Cr(III) dynamic removal in a fixed-bed column by using a co-gasification char

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Abstract
A char (GC) obtained from the co-gasification of rice husk and polyethylene was used in a fixed-bed column with continuous flow for Cr(III) removal assays from synthetic and industrial wastewaters. For comparison purposes, a commercial activated carbon (CAC) was also used. The best experimental conditions in the continuous removal assays were the following ones: Cr(III) inflow concentration = 5 mg L⁻¹, feed flow rate = 3 mL min⁻¹, mass of adsorbent in the column = 0.8 g, and inflow temperature = 50 °C. Under these conditions, the highest uptake capacities were 1.60 and 2.14 mg g⁻¹ in the synthetic solution, and 3.25 and 7.83 mg g⁻¹ in the industrial wastewater, for GC and CAC, respectively. These results are different from those obtained under batch conditions in which GC performed better than CAC. Cr(III) removal by both adsorbents occurred due to precipitation, but CAC presented a slightly higher amount of Cr(III) removed due to its highest porosity. The regeneration of GC and CAC was also studied, but both adsorbents showed no capacity to be used in more than one cycle. This study highlighted the importance of studying Cr(III) removal under continuous conditions, as the removal mechanisms may be completely different from the batch assays, affecting the adsorbents’ performance.

Keywords | Chars · Cr(III) recovery · Fixed-bed column · Rice wastes · Wastewater

Introduction
Gasification is a thermochemical process that occurs in a partial oxidation environment under a sub-stoichiometric amount of oxygen. Through gasification, wastes can be thermally converted into high-added value products. Syngas is the main energy product of gasification, being composed of CO, H₂, CH₄, and a mixture of other minor gases (Guo et al. 2016). However, a carbonaceous solid by-product, with a relatively high ash content, commonly known as char, is also produced (You et al. 2017). This char can be used as-produced or activated for catalytic and adsorption applications (Benedetti et al. 2018; Buentello-Montoya et al. 2019).

In the last decade, an increasing interest in using chars in wastewater treatment has been noticed in the literature (Fu and Wang 2011; Peng et al. 2014; Inyang et al. 2016; Bernardo et al. 2017; Li et al. 2020). The specific properties of chars that make them useful as adsorbents of pollutants include a relatively porous structure, functional groups, and/or mineral clusters over the surface (You et al. 2017). As adsorbents, chars resemble some properties of activated carbons which are frequently used for the removal of diverse pollutants from water and wastewaters. Compared to the commercial activated carbons, chars are cheaper and with effective adsorption capacity. The feedstocks for char production are abundant and of low-cost, being mainly obtained from agroforestry biomass and solid bio-wastes (Palanivelu et al. 2020).

Given the high potential of chars as metal adsorbents through precipitation, complexation, electrostatic attraction, and ion exchange mechanisms (Abbas et al. 2018), the authors previously studied the removal of Cr(III) from...
The column (Aksu and Gönen 2004; Patel 2019). In fact, most of the published studies have been devoted to the use of pyrolysis-derived chars as metal adsorbents (Wang et al. 2019), being scarce the use of gasification chars for this same purpose (Runtti et al. 2014). However, as the authors have demonstrated in a previous work (Godinho et al. 2017), the gasification chars can perform better than the pyrolysis chars in Cr(III) removal due to their high mineral content. Given the high uptake capacity of trivalent chromium by rice wastes gasification chars under batch conditions demonstrated in a previous work (Dias et al. 2018b), the authors have decided to study the Cr(III) removal under dynamic conditions by using the char that showed the highest Cr(III) uptake capacity.

Most studies regarding adsorption use batch systems, as these systems are cheaper and easier to operate than the dynamic ones (Patel 2019; Wojnicki et al. 2020). Although continuous systems are preferred in industrial processes for wastewater treatment through adsorption (Pérez Marín et al. 2009; de Franco et al. 2018), there is a lack of data concerning the operation of continuous flow systems and their regeneration, particularly for recent adsorbents such as chars. Despite this lack of information, the data obtained under batch conditions are only hardly applied to dynamic treatment processes operating by column systems (Farooq et al. 2013). Thus, it is mandatory to study the adsorption mechanisms under conditions closer to industrial applications, which means that adsorption studies must move forward to dynamic conditions.

The fixed-bed column is an example of a dynamic system allowing continuous flow processing by means of adsorption/desorption/regeneration cycles. After the column saturation, the adsorbent may be regenerated using suitable solutions (Cossich et al. 2004). In the case of metals, acids (such as HCl, HNO₃, and H₂SO₄), chelating agents, among other compounds, are commonly used (Abdolali et al. 2017; Arim et al. 2018; Baharlouei et al. 2018; Kegl et al. 2020). Cyclic adsorption/desorption/regeneration processes can be applied to a fixed-bed column, making use of the adsorbent concentration gradient and osmotic pressure as the driving forces for adsorption/desorption; also, the dynamic adsorption/desorption cycles allow more efficient utilization of the adsorbent capacity (Aksu and Gönen 2004). Other advantages of the fixed-bed column systems are the following: (a) it can be easily scaled up from a laboratory-scale system, (b) the adsorption/desorption protocol can be automated, (c) high degrees of purification can often be achieved in a single-step process, and (d) a large volume of wastewater can be continuously treated using a defined mass of adsorbent in the column (Aksu and Gönen 2004; Patel 2019).

