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MDF and PB activated carbons for adsorption of dyes from liquid phase

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Abstract

The presence of pollutants in water is a recurring issue that is continuously addressed by governmental, intergovernmental, hybrid and non-governmental organizations and their action programs. Activated carbons (ACs) are currently used as adsorbents for waste water treatment. Combining the need to create and improve new carbon materials with the use and recovery of industrial by-products as precursors, we can achieve a balance between the high performance of these type of carbon adsorbents, cheap and sustainable sources of precursors.

AC samples were produced from medium-density fibreboard (MDF) and particleboard (PB) in monolithic form through physical activation with carbon dioxide (CO₂) and chemical activation with K₂CO₃. Physical activated carbons were found to be essentially microporous with narrow pores and apparent surface areas (A_{BET}) between 804 and 926 m²/g and chemical activated samples present wider pores, with A_{BET} ranging from 951 to 1032 m²/g.

Liquid phase adsorption studies were made for several dyes both in a static and dynamic adsorption modes. In static mode high values of removal were achieved after 5h, being this the time period used in the dynamic experiments, where some samples reached almost 100% removal.

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1. Introduction

Currently one of the biggest challenges of societies is the sustainability of the systems. One of the strategies to achieve this equilibrium consists in wastes valorisation by producing new materials of added value, in particular, when they are produced in large amounts, without significant commercial value and containing toxic substances [1,2].

The production of wood agglomerates, containing synthetic polymers, presents a considerable increment in the last few years as result of the growth of the

applications range and the amounts of consumption in areas related with furniture, construction, floor, coverings, among others. In this class of agglomerates, the most important are MDF (Medium Density Fibreboard) and PB (Particle Board) with annual high values of production in the order of ~14.5 and ~39 million m³, as example only in Europe on 2013, respectively [3]. These amounts, sooner or later, generate significant quantities of wastes of those composites, which usually finish incinerated in a waste incineration plant for energy production.

In another perspective, it is known the possibility to produce carbon adsorbents, among them the activated carbons, from polymeric precursors of lignocellulosic origin and also of synthetic nature [4]. These adsorbents present more and more applications in different areas, ranging from the environment to

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health, along with food and technological industries [5].

Having in mind this reality, the hypothesis of using MDF and PB wastes as precursors for activated carbons was taken in consideration, as well as the usage of these materials for the removal of specific molecules, such as dyes, was evaluated. The analysis of the adsorption process of those molecules on porous solids, besides their toxicity they are considered probe molecules, will bring information at the chemical and structural level of these materials and about the interaction with these chemical species [6].

This work contributes to evaluate the potential to obtain activated carbons from the MDF and PB wastes, a topic little explored until now [7], and its application in the removal of pollutants from the liquid phase, contributing decisively to the valorisation of those residues whose hazard is not negligible.

2. Experimental

2.1. Materials production

Activated carbon materials were produced by physical and chemical activation in a horizontal tubular furnace.

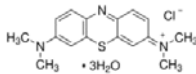
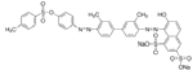
Monolithic raw materials were obtained from MDF and PB wastes provided by SONAEINDUSTRIA.

Physical activated carbons were obtained using carbon dioxide as activating agent. Samples were subjected to a two-step carbonization process, under nitrogen flow, followed by a dwell time for the activation under CO₂ flow during different times in order to achieve the desired burn-off rates, at a maximum temperature of 1073.15 K.

The chemical activated materials were obtained through a predetermined temperature program, with a heating ramp from room temperature to 1073.15 K, followed by a 2h dwell under a nitrogen atmosphere. Prior to the heat treatment step, the raw materials were subjected to the contact with 20 wt.% aqueous solution of K₂CO₃, maintaining a raw material to chemical agent ratio of 1:0.25. Chemical activated materials were washed with distilled water until pH ≈ 7.

The designation of the samples tested is made according to the raw material used and the type of activation process/type of activated carbon obtained, having as examples, MDF-CARB, for a MDF carbonized material, or PB-CHEM, for a PB chemical activated material.

Table 1. Adsorptive properties.

