Full Paper

New Regeneration Process of Heavy-Metal-Loaded Chelating Resins

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An alternative to the classical acid-base regeneration of chelating resins loaded with heavy metals is investigated. The new process consists in recovering the heavy metals with recyclable soluble complexing agents. The semiclosed reactor includes a fixed bed and a stirred tank. A three-parameter model, which implies a double equilibrium in series, is introduced. When less than 10 % of the metal is still fixed on the resin at the end of the desorption, a simplified form of the model with two parameters, which describes a quick equilibrium followed by a first-order kinetics reaction, is proposed. Both forms of the model can simulate results for different experimental conditions (polymer and metal types, polymer initial concentration). It was observed for both cases that the first equilibrium constant depends on the polymer type and that the rate constant of desorption depends on the metal type. The scale-up of desorption is then conducted at mini-pilot scale. Scale-up criteria tend to minimize the desorption time and the soluble polymer quantity used.

1 Introduction

Adsorption to chelating resins is a common method to recover heavy metals from wastewater containing very small concentrations of heavy metals. The main advantage of the chelating resins compared to classical ion exchangers is their ability to form strong complexes with heavy metals. The stability of the complexes is very well described by adsorption constant K [1]. A favorable adsorption, with a high adsorption constant, implies indeed that it will be difficult to detach the metal from the resin in the regeneration step.

Classical resin regeneration is based on the pH dependence of the adsorption constants, which tend to decrease by lowering the pH. An acidic solution can solubilize the heavy metal and the resin is then regenerated under alkaline conditions to perform a further metal adsorption. Both acid and base are used in excess quantities. It was shown [2] for the system Cu^{2+}/Chelamine (see Materials and Methods) that a molar ratio $Cu^{2+}/H_2SO_4/NaOH$ of 1/5/4 is required to perform a full desorption/regeneration of the resin. The regeneration process leads therefore to a consumption of acid and bases and thus a considerable production of salts.

In order to avoid this consumption of chemicals and salt production, a new recovery method of the metallic ion by use of recyclable chemicals was developed [3]. The idea is to solubilize the heavy metal with soluble strong complexing agents (for example ethylenediamine tetraacetate, EDTA). The so-formed metallic complex is electrolyzed in a further step and the complexing agent is recycled for a further regeneration cycle.

The main problems to overcome are:
- loss of the complexing agent by degradation
- dilution of the complexing agent solution due to washing processes

The solution needs to be reconcentrated by a membrane process (see Fig. 1). The use of high-molecular-weight complexing agents, like soluble chelating polymers, greatly facilitates the concentration step: reverse osmosis, used for the separation of small molecules, like metal complexes of EDTA, can be replaced by an ultrafiltration module.
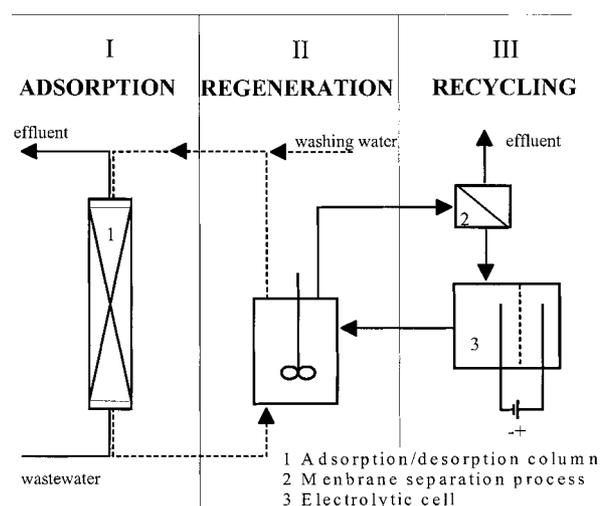
Figure 1. Global metal recovery process.

Several researchers investigated the feasibility of desorption of loaded resins with strong soluble complexing agents. Bolto *et al.* [4] proposed a regeneration process of weak-acid resins loaded with cadmium with *EDTA* or nitrilotriacetate (*NTA*). Tipnis and Dasare [5] compared different desorptions of resins loaded with mercury. The entire mercury picked up by weakly basic anion exchangers was eluted by 0.5 N or 1.0 N nitric acid solutions. Compared to nitric acid, *EDTA* buffered at pH 10 appears to be the best eluting agent for mercury. However, none of these authors tried to describe the kinetic characteristics of the desorption process with strong complexing agents.

The purpose of this work is to study the regeneration of a loaded resin with different strong complexing agents. A kinetic model will be developed in order to understand the

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fundamentals of this regeneration process, especially the influence of the molecular size of the complexing agents on the desorption.

