

## Research Article

# Recovery Process for Critical Metals: Selective Adsorption of Nickel(II) from Cobalt(II) at Acidic Condition and Elevated Temperature

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Effective and sustainable separation processes for critical metals, especially for the physicochemically similar elements nickel and cobalt in battery recycling, are of great interest in the future. Selective adsorption represents a highly potential process for this purpose. In this publication, a silica adsorbent functionalized with an amino-polycarboxylate derivate (HSU331) was investigated regarding the selective adsorption of Ni(II) in the presence of Co(II) in acidic solution (pH range at equilibrium 1.8–2.3) at elevated temperature. Comparable maximum equilibrium loadings ( $q_{\max}$ ) for Ni(II) and Co(II) of  $0.59 \mu\text{mol}(\text{Ni}(\text{II})) \cdot \mu\text{mol}(\text{Ligand})^{-1}$  ( $18.3 \text{ mg}(\text{Ni}(\text{II})) \cdot \text{g}(\text{Adsorbent})^{-1}$ ), and  $0.52 \mu\text{mol}(\text{Co}(\text{II})) \cdot \mu\text{mol}(\text{Ligand})^{-1}$  ( $16.0 \text{ mg}(\text{Co}(\text{II})) \cdot \text{g}(\text{Adsorbent})^{-1}$ ), respectively, were achieved at  $T = 50^\circ\text{C}$  in single-component experiments. Under competitive conditions, the Ni(II) loading remained constant at  $0.60 \mu\text{mol}(\text{Ni}(\text{II})) \cdot \mu\text{mol}(\text{Ligand})^{-1}$  ( $18.4 \text{ mg}(\text{Ni}(\text{II})) \cdot \text{g}(\text{Adsorbent})^{-1}$ ), while the Co(II) loading drastically decreased to  $0.09 \mu\text{mol}(\text{Co}(\text{II})) \cdot \mu\text{mol}(\text{Ligand})^{-1}$  ( $2.7 \text{ mg}(\text{Co}(\text{II})) \cdot \text{g}(\text{Adsorbent})^{-1}$ ) in an equimolar dual-component system. Calculated stability constants of  $3 \cdot 10^3$  and  $0.7 \cdot 10^3 \text{ L} \cdot \text{mol}^{-1}$ , respectively, for the formed metal ion complexes of Ni(II) and Co(II) onto the adsorbent HSU331, clarify the clear selectivity of the adsorbent towards Ni(II) in the presence of Co(II) even at elevated temperature ( $T = 50^\circ\text{C}$ ).

## 1. Introduction

Rising global warming requires an energy transition away from fossil fuel-based power generation to a sustainable generation from wind and solar energy. For the success of energy transition, electricity storage systems for wind power and photovoltaic systems or electric vehicles are mandatory. As a result, state-of-the-art lithium-ion batteries (LIB), whose mixed oxide cathodes consist of lithium (Li) and certain transition metals such as cobalt (Co) and nickel (Ni), will be increasingly demanded in the future. In 2015, 49% of the globally produced refined Co was already used in the rechargeable battery market [1] and the European Union (EU) classified this metal already as critical raw material [2]. According to estimates, the application of Ni in batteries for electric vehicles will grow by 39% annually until 2025. At similar growth rates, this corresponds to a

Ni requirement in 2030 of more than 50% of the current global Ni production [3].

From 2030 onwards, the EU thus demands material recovery rates from batteries, i.a. for Ni and Co of 95% each [4]. Klimenko et al. postulate that an improvement of current global Co recycling rates from 30 to 50% is imperative to address an otherwise inevitable Co shortage by the middle of the century [5]. Consequently, accelerated development of effective and sustainable recycling approaches for end-of-life Li batteries becomes an essential technological task.

Today, LIB recycling e.g. based on the Batec, and Duesenfeld process, respectively, which combine mechanical and thermal treatments with hydrometallurgical methods, mainly acidic leaching in the presence of reductants [6, 7]. After leaching, Ni and Co normally exist as Ni(II) and Co(II) in an acidic aqueous phase, from which they are subsequently recovered by solvent extraction, and precipitation,

respectively. Depending on the leaching agent employed, the recovery rates for Co(II) and Ni(II) range from approximately 80 to 99% [6, 8, 9]. Thus, considerable amounts of up to 20% of these valuable metals get lost via wastewater. In view of the required economic and ecological sustainability of industrial processes, further treatment of such sewage effluents are expedient. Another typical industrial process is electroplating [10–12], where Ni(II) and Co(II) are removed from acidic wastewater during plating or at the end of the process [10–13].

Common separation technologies for bivalent metal ions from aqueous solution are based on adsorption methods, membrane techniques, or electrochemical methods [14]. Especially, Ni(II) and Co(II) separation processes from aqueous solution include complexation by chelating agents [10, 15] combined with electrodialysis [16, 17], adsorption [11, 13, 18, 19], and precipitation [20, 21]. Nevertheless, a selective separation of Ni(II) from Co(II) is challenging because of their similar physicochemical properties [7, 20].

Particularly, adsorption represents an advantageous elimination method for heavy metal ions in aqueous phase because of low operational costs, efficient separation at low concentrations, and an adjustable selectivity towards a specific target component [14, 18, 22, 23]. Adsorption selectivity can be achieved by surface modification of an adsorbent matrix, like porous silica gels, with target-directed ligands [24, 25]. These matrix materials offer adjustable porosities according to the selected process conditions, defined structures, and immense possibilities of specific surface functionalization [25, 26].

Generally, amino-polycarboxylic acids in a non-immobilized form show high complex stabilities with Ni(II) and Co(II) [27] and are consequently suitable for functionalization of adsorbents for heavy metal recovery. For instance, Repo et al. [28] showed high adsorption capacities for Ni(II) and Co(II) using silica gels functionalized with amino-polycarboxylic acids. A selectivity towards Ni(II) was suggested when utilizing chitosan [29, 30] as matrix matter. Several other matrices, e.g. acrylonitrile-divinylbenzene copolymer (AN-DVB) [31] or silica polyamine composites [32], were functionalized with amino-polycarboxylic acid derivatives which showed high adsorption capacities for Ni(II) and Co(II).

In this article, we demonstrate the outstanding performance of a mesoporous silica gel functionalized with an amino-polycarboxylate derivative for the selective adsorption of Ni(II) from Co(II) from an acidic model laboratory solution (pH = 1–4) at elevated temperature ( $T = 50^\circ\text{C}$ ), which represents characteristic conditions for Ni(II) and Co(II) containing industrial process waters [16, 33, 34]. These aspects complicate the search of suitable adsorbents for integrated or attached recycling steps in industrial processes because adsorption is usually an exothermic process, which implicates that higher temperatures support desorption [35]. Moreover, low pH values favor desorption of cations, here Ni(II) and Co(II) [24].

Equilibrium batch experiments were performed in order to investigate its adsorption behavior in single- and dual-component systems and the influence of different experi-

mental parameters (temperature, pH, and various molar ratios) on the selective Ni(II) adsorption. Furthermore, a desorption method at  $20^\circ\text{C}$  is presented.

This study provides substantial information for the development of a selective adsorption-based separation process as a basis for a sustainable Ni(II) and Co(II) recovery in lithium-ion battery recycling and for a process-integrated Ni(II) and Co(II) recovery step in electroplating.

