

Designing Activated Carbons from Natural and Synthetic Raw Materials for Pollutants Adsorption

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Abstract. Over the last decades the literature has shown the possibility of producing activated carbons (AC) from a wide variety of raw materials, and to use them as one of the most environment-friendly solutions for waste disposal [1]. Simultaneously, it has been shown that the adsorption of pollutants from different sources by activated carbons is one of the most efficient techniques for remediating or solving this kind of problem [2]. In this context, phenolic compounds represent one of the most important classes of pollutant present in the environment [3]. In this perspective, we present a study involving the production of AC from cork (*Quercus suber* L.), PEEK (polyetheretherketone) wastes or granulated recycled PET (polyethyleneterephthalate) and their applicability for the adsorption of phenolic compounds from the liquid phase. All samples were characterised in relation to their structural properties and chemical composition, by different techniques, including nitrogen adsorption at 77 K, elemental analysis (C, H, N, O and S) and point of zero charge (PZC).

The activated carbons produced demonstrated high adsorption capacities both in the gas and liquid phase as exemplified by N₂ and phenolic compounds adsorption experiments. Based on the structural and chemical properties, and on the kinetic and equilibrium studies of liquid phase adsorption, it is possible to conclude that it is the porous volume of the ACs that predominantly controls the process of phenolic compounds adsorption.

Introduction

In the present days one of the greatest challenges to humanity is to diminish or remediate the pollution of the earth's environment produced by human activities [1]. Organic compound pollution has become a major concern in the production of safe drinking water and in many countries there are strict regulations that limit the concentration of these compounds. Phenolic compounds are among the most frequent contaminants of water [4]. And particularly, chlorophenol derivatives are toxic to a wide range of micro-organisms and to man, and concentrations as low as one part per thousand million can contaminate water [5]. In this work, 4-chlorophenol was chosen for investigation due to its unpleasant odour, its harmful properties against the environment and due to its wide presence.

Another very important class of pollutants is dyes that are not biodegradable. Essential sources of this pollution are petroleum refining, plastics, textile and dyeing industries. The persistent colour and the non-biodegradable nature of the spent dyebaths represent serious problems to the environment. Although the primary concern about industrial coloured effluent is its undesirable visual impact in receiving waters, a lot of wastewater from diverse sources also contains different types of phenol compounds [6].

High temperature, biodegradation, precipitation, flocculation and adsorption are some of the methods used to diminish or solve the contamination problem. On most occasions, thermal treatments present considerable emission of other hazardous compounds. The biological treatments require a long residence time for microorganisms to degrade the pollutant and they can be affected

by toxicity and temperature changes. Frequently, the other techniques such as flocculation, precipitation and adsorption on activated carbon require a post-treatment step. However, between those processes, adsorption represents one of the most important and more efficient techniques used to retain the contamination [1-4, 6]. Activated carbons are amongst the materials commonly employed as adsorbent and adsorption is one of the most studied techniques and seems a successful efficient alternative for the removal of organic compounds and dyes in low concentrations [3-8]. Adsorption on granular activated carbon has been cited as having a great potential and is usually used in the water treatment industry [9].

Basically, adsorption is a mass transfer process in which a substance is transferred from the liquid phase to the surface of a solid, and becomes bound by physical and/or chemical interactions. However, the adsorption process of aromatic compounds by activated carbons is more complex than the simple explanation and there still exists considerable difficulty in entirely explaining the results of adsorption studies [10].

The AC efficiency for applications in the liquid-phase is due to their high porous volume and pore size distribution, conjugated with surface chemistry and fast adsorption kinetics. Among the characteristics of the adsorptive that mainly influence the adsorption process are its molecular size, the water solubility and the pKa. The molecular size is related to access of the adsorbate to the pores and the solubility influences the hydrophobic interactions with the adsorbent surface [8].