2 Materials and Methods

2.1 Chelating Resin

The resin used for this application was the Chelamine Standard (JPS-Chimie, Neuchâtel, Switzerland). It was synthesized using a polyacrylamide gel with tetraethylene pentamine chelating groups. Before each use, the resin was treated in a fixed bed with a solution of sulfuric acid (pH 1), then washed with demineralized water. In a further step the resin underwent a regeneration with a sodium hydroxide solution (pH 11.5) and a wash with demineralized water to a defined pH (pH_0). If not mentioned otherwise, pH_0 was equal to 9.5.

The mean radius of the resin particles r_p was measured by laser diffraction (Particle Sizer 2600 E, Malvern Instruments, England) and was $1.730 \cdot 10^{-4}$ m for unloaded Chelamine and $1.524 \cdot 10^{-4}$ m for the Chelamine loaded with Cu^{2+}. The porosity of the fixed bed was determined by the measurement of the residence-time distribution of a void volume marker. β-D(+) glucose (Sigma, St-Louis, USA) was used to measure the total void volume in the fixed bed. The global porosity of a fixed bed of Chelamine was estimated to a value of $\varepsilon_r = 0.87$.

2.2 Complexing Agents and Adsorbate

The soluble polymers were the polyacrylic acid (*PAA*) and the polyethyleneimineacetic acid (*PEIAC*). The *PAA* ($M_w = 20'000$ g mol^{-1}) was purchased from Fluka AG (Buchs, Switzerland) and was used without prior treatment. The *PEIAC* ($M_w = 5'000$ and $750'000$ g mol^{-1}) was synthesized by Dr. G. Jeanneret-Gris (JPS Chimie, St-Aubin, Switzerland) from polyethyleneimine (Aldrich, USA) according to Geckeler *et al.* [6]. It was purified by ultrafiltration according to a method described by Menoud [7]. All sulfates of hydrated metallic cations (purity: purum p.a.) used in this work were purchased from Fluka AG. The absorbance of the complexes PM^{2+} was measured by a UV-VIS spectrophotometer (Diode Array HP 8452A, Hewlett Packard, Palo Alto, USA). The measured absorbance was transformed into concentration according to the Lambert-Beer's law: extinction coefficients $\varepsilon_{PM,\lambda}$ obtained by an appropriate calibration are given in Tab. 1.

2.3 Experimental Procedure

The regeneration installation included a fixed-bed column and a continuous stirred tank reactor (CSTR) as depicted in Fig. 2. A pump located between the fixed-bed column and the CSTR ensured a constant flow rate Q. A pH-stat (Impulso-

Table 1. Wavelengths and molar absorption coefficients for heavy metal complexes.

Polymer	Metal	λ [nm]	$\varepsilon_{PM,\lambda}$ [M^{-1} cm^{-1}]
PAA 20'000	Cu^{2+}	690	42.03
	Ni^{2+}	398	8.90
PEIAC 25'000	Cu^{2+}	582	43.00
		686	87.40
	Ni^{2+}	582	10.44
		686	4.05
PEIAC 750'000	Ni^{2+}	578	11.06
EDTA	Cu^{2+}	382	4.26
		732	93.83
	Ni^{2+}	382	13.26
		732	1.94

mat, Dosimat, pH-Meter, Metrohm, Herisau, Switzerland) adjusted the pH in the CSTR to a defined constant pH (the "work pH") with adjunction of an *NaOH* solution. The UV-VIS spectrophotometer measured the on-line concentration of the complex PM^{2+} at the outlet of the CSTR. The column and the UV-VIS cell were thermostatted at 20 °C. Two scales of equipment were used for these experiments: the laboratory-scale apparatus (column diameter $d_t = 0.015$ m) and the pilot plant ($d_t = 0.052$ m).
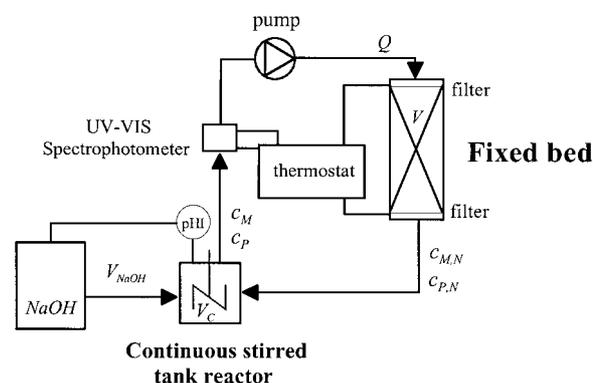
Figure 2. Schematic diagram of experimental apparatus.