The objective of this work was to use a char obtained from the co-gasification of rice wastes in the removal of Cr(III) from aqueous solutions by using fixed-bed columns operated under continuous flow, giving continuity to the previous study under batch conditions. The removal of Cr(III) under continuous flow was tested in a synthetic solution and in a leather tanning wastewater to simulate a real scenario of use.

Date and location of the research

Gasification experiments have been carried out at Unidade de Bioenergia e Biorrefinarias (UBB)—Laboratório Nacional de Energia e Geologia (LNEG) in 2014–2015. Cr(III) removal assays and quantification of Cr(III) were done at the Department of Chemistry and at the Department of Sciences and Technology of Biomass from Faculdade de Ciências e Tecnologia—NOVA University of Lisbon, between 2018 and 2019. The industrial wastewater was collected at SIRECRO-AUSTRA—a chromium recovery plant from leather tanning wastewaters located at Alcanena, Portugal—in November 2017.

Materials and methods

Origin of the gasification char (GC)

80% rice husk (RH) and 20% polyethylene (PE) were submitted to co-gasification in a bubbling fluidized bed gasifier with 0.08 m internal diameter and 1.5 m height (Pinto et al. 2002). The gasification conditions were as follows: \( T = 850 \, ^\circ C \); reaction time = 90–120 min; fuel flow = 5 g min⁻¹ (dry ash-free basis, daf); gasification agent = \( O_2 \); equivalent ratio (g oxygen/g fuel daf) = 0.2; and vapour flow = 5 g min⁻¹. These operational conditions were defined to increase the char yield. The bed material was composed of fine sand previously washed to remove free minerals.

After the co-gasification process, the mixed bed material (a mixture of sand and char) was collected at the bottom of the gasifier and sieved to separate the chars from sand. The syngas produced was passed through a cyclone, a gas condensation system, and filters, before being collected for further characterization. The yield of bed chars in the gasification assays was in the range of 6–13% (w/w).

The study on syngas composition was the main objective of other works (André et al. 2014; Pinto et al. 2015).

RH was supplied by Orivárzea, a rice production and processing company owning rice fields in Ribatejo region (Portugal). RH was collected from husk silos at the rice
processing mill. PE bags were obtained from rice farmers, after their use in the transportation of rice seeds to the crop fields. The characterization of RH and PE was shown in a previous study (Dias et al. 2017).

For comparison purposes, a commercial activated carbon (CAC) (Norit GAC 1240) was also used.

Both GC and CAC were milled and sieved to a particle size of 50–100 µm. The characterization of GC and CAC was previously studied (Dias et al. 2017, 2018a, b) and is summarized in Supplementary Material, Table S1.

**Experimental set-up of column assays**

The experimental set-up of the column assays is presented at Supplementary material (Fig. S1). Briefly, the initial Cr(III) solution (1), which was prepared with known concentrations, was pumped into the fixed-bed column (diameter = 0.5 cm; height = 10.0 cm) (4) from bottom to top, through a hose (3) by using a peristaltic pump (2). The adsorbent (4a) was fixed in the column by using filter papers (4b) of 2.5 µm pore-size diameter on both top and bottom of the column. At the top of the column, a new hose (5) led the solution (post-removal assay) to a collector flask (6). To control the temperature of the assays, a circulating water bath (7) was used. The bath tank was filled up with deionized water (8) and set to a desired temperature. The water was recirculated through a water chamber involving the fixed-bed column, from bottom to top, by using recirculating hoses (9).

**Cr(III) removal assays from synthetic solution**

The synthetic chromium solution was prepared with CrN3O3.9H2O salt (99%).

The performance of a fixed-bed column is studied through the outflow concentration over time. This is represented by a breakthrough curve (Calero et al. 2009; Patel 2019). For a fixed-bed height, these curves are usually expressed as the ratio between the absorbate concentrations in the outflow and inflow \( \left( \frac{C_t}{C_0} \right) \) of the column, as a function of time or outflow volume (Calero et al. 2009; Patel 2019). For this purpose, several samples were collected over the testing time, throughout each adsorption test. The pH of each sample was measured. Finally, the samples were acidified with HNO3 for pH < 2, before Cr quantification by inductively coupled plasma atomic emission spectrometry (ICP-AES). All Cr(III) removal assays were performed with a fixed flow rate of 3 mL min\(^{-1}\).

The adsorption process in fixed-bed columns is influenced by several parameters, such as the initial absorbate concentration, mass of adsorbent (or height of the bed column), flow rate, and temperature (Calero et al. 2009; de Franco et al. 2018). With the objective to maximize the removal potential of the adsorbent, different conditions were tested in the column assays, namely different Cr(III) inflow concentrations, adsorbent masses, and temperatures. At the end of each assay, several parameters were analysed:

(a) Breakthrough time \( (t_b) \) — Time at which Cr(III) concentration in the outflow is 5% of the inflow concentration \( \left( \frac{C_t}{C_0} = 0.05 \right) \) (min).

(b) Saturation time \( (t_s) \) — Time at which Cr(III) concentration in the outflow is 95% of the inflow concentration \( \left( \frac{C_t}{C_0} = 0.95 \right) \) (min).

(c) pH \( t_b \) and pH \( t_s \) — pH value at breakthrough and saturation time, respectively (Sørensen scale).

