

**Predictive Simulation for Separation of Toxic Metal Ions  
by Ion-Exchange Resins in Complex Media**

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**Abstract**

A calculation program based upon predictions was developed to foresee the separation conditions by ion exchange for two divalent metal ions often encountered together. The simulations were compared to experimental results obtained in similar conditions in complex media. Whilst the separation by batch method was found unlikely for these metals on Dowex-50-X8 resin in these conditions, our program shows that quantitative separation of these species in column is achieved by sequential elutions with chelating agent solution and the correlation with experimental verification applicable. The simulations described could be a didactic illustration for selective separation using these types of resins.

**Key words:** Ion-Exchange, Heavy metals, Zinc, Cadmium, Separation

**Introduction**

Heavy toxic metals often present in liquid industrial wastes and polluted natural waters and soils are very harmful to the environment [1-4]. Although much work has been devoted to this topic over the past decades and relatively recent methods as ion exchange chromatography and solvent extraction have been widely used for trace metals recovery [5-12], the separation of metals with similar properties remains difficult. Selective separation is practically impossible in the absence of complexing agents. Complexation by different ligands allowed to highlight the role of the medium and could lead to improve the separations, whatever the method used [13-23].

Furthermore, the analysts have proven it is well worthy to achieve metal ion separations based upon theoretical predictions which are less time consuming while purely experimental verifications can be minimized as required [24]. The theoretical aspects, especially those introducing the conditional constants, have been established by the pioneers in analytical chemistry [25-29]. Indeed conventional stability constants give little information about the actual stability of compounds in presence of masking agents while conditional stability constants purposely point out the actual speciation and the opportunity to analyze separately metallic ions.

Model heavy metal ions like cadmium, zinc and copper are often used as probes to study the exchange properties of different solid–water interfaces at different media and to understand the mechanisms involved. In this topic, it is interesting to develop a simulation program for heavy metal ions distribution that can fit experimental data and provide predictive results. For this purpose, synthetic solutions consisting of mixtures of two metals, cadmium and zinc were made and interacted with an ion exchange resin. Experimental analytical results were compared to the calculations made with the simulation program for the same pH conditions.

Our aim is to study the contribution of the complexation on the separation of two given elements, with similar properties like cadmium and zinc, often encountered in certain liquid and solid forms of wastes or eventually in drinking waters.

**Theoretical background**

**A. Batch Method**

The batch method consists of bringing into contact the solution containing the metallic ions to be separated with a known amount of the ion exchange resin in a vessel (preferably of polyethylene matter to avoid sorption on the walls). The resin and the solution are therefore stirred with an appropriate agitation item during the time required to reach equilibrium. The very weak concentrations of these metals justify the use of the concentrations instead of activities. At low ionic strength accuracy of estimation of formation constants is generally sufficient [24].

The amount of metal (M) sorbed can be calculated with determining its conditional distribution coefficient given

by:

$$D^M = \frac{[M]_{\text{res}}}{[M]_{\text{sol}}} \quad (1)$$

where:  $[M]_{\text{res}}$  is the metal M concentration in the resin;  
 $[M]_{\text{sol}}$  is the total metal M concentration in the solution.

Thus, for the separation of the divalent metal Cd, at the  $[Cd]_0$  concentration, from the divalent metal Zn, at the  $[Zn]_0$  concentration, on a cation exchange resin,  $Na^+$ -form, in presence of complexing agent L, at the concentration  $[L]_0$ , the exchange reactions and equilibrium constants are given by:



with

$$K_{2Na}^M = \frac{[M^{2+}]_{\text{res}}}{[M^{2+}]_{\text{sol}}} \cdot \left( \frac{[Na^+]_{\text{sol}}}{[Na^+]_{\text{res}}} \right)^2 \quad (3)$$

where M represents zinc and cadmium separately, and  $K_{2Na}^M$  is the selectivity coefficient for the divalent metal M to the exchangeable sodium cation of the resin.

If  $Q_{M(\text{res})}$  is the amount of metal M in the resin and  $Q_{M(\text{sol})}$  that remaining in the solution, it follows:

$$\frac{Q_{M_{\text{res}}}}{Q_{M_{\text{sol}}}} = \frac{m_{\text{res}} [M]_{\text{res}}}{V [M]_{\text{sol}}} = \frac{m_{\text{res}}}{V} D^M \quad (4)$$

where:  $m_{\text{res}}$  is the mass of dry resin;  
 $V$  is the solution volume;

Thence, the separation will be possible as follows:

- To keep less than 0.1% of the metal M in the solution (more than 99.9% sorbed in the resin), the following condition must be satisfied:

$$Q_{M_{\text{sol}}} < 0.1\% Q_{M_{\text{res}}} \quad \text{or} \quad \frac{Q_{M_{\text{res}}}}{Q_{M_{\text{sol}}}} > 1000 \quad (5)$$

Thus:

$$D^M > \frac{V}{m_{\text{res}}} \cdot 10^3 \quad (6)$$

- On the other hand, to keep at least 99.9% of the metal M in the solution (less than 0.1% sorbed in the resin, or zero fixation), the following condition must be satisfied:

$$Q_{M_{\text{res}}} < 0.1\% Q_{M_{\text{sol}}} \quad \text{or} \quad \frac{Q_{M_{\text{res}}}}{Q_{M_{\text{sol}}}} < 0.001 \quad (7)$$

Thus:

$$D^M < \frac{V}{m_{\text{res}}} \cdot 10^{-3} \quad (8)$$

Consequently, we have to determine the theoretical range of pH in which the metal Cd remains completely in solution while the other metal Zn passes completely in the resin or conversely. The conditional distribution coefficients (depending of the pH of the solution) must then be calculated using equation (1). As recommended by the International Union of Pure and Applied Chemistry (IUPAC), the notation is abridged as follows: H, OH, M, L, ... instead of  $H^+$  (or  $H_3O^+$ ),  $OH^-$ ,  $M^{n+}$ ,  $L^m$ , ... with a view of simplification.