## 2. Materials and Methods

**2.1. Materials.** For the selective adsorption experiments, a silica-based adsorbent, designated as HSU331, with the following characteristics was applied: specific surface area of  $510\text{ m}^2\cdot\text{g}^{-1}$ , pore diameter of  $58\text{ \AA}$ , pore volume of  $0.74\text{ mL}\cdot\text{g}^{-1}$ . It consisted of an irregular silica matrix (particle size:  $40\text{--}63\text{ }\mu\text{m}$ , pore diameter:  $60\text{ \AA}$ ), functionalized with an aminopolycarboxylate ligand. Ultrapure water of type 1 was utilized in all experiments and generated with the water purification system B30 Integrity (AQUAlab, Höhr-Grenzhausen, Germany). Cobalt(II) nitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2\cdot(\text{H}_2\text{O})_6$ , purity > 98%), purchased from Carl Roth (Karlsruhe, Germany), and Nickel(II) nitrate hexahydrate ( $\text{Ni}(\text{NO}_3)_2\cdot(\text{H}_2\text{O})_6$ , purity 99%) as well as 65 wt% Suprapur® nitric acid, delivered from Merck (Darmstadt, Germany), were applied for sample preparation.

**2.2. Elemental Analysis of the Functionalized Silica Gel.** The amount of functionalized ligands onto the silica surface (surface coverage  $F$ ) was obtained by elemental analysis using a Vario EL Cube Elemental Analyzer (Elementar Analysensysteme, Langensfeld, Germany) with helium as carrier gas and sulphanic acid (p.a., Merck, Darmstadt, Germany) as calibration standard. Each sample consisted of 10 mg adsorbent and was analyzed in triplicate.

**2.3. Metal Ion Quantification.** Ni(II) and Co(II) concentrations in the experimental samples were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) with an Agilent 7800 system (Agilent Technologies, Waldbronn, Germany) according to Kriese et al. [36].

**2.4. Adsorption Experiments.** Discontinuous adsorption experiments with 50 mg HSU331 in differently concentrated aqueous metal samples ( $V = 5\text{ mL}$ ) were performed in 15 mL centrifuge tubes (VWR International, Darmstadt, Germany) at  $T = 20^\circ\text{C}$  and  $T = 50^\circ\text{C}$  in triplicate ( $n = 3$ ). Metal samples were prepared from corresponding metal stock solutions ( $c = 30\text{ mmol}\cdot\text{L}^{-1}$ ) by dilution with nitric acid (0.1 wt%). In single-component samples, the initial Ni(II) and Co(II) concentrations ( $c_0(\text{M}(\text{II}))$ ) comprised between  $0.030$  and  $17\text{ mmol}\cdot\text{L}^{-1}$  (Table 1). In the case of equimolarity (1:1) in dual-component samples, the adjusted concentrations of each metal ion ranged between  $1.0$  and  $15\text{ mmol}\cdot\text{L}^{-1}$ . For the molar ratio of 1:3, the concentrations of the surplus component (Co(II)) also varied between  $1.0$  and  $15\text{ mmol}\cdot\text{L}^{-1}$ , and those of the minor component (Ni(II)) between  $0.33$  and  $5.0\text{ mmol}\cdot\text{L}^{-1}$  (Table 1).

Initially, the pH value of each sample solution was adjusted to 3.5 with 65 wt% nitric acid. For equilibrium achievement, the centrifuge tubes rotated in an overhead

TABLE 1: Initial concentrations of metal ions in the prepared single- and dual-component systems (molar ratio Ni(II) : Co(II) of 1 : 1 and 1 : 3) for the different adsorption experiments.

Single-component system $c_0(\text{M(II)})$ (mmol · L <sup>-1</sup> )	Dual-component system $c_0(\text{M(II)})$ (Ni(II) and Co(II)) (mmol · L <sup>-1</sup> )	
	1 : 1	1 : 3
—	—	—
0.030	—	—
1.0	1.0 + 1.0	0.33 + 1.0
2.8	2.8 + 2.8	0.93 + 2.8
4.5	4.5 + 4.5	1.5 + 4.5
5.6	5.6 + 5.6	1.9 + 5.6
11	11 + 11	3.7 + 11
17	15 + 15	5.0 + 15

rotator (Sunlab, Mannheim, Germany) with 40 rpm for 24 h at 20°C. Subsequently, an analogous series of experiments at  $T = 50^\circ\text{C}$  proceeded in a temperature-controlled heating cabinet. After 24 h, aliquots ( $V = 0.15$  mL) of each sample solution were diluted with 5 mL 0.65 wt% of nitric acid and analyzed with the ICP-MS. The equilibrium pH value ( $\text{pH}_{\text{eq}}$ ) in all sample solutions was measured in order to determine the ratio of released protons ( $n(\text{H}^+, \text{released})$ ) per adsorbed metal ion ( $n(\text{M(II)}, \text{adsorbed})$ ) during adsorption. This ratio represents the number of ligand dentates that coordinate one metal ion, which is a measure of the resulting complex structure and was calculated as follows:

$$\frac{n(\text{H}^+, \text{released})}{n(\text{M(II)}, \text{adsorbed})} = \frac{(10^{-\text{pH}_{\text{eq}}} - 10^{-\text{pH}_0}) \cdot 10^6}{(c_0(\text{M(II)}) - c^*(\text{M(II)}))}, \quad (1)$$

where  $c_0(\text{M(II)})$  constitutes the initial and  $c^*(\text{M(II)})$  the equilibrium concentration in the sample solution and  $\text{pH}_0$  gives the initial pH value.

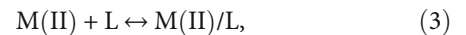
Based on the measured equilibrium concentrations compared to the initial ones, specific dynamic and thermodynamic equilibrium parameters (equilibrium loading, stability constant, enthalpy, entropy, and free enthalpy of formation) were calculated to clarify the underlying adsorption mechanism and to verify the selectivity of HSU331 (expressed by the selectivity coefficient and reaction engineering selectivity).

According to the measured experimental concentrations in  $\mu\text{mol} \cdot \text{L}^{-1}$ , each corresponding molar equilibrium loading  $q^*$  in  $\mu\text{mol}(\text{M(II)}) \cdot \mu\text{mol}(\text{Ligand})^{-1}$  yields as:

$$q^* = \frac{(c_0(\text{M(II)}) - c^*(\text{M(II)})) \cdot V}{m_{\text{ad}} \cdot F}, \quad (2)$$

where  $V$  represents the sample volume in L,  $m_{\text{ad}}$  the adsorbent mass in g, and  $F$  the functionalization degree in  $\mu\text{mol}(\text{Ligand}) \cdot \text{g}(\text{Adsorbent})^{-1}$  (determined according to Section 2.2).

Usually, the adsorption of bivalent metal ions on functionalized surfaces proceeds according to the following equilibrium reaction:



in which the M(II) ions and the adsorbent ligand L form ion ligand complexes. Considering the equilibrium concentrations ( $\mu\text{mol} \cdot \text{L}^{-1}$ ) of the formed complexes  $c^*(\text{M(II)/L})$ , non-adsorbed metal ions  $c^*(\text{M(II)})$ , and free ligands  $c^*(\text{L})$ , the stability constant ( $K_{\text{ML}}$ ) of the metal ion ligand complex was determined according to

$$K_{\text{ML}} = \frac{c^*(\text{M(II)/L})}{c^*(\text{M(II)}) \cdot c^*(\text{L})}. \quad (4)$$

The enthalpy ( $\Delta H^0$ ) and entropy ( $\Delta S^0$ ) were derived from the linear van't Hoff equation [37], which describes the equilibrium position of a chemical reaction as a function of temperature:

$$\ln K_{\text{ML}} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R \cdot T}. \quad (5)$$

By plotting  $\ln K_{\text{ML}}$  (ordinate) against  $1/T$  (abscissa) [38],  $\Delta H^0$  and  $\Delta S^0$  resulted from the slope, and the intercept of the linear curve, respectively.