(d) Cr(III) mass retained \( (m_{\text{Cr(III)}\text{-ads}}) \) — Total mass of Cr(III) retained until saturation time (mg), which was calculated through Eq. 1 (de Franco et al. 2018):

\[
m_{\text{Cr(III)}\text{-ads}} = \frac{Q \times C_0}{1000} \times \int_0^{t_s} \left( 1 - \frac{C_t}{C_0} \right) dt \quad (1)
\]

where \( Q \) is the flow rate of the solution passing through the column (mL min\(^{-1}\)), \( C_0 \) is the Cr(III) concentration in the inflow (mg L\(^{-1}\)), and \( C_t \) is the Cr(III) concentration in the outflow on time \( t \) (mg L\(^{-1}\)).

(e) Cr(III) removal efficiency \( (\eta) \) — Ratio between the total mass of Cr(III) retained by the column and total mass of Cr(III) that was passed through the column (Eq. 2), expressed in % (Aksu and Gönen 2004):

\[
\eta = \frac{m_{\text{Cr(III)}\text{-ads}}}{m_{\text{Cr(III)}\text{-total}}} \times 100 \quad (2)
\]

where \( m_{\text{Cr(III)}\text{-total}} \) is the total mass of Cr(III) that passed through the column (Eq. 3) (Aksu and Gönen 2004):

\[
m_{\text{Cr(III)}\text{-total}} = \frac{Q \times C_0 \times t_s}{1000} \quad (3)
\]

where all the variables have the same meanings and units as for the previous equations.

(f) Total uptake capacity \( (q_{\text{total}}) \) — Removal capacity of the column in the saturation time \( (t_s) \) or total uptake capacity of the column (mg Cr(III) g\(^{-1}\) adsorbent) (4) (de Franco et al. 2018):

\[
q_{\text{total}} = \frac{m_{\text{Cr(III)}\text{-ads}}}{m_{\text{ads}}} \quad (4)
\]

where \( m_{\text{ads}} \) is the mass of adsorbent in the column (g) and \( m_{\text{Cr(III)}\text{-ads}} \) has the same meaning and units as defined for Eq. (1).
Effect of Cr(III) concentration in the inflow

Five inflow concentrations \( (C_0) \) were tested: 2.5, 5, 10, 25, and 50 mg L\(^{-1}\). These assays were performed under the following conditions: \( Q = 3 \text{ mL min}^{-1} \); \( T = 25 ^\circ \text{C}; t = \text{up to 70 min (until the saturation has been reached)} \).

The inflow concentration that originated the assay with the highest uptake capacity was selected for the next assays.

Effect of adsorbent mass

To test the effect of adsorbent mass \( (m_{ads}) \) in the removal process, three masses were tested: 0.2, 0.4, and 0.8 g (column height: 1.1, 2.1, and 4.2 cm, respectively). These assays were performed under the following conditions: \( Q = 3 \text{ mL min}^{-1}; T = 25 ^\circ \text{C}; t = \text{up to 150 min (until the saturation has been reached)} \); \( C_0 = 5.0 \text{ mg L}^{-1} \).

The adsorbent mass that originated the assay with the highest uptake capacity was selected for the next assays.

Effect of temperature

To test the influence of the temperature \( (T) \) in the removal process, three temperatures were tested: 25, 40, and 50 ^\circ \text{C}. These assays were performed under the following conditions: \( Q = 3 \text{ mL min}^{-1}; T = 25 ^\circ \text{C}; t = \text{up to 210 min (until the saturation has been reached)} \); \( C_0 = 5.0 \text{ mg L}^{-1}; m_{ads} = 0.8 \text{ g} \).

The temperature that originated the assay with the highest uptake capacity was selected for the next assays.

Control assay with a commercial activated carbon (CAC)

The conditions used in the assays with CAC were the following: \( Q = 3 \text{ mL min}^{-1}; T = 25 ^\circ \text{C}; t = \text{up to 10 min (until the saturation has been reached)} \); \( C_0 = 5.0 \text{ mg L}^{-1}; m_{ads} = 0.8 \text{ g} \).

Cr(III) recovery and adsorbent’s regeneration

To understand the regeneration capacity of the adsorbent, adsorption and desorption cycles were performed. The conditions of these assays were the same as in Sect. Control assay with a commercial activated carbon (CAC) and comprised the following steps:

(a) Adsorption assay until the saturation has been reached.
(b) Desorption assay with acetic acid \( (0.2 \text{ mol L}^{-1}) \) until the Cr(III) concentration in the column outflow has reached <0.2 mg L\(^{-1}\). The acetic acid was chosen for being a greener acid than the typical acids used in column desorption processes, such as HCl (Abdolali et al. 2017; Baharlouei et al. 2018). The concentration of 0.2 mol L\(^{-1}\) has been chosen because at that concentration the acetic acid provides a pH of 3, capable to solubilize the retained Cr.
(c) Desorption assay with ultrapure water until Cr(III) concentration in the column outflow has reached a value <0.02 mg L\(^{-1}\). This ensures the removal of excess acid from the column and the stabilization of its pH.
(d) Repetition of the steps (a), (b), and (c) until the maximum regeneration capacity has been reached.

For comparison purposes, the same test was performed for CAC.

