

# Lead Removal Process Modeling in Natural Zeólita Clinoptilolita through Dynamic and Batch Systems

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In this work, the uptake capacity of lead ions in clinoptilolite zeolite was investigated. The experiments were carried out in continuous system, at pH=5.0, with a flow rate of 25mL/min, an average particle size of 0.65mm and concentration of 300, 400, 600 and 700 ppm. A mathematical model was also applied to represent the dynamics of the column's sorption. The equilibrium data were correlated using the Langmuir isotherm. The parameters necessary for this correlation were obtained using batch system. The results of the lead simulation converged very well with the experimental dynamic data. The mass transfer in the solid (K) was influenced by the initial metal concentration in the range studied.

Palavras-chave: Ion exchange, Fixed-bed, Clinoptilolite, Isotherm, Modeling.

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## 1. INTRODUCTION

Clinoptilolite belongs to the group of the heulandite and is among the most studied natural zeolite studied as well as the most abundant among the 40 natural species. Its chemical formula is  $\text{Na}_6[(\text{AlO}_2)_6(\text{SiO}_2)_{30}]\cdot 24\text{H}_2\text{O}$  typically [1]. Its ion exchange capacity with heavy metals such as  $\text{Pb}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{3+}$ ,  $\text{Fe}^{3+}$  has been investigated by several authors, demonstrating high selective attraction for these metals. These studies presented different selective orders of the zeolite for several metals and all indicate that clinoptilolite presents high affinity for lead [1-5].

Adsorption can be qualitatively evaluated through the adsorption isotherms. Many theoretical and empirical equations (Langmuir, Freundlich, Henry, Temkin, Giles, Tóth and Brunauer, Emmett, Teller (BET)) have been developed to represent the adsorption equilibrium state and relate directly the quantity of metal adsorbed with the initial solution concentration. The most widely explored model has been considered the Langmuir for monolayers due to its good correlation with experimental equilibrium data [6-9].

The ion exchange equilibrium conditions or adsorption can be developed in a batch or dynamic process. Great part of the bench scale ion exchange operations are done under dynamic conditions using fixed bed systems, once it's considered a highly selective technique capable of removing even metal traces out of great volumes of diluted solutions.

During the dynamic step, that is away from the equilibrium the ion exchange occurs more closely to the industrial processes. In many cases the isotherms are investigated through batch systems what, most probably does not represent the retention mechanism observed in continuous systems once the ion removal in this case happens through a constant rate and the pH variation tends to be much smoother compared to the batch process. Therefore, for a good representation of continuous processes it is recommended obtaining isotherm generated from continuous systems [9].

On copper study removal using marine algal *Sargassum* sp, greater copper removals have been found in the continuous system compared to the batch system [7].

The Langmuir isotherm parameters obtained in batch system were employed to model and simulate the experimental breakthrough curves in continuous regime and have presented adequate for the equilibrium continuous flow representation in fixed bed [6,9].

The copper and zinc adsorption capacity of the marine algal *C. nodosa* was investigated and it was observed that the maximum copper adsorption capacity did not depend of the operation system: the batch and continuous systems have brought out practically the same results.

Nevertheless, in the case of zinc the adsorption capacity did depend on the system used and the continuous operation resulted in higher values of removal [6].

Therefore, depending on the metallic ion which is being removed the equilibrium data obtained in batch systems not always can be used to represent properly the experimental breakthrough curves data.

This paper intends to expose the modeling generated for the lead removal experimental breakthrough curves obtained using zeolite clinoptilolite. The equilibrium data was collected from both dynamic and batch systems and a mathematical model was explored in order to adjust the experimental breakthrough curve data. The model used was developed by Silva [10] and adjusted properly copper and chromium removal data in marine algal *Sargassum* sp and chromium (III) in zeolite NaX [7-9].