Compound (generic name)	Methylene Blue (MB)	Acid Red 114 (AR 114)
Chemical structure		
Molecular formula	C ₁₆ H ₁₈ ClN ₃ S·3H ₂ O	C ₃₇ H ₂₈ N ₄ Na ₂ O ₁₀ S ₃
Mw (g/mol)	373.90	830.81
λ _{max.} (nm)	666	525

2.2. Materials characterization

Activated carbon samples were physically characterized by nitrogen adsorption at 77 K and He pycnometry. Nitrogen adsorption isotherms were determined using a Quadrasorb SI gas adsorption manometric equipment from Quantachrome Instruments, using 99.999% nitrogen supplied by Air Liquide. All samples were outgassed on a Master Prep unit from Quantachrome Instruments, for 5h at 573.15 K, reached with a heating rate of 2 K/min. He pycnometry was determined with a Micromeritics AccuPyc 1330 Helium pycnometer, using helium of 99.996% purity supplied by Linde. Chemical characterization was determined by elemental analysis, CHNS-O and FTIR. The first was carried out with a EuroVector – EuroEA elemental analyser. FTIR spectra were determined using a Perkin Elmer Spectrum Two FT-IR Spectrophotometer by the KBr disk method, with a resolution of 4 cm⁻¹ and 16 scans between 4000 and 450 cm⁻¹. Point of zero charge (pzc) was determined using a modified version of a simple method proposed by Noh and Schwarz, following procedures detailed in previous work [8].

2.3. Liquid phase adsorption

Liquid phase adsorption studies were performed for methylene blue (MB) (Pure, Himedia) and acid red 114 (AR 114) (dye content 45%, Sigma-Aldrich).

2.3.1. Batch adsorption studies

Batch adsorption studies were carried out in 50 mL Erlenmeyer flasks covered with rubber stoppers inserted in a Grant OLS 200 thermostatic orbital shaking bath with cooling unit, at 298.15 K, for 24h. Each flask contained a fixed amount of adsorbent and

specific volume of a dye solution. The residual concentration of the compound in study was determined at the corresponding maximum wavelength with a Thermo Nicolet Evolution 300 UV-Vis spectrophotometer, after decantation of the supernatant.

2.3.2. Dynamic adsorption studies

The adsorption studies in dynamic mode were performed with selected samples from both precursors, one physically and one chemically activated.

The adsorbent material was encapsulated in a plastic container connected to a flow cell, obtained from Hellma Analytics, in the UV-Vis spectrophotometer enabling a real time measure of the residual concentration. The experimental assembly was designed and built, especially for this study, as per the sketch in Fig. 1. Experiments were carried out recirculating 200 mL of an aqueous solution of the MB through about 0.4 g of AC.

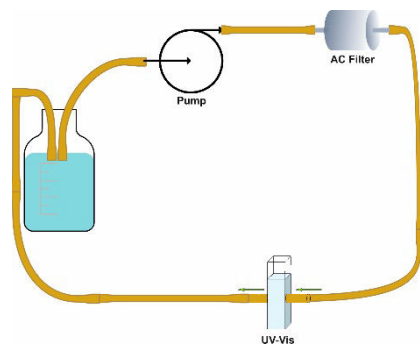


Fig. 1. Flow adsorption experimental assembly.

3. Results and Discussion

3.1. Materials characterization

Textural characterization of the samples was performed by the adsorption of N_2 at 77 K, being the resulting isotherms analysed through the application of BET and DR equations and α_s method. The obtained parameters for these samples are summed in Table 2.

Adsorption isotherms, not shown here for simplicity, can be classified as type I, according to IUPAC classification [9], characteristic of microporous materials, as can be seen, on these samples, by the difference between the total pore volume (V_s) and the micropore volume (V_0).

Apparent surface areas (A_{BET}) present higher values for the chemical activated samples than the physical activated samples, trend followed for the V_s and V_0 . In another way the pore width (L_0) decreases, in the previous relation, indicating a presence of narrower pores, and correlating with the difference between the pore volumes, a narrower pore size distribution.

Through the elemental analysis it's visible, in the physical activated samples, the decrease of the carbon content with the increase of the activation process, instead to what occurs with the oxygen content. Chemical activated samples present a higher carbon content, in comparison with the physical activated, and a lower, or inexistent, content of the other heteroatoms, characteristic of this activation process.