The IUPAC notation using the overall constants leads therefore to write:

$$[M]_{\text{sol}(\text{tot})} = [M^{2+}] \alpha_{M(L,OH)} \quad (9)$$

where the cumulative coefficients  $\alpha_{M(L,OH)}$  of complexation by L and OH ligands, and  $\alpha_{M(L)}$  and  $\alpha_{M(OH)}$  the "individual" coefficients of complexation by L and OH respectively, are given below (without indicating the charges of the species, as recommended by IUPAC and noted above):

$$\alpha_{M(L,OH)} = \alpha_{M(L)} + \alpha_{M(OH)} - 1 \quad (10)$$

$$\alpha_{M(L)} = 1 + \sum_i K_{ML_i}^{iL} [L]^i \quad (11)$$

$$\alpha_{M(OH)} = 1 + \sum_i K_{M(OH)_i}^{iOH} [OH]^i \quad (12)$$

The constants  $K_{ML_x}^{xL}$  and  $K_{M(OH)_y}^{yOH}$  are the so called overall formation (or cumulative or else global) constants of the complexes of the metals Cd and Zn with the ligands L and OH<sup>-</sup>. The conditional distribution coefficients of the two metals are written as follows:

$$D^M = \left( \frac{[Na^+]_{res}}{[Na^+]_{sol}} \right)^2 \frac{K_{2Na}^M}{\alpha_{M(L,OH)}} \quad (13)$$

The concentration of the free ligand (not bound to the metals), noted as [L'] may be expressed by:

$$[L'] = [L] + \sum_i [LH_i] = [L] \alpha_{L(H)} \quad (14)$$

where

$$\alpha_{L(H)} = 1 + \sum_i K_{LH_i}^{iH} [H]^i \quad (15)$$

and L would be a polybase (a mono-, bi-, or mostly a tri-, tetra-, penta-, or hexa-base) like chloride, iodide, oxalate, citrate, EDTA, DCTA, EGTA, ...

The latter masking agents have been found earlier by Schwartzenbach and contemporaries [25, 26] to be very useful in analytical chemistry since the complexation could be reinforced by the chelate effect. The most important of these so-called aminopolycarboxylic acids is ethylenediaminetetra-acetic acid: EDTA because of its powerful complexing action and availability [25, 26].

Other complexing agents (complexones) include (a) nitrilotriacetic acid: NITA or NTA, (b) trans-1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid whose abbreviated name is CDTA, DCyTA or DCTA, (c) 2,2'-ethylenedioxybis {ethyliminodi(acetic acid)} also known as ethylene glycolbis(2-aminoethyl ether)N,N,N',N'-tetraacetic acid (EGTA), and (d) triethylenetetramine-N,N,N',N'',N''',N''''-hexaacetic acid (TTHA). EDTA is also used as Fe-EDTA complex against anemia in medicine as well in other fields like environmental studies [30].

In most cases, the metals are present in trace amounts, so the amounts of exchanged counter-ion (sodium) will be negligible and we can consider that  $[Na^+]_{sol}$  is constant and then:

$$[Na^+] \cong C_E \quad (16)$$

where  $C_E$  is the exchange capacity of the resin.

When the metal ions  $Cd^{2+}$  and  $Zn^{2+}$  are present together, the total concentration of the ligand is given by:

$$[L]_0 = [L'] + \sum_i [CdL_i] + \sum_j [ZnL_j] \quad (17)$$

This can be written as:

$$[L]_0 = [L'] + [Cd^{2+}] \sum_i (i K_{CdL_i}^{iL} [L]^i) + [Zn^{2+}] \sum_j (j K_{ZnL_j}^{jL} [L]^j) \quad (18)$$

Thence:

$$[L] = \frac{[L]_0 - [Cd^{2+}] \sum_i (i K_{CdL_i}^{iL} [L]^i) - [Zn^{2+}] \sum_j (j K_{ZnL_j}^{jL} [L]^j)}{\alpha_{L(H)}} \quad (19)$$

In addition, the total concentration of the metals can be given by:

$$[M^{2+}]_0 = [M^{2+}]_{\text{sol(tot)}} + [M^{2+}]_{\text{res}} \quad (20)$$

Therefore:

$$D^M = \frac{[M]_0}{[M^{2+}] \alpha_{M(L,OH)}} - 1 \quad (21)$$

This leads to:

$$[M^{2+}] = \frac{[M]_0}{\left( \frac{[Na^+]_{\text{res}}}{[Na^+]_{\text{sol}}} \right)^2 K_{2Na}^M + \alpha_{M(L,OH)}} \quad (22)$$

#### B. Dynamic Method (1-line space)

In this case, only the total or null retention conditions change. Actually, according to Ringböm [24], the assumptions are the followings:

○ The metal M will be completely retained by the resin if:  $D^M > 5 \frac{V}{m_{\text{res}}} \quad (23)$

○ It will be completely eluted away from the resin if:  $D^M < \frac{V}{5m_{\text{res}}} \quad (24)$

○ The maximal elution volume is:  $V_{\text{max}} = D^M \cdot m_{\text{res}} + V_i \quad (25)$

○ The critical elution volume is:  $V_{0.1\%} = V_{\text{max}} \left( 1 - 3.09N^{-\frac{1}{2}} \right) \quad (26)$

○ The total elution volume is:  $V_{99.9\%} = 2V_{\text{max}} - V_{0.1\%} \quad (27)$