The fixed-bed column was filled with a quantity of resin *m*. The resin was loaded to saturation with a concentrated metal solution ($c_0 = 5$ kg m^{-3}) and washed with distilled water. The CSTR contained a volume $V_{C,0}$ of a polymer solution with a concentration $c_{P,0}$. At the beginning of the regeneration (time $t = 0$), the on-line UV-VIS measurement, the pump and the pH-stat were switched on. The constancy of the flow rate was checked and the volume of the added *NaOH* solution V_{NaOH} was recorded. The regeneration was over when the absorbance at the outlet of the CSTR reached a constant value. In case of partial metal desorption, the heavy metal remaining on the resin was desorbed with a solution (100 mol m^{-3}) of the strong ligand *EDTA* and washed with distilled water for a further regeneration.

The determination of the initial concentration of metal on the resin q_0 and the polymer capacity q_P was determined by a method described by Menoud [2].

For all laboratory experiments, 0.4 g of resin was used (17.05 g for the pilot plant). As the volume of the fixed bed increased by a factor 2 when metal was totally desorbed from the resin, an average value of the reactor volume $V = 2.425 \; 10^{-6} \; m^3$ was used (large scale: $1.115 \; 10^{-4} \; m^3$).

The initial volume of the CSTR $V_{C,0}$ was $7.5 \; 10^{-5} \; m^3$ (large scale: $2.528 \; 10^{-3} \; m^3$). The dead volume V_M included the volumes of the pipes and of the liquid at the top of the fixed bed and was $3.05 \; 10^{-6} \; m^3$ (large scale: $2.50 \; 10^{-4} \; m^3$).

The molar ratio γ between the initial free sites of the complexing agent and the initial metallic cations present on the resin in the desorption reactor is given by[1]:

$$\gamma \;=\; \frac{c_{P,0} \; V_{C,0}}{m \; q_0} \tag{1}$$

3 Theoretical Basis and Model

3.1 Reactor Model

The final process consists of a fixed bed modeled by a cascade of N ideal continuous stirred tanks, a dead volume and a CSTR. The value of N is determined from a residence-time distribution and is found to be equal to 3.

At the beginning of the desorption process, the viscous polymer solution was only slowly mixed with the low-viscous medium. This led to the formation of dead volume near the walls and channeling. Therefore, an initial by-pass $r = 0.3$ ($r = 0.1$ for the pilot plant) was included in the model [2].

3.2 Kinetic Model

A loaded chelating resin (RM^{2+}) is desorbed by a chelating-soluble polymer (P). A kinetic model and a simplification of this model is developed in this section. Simulation results with a diffusion model show that pore diffusion and external mass transfer are not rate-limiting for all chemicals participating in the reaction (P, PM^{2+} and co-ions like Na^+). The kinetics is governed by the desorption reaction on the active sites of the resin. The kinetic model includes a double equilibrium as follows (the concentrations of each species is given on the second line):

$$RM^{2+} + P \; \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \quad \{RM^{2+}P\} \quad \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \quad R + PM^{2+} \tag{2}$$

$$(q_i - q_{c,i}) \, c_{P,i} \qquad\qquad q_{c,i} \qquad\qquad (q_0 - q_i) \, c_{M,i}$$
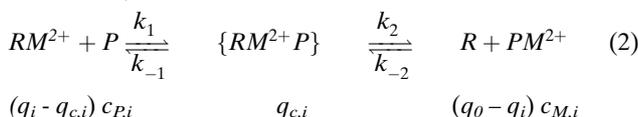
The loaded resin reacts with the soluble polymer and forms an intermediate complex ($\{RM^{2+}P\}$) which splits into a complex (PM^{2+}) and an unloaded resin site (R). The same

type of kinetics is encountered in inorganic chemistry for the substitutions in octahedral complexes in solution, described by the Eigen-Wilkins mechanism [7]. The first step corresponds to the formation of a pair of ions: this step is not depending on the nature of the metallic cation. The second step is an exchange of a molecule of water with a molecule of ligand. This step depends on the nature of the metallic cation. The concentration c_{P_i} represents the concentration of free polymer sites in the tank i of the fixed bed. The first equilibrium is assumed to be reached much faster than the second one, one can thus write:

$$\frac{dq_{c,i}}{dt} = k_1 \, (q_i - q_{c,i}) \, c_{P,i} \; - \; k_{-1} \, q_{c,i} \tag{3}$$