Cr(III) removal assays from industrial wastewater

To replicate real conditions of use, the column assays were also performed with an industrial wastewater rich in Cr. The industrial wastewater was collected in SIRECRO-AUSTRA—a chromium recovery plant from leather tanning wastewaters (Alcanena, Portugal). The wastewater sample was collected at the plant inflow, after the screening operation unit, where the concentration of Cr(III) in the solution is around 2000 mg L\(^{-1}\). This high concentration remains dissolved as the pH is <4.0. The characterization of the industrial wastewater was already shown in a previous work (Dias et al. 2018b).

As in the removal assays from the synthetic solution, several samples were collected throughout each test at the outflow of the column to define the breakthrough curves. The pH of each sample was measured. These samples were then acidified with HNO\(_3\) for pH <2 before the Cr quantification by ICP-AES. The parameters characterized for Cr(III) removal assays from the synthetic solution (Sect. Cr(III) removal assays from synthetic solution) were also used in the removal assays with the industrial wastewater. The experimental conditions were the same as defined in Sect. Control assay with a commercial activated carbon (CAC). Once again, CAC was used for comparison purposes.

Kinetic modelling

The experimental data were adjusted to Thomas’ nonlinear model (Eq. 5) (Thomas 1948):

\[
\frac{C_t}{C_0} = \frac{1}{1 + e^{(k_q q_0 C_{ads})/(m_{ads} C_0 t)} - (k_q C_0 t)}
\]

where \( C_t \) (mg L\(^{-1}\)) is the Cr(III) concentration in the column outflow on time \( t \) (min), \( C_0 \) is the Cr(III) concentration in the column inflow (mg L\(^{-1}\)), \( k_q \) is the Thomas rate constant (mL min\(^{-1}\) mg\(^{-1}\)), \( q_0 \) is the maximum removal capacity of the adsorbent (mg Cr(III) g\(^{-1}\) adsorbent), \( m_{ads} \) is the mass of adsorbent
in the column (g), and \( Q \) is the flow rate of the solution passing through the column (mL min\(^{-1}\)).

Thomas model has been the most used kinetic model in column studies. It assumes that under conditions where the external and internal diffusion resistances are very low, the experimental data follow Langmuir adsorption isotherm without axial dispersion, considering that the rate driving force obeys to a second-order reversible reaction kinetic (Rosales et al. 2017; Patel 2019).

The model adjustment was done through the minimum of the least-square method by using SOLVER function of MS Excel 2016 (Eq. 6):

\[
\text{Min} \left[ \sum \text{Least squares} \right] = \text{Min} \left[ \sum (q_{\exp} - q_{\text{cal}})^2 \right] \quad (6)
\]

where \( q_{\exp} \) is the experimental Cr(III) uptake capacity (mg Cr(III) g\(^{-1}\) adsorbent) and \( q_{\text{cal}} \) is the calculated/modelled Cr(III) uptake capacity (mg Cr(III) g\(^{-1}\) adsorbent).

**Results and discussion**

**Cr(III) removal assays from the synthetic solution**

**Effect of the inflow Cr(III) concentration**

The results of the column assays with GC for Cr(III) removal from synthetic solution at different inflow concentrations are shown in Fig. 1 and Table 1. The initial pH values of the synthetic solution for 2.5, 5.0, 10, and 25 mg L\(^{-1}\) were 4.49, 4.22, 4.05, 3.74, and 3.66, respectively. The differences in pH values are related to the dissociation of water molecule. Cr(III) promotes the release of H\(^+\) and consequently acidifies the solution. The higher the Cr(III) concentration is, the lower the pH will be (Godinho et al. 2017).

Fig. 1  a Breakthrough curves and b pH values for the column assays using GC for Cr(III) removal from the synthetic solution at different inflow concentrations (black symbols represent the experimental breakthrough and saturation times; lines represent the Thomas model adjustment. Experimental conditions: \( m_{\text{ads}} = 0.2 \) g; \( Q = 3 \) mL min\(^{-1}\); \( T = 25 \) °C; \( t = \) up to 70 min
The assays with Cr(III) inflow concentrations \(C_0\) of 50 and 25 mg L\(^{-1}\) presented very similar results, reaching the adsorbent saturation very fast (≤ 2.72 min). Consequently, it was not possible to quantify the breakthrough time \(t_b\) for these assays. Although the assay with a \(C_0\) of 10 mg L\(^{-1}\) presented a slightly higher saturation time \(t_s\) (9.55 min), \(t_b\) was still not quantifiable. Only in the assays with \(C_0\) of 5 and 2.5 mg L\(^{-1}\), it was possible to quantify \(t_b\) (0.546 and 3.19 min, respectively). Regarding \(t_s\), the values increased to 25.8 and 47.0 min, respectively.

The breakthrough curves become flattered for lower initial concentrations, indicating a lower diffusion, and probably this was the rate-limiting step. Therefore, lower concentrations led to higher breakthrough and saturation times. For higher concentrations, there was a higher driving force causing a faster transport of Cr ions and sharper breakthrough curves.

The pH \(t_b\) was very close in all the assays, varying between 5.65 and 6.05. This indicates that precipitation was ruling Cr(III) removal, once Cr(III) precipitation occurs at pH > 5 (Li et al. 2010). As the initial pH of all synthetic solutions was below 5, the high ash content and consequently the mineral content of GC (Supplementary material, Table S1) played an important role on increasing the pH of the solution and removing Cr(III) by precipitation.