The symbols and units used here are explained as follows:

- V is the eluted volume (in mL) ;
- $V_i$  is the interstitial volume of the ion-exchange column (The relative interstitial volume is given by  $V_i/V_r$  and has values generally in the range 30% to 40% ;  $V_r$  is the resin bed volume);
- N is the number of theoretical plates ;
- $m_{\text{res}}$  is the mass of the resin (g) ;
- the number « 5 » is derived from « the fifth and fivefold » volume of the eluted one.
- Actually, it has been assumed that:
- the metal M is not found in the eluate in the first fifth volume of the elution peak, which can be expressed as:

$$V < \frac{V_{\text{max}}}{5} = \frac{D^M \cdot m_{\text{res}} + V_i}{5} \quad (28)$$

then  $D^M > \frac{5V - V_i}{m_{\text{res}}} \quad (29)$

- the elution of M is complete when the eluted volume is the quintuple of the peak volume.

Therefore, this is expressed by:

$$V > 5V_{\text{max}} = 5(D^M \cdot m_{\text{res}} + V_i) \quad (30)$$

then  $D^M < \frac{\left( \frac{V}{5} - V_i \right)}{m_{\text{res}}} \quad (31)$

Considering all the preceding equations, it is obvious that, for a given value of pH, the distribution coefficients can be conveniently calculated by numerical simulation. The flowchart of the Turbo-Pascal program specially conceived for this and named "Seplon" is given in Figure 1).

When the constants of the complexes formed differ from one another with at least five powers of ten, the separations will become very easy [24].

To illustrate the method, we present an application to the quantitative separation of Zn(II) and Cd(II) on Dowex-50 X8 with the conditions:

- The complexing agents (noticed L) studied are EGTA, Oxalate, Tartrate and Acetate ;
- The initial concentration of the metals is:  $10^{-5}$  mole/L;
- The total concentration of the complexing agent used is:  $10^{-3}$  mole/L;
- The selectivity coefficient of the zinc is: 0.6;
- The selectivity coefficient of the cadmium is: 0.76;
- The ion exchange capacity of the resin is: 5 meq/g;
- The concentration of  $\text{Na}^+$  ions in solution is: 0.1 mole/L;
- The succeeding formation constants of the ligands L with  $\text{H}^+$  ions are given in Table 1.
- The global complex formation constants of the ligands L with Zn(II) and Cd(II) are given in Table 2 below.

Table 1: Logarithms of the stepwise formation constants of the ligands noticed L with  $\text{H}^+$  ions at ionic strength  $\mu = 0.1$  (when needed, the values were converted to  $\mu = 0.1$  using the approached conversion abacus), according to Ringböm [24].

Ligand (L)	$\text{LogK}_{\text{HL}}^{\text{H}}$	$\text{LogK}_{\text{H}_2\text{L}}^{2\text{H}}$	$\text{LogK}_{\text{H}_3\text{L}}^{3\text{H}}$	$\text{LogK}_{\text{H}_4\text{L}}^{4\text{H}}$
EGTA	9.54	8.93	2.73	2.08
Oxalate	4.0	1.1	-	-
Tartrate	4.1	2.9	-	-
Acetate	4.65			

Table 2: Logarithms of the global complex formation constants of the ligands L with Zn(II) and Cd(II) at ionic strength  $\mu = 0.1$  (when needed, the values were converted to  $\mu = 0.1$  using the approached conversion abacus), according to Ringböm [24].

Ligand L	EGTA	Oxalate		Tatrate	Acetate				$\text{OH}^-$			
	ML	ML	$\text{ML}_2$	ML	ML	$\text{ML}_2$	$\text{ML}_3$	$\text{ML}_4$	ML	$\text{ML}_2$	$\text{ML}_3$	$\text{ML}_4$
Cd	15.6	3.24	5.04	3.14	1.19	2.37	2.27	1.86	4.49	8.17	10.77	12.56
Zn	12.8	4.04	6.34	2.74	1.3	2.1	-	-	4	10.66	13.76	15.02

1. Batch method:
  - The masse of the dry resin used is: 0.5g;
  - The volume of the solution is: 25 mL;
2. Column method:
  - The mass of the dry resin used is: 10g ;
  - The volume of the solution to percolate is: 240 mL;
  - The height of the resin bed is: 90 mm;
  - The internal diameter of the column is: 16 mm;
  - The interstitial volume of the column is: 7.12 mL;

The calculation steps of the "Seplon" program are illustrated by the flowchart given below (Figure 1).