Assuming a thermodynamic equilibrium the concentration of the intermediate $\{RM^{2+}P\}$ is given by:

$$q_{c,i} \;=\; \frac{K_1 \, c_{P,i} \, q_i}{1 + K_1 \, c_{P,i}} \tag{4}$$

with the first equilibrium constant:

$$K_1 \;=\; \frac{k_1}{k_{-1}} \tag{5}$$

The second step is described by the following equation:

$$\frac{dq_{c,i}}{dt} = \frac{dq_i}{dt} = -k_2 \, q_{c,i} \; + \; k_{-2} \, (q_0 - q_i) \, c_{M,i} \tag{6}$$

A combination of (4) and (6) gives the kinetic equation for the model:

$$\frac{dq_i}{dt} \;=\; -k_2 \left(\frac{K_1 \, c_{P,i}}{1 + K_1 \, c_{P,i}} \right) q_i \; + \; k_{-2} \, (q_0 - q_i) \, c_{M,i} \tag{7a}$$

A simplification of the model is obtained when the constant k_{-2} is sufficiently small to be neglected. The simplified model postulates that the desorption goes on as long as loaded resins RM^{2+} and free polymers sites P are available. The desorption of loaded resin through a polymer is then:

$$\frac{dq_i}{dt} \;\cong\; -k_2 \left(\frac{K_1 \, c_{P,i}}{1 + K_1 \, c_{P,i}} \right) q_i \tag{7b}$$

This behavior is sometimes called "saturation kinetics". Its mathematical representation is a hyperbola. For a high concentration of soluble polymer ($K_1 \, c_{P_i} \gg 1$), the desorption rate is simplified to a first-order rate independent from the polymer concentration:

$$\frac{dq_i}{dt} \;\cong\; -k_2 \, q_i \tag{8}$$

A second-order kinetics describes the situation at low polymer concentrations ($K_1 \, c_{P_i} \ll 1$):

$$\frac{dq_i}{dt} \;\cong\; -k_2 \, K_1 \, c_{P,i} \, q_i \tag{9}$$

Numerical solutions of the differential equations for the different models developed were obtained with the software Simusolv (The Dow Chemical Company, Midland, Michigan, USA). The integration method used was a Gear algorithm

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1) List of symbols at the end of the paper.

(BDF-DIFSUB) with variable step and order. Kinetic parameters for the models were estimated by curve fitting.

4 Results and Discussion

A wide range of experimental parameters can affect the desorption of metal ions with a soluble polymer, for example:
- the residence time τ in the fixed bed
- the pH of the polymer solution
- the molar ratio γ
- the type of metal adsorbed on the resin
- the type and the molecular weight of soluble polymer

Preliminary experiments studying the effects of the residence time τ in the fixed bed and the pH of the polymer solution lead to the following conclusions:
- the loaded soluble polymer precipitates at low pH solutions (pH <5.3).
- a high pH involves a large consumption of *NaOH* for the preparation of the alkaline solutions and precipitation of the metal ions as hydroxide.

Thus, an intermediate pH value of 7.3 was selected. In order to avoid any gradient of pH the residence time in the fixed bed has to be low compared to the characteristic desorption time [2].

4.1 Influence of the Soluble Polymer Concentration

Fig. 3 describes several desorptions of the Ni^{2+}-loaded resin Chelamine with the *PEIAC* 25'000. The experimental conditions for these desorptions are given in Tab. 2. The evolution of the reaction is given by the elution volume, V_E ($V_E = Q\,t$) and the ordinate indicates the concentration of metallic complex c_M [mol m^{-3}] in the CSTR. The effect of the initial polymer concentration $c_{P,0}$ (corresponding to changing γ) at pH 7.3 was studied.

The simplified model (7b) gives a good representation of the experimental values. The optimized kinetic parameters remain constant from one experiment to the other, $K_1 \cong 0.035$ m^3 mol^{-1} for each run and the average value of $k_2 = 8.0$ 10^{-3} s^{-1}. The value of K_1 obtained with the complete model is maintained, as this parameter is totally independent of ($K_2 = k_2/k_{-2}$).

It is important to notice that a γ lower than 1 corresponds to a lack of soluble polymer. REG124 is such a run, from which the capacity of the complexing agent can be determined $q_P = 2.076$ mol kg^{-1}. An increase in γ (and in concentration $c_{P,0}$) shortens the desorption time. However, if some polymer is lost during the global recovery process presented in the introduction (during ultrafiltration or electrolysis), it is important to mini-
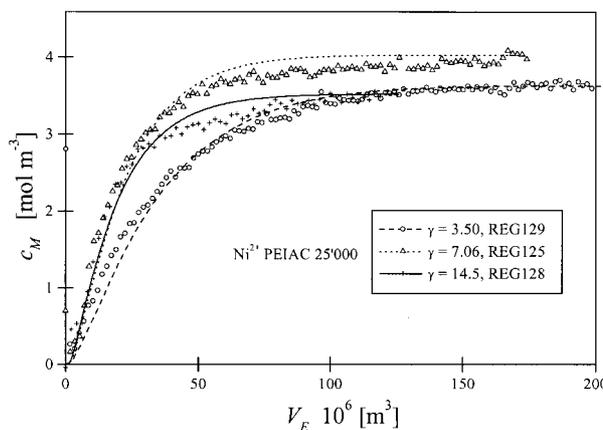
Figure 3. Effect of polymer concentration (*PEIAC* 25'000) on the desorption of the resin Chelamine loaded with Ni^{2+}. $m = 0.4$ g, pH = 7.3, simplified model, (7b).

