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From MDF and PB wastes to adsorbents for the removal of pollutants

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ABSTRACT

The production of activated carbons in powder and monolith forms, by physical activation with CO_2, with specific surface areas between 804 and 1469 $m^2\ g^{-1}$, porous volume between 0.33 and 0.59 $cm^3\ g^{-1}$, with basic nature (PZC ~ 9.6–10.6) was achieved in our lab, from medium density fibreboard (MDF) and particleboard (PB), engineered wood composites wastes.

These highly porous adsorbents were applied in kinetic and equilibrium adsorption studies, in batch and dynamic modes, in powder and monolith forms, of specific adsorptives, considered pollutants, namely phenol (P), p-nitrophenol (PNP) and neutral red (NR). In batch the maximum adsorbed amount was 267, 162 and 92 mg g^{-1}, for PNP, P and NR, respectively. The application of different kinetic models (pseudo-first order, pseudo-second order and intraparticle diffusion model) leads to a better knowledge of the adsorption mechanisms of those adsorptives.

The results obtained in the kinetic and equilibrium tests show that the combination of the structural features and the surface chemistry nature of the adsorbents, with the adsorptives properties, establish the kinetic performance, the type and amount adsorbed for each system. This work confirms the potential of these types of wastes in the production of activated carbons and its application in adsorption from liquid phase.

1. Introduction

Adsorption, as a technique with increasingly innovative applications, in number and type, is a focus of a growing attention among the scientific and industrial communities. The target is on obtaining and developing adsorbents with structural and chemical properties with potential for application in specific situations, from the environmental area to the food industry, and from energy to health, among others. In parallel, there is a concern in adopting sustainable strategies in the production process, which involves variables as: precursor materials, processes of production, means of usage, reuse and recovery [1–3].

The combination of these variables, along with a greater concern on the environment, fits perfectly to the production of activated carbon from polymer waste of any source, natural or synthetic, by physical activation processes and with the goal aimed on the removal of pollutants from the liquid phase [4–7]. There is a constant demand for cheap and renewable precursors, which have the potential to produce adsorbents with well-developed porous structure and adequate surface chemistry, suitable to be applied not only in powder form, but also as larger structures, like monoliths [8,9].

Wood composites industry, in particular the production of MDF, medium density fibreboard, and PB, particleboard, along with all the activities where those materials are used, appears as a potential supplier of precursors for the production of carbon adsorbents [8,10–14]. In this way we contribute to the enhancement of these wastes through the production of added value materials, with a growing demand [15], and also decisively to the reduction of their environmental impact by the recovery, reuse and recycling of those engineering composites materials, composed of a polymer mixture of natural origin (lignocellulose) and also synthetic origin (resins and others).

In liquid phase applications, aspects as the adsorption medium characteristics (ex. pH), the shape of the adsorbent, the contact time and the kinetics of the liquid phase (in static or dynamic mode), are variables that have been increasingly taken into account. It is important to evaluate the performance of adsorbents in the removal of specific molecules that gather a set of characteristics such as molecular weight, size, and chemical nature, among others, with interest in its hazardous nature but also by the fact that they are considered as probe molecules and allow the comparison of those adsorbents with others [2,16].

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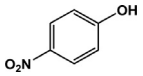
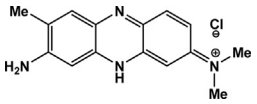
Table 1
Properties of phenol, p-nitrophenol and neutral red adsorptives.

Compound (generic name)	Phenol (P)	p-Nitrophenol (PNP)	Neutral red (NR)
Chemical structure			
Molecular formula	C_6H_6O	$C_6H_5NO_3$	$C_{15}H_{17}ClN_4$
Mw ($g\,mol^{-1}$)	94.11	139.11	288.78
pK_a	10.0	7.2	6.7
λ_{max} [a] (nm)	269/–	317/402	527/459

[a] Adsorptive characteristic wavelengths of maximum absorbance used in is determination and posterior quantification (acid/basic medium). Always acid in dynamic mode, and in batch, acid (for P) and basic (PNP and NR).

These are the assumptions of this work, in which wastes of MDF and PB were used for the production of activated carbons from precursors in monolithic perforated discs, form which originate adsorbents that retained the initial shape, enabling the usage in powder or monolith form. The powder activated carbons were used in adsorption of three common adsorptives in an appropriated concentration range in static mode, while the monolith activated carbons were tested in a dynamic mode, along with the powdered samples, allowing the evaluation of their performance when subjected to a pollutant solution flow with a fixed initial concentration. The kinetic aspects have been assessed with particular focus in dynamic mode.