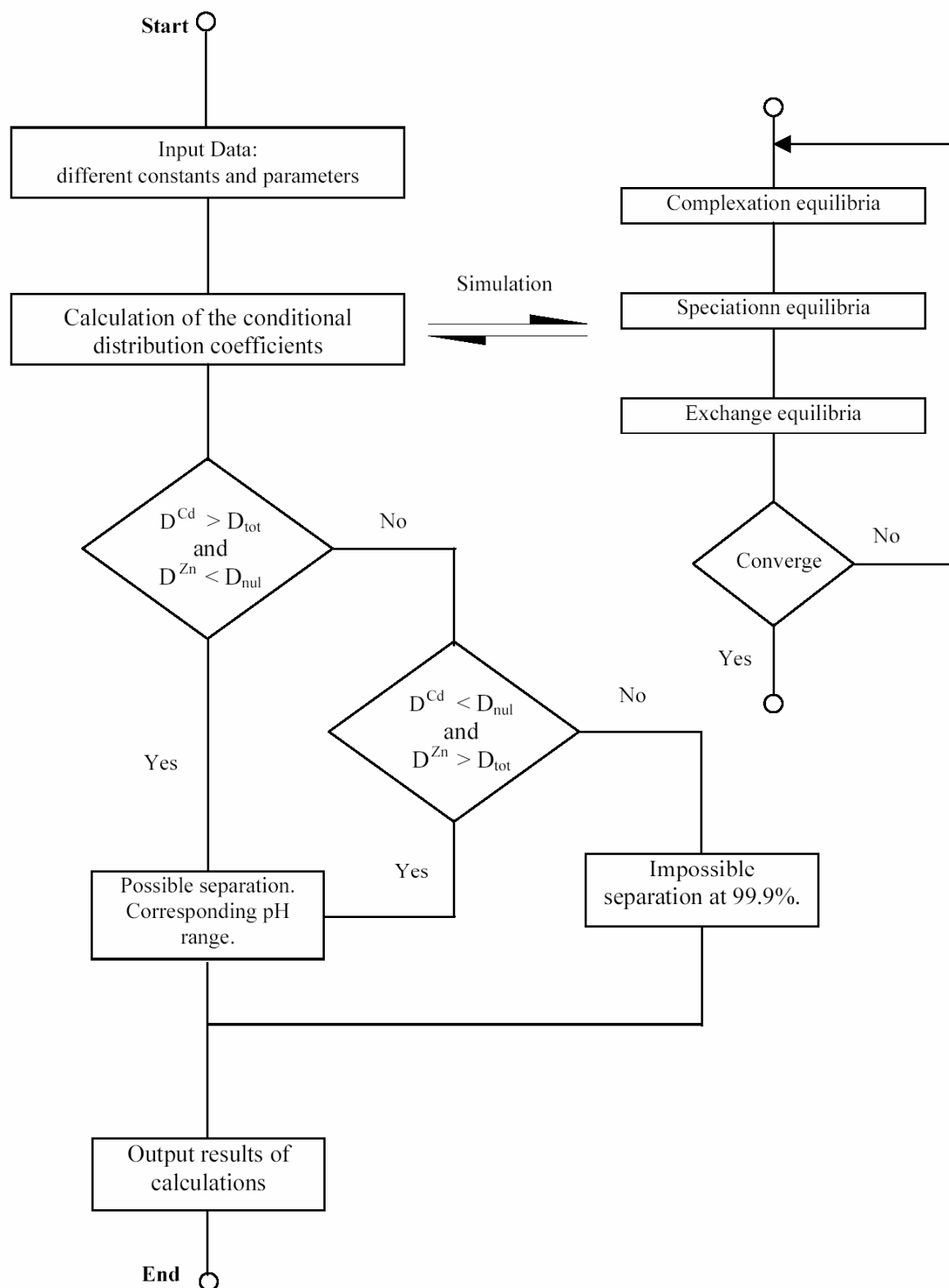


Figure 1 Flowchart of the calculation program "Seplon".  $D$ , conditional distribution coefficients.  $D_{tot}$  and  $D_{nul}$ , limits of the total and null fixation respectively.

## Experiment

To verify the simulating results, batch and column experiments were carried out under conditions as similar as possible to those chosen for the theoretical calculations. Dowex-50 X8 (Na<sup>+</sup> form, 71-125 μm) was used as the cation exchanger resin. EGTA, oxalate, tartrate and acetate were used as the complexing agents for the batch method while EGTA and oxalate at convenient pH values were used as the eluent systems for the column method.

The batch experiments were carried out using polyethylene bottles. In order to set the required shaking time, kinetic experiments were carried out. In this case, 0.5 g of a Dowex-50 X8 resin was added to 25 mL of a solution containing the metallic ions M<sup>2+</sup> at a concentration of 5 mmol.L<sup>-1</sup> and the mixture was shaken at 120 knocks/min. The amounts of sorbed M<sup>2+</sup> on the solid phase were then determined for different contact times. For the separation experiments, 25 mL of the solution containing both Cd<sup>2+</sup> and Zn<sup>2+</sup> at a concentration of 0.01 mmol.L<sup>-1</sup> were mixed with 0.5 g of the resin in the presence of 1 mmol.L<sup>-1</sup> of the complexing agent and the mixture was shaken at 120 knocks/min during 60 min.

The dynamic experiments were carried out with columns of 16 mm internal diameter and the height of the bed resin was 9 cm (corresponding to 10 g of the resin used). A small volume of 2.5 mL of a solution containing 0.2696 mg of cadmium and 0.1738 mg of zinc was poured on the top of the resin bed. After that the adsorbed metal mixture was eluted (the flow rate was about 3-4 mL/min) by 240 mL of a solution containing a complexing agent (EGTA or oxalate) at appropriate conditions of concentration and pH, allowing the separation of the two elements.

A plasma vista AX CCD simultaneous ICP-AES spectrometer was used to determine the amount of ions remaining in solution. The amounts of metallic ions in the resin phase were determined after an elution (desorption) with 0.1 N nitric acid. The selectivity coefficients  $K_{2Na}^M$  were determined by studying the sorption of Cd<sup>2+</sup> and Zn<sup>2+</sup> (individually) on Dowex-50 X8 resin in batch equilibrium at room temperature (21 ± 0.1°C) as a function of the contact time. After the equilibration time reached, corresponding to maximum sorption stage, the amounts of Cd<sup>2+</sup> and Zn<sup>2+</sup> fixed on the resin and those remaining in solution as well as the quantity of Na<sup>+</sup> in both the solid and aqueous phases were determined. This allowed us to evaluate the selectivity coefficients according the equation 3 given above.

The values of  $K_{2Na}^M$  used herein for theoretical calculation are the average of the results of several experiments.

## Results and discussion

The results of the theoretical calculations by Seplon program are given below and reported in Figures 2-5.