Surface chemical characterization was obtained by FTIR analysis, and point of zero charge. In the physical ACs the resulting spectra are somewhat poor, only being noticeable the presence of aromatic structures, with a band at around 1500 cm^{-1} related to the C-H bond stretching, and the presence of hydroxyl groups, commonly found on these kind of materials, with bands between 1200 and 1100 cm^{-1} for the C-O bond stretching, that can be attributed to phenol groups. Chemical ACs present a richer surface, mainly due to the interaction of the activating agent and the surface groups present in the precursor material. These samples present bands related to alcohol groups at 3300 cm^{-1} for the O-H bond, confirmed at 1030 cm^{-1} with the stretching of the C-O bond and the deformation of the O-H bond at 1430 cm^{-1} . Alkanes are noticeable through the asymmetric stretching of C-H at about 2900 cm^{-1} and the symmetric stretching at 2850 cm^{-1} .

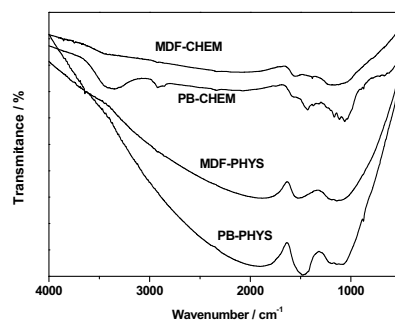


Fig. 2. FTIR spectra of physical and chemical activated carbons.

Ethers can be foreseen by the antisymmetric stretching of the C-O-C bond at 1060 cm^{-1} and the symmetric stretching at 900 cm^{-1} for the same bond.

Table 2. Textural and chemical characterization.

Sample	Porosity						Elemental composition (wt.%)				Ash (wt.%)	Density by He (g/cm)	PZC (pH)
	BET		DR										
	A_{BET} (m ² /g)	α_s (m ² /g)	V_S (cm ³ /g)	V_0 (cm ³ /g)	E_0 (kJ/mol)	L (nm)	N	C	H	O			
MDF-CARB	^a	^a	^a	^a	^a	^a	3.5	87.1	0.6	5.9	1.0	1.72	9.6
MDF-PHYS	804	14.28	0.33	0.31	27.70	0.66	3.5	71.6	0.9	9.7	1.3	1.82	10.3
MDF-CHEM	1032	8.34	0.42	0.40	28.41	0.63	0.4	78.3	-	^b	^b	^b	7.3
PB-CARB	88	14.37	0.07	^a	^a	^a	1.9	84.9	0.8	5.4	2.6	1.97	10.0
PB-PHYS	926	11.81	0.38	0.36	24.90	0.80	2.5	72.6	0.9	8.2	2.5	2.54	10.5
PB-CHEM	951	18.99	0.38	0.37	26.44	0.72	0.3	78.4	0.6	^b	^b	^b	7.4

^a Null adsorption of N₂ at 77 K

^b Not determined

The pzc values, greater than 10, indicate that the physical AC samples present a clearly basic surface, and the chemical activated ones present a pH around 7, indicating a neutral surface (Table 2).

As per described [5], the increase of density observed in the physical activated carbons is related to the opening of inaccessible porosity, hence, the increase of surface area.

3.2. Batch adsorption studies

All samples presented above were studied for the adsorption of MB and AR 114 from diluted aqueous solutions in order to evaluate their capabilities as an adsorbent for these dyes. Relating the adsorption behaviour of activated samples with their structural and chemical characteristics, it is clear that the adsorbed amounts are higher with MB dye for chemical activated samples (Fig. 3).

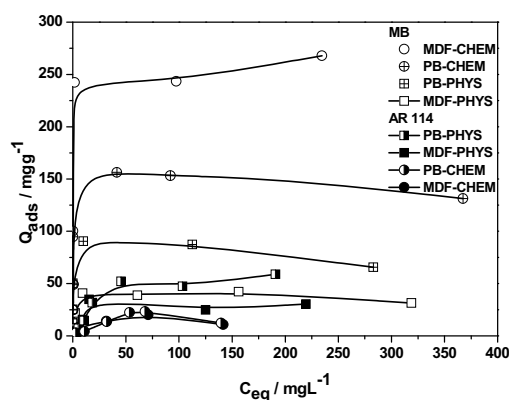


Fig. 3. Experimental adsorption isotherms of methylene blue and acid red 114 on physical and chemical activated carbons.

