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To cite this article: Patrícia da Luz Mesquita, Cássia Ribeiro Souza, Nilza Tatiane G. Santos & Sônia Denise Ferreira Rocha (2018) Fixed-bed study for bone char adsorptive removal of refractory organics from electrodialysis concentrate produced by petroleum refinery, Environmental Technology, 39:12, 1544-1556, DOI: 10.1080/09593330.2017.1332691

To link to this article: https://doi.org/10.1080/09593330.2017.1332691
Fixed-bed study for bone char adsorptive removal of refractory organics from electrodialysis concentrate produced by petroleum refinery

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ABSTRACT
Water reuse in industrial processes has been an increasing need encouraged in recent years. However, as the streams are recycled, solutes accumulate, thus requiring purification techniques. Membrane processes (reverse osmosis and electrodialysis) have been implemented and in order to increase the reuse of water at its highest level, crystallization has been evaluated to remove salts from the concentrate produced and get a feasible disposal. Nevertheless, contaminants affect the crystallization performance, thus making the removal of residual organics important for both the efficiency of crystallization and the increase of water reuse. In this context, aiming at establishing a sustainable virtuous circle, bone char (0.5–1.4 mm particle size, mesoporous structure) was used to remove refractory organics from an electrodialysis concentrate effluent (C-EDR) from a Brazilian petroleum refinery, at a lab-scale, in a fixed-bed adsorption column. Bone char selectively and partially removed the refractory organics, a complex mixture of long-chain hydrocarbons, aromatic compounds, carboxylic acids, amines and amides. The maximum adsorption capacity increased with the increase in bed depth and reduction in flow rate. A maximum removal of 35.60 mg g\(^{-1}\) was achieved for the highest bed depth evaluated (12.9 cm). The breakthrough curves indicated that bone char could adsorb part of the organic compounds from the C-EDR. The scaling up was possible for the C/C\(_{0}\) ratios of 0.55, 0.60 and 0.65, providing a service time at about 16 days for 45% removal efficiency for typical real operational conditions used in the refinery.

1. Introduction
The improvement of consolidated technologies and the search for viable and low-cost alternative processes for water reuse in industry have been increasingly encouraged in a water scarcity scenario [1–3]. The petrochemical industry, one of the most relevant sectors in Brazil, requires, during the process of oil refining, an average of 246–340 l of water/day per barrel of crude oil. Additionally, a quantity of wastewater around 0.4–1.6 times the volume of oil processed is generated [4]. Due to this high water demand, reuse can significantly reduce the processing costs in oil refineries. Consequently, it is necessary to implement water management systems that include both water use rationalization and the choice of the best treatment system.

Nevertheless, water reuse requires advanced (tertiary) treatment such as adsorption onto activated carbon, advanced oxidation processes and membrane separation processes (e.g. reverse osmosis or electrodialysis), to remove dissolved organic or/and inorganic compounds [5–9]. Membrane processes bring many advantages [10] and a high-quality permeate for reuse is produced; however, as water recirculates, increasing salinity is inevitably observed in concentrate streams. Crystallization of salts is an option for destination of such brines, but it is affected by the presence of diverse contaminants, including low-solubility salts and organic compounds [11].

Refractory organics from petroleum processing are also of great concern because they may bring corrosion, toxicity and carcinogenicity to streams. Typical organic contaminants, such as long-chain hydrocarbons, aromatic compounds (such as benzene and phenolic ones), amines and amides, have been identified in the concentrate from electrodialysis [11,12].

In this context, adsorption, a consolidated process, is a potential technique to be included in these systems. Bhatnagar et al. [13], Hashemi [14] and Brunson and Sabatini [15], among other authors, highlight its usual low-cost, operational simplicity and low area demand, compared to other advanced wastewater treatment processes such as advanced oxidation processes and reverse
osmosis. In particular, the adsorption process is suitable for removal of low-concentration or highly toxic contaminants that cannot be removed by the conventional biological treatment [16].

However, the organics removal by adsorption in charcoal has already been carried out, but with high cost and the performance was affected by increasing salinity. In this context, low-cost alternatives, such as adsorbents produced from wastes, are becoming more and more attractive. Among them, bone char may be highlighted produced from wastes, are becoming more and more attractive. Among them, bone char may be highlighted.

Bone char (consisting of 70–90% of calcium phosphate, low amounts of calcium carbonate and only 10% in weight of carbon) differs from the conventional activated carbons (mainly constituted of C). It presents moderate specific surface area (around 120 m² g⁻¹), as well as carbonates from its preparation process, characteristics that make it singular for wastewater treatment applications and industrial demands of water reuse, including metals removal [14,15,22,28,29]. Bone char can also be promising to compose a sustainable cycle, as it is produced from a voluminous waste from tannery, food industry and cattle breeding. After its use and exhaustion in the adsorption process, it could be possible to reuse the apatite, precariously crystallized in the bone char, as a renewable and efficient phosphate fertilizer for deficient soils [18,31].

Studies for organic and inorganic compounds removal by bone char have been reported in the literature; however, most of them use synthetic aqueous solutions, especially for fluoride removal [14,15,23,25,31–39]. No previous investigation was found on the applications for removal of refractory organics in real concentrate streams from electrodialysis in the petroleum industry. Thus, this is the focus of the present work, which presents the use of bone char in the removal of organics from real electrodialysis concentrate in a continuous lab-scale fixed-bed column.

