiveness particularly in removal of ions of low concentrations. The example can be application of chelating ions of aminophosphonic, iminodiacetate, bispicoliloamine groups and also cation exchangers of carboxylic groups and low-cost sorbents for removal of Ni(II) ions from waters and waste waters [1 ÷ 6].

The paper presents the possibility of Ni(II) ions removal in the presence of polyaspartic acid (DS) on the ion exchangers Lewatit MonoPlus M 800 and Lewatit MK-51. Sodium salt of polyaspartic acid (Baypure DS 100, in the paper designated DS) is formed in the process of thermal, polymerization of aspartic acid, then basic hydrolysis according to the equation:



The way the synthesis is carried out affects the chemical structure of formed polyasparagines and decides about their molecular weight and structure. DS is characterized by very good anticorrosive properties, stability and low toxicity [7]. It was proved that asparagines residues take part in the metal ions binding, whereby for the, polymer of the mass 10000, 72 asparagine residues should be treated as 18 molecules of polyaspartic acid (H₄ds). It was additionally found that at pH 1 about 100% DS occurs as H₄ds, for pH 3.0 about 70% is H₃ds⁻, for pH > 4.0 about 48% is H₂ds²⁻, at pH 4.8 about 65% is Hds³⁻ and at pH > 7.0 practically 100% is ds⁴⁻ [8]. The general reaction of formation of M(II) with Ds complexes can be presented according to the equation below (where n = 0-3):



The M(II) – DS = 1:1 complexes show much smaller values of conditional stability constants compared to the analogous complexes with EDTA (etylenediaminetetraacetic). Figure 1 includes the comparison of the values for some complex with DS and EDTA.

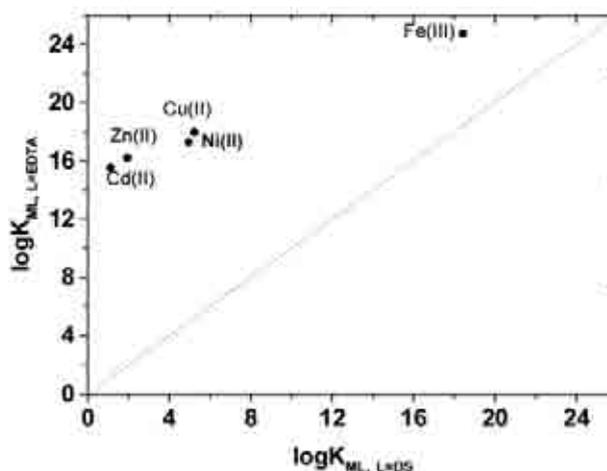


Fig. 1. Comparison of conditional stability constants values of same complexes of metals with EDTA and DS

Pharmaceutical and medical industries make use of biological non – toxicity and neutrality of polyasparagines for production of biomedical materials and sanitary agents. Polyaspartic acid as a super absorber is also applied in agriculture (AmiSorb®). DS can be used as an anticorrosion agent, dispersive and retarding the process of boiler scale formation and also as a component of detergents.

In the presented paper the studies were carried out by means of the static method. The effect of the phase contact time, pH, temperature and concentration of Ni(II) ions and DS in the solution on the process effectiveness was determined based on them.

Experimental part

The studies were carried out using the static method in the 0.001M Ni(II)- Ds 1:1system. The complex solutions of Ni(II) with DS were prepared by mixing the solutions: NiCl₂ · 6H₂O with the solution Baypure DS 100. The basic physicochemical properties the ion exchangers in question are presented in Table I.

Table I

Characterization of the ion exchangers Lewatit MonoPlus M 800 and Lewatit MK-51

Ion exchanger	Skeleton	Type of functional groups	Structure	Capacity
Lewatit MonoPlus M800	PS-DVB	quaternary ammonium type I	gel	1.4 val/dm ³
Lewatit MK 51	PS-DVB	methylglucamine	macroporous	1.1 val/dm ³

The static studies were carried out in the cone flasks of 100 cm³ volume sealed tightly with a silicone cork. 0.2 g of the ion exchanger in the appropriate form and 20cm³ of the aqueous solution containing the above mentioned complexes in the amounts of from 1x10⁻³M to 6x10⁻³M was added to the flasks. Then they were placed in the mechanical shaker (Elphin 357, Elphin Plus Poland) and their content was mixed at room temperature at fixed time (from 1 to 120 min). When the intensive shaking was over, the mixture was filtered to separate the ion exchanger from the solution. The nickel content in the solution was determined using the atomic absorption spectrometry (AAS) method by means of Spectra 240 FS (Varian, Australia).