## 2. MATERIALS E METHODS

Natural zeolite Clinoptilolite supplied by Steelhead Specialty Minerals, Spokane, Washington (USA) was used as the adsorbent material studied. The solid was prepared and classified in order to obtain an average diameter of 0.65 mm and its physical and chemical properties were supplied by Steelhead Specialty and is given by Tables 1 and 2.

*Tabela 1: Clinoptilolite's Physic characterization*

|                          |                       |
|--------------------------|-----------------------|
| Density                  | 1.6 g/cm <sup>3</sup> |
| Average pore diameter    | 4.0 Å                 |
| Porosity                 | 15%                   |
| Cation exchange capacity | 1.8meq/g              |
| Acid stability           | pH 3-7                |
| Basic stability          | pH 7-10               |
| Thermal stability        | 650°C                 |
| Specific surface area    | 40m <sup>2</sup> /g   |

*Table 2: Clinoptilolite's Chemical composition*

|                                    |        |                        |       |                                    |        |
|------------------------------------|--------|------------------------|-------|------------------------------------|--------|
| <b>SiO<sub>2</sub></b>             | 66.03% | <b>MgO</b>             | 0.58% | <b>K<sub>2</sub>O</b>              | 1.81%  |
| <b>Al<sub>2</sub>O<sub>3</sub></b> | 10.47% | <b>TiO<sub>2</sub></b> | 0.13% | <b>Fe<sub>2</sub>O<sub>3</sub></b> | 1.12%  |
| <b>CaO</b>                         | 1.55%  | <b>Na<sub>2</sub>O</b> | 3.25% | <b>MnO</b>                         | 0.027% |

The column composed of acrylic with 13.3 cm of height and 1.4 cm of internal diameter was used and is illustrated in Fig. 1. The solution containing the adsorbate was prepared from analytical grade Pb(NO<sub>3</sub>)<sub>2</sub>, adjusting the pH to 5 with also analytical grade HNO<sub>3</sub> and NaOH. The lead concentration analysis were conducted through an atomic absorption spectrometry.

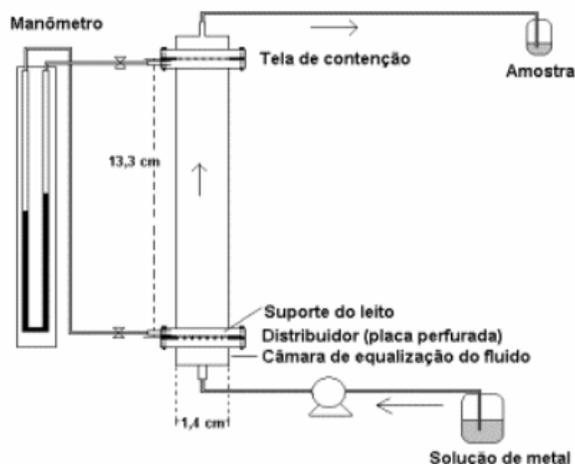


Figure 1: Schematic Figure of the fixed bed column set.

The fluid dynamic study was conducted in the column packed with 18 g of zeolite of 0.65 mm of diameter and through it the operation flows were defined below 50mL/min in order to meet the Darcy flow range and reduce pumping energy consumption.

The column void fraction,  $\epsilon_L$ , was determined measuring the void volume (volume of distilled water required to fill the bed).

The column was filled with zeolite and distilled water was added to fill completely the bed. The water was then drained from the bottom of the column using a minimum period of 24 h and the void volume was determined from the drained volume. The zeolite was then removed, and a peristaltic pump was used to fill the column from a reservoir, which contained a defined volume of distilled water. The bed's volume was obtained by the difference between the initial volume in the reservoir and the volume remaining in the reservoir at the end.

The column void fraction was calculated using the following equation:

$$\epsilon_L = \frac{V_v}{V_b} \quad (1)$$

where  $V_v$  is the bed void volume and  $V_b$  is the bed volume. The value found was of 0.68.