For large-scale processes, continuous systems are preferable and often more economical and effective [40], which motivates this work. Three steps govern the adsorption process in fixed beds: the external mass transfer, the internal diffusion and the adsorption itself, being the operational conditions, such as flow rate, bed depth and initial concentration of the contaminant of great relevance. The breakthrough curve, which describes the dynamic behavior and efficiency of a fixed-bed adsorption column [41], gives parameters that provide input information for modeling and future scale up of the system [7,42]. Generally, the breakthrough point is chosen as the point at which the concentration of adsorbate leaving the column reaches 5% of the initial concentration. However, this value can be chosen specifically for each application. Similarly, a concentration around 90–95% of the initial concentration can be used as a parameter to determine the exhaustion point [41]. The mass transfer zone (MTZ) is the region located between the breakthrough point and the point of exhaustion and it determines the region where mass transfer occurs within the column.

Therefore, this work aims at describing the use of bone char for the removal of refractory organics present in the electrodialysis saline concentrate effluent produced by petroleum refinery, using a lab-scale fixed-bed adsorption column. This represents a new contribution to support the association of reverse electrodialysis, evaporative crystallization, already in pilot-scale evaluation in an existent oil refinery, and adsorption, aiming at improving water recovery in oil refineries and an overall minimization of residues.

2. Experiments

2.1. Preparation of adsorbent and samples

2.1.1. Bone char

Bone char, supplied by Bonechar Carvão Ativado do Brasil, Maringá, Brazil, was produced at 700–750°C, in a furnace with limited supply of air for 8 h [17]. Sampling was carried out according to Brazilian technical standards [43] and particle size analysis was done by sieving in the vibrating system (Bertel Indústria Metalúrgica Ltda) using sieves of 6, 12, 32, 48, 60 and 100 mesh (6300, 3350, 1400, 500, 300 and 152 μm, respectively), for 15 min at 5 rpm. Particles of 12–32 mesh size (0.5–1.4 mm) were selected for the adsorption experiments, and prior to their use were washed four times using distilled water (2 L water/500 g of bone char) to remove any tiny particles adhered to their surfaces. Finally, bone char was dried in a furnace (Sterilifer SX1.1 DTME, series 0057) at 120°C for 2 h.

2.1.2. Electrodialysis concentrate effluent (C-EDR)

The real effluent used was obtained from the saline concentrate stream of electrodialysis, the last step of advanced wastewater treatment, in 10–20 L plastic flasks, after being appropriately cleaned, washed and rinsed. The characterization of the effluent was carried out according to Standard Methods for Analysis of Water and Wastewater [44]. Refractory organics qualitative characterization for equilibrium study was carried out at Federal University of São Paulo (USP) and determined by gas chromatography/mass spectrometry (GC/MS Shimadzu QP 2010 plus; capillary column.
Adsorption continuous tests were carried out in a polycarbonate fixed-bed column (12.9 cm height and internal diameter of 2.2 cm). Bone char was packaged between two layers of glass beads. In order to evaluate the effect of bed depth, five continuous experiments with fixed flow rate (Q) and initial concentration (C₀) (Q = 3.00 mL min⁻¹ and C₀ = 63 mg L⁻¹) were carried out, but with varying bed depths (h = 2.6, 3.5, 5.0, 7.7 and 12.9 cm). In order to check the flow rate effect, bed height (h) and C₀ were kept constant (h = 7.7 cm and C₀ = 63 mg L⁻¹) and three flow rate conditions were compared (Q = 1.50, 3.00 and 6.00 mL min⁻¹). Finally, the effect of input organic concentration for C₀=63 and 93 mg L⁻¹ was evaluated, keeping the flow rate and the bed depth constant at 6.00 mL min⁻¹ and 7 cm, respectively. Temperature and pH were monitored (HANNA pH 21) in each run, being measured at least in triplicate. In order to guarantee homogeneity, C-EDR effluent was magnetically stirred (Thelga TMA10 CFI). The effluent was pumped upstream (MS Tecnopon Instrumentation DMC-100 peristaltic pump) through the bone char bed, as shown in Figure 1.

The operational parameters that describe the behavior of the breakthrough curves were calculated from the results. For determination of t₀ and tₐ, the volume of effluent at the breakthrough points was obtained considering C/C₀ 5% higher than the initial C/C₀ ratio and the exhaustion times were determined taking 5% less than the final C/C₀ ratio.

The necessary time to move the adsorption zone through the adsorption column is given by [45]

\[ t_z = \frac{V_E - V_b}{Q} \]  

where t₂ is the necessary time to move the adsorption zone through the adsorption column (h), Vₑ is the effluent volume at the exhaustion point (L), V₀ is the effluent volume at the breakpoint (L) and Q is the flow rate (L h⁻¹).

The time to establish the MTZ, or exhaustion time, tₑ (h), was determined according to Equation (2) [45], where Vₑ is the volume of exhaustion (L) and Q is the volumetric flow rate (L h⁻¹)

\[ t_E = \frac{V_E}{Q} \]  

In order to calculate the time required for the adsorption zone to be initially formed, it was necessary to calculate the fractional capacity of the adsorbent in the adsorption zone, which is given by [45]

\[ F = \frac{\int_{V_b}^{V_E} (C_0 - C) dV}{C_0(V_E - V_b)} \]  

where F is the fractional capacity of the adsorbent in the adsorption zone, C₀ is the effluent inlet concentration (mg L⁻¹) and C is the effluent concentration varying with the time.

The time required for the adsorption zone to be initially formed (t₁) may be obtained by [45]

\[ t_t = (1 - F)t_z \]  

The moving adsorption zone rate (U) and the adsorption zone depth (cm) could be obtained by Equations (5) [45] and (6) [45], respectively, where U is the moving adsorption zone rate (cm/h), X is the total bed depth (cm) and X₂
is the adsorption zone depth (cm)

\[ U = \frac{X_2}{t_2} = \frac{X}{t_e - t_f}, \]  

(5)

\[ X_2 = \frac{X(t_2)}{t_e - t_f}. \]  

(6)

Finally, the column saturation (S) is calculated as shown below [45]:

\[ S(\%) = \frac{X + (F - 1)X_2}{X} \times 100. \]  

(7)

2.2.1. Determination of bed adsorptive capacities (q)

Bed adsorption capacities were calculated by numerical integration of experimental breakthrough curves, using Curve Expert® software, and taking into account the flow rate and bone char mass in the column for each experiment. The refractory amount of organics was subtracted from the total value obtained from the integration to determine the real value for q.

