

## Activated Carbons from the Co-pyrolysis of Rice Wastes for Cr(III) Removal

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Rice husk and polyethylene were mixed (50 % w/w each) and submitted to a pyrolysis assay. Four physical activations with CO<sub>2</sub> were performed on the resulting co-pyrolysis char (PC). The activation at 800 °C, for 4h, generated the activated carbon (PAC3) with the best textural properties. PC, PAC3 and a commercial activated carbon (CAC) were characterized and submitted to Cr(III) removal assays. PC had a high percentage of volatile matter that was removed after the physical activation, resulting in more available pores in the final material (PAC). In the Cr(III) removal assays, two S/L ratios were tested: 5 and 10 g L<sup>-1</sup>. PC did not remove any Cr(III) from the solutions, but PAC presented similar results to CAC. At the S/L of 5 g L<sup>-1</sup>, Cr(III) removal was of 58.5 % for PAC and 62.5 % for CAC, both by adsorption mechanism; at the S/L of 10 g L<sup>-1</sup>, Cr(III) removal was almost complete due to precipitation caused by pH increase. The highest uptake capacities were of 7.92 mg g<sup>-1</sup> for PAC and 8.71 mg g<sup>-1</sup> for CAC, at the S/L of 5 g L<sup>-1</sup>. The results indicated that PAC3 may be a viable alternative to CAC on Cr(III) removal from aqueous media.

### 1. Introduction

Rice is the second most produced cereal in the world; in Europe, Italy and Portugal are the main producer and consumer countries, respectively. With a world production of 756.7 million tonnes in 2017 (FAO, 2017), this crop generates high quantities of wastes, mostly rice husk (RH), rice straw (RS) and plastics (mainly polyethylene – PE) from the transportation of seeds and fertilizers to the cultivation fields. Currently, some destinations of these wastes are not the most environmentally sound; new routes of valorisation are therefore necessary (Lim et al., 2012).

Due to their calorific values, these wastes can be used in thermo-chemical processes, such as pyrolysis, generating liquids and gases that can be used as renewable energy sources (Costa et al., 2007; Pütün et al., 2004; Quispe et al., 2017). Additionally, another material is formed during pyrolysis – the char.

Although the char is a by-product of pyrolysis process, several studies have been conducted in order to valorize this material (Cha et al., 2016; Kuppens et al., 2014). One of the most promising routes for the pyrolysis char is its use as an adsorbent material for removing pollutants from aqueous medium (Bernardo et al., 2017; Dias et al., 2017; Godinho et al., 2017). Being a more economic and sustainable material, char can be a viable alternative to the commercial activated carbons, which are the most traditional materials used for adsorption of contaminants.

One of the most problematic pollutants in water is chromium (Cr). Aside the environmental risks, Cr is also a very important raw material used in many applications of metallurgic industry, leather tanning, wood preservation, and even in chemical industry as catalyst.

In 2011, the European Commission published a report regarding the critical raw materials for the European industry. This list took into consideration the supply risk and economic importance of raw materials. In 2015 and 2017, the report was revised; in the three reports, Cr was classified as one of the most important materials, due to its economic importance (EC, 2017). Therefore, the recovery of this raw material from industrial wastes and wastewaters is a topic of utmost importance.

Although there are some studies on the recovery of Cr by chars from aqueous medium (Agrafioti et al., 2014; Pan et al., 2013), the use of chars from the co-pyrolysis of rice wastes is not an explored topic.

The aim of this work was to use a char, resulting from the co-pyrolysis of rice wastes, and an activated carbon, produced from the activation of the char, in the removal of Cr(III) from a synthetic medium – aqueous medium spiked with Cr(III). A commercial activated carbon was also used in this study for comparison purposes.

## 2. Materials and Methods

### 2.1 Co-pyrolysis assays

Several mixtures of rice wastes with different experimental conditions were tested in co-pyrolysis assays. The assays were performed in a 1 L batch reactor and the chars were separated from the liquid fraction through settling and extraction with hexane (Soxhlet extraction) with a hexane/char ratio of 17 mL g<sup>-1</sup>, for 3 h.

For this study, it was used the char (PC) resulting from the pyrolysis of 50% (w/w) RH and 50% (w/w) PE under the following reactional conditions: T = 390 °C; P = 6 bar; t = 35 min. This assay was selected because it produced the highest char yield.