In an effort to find highly available–low cost raw materials for the production of activated carbons, this study was conducted in order to check the suitability of selected precursor materials, not extensively investigated and report their adsorbing capacities. An attempt is made to interpret the differences in adsorption capacities. Furthermore, some of the adsorbents developed are not really low-cost materials to permit widespread use. Efforts are therefore still needed to have low-cost adsorbents that have a high-adsorption capacity for phenolic compounds.

Experimental

Materials. In this study we used a set of samples prepared from cork oak (*Quercus suber* L.) wastes, recycled granulated PET and PEEK wastes. The series of activated carbons prepared in our laboratory were activated by physical activation with carbon dioxide (later identified by *DC*) or chemical activation with potassium hydroxide (later identified by *PH*).

In physical activation the samples are first carbonised in a flux of dry nitrogen. Subsequently, in a second step, the activation is made by switching the flux to CO₂ (*DC* activation). All the process is controlled by using a specific heating rate, final temperature and residence time. The activation temperature was 973 K for cork and 1173 K for PEEK samples, and a variable time of activation to achieve different levels of burn-off. For cork and PEEK samples the burn-off was 70 and 74 %, respectively.

In chemical activation the raw materials were dry impregnated with solid potassium hydroxide. After that mixing step, in impregnant/precursor mass ratio of 2, all the mixture was submitted to pyrolysis. The activation was carried out by heating the sample in a horizontal tubular furnace in a flux of dry nitrogen with flow rate 85 cm³ min⁻¹. The maximum temperature was 973 K for cork and PET, or 1173 K for PEEK with a maximum dwell time of 120 min. The pyrolysed samples were washed until complete removal of the impregnant and then dried at 373 K during 3 days. The designation of the samples starts with the initials of the precursor, followed by the activating agent and the level of burn-off (in the case of physical activation): CORK-DC-68, CORK-PH, PEEK-DC-74, PEEK-PH and PET-PH.

The adsorptives used in liquid-phase adsorption were two phenolic compounds, 4-chlorophenol (PCP), and phenol (P), both from Aldrich with purity greater than 99%.

Methods. All AC were structurally and chemically characterised, by nitrogen adsorption at 77 K, elemental analysis (C, H, N, O and S) and by their point of zero charge.

The batch and kinetic studies of adsorption of phenolic compounds were carried out at 298 K in an acid pH medium. In these studies a fixed quantity of activated carbon was added to an aqueous solution of the mono-phenolic compound (with specific concentrations). The erlenmeyer flasks with stopper were placed in a thermostated shaker bath for different times, to establish the equilibrium time (4 days). The filtrate was analysed by UV/visible spectrophotometry at appropriate wavelength (280 and 269 nm for PCP and P). The amount of phenolic compound was fixed in appropriate conditions of pH that ensured only one of the forms of the compound was present. The amounts adsorbed on the activated carbons were determined from the measured concentration, and the adsorption isotherms were obtained.

Results and Discussion

All of the nitrogen adsorption isotherms, presented in Fig.1, are type I of the IUPAC classification, with some variation in terms of pore volume, external surface area and micropore size. The elemental analysis and point of zero charge also reflect differences between the activated carbons, namely the acid or basic character and the content in carbon and oxygen. In Table 1 a summary of these results is given.

There is a clear difference between the natural polymer, cork, and the synthetic polymer precursors, when submitted to a physical or chemical activation, as was reported in the literature [11-13]. With cork, there is an increase of the pore volume, of approximately double, when the activation is made with PH (from 0.33 to 0.64 cm³ g⁻¹). On the other hand, the mean pore width decreases with chemical activation, obtaining a more microporous material in this case. With PEEK, the physical activation with DC leads to an AC with a higher micropore volume and surface area (1.27 cm³ g⁻¹ and 38.6 m² g⁻¹) when compared with those obtained by chemical activation with PH (0.74 cm³ g⁻¹ and 12.0 m² g⁻¹ respectively). When we compare the two precursors, in terms of mean pore width, there is clearly a narrowing of the pore size when there is a change from physical to chemical activation.