Although the Cr(III) removal efficiency \(\eta\) increased by decreasing \(C_0\) from 5.0 to 2.5 mg L\(^{-1}\), the highest uptake capacities for both the experimental data \(q_{\text{total}}\) and Thomas model \(q_0\) were found in the assay with a \(C_0\) of 5.0 mg L\(^{-1}\) (0.995 and 0.923 mg g\(^{-1}\), respectively). Taking into consideration these results, the \(C_0\) of 5.0 mg L\(^{-1}\) was selected for the next assays.

### Effect of the adsorbent mass

The results of the column assays for Cr(III) removal from the synthetic solution by using GC in different masses are shown in Fig. 2 and Table 1. The initial pH values of the synthetic solution for 0.2, 0.4, and 0.8 g of adsorbent were 4.22, 4.20, and 4.24, respectively.

Increasing the mass of adsorbent \(m_{\text{ads}}\) also increased all experimental parameters (except the pH). A higher mass of adsorbent (and higher bed height) also caused longer \(t_b\) and \(t_s\) since the mass transfer zone is much higher. These differences were reflected on the removal efficiency \(\eta\) and uptake capacities \(q_{\text{total}}\) and \(q_0\). The assay with a \(m_{\text{ads}}\) of 0.4 g obtained a \(\eta\) of 56.8%, a \(q_{\text{total}}\) of 1.02 mg g\(^{-1}\), and a \(q_0\) of 1.03 mg g\(^{-1}\), while in the assay with a \(m_{\text{ads}}\) of 0.8 g those values slightly increased to 58.4%, 1.26 mg g\(^{-1}\), and 1.24 mg g\(^{-1}\), respectively. If the differences between the uptake capacities for the assays with masses of 0.2 and 0.4 g were not very significant, in the assay with a \(m_{\text{ads}}\) of 0.8 g those discrepancies were more relevant, with an increase of 26.6% for \(q_{\text{total}}\) and 34.4% for \(q_0\), when compared to the initial assay \(m_{\text{ads}} = 0.2 \text{ g}\). Still, in general, these uptake capacities were low.

### Table 1

| \(C_0\) (mg L\(^{-1}\)) | Experimental data parameters | Thomas model parameters |
|------------------------|----------------------------|-------------------------|
| \(C_0\) (mg L\(^{-1}\)) | \(t_b\) (min) | \(pH_{t_b}\) | \(t_s\) (min) | \(pH_{t_s}\) | \(m_{\text{Cr(III)}_{\text{ads}}}\) (mg) | \(\eta\) (%) | \(q_{\text{total}}\) (mg g\(^{-1}\)) | \(k_{\text{th}}\) (mL min\(^{-1}\) mg\(^{-1}\)) | \(q_0\) (mg g\(^{-1}\)) | \(R^2\) |
| 2.5                    | 3.19                      | 9.28                    | 47.0              | 6.05              | 0.182                       | 54.0                   | 0.912                           | 59.7                               | 0.900                        | 0.995 |
| 5.0                    | 0.546                     | 9.44                    | 25.8              | 5.88              | 0.200                       | 49.2                   | 0.995                           | 40.8                               | 0.923                        | 0.995 |
| 10.0                   | n.q                       | n.q                     | 9.55              | 5.75              | 0.137                       | 46.8                   | 0.683                           | 57.6                               | 0.674                        | 0.991 |
| 25.0                   | n.q                       | n.q                     | 2.67              | 5.65              | 7.59 \times 10^{-2}         | 35.5                   | 0.379                           | 55.8                               | 0.226                        | 0.992 |
| 50.0                   | n.q                       | n.q                     | 2.72              | 5.87              | 9.91 \times 10^{-2}         | 25.3                   | 0.495                           | 22.0                               | n.q                           | 0.977 |

\(m_{\text{ads}}\) (mg): 0.2, 0.4, 0.8 g

\(T\) (°C): 25, 40, 50

n.q.—not quantifiable

The pH \(t_b\) was very close in all the assays, varying between 5.65 and 6.05. This indicates that precipitation was ruling Cr(III) removal, once Cr(III) precipitation occurs at pH > 5 (Li et al. 2010). As the initial pH of all synthetic solutions was below 5, the high ash content and consequently the mineral content of GC (Supplementary material, Table S1) played an important role on increasing the pH of the solution and removing Cr(III) by precipitation.
Regarding pH, while the pH$_{tb}$ decreased with the increase in mass, the pH$_{ts}$ was again in the same range as in the previous assays (between 5.73 and 5.94). This means that precipitation played an important role in Cr(III) removal, emphasizing the importance of the high ash and mineral content of GC (Supplementary material, Table S1) on the Cr(III) removal.

The sharper breakthrough curve for the assay with 0.2 g of char is reflected in a high Thomas kinetic constant since the removal kinetics are much higher. It can be concluded that no relevant advantage on Cr(III) removal will be achieved by increasing the mass of adsorbent from 0.2 to 0.4 g, while the increase from 0.4 to 0.8 g may significantly increase the overall efficiency of the removal process. For that reason, 0.8 g was the adsorbent mass selected to be used in the next assays.

Effect of temperature

The results of the column assays for Cr(III) removal from synthetic solution using GC at different temperatures are shown in Fig. 3 and Table 1. The initial pH values of the synthetic solution for 25, 40, and 50 °C were 4.24, 4.18, and 4.16, respectively.