### 2.2 Activation of PC

To improve its adsorption capacity, PC was physically activated with CO<sub>2</sub>; N<sub>2</sub> was used for heating up and cooling down the char during activation, to ensure that no oxidation occurred during the process. Both CO<sub>2</sub> and N<sub>2</sub> flows were of 150 ml min<sup>-1</sup>. Four activations were performed (Table 1) in a quartz reactor placed inside an electric vertical tube furnace.

*Table 1: Experimental conditions of PC activations*

Activation	Code	Time (h)	Temperature (°C)
1	PAC1	2	800
2	PAC2	2	850
3	PAC3	4	800
4	PAC4	4	850

Solid yield ( $\hat{Y}$ , expressed in %) of each physical activation was calculated through equation 1:

$$\hat{Y} = \frac{m_f}{m_0} \times 100 \% \quad (1)$$

where  $m_0$  is the initial PC mass (g) (char mass) and  $m_f$  is the PAC mass (g) (mass of activated carbon obtained after the physical activation of char).

PC and PAC samples were characterized; afterwards, both PC and PAC sample with the best textural properties were used on the adsorption assays.

For comparison purposes, a commercial activated carbon (CAC) (Norit GAC 1240) was also characterized and used on the adsorption assays. Norit GAC 1240 is a granular activated carbon produced by steam activation of select grades of coal.

### 2.3 Characterizations of the adsorbents

All adsorbents (PC, PAC and CAC) were milled, sieved to 100 µm and characterized for:

(a) Textural analysis – surface area and pore volume distribution were determined through N<sub>2</sub> adsorption-desorption isotherms at 77 K, with previous sample degasification under vacuum conditions at 150 °C;

(b) Proximate analysis – moisture content (M) (EN 14774-1), volatile matter (VM) (EN 15148), and ashes (Ash) (EN 14775) were determined by gravimetric method;

(c) Elemental composition – CHNS contents were determined by ASTM D 5373 and ASTM D4239 standards;

(d) pH<sub>pzc</sub> – the adsorbents were placed in 0.1 M NaCl solutions with an initial pH (pH<sub>i</sub>) between 2 and 12, at a solid/liquid ratio (S/L) of 5 g L<sup>-1</sup>. The solutions were stirred in a roller-table device, at 150 rpm, for 24 h. At the end of agitation time, final pH (pH<sub>f</sub>) was measured. The pH<sub>pzc</sub> value corresponded to the point where pH<sub>i</sub> = pH<sub>f</sub>.

## 2.4 Cr(III) removal assays

The Cr(III) synthetic medium used in the removal assays was prepared by using a standard Cr(NO<sub>3</sub>)<sub>3</sub> solution of 1000 mg Cr(III) L<sup>-1</sup> in 0.5 M of HNO<sub>3</sub> (Merck) and ultrapure water. The initial concentration of Cr(III) in the medium was of 70 mg L<sup>-1</sup>. The initial pH of the medium was corrected for 4.5 with NaOH, once Cr(III) starts to precipitate at a pH above 5. Batch assays were performed with two S/L ratios of 5 and 10 g L<sup>-1</sup>, under constant stirring of 150 rpm (in a roller-table shaker) for 24h at room temperature (25 ± 1 °C). The samples were then filtered through 0.45 µm cellulose nitrate membranes and the pH of filtrates was measured. The filtrates were then acidified with HNO<sub>3</sub> for a pH below 2 before Cr quantification by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).

Cr(III) removal efficiency ( $\eta$ , expressed in %) and adsorbent uptake capacity ( $q_e$ , expressed in mg g<sup>-1</sup>) of each assay were calculated through equations 2 and 3, respectively:

$$\eta = \frac{(C_0 - C_f)}{C_0} \times 100\% \quad (2)$$

$$q_e = \frac{(C_0 - C_f)}{m} \times V \quad (3)$$

where  $C_0$  and  $C_f$  are Cr(III) concentrations (mg L<sup>-1</sup>) before and after the batch assays, respectively,  $m$  is the adsorbent mass (g) and  $V$  the volume of Cr(III) solution (L).

## 3. Results and Discussion

### 3.1 Activation of PC and characterizations

Table 2 shows the solid yield of physical activations and textural properties of the samples.

PC char, being a non-activated sample has no porous structure that can be characterized with N<sub>2</sub> isotherm technique.

PAC4 had the lowest solid yield of all activated carbons and its textural analysis indicated that the activation conditions were very aggressive, promoting the collapse of porous structure. For the other samples, all surface areas and pore volumes increased, indicating successful activations. PAC3 had the lowest solid yield (66.1 %) meaning that more volatile matter was removed during this activation, providing more available pores, and consequently increasing the surface area (325 m<sup>2</sup> g<sup>-1</sup>) and total volume (0.18 cm<sup>3</sup> g<sup>-1</sup>) of the (Seixas et al., 2017). Still, these results were lower than for CAC.

