Kinetics analysis of zinc sorption in fixed bed column using a strongly basic anionic exchange resin
Emilia Gîlçă, Andrada Măicăneanu and Petru Ilea

ABSTRACT
The aim of this study was to examine the capacity of anionic resins to remove zinc as zinc chloride complexes in fixed bed. The applicability of the kinetics models and the characteristics of the bed (sorption capacity, breakthrough curve, depth of the adsorption zone) were taken into account. The influence of the process parameters, such as resin quantity (bed height) and zinc initial concentration, on the removal process was also considered. The obtained results (Amberlite IRA410) were analyzed using sorption kinetic models such as Thomas, Adam-Bohart, and Clark, by linear regression analysis. Similarly, the concept of the mass transfer zone was applied in order to properly design the fixed bed adsorption process. By comparing various resins, the following series was depicted based on sorption capacities: Amberlite IRA410 > Purolite A103S > Purolite NRW700 > Purolite A400MBOH. The experimental data were in good agreement with the Clark model, while for the other models, lower correlation coefficients were obtained under the same experimental conditions. The MTZ height and rate of movement increased with increasing initial concentration.

Key words | Amberlite IRA410, anionic exchangers, hot-dip galvanizing, kinetics

INTRODUCTION
Metal plating has been identified as an industrial sector that poses an enormous risk concerning the potential hazardous nature of its waste streams since they often contain various amounts of acids and heavy metals (Mansur et al. 2008). The hot-dip galvanizing process generates several types of effluents containing zinc, iron and hydrochloric acid (Carrera et al. 2009). Therefore, it is necessary to use feasible processes to minimize the pollution caused by zinc discharges that give rise to an environmental problem due to their hazardous nature (Carrillo-Abad et al. 2012; Gîlçă et al. 2014). Ion exchange treatment, beside adsorption, is the second most widely used method for metal removal and presents some advantages like valuable metal recovery, selectivity, less sludge produced, low operational costs and high efficiency and also allows handling of large volumes of wastewaters (Abdelwahab et al. 2013; Gîlçă et al. 2014). Zinc chloride in the contaminated effluents from the hot-dip galvanizing process exists as anionic complexes, ZnCl$_3^-$ and ZnCl$_4^{2-}$, with ZnCl$_4^{2-}$ as the predominant species. Ferrous iron will not form an anionic complex in the specific conditions, therefore zinc can be selectively separated by an anion exchange resin (Haines et al. 1973; Miesiac 2005).

In this paper, synthetic solutions of zinc (as zinc chloride complexes) were used to examine the performances of several anionic exchange resins in a fixed bed. Influence of the process parameters such as resin quantity (bed height) and zinc initial concentration were considered. The results obtained on the best anionic exchange resin were analyzed using sorption kinetic models (Thomas, Adam-Bohart, Clark). Characteristics of the adsorption zone and diffusion parameters were also taken into account.

EXPERIMENTAL
Resins and solutions
Four anionic exchange resins, Amberlite IRA410, Purolite A103S, Purolite A400MBOH and Purolite NRW700, were taken into consideration for this investigation. Their characteristics were presented in a previous study (Gîlçă et al. 2014). Before usage, the resins were soaked in double-distilled water for 24 hours and then washed several times.
Initial zinc solutions (300–1,100 mg/L) were prepared by dissolving ZnCl₂ salt in 1 M hydrochloric acid. All used chemicals were of analytical purity.

Apparatus and analytical procedure

A glass column (φ = 12 mm and height 210 mm) was used for the experiments. The column was equipped with a glass frit for support and a layer of glass wool to prevent the escape of the resins beads (1–6 g, 18–108 mm bed heights) during operation. The scheme of the experimental setup is presented in Figure 1.

The synthetic solution (1.36 mL/min flow rate) having zinc concentrations ranging from 300 to 1,100 mg/L was allowed to pass through the column in continuous downflow mode using a peristaltic pump, Ismatec Switzerland). All the experiments were conducted at room temperature (23 ± 2 °C). The treated metal solution (20.5 mL) was collected at the outlet of the column every 15 minutes and analyzed. The concentration of zinc in solutions was determined using an atomic absorption spectrophotometer, Avanta PM GBC (Australia). All the experiments were realized in triplicate and the average value was used.