Subsequently, the free enthalpy of formation ( $\Delta G^0$ ) according to the Gibbs-Helmholtz Equation (Equation (6)) substantiates the endergonic or exergonic character of the adsorption [37]:

$$\Delta G^0 = \Delta H^0 - T \cdot \Delta S^0. \quad (6)$$

Two characteristic parameters, (1) the selectivity coefficient ( $\alpha_{\text{Ni,Co}}$ ) and (2) the reaction engineering selectivity related to the formed Ni/HSU331 complex ( $S_{\text{Ni/L,L}}$ ), were chosen for discussing the selectivity of the adsorbent HSU331 towards Ni(II) and calculated from the results of the dual-component experiments as ratio of the stability constants of the formed Ni(II) and Co(II) complexes (1):

$$\alpha_{\text{Ni,Co}} = \frac{K_{\text{Ni/HSU 331}}}{K_{\text{Co/HSU 331}}}, \quad (7)$$

and as ratio of the amount of formed Ni/HSU331 complexes ( $n^*(\text{Ni/L})$ ) at equilibrium and the difference between the initial amount of the adsorbent's ligands ( $n_0(\text{L})$ ) and the amount of free ligands ( $n^*(\text{L})$ ) at equilibrium (2), which means that the denominator describes the total occupied ligands [39]:

$$S_{\text{Ni/L,L}} = \frac{n^*(\text{Ni/L})}{n_0(\text{L}) - n^*(\text{L})}. \quad (8)$$

**2.5. Desorption Experiments.** Prior to the desorption investigations, corresponding adsorption experiments ( $c_0(\text{M(II)}) = 2.8$  mmol · L<sup>-1</sup>,  $T = 20^\circ\text{C}$ ,  $n = 3$ ) were conducted as described

in Section 2.4. Supernatants were discarded after 24 h and replaced by 5 mL of nitric acid with different pH values (1.0, 0.5, 0.0, and -0.3, respectively) for disclosing the optimal desorption conditions.

After equilibration (24 h) and rejection of the acidic supernatants, two washing steps ( $V = 10$  mL) with ultrapure water took place in rotating sample containers for 15 min at 40 rpm, followed by a second adsorption step. Aliquots of every adsorption, desorption, and washing step were sampled, diluted, and analyzed for dissolved Ni(II), and Co(II), respectively, according to Section 2.3.

The desorption efficiency ( $\eta_{DE}$ ) was calculated appropriate to the following equation:

$$\eta_{DE} = \frac{n_d}{n_a} \cdot 100\%, \quad (9)$$

where  $n_d$  represents the desorbed and  $n_a$  the adsorbed amount of the respective transition metal ion.

### 3. Results and Discussion

**3.1. Surface Coverage.** Elemental analysis of the adsorbent HSU331 determined a nitrogen mass fraction of 2.2 wt% which corresponds to a surface coverage of HSU331 of  $524 \mu\text{mol}(\text{Ligand}) \cdot \text{g}(\text{Adsorbent})^{-1}$ .

**3.2. Single-Component Adsorption.** Investigations of the adsorption performance of HSU331 at  $T = 20^\circ\text{C}$  and  $T = 50^\circ\text{C}$  regarding the single-component systems Ni(II) and Co(II) resulted in Langmuir isotherms for both metal ions (Figure 1). The characteristic isotherm parameters  $q_{\max}$  (maximum adsorption loading at equilibrium) and  $K_L$  (Langmuir equilibrium constant) were determined according to the Langmuir Modell [40]:

$$q^* = \frac{q_{\max} \cdot K_L \cdot c^*}{1 + K_L \cdot c^*}, \quad (10)$$

and are summarized in Table 2. At  $T = 20^\circ\text{C}$ , adsorption of Ni(II) led to the highest  $q_{\max}$  of  $0.72 \mu\text{mol}(\text{Ni(II)}) \cdot \mu\text{mol}(\text{Ligand})^{-1}$ , and  $K_L$  values of  $4.1 \cdot 10^{-2} \text{L} \cdot \mu\text{mol}(\text{Ni(II)})^{-1}$ , whereas Co(II) was adsorbed by one-third less ( $q_{\max} = 0.49 \mu\text{mol}(\text{Co(II)}) \cdot \mu\text{mol}(\text{Ligand})^{-1}$ ) and a fourfold lower  $K_L$  value of  $9.6 \cdot 10^{-3} \text{L} \cdot \mu\text{mol}(\text{Co(II)})^{-1}$ .

In comparison to our results (see Table 2, column 5), Repo et al. [28] reported Ni(II) and Co(II) maximum loadings ( $\text{mg}(\text{M(II)}) \cdot \text{g}(\text{Adsorbent})^{-1}$ ) in the same order of magnitude. However, contrary to our results, the difference between the maximum loadings for Ni(II) and Co(II) was ten times smaller than that in our study, indicating a lower selectivity potential at competitive adsorption conditions.

Taking into account the industrial process conditions (e.g. elevated temperatures) for the Ni(II) and Co(II) separation, the adsorption experiments were also performed at  $T = 50^\circ\text{C}$ . The results showed that the  $q_{\max}$  of Co(II) remained nearly unchanged ( $0.52 \mu\text{mol}(\text{Co(II)}) \cdot \mu\text{mol}(\text{Ligand})^{-1}$ ), while the maximum adsorption of Ni(II) decreased by 20% ( $0.59 \mu\text{mol}(\text{Ni(II)}) \cdot \mu\text{mol}(\text{Ligand})^{-1}$ ). Nev-

ertheless, the  $q_{\max}$  and  $K_L$  values for Ni(II) were higher than those of Co(II), that is HSU331 separated still more Ni(II) than Co(II) at elevated temperature. Overall, these results indicate a higher selectivity of HSU331 towards Ni(II), which will be discussed in more detail for competitive adsorption in the dual-component system.

**3.2.1. Adsorption Mechanism.** By virtue of (1) the observed discoloration of HSU331 after contact with the metal ion solutions and (2) the significant pH shift in the sample solutions by approximately two units into the strongly acidic range at equilibrium, it can be assumed that the adsorption occurred as an adsorptive ligand complexation.

The complexation of Ni(II) and Co(II) resulted in a blue, and pink coloration of HSU331, respectively. Generally, blue octahedral or tetrahedral high-spin Ni(II) complexes and pink octahedral high-spin Co(II) complexes are known from literature [41, 42] supporting our assumption of adsorptive ligand complexation. Additionally, similar pink colored Co(II)/DTPA octahedral complexes, immobilized onto a melamine-formaldehyde resin were reported in [43].

Due to the chelating character of the non-immobilized amino-polycarboxylic acids, e.g. EDTA and DTPA, complex formation of free hexa- or octadentate ligands with Ni(II) or Co(II) ions usually generates octahedral complexes with high stability constants between  $\lg K_{ML} = 16.4$  and  $20.2$  [27, 42, 44]. The considerably lower stability constants determined for the HSU331 complexes, summarized in Table 3 (column 6), are more comparable to those of only tridentate or tetradentate ligands, like N-methyliminodiacetic acid (MIDA) and nitrilotriacetic acid (NTA) with Ni(II) ( $\lg K_{ML}(\text{Ni}/\text{MIDA}) = 8.7$ ;  $\lg K_{ML}(\text{Ni}/\text{NTA}) = 11.5$ ), and Co(II) ( $\lg K_{ML}(\text{Co}/\text{MIDA}) = 7.5$ ;  $\lg K_{ML}(\text{Co}/\text{NTA}) = 10.3$ ), respectively [27]. These results demonstrate a non-optimal exploitation of the immobilized HSU331 ligands, likely due to steric hindrance [28, 45, 46]. In general, metal ion chelate complexes described in the literature reveal constantly higher stability constants for Ni(II) than for Co(II) and, according to the Irving-Williams series, are explicable by a higher ligand field stabilization for Ni(II) in coordination with oxygen or nitrogen-containing ligands [27, 42]. This tendency was also observable for the stability constants ( $\lg K_{ML}$ ) of the corresponding HSU331 complexes determined in this study (Table 3, column 6). Overall, the  $\lg K_{ML}$  values are at least two times smaller and thus less stable than for the non-immobilized complexes discussed above. Immobilization of the ligand molecules of HSU331 lowers their degree of motion, so that possibly more unstable octahedral complexes are formed in which some coordination sites of the metal ions remain occupied by water molecules [42, 47–49].