2.3. Mathematical modeling

Thomas (Equation (8)), Yan (Equation (9) and Equation (10)), Wolborska (Equations (11) and (12)), and bed depth service time (BDST) (Equations (13) and (14)) models were fitted to experimental data according to the literature [16,41,46–49]

\[ \frac{C}{C_0} = \frac{1}{1 + \exp \left[ \frac{K_T q_e m}{Q} \right] - K_T C_0 f}, \]  

(8)

where \( K_T \) is the Thomas constant (L mg\(^{-1}\) min\(^{-1}\)), \( q_e \) is the maximum adsorption capacity (mg g\(^{-1}\)), C is the equilibrium concentration (mg L\(^{-1}\)) at time t (min), \( C_0 \) is the initial concentration (mg L\(^{-1}\)), \( m \) is the adsorbent mass (g), Q is the flow rate (mL min\(^{-1}\)) [41,49]

\[ \frac{C}{C_0} = 1 - \frac{1}{1 + \left( \frac{Q t}{b} \right)^a}, \]  

(9)

\[ q_e = \frac{b C_0}{m}, \]  

(10)

\( a, b \) are parameters of the Yan model, Q is the flow rate (mL min\(^{-1}\)), t is the time (min), \( m \) is the adsorbent mass (g), \( q_e \) is the bed capacity (mg g\(^{-1}\)); C is the equilibrium concentration (mg L\(^{-1}\)) at time t (min), \( C_0 \) is the initial concentration (mg L\(^{-1}\)) [46]

\[ \frac{C}{C_0} = e^{(b q_e C_0 N_0 t - b q_e X) / U}, \]  

(11)

\[ \beta_a = \frac{U^2}{2D} \left( \sqrt{1 + \frac{4 \beta_0 D}{U^2}} - 1 \right), \]  

(12)

where \( \beta_a \) is the external mass transfer kinetic coefficient (h\(^{-1}\)), D is the axial diffusion coefficient (cm\(^2\) h\(^{-1}\)), \( \beta_0 \) is the external mass transfer kinetic coefficient for negligible axial diffusion coefficient, \( N_0 \) is the exchange capacity (mg L\(^{-1}\)), U is the superficial fluid velocity (cm h\(^{-1}\)) and X is the bed depth (cm) [47,48,50]

\[ \ln \left( \frac{C}{C_0} \right) = \ln \left( e^{(K_a N_0 X) / U} - 1 \right) - K_a \cdot C_0 \cdot t, \]  

(13)

\[ t = \frac{N_0}{C_0 U} \frac{X}{1 - \frac{1}{C_0 K_a} \ln \left( \frac{C_0}{C_b} \right)}, \]  

(14)

where \( C_0 \) is the initial solute concentration (mg L\(^{-1}\)), \( C_b \) is the concentration at breakthrough point (mg L\(^{-1}\)), \( K_a \) is the adsorption rate constant (L mg\(^{-1}\) h\(^{-1}\)), \( N_0 \) is the adsorption capacity (mg L\(^{-1}\)), \( X \) is the bed depth (cm), U is the linear flow velocity (cm h\(^{-1}\)), t is the column service time (h) [16].

After the determination of the BDST equation for a specific flow rate and initial concentration, the BDST model was fitted for different C/C\(_0\) ratios (0.25, 0.30, 0.55, 0.60 and 0.65), for bed depths of 5.0, 7.7 and 12.9 cm and flow rate of 2.97 ± 0.03 mL min\(^{-1}\). The equations for each C/C\(_0\) condition were acquired by a linear fit. The angular (a) and linear (b) coefficients, \( K_{BDST} \) and \( N_0 \) values were determined by the following equations:

\[ a = \frac{N_0}{C_0 U}, \]  

(15)

\[ b = \frac{1}{C_0 K_a} \ln \left( \frac{C_0}{C_b} \right). \]  

(16)

Equation (17) was used to determine the critical bed depth, \( X_0 \) the minimum required for the final adsorbate concentration at the outlet of the column to be \( C_b \):

\[ X_0 = \frac{U}{N_0 K_a} \ln \left( \frac{C_0}{C_b} \right). \]  

(17)

In order to evaluate the fit obtained by the BDST model, values of the times required to reach the same C/C\(_0\) ratios, for a bed depth of 7.7 cm, but at a different flow rate (1.5 ± 0.04 mL min\(^{-1}\)) were calculated and compared to experimental data. The deviation was estimated according to the following equation:

\[ \text{Deviation\%} = \left( \frac{T_{\text{exp}} - T_{\text{model}}}{T_{\text{exp}}} \right), \]  

(18)

where deviation (%) is the percentage difference.
between the predicted time \( (T_{\text{model}}) \) and that obtained experimentally \( (T_{\text{exp}}) \).

From the BDST model, the system was scaled up assuming the operational conditions for one industrial column, of area 6.15 m\(^2\), internal diameter of 2.80 m, column height of 1.50 m, completely full of bone char, to treat refractory organics from C-EDR effluent at a flow rate of 13 m\(^3\) h\(^{-1}\) and the initial COD concentration of 61.11 mg L\(^{-1}\). These industrial operational conditions were considered for scaling up based on the dimensions of inactive carbon filters already existing in the refinery, as well as on the operational conditions for the concentrate stream produced by electrodialysis in the real process.