Differing from the previous results, the breakthrough curves of these assays were similar (Fig. 4). Although $t_b$ and $t_s$ have increased with temperature, the differences...
between the assays with temperatures of 25 and 50 °C were not marked. The same happened in the efficiency of Cr(III) removal with values between 54.2% (T = 50 °C) and 58.4% (T = 25 °C). Some differences were only found for the uptake capacities, with values of \( q_{\text{total}} \) varying between 1.19 (T = 40 °C) and 1.42 mg g\(^{-1}\) (T = 50 °C) and of \( q_0 \) varying between 1.15 (T = 40 °C) and 1.38 mg g\(^{-1}\) (T = 50 °C). Higher temperature seems to increase the mass transfer in the column. Also, the removal kinetics increased with the increasing temperature (higher Thomas kinetic constant).

The pH values followed the same tendency of similarity between assays: pH \( t_b \) ranged between 7.48 and 7.82, while pH \( t_s \) presented similar values as in the previous assays (between 5.49 and 5.73), showing again the importance of the mineral properties of GC in Cr(III) removal by precipitation.

The assay with a temperature of 50 °C showed the highest uptake capacities, and, for that reason, this temperature was selected to be used in the following assays.

**Comparison with a commercial activated carbon (CAC)**

Usually, the uptake capacities determined from dynamic tests are lower than those found in batch experiments, as the external diffusion is favoured under vigorous stirring conditions as performed under batch adsorption. With fixed-bed experiments, the mass transfer resistance is higher (usually intra-particle diffusion controls the adsorption rate), resulting in lower uptake capacities. That is why the uptake capacities obtained with GC char were much lower under dynamic conditions (around 1 mg g\(^{-1}\)) than in batch conditions (around 8 mg g\(^{-1}\)) (Dias et al. 2018b).
As specified before (Sect. Materials and methods - Effect of adsorbent mass), GC presented a column height of 4.2 cm for a mass of 0.8 g. However, once CAC is a different material with a different apparent density, the column height was of 6.0 cm for the same mass of adsorbent. The results of the column assays for Cr(III) removal from the synthetic solution using GC and CAC are shown in Table 2. Breakthrough curves and pH are presented in Supplementary material, Fig. S2. The initial pH values of the synthetic solution were 4.16, for the assay with GC, and 4.18, for the assay with CAC. In general, CAC presented better parameters than GC. The $t_b$ of CAC were slightly longer than for GC (59.3 and 51.2 min, respectively), but the difference of $t_s$ was more significant (208 and 145 min, respectively). Although the Cr(III) removal efficiency of CAC was slightly lower than for GC, the uptake capacities were higher for CAC with values of 2.14 mg g$^{-1}$ for $q_{total}$ and of 2.05 mg g$^{-1}$ for $q_0$. Due to the slightly lower pH$_{pzc}$ of CAC (9.13) (Dias et al. 2018b, a) when compared to GC (9.58) (Dias et al. 2018b), the pH values for CAC throughout the assay were, in general, lower than for GC; especially in the beginning of the assay, still the pH values were above 5 for almost all the assay, meaning that chromium precipitation was also important on the removal of Cr(III) by CAC. The pore properties of CAC might also explain the higher Cr removal since this adsorbent is an activated carbon with a high surface area and pore volume (Supplementary material, Table S1). The breakthrough curve for CAC indicates a higher diffusion resistance that can be related to the fact that this carbon presents high microporosity. Cr ions take a longer time to diffuse into the micropores causing slower adsorption kinetics and a lower Thomas constant. Nevertheless, the commercial carbon presented higher uptake of Cr than the char. These results are slightly different from those obtained in an earlier study (Dias et al. 2018b), in which the gasification char was able to remove much more chromium from water under batch conditions than the same commercial carbon. However, in those conditions trivalent chromium was mainly removed by GC through ion exchange, while in dynamic conditions the main mechanism was precipitation induced by pH.

In general, the uptake capacities cited in the literature were higher than the uptake capacities of GC and CAC (Cos-sich et al. 2004; Elangovan et al. 2008; Calero et al. 2009; Pérez Marín et al. 2009; Farooq et al. 2013; Ferraz et al. 2015; Tofan et al. 2015; Arim et al. 2018; Zhang et al. 2019). However, in most of these studies the pH was not monitored throughout the assays, and as already discussed, pH is a very important parameter for Cr(III) removal.

**Cr(III) recovery and regeneration of adsorbents**

Figure 4 presents the four stages of Cr(III) recovery and regeneration for GC and CAC, and Table 3 shows the experimental data and Thomas model parameters of the adsorption cycles. The pH values of those four stages are presented at Supplementary Material, Fig. S3.

The initial pH of the synthetic solution was: (a) 4.24 for GC and 4.21 for CAC concerning the first Cr(III) adsorption cycle; (b) 2.91 for GC and 2.78 for CAC concerning the desorption cycle with acetic acid; (c) 5.45 for GC and 5.08 for CAC concerning the desorption cycle with ultrapure water; and (d) 4.24 for GC and 4.19 for CAC concerning the second Cr(III) adsorption cycle.

As expected, the first adsorption cycle showed similar results to those shown in Sect. Results and discussion - Comparison with a commercial activated carbon (CAC), both for the breakthrough curves (Fig. 4a) and for the pH values (Supplementary material, Fig. S3). However, the differences between GC and CAC were slightly lower. If in the case of $t_b$ and $t_s$ the results were very similar (except the $t_s$ for CAC), in the other parameters the differences were slightly higher. For GC, there was a slightly increase in the Cr(III) removal efficiency (56.9%) and uptake capacities ($q_{total} = 1.60$ mg g$^{-1}$ and $q_0 = 1.55$ mg g$^{-1}$).