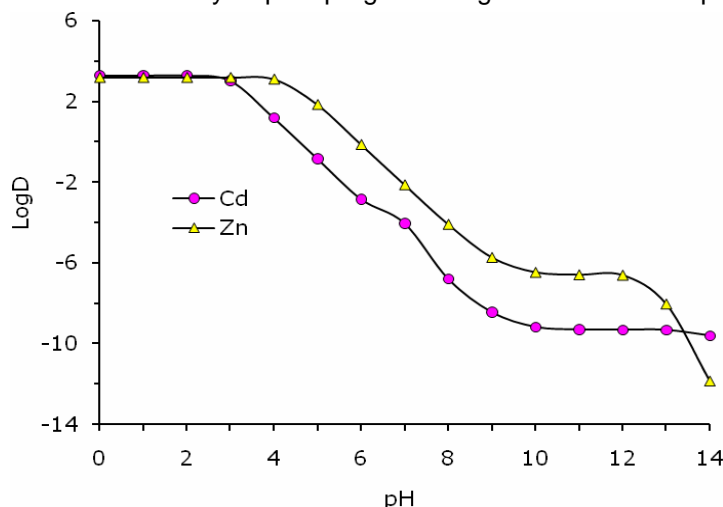


Figure 2 Conditional distribution coefficients of Zn(II) and Cd(II) on Dowex-50 X8 (Na<sup>+</sup> form) in presence of EGTA in solution, calculated with Seplon program.

According to the kinetic experiments, as it is shown by the figure 6 below about 30 min of contact time were widely sufficient for the ion-exchange to reach the equilibrium. Then, for all the other batch experiments the shaking time was fixed to 60 min to ensure the maximum of metal sorption.

To predict the separations of elements, an essential condition obviously appears to be the knowledge of the stability constants of complexes; however, any estimate must be the subject of experimental verification to make sure whether a slow step or unfavorable complex-formation kinetics will not prevail over the advantages offered by a possible difference of the separation factors.

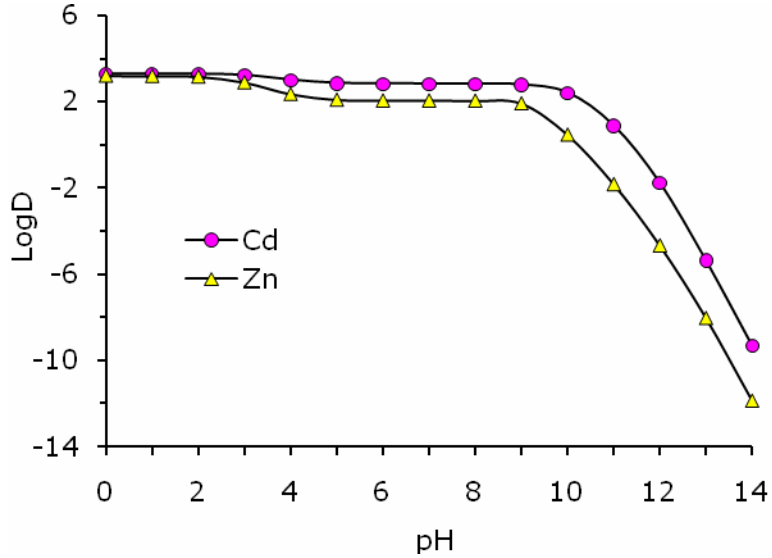


Figure 3 Conditional distribution coefficients of Zn(II) and Cd(II) on Dowex-50 X8 (Na<sup>+</sup> form) in presence of oxalate in solution, calculated with Seplon program

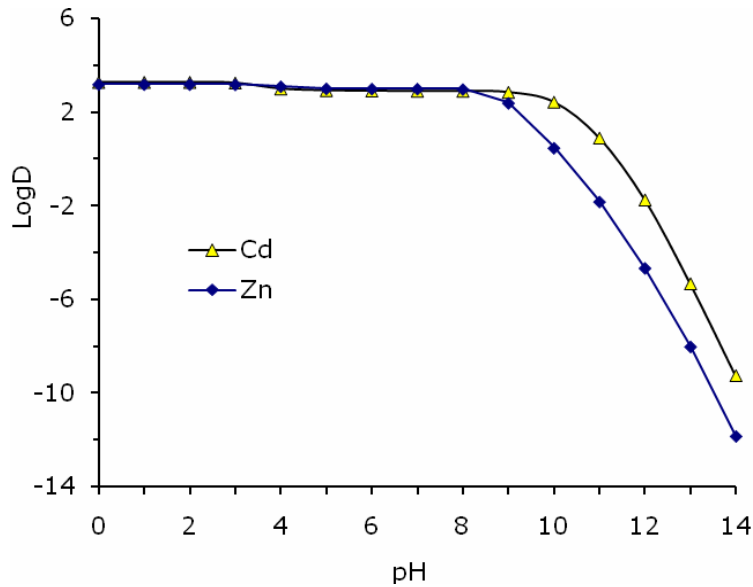


Figure 4 Conditional distribution coefficients of Zn(II) and Cd(II) on Dowex-50 X8 (Na<sup>+</sup> form) in presence of tartrate in solution, calculated with Seplon program.