A pH study was developed in order to determinate the range in which no lead precipitation or changes in the zeolite's properties could occur so as not to interfere in the evaluation of the adsorption process. The tests were done using lead solution of 100 ppm concentration, in which 100mL were transferred to beakers varying the solution's pH within the range of 2.0 to 7.0. The samples with different pHs were left settled for a period of 24 hours at room temperature. After this period the samples were filtered and analyzed.

Fig. 2 shows that between pH 3 and 5 no lead precipitation occurred. Due to this behavior the pH 5.0 was adopted once it also doesn't disturb the zeolite's physical and chemical properties.

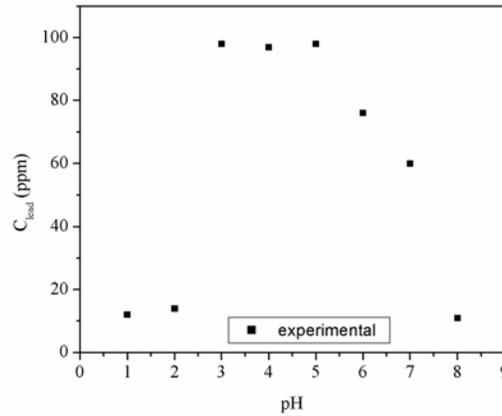


Figure: Effect of pH on lead precipitation process

The dynamic adsorption isotherm was obtained using 25 mL/min of solution flow rate, room temperature, 0.65mm particle diameter, pH 5.0, 25°C and lead concentrations varying from 300 to 700ppm. For the batch isotherm [11] the operational conditions were: pH 5.0, 0.65mm particle diameter, 1g of zeolite mass and lead feeding concentration varying from 200 to 1000ppm.

The isotherms were obtained from the breakthrough experimental data that were collected until the complete saturation. From the breakthrough mass balance the total capacity of the fixed bed was calculated using the following equation:

$$q^* = \frac{C^F Q^*}{1000m} \int_0^t (1 - C|_{Z=L} / C^F) dt \quad (2)$$

The integral represented by Eq. (2) was solved numerically.

In literature, there are a number of mathematical models to describe ion exchange and adsorption dynamics in fixed bed columns [12-15].

The experimental breakthrough curves were adjusted by Silva's model [10]. The proposed modeling methodology for lead ion removal in the outlined fixed bed column is based on the following assumptions: isothermal process, constant bed void fraction, constant physical properties, superficial adsorption and negligible radial dispersion.

The mass balance equations for the fluid phases is:

$$\frac{\partial C}{\partial \tau} + \rho_b \frac{(1 - \epsilon_b)}{\epsilon_b} \frac{\partial q}{\partial \tau} = - \frac{\partial C}{\partial \xi} + \frac{1}{Pe_b} \frac{\partial^2 C}{\partial \xi^2} \quad (3)$$

with the following initial condition:

$$C(\xi, 0) = C_0 \quad (4)$$

and boundaries conditions:

$$\frac{\partial C}{\partial \xi} = Pe_b (C(\tau, 0) - C^F) \text{ in } \xi = 0 \quad (5)$$

$$\frac{\partial C}{\partial \xi} = 0 \quad \text{in } \xi = 1 \quad (6)$$

Moreover, the mathematical model is based on the assumption that the ion exchange is relatively fast, due to the very favorable shape of the isotherms, and the migration in the zeolite pores plays a dominant role in the process [16].

The ion mass transfer mechanism in the adsorbent occurs through diffusion and must be described by Fick's second law, nevertheless, in order to reduce complexity of the differential equation system some authors have been approximating this law using a simpler kinetic expression [17].