In particular, the pH of the equilibrated system is a decisive factor influencing  $K_{ML}$ , which becomes clear from the underlying complex formation reaction:



where  $\text{M}^{2+}$  represents a bivalent metal ion,  $L$  the ligand, and  $n$  the variable number of released protons. Due to Equation (11), the release of one proton per coordination site

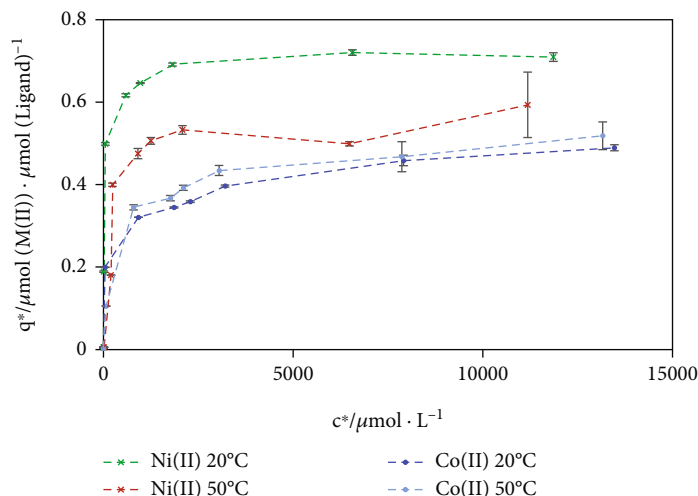


FIGURE 1: Adsorption isotherms for the single-component systems Ni(II), and Co(II) at  $T = 20^\circ\text{C}$  and  $T = 50^\circ\text{C}$ , respectively.

TABLE 2: Characteristic Langmuir isotherm parameters ( $K_L, q_{\max}$ ) depending on adsorptive and temperature.

Adsorptive	$T$ ( $^\circ\text{C}$ )	$K_L$ ( $\text{L} \cdot \mu\text{mol}(\text{M}(\text{II}))^{-1}$ )	$q_{\max}$ ( $\mu\text{mol}(\text{M}(\text{II})) \cdot \mu\text{mol}(\text{Ligand})^{-1}$ )	$q_{\max}$ ( $\text{mg}(\text{M}(\text{II})) \cdot \text{g}(\text{Adsorbent})^{-1}$ )
Ni(II)	20	$4.1 \cdot 10^{-2}$	0.72	22.2
Co(II)	20	$9.6 \cdot 10^{-3}$	0.49	15.1
Ni(II)	50	$9.8 \cdot 10^{-3}$	0.59	18.3
Co(II)	50	$2.9 \cdot 10^{-3}$	0.52	16.0

TABLE 3: Correlation between proton release per adsorbed metal ion during adsorption and stability constant  $K_{ML}$  at  $T = 20^\circ\text{C}$  in a single-component system.

Adsorptive	$c_0(\text{M}(\text{II}))$ ( $\mu\text{mol} \cdot \text{L}^{-1}$ )	Metal ion : ligand ratio ( $\mu\text{mol}(\text{M}(\text{II})) \cdot \mu\text{mol}(\text{Ligand})^{-1}$ )	$\text{pH}_{\text{c}q}$	Released $\text{H}^+$ : adsorbed metal ion ratio ( $\mu\text{mol}(\text{H}^+) \cdot \mu\text{mol}(\text{M}(\text{II}))^{-1}$ )	$\lg K_{ML}$
None	0	—	2.7	—	—
Ni(II)	2800	1 : 2	2.0	3.65	4.30
Co(II)	2800	1 : 2	2.3	2.54	2.71
Ni(II)	5600	1 : 1	1.9	3.68	3.09
Co(II)	5600	1 : 1	2.3	2.22	2.31
Ni(II)	17000	3 : 1	1.8	4.14	2.32
Co(II)	17000	3 : 1	2.2	2.33	1.84

descends the pH into the acidic range over time, thereby shifting the equilibrium of complexation to the left and decreasing the stability of the complexes [50].

During the adsorption experiments, this pH shift was evident. When only adsorbent HSU331 is dispersed into an aqueous phase with an initial  $\text{pH} = 3.5$ , the pH value in equilibrium state shifts to 2.7, which demonstrates the expected net acidity of the HSU331 ligands. After contact of HSU331 with the metal samples, the pH of Ni(II) and Co(II) samples shifted from  $\text{pH} 3.5$  to  $\text{pH} 1.8$ , and 2.2, respectively, which underline the assumption that the adsorption was caused by adsorptive ligand complexation. The ratio of protons released per adsorbed metal ion corre-

lates directly with the number of coordinated ligand dentates, namely for Ni(II) 3 to 4 and for Co(II) 2 to 3 (Table 3, column 5). This result additionally confirms the discussed weaker complexation of Co(II) ions.

**3.2.2. Influence of Temperature on Adsorption.** The fact that at elevated temperature ( $T = 50^\circ\text{C}$ ) the HSU331 adsorption performance, especially for Co(II) adsorption, remains almost unchanged (Table 2, column 4) is discussed on the basis of the estimated thermodynamic state variables enthalpy  $\Delta H^0$ , entropy  $\Delta S^0$ , and free enthalpy  $\Delta G^0$  of formation (Table 4). The negative  $\Delta H^0$  ( $-13.5 \text{ kJ} \cdot \text{mol}^{-1}$ ) of the Ni(II) complexation reflects the exothermic character of this

TABLE 4: Thermodynamic state variables for the adsorption of Ni(II) and Co(II) onto HSU331 in a single-component system (metal ion : ligand ratio of 1 : 1).

	$\Delta H^0$ (kJ · mol <sup>-1</sup> )	$\Delta S^0$ (J · mol <sup>-1</sup> · K <sup>-1</sup> )	$\Delta G^0$ , $T = 20^\circ\text{C}$ (kJ · mol <sup>-1</sup> )	$\Delta G^0$ , $T = 50^\circ\text{C}$ (kJ · mol <sup>-1</sup> )
Ni(II)	-13.5	13.0	-17.3	-17.7
Co(II)	2.8	53.5	-12.9	-14.4

reaction. By increasing the temperature, according to Le Chatelier's law, the reverse reaction proceeds more intensively, which consequently leads to a lower loading of the adsorbent HSU331 (see Figure 1). Conversely, the Co(II) complexation onto the HSU331 surface is weakly endothermic due to the positive enthalpy of formation (2.8 kJ · mol<sup>-1</sup>).

Overall, the more negative free enthalpies ( $\Delta G^0$ ) of formation for Ni(II) adsorption at  $T = 20^\circ\text{C}$  and  $T = 50^\circ\text{C}$  compared to the corresponding free enthalpies for Co(II) adsorption (see Table 4) indicate an elevated spontaneous nature of the Ni(II) adsorption onto HSU331. For both temperatures, this correlates well to the demonstrably higher HSU331 loadings with Ni(II) compared to the loadings with Co(II) (refer to Table 2, column 4).

The positive entropies for Ni(II) and Co(II) adsorption onto HSU331, presumably caused by the release of metal ion-coordinated H<sub>2</sub>O molecules throughout the complexation [38], signified a generation of chelate complexes onto the HSU331 surface, in which a multidentate ligand occupies at least two coordination sites of a central metal ion [27, 42]. As summarized in Table 3, the release of more than two protons per adsorbed metal ion implies an occupation of the same number of metal coordination sites by the ligands' dentates and a simultaneous release of at least two water molecules per adsorbed metal ion causing the observed entropy increase in the system (Table 4, column 3).

A significantly higher  $\Delta S^0$  for the Co(II)/HSU331 complex formation compared to that for the Ni(II)/HSU331 complexing was also found by Smith and Martell [27], who investigated similar non-immobilized amino-carboxylate complexes of Ni(II) and Co(II).

