Critical discussion on activated carbons from bio - wastes - environmental risk assessment

Un análisis crítico del uso de carbones activados obtenidos a partir de bioresiduos – evaluacion de riesgos medioambientales

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Abstract

The use of bio-wastes as precursor materials to prepare porous activated carbons have gained much attention in recent years, mainly due to their abundancy and low cost. Particularly, it has been registered an increasing interest in these waste-derived materials for environmental applications, particularly as adsorbents for water treatment. Activated carbons may retain the mineral matter initially present in the precursors as well as the chemical agents used in the activation process; therefore, it is important to assess the potential environmental impact associated to their use, in order to avoid problems related with secondary environmental pollution.

This review intends to give an insight and provide discussion about the environmental risk assessment of activated carbons derived from bio-wastes.

Resumen

La utilización de bio-residuos como materiales precursores de carbones activados porosos ha ganado mucha atención en los últimos años, principalmente por su abundancia y bajo costo; en particular, sus aplicaciones ambientales adsorbentes para tratamiento de aguas. No obstante, estos carbones activados pueden conservar la materia mineral inicialmente presente en los precursores y también los agentes químicos usados en el proceso de activación. Por lo tanto, es importante evaluar el potencial impacto ambiental asociado a su utilización para evitar problemas de contaminación secundaria.

Esta revisión intenta proporcionar una discusión crítica sobre la evaluación del riesgo ambiental del uso de carbones activados derivados de bio-residuos.

1. Introduction

In the last years, the number of publications concerning the conversion of bio-waste to activated carbon (AC) has significantly increased [1]. Any bio-waste material with a high carbon and low inorganic contents can be used as precursor of AC [2]. Therefore, bio-waste, particularly lignocellulosic wastes, have proved to be suitable, low-cost and abundant alternatives to the conventional raw materials for AC production such as petroleum residues, wood, coal, peat and lignite, which are expensive and the majority non-renewable [1]. Moreover, the use of bio-wastes for the production of AC is a potential pathway to solve the waste management problems of several industries dealing with these type of wastes.

There are two main processes for AC preparation: physical or chemical activation (Figure 1). Physical activation is a two-step process, which means that the raw material is first carbonized in the absence of oxygen in a process named as pyrolysis (usually at temperatures between 400-850 ºC) followed by activation of the resulting char from the carbonization step with oxidant gases such as steam or CO_2 (around