When representing the lead removal rate of the zeolite it is supposed that the mass transfer motive force varies linearly with the solid phase concentration. Therefore, the exchange rate can be expressed by the equation:

$$\frac{\partial q}{\partial \tau} = \beta(q - q^*) \quad (7)$$

where:  $\beta = K \cdot u / L$   
with the initial condition:

$$Q(\xi, 0) = q_0 \quad (8)$$

The equilibrium concentration uptake of lead in the zeolite ( $q^*$ ) was calculated by Langmuir isotherm model, described by the following equation:

$$q^* = \frac{q_{\max} \cdot b \cdot C^*}{1 + b \cdot C^*} \quad (9)$$

The line methods were used in order to solve the partial differential equation system (PDE) given by Eqs. (3) and (7). The initial and boundary conditions used were the ones indicated in Eqs. (4)-(6) and (8). Whilst the equilibrium relation used is the Langmuir given by Eq. (9). Initially the domain of the problem was discretized in (n) elements. This procedure changed the PDE system to an ordinary differential equation (ODE) system. The code DASSL was used to solve the ODE system [18]. This code solves systems of algebraic/differential equations and uses backward differentiation formulae to advance the solution from one time step to the next.

The axial dispersion coefficient (DL) and the adsorption rate constant (K) were estimated using the experimental data of the breakthrough curves and the following objective functions:

$$F = \sum_{i=1}^{np} (C_{\text{out}}^{\text{exp}} - C_{\text{out}}^{\text{mod}})^2 \quad (10)$$

where  $C_{\text{out}}^{\text{exp}}$  is the experimental concentration of the lead in the outlet of the column;  $C_{\text{out}}^{\text{mod}}$ , concentration of the lead determined by the solution of the model in the outlet of the column; np the number of experimental data points.

### 3. RESULTS E DISCUSSION

For heavy metal mathematical modeling it is first necessary to describe the systems equilibrium conditions. The experimental equilibrium data obtained in the measurements done in column for lead adsorption along with the Langmuir model adjusted curve are shown in Fig 3.

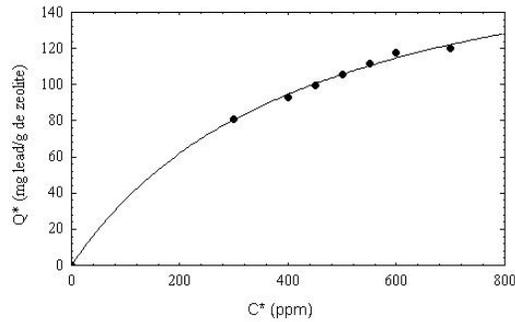


Figure 3: Dynamic isotherm Pb - zeolite clinoptilolita. (●) Experimental points and (–) Langmuir model.

The Langmuir's model parameters for continuous systems  $q_{max}$  and  $b$ , shown in Eq. (9), were estimated using the Quasi-Newton non linear regression method in the STATISTICA for Window® version 5.0 and their values are presented in table 3. The results obtained by [11] are also given with the difference that the Eq (9) was linearized in the format  $Y = A + B.X$ .

Table 3: Langmuir's Parameters

| System             | $Q_{max}$ (mg/g) | $b$ (mg/L) | $R^2$ (%) |
|--------------------|------------------|------------|-----------|
| Batch <sup>1</sup> | 95.10            | 0.50       | 99.00     |
| Dynamic            | 200.54           | 0.00223    | 99.77     |

<sup>1</sup>Zambon [12]

Fig. 3 indicates that Langmuir's isotherm model for the dynamic system fit adequately the equilibrium sorption data and that great quantities of lead can be removed.

The maximum adsorption capacity constant ( $q_{max}$ ) increased for the dynamic system compared to the values obtained in batch system. The energy of adsorption constant ( $b$ ) on the other hand reduced significantly on the continuous flow compared to the batch system. This is most probably due to different equilibrium sorption conditions given in each system.

The Langmuir parameters  $q_{max}$  and  $b$  obtained for each system, batch and dynamic, were incorporated to the mathematical model in order to simulate lead removal in fixed bed. Simulations were done with Langmuir's isotherm for each experimental breakthrough curve in order to describe the system's equilibrium conditions.

The experimental breakthrough curve and results obtained by solution of the mathematical model are shown in Fig. 4. The equilibrium sorption data using the batch conditions did not fit properly to the equilibrium observed in the column due to most probably the limitation in mass transfer in the batch system. Therefore the batch equilibrium most probably isn't capable of representing the dynamic equilibrium for lead in the conditions studied.