**3.3. Competitive Adsorption.** The resulting isotherms for the competitive adsorption onto HSU331 at  $T = 20^\circ\text{C}$  as well as  $T = 50^\circ\text{C}$  in the dual-component system Ni(II):Co(II) are depicted in Figure 2. Isotherm data points are divided into two parts: the first data point at low initial concentration ( $c_0(\text{M(II)}) = 1,000 \mu\text{mol} \cdot \text{L}^{-1}$  for Ni(II), and Co(II), respectively; zoomed area in Figure 2) and the remaining five data points ( $c_0(\text{M(II)}) \geq 2,800 \mu\text{mol} \cdot \text{L}^{-1}$  for Ni(II), and Co(II), respectively). At low initial concentration, the loadings of HSU331 are comparable (0.13/0.17 and 0.14/0.16  $\mu\text{mol}(\text{M(II)}) \cdot \mu\text{mol}(\text{Ligand})^{-1}$  for Co(II)/Ni(II) at  $20^\circ\text{C}$ , and  $50^\circ\text{C}$ , respectively). In this case, the surplus of ligands (metal ion : ligand ratio 0.4:1) avoids a competition for the ligands between both metal ions.

At higher initial concentrations, the adsorption loading of HSU331 with Ni(II) increases steadily until saturation, while the adsorption loading of Co(II) decreased by around 80% with rising initial concentrations compared to that in the single-component system. This can be attributed to the

onset of competitive adsorption from a metal ion : ligand ratio  $\geq 1$ .

Table 5 demonstrates the relations between  $\text{pH}_{\text{eq}}$ , released protons per adsorbed metal ion, and the stability constant  $K_{\text{ML}}$  at  $T = 20^\circ\text{C}$ . For low initial concentrations ( $c_0(\text{M(II)}) = 1,000 \mu\text{mol} \cdot \text{L}^{-1}$  for Ni(II), and Co(II), respectively), the stability constants  $K_{\text{ML}}$  (Table 5, line 1-2) are comparable with those of each single-component system at a similar metal ion : ligand ratio (refer to Table 3, line 2-3). The ratio of released protons per adsorbed metal ion of 3.0 represents the average value of the ratios calculated for the single-component systems Ni(II) and Co(II) at the same concentrations and  $T = 20^\circ\text{C}$ , which implies that also in the dual-component system the respective determined number of ligand dentates (Ni(II): 3.65; Co(II): 2.54; see Table 3), takes part in the coordination of the metal ions.

From an initial concentration of greater than or equal to  $2,800 \mu\text{mol}(\text{Ni(II)/Co(II)}) \cdot \text{L}^{-1}$  (metal ion : ligand ratio  $\geq 1$ ), the stability constants of the Ni(II)/HSU331 complexes always exceed those of the Co(II)/HSU331 complexes (Table 5, column 6), that is Ni(II)/HSU331 complexes are preferentially formed in the presence of ligand deficiency. Additionally, the equilibrium reached at  $\text{pH} 2.0$  is more favorable for Ni(II) than for Co(II) complexation as demonstrated for the single-component system (Table 3, column 4). Overall, the resulting  $K_{\text{ML}}$  values for Ni(II)/HSU331 complexes in the dual-component system are comparable values to those calculated for the single-component system. The release of about two protons (1.8-2.4, see Table 5) signifies that only two ligand dentates are involved in Ni(II) complex formation. This result theoretically allows the separation of a 1.5 to 2-fold higher number of Ni(II) ions compared to the single component system (released H<sup>+</sup> : adsorbed metal ion ratio 3-4). In practice, only an increase of 18% could be achieved, reflected by the slightly higher  $q_{\text{max}}$  of  $0.85 \mu\text{mol}(\text{Ni(II)}) \cdot \mu\text{mol}(\text{Ligand})^{-1}$  at  $T = 20^\circ\text{C}$  and an initial concentration of  $15,000 \mu\text{mol} \cdot \text{L}^{-1}$  (Figure 2), compared to  $0.72 \mu\text{mol}(\text{Ni(II)}) \cdot \mu\text{mol}(\text{Ligand})^{-1}$  for the single-component system (see Table 2).

In general, the temperature rise of  $30^\circ\text{C}$  has no impact on the adsorption performance of HSU331 towards both metal ions (refer to Figure 2). However, the remarkable decrease of the maximum Ni(II) loading at  $T = 50^\circ\text{C}$  (Figure 2) and an initial concentration of  $15,000 \mu\text{mol} \cdot \text{L}^{-1}$  can possibly be attributed to the strong exothermic character of the Ni(II)/HSU331 complexation (refer to Section 3.2.2).

Additionally, an isotherm for the molar ratio of Ni(II) : Co(II) of 1 : 3 was generated in order to investigate the selectivity of HSU331 towards Ni(II) under non-equimolar conditions (Figure 3). Interestingly, even if Ni(II) represents the minor system component, still relative high maximum

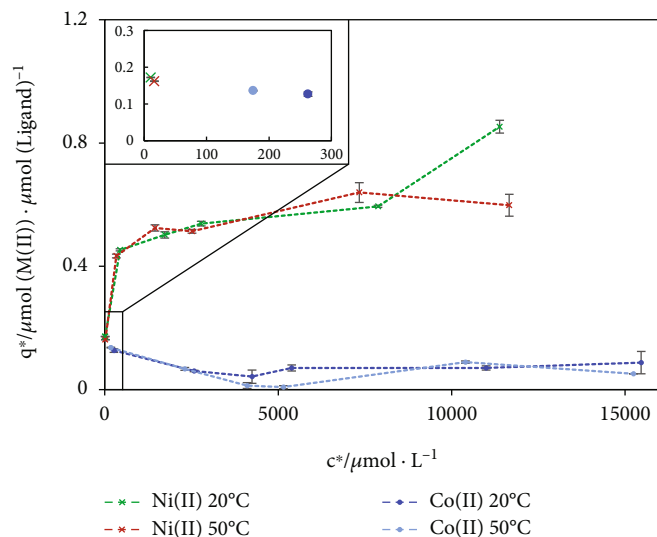


FIGURE 2: Adsorption isotherms of the equimolar dual-component system Ni(II) : Co(II) at  $T = 20^{\circ}\text{C}$ , and  $50^{\circ}\text{C}$ , respectively. The zoomed area depicts the isotherm at low concentrations ( $c_0(\text{M(II)}) = 1000 \mu\text{mol} \cdot \text{L}^{-1}$ ).

TABLE 5: Correlation between proton release per adsorbed metal ion during adsorption, stability constant  $K_{\text{ML}}$ , and molar equilibrium loading  $q^*$  at  $T = 20^{\circ}\text{C}$  in different competitive adsorption experiments at Ni(II) : Co(II) molar ratio of 1 : 1.

Adsorptives	$c_0(\text{M(II)})$ ( $\mu\text{mol} \cdot \text{L}^{-1}$ )	Metal ion : ligand ratio ( $\mu\text{mol}(\text{M(II)}) \cdot \mu\text{mol}(\text{Ligand})^{-1}$ )	$\text{pH}_{\text{eq}}$	Released $\text{H}^+$ : adsorbed metal ion ratio ( $\mu\text{mol}(\text{H}^+) \cdot \mu\text{mol}(\text{M(II)})^{-1}$ )	$\lg K_{\text{ML}}$	$q^*$ ( $\mu\text{mol}(\text{M(II)}) \cdot \mu\text{mol}(\text{Ligand})^{-1}$ )
Ni(II) and Co(II)	1000	0.4 : 1	2.3	3.0	4.36	0.17
Ni(II) and Co(II)	2800	1 : 1	2.2	2.2	3.32	0.45
Ni(II) and Co(II)	5600	2 : 1	2.1	2.4	2.69	0.54
Ni(II) and Co(II)	15000	6 : 1	2.0	1.8	2.76	0.85
					1.47	0.09