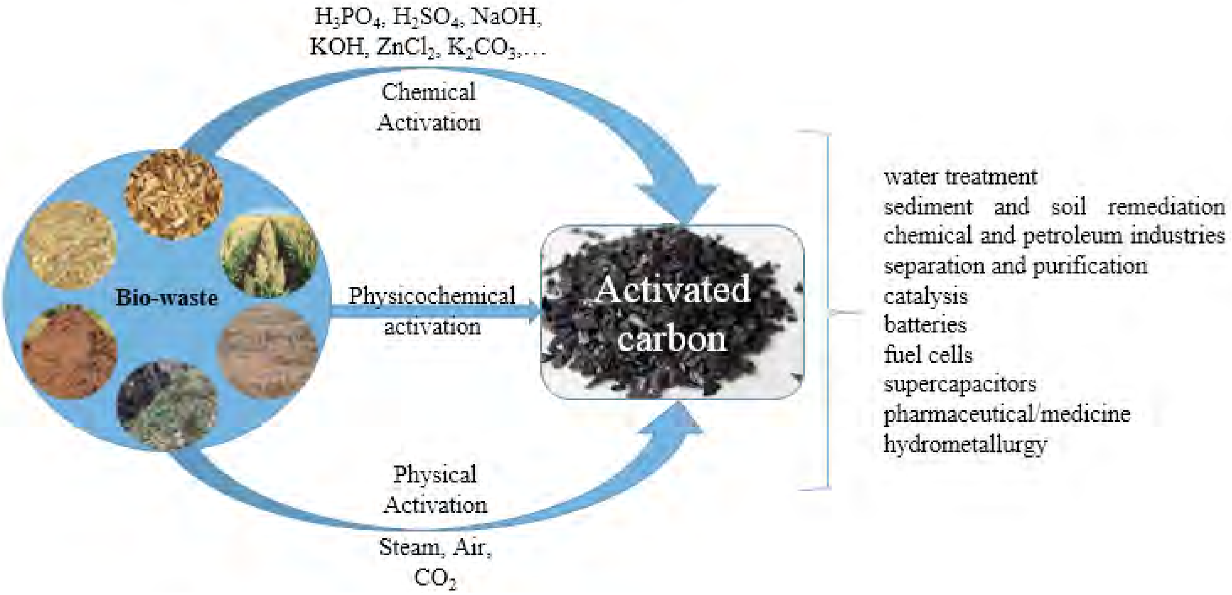

Figure 1. Schematic illustration of bio-wastes-derived activated carbon process and the possible applications.

Figura 1. Ilustración esquemática del proceso de producción de carbones activados derivados de bio-residuos y sus diferentes aplicaciones.

600-1000 ºC) [1-2]. Chemical activation can be a one-step or two-step method for the preparation of AC; it involves the impregnation of the precursor (the biomass or the resulting char from the first step of carbonization) with the chemical agent (dehydrating agents and/or oxidants) followed by heating under inert atmosphere at temperatures between 400-800 ºC) [1-2]. Also, physical and chemical activation can be used simultaneously.

Chemical activation has the advantage of producing AC with high surface area, but the washing of the resulting carbons in order to remove the residuals of reactants and inorganic matter (ash) from the precursor makes the process time and energy consuming, expensive and environmentally non-friendly [3]. On the other hand, physical activation presents some disadvantages: the ACs are obtained in two steps, higher temperatures of activation and poorer control of the porosity [4].

The high adsorption capacity of AC as a result of the high available area due to an extensive internal pore structure, makes them useful materials in several industries and applications: water treatment [5], sediment and soil remediation [6], chemical and petroleum industries [7], separation and purification [8], catalysis [9], energy storage [10], batteries [11], fuel cells [12], supercapacitors [3], pharmaceutical/medicine [13], hydrometallurgy [14], among others.

The valorisation of AC through the application routes described above requires the knowledge of their composition, properties and risk assessment, mainly due to environmental and economic reasons. Specially, the increasing interest in these waste-derived ACs for environmental applications, particularly those related to soil and water remediation, requires studies on the potential environmental impact associated with their use in order to avoid problems of secondary environmental pollution.

2. Environmental risk assessment of ACs derived from bio-wastes

2.1 The concept of ecotoxicity

According to the European Waste Framework Directive [15], an ecotoxic material presents or may present immediate or delayed risks for one or more compartments of the environment. Therefore, ecotoxicity tests must be applied to identify the potential hazardous properties of a particular material with respect to the environment or to assess the risk related to a site-specific exposure scenario.

Ecotoxicity can be estimated using two approaches: a chemical-specific approach and a toxicity-based approach. In the former case, chemical analyses are compared to quality criteria or threshold values to estimate toxicity. In the latter case, toxicity is measured directly using bioassays [16].

The determination of chemical contaminants in complex materials of unknown composition is an extremely difficult task and does not allow a proper prediction of the global ecotoxic effects. On the other hand, bioassays integrate the effects of all contaminants including additive, synergistic and antagonistic effects [16], and are sensitive to the bioavailable fraction of the contaminants only. Therefore, combining chemical analyses with ecotoxicological tests, as an integrated strategy to characterize the environmental impact of a given sample, has the advantage of providing a more complete set of information about its global toxic effect [17].

The evaluation of the ecotoxicity of a sample can be made by applying both chemical analyses and biological tests to the raw materials or to their aqueous extracts (eluates). Assays on the aqueous eluate of the sample are the most commonly employed method for ecotoxicity assessment, particularly for materials directly exposed to water (fresh and salted water environments) or to compartments in which the water is an important component (soil). Indeed, the release of soluble constituents upon contact with water can be regarded as a main mechanism of release, which results in a potential risk to the environment as a consequence of the use of waste-derived materials. Moreover, assessing the ecotoxicity on the aqueous soluble fraction of the material provides a more accurate risk to the environment instead of considering the sample bulk composition which would provide an overestimated prediction of the ecotoxic risk [18].