The amount of adsorbed ions Ni(II) depending on the phase contact time(q_t), pH, temperature and concentration was calculated according to the equation:

$$q_t = \frac{c_0 - c_t}{m} \times V \quad (3)$$

where: C₀ is the initial concentration of Ni(II) ions in the solution [mg/dm³], c_t is the concentration of Ni(II) ions in the solution [mg/dm³] after the sorption time t [min], m is the anion exchange, mass[g], v is the solution volume [dm³].

From the obtained data sorption kinetic parameters were determined. The sorption parameters for the studied systems were determined using the kinetic Ho and McKay equations i.e. the pseudo second order.

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \quad (4)$$

where: k₂ is the rate constant of PS-order sorption (g/mg min). Based on the plots of log(q_e - q_t) vs. t and t/q_t vs. t, the kinetic parameters were calculated.

The adsorption isotherms of the ion exchangers Lewatit MonoPlus M 800 and Lewatit MK-51 were determined shaking 0.2g of the ion exchanger and 20 cm³ of the solution containing the Ni(II) and DS complexes in 100 cm³ flasks. The process proceeded in the concentration range 1x10⁻³–6x10⁻³ M at the constant value of pH for 2h. After shaking it was filtered off and the Ni(II) ions content was

determined in the raffinate in the same way as in the studies of sorption kinetics. The adsorption isotherm equations were determined using the Langmuir model.

Studies of the pH influence on sorption effectiveness were carried out in the range of 4-12.

The pictures of the anion exchanger Lewatit MonoPlus M 800 surface before and after Ni(II) ions sorption in the presence of DS were made by means of the scanning microscope. Ultra plus (Carl Zeiss STM GmbH, Germany). Automatic measurements of 3D grain size and shape were made using an optical – electronic analyser AWK 3D (KAMIKA Instruments). The grain size was analysed according to the Zingg classification which is commonly known and applied in research and can be successfully used in practice.

Results and discussion

Based on the studies by the static method the amount of adsorbed Ni(II) ions in the presence of DS on the ion exchangers Lewatit MonoPlus M800 and Lewatit MK-51 was calculated. The effect of phase contact time, pH, initial solution concentration on the effectiveness of the sorption process was also determined. As follows from the studies sorption effectiveness increases with the increasing phase contact time (Fig. 2a-b).

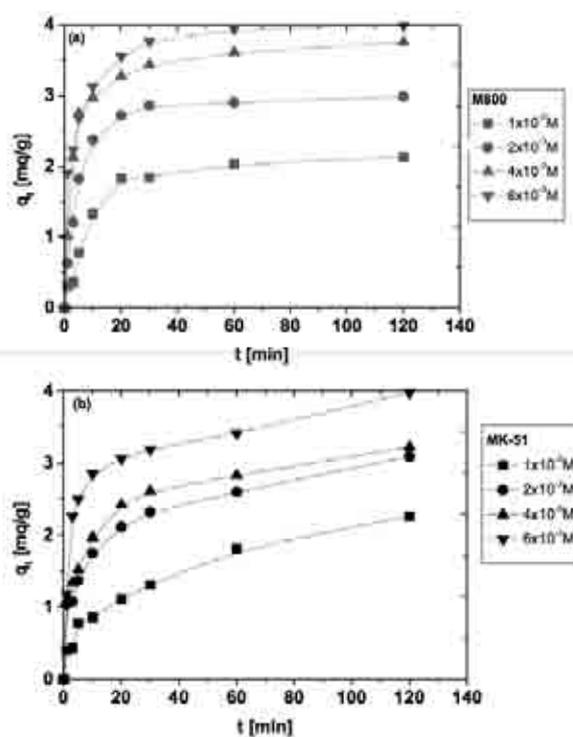


Fig. 2a-b. Effect of phase contact time and concentration on the effectiveness of Ni(II) and DS complex sorption on the ion exchangers Lewatit MonoPlus M 800 and Lewatit MK-51