All the adsorbents were tested in the adsorption of the phenol, p-nitrophenol and neutral red contaminants, being the first two the most widely studied molecules in liquid phase adsorption onto activated carbons, and the latter a medium to large size molecule with several functional groups that can be seen as a probe molecule in this type of studies. Moreover, these molecules belong to the major classes of pollutants, occurring in the wastewaters of several industries and sometimes also in the natural or artificial water reservoirs, like rivers and dams. These aspects, along with the fact that is the first time that adsorption of those molecules is tested simultaneously with ACs in powder and monolith forms and also in static and dynamic modes, illustrate the interest of this work.

2. Experimental

2.1. Sample production

Activated carbon samples were prepared through a two-step method. In the first step, and in order to promote a slower exit of all the water content, as described in [8,17], the sample was subjected to a heating slope of $2\,^{\circ}C\,min^{-1}$ from room temperature to 110 °C, and a dwell of 60 min. Afterwards the carbonization process was undertaken with a heating slope of $10\,^{\circ}C\,min^{-1}$ until 800 °C with a dwell time of 30 min, proceeded with an activation dwell with different times to obtain different characteristic materials. The desiccation and carbonization steps were conducted under a N_2 atmosphere, 99.9997% purity provided by Linde, and the physical activation was performed with CO_2 atmosphere, 99.999% provided by Linde. Samples were named as per the following code *W-P-B*, being *W* the waste used, MDF or PB, *P* the physical shape of the precursor, P for powder and M for monolith, and *B* the burn-off rate. In the case of the non-activated samples (carbonized) the designation used was *W-P-CARB*.

2.2. Materials characterization

Samples were characterized both physical and chemically using the most common techniques for activated carbons, such as nitrogen adsorption at 77 K, CHNS-O elemental analysis, FTIR, point of zero charge and ash content.

Nitrogen adsorption isotherms at 77 K were determined with a Quadrasorb *SI* gas adsorption equipment from Quantachrome Instruments, using nitrogen of 99.999% purity from Air Liquide. Prior to the adsorption isotherms, the samples were outgassed with a MasterPrep unit from Quantachrome Instruments, for 300 min at 300 °C, with a heating rate until the maximum of $2\,^{\circ}C\,min^{-1}$.

Elemental analysis, CHNS-O was determined with a EuroVector – Euro EA elemental analyser, with each analysis being performed in three replicates in order to eliminate operation errors. All elements were determined directly, being CHNS simultaneous and O in separate experiments. The FTIR spectra were determined with a Perkin Elmer Spectrum Two Spectrophotometer by the KBr disc method, resolution of $4\,cm^{-1}$ and 16 scans between 4000 and $450\,cm^{-1}$. Point of zero charge was obtained using a modified method of the one proposed by Noh and Schwarz, as described elsewhere [18]. Ash contents were determined from the residue mass left after combustion of the samples in air, adapted from ASTM D2866-94 [19].

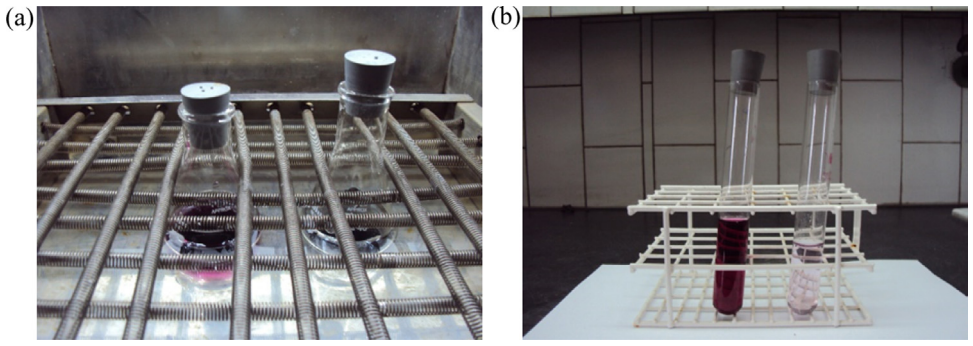


Fig. 1. Experimental setup used in batch adsorption (a) and the outlook of one initial solution of NR and the supernatant after equilibrium adsorption (b).