mize its quantity (γ) in the desorption. A value of $\gamma = 1$ represents a quantity of polymer just sufficient to desorb all the metal from the resin, but the desorption time is large. For very high values of γ, the equation can be further simplified and (8) used.

4.2 Desorption Behavior for Different Types of Metal and Soluble Polymer

First, the desorptions of two different heavy-metal ions with *PEIAC* 25'000, and then with *PAA* 20'000 are compared to determine the influence of the type of metal. Then the desorptions of Ni^{2+} with two different soluble polymers provide information on the influence of the type of soluble polymer. Finally, the desorptions of Ni^{2+} with *PEIAC* of two molecular masses gives the influence of the molecular mass on the desorption. The various desorptions and their parameters used for the simulation are summarized in Tabs. 2 and 3.

It was shown that the desorption of the system *PEIAC* 25'000/Ni^{2+} was complete (REG129). Fig. 4 shows that the desorption with *PEIAC* 25'000 of a resin loaded with Cu^{2+} is partial (REG140). The remainder of the metal ions represents 60 % of the initial amount and their quantity is given by q_{rest} (Tab. 3). An excess of soluble polymer ($\gamma >1$) does not desorb all the Cu^{2+} from the loaded resin. If the stability constant of the complexing agent and heavy metal is high compared to the

Table 2. Overview on the experimental conditions for the desorptions of Ni^{2+} with *PEIAC* 25'000. pH = 7.3, $m = 0.4$ g, simplified model, (7b).

Exp. REG	$Q\,10^7$ m^3 s^{-1}	$c_{P,0}$ mol m^{-3}	q_0 / q_{rest} mol kg^{-1}	γ -	K_1 m^3 mol^{-1}	k_2 s^{-1}
124	0.768	2.58	0.847 / 0.344	0.59	0.035	7.6 10^{-3}
129	0.691	14.45	0.805	3.50	0.035	9.0 10^{-3}
125	0.888	32.48	0.898	7.06	0.035	9.6 10^{-3}
128	0.835	57.80	0.775	14.54	0.036	7.2 10^{-3}
131	0.937	113.80	0.882	25.20	0.035	(19.2 10^{-3})

Table 3. Parameters for regenerations with different soluble polymers and heavy metals. pH = 7.3, m = 0.4 g, except for REG150 m = 17.05 g.

Exp. REG	P/M^{2+}	$Q \cdot 10^7$ m³ s⁻¹	$c_{P,0}$ mol m⁻³	γ -	q_P mol kg⁻¹	q_0/q_{rest} mol kg⁻¹	K_1 m³ mol⁻¹	k_2 s⁻¹	k_{-2} m³ s⁻¹ mol⁻¹	K_2 mol m⁻³
101	*PAA* 20'000/*Cu²⁺*	0.735	36.00	7.60	1.800 [1)]	0.924/0.457	0.100	1.0 10⁻³	3.5 10⁻⁴	3
113	*PAA* 20'000/*Ni²⁺*	0.600	36.00	9.99	1.800 [1)]	0.711	0.100	1.2 10⁻²	-	-
140	*PEIAC* 25'000/*Cu²⁺*	1.010	19.83	4.29	2.000 [2)]	0.900/0.537	0.035	2.1 10⁻³	7.8 10⁻⁴	3
147	*PEIAC* 750'000/*Ni²⁺*	0.976	1.88	0.44	1.438 [3)]	0.826/0.460	0.010	8.0 10⁻³	-	-
148	*PEIAC* 750'000/*Ni²⁺*	2.179	17.72	5.04	1.438 [3)]	0.686/0.090 [4)]	0.010	10.6 10⁻³	8.7 10⁻⁵	120
150	*PEIAC* 25'000/*Ni²⁺*	33.95	10.38	1.96	2.076 [5)]	0.784/0.065	0.035 [6)]	8.0 10⁻³ [6)]	-	-
143	*PEIAC* 25'000/*Ni²⁺* /*Cu²⁺*	0.903	33.51	8.81	2.076 [5)]	0.317 / 0.425/0.308	0.035 / 0.035	8.0 10⁻³ / 2.1 10⁻³	- / 5.7 10⁻³	- / 0.4

stability constant of the resin-metal complex, complete desorption is impossible even at $\gamma > 1$.