3. Results and discussion

3.1. Breakthrough curves and bed capacities

The breakthrough curves were obtained for different operational conditions in continuous experiments using bone char in a fixed-bed column for C-EDR refractory organics removal, as shown in Table 1 and in Figures 2–4.

It is interesting to note different patterns in the shape of breakthrough curve for the system. This can be especially highlighted in Figure 2(e), condition under which the column worked completely full of bone char (bed depth = column height), the curve ongoing at \( C/C_0 \) at approximately 0.2, differently from what is normally expected and reported in the literature, \( C/C_0 \) starting from zero (0). An ideal rupture curve assumes a total adsorption of the adsorbate between the initial stages of operation and the point of rupture \( (C_0) \). According to Metcalf & Eddy [7], when the breakthrough curve does not start from 0 (zero), the presence of compounds that can be adsorbed and others which cannot be adsorbed is indicated [7]. In other words, the C-EDR contained organics that bone char was not able to retain. In fact, this was confirmed by GC/MS analysis for previous equilibrium studies, when it was observed that after the equilibrium was reached, some of the 70 organic compounds present in C-EDR were also present in the treated C-EDR, the maximum removal being achieved at around 60\% \( (C/C_0 = 0.4) \) for equilibrium conditions. The influent was a mixture of long-chain hydrocarbons, mostly alkanes and alkenes. Indeed, alkanes are not very reactive and have low biological activity, the reason why they were found in the concentrate stream. In addition, aromatics, carboxylic acids, amines and amides had also been identified [51]. The most pronounced peaks were: 9-octadecenamide, \((Z)\)-docosane, 1,22-dibromododecane, d-ribose, 2-deoxy-bis(thio-heptyl)-, eicosanoic acid, 2,3-bis[(trimethylsilyl)oxy]propyl ester, octadecanoic acid, 3-oxo-, methyl ester, phenol, 2,4-bis(1,1-dimethylheptyl)-, undecane, 4-ethyl-, 1H-indene, 1-hexadecyl-2,3-dihydro. After adsorption, it was observed that, from the 70 refractory organics in the influent, 25 were not identified in the effluent any longer; therefore, they had been retained onto the bone char.

Another curious point to consider is about the shape of the breakthrough curve, shown in Figure 2(e), which did not follow the exact sigmoidal form reported by the literature. In fact, COD removal curves throughout the entire experiment for the completely filled column (11 days) seemed to be an assembly of several sigmoidal breakthrough curves. \( C/C_0 \) started at approximately 0.15–0.20 and stabilized for the first time around \( C/C_0 = 0.45 \). After this time, the organic concentration in the treated effluent remained approximately constant, suggesting a possible exhaustion. However, after 115 h (almost 5 days) of experiment, \( C/C_0 \) began to increase again, until new steadying was reached, around \( C/C_0 = 0.65, 0.70 \). After about 190 h (or ~8 days) of experiment, \( C/C_0 \) arose again, reaching its last level of stability at about \( C/C_0 = 0.85 \). This behavior reinforced the hypothesis of adsorption in multilayers, in which each layer of adsorbate constitutes new adsorption sites.

Table 1. Operational conditions of the continuous tests to verify the interference of bed depth \((X)\), flow rate \((Q)\) and initial concentration of organics, in terms of COD \((C_0)\) on the adsorptive process: desired values and measured values.

<table>
<thead>
<tr>
<th>Bed depth influence</th>
<th>Flow rate, ( Q ) (goal) (mL min(^{-1}))</th>
<th>Flow rate, ( Q ) (real) (mL min(^{-1}))</th>
<th>( C_0 ) (goal) (mg L(^{-1}))</th>
<th>( C_0 ) (real) (mg L(^{-1}))</th>
<th>pH</th>
<th>T (°C)</th>
<th>Figure</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.6</td>
<td>3.00</td>
<td>3.09 ± 0.04</td>
<td>63</td>
<td>67 ± 9</td>
<td>7.8 ± 0.2</td>
<td>22.7 ± 0.8</td>
<td>2(a)</td>
</tr>
<tr>
<td>3.5</td>
<td>3.00</td>
<td>3.07 ± 0.07</td>
<td>63</td>
<td>65 ± 3</td>
<td>7.7 ± 0.1</td>
<td>24 ± 1</td>
<td>2(b)</td>
</tr>
<tr>
<td>5.0</td>
<td>3.00</td>
<td>3.00 ± 0.15</td>
<td>63</td>
<td>60 ± 5</td>
<td>7.7 ± 0.2</td>
<td>22 ± 1</td>
<td>2(c)</td>
</tr>
<tr>
<td>7.7</td>
<td>3.00</td>
<td>2.94 ± 0.05</td>
<td>63</td>
<td>66 ± 1</td>
<td>7.7 ± 0.2</td>
<td>23.9 ± 0.7</td>
<td>2(d)</td>
</tr>
<tr>
<td>12.9*</td>
<td>3.00</td>
<td>2.98 ± 0.09</td>
<td>63</td>
<td>60 ± 1</td>
<td>7.9 ± 0.4</td>
<td>26 ± 2</td>
<td>2(e)</td>
</tr>
<tr>
<td>Flow rate influence</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>7.7</td>
<td>1.50</td>
<td>1.50 ± 0.04</td>
<td>63</td>
<td>62 ± 5</td>
<td>8.3 ± 0.3</td>
<td>25 ± 2</td>
<td>3(a)</td>
</tr>
<tr>
<td>7.7</td>
<td>3.00</td>
<td>2.94 ± 0.05</td>
<td>63</td>
<td>66 ± 1</td>
<td>7.7 ± 0.2</td>
<td>23.9 ± 0.7</td>
<td>3(b)</td>
</tr>
<tr>
<td>7.7</td>
<td>6.00</td>
<td>5.81 ± 0.16</td>
<td>63</td>
<td>62 ± 8</td>
<td>7.4 ± 0.4</td>
<td>25 ± 2</td>
<td>3(c)</td>
</tr>
<tr>
<td>Initial concentration influence</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.7</td>
<td>6.00</td>
<td>5.81 ± 0.16</td>
<td>63</td>
<td>62 ± 8</td>
<td>7.4 ± 0.4</td>
<td>25 ± 2</td>
<td>4(a)</td>
</tr>
<tr>
<td>7.7</td>
<td>6.00</td>
<td>6.15 ± 0.19</td>
<td>93</td>
<td>93 ± 1</td>
<td>8.2 ± 0.3</td>
<td>25 ± 2</td>
<td>4(b)</td>
</tr>
</tbody>
</table>
reports that since the main phase present in bone char is hydroxyapatite, most surface groups (phosphates, hydroxyls and carbonates) are negative at pH above 5 [22,39], which was the case in this investigation. Therefore, at the beginning, possible interactions with the organic compounds would occur through hydrogen bonds between electronegative heteroatoms such as oxygen, present in the phosphate, carbonate and hydroxyl groups of bone char, and hydrogen from O–H and N–H of the carboxylic acids, phenols, amines and amides contained in the effluent. Then, weak interactions, such as van der Waals, among long chains of hydrocarbons adhered to the solid, could be present [51]. In fact, the type of isotherm obtained from bone char characterization for determination of surface area and porosity by the Brunauer–Emmet–Teller method was the type 5 isotherm [51], typical for relatively weak adsorbate–adsorbent interactions [51,52]. Therefore,