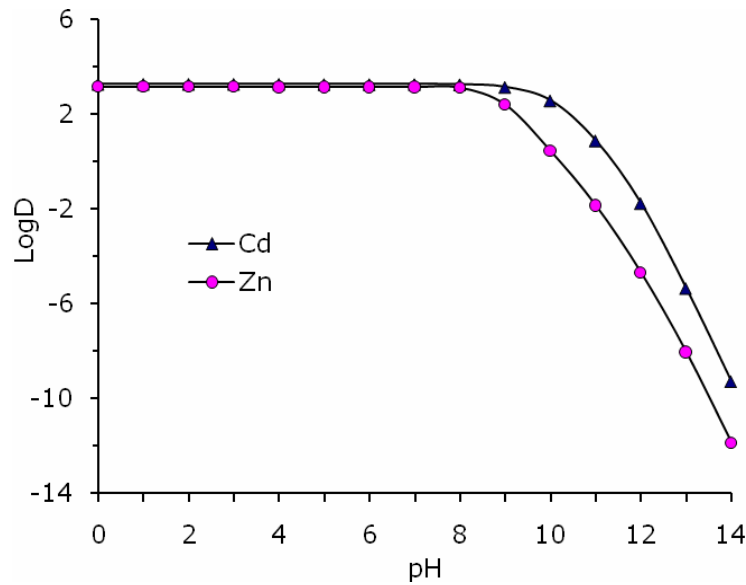


Figure 5 Conditional distribution coefficients of Zn(II) and Cd(II) on Dowex-50 X8 (Na<sup>+</sup> form) in presence of acetate in solution, calculated with Seplon program.

This separation will become possible in a media containing a complexing agent under optimal conditions such as pH regions allowing a retention efficiency of nearly 100% for a chosen metal, while the anionic or neutral species formed with the other cations are not retained by the cation-exchanger. The separation of the metals will then occur by eluting the resin with a solution containing the complexing agent at the chosen pH.

As already pointed out, there are many parameters involved, and it is essential to perform several calculations by taking into account all these factors. However, ion-exchange experiments have been conducted in similar conditions in order to corroborate them with the simulation results. A comparative experimental study was done with “targeting” a difficult case, to separate cadmium and zinc whose properties are quite often similar even with using common complexing agents.

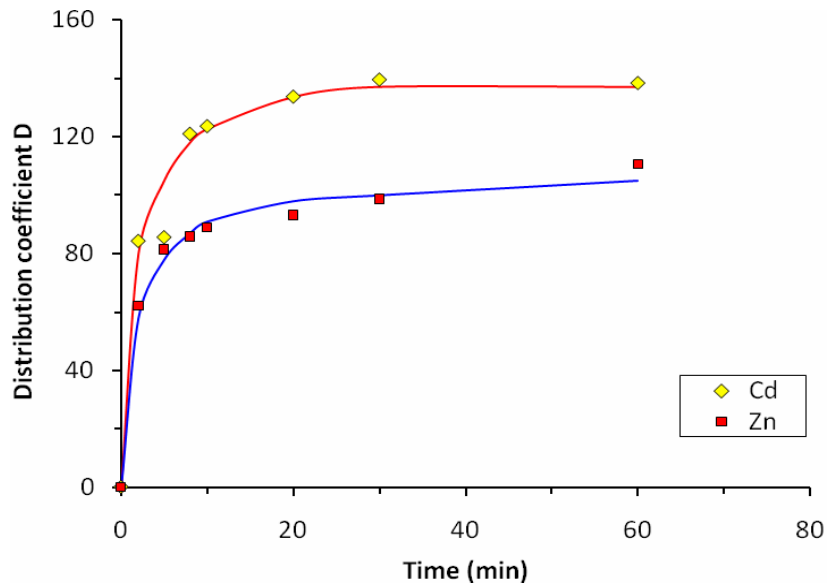


Figure 6 Dependence of the distribution coefficients of Cd and Zn between the Dowex-50 X8 resin and the aqueous solution as a function of the shaking time.

The theoretical calculation for batch equilibrium (Figures 2-5 and Tables 3-6) showed the impossibility of the separation of Zn(II) and Cd(II) under these conditions.

For column method, the theoretical simulations showed that Zn(II) and Cd(II) could be separated at 99.9% within pH 4.27-4.88 in presence of EGTA where Zn(II) passes completely into the resin and Cd(II) remains in solution, and that Zn(II) could then be eluted (for example) with 234 mL of a solution of EGTA 0.001M at pH 5.3.

Also, it showed that Zn(II) and Cd(II) could be separated at 99.9% within pH 9.91-10.32 in presence of oxalate where Cd(II) passes completely into the resin and Zn(II) remains in solution, and that Cd(II) could then be eluted (for example) with 260.76 mL of a solution of oxalate 0.001M at pH 10.8.

Table 3: Results of Seplon calculations for Cd and Zn separation by batch method in presence of EGTA as complexing agent in solution.

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Separation of Cd and Zn by BATCH METHOD

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Fixation of Cd and Zn on the resin Dowex-50 X8 (Na<sup>+</sup>-form)  
 In presence of the competing agent EGTA (noticed L) vs pH:  
 $K_{2NaCd} = 0.76$ ,  $K_{2NaZn} = 0.60$   
 $C_e = 5.00$  meq/g,  $[Na]_{sol} = 0.10$  M,  
 $[L]_o = 0.0010$  M,  $[Cd]_o = 0.000010$  M,  $[Zn]_o = 0.000010$  M  
 $m_r = 0.50$  g,  $v = 25.00$  ml.

pH	Log $\alpha_{Cd(L,OH)}$	Log $\alpha_{Zn(L,OH)}$	Log $\alpha_{L(H)}$	Log D <sub>Cd</sub>	Log D <sub>Zn</sub>
0	0.00	0.00	23.28	3.28	3.18
1	0.00	0.00	19.32	3.28	3.18
2	0.00	0.00	15.58	3.28	3.18
3	0.26	0.00	12.67	3.02	3.18
4	2.10	0.00	10.49	1.18	3.10
5	4.12	1.34	8.47	-0.84	1.84
6	6.12	3.32	6.47	-2.84	-0.14
7	8.12	5.32	4.48	-4.84	-2.14
8	10.07	7.27	2.52	-6.79	-4.10
9	11.72	8.92	0.87	-8.44	-5.74
10	12.45	9.65	0.14	-9.17	-6.48
11	12.58	9.78	0.01	-9.30	-6.60
12	12.59	9.79	0.00	-9.31	-6.62
13	12.60	11.23	0.00	-9.32	-8.05
14	12.88	15.04	0.00	-9.60	-11.87

Total fixation at more than 99.9% (Log D > 4.70) for :

Cd : no total fixation at 99.9%

Zn : no total fixation at 99.9%

Zero fixation at less than 0.1% (Log D < -1.30) for :

Cd at pH > 5.23

Zn at pH > 6.57

There is no possibility of separation in these conditions !