The amount of sorbed zinc (sorption capacity), at time $t$, was calculated using the following equation:

$$q_t = \frac{(C_0 - C_t)V}{m} + q_{t-1}$$

where $C_0$ and $C_t$ are the initial and time $t$ zinc ion concentrations (mg/L), $q_t$ and $q_{t-1}$ are the amount of metal ions sorbed at times $t$ and $t-1$, respectively (mg/g), $V$ is the volume of zinc solution (L), $m$ is the mass of the resin (g), and $q_t$ is the value calculated at the end of the experiment.

Methods

Thomas, Adam-Bohart, and Clark models, the most commonly used models to predict and analyze the dynamic behavior in a fixed-bed column, are used in this study.

The Thomas model is one of the most widely used models in assessing column performance. This model assumes that no axial dispersion is derived with the adsorption and that the rate driving force obeys second-order reversible reaction kinetics (Malkoc & Nuhoglu 2006).
The kinetic expression of the Thomas model is given below:

\[
\ln \left( \frac{C_0}{C_t} - 1 \right) = \frac{k_{TH} q_0 X}{Q} - \frac{k_{TH} C_0}{Q} V_{eff} \tag{2}
\]

where \( C_0 \) and \( C_t \) are the initial and time \( t \) zinc ion concentrations (mg/L), \( k_{TH} \) is the Thomas rate constant (L/min·mg), \( q_0 \) is the predicted adsorption capacity (mg/g), \( X \) is the amount of adsorbent in the column (g), \( Q \) is the flow rate (L/min), \( V_{eff} \) is the effluent volume (L) (Malkoc & Nuhoglu 2006).

The Adam-Bohart model is based on the assumption that the rate of adsorption is proportional to the concentration of the adsorbing species and the residual capacity of the adsorbent, and is used for the description of the initial part of the breakthrough curve (Hamdaoui 2009; Ahmad & Hameed 2010).

The Adam-Bohart expression is given as

\[
\ln \left( \frac{C_t}{C_0} \right) = k_{AB} N_0 Z Q - k_{AB} C_0 t \tag{3}
\]

where \( k_{AB} \) is the kinetic constant (L/mg·min), \( N_0 \) is the saturation concentration (mg/L) and \( Z \) is the bed height of the column (cm).

The Clark model is based on the use of a mass-transfer concept in combination with the Freundlich isotherm (Hamdaoui 2009). The Clark model expression is given below:

\[
\ln \left( \frac{C_0}{C_t} \right) ^ {n-1} - 1 = -rt + \ln A \tag{4}
\]

where \( n \) is the Freundlich constant, \( A \) and \( r \) (1/min) are the Clark constants (Hamdaoui 2009).

### RESULTS AND DISCUSSION

**Ionic exchange capacity of anionic exchange resins**

The same four anionic exchange resins previously tested in batch mode were tested in the present study, in a fixed bed column, using 2 g of resin with 1,000 mg/L zinc solution at a flow rate of 1.36 mL/min (Figure 2).

The results showed the highest sorption capacity of about 45 mg/g for Amberlite IRA410 and the lowest sorption capacity of about 36 mg/g for Purolite A400MBOH. Based on the obtained data the following series was depicted taking into account their sorption capacity: Amberlite IRA410 > Purolite A103S > Purolite NRW700 > Purolite A400MBOH. The same series was obtained in batch mode (Gilca et al. 2014). The zinc uptake on Amberlite IRA410 and Purolite A103S was almost the same, but we chose to make the following tests on Amberlite IRA410 resin in order to compare its capacity for zinc sorption in a fixed bed column with the results obtained in batch mode from our previous study (Gilca et al. 2014).

**Effect of resin quantity**

The breakthrough curves for zinc sorption on Amberlite IRA410 at various resin quantities, 1–6 g (various bed heights, 18–108 mm), at an inlet concentration of 500 mg/L and a flow rate of 1.36 mL/min are shown in Figure 3.

As we expected, at 500 mg/L initial concentration, zinc sorption was very fast in the first minutes, then the concentration at the column outlet was rapidly increasing as the resin was getting saturated. The final sorption capacity
decreased with an increase in resin quantity (high uptake was observed at the highest bed height due to an increase in the surface area of the resin, which provided more binding sites for the sorption (Padmesh et al. 2005).

The breakthrough curves shown in Figure 3 did not follow the typical ‘S-shape’ curves which are typically formed in ideal adsorption systems. The deformed breakthrough curves were obtained due to the slow kinetics of zinc on the resin (Al-Degs et al. 2009).