The structural properties and the suitable surface chemistry for this cationic dye justified these good adsorption results.

On the other hand, the chemical nature and size of AR 114 dye limited the adsorption process. In particular, only with the physical activated samples, basic ACs, the results are not so bad [6].

3.3. Dynamic adsorption studies

Presently, the dynamic aspects of the adsorption process are of increasing importance for real systems. Following this goal, the adsorption process of MB on ACs samples was evaluated in detail.

The adsorption kinetics were detailed in a period of 5 h, around the equilibrium time for these systems in static adsorption mode. From Fig. 4 it's clear that chemical ACs show kinetic profiles more favourable than the physical ACs. In detail, the equilibrium is faster reached with PB-CHEM and almost with MDF-CHEM samples. These outlines can be justified by the good structural and chemical features of those ACs.

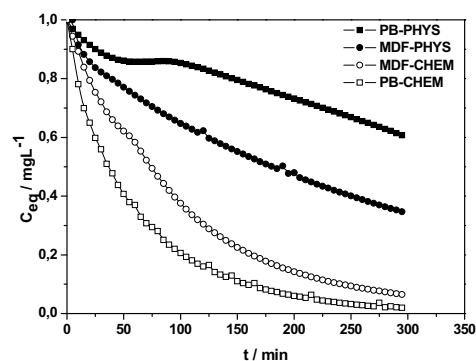


Fig. 4. Adsorption kinetics of methylene blue onto physical and chemical activated carbons.

A longer time period is necessary to MDF-PHYS and in the case of PB-PHYS two different periods are observed. A fast previous equilibrium is reached (~100 min) followed by other segment where the C_{eq}

decreases slowly without reaching an equilibrium. Structural parameters like pore width and volume can explain this fact. During the initial period the higher pore size benefits a non-orientated adsorption, probably leading to the blocking of the porous structure entrance. As time develops a rearrange of the adsorbate occurs and the adsorption proceeds.

To understand more about the adsorption process mechanism, the adsorption kinetics were studied with the two simplified models most widely used, the pseudo-first and pseudo-second orders equations, respectively Eqs. 1 and 2, given by [10,11]:

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303} t \quad (1)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \quad (2)$$

where Q_e and Q_t are the amounts adsorbed at equilibrium and at time t , respectively, k_1 and k_2 are the rates constant of pseudo-first-order and pseudo-second-order adsorption, respectively.

To establish similar analysis conditions, the equations were fitted to experimental data in the first 200 min with correlation coefficients $R^2 \geq 0.8742$ and ≥ 0.9078 , respectively for pseudo 1st and 2nd orders equations. From the analysis of the adsorption kinetics profile (Fig. 3), the experimental and calculated adsorbed amounts (Table 3), the agreement for chemical ACs and for MDF-PHYS is quite good.

Table 3. Comparison of experimental amount adsorbed and the parameters estimated by the pseudo 1st and 2nd orders equations for the adsorption of MB on ACs.

Sample	Exp	1 st order		2 nd order	
	(Q_{ads}) (mg/g)	k_1 (min ⁻¹)	(Q_e) _{1st} (mg/g)	k_2 (g/(mg min))	(Q_e) _{2nd} (mg/g)
PB-PHYS	1.05	0.004	0.85	0.030	0.74
MDF-PHYS	1.50	0.007	1.33	0.007	1.61
PB-CHEM	3.12	0.013	2.29	0.007	3.55
MDF-CHEM	2.77	0.011	2.78	0.003	3.76

4. Conclusions

The MDF and PB wastes are adequate for the production of ACs adsorbents with potential applications on the adsorption of dyes from liquid-phase. The precursors show different answers to the

activation process with CO₂ or K₂CO₃, presenting apparent surface areas between ~800 and 1030 m²/g and pore volumes from 0.36 to 0.42 cm³/g. All the adsorbents are essentially microporous materials with pore width between 0.63 to 0.80 nm.

The surface chemistry and structural properties of the materials enable their use on the adsorption of MB and AR 114 from liquid-phase. The adsorbed amounts in the case of the cationic dye, MB, are higher than the AR 114, an acidic dye, which is due to the different size and chemical nature of those adsorptive.

The MDF and PB chemical activated samples have a good behaviour, not only on batch, but also in dynamic adsorption studies.

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