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Table 4: Results of Seplon calculations for Cd and Zn separation by batch method in presence of Oxalate as complexing agent in solution.

Separation of Cd and Zn by BATCH METHOD

Fixation of Cd and Zn on the resin Dowex-50 X8 (Na<sup>+</sup>-form)  
 In presence of the competing agent Oxalate (noticed L) vs pH:  
 $K_2NaCd = 0.76$ ,  $K_2NaZn = 0.60$   
 $C_e = 5.00$  meq/g,  $[Na]_{sol} = 0.10$  M,  
 $[L]_o = 0.0010$  M,  $[Cd]_o = 0.000010$  M,  $[Zn]_o = 0.000010$  M  
 $m_r = 0.50$  g,  $v = 25.00$  ml.

pH	Log $\alpha_{Cd(L,OH)}$	Log $\alpha_{Zn(L,OH)}$	Log $\alpha_{L(H)}$	Log $D_{Cd}$	Log $D_{Zn}$
0	0.00	0.00	5.13	3.28	3.18
1	0.00	0.00	3.35	3.28	3.17
2	0.01	0.04	2.06	3.27	3.14
3	0.06	0.30	1.05	3.22	2.87
4	0.28	0.85	0.30	3.00	2.33
5	0.43	1.11	0.04	2.85	2.07
6	0.45	1.15	0.00	2.83	2.03
7	0.45	1.15	0.00	2.82	2.03
8	0.46	1.15	0.00	2.78	2.02
9	0.50	1.28	0.00	2.82	1.90
10	0.87	2.72	0.00	2.41	0.45
11	2.39	5.02	0.00	0.89	-1.84
12	5.04	7.86	0.00	-1.76	-4.68
13	8.63	11.21	0.00	-5.35	-8.04
14	12.57	15.04	0.00	-9.29	-11.87

Total fixation at more than 99.9% (Log D > 4.70) for :

Cd : no total fixation at 99.9%

Zn : no total fixation at 99.9%

Zero fixation at less than 0.1% (Log D < -1.30) for :

Cd at pH > 11.85

Zn at pH > 10.78

There is no possibility of separation in these conditions !

Table 5: Results of Seplon calculations for Cd and Zn separation by column method in presence of EGTA as complexing agent in solution.

Separation of Cd and Zn by COLUMN METHOD

Fixation of Cd and Zn on the resin Dowex-50 X8 (Na<sup>+</sup>-form)  
 In presence of the competing agent EGTA (noticed L) vs pH:  
 $K_2NaCd = 0.76$ ,  $K_2NaZn = 0.60$   
 $C_e = 5.00$  meq/g,  $[Na]_{sol} = 0.10$  M,  
 $[L]_o = 0.0010$  M,  $[Cd]_o = 0.000010$  M,  $[Zn]_o = 0.000010$  M  
 $m_r = 10.00$  g,  $V = 240.00$  ml.  
 The height of the resin bed:  $L_c = 90.00$  mm  
 The internal diameter of the column:  $i_d = 16.00$  mm

pH	Log $\alpha_{Cd(L,OH)}$	Log $\alpha_{Zn(L,OH)}$	Log $\alpha_{L(H)}$	Log $D_{Cd}$	Log $D_{Zn}$
0	0.00	0.00	23.28	3.28	3.18
1	0.00	0.00	19.32	3.28	3.18
2	0.00	0.00	15.58	3.28	3.18
3	0.26	0.00	12.67	3.02	3.18
4	2.10	0.08	10.49	1.18	3.10
5	4.12	1.34	8.47	-0.84	1.84
6	6.12	3.32	6.47	-2.84	-0.14
7	8.12	5.32	4.48	-4.84	-2.14
8	10.07	7.27	2.52	-6.79	-4.10
9	11.72	8.92	0.87	-8.44	-5.74
10	12.45	9.65	0.14	-9.17	-6.48
11	12.58	9.78	0.01	-9.30	-6.60
12	12.59	9.79	0.00	-9.31	-6.62
13	12.60	11.23	0.00	-9.32	-8.05
14	12.88	15.04	0.00	-9.60	-11.87

Total fixation at more than 99.9% (Log D > 2.08) for :

Cd at pH < 3.56

Zn at pH < 4.88

Zero fixation at less than 0.1% (Log D < 0.62) for :

Cd at pH > 4.27

Zn at pH > 5.61

Cd and Zn could be separated within  $4.27 < \text{pH} < 4.88$

region where Zn passes completely into the resin and Cd remains in solution

Zn could be eluted with a solution of EGTA ( $[EGTA]_o = 0.0010$  M) at pH = 5.3

The critical volume of elution for Zn is :  $V(0.1\%) = 118.97$  mL

The volume of total elution for Zn is :  $V(99.9\%) = 233.90$  mL

Table 6: Results of Seplon calculations for Cd and Zn separation by column method in presence of oxalate as complexing agent in solution.