Considering these results, PAC3 was the activated carbon selected to be further characterized and used on the adsorption assays.

Table 2: Solid yield of the physical activations and textural properties of the samples

Samples	$\hat{Y}$ (%)	Textural properties			
		S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	V <sub>total</sub> (cm <sup>3</sup> g <sup>-1</sup> )	V <sub>micro</sub> (cm <sup>3</sup> g <sup>-1</sup> )	V <sub>meso</sub> (cm <sup>3</sup> g <sup>-1</sup> )
PC	n.a.	2.2	n.d.	n.d.	n.d.
PAC1	79.1	190	0.11	0.06	0.044
PAC2	70.0	223	0.12	0.07	0.042
PAC3	66.1	325	0.18	0.10	0.071
PAC4	32.6	n.d.	n.d.	n.d.	n.d.
CAC	n.a.	1030	0.56	0.304	0.253

n.a.: not applicable; n.d.: not determined.

#### 3.1.1 Proximate and elemental analysis

Proximate and elemental analysis of the adsorbents (Table 3) showed that PC was mainly composed by fixed carbon (46.0 % w/w), but still with a high percentage of volatile matter (22.7 % w/w) and ashes (30.0 % w/w). While the ashes could be interesting for contributing with ions for ion exchange mechanism with Cr(III), the volatile matter hindered the adsorbent pores.

The physical activation (PAC3) removed significant volatile matter from the material (a decrease of 81.3% was registered), which led to more available pores as it was seen in the textural properties (Table 2); however, it caused a higher concentration of ashes on the resulting activated carbon.

As expected, CAC was mainly composed by fixed carbon (74.2 % w/w).

Table 3: Proximate and elemental analysis of the adsorbents

Parameter	Adsorbent		
	PC	PAC3	CAC
<i>Proximate analysis (% w/w ar)</i>			
Moisture content	1.38	4.36	13.1
Volatile matter	22.7	4.25	7.04
Fixed carbon	46.0	51.0	74.2
Ashes	30.0	40.4	5.70
<i>Elemental analysis (% w/w daf)</i>			
C	59.7	50.2	86.3
H	4.46	0.26	0.47
N	0.51	0.47	0.16
S	< 0.03	< 0.03	0.57

ar: as received; daf: dry ash-free.

### 3.1.1 $pH_{pzc}$

Figure 1 presents the  $pH_{pzc}$  of adsorbents.

PC presented a neutral to slightly acidic  $pH_{pzc}$  (6.4), but after the physical activation (PAC3), the  $pH_{pzc}$  increased significantly to 9.9, which characterized PAC3 sample as an alkaline material. This happened because the activation removed most volatile matter, thus concentrating the ashes which are responsible for the alkalinity of the adsorbent.  $pH_{pzc}$  of CAC (9.1) was also alkaline although slightly lower than for PAC3.

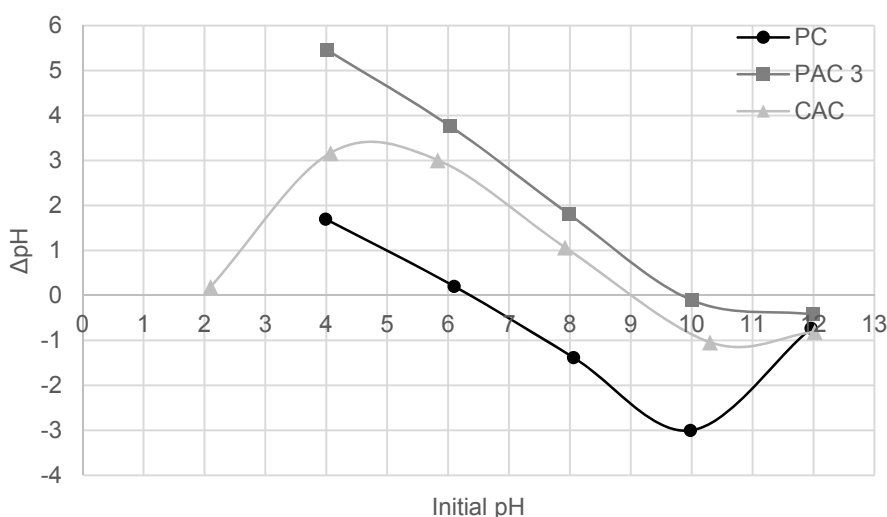


Figure 1:  $pH_{pzc}$  of adsorbents.