The breakthrough time decreased with a decrease of bed depth from 108 to 18 mm (6-1 g). At low bed depth, the zinc species do not have enough time to diffuse onto the surface of the resin due to axial dispersion phenomena in the mass transfer. Hence, by increasing the bed depth, the residence time and zinc diffusion increased as well (Taty-Costodes et al. 2005).

**Effect of initial zinc concentration**

The experiments were carried out using a fixed bed containing 5 g of resin, 1.36 mL/min flow rate and various initial concentrations ranging between 300 and 1,100 mg/L. The obtained results for the sorption of zinc by Amberlite IRA410 starting from different initial concentrations are presented in Figure 4 (breakthrough curves).

In this range of concentrations, zinc sorption was very fast in the first 15 minutes, from the initial concentration until 0 in all cases. Afterwards, the sorption rate slowly decreased (concentration at the column outlet was increasing) as the resin was getting saturated, while closer to the exhaustion point the sorption rate was very small (concentration at the column outlet was increasing very slowly).

In Table 1 the values of the following parameters are presented: breakthrough time \( t_b \) of the breakthrough curves obtained when different initial concentrations and sorption capacities were used at exhaustion time \( t_s \), 7.5 hours. It can be observed that the values of \( t_b \) decreased when zinc concentration was increasing. Sorption capacity values were increasing with an increase of the concentration from 28 mg/g (300 mg/L) to 45 mg/g (1,100 mg/L). High concentrations quickly saturated the resin, thereby decreasing the breakthrough time. As a result, an increase in the concentration modified the adsorption rate through the bed and increased the bed adsorption capacity. Thus, the diffusion process depends on the inlet concentration, and the saturation of the adsorbent requires much more time (Taty-Costodes et al. 2005).

**Reaction kinetic models**

In order to study the kinetics of zinc sorption on Amberlite IRA 410, the Thomas, Adam-Bohart, and Clark models were considered.

The Thomas kinetic coefficient, \( k_{TH} \), and the sorption capacity of the adsorbent, \( q_0 \) were determined from the \( \ln(C_t/C_0) \) vs. \( V_{eff} \) plot.

The determined coefficients and relative constants were obtained using linear regression analysis and the results are shown in Table 2. As can be inferred from Table 2, the \( k_{TH} \) values increased as resin quantity increased up to 5 g and afterwards slowly decreased with a further increase of the resin quantity. In contrast, \( k_{TH} \) decreased with increasing initial zinc concentration.

The data obtained in column in continuous down-flow mode studies were used to calculate maximum solid phase concentration of zinc on Amberlite IRA410 beads. Parameters describing the characteristic operations of the column \( (k_{AB} \) and \( N_0) \) were determined from a linear plot of \( \ln(C_t/C_0) \) vs. time \( t \), as the intercept and slope, respectively (Hamdaoui 2009; Ahmad & Hameed 2010).

The values of \( k_{AB} \), Table 2, decreased with an increase of the initial concentration and an increase of the bed height, which pointed out that the overall system kinetics was dominated by external mass transfer in the initial part of adsorption in the column (Ahmad & Hameed 2010).

### Table 1

<table>
<thead>
<tr>
<th>( C_0 ) (mg/L)</th>
<th>300</th>
<th>500</th>
<th>700</th>
<th>900</th>
<th>1,100</th>
</tr>
</thead>
<tbody>
<tr>
<td>( t_b ) (h)</td>
<td>2.50</td>
<td>2.25</td>
<td>2.00</td>
<td>1.75</td>
<td>1.50</td>
</tr>
<tr>
<td>( q_t ) (mg/g)</td>
<td>28.32</td>
<td>30.10</td>
<td>39.57</td>
<td>37.43</td>
<td>45.26</td>
</tr>
</tbody>
</table>

**Figure 4** Breakthrough curves for zinc sorption onto Amberlite IRA410 using different initial zinc concentrations.
On the basis of the correlation coefficients shown in Table 2, it was concluded that the Adam-Bohart model does not adequately fit the experimental data for the Amberlite resin; so model assumptions were not validated.

In previous equilibrium studies, it was found that the Freundlich model was valid for the zinc adsorption on Amberlite IRA410, which allowed the use of the Freundlich constant ($n=1.29$) (Gîlca et al. 2014) to calculate the parameters in the Clark model (Equation (4)).