Separation of Cd and Zn by COLUMN METHOD

Fixation of Cd and Zn on the resin Dowex-50 X8 (Na<sup>+</sup>-form)  
 In presence of the competing agent Oxalate (noticed L) vs pH:  
 $K_{2NaCd} = 0.76$ ,  $K_{2NaZn} = 0.60$   
 $C_e = 5.00$  meq/g,  $[Na]_{sol} = 0.10$  M,  
 $[L]_o = 0.0010$  M,  $[Cd]_o = 0.000010$  M,  $[Zn]_o = 0.000010$  M  
 $m_r = 10.00$  g,  $V = 240.00$  ml.  
 The height of the resin bed:  $L_c = 90.00$  mm  
 The internal diameter of the column:  $i_d = 16.00$  mm

pH	Log $\alpha_{Cd(L,OH)}$	Log $\alpha_{Zn(L,OH)}$	Log $\alpha_{L(H)}$	Log $D_{Cd}$	Log $D_{Zn}$
0	0.00	0.00	5.13	3.28	3.18
1	0.00	0.00	3.35	3.28	3.17
2	0.01	0.04	2.06	3.27	3.14
3	0.06	0.30	1.05	3.22	2.87
4	0.28	0.85	0.30	3.00	2.33
5	0.43	1.11	0.04	2.85	2.07
6	0.45	1.15	0.00	2.83	2.03
7	0.45	1.15	0.00	2.82	2.03
8	0.46	1.15	0.00	2.82	2.02
9	0.50	1.28	0.00	2.78	1.90
10	0.87	2.72	0.00	2.41	0.45
11	2.39	5.02	0.00	0.89	-1.84
12	5.04	7.86	0.00	-1.76	-4.68
13	8.63	11.21	0.00	-5.35	-8.04
14	12.57	15.04	0.00	-9.29	-11.87

Total fixation at more than 99.9% (Log D > 2.08) for :

Cd at pH < 10.32  
 Zn at pH < 4.94

Zero fixation at less than 0.1% (Log D < 0.62) for :

Cd at pH > 11.12  
 Zn at pH > 9.91

Cd and Zn could be separated within  $9.91 < \text{pH} < 10.32$   
 region where Zn passes completely into the resin and Cd remains in solution  
 Zn could be eluted with a solution of Oxalate ( $[Oxalate]_o = 0.0010$  M) at pH = 5.3

The critical volume of elution for Zn is :  $V(0.1\%) = 132.63$  mL  
 The volume of total elution for Zn is :  $V(99.9\%) = 260.76$  mL

From Figure 7 showing the plot of both theoretical and experimental results in a same figure with a region of expanded scale, it could be presumed that the correlation between them is reasonably relevant, notwithstanding the lack of data.

The fact that either the constant values used in the simulating program are somewhat erroneous or to the operating conditions which are not rigorously the same could explain the deviations of the experimental results from the theoretical ones.

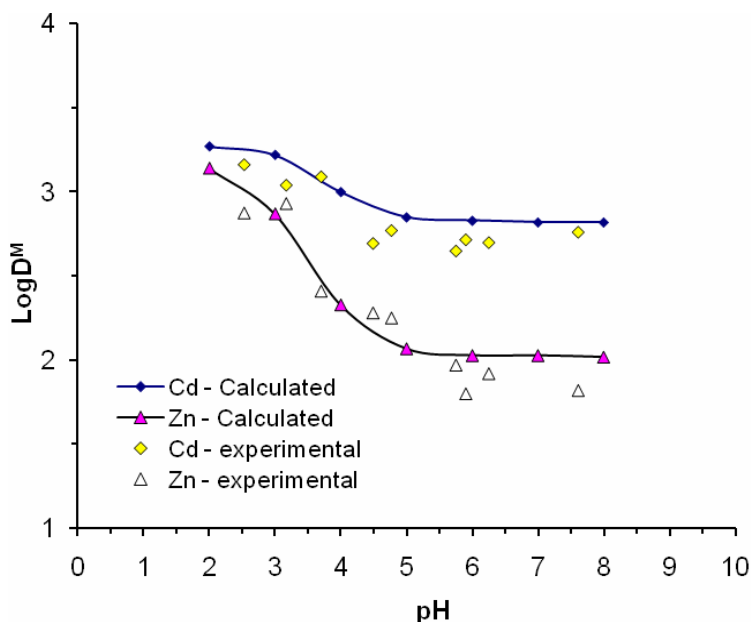


Figure 7 Correlation of some experimental results with theoretical conditional distribution coefficients of Zn(II) and Cd(II) on Dowex-50 X8 ( $\text{Na}^+$  form) in presence of EGTA in solution calculated with Seplon program.

The experiments in the ranges of pH 0-2 and pH 8-14 have not been conducted because of the detrimental effects of the acidity and the alkalinity, respectively. In acidic media, the complexes are not very stable and the only forms present are thought to be the free cationic metals.

The formation of hydroxides and mixed MOHL as well as MHL complexes in alkaline and acidic media respectively may occur and compete with the  $\text{ML}_i$  complexes [24, 25, 28, 29]. Therefore the actual speciation would be completely modified and the statements distorted. So, in practice the separation of  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  is considered to be unlikely in these two pH ranges.

### Conclusion

The theoretical background used here is obtainable in the literature, but the availability of microcomputing facilities and their widespread use justifies renewed interest in affordable simulation programs. Beside our experimental studies, we have developed a computing program concerned with the separation of two divalent metals by ion-exchange chromatography taking into account all aspects of the complexation phenomenon. The column studies showed that the experimental verification is quite relevant in a wide pH range and the separation by sequential elutions is possible and quantitative. We hope that this didactic contribution, after its improvement with a required development taking into account the actual speciation, will serve to illustrate how calculations can help to determine rapidly best conditions for selective metal removal from contaminated waters.

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