### 3.2 Cr(III) removal assays

Cr(III) removal assays (Figure 2) revealed that PC removed almost no Cr(III) from the solution (0 % at S/L of 5 g L<sup>-1</sup> and 3.66 % at S/L of 10 g L<sup>-1</sup>); this can be explained by the fact that this is a non-porous material (Table 2). However, after its physical activation, the resulting material (PAC3) showed interesting results for Cr(III) removal assays, comparable to those obtained for CAC. At a S/L of 10 g L<sup>-1</sup>, both activated carbons (PAC3 and CAC) removed almost all Cr(III) present in the solution (99.9 % for PAC3 and 98.1 % for CAC). However, in both cases, the final pH of filtrates was above 5, indicating that the removal was mainly driven by precipitation. On the other hand, at a S/L of 5 g L<sup>-1</sup>, both assays presented filtrates with a final pH below 5, indicating that precipitation mechanism has not dominated, and adsorption could have explained Cr(III) removal. Although the surface area and pore volume of PAC3 were much lower than those for CAC (Table 2), the performance of both adsorbents was very similar: PAC3 removed 58.8 % of Cr(III) from the solution and CAC removed 62.5 %. These results suggest that the adsorption of Cr(III) by PAC3 was not only by pore filling, but also by ion exchange, due to the high ash content of PAC3, composed by minerals that can exchange ions with Cr, such as K, Ca, Na and Mg (Dias et al., 2017).

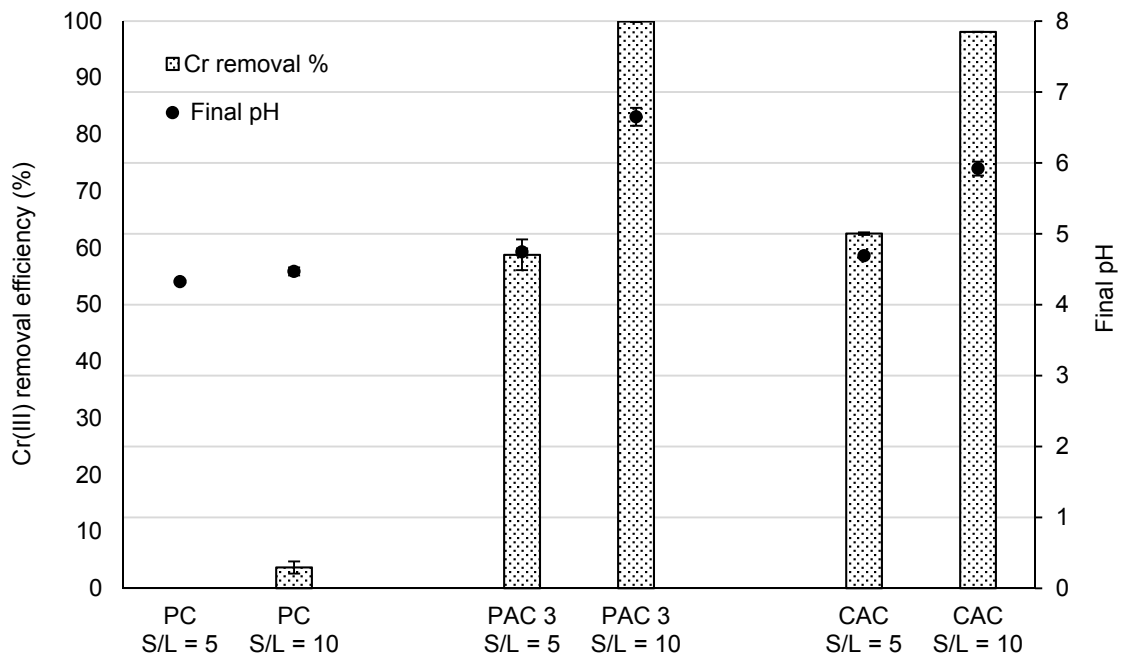


Figure 2: Cr(III) removal efficiency of adsorbents and final pH of filtrates (S/L expressed in g L<sup>-1</sup>).

