Journal of Hazardous Materials 321 (2017) 173–182

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Adding value to gasification and co-pyrolysis chars as removal agents of Cr^{3+}

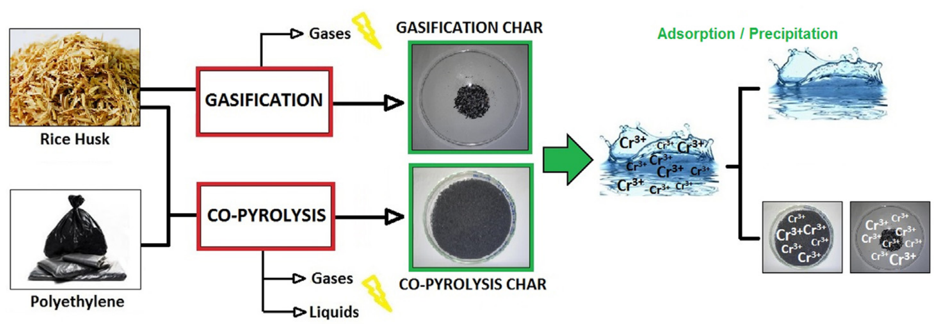
D. Godinho[a], D. Dias[a], M. Bernardo[b], N. Lapa[a,*], I. Fonseca[b], H. Lopes[c], F. Pinto[c]

[a] LAQV-REQUIMTE, Departamento de Ciências e Tecnologia da Biomassa, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal
[b] LAQV-REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal
[c] Unidade de Bioenergia, Laboratório Nacional de Energia e Geologia, Estrada do Paço do Lumiar, Ed. J, 1649-038 Lisboa, Portugal

HIGHLIGHTS

- Rice wastes and their blends are valorised through pyrolysis and gasification.
- Chars are fully characterised and used in the removal of Cr^{3+} from liquid medium.
- The gasification char presents a high performance on the removal of Cr^{3+}.
- The chars, namely from gasification, get a high added-value for the Cr^{3+} recovery.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 24 May 2016
Received in revised form 17 August 2016
Accepted 3 September 2016
Available online 6 September 2016

Keywords:
Chars
Co-pyrolysis
Cr^{3+} removal
Gasification
Rice wastes

ABSTRACT

The present work aims to assess the efficiency of chars, obtained from the gasification and co-pyrolysis of rice wastes, as adsorbents of Cr^{3+} from aqueous solution. GC and PC chars, produced in the gasification and co-pyrolysis, respectively, of rice husk and polyethylene were studied. Cr^{3+} removal assays were optimised for the initial pH value, adsorbent mass, contact time and Cr^{3+} initial concentration.

GC showed a better performance than PC with about 100% Cr^{3+} removal, due to the pH increase that caused Cr precipitation. Under pH conditions in which the adsorption prevailed (pH < 5.5), GC presented the highest uptake capacity (21.1 mg Cr^{3+} g^{-1} char) for the following initial conditions: 50 mg Cr^{3+} L^{-1}; pH 5; contact time: 24 h; L/S ratio: 1000 mL g^{-1}.

The pseudo-second order kinetic model showed the best adjustment to GC experimental data. Both the first and second order kinetic models fitted well to PC experimental data.

The ion exchange was the dominant phenomenon on the Cr^{3+} adsorption by GC sample. Also, this char significantly reduced the ecotoxicity of Cr^{3+} solutions for the bacterium *Vibrio fischeri*.

GC char proved to be an efficient material to remove Cr^{3+} from aqueous solution, without the need for further activation.

1. Introduction

Chromium (Cr) is a chemical element related to both beneficial and detrimental effects in environment and human health. It occurs in aquatic environments mainly in the trivalent and hexavalent oxi-

* Corresponding author at: UNL-FCT-DCTB, LAQV-Requimte, Campus da Caparica, Ed. Departamental, Piso 3, Gab. 362, 2829-516 Caparica, Portugal.
E-mail address: ncsn@fct.unl.pt (N. Lapa).

http://dx.doi.org/10.1016/j.jhazmat.2016.09.006
0304-3894/

dation states, showing different levels of toxicity [1]. Cr^{6+} is easily bioavailable and has a higher toxicity than Cr^{3+} [2]. Cr^{3+} is essential for mammal metabolism in vestigial concentrations, because it reduces both glycose and cholesterol concentrations in blood [3].

Cr^{3+} is widely used in industry, such as metal finishing, wood preservation, and leather tanning. Therefore, it can be found in several industrial wastewaters as a contaminant [4]. The leather tanning industry, for example, is an important industry sector worldwide [5]. In Portugal, 60 companies are still active in this sector, being dependent on Cr supply as a raw material [6]. Cr is also one of the twenty EU critical raw materials for the European industry [7]. Consequently, Cr recovery from industrial wastewaters is an important research topic, not only for environmental and public health issues, but also for the sustainability of industrial processes.

There are several methods to remove Cr from liquid effluents: addition of alkalis and subsequent precipitation of Cr salts; adsorption; chelation; ion exchange; solvent extraction; membrane separation; precipitation by electrolysis [8]. In Portugal, AUSTRA Company (Alcanena Municipality) is the managing entity of one of the most important Cr recovery systems from tannery effluents. Alcanena Municipality comprises one of the biggest tannery areas in Portugal using high amounts of Cr^{3+}. The Cr^{3+} recovery technology used by AUSTRA comprises: sieving and sedimentation; Cr removal by precipitation as $Cr(OH)_3$; pressing of Cr-enriched cake; Cr solubilisation with sulfuric acid; removal of contaminants with diatom sand. This chemical technology is relatively reliable, but requires chemical reagents that increase the Cr cost [3,9].