Figure 2. Breakthrough curves for different bed depths obtained in lab-scale fixed-bed experiments. $C_0 = 63 \pm 4$ mg L$^{-1}$; $Q = 3.01 \pm 0.06$ mL min$^{-1}$: (a) $Z = 2.6$ cm; (b) $Z = 3.5$ cm; (c) $Z = 5.0$ cm; (d) $Z = 7.7$ cm; (e) $Z = 12.9$ cm.
there was formation of a first layer, on the surface of the adsorbent, until its complete saturation occurred (‘first’ breakthrough). From this moment, the adsorption zone was occupied until its ‘first’ exhaustion occurred. When the bed was exhausted, the concentration of the treated effluent was not affected any longer.

Nevertheless, as more and more effluent flew upstream through the column and more organics contacted the bone char, new active sites appeared by the overlapping of long-chain C-EDR compounds. It seemed that the process restarted, adsorption continued leading to a new saturation (and, therefore, a new breakthrough)

**Figure 3.** Breakthrough curves for different flow rates obtained in lab-scale fixed-bed experiments. $C_0 = 63 \pm 4 \text{ mg L}^{-1}; Z = 7.7 \text{ cm}$: (a) $Q = 1.50 \pm 0.04 \text{ mL min}^{-1}$; (b) $Q = 2.94 \pm 0.05 \text{ mL min}^{-1}$ and (c) $Q = 5.81 \pm 0.16 \text{ mL min}^{-1}$.

**Figure 4.** Breakthrough curves for different initial C-EDR COD concentrations obtained in lab-scale fixed-bed experiments. $Q = 5.98 \text{ mL min}^{-1}; Z = 7.7 \text{ cm}$: (a) $C_0 = 62 \pm 8 \text{ mg L}^{-1}$ and (b) $C_0 = 93 \pm 1 \text{ mg L}^{-1}$. 
point) and new exhaustion. This was repeated three times for the deepest bed possible at the experimental conditions. At lower bed depths, the breakthrough curves obtained seemed to be portions of the complete curve, for a bed depth of 12.9 cm. For 7.7 cm depth, it was possible to notice two distinct regions and the entire range of \( C/C_0 \) (from 0.2 to 0.9) was also observed, in stages of breakthrough and exhaustion, but with shorter times and smaller volumes of treated effluent. When the bed depth was 5.0 cm, the curve started at 0.20 and stabilized at approximately 0.65, only two regions could be observed. At lower bed depths \((Z = 3.5 \text{ and } 2.6 \text{ cm})\), it was not possible to observe either the breakthrough or \( C/C_0 \) regions before 0.5, 0.6, going to 0.7 and 0.85, respectively. Therefore, as mentioned by McCabe et al. [53], deep bed layers affected the treatment efficiency, since the adsorption rate in liquids is slower when compared to the gas adsorption.

Concerning bed capacities, a variation from around 6.00 to 35.60 mg g\(^{-1}\) was observed for the different bed depths applied, as shown in Table 2. The maximum value of \( q \) (35.60 mg g\(^{-1}\)) obtained for the deepest bed (12.9 cm) was due to the larger amount of the adsorbent, which resulted in a greater availability of active sites to adsorb organics [54] and superior opportunity of adsorbent–adsorbate.

A breakthrough curve profile very similar to that obtained for bed depth variation could be observed due to flow rate variations. At low flow rates, for example, the curves seemed to be composed of more than one breakthrough–exhaustion region, suggesting once again the recovery of adsorptive capacity over time (or with greater volume of treated effluent), with more adsorbate being incorporated (multilayers). The lowest flow rate \((1.5 \text{ mL min}^{-1})\) was the condition under which higher levels of removal were achieved \((q = 29.95 \text{ mg g}^{-1})\), since the curve started from \( C/C_0 \) of approximately 0.20, reaching 0.85 in the ‘last’ exhaustion. Indeed, as can be seen in Table 3, bed adsorption capacity almost doubled when the lowest flow rate \((Q = 1.5 \text{ mL min}^{-1})\) was compared to \( Q = 2.94 \text{ mL min}^{-1} \) (29.95 against 15.39 mg g\(^{-1}\), respectively) and was more than three times superior, when compared to \( Q = 5.81 \text{ mL min}^{-1} \). This increase was due to greater residence time of the solution inside the column when smaller flow rates were employed [46], which also favored the adsorbent–adsorbate contact.