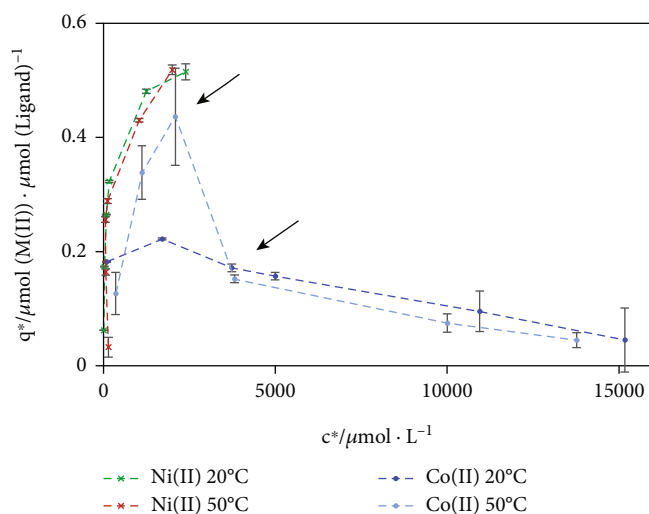


FIGURE 3: Adsorption isotherms of HSU331 for the dual-component systems with a molar ratio of Ni(II) : Co(II) 1 : 3 at  $T = 20^{\circ}\text{C}$  and  $50^{\circ}\text{C}$ . Arrow marked data points denote the limit values from which the metal ion : ligand ratios are  $\geq 1$ . Each isotherm consists of six data points.

adsorption loadings of HSU331 with Ni(II) ( $0.52 \mu\text{mol}(\text{Ni(II)}) \cdot \mu\text{mol}(\text{Ligand})^{-1}$ ) at both temperatures are achievable (Figure 3), which can be explained with the about 1.5 times higher  $\lg K_{\text{ML}}$  values of Ni(II)/HSU331 complexes (refer to Table 3).

In the experiments, where the total metal ion amounts were lower than the amount of ligands (Figure 3, first three data points), Co(II) was still adsorbed with a  $q_{\text{max}}$  of  $0.22 \mu\text{mol}(\text{Co(II)}) \cdot \mu\text{mol}(\text{Ligand})^{-1}$ , and  $0.44 \mu\text{mol}(\text{Co(II)}) \cdot \mu\text{mol}(\text{Ligand})^{-1}$  at  $20^\circ\text{C}$ , and  $50^\circ\text{C}$ , respectively. The higher Co(II) loading of HSU331 at  $T = 50^\circ\text{C}$  can be explained by the endothermic character of Co(II) complexation (Table 4). However, with respect to a possible selectivity of HSU331 towards Co(II) at  $50^\circ\text{C}$ , it should be noted that despite the discussed higher loading for Co(II) at this temperature, the removal efficiency for Ni(II) reaches 96%, and for Co(II) only 52%, respectively.

The decrease of the Co(II) loadings (Figure 3, data points with a metal ion : ligand ratio  $> 1$ ) can be explained by the replacement of central Co(II) ions in the Co(II)/HSU331 complexes through Ni(II) ions, as already discussed for the equimolar system.

Calculated selectivity coefficients ( $\alpha_{\text{Ni,Co}}$ ) (refer to Equation (7)) strongly varied between 0.8 and 173 without any tendency regarding molar ratio, initial metal ion concentration, and temperature. All selectivity coefficients  $> 1$  indicated a selectivity of HSU331 towards Ni(II). Comparable selectivity coefficients at  $T = 20^\circ\text{C}$  between 37 and 129 were also found by Repo et al. [29], who examined several amino-polycarboxylic acid ligands bound to chitosan.

Since the calculated selectivity coefficients showed no trend, the reaction engineering selectivity related to the formed Ni(II)/HSU331 complex ( $S_{\text{Ni/L,L}}$ , refer to Equation (8)) was used instead as a parameter (Table 6) for evaluating the exploitation of the occupied ligands for the Ni(II) adsorption.

In the equimolar system,  $S_{\text{Ni/L,L}} > 0.5$  signifies a selectivity of the adsorbent HSU331 towards Ni(II), because more than half of the occupied ligands are coordinated with Ni(II), while at a molar ratio of 1:3, a  $S_{\text{Ni/L,L}}$  value  $> 0.25$  indicates the Ni(II) selectivity of adsorbent HSU331.

According to the calculated  $S_{\text{L-Ni,L}}$  values for  $c_0(\text{M(II)}) \geq 2,800 \mu\text{mol} \cdot \text{L}^{-1}$  in the equimolar system (Table 6, columns 2-3), at least 82% and up to 98% of the HSU331 ligands were coordinated with Ni(II), which clearly evidenced the selectivity of HSU331 towards Ni(II). Even in the presence of an Co(II) excess (molar ratio Ni(II):Co(II) 1:3), up to 92% (Table 6, columns 4-5) of the occupied ligands are preferably coordinated to Ni(II) at high initial concentrations ( $c_0(\text{M(II)}) = 15 \text{ mmol}(\text{Co(II)}) \cdot \text{L}^{-1}/5.0 \text{ mmol}(\text{Ni(II)}) \cdot \text{L}^{-1}$ ).

**3.4. Desorption Studies.** In order to find suitable desorption conditions for Ni(II) and Co(II), nitric acid with varying concentrations of 0.1 to 2 M (pH 1 to -0.3) was investigated as desorption solution (DS). Desorption efficiencies for both metal ions depending on the acidity of the DS are presented in Figure 4. The application of a DS with a  $\text{pH} \leq 0.5$  ( $c(\text{HNO}_3) \leq 0.32 \text{ M}$ ) led to a complete desorption

TABLE 6: Selectivity of reaction engineering ( $S_{\text{Ni/L,L}}$ ) for the Ni(II) adsorption onto HSU331 in dependence of molar ratio, initial concentration, and temperature.

$c_{0,\text{major component}}$ ( $\mu\text{mol} \cdot \text{L}^{-1}$ )	$S_{\text{Ni/L,L}}$			
	Ni(II):Co(II) molar ratio 1:1		Ni(II):Co(II) molar ratio 1:3	
	$20^\circ\text{C}$	$50^\circ\text{C}$	$20^\circ\text{C}$	$50^\circ\text{C}$
1000	0.58	0.54	0.25	0.20
2800	0.88	0.86	0.44	0.33
5600	0.88	0.98	0.67	0.55
15000	0.82	0.88	0.92	0.92

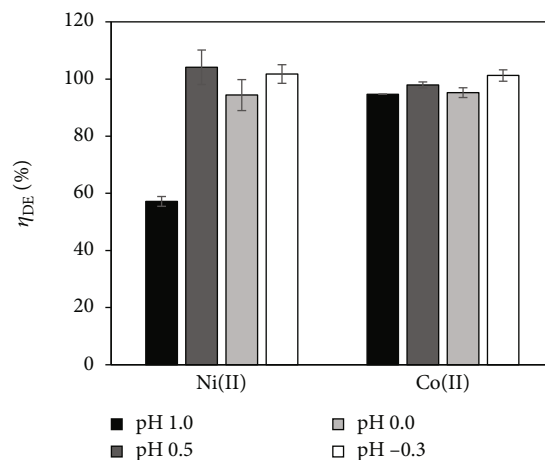


FIGURE 4: Desorption Efficiency ( $\eta_{\text{DE}}$ ) for Ni(II) and Co(II) at  $T = 20^\circ\text{C}$  depending on the pH of the desorption solution (DS). Adsorption loadings before the desorption amounted on average  $0.49 \mu\text{mol}(\text{Ni(II)}) \cdot \mu\text{mol}(\text{Ligand})^{-1}$  and  $0.35 \mu\text{mol}(\text{Co(II)}) \cdot \mu\text{mol}(\text{Ligand})^{-1}$ .

of Ni(II) ( $\eta_{\text{DE}} \sim 100\%$ ), whereas 0.1 M nitric acid ( $\text{pH} = 1$ ) was only able to desorb 50% of Ni(II). In contrast, Co(II) was almost completely released from HSU331 already at  $\text{pH} = 1$ . These results correlate with the discussed higher stability constants of Ni(II)/HSU331 complexes at different pH values (see Section 3.2.1). Moreover, it is most likely that the protonated HSU331 ligands represent the more stable molecular form, since, e.g. non-immobilized EDTA molecules predominantly exist as protonated  $\text{H}_5\text{EDTA}^+$  molecules in aqueous solution at  $\text{pH} = 0.5$  [51].