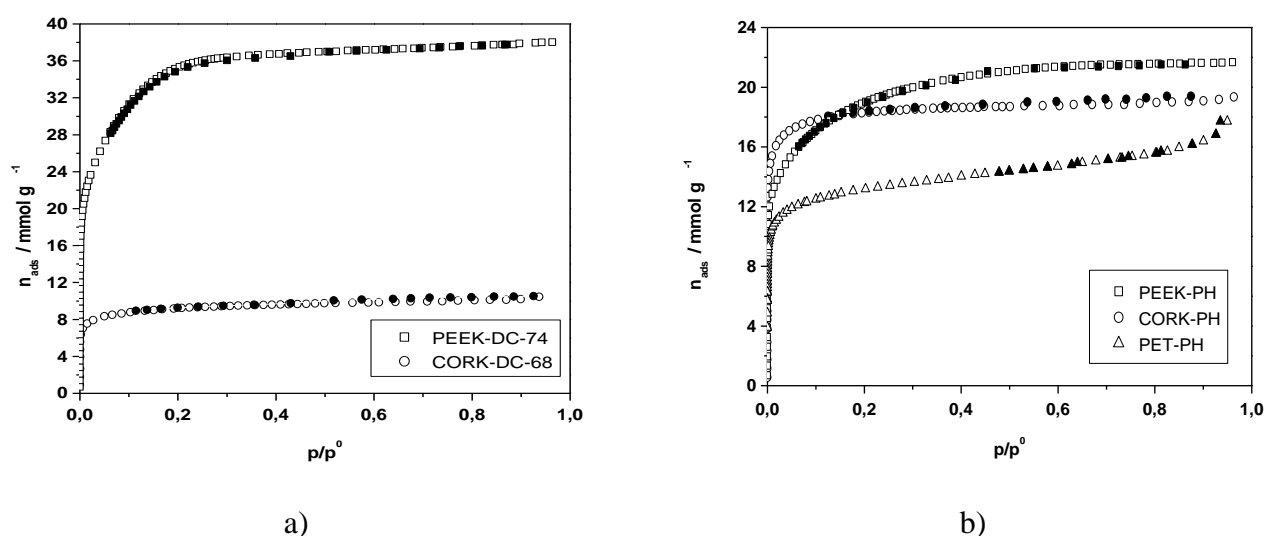


Figure 1. N₂ / 77 K adsorption isotherms determined on samples prepared by physical activation (a), and by chemical activation (b). Open symbols represent adsorption, closed symbols represent desorption.

Table 1. Structural and chemical parameters of carbon samples obtained by different techniques (A - surface area, V - pore volume, L_0 - mean pore width; BET, S and O subscripts correspond to BET, α_S and DR methods, respectively).

Activated Carbon	N ₂ Adsorption					N	Elemental Analysis			PZC pH
	A _{BET} [m ² g ⁻¹]	A _S [m ² g ⁻¹]	V _S [cm ³ g ⁻¹]	V ₀ [cm ³ g ⁻¹]	L ₀ [nm]		C [%]	H [%]	O [%]	
CORK-DC-68	787	20.4	0.33	0.31	1.18	0.8	58.5	0.8	20.1	10.1
PEEK-DC-74	2874	38.6	1.27	0.99	2.17	0.22	75.5	0.03	1.1	9.4
CORK-PH	1616	16.5	0.64	0.61	0.89	1.1	65.2	0.4	15.5	5.9
PEEK-PH	1572	12.0	0.74	0.54	1.21	---	---	---	2.2	7.7
PET-PH	892	102	0.45	0.43	1.38	0.03	63.5	0.02	8.5	8.8