The Fig. 4 also shows how the simulation using the Langmuir's parameters in the dynamic system fit very closely to the experimental breakthrough curves.

For operations in column, the concentrations in the fluid and solid phases vary with time and position throughout the column. This can explain why the phase equilibrium obtained by the dynamic isotherm represented more adequately the experimental data than the isotherm in batch system.

It still is possible to notice through the experimental breakthrough curves behavior that the zeolite saturates faster under greater initial lead concentrations and that the breakthrough time reduces with the increase of initial lead concentration. Therefore, the initial lead concentration variation had a significant effect over the breakthrough curve's shape.

The global mass transfer coefficient and the axial dispersion coefficient values used in the simulations are presented in Table 4 and were adjusted using Eq. (10).

These results prove that either the change of concentration gradient affected the rate and exchange capacity, or the diffusion process was concentration dependent. This trend was also observed in chromium (III) removal using NaX zeolite as well as in copper removal using *Sargassum sp* alga marine [7,9].

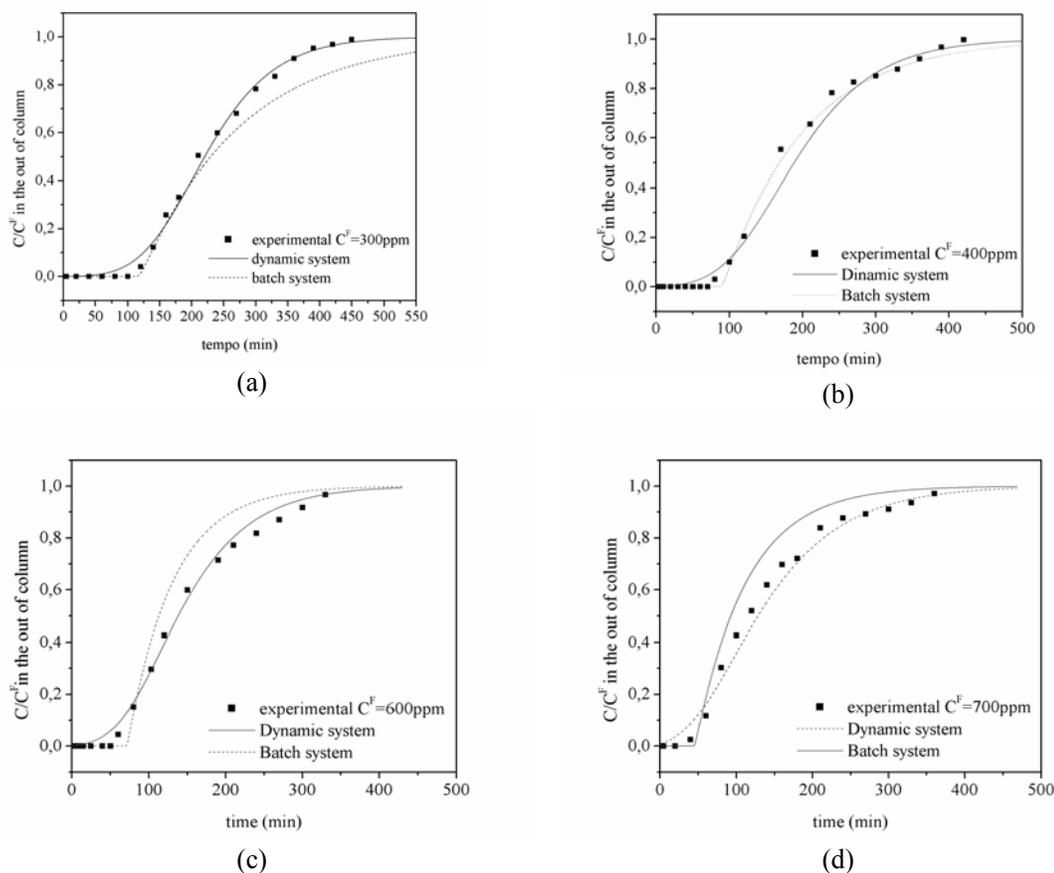


Figure 4: Experimental breakthrough curve and simulated breakthrough curves (dynamic and batch) of Pb-zeolite clinoptilolite.

