



Evaluation of heavy metal ions removal from acidic waste water streams



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HIGHLIGHTS

- Iminodiacetate resins were used for heavy metals (HM) ions removal from solutions.
- The sorption was favoured at pH range of 4.0–7.0 and high concentrations of NaCl.
- Recommendation to use Lewatit TP 207 and Lewatit TP 208 as effective ion exchangers was made.

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ABSTRACT

This study presents some purification processes of acidic waste streams including such heavy metals as Cu(II), Zn(II) and Ni(II) in the low and adjusted pH range as well as high NaCl concentrations, which are typical industrial conditions. A novel approach to the assembly of previously used processes skips the step of pH adjustment of the treated waste streams, which further reduces maintenance costs of waste streams.

The study was conducted using macroporous ion exchange resins based on the polystyrene–divinylbenzene matrix: Lewatit TP 207 and Lewatit TP 208 – the chelating ion exchangers with the iminodiacetate functional groups and the medium base anion exchange resin Lewatit MonoPlus MP 64 with the quaternary ammonium and tertiary amine functional groups. Ion exchangers are characterized by high resistance to osmotic shock. The macroporous structure provides an ideal diffusion of Cu(II), Zn(II) and Ni(II), allowing the efficient exhaustion and regeneration. Beside the commercial form, Lewatit TP 207 and Lewatit TP 208 were used in the mono- and disodium forms.

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1. Introduction

Due to the increasing deterioration of the environment, European industry is forced to run its business in a manner least disruptive to the surroundings [1]. A major threat to the environment constitute such contaminants as heavy metal ions. Their sources include metal finishing industry, where electrochemical methods are used. In recent years, there has appeared a trend towards elimination of certain heavy metal ions in these processes [2], but this is not always possible due to the lack of alternative technologies. In this case one can only do the activities eliminating hazardous chemicals from waste streams and recycle them [3,4]. In purification of waste waters from metal surface treatment by electrochemical methods the ion exchange method one is of significant importance.

Natural inorganic exchangers such as zeolites, oxides and clay minerals have wide applications especially in treatment of nuclear wastes due to their resistance to decomposition in the presence of ionizing radiation or at high temperatures. They are also characterized by high selectivity towards certain ions therefore they may be suitable for certain hydrometallurgic applications [5–7]. However, waste water treatment technologies generally apply macroporous ion exchangers [8] with the functional groups characterized by chelating properties. The use of chelating resins allows for selective removal of metal ions from waste streams [9]. Selective ion exchange considerably increases the ion exchange capacity due to the fact that the active sites are filled only by specific (not selected) metal ions without unnecessary ballast. The additional advantages of ion exchange include the possibility of recovering valuable metal ions, low amounts of sludge formation and the ability to reach the limit for discharge, small footprint and low installation costs or the concentration factor larger than 200 [10]. For example by using sulfuric acid as regenerating solution copper

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can be directly recovered by electrowinning (at the same time the regenerant acid is recovered). In default of electrowinning the spent regenerant has to be treated by precipitation, but to a much smaller extent than when precipitation is a stand-alone treatment.

The ion exchange method using ion exchange resins is usually used for low and medium levels of metal ions, while extraction is used for medium and high concentrations of metal ions. The combination of both techniques allows for the recovery of metal ions over a range of concentrations. Extraction processes are high-speed ones not requiring a large area for apparatus, but ion exchange techniques require much larger equipment (due to much lower reaction kinetics) [11]. An attempt to avoid these disadvantages is the use of impregnated resins (SIRs) with suitable extractants [12]. In some applications it is possible to use ion exchange resins in the form of fibers, which are characterized by very high ion exchange kinetics due to a large surface area of contact interface [13,14]. Therefore a potential area of fibrous ion exchangers are wastewater treatment processes. So far this method has been in the initial stage of investigations. Numerous studies have been carried out on the removal of metal ions from solutions using strongly acidic cation exchangers (SAC) and chelating ion exchangers [15–17].

This paper presents the possibility of removal from acidic waste streams (such as spent bathing, washing effluents or spent hydrochloric acid from metal etching) of heavy metal ions in the low, deliberately not corrected pH and often high concentrations of NaCl. These conditions are found in industry. To this end the weakly acidic ion exchangers (WAC) were used. There is a clear change in the approach compared to the previous assumptions, since the currently accepted procedures usually require the preliminary, more expensive stage of adjusting the acidity of solutions to the pH range from 1 to 5 or from 9 to 10, causing precipitation of metals [18]. Additionally, the neutralization equipment and supplies must be available. Moreover, it should be also mentioned that some waste waters for example containing cyanides cannot be neutralized because of the possibility of generation of toxic fumes, for example hydrogen cyanide. On the other hand, using NaOH the equilibrium pH control is difficult and over neutralization to pH 13 is possible or using HCl the acid forms a very corrosive mist [19,20].