### Table 2 Experimental data and Thomas model parameters of column assays for Cr(III) removal from the synthetic solution and industrial wastewater using GC and CAC

| Synthetic solution | Experimental data parameters | Thomas model parameters |
|--------------------|-----------------------------|------------------------|
|                    | $t_b$ (min) | pH | $t_s$ (min) | pH | $m_{Cr(III)}$ (mg) | $\eta$ (%) | $q_{total}$ (mg g$^{-1}$) | $k_t$ (mL min$^{-1}$ mg$^{-1}$) | $q_0$ (mg g$^{-1}$) | $R^2$ |
| GC                 | 51.2        | 7.48 | 145          | 5.49 | 1.14 | 54.2 | 1.42 | 17.3 | 1.38 | 0.992 |
| CAC                | 59.3        | 6.39 | 208          | 5.10 | 1.72 | 52.2 | 2.14 | 9.09 | 2.05 | 0.991 |
| Wastewater         |             |     |              |     |     |     |     |     |     |      |
| GC                 | 2.25        | 10.0 | 538          | 5.15 | 2.68 | 31.6 | 3.35 | 3.25 | 3.00 | 0.980 |
| CAC                | 44.2        | 6.77 | 1 100        | 4.75 | 6.26 | 34.8 | 7.83 | 1.46 | 6.66 | 0.977 |
On the other hand, CAC presented a similar efficiency but slightly lower uptake capacities ($q_{\text{total}} = 1.86 \text{ mg g}^{-1}$ and $q_0 = 1.76 \text{ mg g}^{-1}$). In this assay, although CAC still presented slightly better results than GC, the differences between both adsorbents were much lower.

The differences between the results of the assays in this section and those in Sect. Results and discussion - Comparison with a commercial activated carbon (CAC) may be related to two factors: (a) the assays in Sect. Results and discussion - Comparison with a commercial activated carbon (CAC) were performed beyond the saturation time (210 min for GC and 270 min for CAC), while in this section the assay was stopped at the saturation time (150 min for GC and 210 min for CAC); (b) heterogeneity of adsorbent samples, especially in the case of GC.

The desorption step with acetic acid (Fig. 4b) showed discrepancies between both adsorbents. For GC, the desorption was very fast, starting with higher concentrations of

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**Table 3** Experimental data and Thomas model parameters for Cr(III) column adsorption cycles from synthetic solution using GC and CAC

| Adsorbent | Adsorption Cycle | Experimental data parameters | Thomas model parameters |
|-----------|------------------|------------------------------|-------------------------|
|           | $t_b$(min) | pH $t_b$ | $t_s$(min) | pH $t_s$ | $m_{\text{Cr(III) ads}}$(mg) | $\eta$(%) | $q_{\text{total}}$(mg g$^{-1}$) | $k_{th}$(mL min$^{-1}$ mg$^{-1}$) | $q_0$(mg g$^{-1}$) | $R^2$ |
| GC        | 1$^{st}$      | 54.1   | 7.51     | 150      | 5.77   | 1.28 | 56.9 | 1.60 | 14.8 | 1.55 | 0.990 |
|          | 2$^{nd}$      | n.q    | n.q      | 6.42     | 5.05   | 2.08×10$^{-2}$ | 21.4 | 2.59×10$^{-2}$ | 21.4 | 116 | 7.50×10$^{-3}$ | 0.986 |
| CAC       | 1$^{st}$      | 60.7   | 6.46     | 181      | 5.13   | 1.49 | 53.8 | 1.86 | 14.6 | 1.76 | 0.991 |
|          | 2$^{nd}$      | 0.17   | 4.92     | 127      | 5.30   | 0.349 | 18.6 | 0.436 | 37.0 | 0.125 | 0.878 |

n.q.—not quantifiable
Cr(III) desorbed, which quickly decreased. At time 0 (i.e., the first drops of solution after passing the acid through the column), the concentration of Cr(III) ($C_t$) was 9.78 mg L$^{-1}$, but only 3 min later $C_t$ was already at 1.67 mg L$^{-1}$, showing that the highest recovery of Cr(III) occurred in the first minutes. After 30 min, $C_t$ was already below 0.2 mg L$^{-1}$, and after 60 min the assay stopped with a $C_t$ around 0.1 mg L$^{-1}$.

On the other hand, for CAC there was an increase in the concentration of Cr(III) desorbed at the beginning of the process and only then a slow decrease in the desorption process was registered. At time 0, $C_t$ was of 1.50 mg L$^{-1}$ and increased to the highest value of 3.52 mg L$^{-1}$ after 2 min. Then, $C_t$ slowly decreased and the assay was stopped at 150 min, when $C_t$ reached a value slightly lower than 0.2 mg L$^{-1}$. The lower desorption of chromium with CAC might be also related to the fact that Cr ions were trapped inside the carbon micropores. In the case of GC, the chromium was almost all precipitated in its surface, being solubilized very fast.

The third stage of the process (Fig. 4c) was mainly to wash out the acetic acid from the adsorbent. However, in the beginning of the process there was still some desorption of Cr(III), especially in the case of CAC where $C_t$ was of 1.76 mg L$^{-1}$ at time 0. The washing step induced a pH increase from 3.28 to 4.55, in GC, and from 2.87 to 4.56 in CAC (Supplementary material, Fig. S3).