In the initial stage of the process (1-5 min) it was found that a little higher values q_t were obtained for the ion exchanger Lewatit MonoPlus M800. As follows from the pictures of the above mentioned ion exchangers before and after sorption their surface is characterized by much smaller roughness. Coarseness of the surface also called roughness is one of the elements which can explicitly indicate the sorption mechanism. Decrease in the surface coarseness can be helpful in establishing the sorption mechanism. Rapid decrease of this parameter indicates e.g. formation of coordination bonds between the sorbent functional groups and the removed ion on the sorbent surface. One of the methods allowing to measure surface coarseness values and thus to determine such parameters as maximal and minimal values of inequalities as well as arithmetic means of profile diversion of a given sorbent is the use of atomic force microscopy or scanning electron microscope.

The decrease in the above mentioned quantities was about 6% for Lewatit MonoPlus M 800 and about 10% for Lewatit MK-51. The exemplary pictures of the anion exchanger Lewatit MonoPlus M800 are presented in Figures 3a-b.

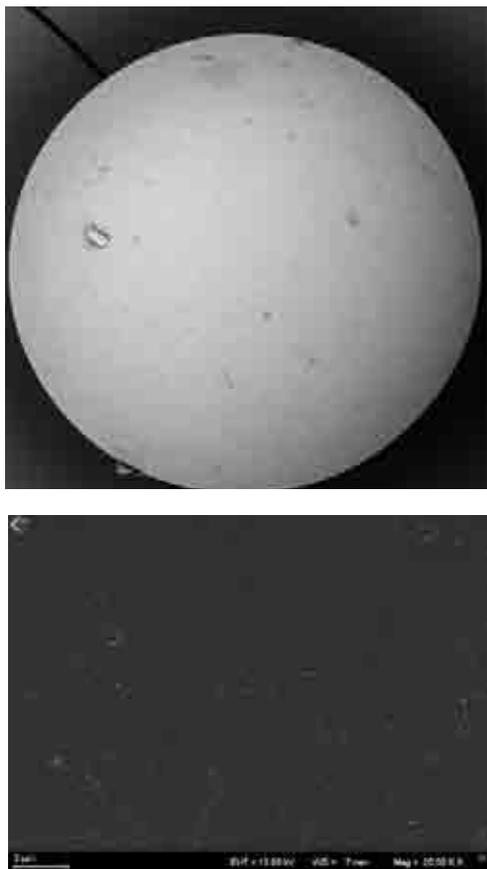
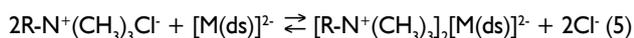
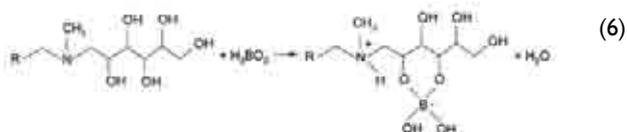


Fig. 3a-b. SEM pictures of the ion exchanger Lewatit MonoPlus M800 – magnification $\times 400$ before sorption (a), $\times 20.000$ after sorption (b)

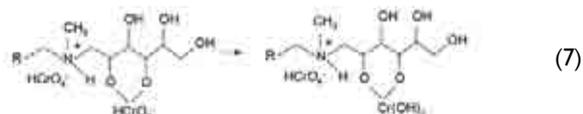
With higher values of phase contact time the sorption kinetics is more advantageous for the anion exchanger Lewatit MonoPlus M800. For his anion exchange the equilibrium state is established with the phase contact time about 60 min and sorption proceeds according to the anion exchange mechanism:



However, for the ion exchange of the N-methyl (polyhydroxohexylo) amine groups also called methylglutamine (Lewatit MK-51) the equilibrium state is established within 240 min. The chelating ion exchanges containing this type of functional groups such as Amberlite IRA 743, Duolite ES 371, Diaion CRB 02, Dowex BSR 1, Purolite S 108 are characterized by great selectivity towards boron (in the form of trioxoboric acid H_3BO_3) [8]. The sorption of borate proceeds according to the scheme:



Whereas when the sorption of chromate(VI) ions proceeds due to both electrostatic interactions with the protonated amine group and the reduction of Cr(VI) to Cr(III)



However, in case of anion Ni(II) and DS complexes of the type $[Ni(ds)]^{2-}$ sorption proceeds according to the anion exchange mechanism for low pH values but for higher pH values decomposition of the above mentioned complexes and Ni(II) ions complexation in the ion exchange phase take place:



It should be stressed that sorption effectiveness increases with the increasing Ni(II) ions concentration in the solution.