Similar findings were reported by Repo et al. [28]. They demonstrated that Ni(II) was still adsorbed at  $\text{pH} = 1.0$  but Co(II) only marginally by amino-polycarboxylic functionalized surfaces. Additionally, a complete desorption of Ni(II) and Co(II) was accomplished with 2 M nitric acid. Our results prove that already 0.1, and 0.32 M nitric acid are sufficient for the selective desorption of Co(II), and Ni(II) from HSU331, respectively. As the adsorption performance of HSU331 for Ni(II) and Co(II) (data not shown) was maintained at a second adsorption after desorption, it can be assumed that a complete regeneration of the adsorbent was achieved.



## 4. Conclusion

Our experimental results evidence that the investigated adsorbent HSU331 selectively separates Ni(II) from Co(II) at 20°C and 50°C in acidic aqueous solution (pH < 3.5). An approximately seven- to nine-fold higher loading of HSU331 was obtained with Ni(II) compared to Co(II) due to the higher stability constants for the proposed Ni(II) chelate complexes. Low equilibrium pH values of 2.0 to 2.2 in the dual-component system reinforce the selectivity for Ni(II)/HSU331 complexes, while the Co(II)/HSU331 complexes exhibit significant lower stability constants ( $\lg K_{ML} \leq 1.68$ ).

Determined positive entropies of formation indicated that the generation of metal ion chelate complexes during adsorption is very likely. The thereby accompanied decrease of free enthalpies at  $T = 50^\circ\text{C}$  demonstrate that a temperature increase by 30°C does not limit the metal ion adsorption.

Furthermore, based on our results from the desorption experiments, a two-step desorption process can be developed in which the selectivity of the adsorbent HSU331 is maintained. In terms of the recovery of both critical metals, the achieved results demonstrate the outstanding performance of HSU331 for a development of selective and thereby sustainable industrial processes for nickel and cobalt separation.

## Data Availability

The experimental data used to support the findings of this study are available from the corresponding author upon reasonable request.

## Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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## References

- [1] P. Alves Dias, D. Blagoeva, C. Pavel, and N. Arvanitidis, *Cobalt: Demand-supply balances in the transition to electric mobility*, vol. 10, article 97710, Publications Office of the European Union, 2018.
- [2] European Commission, *Study on the review of the list of critical raw materials: Final report*, Publications Office of the European Union, 2020.
- [3] M. Henckens and E. Worrell, "Reviewing the availability of copper and nickel for future generations. The balance between production growth, sustainability and recycling rates," *Journal of Cleaner Production*, vol. 264, article 121460, 2020.
- [4] European Commission, *Proposal for a regulation of the European Parliament and the Council Concerning Batteries and Waste Batteries, Repealing Directive 2006/66/EC and Amending Regulation (EU) No 2019/1020*, Publications Office of the European Union, 2020.
- [5] V. V. Klimenko, S. V. Ratner, and A. G. Tereshin, "Constraints imposed by key-material resources on renewable energy development," *Renewable & Sustainable Energy Reviews*, vol. 144, article 111011, 2021.
- [6] L. Duan, Y. Cui, Q. Li, J. Wang, C. Man, and X. Wang, "Recycling and direct-regeneration of cathode materials from spent ternary lithium-ion batteries by hydrometallurgy: Status quo and recent developments economic recovery methods for lithium nickel cobalt manganese oxide cathode materials," *Johnson Matthey Technology Review*, vol. 65, no. 3, pp. 431–452, 2021.
- [7] S. Windisch-Kern, E. Gerold, T. Nigl et al., "Recycling chains for lithium-ion batteries: A critical examination of current challenges, opportunities and process dependencies," *Waste Management*, vol. 138, pp. 125–139, 2022.
- [8] X. Chen, Y. Chen, T. Zhou, D. Liu, H. Hu, and S. Fan, "Hydrometallurgical recovery of metal values from sulfuric acid leaching liquor of spent lithium-ion batteries," *Waste Management*, vol. 38, pp. 349–356, 2015.
- [9] E. Mossali, N. Picone, L. Gentilini, O. Rodríguez, J. M. Pérez, and M. Colledani, "Lithium-ion batteries towards circular economy: A literature review of opportunities and issues of recycling treatments," *Journal of Environmental Management*, vol. 264, article 110500, 2020.
- [10] M. Rahman, S. M. Sarkar, and M. M. Yusoff, "Efficient removal of heavy metals from electroplating wastewater using polymer ligands," *Frontiers of Environmental Science & Engineering*, vol. 10, no. 2, pp. 352–361, 2016.
- [11] M. Ajmal, R. A. K. Rao, R. Ahmad, and J. Ahmad, "Adsorption studies on *Citrus reticulata* (fruit peel of orange): Removal and recovery of Ni(II) from electroplating wastewater," *Journal of Hazardous Materials*, vol. 79, no. 1–2, pp. 117–131, 2020.
- [12] L. J. Durney, "Electrochemical and Chemical Deposition," in *Ullmann's Encyclopedia of Industrial Chemistry*, vol. 12, pp. 161–219, Wiley-VCH, Weinheim, 2012.
- [13] S.-K. Pang and K.-C. Yung, "Chelating resin for removal of nickel impurities from gold electroplating solutions," *Industrial & Engineering Chemistry Research*, vol. 52, no. 6, pp. 2418–2424, 2013.
- [14] F. Fu and Q. Wang, "Removal of heavy metal ions from wastewaters: A review," *Journal of Environmental Management*, vol. 92, no. 3, pp. 407–418, 2011.
- [15] A. Izzati, H. Petrus, and A. Prasetya, "Nickel recovery from precipitate of NCA lithium-ion battery leach liquor by using disodium ethylene diamine tetraacetate," *IOP Conference Series: Earth and Environmental Science*, vol. 882, no. 1, article 012002, 2021.
- [16] A. Iizuka, Y. Yamashita, H. Nagasawa, A. Yamasaki, and Y. Yanagisawa, "Separation of lithium and cobalt from waste lithium-ion batteries via bipolar membrane electrodialysis coupled with chelation," *Separation and Purification Technology*, vol. 113, pp. 33–41, 2013.
- [17] A. J. Chaudhary, J. D. Donaldson, S. M. Grimes, and N. G. Yasri, "Separation of nickel from cobalt using electrodialysis