From the linear plot of $\ln(C_0/C_t)^{1/n} - 1$ vs. time ($t$) the values of $r$ and $A$ were determined from the intercept and slope of the plot and are presented in Table 2.

From the experimental results and regression analysis, the Clark model provided an acceptable correlation of the effects of bed height and concentration.

The Yoon and Nelson, and Wolborska models were also applied for zinc sorption, when small correlation coefficients were obtained, thus proving that the considered models do not fit properly the experimental data for the Amberlite resin.

Therefore, it can be concluded that only the Clark kinetic equation indicates a good applicability of zinc removal on Amberlite resin, conclusion confirmed by high values of the correlation coefficients.

### Characteristics of the adsorption zone

In order to properly design and operate a fixed bed adsorption process, the concept of the mass transfer zone (MTZ) was applied (Namane & Hellal 2006; Hanen & Abdelmottaleb 2013). MTZ is formed at the front of the column where adsorption takes place. The depth of MTZ is controlled by factors like resin quantity, inlet concentration, and flow rate, which considerably affects the lifetime of the column. Once formed, MTZ moves down through the adsorbent bed until it reaches the adsorbent end, where the effluent concentration of solute begins to rise in the aqueous phase (Al-Degs et al. 2009). Three characteristics determine the mass transfer zone: fractional capacity ($E$), height of MTZ ($H_Z$) and rate of the movement of the MTZ ($U_Z$) (Namane & Hellal 2006).

The fractional capacity of the adsorbent bed is defined as the amount involved in the adsorption phenomenon ($A_Z$, mg) as compared to the total amount of adsorbent ($A_{max}$, mg) (Namane & Hellal 2006; Hanen & Abdelmottaleb 2013) was calculated by the ratio:

$$E = \frac{A_Z}{A_{max}} = \frac{\int_0^{t_b} (C_0 - C_t)dt}{C_0(t_s - t_b)}$$  \hspace{1cm} (5)

If $E = 1$, the adsorbent is entirely saturated, while if $E = 0$, the adsorbent contains no adsorbate and the zone-formation time should be very short (Namane & Hellal 2006). In the studied range of concentrations and bed heights (resin quantities) the values of $E$ were between 0.6–0.8 and 0.4–0.9, respectively; therefore the resin was not completely saturated.

The height of MTZ is the area where the adsorption phenomenon takes place and gives indications about the diffusion resistances. The lower resistance to the transfer is, the faster the kinetics of adsorption is and the smaller

<table>
<thead>
<tr>
<th>$m/C_0$ (g)</th>
<th>$q_0$ (mg/g)</th>
<th>k\text{r} 10^{-5} (L/min·mg)</th>
<th>$R^2$</th>
<th>k\text{ad} 10^{-5} (L/mg·min)</th>
<th>$N_0$ (mg/L)</th>
<th>$R^2$</th>
<th>$A$</th>
<th>$r10^{-2}$ (1/min)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/500</td>
<td>2.66</td>
<td>3.11</td>
<td>0.82</td>
<td>0.61</td>
<td>86.20</td>
<td>0.50</td>
<td>0.37</td>
<td>1.3</td>
<td>0.85</td>
</tr>
<tr>
<td>2/500</td>
<td>30.93</td>
<td>4.22</td>
<td>0.80</td>
<td>2.05</td>
<td>35.15</td>
<td>0.55</td>
<td>0.01</td>
<td>1.5</td>
<td>0.88</td>
</tr>
<tr>
<td>3/500</td>
<td>26.76</td>
<td>6.51</td>
<td>0.91</td>
<td>3.70</td>
<td>22.40</td>
<td>0.70</td>
<td>0.04</td>
<td>2.3</td>
<td>0.98</td>
</tr>
<tr>
<td>4/500</td>
<td>25.63</td>
<td>6.29</td>
<td>0.97</td>
<td>4.32</td>
<td>18.76</td>
<td>0.88</td>
<td>0.35</td>
<td>1.9</td>
<td>0.99</td>
</tr>
<tr>
<td>5/500</td>
<td>25.76</td>
<td>8.56</td>
<td>0.90</td>
<td>7.82</td>
<td>15.27</td>
<td>0.86</td>
<td>0.92</td>
<td>1.9</td>
<td>0.97</td>
</tr>
<tr>
<td>6/500</td>
<td>24.56</td>
<td>8.07</td>
<td>0.95</td>
<td>7.62</td>
<td>14.26</td>
<td>0.94</td>
<td>0.98</td>
<td>1.7</td>
<td>0.98</td>
</tr>
<tr>
<td>5/500</td>
<td>31.04</td>
<td>4.39</td>
<td>0.92</td>
<td>3.47</td>
<td>20.79</td>
<td>0.86</td>
<td>0.33</td>
<td>0.8</td>
<td>0.96</td>
</tr>
<tr>
<td>5/700</td>
<td>46.97</td>
<td>2.49</td>
<td>0.83</td>
<td>1.58</td>
<td>37.79</td>
<td>0.67</td>
<td>0.10</td>
<td>1.1</td>
<td>0.92</td>
</tr>
<tr>
<td>5/900</td>
<td>49.41</td>
<td>2.41</td>
<td>0.86</td>
<td>1.32</td>
<td>43.65</td>
<td>0.62</td>
<td>0.21</td>
<td>1.4</td>
<td>0.95</td>
</tr>
<tr>
<td>5/1,100</td>
<td>57.12</td>
<td>1.75</td>
<td>0.78</td>
<td>1.01</td>
<td>50.68</td>
<td>0.57</td>
<td>0.11</td>
<td>1.2</td>
<td>0.88</td>
</tr>
</tbody>
</table>