Evaluating the influence of the initial concentration of organics, bed capacities did not vary significantly for the range of \( C_0 \) investigated, as they differed less than 5% in the conditions tested \((X = 7.7 \text{ cm} \text{ and } Q \sim 6.0 \text{ mL min}^{-1})\), from 8.80 to 9.29 mg g\(^{-1}\) from \( C_0 \sim 63 \text{ mg L}^{-1} \) to \( C_0 = 93 \text{ mg L}^{-1} \), respectively.

The operational parameters describing the breakthrough curve obtained from each experimental condition, calculated from the equations presented in the previous section, are shown in Table 4. The breakthrough points were determined considering \( C/C_0 \) 5% higher than the initial \( C/C_0 \) ratio, in each region of the curve. The exhaustion times were determined taking 95% of the final \( C/C_0 \) ratio for each region.

For those conditions where more than one breakthrough–exhaustion region was noticed, the curve was sectioned in each region and the parameters obtained were calculated for each of the regions. The time to the MTZ to move, \( t_x \), was proportional to the volume of treated effluent between the breakthrough point and the point of exhaustion, and this value increased with the rise of bed depth, with the reduction of the flow rate and initial concentration.

Regarding the bed depth, breakthrough curves became steeper when the bed depth diminished, indicating a reduction in mass transfer resistance [41]. In addition, breakthrough time increased with growing bed depth. This was due to the larger amount of the adsorbent, which resulted in a greater availability of active sites to adsorb organics [54] and due to solution residence time increasing inside the column [46], favoring adsorbent–adsorbate contact, as discussed previously. Regarding the flow rate, breakthrough was reached more quickly when the flow rate increased. This was because, as the flow rate increases, mass transfer resistance decreases. Therefore, it was notorious that the service time increased with the reduction of flow rate, leading to a greater volume of effluent treated up to the breakthrough point. Liu et al. stated that flow rate is an important issue to control the delay factor, residence time and hydraulic conductivity in a treatment system and its increase raises the rates of external mass transfer and internal diffusion, leading to a faster saturation compared to lower flow rates [55], what was observed in this study.

Column saturation up to breakthrough point increased with the decrease of adsorption zone depth,

---

**Table 2.** Bed adsorptive capacities for different bed depths \((Q \sim 3.0 \text{ mL min}^{-1} \text{ and } C_0 \sim 63.0 \text{ mg L}^{-1})\).

<table>
<thead>
<tr>
<th>Operational conditions (goals)</th>
<th>( Q \sim 3.0 \text{ mL min}^{-1} \text{ and } C_0 \sim 63.0 \text{ mg L}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bed depths, ( X ) (cm)</td>
<td>2.6 \quad 3.5 \quad 5.0 \quad 7.7 \quad 12.9</td>
</tr>
<tr>
<td>Adsorptive capacity, ( q ) (mg g(^{-1}))</td>
<td>7.24 \quad 5.96 \quad 12.00 \quad 15.39 \quad 35.60</td>
</tr>
</tbody>
</table>

**Table 3.** Bed adsorptive capacities for different flow rates \((X = 7.7 \text{ cm} \text{ and } C_0 \sim 63.0 \text{ mg L}^{-1})\).

<table>
<thead>
<tr>
<th>Operational conditions (goals)</th>
<th>( X = 7.7 \text{ cm} \text{ and } C_0 \sim 63.0 \text{ mg L}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Q ) (mL min(^{-1}))</td>
<td>1.50 \quad 2.94 \quad 5.81</td>
</tr>
<tr>
<td>( q ) (mg g(^{-1}))</td>
<td>29.95 \quad 15.39 \quad 8.80</td>
</tr>
</tbody>
</table>
with the increase of the flow rate and increase of the initial concentration. Gupta et al. also found the same trend while studying the removal of heavy metal ions in columns using an activated carbon from fertilizer residues [45] as adsorbent.

### 3.2. Mathematical modeling

Thomas, Yan, Wolborska and BDST models were fitted to experimental data and this mathematical modeling showed precarious fitting ($R^2 < 0.90$) for most cases. The Yan model fit was poor for all the operational conditions ($R^2 < 0.90$), thus, Yan parameters results were suppressed. Thomas, Wolborska and BDST models also failed to describe the system for the conditions of lower bed depths (2.6, 3.5 and 5.0 cm), highest initial concentration ($C_0 = 93 \pm 1$) and lowest flow rate ($Q = 1.50 \pm 0.04$).

Nevertheless, for the operational conditions under which the determination coefficient $R^2$ was around 0.90 or superior for Thomas, Wolborska and BDST modeling, the parameters obtained are presented in Table 5. Such operational conditions also allowed comparison of bed depths and flow rates effect.

As far as Thomas, Wolborska and BDST models are concerned, it can be highlighted that, as mentioned by Xu et al., every model has its limitations because they are derived from specific conditions and situations. Moreover, still according to Xu et al. [16], ‘breakthrough curves deviate from the ideal S shape, prediction derived from any model usually cannot meet the demands’ (p. 172) and, as discussed previously, this was the case in this study.