The results of uptake capacity (Figure 3) were in agreement with the Cr(III) removal efficiencies (Figure 2). PC presented very low uptake capacities for both assays (below 0.27 mg g<sup>-1</sup>). PAC3 and CAC presented higher values at the S/L of 5 g L<sup>-1</sup>, even though at the S/L of 10 g L<sup>-1</sup> all Cr(III) was removed. These results show that Cr(III) removal by adsorption mechanism (pH below 5) requires less adsorbent mass than the removal by precipitation (pH above 5). The difference in the uptake capacities for both activated carbons at S/L of 5 g L<sup>-1</sup> (7.92 mg g<sup>-1</sup> for PAC3 and 8.71 mg g<sup>-1</sup> for CAC) was not significant; it can be concluded that, under these conditions, PAC3 showed good properties to be an efficient renewable alternative to the commercial activated carbon tested in this study.

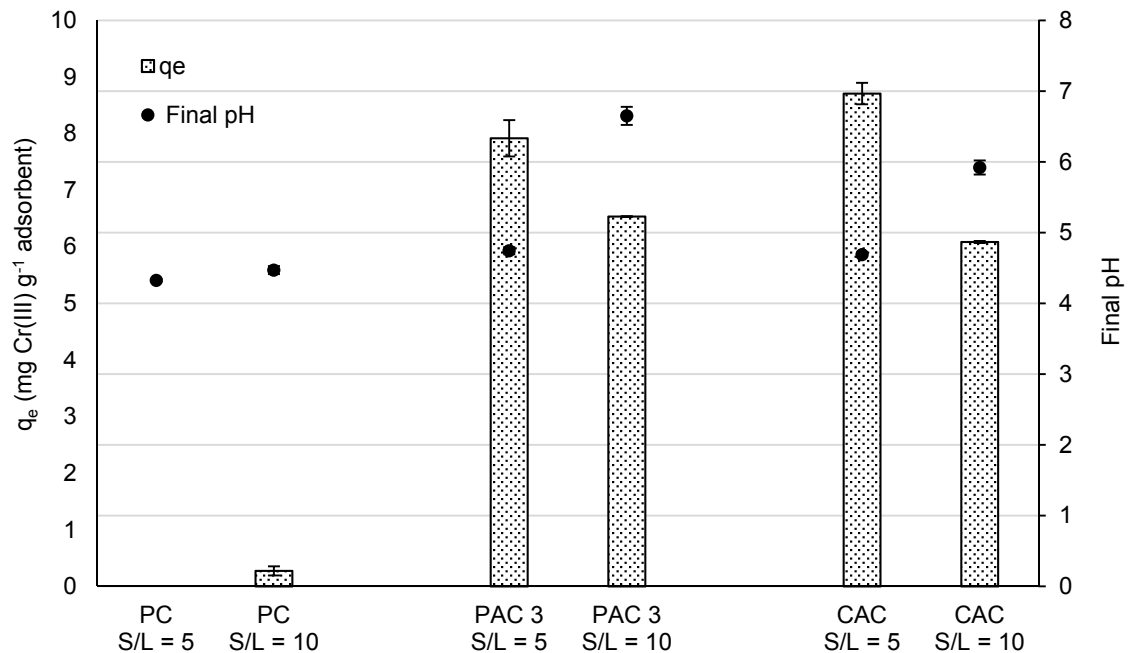


Figure 3: Uptake capacity of adsorbents (q<sub>e</sub>) and final pH of filtrates (S/L expressed in g L<sup>-1</sup>).

## 4. Conclusions

PC was a non-porous material due to its high percentage of volatile matter (22.7 % w/w), which was blocking the char pores. For that reason, Cr(III) was not removed by PC sample.

The most favourable condition in the physical activations of PC sample was 800 °C for 4h, once PAC3 revealed the best textural properties of all PAC samples, with a surface area of 325 m<sup>2</sup> g<sup>-1</sup> and a total volume of 0.18 cm<sup>3</sup> g<sup>-1</sup>. This material was composed mainly by fixed-C (51.0 % w/w) and ashes (40.4 % w/w), indicating that the volatile matter was removed during the activation, which led to more available pores.

These results were confirmed by Cr(III) removal assays. At the S/L of 5 g L<sup>-1</sup>, PAC3 removed 58.3% of Cr(III) by adsorption, almost the same as CAC (62.5 %). At the S/L of 10 g L<sup>-1</sup>, PAC3 removed 99.9 % of Cr(III) by precipitation, even higher than CAC (98.1 %).

The highest uptake capacity was found at the S/L of 5 mg/L<sup>-1</sup> with a value of 7.92 mg g<sup>-1</sup>.

Although less porous than CAC, PAC3 obtained very similar results to CAC on Cr(III) removal assays, which can be attributed also to its high mineral content.

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