The desorptions of Ni^{2+} (REG113) and Cu^{2+} (REG101) with *PAA* 20'000, leads to the same conclusions (Tab. 3). The desorption of Ni^{2+} is complete, whereas the desorption of Cu^{2+} is partial. 50 % of the metal ions remain on the resin at equilibrium. Thus, the *PAA* 20'000 is slightly more efficient than the *PEIAC* 25'000 for the desorption of Cu^{2+}.

The influence of the molecular mass of the complexing agent has been studied for the desorption of Ni^{2+}. Fig. 4 shows a typical desorption of Ni^{2+} with the *PEIAC* 750'000 (REG148). The desorption of Ni^{2+} is partial. The equilibrium is not totally reached after an elution volume V_E = 300 ml, because there is a kinetic effect. The remainder of the metal ions at equilibrium, reached after an elution volume V_E = 600 ml, represents 13 % of the initial amount.
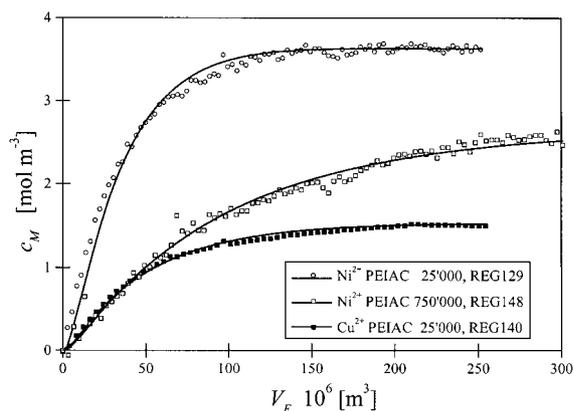
Figure 4. Effect of the type of metal (Ni^{2+} and Cu^{2+}) on the desorption of the resin Chelamine with PEIAC 25'000. m = 0.4 g, pH = 7.3, simplified model for Ni^{2+}. Desorption of Ni^{2+} from the resin Chelamine with *PEIAC* 750'000. m = 0.4 g, pH = 7.3.

The constant K_1 for *PEIAC* 750'000 is lower than for *PEIAC* 25'000 and this latter than for *PAA* 20'000. The parameter k_2 is smaller for Cu^{2+} than for Ni^{2+} and changes slightly when the simplified model is used (Tabs. 2 and 3). The values for K_2 describing the second equilibrium show that the systems *PEIAC* 25'000/Cu^{2+} or *PAA* 20'000/Cu^{2+} are less favorable than the system *PEIAC* 750'000/Ni^{2+}, thus the quantity of remaining metal ions on the resin at equilibrium is greater for

the first two systems. The results led to the following conclusions:
- For a given polymer and a given molecular mass, the parameter K_1 remains identical.
- The parameter k_2 depends on the type of metal.

4.3 Simultaneous Desorption of the Resin Loaded with Cu^{2+} and Ni^{2+}

A simultaneous desorption of Cu^{2+} and Ni^{2+} with *PEIAC* 25'000 (REG143) is presented in this section. The resin was loaded with an almost equimolar solution of Cu^{2+} and Ni^{2+}, therefore the resin was saturated as there was an excess of metal ions.

Ni^{2+} is totally desorbed (analytical limit) while a large portion of Cu^{2+} (70 %) is still in equilibrium with the resin and the polymer. Fig. 5 gives the desorption concentrations profiles of both metal ions in the CSTR. The small absorbance of the complex *PEIAC/Ni²⁺* explains the poor quality of the Ni^{2+} desorption curve.
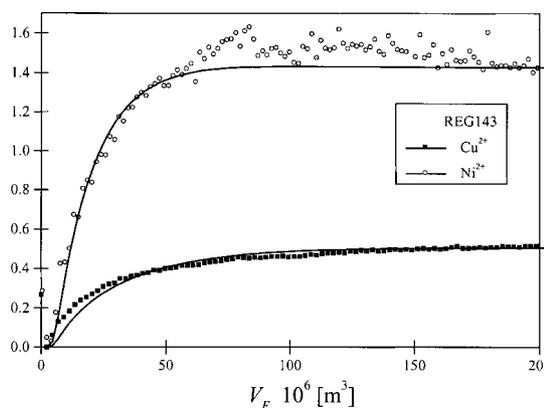
Figure 5. Simultaneous desorption of Cu^{2+} and $Ni2+$ from the resin Chelamine with *PEIAC* 25'000. $c_{P,0}$ = 33.51 mol m⁻³, m = 0.4 g, pH = 7.3, γ = 8.81, K_1 = 0.035 m³ mol⁻¹, $k_{2,Cu}$ = 2.1 10⁻³ s⁻¹, $k_{-2,Cu}$ = 5.7 10⁻³ m³ s⁻¹ mol⁻¹, $k_{2,Ni}$ = 8.0 10⁻³ s⁻¹, simplified model for Ni^{2+}.