The Thomas model, for example, in spite of being one of the most widely used models, as mentioned by Lezehari et al. and Song et al. [48,56,57], was developed to describe mathematically the performance of a cation exchange column. It presents a relatively general flowing system equation, assuming the second-order reversible reaction kinetics (which was the case in the real system, one of the reasons why the Thomas model was tested). The model neglects axial dispersion and in this study, we could admit that axial dispersion was not relevant for Thomas model fitting. In this study, despite $L$ (bed length)/$D$ (internal diameter) ratio was close to 6, far from the ratio $L/D > 20$, value cited in the literature as the conservative value to guarantee that axial dispersion can be neglected, some authors take negligible axial dispersion into account at lower $L/D$ values, depending on other characteristics of the system and operational conditions. Apud Delgado [58] mentions that the variations of the fluid velocity, porosity and dispersion coefficient, in radial position, can be negligible if $D$ (column diameter)/$d$ (particle diameter) > 15, which was the case in this

### Table 4: Operational Parameters to describe breakthrough for bone char-C-EDR refractory organics system.

<table>
<thead>
<tr>
<th>Bed depth (cm)</th>
<th>X (cm) (regions)</th>
<th>Flow rate $Q$ (mL min$^{-1}$)</th>
<th>Initial concentration $C_0$ (mg L$^{-1}$)</th>
<th>Breakthrough time $t_b$ (h)</th>
<th>Exhaustion time $t_e$ (h)</th>
<th>Time to move MTZ $t_z$ (h)</th>
<th>Bed depth/time $U_z$ (cm/h)</th>
<th>Adsorption zone depth $X_z$ (cm)</th>
<th>Column saturation %</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.6</td>
<td>3.5</td>
<td>3.09 ± 0.04</td>
<td>3.07 ± 0.07</td>
<td>3.00 ± 0.15</td>
<td>3.00 ± 0.15</td>
<td>3.00 ± 0.15</td>
<td>0.54</td>
<td>3.52</td>
<td>12.5</td>
</tr>
<tr>
<td>3.5</td>
<td>3.0</td>
<td>2.54 ± 0.04</td>
<td>2.49 ± 0.05</td>
<td>2.50 ± 0.04</td>
<td>2.50 ± 0.04</td>
<td>2.50 ± 0.04</td>
<td>0.34</td>
<td>1.30</td>
<td>82.7</td>
</tr>
<tr>
<td>5.0</td>
<td>2.6</td>
<td>2.84 ± 0.04</td>
<td>2.79 ± 0.05</td>
<td>2.75 ± 0.04</td>
<td>2.75 ± 0.04</td>
<td>2.75 ± 0.04</td>
<td>0.25</td>
<td>2.90</td>
<td>80.6</td>
</tr>
</tbody>
</table>

*Conditions for which breakthrough curves were splitted in two or three regions of breakthrough/exhaustion, results per region.*
study \( D/d \sim 23 \). Celenza reports as usual a ratio \( L/D > 4 \) [58,59].

Modeling according to Wolborska was tried because of the real system investigated in this study and Wolborska and Wolborska and Pustelnik studied the adsorption of an organic compound (\( p \)-nitrophenol) on activated carbon [16,60,61].

The BDST model is derived from the Bohart–Adams model and they have been successful in predicting several breakthrough curves [16,48,62]. Due to its simplicity associated with the assumption that adsorption is governed by the surface reaction between the adsorbate and the unused capacity of the adsorbent, this model was used in the present work, also aiming at providing helpful information to scale up the process as it is discussed in the following section.

From Table 5 analysis, it was observed that, although numerical values of adsorption capacity parameters obtained by the Thomas model were diverse from real ones due to the fit, the same trend as observed for calculated capacity values was confirmed: deeper beds and low flow rates give better results of adsorption capacity. This trend was similar to that found by Singh et al. in their continuous adsorption studies, for the removal of furfural, from aqueous solutions using activated charcoal as adsorbent [63]. Indeed, as the bed depth increased and the flow rate decreased, the residence time of the solution in the column became larger, allowing the diffusion of the adsorbate deeper into the porous of the adsorbent, so that both the saturation time and the capacity of adsorption increased [46]. From the results with higher determination coefficients for BDST modeling, it was noticed that the increase in bed depth and the decrease in the flow rate led to a reduction in the adsorption rate, indicating that the process became slower. In fact, the reduction of the rate contributed to the increase of adsorption capacity by improving the adsorbent–adsorbate contact. For Wolborska parameters, the same conclusions could be drawn for the effects of bed depth and flow rate, in cases where the fit was satisfactory. \( \beta \) parameter decreased for greater bed and lower flow rate; then, mass transfer occurred more slowly in these cases, corroborating previous discussions. In fact, Hamdaoui stated that the increase in the flow rate increases \( \beta \), since there is a decrease of the boundary layer around the adsorbent with higher turbulence [47].

The effect of the initial concentration on the maximum adsorptive capacity obtained by the models could not be evaluated, since the fit to all the models for these conditions was precarious (\( R^2 = 0.4494 \)).

### 3.3. Scale up

Figure 5 shows the BDST model for different \( C/C_0 \) ratios (0.25, 0.30, 0.55, 0.60 and 0.65) for bed depths of 5.0, 7.7 and 12.9 cm at a flow rate of 2.97 ± 0.03 mL min\(^{-1} \). From the angular and linear coefficients obtained for each \( C/C_0 \) ratio, \( K_{BDST} \) and \( N_0 \) were calculated as described in the experimental section. Critical depth \( (X_0) \) was determined and the results are shown in Table 6.