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**Table 2** Thomas, Adam-Bohart and Clark parameters for sorption of zinc on Amberlite IRA410 for different resin quantities and initial concentrations

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*E. Gîlca et al. | Kinetics analysis of zinc sorption in fixed bed column | Water Science & Technology | 71.11 | 2015*
the depth of the zone of mass transfer is (Namane & Hellal 2006).

The height of MTZ, \( H_z \) (Hanen & Abdelmottaleb 2013) was calculated using the following equation:

\[
H_z = \frac{H_b(t_z - t_l)}{t_z - t_b} + E(t_z - t_b)
\]

(6)

where \( H_b \) is the height of the adsorbent bed (cm).

From the obtained experimental results, it can be concluded that the adsorption phenomenon takes place between 7.90 and 8.56 cm (Table 3) in the studied range of concentration and 1.70 and 4.75 cm in the studied range of the resin quantity. An increase of the concentration (more molecules of solute) is leading to an increase in the residence time of molecules in the column, due to the steric effect. Thus, the mass transfer zone increases its height and offers more sites to the molecules. In contrast, an increased bed depth gives a greater number of adsorption sites for an equivalent number of molecules, which means an easier choice of the site, and consequently an acceleration of the process. In conclusion, it can be said that an increase in bed depth improves the adsorption kinetics (Namane & Hellal 2006).

The rate of the movement of the MTZ depends on the capacity of the adsorbent and was calculated using the following equation (Hanen & Abdelmottaleb 2013):

\[
U_z = \frac{H_z}{t_z} = \frac{H_z}{t_z - t_b} = \frac{H_b}{t_z - t_l}
\]

(7)

where \( t_z \) is the time required for the adsorption zone to travel its own length when established (h), and \( t_l \) is the time required for the formation of the transfer zone (h).

The smaller is the depth of MTZ, the more quickly is the rate of transfer, and the more rapid is the saturation of the bed (Namane & Hellal 2006).

When increasing the height of the bed, hydrodynamic conditions remain unchanged, but the specific characteristics of the MTZ change (\( H_z \) increases). Increasing the concentration of effluent determines an increase in the height of MTZ and its rate of movement; so the resin bed is rapidly exhausting (Namane & Hellal 2006).

The value of \( t_l \) (Hanen & Abdelmottaleb 2013) can be calculated as:

\[
t_l = (1 - E) t_z
\]

(8)

The time required to form MTZ (\( t_l \)) greatly increased at 300 mg/L initial concentration but when the concentration increased the time decreased (Table 3). Therefore it takes 1.62 hours for MTZ to form at 300 mg/L and less than 1 hour at higher concentration between 900 and 1,100 mg/L. So, the earlier formation of MTZ reflected the earlier exhaustion of the resin (Al-Degs et al. 2009). The same explanation can be also attributed for the effect of resin quantity.