The application of (7a) to the simultaneous desorption of Cu^{2+} and Ni^{2+} requires the introduction of mass balances (in each part of the reactor) and an additional kinetics equation for the second

metal. The same equilibrium K_1 is applied to both kinetic equations, as this constant does not depend on the type of metal. The model applied to the desorption of Cu^{2+} and Ni^{2+} includes four parameters: $K_1, k_{2,Cu}, k_{-2,Cu}$ and $k_{2,Ni}$. The mean parameters determined separately for each metal without any optimization are used for the simulation (Tab. 3). A correction on constant $k_{-2,Cu}$ (by a factor 7) is necessary to obtain a correct description. This can be explained by the competition of desorption due to different kinetics of desorption of both metal.

4.4 Validation of the Model for a Pilot Fixed Bed

The purpose of this section is to show the validity of the simplified kinetic model at a scale 40 times bigger. The values and operating conditions used are summarized in Tab. 4.

Fig. 6 shows the pilot desorption of Ni^{2+} from the resin Chelamine with *PEIAC* 25'000. The parameters used for the calculations were those obtained at laboratory scale for the simplified model ($K_1 = 0.035\ \mathrm{m^3\ mol^{-1}}, k_2 = 8.0\ 10^{-3}\ \mathrm{s^{-1}}$) without adjustment, as well as the measured values for flow rate, resin capacity and initial concentration of the polymer free sites.

The result for the pilot desorption shows that the desorption kinetics remains valid at mini-pilot scale. The metal ions still fixed on the resin ($q_{rest} = 0.065\ \mathrm{mol\ kg^{-1}}$) do not induce any problem in the global regeneration process as these correspond to less than 8 % of the total desorbed metal ions. This experiment proves that valid calculated simulations can be obtained if one of the experimental parameters is changed. The molar ratio between the *NaOH* added in the CSTR and the desorbed Ni^{2+} is also analyzed. A value of 1.97 is obtained for the pilot desorption. If the added base compensates the decrease in pH due to desorption, the complexation mechanism between the metal ions and the polymer proposed by Geckeler *et al.* [8] is confirmed, i.e., the adsorption of each metallic divalent cation to the polymer discharges two protons H^+.

5 Conclusions

The new regeneration system presented in this study is part of a global process of regeneration of heavy-metal-loaded chelating resins [3]. The global process consists of a coupling of the adsorption of the heavy-metal ions in a fluidized bed, desorption with soluble polymer in a fixed bed, reverse osmosis or ultrafiltration to concentrate the desorption solution of the complex polymer/M^{2+} and electrolysis of the solution to recover the metal.

A complete model describing the kinetics of desorption of heavy-metal-loaded resin has been proposed. It allows the description of partial desorption and can be simplified for a total desorption. The variation of operating conditions, as well

Table 4. Parameters for the pilot experiment. Desorption of Ni^{2+} from the resin Chelamine with *PEIAC* 25'000. Simplified model, (7b).

$c_{P,0}$	10.0	mol m^{-3}	k_2	8 10^{-3}	s^{-1}
Q	3.395 10^{-6}	m^3 s^{-1}	m	17.05	g
$V_{C,0}$	2.528 10^{-3}	m^3	q_0	0.9	mol kg^{-1}
V_{NaOH}	-	-	q_P	2.0	mol kg^{-1}
γ	1.65	-	V	1.115 10^{-4}	m^3
final c_M	4.8	mol m^{-3}	ε_r	0.87	-
K_1	0.035	m^3 mol^{-1}	V_M	2.50 10^{-4}	m^3
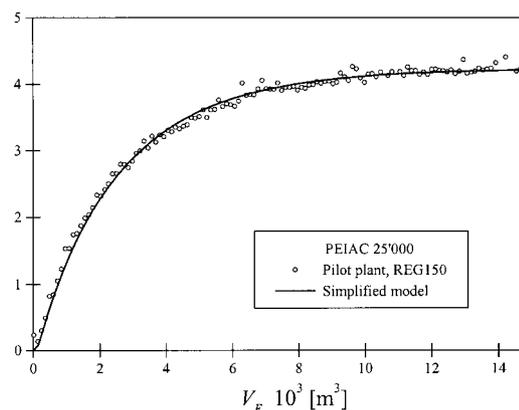
Figure 6. Pilot desorption of Ni^{2+} from the resin Chelamine with *PEIAC* 25'000. $c_{P,0} = 10.38$ mol m^{-3}, $m = 17.05$ g, pH = 7.3, $K_1 = 0.035$ m^3 mol^{-1}, $k_2 = 8.0$ 10^{-3} s^{-1}, $Q = 3.395$ 10^{-6} m^3 s^{-1}, $r = 0.1$, simplified model.