An important parameter affecting, among others, sorption kinetics is the size and shape of the ion exchanger, grains. Therefore using the method of falling grain scanning two basic shapes of grains i.e. disk and sphere we distinguished according to the Zingg classification. It was proved that for the studied ion exchangers the of grain sizes has an effect on the Gauss curve shape. These ion exchangers possess a larger number of disk shaped grains. As follows from Figures 4 a-b spherical grains occur in a small percentage. Let us take an example the percentage content of the grain fraction for $c/b = 0.6$ (where is the width, c is the grain height) for the anion exchanger Lewatit MonoPlus M 800 is 32%, However, for the ion exchanger Lewatit MK-51 $c/b = 0,7$ it is 48%.

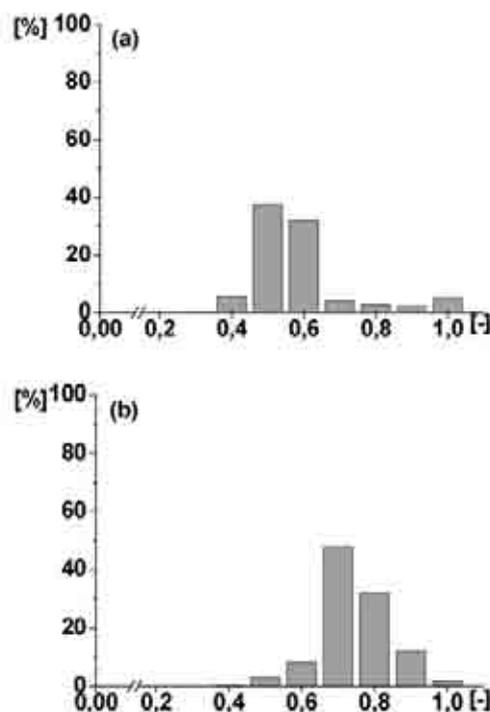


Fig. 4a-b. Distribution of the grain sizes (a) Lewatit MonoPlus M 800 and (b) Lewatit MK-51 based on the Zingg classification

Another factor braving an influence on sorption effectiveness is pH value. It was found that the maximum percentage of removal of the Ni(II)-DS complexes = 1:1 is achieved for the above mentioned ion exchanges with the value $pH > 7.0$. The temperature increase causes slight decrease of sorption effectiveness on all ion exchangers. In the last stage based on the linear dependence of the Langmuir isotherm:

$$\frac{c_e}{q_e} = \frac{1}{q_o b} + \frac{c_e}{q_o} \quad (10)$$

where: q_e is the mass of adsorbed Ni(II) ions, c_e is the concentration of Ni(II) ions in the equilibrium $[mg/dm^3]$ were determined the maximal sorption capacity (q_o) and the Langmuir constant (b) for the

complexes Ni(II)-DS=1:1. Which were for Lewatit MonoPlus M 800 ($q_0 = 4.45 \text{ mg/g}$, $b = 0.221 \text{ dm}^3/\text{mg}$) and for Lewatit MK-51 ($q_0 = 6.15 \text{ mg/g}$, $b = 0.128 \text{ dm}^3/\text{mg}$). It is worth noting that 1 M HCl solution proved to be a regenerating agent for the studied anion exchangers.

Conclusions

Based on the studies it was found that:

1. The amount of sorbed Ni(II) ions in the presence of DS depends on the kind of functional groups of the ion exchangers under investigation
2. based on the Langmuir isotherm model larger values of maximal sorption capacities were obtained for the ion exchanger Lewatit MK-51 compared to those for the anion the exchanger Lewatit MonoPlus M 800
3. The amount of sorbed Ni(II) ions retention on both Lewatit MK-51 and Lewatit MonoPlus M 800 increases with the increasing initial concentration of the solution
4. pH and phase contact time affect the sorption process
5. The pseudo second order agnation describes well the sorption as confirmed by the statistical evaluation

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