Preventing from such a phenomenon as well as eliminating one of the stages in the existing technologies, selection of appropriate and stable ion exchangers, checking their resistance to osmotic shock and examination of their selectivity in the process of Cu(II), Zn(II) and Ni(II) separation was proposed. It should be emphasized that in view of the applicable character of the obtained results, the commercially available ion exchange resins were selected to this end. They are characterized by high affinity for divalent metal ions and a much higher capacity than SAC.

2. Experimental

2.1. Materials and solutions

The following polystyrene–divinylbenzene (PS–DVB) ion exchangers, produced by Lanxess, Germany, were used in the investigations: Lewatit TP 207, Lewatit TP 208 and Lewatit MonoPlus MP 64. Brief characteristics of these chelating resins is presented below and their detailed properties are given in Table 1.

Lewatit TP 207 is a weakly acidic, macroporous cation exchange resin with the iminodiacetate functional groups used for the selective sorption of heavy metal cations from aqueous solutions, the total ion exchange capacity of 2.2 meq/cm³, the particle size of 0.4–1.25 mm and the thermal stability of up to 313 K.

Lewatit TP 208 is a weakly acidic, macroporous cation exchange resin with the iminodiacetate functional groups used for the selective extraction of heavy metal cations from aqueous solutions, the total ion exchange capacity of 2.9 meq/cm³, the particle size of 0.4–1.25 mm and the thermal stability of up to 313 K.

Lewatit MonoPlus MP 64 is a medium base anion exchange resin with the quaternary ammonium and tertiary amine functional groups. It is recommended by the manufacturer for the selective removal of alkaline earth metals from industrial effluents, the total ion exchange capacity of 1.3 meq/cm³, the particle size of 0.59 ± 0.05 mm and the thermal stability of up to 313 K.

Prior to their use they were washed with NaOH and HCl (7.5% in an amount of 140 g per 1000 cm³) to remove organic and inorganic impurities and then washed several times with deionized water. The resins were finally converted to the appropriate form. In order to obtain the monosodium and disodium forms, 100 cm³ of the ion exchanger samples were shaken for 2 h with 160 cm³ or 320 cm³ of 4% sodium hydroxide solution, respectively. The amount of NaOH solution was selected based on the manufacturer's data. After that the resins were washed with deionised water.

Copper(II), zinc(II) and nickel(II) salts (POCh, Poland) of analytical grade were used. The stock solutions (1 × 10⁻² M) of the above-mentioned ions were prepared by dissolving the exact quantity of respective salts in distilled water. The stock solutions were further diluted to the required experimental concentration. The other chemicals used were of analytical grade.

2.2. Static (batch) studies

The static tests were carried out to obtain the sorption percentage (%S) of Cu(II), Ni(II) and Zn(II) ions for Lewatit TP 207, Lewatit TP 208 and Lewatit MonoPlus MP 64, depending on the phase contact time, pH, concentration of NaCl and the operational form of ion exchanger. The studies were carried out in 250 cm³ shake flasks, placed in an orbital thermostatted shaker allowing to achieve 250 rpm (ELPHINE type 357, Poland). To a dry flask 2 g of the ion

Table 1
Detail characteristic of the Lewatit TP 207, Lewatit TP 208 and Lewatit MonoPlus MP 64.

Properties	Lewatit TP 207	Lewatit TP 208	Lewatit MonoPlus MP 64
Matrix	PS–DVB macroporous	PS–DVB macroporous	PS–DVB macroporous
Functional groups	–CH ₂ N(CH ₂ COOH) ₂	–CH ₂ N(CH ₂ COOH) ₂	–N ⁺ R ₃ /–NR ₂
Physical form	Opaque, white	Opaque, white	Opaque, white
Ionic form as shipped	Na ⁺	Na ⁺	Free base
Beads size mm	0.4–1.25	0.4–1.25	0.59 ± 0.05
Total exchange capacity	2.2	2.9	1.3
Moisture holding capacity (%)	53–58	55–60	61–66
Shipping weight (±5%) (g/dm ³)	720	790	660
Uniformity coefficient	1.7	1.8	1.04
Swelling Na ⁺ > H ⁺ (%)	30	40	n.a.
pH range	0–14	0–14	0–14
Maximum temperature (K)	313	313	313

n.a. – not available

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