The percentage of the total column saturated (Hanen & Abdelmottaleb 2013) at breakthrough is

\[
\text{%saturation} = \left( \frac{H_b + (E - 1)H_z}{H_b} \right) 
\]

(9)

The values obtained are presented in Table 3. At 1,100 mg/L the saturation was approximately 89%; a further decrease in concentration will lead to a slow decrease in the percentage saturation. At 300 mg/L only 72% saturation at breakthrough point was obtained. In the case of varying the resin quantity, the percentage saturation will increase by decreasing the resin quantity.

It can be concluded that by increasing the effluent concentration, the height of MTZ also increases (the resin bed is rapidly exhausting). Thereby, with the increase of the height of MTZ, the rate of the MTZ movement also increases (Namane & Hellal 2006).

**Diffusion parameters**

To determine the controlling mechanism, in the case of mass transfer controlled systems, the Miura and Hashimoto

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**Table 3 |** Basic design parameters of the sorption column starting from different initial concentrations and bed heights (resin quantities)

<table>
<thead>
<tr>
<th>( C_0 ) (mg/L)</th>
<th>( H_b ) (cm)</th>
<th>( E )</th>
<th>( H_z ) (cm)</th>
<th>( U_z ) (cm)</th>
<th>( t_l ) (h)</th>
<th>( t_f ) (h)</th>
<th>Saturation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>9</td>
<td>0.67</td>
<td>7.66</td>
<td>1.53</td>
<td>1.62</td>
<td>5</td>
<td>72.29</td>
</tr>
<tr>
<td>500</td>
<td>9</td>
<td>0.73</td>
<td>7.73</td>
<td>1.47</td>
<td>1.39</td>
<td>5.25</td>
<td>77.19</td>
</tr>
<tr>
<td>700</td>
<td>9</td>
<td>0.78</td>
<td>7.83</td>
<td>1.42</td>
<td>1.18</td>
<td>5.5</td>
<td>81.22</td>
</tr>
<tr>
<td>900</td>
<td>9</td>
<td>0.82</td>
<td>7.94</td>
<td>1.38</td>
<td>0.98</td>
<td>5.75</td>
<td>84.87</td>
</tr>
<tr>
<td>1,100</td>
<td>9</td>
<td>0.87</td>
<td>8.00</td>
<td>1.33</td>
<td>0.75</td>
<td>6</td>
<td>88.85</td>
</tr>
<tr>
<td>500</td>
<td>1.8</td>
<td>0.98</td>
<td>1.70</td>
<td>0.48</td>
<td>0.05</td>
<td>3.5</td>
<td>98.61</td>
</tr>
<tr>
<td>500</td>
<td>3.6</td>
<td>0.95</td>
<td>3.24</td>
<td>0.99</td>
<td>0.14</td>
<td>3.25</td>
<td>95.92</td>
</tr>
<tr>
<td>500</td>
<td>5.4</td>
<td>0.92</td>
<td>4.18</td>
<td>1.52</td>
<td>0.19</td>
<td>2.75</td>
<td>94.38</td>
</tr>
<tr>
<td>500</td>
<td>7.2</td>
<td>0.84</td>
<td>4.75</td>
<td>2.11</td>
<td>0.34</td>
<td>2.25</td>
<td>90.01</td>
</tr>
<tr>
<td>500</td>
<td>10.8</td>
<td>0.46</td>
<td>2.41</td>
<td>3.22</td>
<td>0.39</td>
<td>0.75</td>
<td>88.07</td>
</tr>
</tbody>
</table>
model can be applied. They defined the mechanical parameter ($\zeta$), as follows (Inglezakis & Zorbas 2012):

$$\zeta = \frac{k_l \cdot a_u}{K \cdot \frac{q_{\text{max}}}{C_0}}$$  \hspace{1cm} (10)

$$K = \frac{15 \cdot D_s \cdot \rho_b}{R^2}$$  \hspace{1cm} (11)

$$a_u = \frac{6 \cdot (1 - \varepsilon)}{d_p}$$  \hspace{1cm} (12)

where $k_l$ is the mass-transfer coefficient (cm/s), $a_u$ is the total external solid surface area per unit bed volume (1/cm), $K$ is the solid-side mass transfer coefficient (g/s·cm³), $q_{\text{max}}$ is the operating capacity (mg/g), $D_s$ is the solid diffusion coefficient (cm²/s), $\rho_b$ is the bed density (g/cm³), $R$ is the particle radius (cm), $\varepsilon$ is the bed voidage, $d_p$ is the particle diameter (cm) (Inglezakis & Pouloupolou 2006; Inglezakis & Zorbas 2012).