According to Table 4, for dynamic systems it is noticed that the values of  $k$  reduce with the concentration increase. The batch data on the other hand had the inverse variation:  $k$  increased with the concentration increase.

Table 4: Overall mass transfer in zeolite, axial dispersion coefficients estimated by model in the batch and dynamic system

| System  | Feed concentration (ppm) | $K \times 10^{-2}$ (per min) | $D_L \times 10^{-2}$ (cm <sup>2</sup> /min) |
|---------|--------------------------|------------------------------|---|
| Dynamic | 300                      | 2.90                         | 1.85  |
| Batch   |                          | 0.65                         | 2.57  |
| Dynamic | 400                      | 2.35                         | 2.02  |
| Batch   |                          | 0.91                         | 3.02  |
| Dynamic | 600                      | 2.04                         | 2.18  |
| Batch   |                          | 1.70                         | 1.95  |
| Dynamic | 700                      | 1.67                         | 2.26  |
| Batch   |                          | 1.50                         | 2.45  |

The axial dispersion coefficient  $D_L$  in dynamic systems increases with the concentration increase and once again the behavior observed in batch system was the inverse: the increase of concentration reduces the  $D_L$  coefficient value.

#### 4. CONCLUSIONS

Lead removal using clinoptilolite zeolite in dynamic systems was favorable, according to the observed in the isotherm, (Fig.3).

The equilibrium data obtained using continuous flow conditions fit well on to the experimental breakthrough curves using Langmuir's isotherm and these model constants indicate that the maximum adsorption capacity is of 200.54 mg of Pb/g of zeolite.

The results obtained in the breakthrough curves simulations using Langmuir's isotherm in continuous flow and batch conditions generated diverse results.

The equilibrium data in the batch system didn't represent well the column's equilibrium. The simulation observed using the dynamic equilibrium conditions on the other hand agreed quite closely to the experimental breakthrough curves.

Mass transfer in the solid and the axial dispersion coefficient vary with the initial lead concentration.

#### Nomenclature

|                   |   |
|-------------------|---|
| b                 | Langmuir isotherm constant (mg/L)                               |
| C                 | lead concentration in the bulk fluid phases (ppm)               |
| C*                | equilibrium lead concentration in the bulk fluid phases (ppm)   |
| C <sup>0</sup>    | initial lead concentration in the bulk fluid phases (ppm)       |
| C <sup>f</sup>    | lead concentration in the inlet in the column (ppm)             |
| C  <sub>z=L</sub> | lead concentration in the outlet in the column (ppm)            |
| D <sub>L</sub>    | axial dispersion coefficient (cm <sup>2</sup> /min)             |
| K                 | overall mass transfer coefficient (per min)                     |
| L                 | length of the bed (cm)  |
| m                 | zeolite's dry weight (g)  |
| q                 | lead concentration adsorption in the zeólita (mg/g)             |
| q*                | equilibrium lead concentration adsorption in the zeólita (mg/g) |
| q <sub>max</sub>  | Langmuir's isotherm parameter (mg/g)                            |
| Q*                | volumetric flow rate (cm <sup>3</sup> /min)                     |
| t                 | time (min)  |
| u                 | interstitial velocity (cm/min)                                  |
| z                 | axial coordinate in the column (cm)                             |
| ε                 | column void fraction  |

#### Dimensionless group

|                 |  |
|-----------------|--|
| Pe <sub>b</sub> | Peclet number for the bed (Lu/D <sub>L</sub> ) |
| ρ <sub>b</sub>  | fixed-bed density (g/l)                        |
| τ               | dimensionless time coordinate (tu/L)           |
| ξ               | dimensionless axial coordinate (z/L)           |

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