Lapa et al. [19] proposed a methodology to assess the ecotoxicity of a given material: both chemical and ecotoxicological characterizations are performed on the resulting eluates and both are used as positive criterions, i.e., the presence of at least one pollutant in a concentration higher than the threshold values or if at least one of the biological tests is positive, the material shall be classified as ecotoxic. The negative criterion presumes that only the negative response to all of the ecotoxicological tests, and if only all the chemical parameters are below the limit values allows the classification as non-ecotoxic. An adaptation of this methodology to the materials focused in this review is presented on Figure 2.

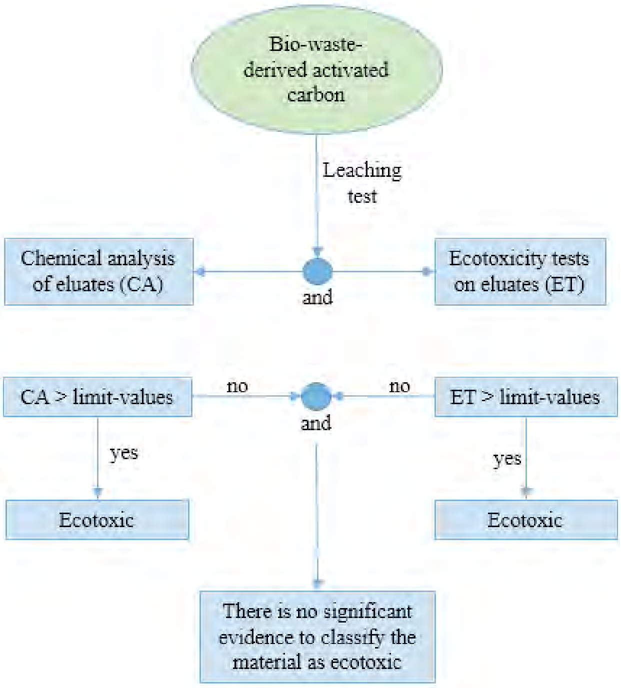

Figure 2. Possible criterion to assess the ecotoxicity of biowaste-derived ACs.

Figura 2. Criterio posible para evaluación de la ecotoxicidad de carbones activados derivados de bio-residuos.

There is a significant lack of studies dealing with the ecotoxicological characterization of bio-waste-based

ACs through bioassays. To the authors' knowledge, there is only the work of Yeung et al. [20] that prepared AC from coffee wastes by phosphoric acid and potassium hydroxide activation; all the AC samples produced by those authors showed no ecotoxicity towards the bacterium *Escherichia coli*.

2.2 Leaching behaviour

In order to generate a water extract from a solid material, several leaching methods have been developed and a wide variety of test protocols is available in literature [21-22].

Even with a washing step, ACs may retain the mineral matter initially present in the precursors, as well as the chemical agents used in the activation process or in carbons surface modification. Therefore, the release of potential environmental contaminants is a possibility that might restrict their applications. The use of leaching tests on bio-waste-derived ACs will allow the prediction of contaminants mobility.

In spite of the importance of leaching tests, there is a lack of studies dealing with the application of these methodologies for environmental risk analysis of AC materials.

Rozada et al. [23] produced sewage sludge ACs for liquid phase adsorption through $ZnCl_2$ activation; the authors investigated the amount of Zn from the activating agent leached to the liquid phase from the produced ACs and found that it was significant (176 mg L^{-1} g^{-1}). As Bernardo et al. [17] showed, there is a relationship between Zn concentration in eluates from carbon materials and their ecotoxicity behaviour suggesting the necessity of controlling zinc mobility.

Fitzmorris et al. [24] converted municipal sludge and poultry manure into ACs by steam activation. The resulting ACs presented high ash fraction and were washed with 0.1 M HCl solution. The authors submitted the washed ACs to a leaching step (L/S ratio of 100 L kg^{-1}, stirring for 4 hours) with solutions at different pHs and monitored the release of several metals such as As, Cr, Cu, Ni, Pb, Se and Zn. Under acidic conditions (0.1 M HCl, pH = 1), all the metals were released, but particularly Cu (1000 – 1600 mg kg^{-1}) and Zn (400 – 1800 mg kg^{-1}) were leached in higher amounts, also because they were the metals present with high concentrations on ACs. Poultry derived ACs also released considerable amounts of Ni (300 mg kg^{-1}) under acidic pH. At pH 5 (water adjusted with 2% HNO_3), a much smaller amount of each metal was released. The highest concentration determined was for Zn in the municipal sludge-based carbon (300 mg kg^{-1}) and Ni (200 mg kg^{-1}) in the poultry litter-based carbon. Only residual amounts of the other metals were quantified in solution. At pH 7, only some residual Zn was still released from the sludge-based carbon (<200 mg kg^{-1}). In almost cases, no metals were detected in solution.