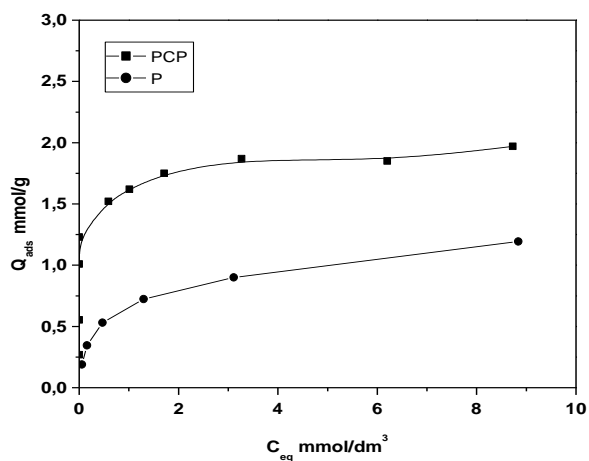
The samples prepared from PEEK, in almost the same experimental conditions, present a higher micropore volume than those prepared with PET or cork. The presence of a high volume and a large pore size is a good condition for application in the liquid phase, principally for adsorption of large adsorbate molecules. The activation with DC leads to AC which are predominantly basic. Whereas the chemical activation with KOH, but only in the case of the cork oak, led to a slightly acid character for one adsorbent, which may result from the different composition of the precursor.

The experimental isotherms show good results for the phenolic adsorbates. In particular 4-chlorophenol shows a very regular behaviour, with higher and uniform adsorption capacities for all AC. It means, that in this range of concentrations, the adsorption is ruled by the principle of solubility and not by the molecular size of the adsorbate. That is, if the sorption were governed only by the porosity of the AC, the capacity adsorption at equilibrium should be a decreasing function of adsorbate molecular size. The adsorptive presenting a higher solubility will be less adsorbed by the adsorbent material. For the phenol and 4-chlorophenol, the solubilities in water are around 9.3 g / 100mL and 2.7 g / 100mL, respectively, at 298 K [6].

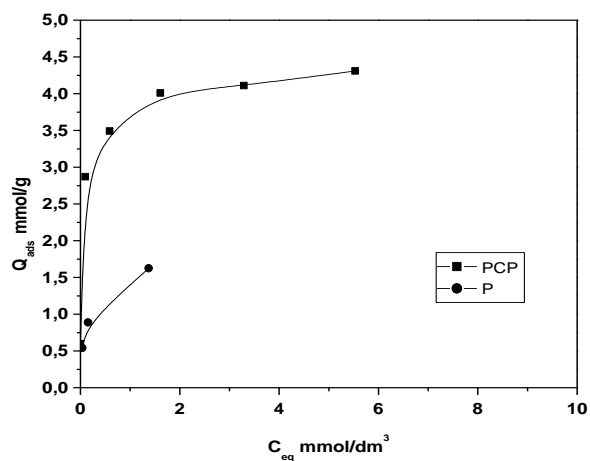
From Fig. 2, it is possible to infer that the phenolic compounds experimental isotherms are characterised by a large increase in the amount adsorbed at low concentrations and stabilizing around an equilibrium concentration of 2 mmol dm⁻³ in the case of CORK samples (Fig. 2 a) and b)). For higher concentrations a tendency to establish a plateau emerges. When the comparison is established between physical and chemical activation, we denote a decrease in the oxygen content, pore size diameter and point of zero charge, but we also find an increase in micropore volume, which corresponds to an increase in the adsorption capacity of phenolic compounds.

For PEEK and PET activated carbons this behaviour is a little different, and limit equilibrium concentration happens in high range concentrations around 4 mmol dm⁻³. With PEEK AC, when the comparison is established between physical and chemical activation, we denote an increase in the oxygen content and a decrease in the pore size diameter, PZC and micropore volume, that correspond to a decrease in the adsorption capacity of phenolic compounds.