The best fit was observed for \( C/C_0 \) of 0.55. Calculated critical depths \( (X_0) \) confirmed experimental results, for example, for \( C/C_0 = 0.25 \), \( X_0 \) was 4.87 cm and at bed heights of 2.6 and 3.5 cm it was only possible to identify the breakthrough curve from \( C/C_0 = 0.60 \) and 0.55, respectively; and at 5.0 cm bed depth, \( C/C_0 = 0.25 \) was identified. For \( C/C_0 = 0.55 \) (best fit), the predicted critical depth was 3.6 cm. In fact, at 3.5 cm bed depth, experimentally evaluated, it was possible to identify \( C/C_0 \) of 0.55 (which was not the case at lower depth, such as that of 2.6 cm). For the BDST scale-up method, validation testing at a lower flow rate \( (Q = 1.5 \pm 0.04 \text{ mL min}^{-1}) \) was carried out and deviation between theoretical and experimental values is presented in Table 7.

![Figure 5. Bed depth service time model for bed depths of 5.0, 7.7 and 12.9 cm and flow rate of 2.97 ± 0.03 mL min\(^{-1} \) with \( C/C_0 \) of 0.25, 0.30, 0.55, 0.60 and 0.65.](image)
Table 6. BDST model parameters for different C/C0.

<table>
<thead>
<tr>
<th>C/C0</th>
<th>( k_{BDST} ) (L mg(^{-1}) h(^{-1}))</th>
<th>( N_0 ) (mg L(^{-1}))</th>
<th>( X_0 ) (cm)</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>( 2.62 \times 10^{-3} )</td>
<td>4038.18</td>
<td>4.87</td>
<td>0.9123</td>
</tr>
<tr>
<td>0.30</td>
<td>( 1.67 \times 10^{-3} )</td>
<td>5202.71</td>
<td>4.59</td>
<td>0.9068</td>
</tr>
<tr>
<td>0.55</td>
<td>(-6.92 \times 10^{-5})</td>
<td>37.661.74</td>
<td>3.61</td>
<td>0.9910</td>
</tr>
<tr>
<td>0.60</td>
<td>(-13.2 \times 10^{-5})</td>
<td>39.991.95</td>
<td>3.61</td>
<td>0.9879</td>
</tr>
<tr>
<td>0.65</td>
<td>(-18.6 \times 10^{-5})</td>
<td>42.634.58</td>
<td>3.67</td>
<td>0.9865</td>
</tr>
</tbody>
</table>

Table 7. Column service time for C/C0 = 0.25, 0.30, 0.55, 0.60 and 0.65: model (previewed by BDST model) and experimental (through breakthrough curves, \( h = 7.7 \) cm and \( Q = 1.5 \pm 0.04 \) mL min\(^{-1}\)).

<table>
<thead>
<tr>
<th>Time (h) to reach C/C0</th>
<th>Experimental</th>
<th>Model</th>
<th>Deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25(^a)</td>
<td>7.00</td>
<td>14.62</td>
<td>−108.86(^*)</td>
</tr>
<tr>
<td>0.30(^a)</td>
<td>14.00</td>
<td>19.35</td>
<td>−38.21(^*)</td>
</tr>
<tr>
<td>0.55</td>
<td>172.00</td>
<td>152.87</td>
<td>11.12</td>
</tr>
<tr>
<td>0.60</td>
<td>180.00</td>
<td>162.33</td>
<td>9.82</td>
</tr>
<tr>
<td>0.65</td>
<td>188.00</td>
<td>172.18</td>
<td>8.41</td>
</tr>
</tbody>
</table>

\(^a\)Huge deviations, more than 30%.

For C/C0 of 0.25 and 0.30, the deviations were huge (more than 100% for the first case and more than 35% for the second case). On the other hand, a deviation close to 10% was observed for prediction of breakthrough time by theoretical calculation for C/C0 of 0.55, 0.60 and 0.65, which can be considered acceptable, since C-EDR effluent is a real complex mixture of organic and inorganic compounds on which several intervening factors can act [11]. Thus, the last three C/C0 ratios were taken for scaling up and results are presented in Table 8. Therefore, scaling up predicted a service time for a single adsorption column operating under the above-mentioned conditions of about 16 days to reach 45% efficiency of removal of refractory organic (C/C0 = 0.55) in terms of COD.

4. Conclusions

Refractory organics from saline stream from electrodialysis (C-EDR) were partially removed by bone char in an adsorption column in a lab scale. The effluent C-EDR contained organic compounds with opposite affinity by the bone char in the conditions employed. The maximum adsorption capacity of organics by bone char \( q \) increased with increasing bed depth and decreasing flow rate, due to the greater availability of active sites and greater adsorbent–adsorbate contact, reaching 35.60 mg g\(^{-1}\) for the deepest bed evaluated \( (12.9 \) cm) (at \( Q \sim 3.0 \) mL min\(^{-1}\) and \( C_0 \sim 63.0 \) mg L\(^{-1}\)). Variation in the initial concentration did not affect the bed capacity significantly in the range of \( C_0 \) employed. It was possible to predict satisfactorily the breakthrough time by the BDST model (deviation near 10%) for C/C0 of 0.55, 0.60 and 0.65, which was considered a very good result, due to the complexity of the effluent. Scaling up for a single adsorption column using real process conditions and dimensions of an inactive carbon filter already existent in the refinery predicted a service time of 16 days to remove, with 45% of efficiency (C/C0 = 0.55), the refractory organics present in the effluent.

Acknowledgements

The authors gratefully acknowledge University of São Paulo (USP), Bonechar Carvão Ativado do Brasil and Petrobras.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

The authors gratefully acknowledge Brazilian Agencies CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) [482165/2013-8], FAPEMIG (Fundação de Amparo à Pesquisa do Estado de Minas Gerais) [APQ0268814], and CAPES-PROEX (Comissão de Aperfeiçoamento de Pessoal do Nível Superior - Programa de Excelência Acadêmica) for financial support.

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