- in the presence of EDTA," *Journal of Applied Electrochemistry*, vol. 30, no. 4, pp. 439–445, 2000.
- [18] M. Ferri, S. Campisi, and A. Gervasini, "Nickel and cobalt adsorption on hydroxyapatite: A study for the de-metalation of electronic industrial wastewaters," *Adsorption - Journal of the International Adsorption Society*, vol. 25, no. 3, pp. 649–660, 2019.
- [19] C. Ribeiro, F. B. Scheufele, F. R. Espiñoza-Quinones et al., "A comprehensive evaluation of heavy metals removal from battery industry wastewaters by applying bio-residue, mineral and commercial adsorbent materials," *Journal of Materials Science*, vol. 53, no. 11, pp. 7976–7995, 2018.
- [20] E. Gerold, S. Luidold, and H. Antrekowitsch, "Selective precipitation of metal oxalates from lithium ion battery leach solutions," *Metals*, vol. 10, no. 11, article 1435, 2020.
- [21] A. Fernandes, J. C. Afonso, and A. J. B. Dutra, "Separation of nickel(II), cobalt(II) and lanthanides from spent Ni-MH batteries by hydrochloric acid leaching, solvent extraction and precipitation," *Hydrometallurgy*, vol. 133, pp. 37–43, 2013.
- [22] S. E. Bailey, T. J. Trudy, R. M. Bricka, and D. D. Adrian, "A review of potentially low-cost sorbents for heavy metals," *Water Research*, vol. 33, no. 11, pp. 2469–2479, 1999.
- [23] H. Rosenfeld, S. Peper, T. Täffner et al., "Effektive Stofftrennung in Gas- und Flüssigphase durch selektive Adsorption," *Chemie Ingenieur Technik*, vol. 8, no. 83, pp. 1229–1236, 2011.
- [24] E. Da'na, "Adsorption of heavy metals on functionalized-mesoporous silica: A review," *Microporous and Mesoporous Materials*, vol. 247, pp. 145–157, 2017.
- [25] P. H. Thiesen and B. Niemeyer, "Maßgeschneiderte Adsorbentien im Anwendungsspektrum Bio-, Medizin- und Umwelttechnik," *Chemie Ingenieur Technik*, vol. 77, no. 4, pp. 373–383, 2005.
- [26] O. Braaß, P. H. Thiesen, V. Behrens, and B. Niemeyer, "Adsorptionskinetik von geruchsaktiven Substanzen an funktionalisierten Silicagelen und Aktivkohle," *Chemie Ingenieur Technik*, vol. 74, no. 9, pp. 1331–1334, 2002.
- [27] R. M. Smith and A. E. Martell, "Critical stability constants, enthalpies and entropies for the formation of metal complexes of aminopolycarboxylic acids and carboxylic acids," *Science of the Total Environment*, vol. 64, no. 1-2, pp. 125–147, 1987.
- [28] E. Repo, T. A. Kurniawan, J. K. Warchol, and M. E. T. Sillanpää, "Removal of Co(II) and Ni(II) ions from contaminated water using silica gel functionalized with EDTA and/or DTPA as chelating agents," *Journal of Hazardous Materials*, vol. 171, no. 1-3, pp. 1071–1080, 2009.
- [29] E. Repo, J. K. Warchol, T. A. Kurniawan, and M. E. T. Sillanpää, "Adsorption of Co(II) and Ni(II) by EDTA- and/or DTPA-modified chitosan: Kinetic and equilibrium modeling," *Chemical Engineering Journal*, vol. 161, no. 1-2, pp. 73–82, 2010.
- [30] K. Inoue, K. Yoshizuka, and K. Ohto, "Adsorptive separation of some metal ions by complexing agent types of chemically modified chitosan," *Analytica Chimica Acta*, vol. 388, no. 1-2, pp. 209–218, 1999.
- [31] M. V. Dinu and E. S. Dragan, "Heavy metals adsorption on some iminodiacetate chelating resins as a function of the adsorption parameters," *Reactive and Functional Polymers*, vol. 68, no. 9, pp. 1346–1354, 2008.
- [32] M. A. Hughes and E. Rosenberg, "Characterization and applications of poly-acetate modified silica polyamine composites," *Separation Science and Technology*, vol. 42, no. 2, pp. 261–283, 2007.
- [33] C. Lupi and D. Pilone, "Electrodeposition of nickel-cobalt alloys: The effect of process parameters on energy consumption," *Minerals Engineering*, vol. 14, no. 11, pp. 1403–1410, 2001.
- [34] G. Gao, X. He, X. Lou et al., "A citric acid/ $\text{Na}_2\text{S}_2\text{O}_3$  system for the efficient leaching of valuable metals from spent lithium-ion batteries," *JOM*, vol. 71, no. 10, pp. 3673–3681, 2019.
- [35] A. Schönbacher, *Thermische Verfahrenstechnik: Grundlagen und Berechnungsmethoden für Ausrüstungen und Prozesse*, Springer, Berlin, 2013.
- [36] F. Kriese, S. Lassen, and H. Horn, "A pitfall in heavy metal separation with amino-modified silica adsorbents from aqueous solution: The occurring pH shift," *ChemistryOpen*, vol. 11, no. 5, article e202200034, 2022.
- [37] G. Wedler and H.-J. Freund, *Lehrbuch der physikalischen Chemie*, vol. 1, Wiley-VCH, Weinheim, 2012.
- [38] A. A. Atia, A. M. Donia, S. A. El-Enein, and A. M. Yousif, "Effect of chain length of aliphatic amines immobilized on a magnetic glycidyl methacrylate resin towards the uptake behavior of Hg(II) from aqueous solutions," *Separation Science and Technology*, vol. 42, no. 2, pp. 403–420, 2007.
- [39] E. Müller-Erlwein, *Chemische Reaktionstechnik*, Springer, Wiesbaden, 2015.
- [40] I. Langmuir, "The adsorption of gases on plane surfaces of glass, mica and platinum," *Journal of the American Chemical Society*, vol. 40, no. 9, pp. 1361–1403, 1918.
- [41] J. D. Donaldson and D. Beyersmann, "Cobalt and Cobalt Compounds," in *Ullmann's Encyclopedia of Industrial Chemistry*, vol. 9, pp. 429–465, Wiley-VCH, Weinheim, 2003.
- [42] N. Wiberg, E. Wiberg, and A. F. Holleman, *Lehrbuch der anorganischen Chemie*, Walter de Gruyter, Berlin, 2007.
- [43] A. Baraka, P. Hall, and M. Heslop, "Preparation and characterization of melamine-formaldehyde-DTPA chelating resin and its use as an adsorbent for heavy metals removal from wastewater," *Reactive and Functional Polymers*, vol. 67, no. 7, pp. 585–600, 2007.
- [44] V. L. Silva, R. Carvalho, M. P. Freitas, C. F. Tormena, and W. C. Melo, "Structural determination of Zn and Cd-DTPA complexes: MS, infrared,  $^{13}\text{C}$  NMR and theoretical investigation," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 68, no. 5, pp. 1197–1200, 2007.
- [45] L. Yang, Y. Li, X. Jin et al., "Synthesis and characterization of a series of chelating resins containing amino/imino-carboxyl groups and their adsorption behavior for lead in aqueous phase," *Chemical Engineering Journal*, vol. 168, no. 1, pp. 115–124, 2011.
- [46] J. Huang, M. Ye, Y. Qu et al., "Pb(II) removal from aqueous media by EDTA-modified mesoporous silica SBA-15," *Journal of Colloid and Interface Science*, vol. 385, no. 1, pp. 137–146, 2012.
- [47] B. Nowack and L. Sigg, "Adsorption of EDTA and metal-EDTA complexes onto goethite," *Journal of Colloid and Interface Science*, vol. 177, no. 1, pp. 106–121, 1996.
- [48] L. Piszczek, A. Ignatowicz, and J. Kielbasa, "Application of cyclic voltammetry for stoichiometry determination of Ni(II), Co(II), and Cd(II) complex compounds with polyaminopolycarboxylic acids," *Journal of Chemical Education*, vol. 65, no. 2, pp. 171–173, 1988.
- [49] Y. Shiraishi, G. Nishimura, T. Hirai, and I. Komasa, "Separation of transition metals using inorganic adsorbents modified with chelating ligands," *Industrial & Engineering Chemistry Research*, vol. 41, no. 20, pp. 5065–5070, 2002.

- [50] O. K. Júnior, L. V. A. Gurgel, R. P. de Freitas, and L. F. Gil, "Adsorption of Cu(II), Cd(II), and Pb(II) from aqueous single metal solutions by mercerized cellulose and mercerized sugarcane bagasse chemically modified with EDTA dianhydride (EDTAD)," *Carbohydrate Polymers*, vol. 77, no. 3, pp. 643–650, 2009.
- [51] D. C. Harris, *Lehrbuch der Quantitativen Analyse*, Springer, Berlin, 2014.