The solid diffusion coefficient is theoretically independent of the flow type and rate (Inglezakis & Zorbas 2012) and was calculated using diffusion models in batch reactor (Gilcă et al. 2014).

In order to calculate the $k_l$ parameter, the Kataoka correlation was used (Inglezakis & Zorbas 2012):

$$k_l = 1.85 \cdot (\text{Re} \cdot \text{Sc})^{2/3} \cdot \frac{U_s}{\varepsilon} \cdot \left(\frac{1 - \varepsilon}{\varepsilon}\right)^{-1/3}$$  \hspace{1cm} (13)

$$\text{Sc} = \frac{\nu}{D_l}$$  \hspace{1cm} (14)

$$\text{Re} = \frac{d_p \cdot U_s}{\nu}$$  \hspace{1cm} (15)

where Re is the particle Reynolds number, Sc is the Schmidt number, $\nu$ is the liquid kinematic viscosity (cm²/s), $D_l$ is the diffusion coefficient of the solute in the liquid phase (cm²/s) and $U_s$ is the superficial liquid velocity (cm/s); $D_{l,\text{Zn}} = 0.76 \cdot 10^{-5}$ cm²/s (Marcinkowsky et al. 1965).

Essentially, the mechanical parameter represents the ratio of the diffusion resistances (solid and liquid film). According to Miura and Hashimoto, if $\zeta < 1$, then liquid film diffusion is controlling the process rate, while if $\zeta > 1$, then the solid diffusion is controlling the process rate (Inglezakis & Zorbas 2012).

According to the obtained values presented in Table 4, the solid diffusion is controlling the process rate at concentrations between 300 and 900 mg/L (the $\zeta$ values are nearly all much higher than 1) and liquid film diffusion is controlling the process rate at higher concentrations, 1,100 mg/L (the $\zeta$ value is much lower than 1).

These developed correlations, which express the Reynolds and Schmidt numbers, give a satisfactory prediction of the individual liquid-film mass transfer coefficient in a column adsorption experiment (Pan et al. 2005). The Reynolds value (Table 4) indicates a laminar flow (Re < 4,000) (Abraham et al. 2011), which is in concordance with the small value used to realize the experiments (1.36 mL/min).

### Table 4 | The kinetic parameters for the estimation of the controlling mechanism

<table>
<thead>
<tr>
<th>$C_0$ (mg/L)</th>
<th>$K$ (g/s·cm³)</th>
<th>$\zeta$</th>
<th>$k_f 10^{-3}$ (cm/s)</th>
<th>$a_u$ (1/cm)</th>
<th>Re</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0.02</td>
<td>4.72</td>
<td>226.08</td>
<td>11.48</td>
<td>76.5</td>
</tr>
<tr>
<td>500</td>
<td>0.01</td>
<td>10.57</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>700</td>
<td>0.01</td>
<td>11.24</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>0.14</td>
<td>1.52</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,100</td>
<td>1.09</td>
<td>0.19</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### CONCLUSIONS

A series of anionic exchange resins was tested for zinc removal (as chloride anion complexes) in a fixed bed column. The following series was depicted based on sorption capacities: Amberlite IRA410 > Purolite A103S > Purolite NRW700 > Purolite A400MBOH. Further on, influence of the process parameters, such as resin quantity (bed height) and zinc initial concentration over the sorption process were considered for zinc sorption on Amberlite IRA410. The obtained values showed a classic behaviour: as the quantity of resin (bed heights) increased, the sorption capacity decreased, while with an increase of the initial concentration, the sorption capacity increased. In order to evaluate the performance of the column, different kinetics models were applied. The following series was depicted: Clark > Thomas > Adam-Bohart based on $R^2$ values. The $R^2$ values for the Clark model indicate a good linearity, while $R^2$ for the Adam-Bohart model was generally lower than the Thomas model under the same experimental conditions. Consequently, it can be concluded that the Clark model describes best the zinc sorption (as chloride anion complexes) process in continuous fixed bed mode on
Amberlite IRA410 resin. Calculated parameters of the mass transfer zone were presented and discussed in detail. The value of the mechanical parameter showed that the rate-controlling mechanism was the liquid film diffusion and solid diffusion.

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