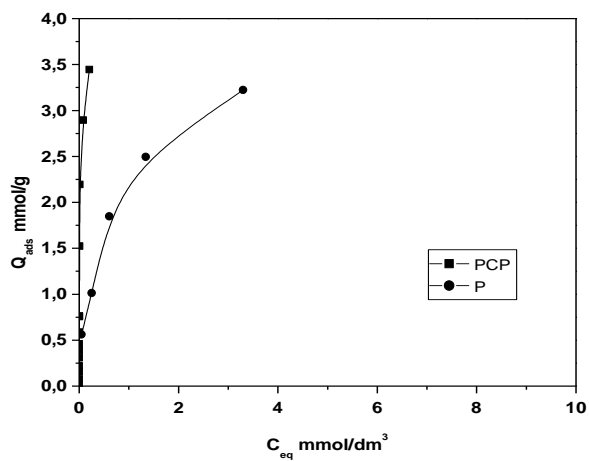
As reported by Ania et al., the adsorption of phenol in particular requires the presence of basic surface oxygen groups [14]. However, correlating the structural and chemical properties of the AC and the results of the experimental adsorption isotherms in liquid phase, it is evidently that in general it is the porous volume that controls the adsorption and not the oxygen content or the PZC.



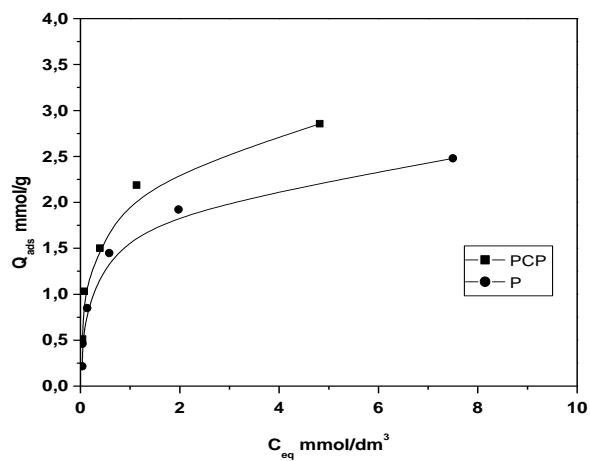
a)



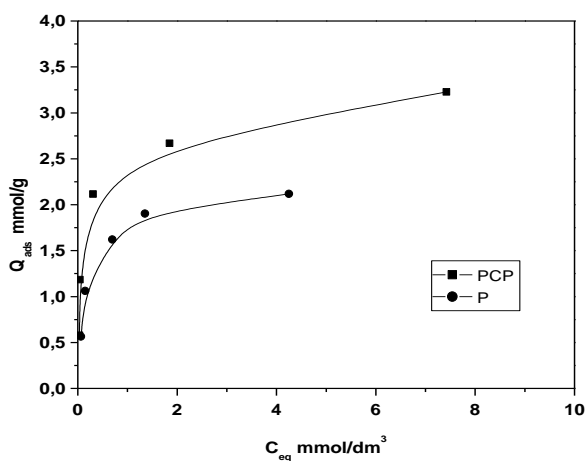
b)



c)



d)



e)

Figure 2. Experimental adsorption isotherms of CORK-DC-68 (a), CORK-PH (b), PEEK-DC-74 (c), PEEK-PH (d) and PET-PH (e), on activated carbons (nomenclature of samples: square symbols—PCP, circle symbols—P).

Conclusion

This work confirms the possibility of producing activated carbon with potentialities of use in liquid phase, namely for the adsorption of phenolic compounds, from waste of low commercial value. The performance of the activated carbons prepared from waste of three polymers, two synthetic ones (PEEK and PET) and of a natural one is compared.

The response of the precursors to the activation processes is clearly different. On the one hand, with cork oak, a better structural development is reached with chemical activation with KOH. On the other, the opposite occurs with PEEK and PET and the AC produced by physical activation present a higher pore size diameter and micropore volume.

In terms of performance in liquid phase, in the majority of the systems it is the porous volume that controls the adsorption process and it seems valid for our systems. However, in this moment we are doing more structural and chemical studies with more samples and different pollutants to explore in a detailed way these first conclusions.

Acknowledgements

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