The fourth and last stage of the process (second adsorption cycle) (Fig. 4d) showed that the use of GC in more than one adsorption cycle was not advantageous, as $t_s$ was reached at 6.42 min and $t_b$ was not even quantifiable. For

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**Fig. 5**  
(a) Breakthrough curves and (b) pH values of the column assays for Cr(III) removal from industrial wastewater using GC and CAC (black symbols represent the breakthrough and saturation times; lines represent the Thomas model adjustment). Experimental conditions: $Q = 3$ mL min$^{-1}$; $t = $ up to 270 min; $C_0 = 5.0$ mg L$^{-1}$; $m_{ads} = 0.8$ g; $T = 50$ °C.
that reason, the Cr(III) removal efficiency (21.4%) and especially the uptake capacities \( q_{\text{total}} = 2.59 \times 10^{-2} \text{ mg g}^{-1} \) and \( q_0 = 7.50 \times 10^{-3} \text{ mg g}^{-1} \) were considered to be very low. Regarding CAC, although a second adsorption cycle was performed, the performance was much lower than in the first cycle; therefore, a second adsorption cycle is also not viable.

Opposing to all the other assays, the pH of CAC in this assay (Supplementary material, Fig. S3) increased in the beginning, reaching an equilibrium from about 30 min to 103 min and slowly decreased until pH 4.4 at 210 min. This may suggest that the release of minerals from CAC was much slower and gradual than in GC. Other possibility is that there was still some acid in the column which made the initial pH of the assay to be lower than expected. No other desorption/adsorption cycles were performed as both GC and CAC showed poor properties in the second adsorption cycle.

**Cr(III) removal assays from the industrial wastewater**

The results of the column assays for Cr(III) removal from the industrial wastewater by using GC and CAC are shown in Fig. 5 and Table 2. The initial pH of the industrial wastewater was 4.78.

Both adsorbents performed better in the industrial wastewater than in the synthetic solution. In both cases, \( t_b \) was lower (2.25 min for GC), but \( t_c \) was much higher (538 and 1100 min for GC and CAC, respectively), indicating that the removal occurred for a much longer period of time (more than 3.7 times for GC and 5.27 times for CAC). Although Cr(III) removal efficiencies decreased slightly (31.6% for GC and 34.8% for CAC), the uptake capacities increased significantly: GC obtained a \( q_{\text{total}} \) of 3.25 mg g\(^{-1}\) and \( q_0 \) of 3.00 mg g\(^{-1}\), while in CAC these values increased to 7.83 ad 6.66 mg g\(^{-1}\), respectively. This means that the uptake capacities increased 2.35 times for GC and 3.65 times for CAC, which highlights the better results in the industrial wastewater.

CAC performed better than GC for the industrial wastewater, as recorded in the synthetic solution. The pH values of the assays may explain this fact. For GC, at saturation time (538 min) the pH was 5.15, suggesting that the Cr(III) removal by this adsorbent was ruled by precipitation. At that same time, the pH for CAC was similar (5.24). However, at about 660 min, the pH of CAC was already below 5, indicating that porosity started to rule the removal process. The \( t_c \) for CAC was 1100 min with a pH of 4.75, meaning that almost half of the assay was ruled by CAC porosity. In these circumstances, the higher porosity of CAC seemed to be more significant than the highest mineral content of GC for Cr(III) removal.

**Conclusion**

The experimental conditions that promoted the best results for Cr(III) removal from the synthetic solution were the following: \( Q = 3 \text{ mL min}^{-1}; t = 210 \text{ min for GC and 270 min for CAC}; C_0 = 5 \text{ mg L}^{-1}; m_{\text{ads}} = 0.8 \text{ g}; T = 50 ^\circ\text{C}. \) Under these conditions, the highest uptake capacities were found at a \( t_c \) of 150 min for GC and 208 min for CAC, with a \( q_{\text{total}} \) of 1.60 and 2.14 mg g\(^{-1}\), respectively.

Both GC and CAC showed no capacity to be used in more than one adsorption cycle.

Both adsorbents performed better in the industrial wastewater with a \( t_c \) of 538 min for GC and 1100 min for CAC, obtaining a \( q_{\text{total}} \) of 3.25 and 7.83 mg g\(^{-1}\), respectively.

CAC presented higher chromium removal than GC for both the synthetic solution and industrial wastewater. Besides precipitation, the high surface area and pore volume were the important features on Cr(III) removal by CAC.

The results obtained in this study highlight the need to study the removal of a contaminant through continuous flow fixed-bed columns since in the practical operation of a full-scale sorption this is the preferred option. The dynamic behaviour can be completely different from the batch sorption experiment of a given adsorbent, being essential to quantify its performance under different conditions to design and optimize an industrial adsorption process.

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**Authors’ contributions** DD contributed to methodology, validation, formal analysis, investigation, data curation, and writing—original draft; MB performed conceptualization, methodology, formal analysis, investigation, writing—review and editing, supervision, and funding acquisition; FP contributed to conceptualization, investigation, resources, writing—review and editing, supervision, and funding acquisition; IF performed conceptualization, resources, writing—review and editing, project administration, and funding acquisition; NL contributed to conceptualization, methodology, validation, writing—review and editing, supervision, project administration, and funding acquisition.

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Declarations

Conflict of interests The authors declare that they have no competing interests.

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