as the types of complexing agents and heavy-metal ions, has shown that the desorption can be described in all cases studied. The kinetic model was used successfully for a scale-up. In the global process of heavy metal recovery, this semiclosed desorption allows almost total recycling of the desorption agent and avoids large consumption of chemicals, as is the case for classical acid-base regeneration. The kinetic study reported in this paper leads to the following conclusions:

1) The type of complexing agent dictates the first equilibrium. The K_1 constant represents the strength of the complexing agent with regard to the desorption.

2) The second equilibrium (or the reaction described by the constant k_2 for the simplified model) depends on the type of heavy metal. The desorption is not complete for the systems *PEIAC* 25'000/Cu^{2+}, *PEIAC* 750'000/Ni^{2+} and *PAA* 20'000/Cu^{2+}, and a final equilibrium is reached.

From the presented results, it can be concluded that the method proposed is simple and effective for the removal of metal ions from dilute solutions and for an efficient desorption of loaded chelating resins with strong complexing agents.

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Symboles used

$c_{P,i}$	[mol m^{-3}]	free polymer sites concentration in the tank *i* of the fixed bed
$c_{P,0}$	[mol m^{-3}]	initial free polymer sites concentration in the CSTR
c_0	[kg m^{-3}]	metal ion concentration of the loading solution
$c_{M,i}$	[mol m^{-3}]	concentration of the polymer-complexed sites PM^{2+} in the tank *i* of the fixed bed
d_t	[m]	column diameter
k_1	[m^3 mol^{-1} s^{-1}]	kinetic constant
k_{-1}	[s^{-1}]	kinetic constant
k_2	[s^{-1}]	kinetic constant
k_{-2}	[m^3 mol^{-1} s^{-1}]	kinetic constant
K_1	[m^3 mol^{-1}]	equilibrium constant
K_2	[mol m^{-3}]	equilibrium constant
m	[kg]	mass of resin in the reactor
M_w	[g mol^{-1}]	mass molecular weight
N	[–]	number of stirred tanks in the fixed bed
Q	[m^3 s^{-1}]	flow rate
q_P	[mol kg^{-1}]	polymer capacity
$q_{c,i}$	[mol kg^{-1}]	metal ion concentration in the intermediary form $\{RM^{2+P}\}$ in the tank *i* of the fixed bed
q_{des}	[mol kg^{-1}]	concentration of desorbed metal
q_i	[mol kg^{-1}]	sum of the metal ion concentrations on the resin RM^{2+} and in the form of intermediary $\{RM^{2+}P\}$ in the tank *i* of the fixed bed
q_{rest}	[mol kg^{-1}]	metal ion concentration remaining on the resin
q_0	[mol kg^{-1}]	initial metal ion concentration on the resin (in equilibrium with concentration c_0)
r_p	[m]	mean radius of the particles
r	[–]	fraction of flow rate going through the dead volume
t	[s]	time
V	[m^3]	volume of the reactor
V_E	[m^3]	volume of liquid passed through the fixed bed
V_M	[m^3]	dead volume
V_C	[m^3]	volume of the CSTR
$V_{C,0}$	[m^3]	initial volume of the CSTR
V_{NaOH}	[m^3]	volume of *NaOH* solution added in the CSTR

Greek letters

γ	[–]	molar ratio P/M^{2+}
$\varepsilon_{PM,\lambda}$	[M^{-1} cm^{-1}]	absorption molar coefficient of the complex PM^{2+}
ε_r	[–]	reactor porosity
λ	[nm]	wave length
τ	[s]	reactor residence time

Abbreviations

CSTR	continuous stirred tank reactor
EDTA	ethylenediamine tetraacetate
M^{2+}	divalent metallic cation
NTA	nitrilotriacetate
P	polymer free site
PAA	polyacrylic acetate
PEIAC	polyethyleneimineacetic acetate
PM^{2+}	complexed-polymer site
R	resin-free site
RM^{2+}	resin site loaded with metal ions
$\{RM^{2+}P\}$	intermediary complex

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