Guo et al. [25] studied the leaching of inorganic constituents (dissolved nitrogen, dissolved phosphorus, Cu, Pb, Zn, Cd and As) from poultry litter ACs also produced by steam activation. The produced ACs were washed with 0.1 M HCl solution and then rinsed with water. The washed ACs were then leached (L/S ratio of 10 L kg^{-1}, stirring for 24 h) with deionised water, hot water and HCl 0.1 M solution. All the chemical elements analysed were more readily extracted with hot water, but especially with the acidic solution. Dissolved nitrogen (10.66 – 22.35 mg kg^{-1}) and dissolved phosphorus (74.02 – 1326.9 mg kg^{-1}) were released from the poultry litter derived ACs. The release of heavy metals such as Cu, Pb, Zn and Cd was negligible for all leaching agents, however, As was leached in considerable amounts (5.36 – 9.71 mg kg^{-1}).

These studies demonstrated that the pH of the liquid medium played a significant role in the amount of metal and non-metal ions that can be released from these type of bio-waste-derived ACs. The mobility of inorganic contaminants is, in general, significantly higher for acidic conditions. Therefore, if these ACs would be considered for environmental applications, the control of pH conditions could be critical.

2.3 Life Cycle Assessment (LCA)

The potential environmental impacts associated with AC production process from bio-wastes can be evaluated through the life cycle assessment (LCA) tool. LCA allows to assess the environmental impacts during the entire life of a product (from the raw material extraction and energy production and use, up to the treatment, recycling and final disposal of the wastes generated) [26], in terms of inputs of energy and natural resources and of outputs of wastes and emissions to the different environmental compartments (air, water and soil) [27].

Hjaila et al. [26] applied the LCA tool to assess the environmental impact associated with activated carbon preparation from olive-waste cake in Tunisia by chemical activation using phosphoric acid. The authors considered the steps of impregnation, pyrolysis, cooling and drying the final AC product. The steps involving transport, raw material drying, crushing, and washing the final AC were excluded from the impact assessment. The results showed that the environmental impacts are dominated by impregnation, followed by pyrolysis of the impregnated precursor, and finally by drying the washed AC. The global warming potential impact was found to be 11.10 kg CO_2 eq/kg AC. If transportation, raw material drying, crushing, and AC washing would be included, the environmental impact could be higher than those quantified by authors.

Arena et al. [27] used LCA to quantify all the interactions with the environment across all stages of the life cycle of steam activated coconut shell AC in Indonesia. The boundaries of this study included processes and transportations from raw material acquisition to the delivery of the product, but the use and final disposal of the AC have not been taken into account, which could affect the final results. The authors concluded that the overall environmental performance of the manufacturing process is dominated by the stages of crushing and tumbling (where the coconut, or the AC product, are crushed to obtain powdered or granulated material) and that of heat recovery and steam generation, mainly due to the high consumptions of electrical energy.

No studies were identified on LCA taking into account the entire life of ACs, being possible to conclude that there is a lack of information about the environmental performance of the overall chain of bio-waste-derived activated carbons.

Conclusions

From the survey literature, it became clear that there is a significant lack of studies dealing with the assessment of the ecotoxic properties of bio-waste-based ACs. Particularly, the evaluation of the AC ecotoxicity through the application of biological assays with test organisms representing different ecological chain levels needs more attention in order to prove their value and sustainability.

LCA of these waste-derived materials has to be much more applied to understand all the environmental aspects involved from raw biomass waste through production, use, disposal and/or recycling. LCA results will allow to indicate the operations with the greatest effects on the environmental performance of ACs production and hence where improvements are necessary.

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