Cr removal from the liquid effluents can also be performed by adsorption, using activated carbon as adsorbent. The adsorption process involves a solid substrate (adsorbent) that is used to remove substances (adsorbates) from aqueous solutions. This process occurs due to the affinity between the adsorbate and adsorbent [10], which is due to either chemical or physical interactions [11]. This is, however, an expensive method, due to the high cost of activated carbon. Several studies have been developed on the use of low cost adsorbents, such as biochars [12–14].

On the other hand, rice is the second most produced cereal worldwide [15,16]. Its production and processing generate different types of wastes characterised by medium to high Lower Heating Values: rice straw (12.4 MJ kg^{-1}) [17], rice husk (12.9 MJ kg^{-1}) [15] and plastics, mainly polyethylene (43.9 MJ kg^{-1}) from big-bags used in the transportation of seeds and fertilisers [18]. These wastes can be used in energy production systems, such as gasification and pyrolysis [17], being more efficient if they are blended [19,20]. A solid fraction, named as char, is produced in these thermal systems that can be valorised as an adsorbent material [21].

Chars are carbonaceous solid materials that retain the mineral fraction present in the feedstock. Chars may have several characteristics that make them effective as metal adsorbents, namely, the presence of an aromatic carbon matrix with a relatively porous structure, and the presence of functional groups or inorganic chemical species in the adsorbent surface, such as exchangeable cations and mineral oxides, providing active sites able to interact with polar and charged metals [21,22].

Several studies on the use of low cost adsorbents for Cr^{3+} removal can be found in literature, namely biochars from municipal sewage sludge [23], *Firmiana simplex* ornamental tree [24] and rice straw [25]. However, the use of chars resulting from both gasification and pyrolysis of different rice wastes are not yet reported in literature. Moreover, the use of chars resulting from blends of these wastes has not been studied. The effect of pH induced by chars on metal removal are also not fully explored in literature.

The main aim of this study was to assess the Cr^{3+} removal from aqueous solution by using chars produced in both gasification of rice husk and co-pyrolysis of a blend of rice husk and polyethylene. The pH effect and the main mechanism associated to Cr removal were also evaluated. The study focuses mainly in the adsorption process of Cr^{3+} onto the chars under acidic conditions (pH < 5.5), even if an efficient chromium removal was registered for pH > 5.5. The adsorption process under acidic conditions was particularly evaluated in this study because (i) the natural pH values of Cr^{3+} solutions are <5.5, and (ii) the Cr precipitation process for pH values >5.5 is already well-known.

2. Material and methods

2.1. Feedstock materials

Rice husk (RH) and polyethylene (PE) were used as feedstock materials. They were collected in the rice processing mill and rice fields of Orivárzea Company.

2.2. Gasification and co-pyrolysis assays

The gasification assay was carried out in a bubbling fluidized bed gasifier (1.5 m height x 0.08 m internal diameter). The experimental conditions were the following – fuel: 100% w/w RH; fuel flow: 5 g dry ash-free (daf) min^{-1}; steam flow: 5 g min^{-1}; equivalence ratio: 0.2; gasification agent: O_2; fluidizing agent: fine sand; temperature: 850 °C. The syngas obtained went through a cyclone, and it was condensed and filtered before being collected in Tedlar bags. The syngas characterisation was the main aim of another study [19]. The gasification char (GC) was collected at the bottom of the gasifier and split from the fluidizing agent through sieving.

The co-pyrolysis assay was performed in a 1 L stirred batch reactor (Parr Instruments), built in Hastelloy C276 [20]. The experimental conditions were the following – fuel mixture: 20% w/w RH + 80% w/w PE; reaction temperature: 390 °C; inert gas: N_2; gas pressure: 0.6 MPa; reaction time at 390 °C: 35 min. The solid and liquid fractions were split through settling. The solid fraction was submitted to a Soxhlet extraction with a hexane/char ratio of 17 mL g^{-1}, during 3 h.

2.3. Characterization of chars

2.3.1. Proximate analysis, mineral content and elemental analysis

GC and PC chars were characterised for proximate analysis (ASTM D 1762-84): moisture content (M) was determined at 105 °C, ashes (Ash) at 750 °C and volatile matter (VM) at 950 °C. Fixed-carbon was calculated as [100%–M–A–VM].

The chars were submitted to a microwave-assisted acid digestion for mineral content quantification: 3 mL H_2O_2 (30% v/v) + 8 mL HNO_3 (65% v/v) + 2 mL HF (40% v/v) (EN 15290). The concentrations of several metals and metalloids were determined by Atomic Absorption Spectrometry (AAS) (Thermo-Scientific spectrometer, Solaar S series).

The elemental analysis comprised the quantification of CHNS in a LECO analyser (ASTM D 5373 for CHN and ASTM D 4239 for S). Oxygen was determined as [100%–C + H + N + S + Ash].

2.3.2. X-ray diffraction

The chars were characterised by X-ray diffraction (XRD) using a benchtop X-Ray diffractometer (RIGAKU, MiniFlex II), operating at 30 kV and 15 mA, and using Cu X-ray tube. The diffractograms were obtained by continuous scanning from 15 to 80° (2θ) with 0.01° (2θ) step size.

2.3.3. Textural properties

The textural properties of chars were determined by N_2 adsorption-desorption isotherms at −196 °C (ASAP 2010 Micromeritics). The samples were previously degasified under