

Modification and Optimization of Activated Carbons for Phenolic Compounds Removal

Isabel .P.P. Cansado,^a Paulo A.M. Mourão^b, Ana I. Falcão^c, M. Manuela L. Ribeiro Carrott^d and Peter J.M. Carrott^e

Centro de Química de Évora and Departamento de Química, Universidade de Évora
Rua Romão Ramalho n°59, 7000-671 Évora – Portugal

^a ippc@uevora.pt, ^b pamm@uevora.pt, ^c anaisafalcao@gmail.com ^d manrc@uevora.pt,
^e peter@uevora.pt,

1. Introduction – Phenolic compounds are generally considered to be one of the important organic pollutants discharged into the environment causing unpleasant taste and odour of drinking water [1,2]. So, removal of phenolics compounds from industrial effluents is required before sewage disposal. The development of inexpensive adsorbents from industrial wastes for the treatment of wastewaters is an important area in environmental sciences. For the phenolic compounds removal, it appears that the pH of the solution, the real surface area of the solid and functional groups play a major role. Adsorption onto activated carbons (AC) is often considered, amongst the methods currently employed to remove inorganic and organic pollutants, from aqueous or gaseous phases, as the most efficient and one of the most economical. A detailed characterization of physical and chemical surface properties of an AC has become one of the most important issues in adsorption technology because it ascertain its suitability for one or more of the application fields [1- 8].

It was reported in the literature, that activated carbon presenting a basic character and also a high nitrogen content show a higher adsorption capacity for phenolic compounds from liquid media [9]. Naturally, the post treatment modification of activated carbon leading to the formation of surface nitrogen compounds, basic groups and carbonyls will contribute to an increase in the phenolics compounds removals capacity. For this also contribute the fine structural changes occurring in this type of post-modification.

Concerning the liquid phase adsorption, various kinetic models have been reported in the literature to describe this process. However, the most widely used isotherm equation for modelling equilibrium is the Langmuir equation given by Eq. (1):

$$n_{ads} = \frac{n_{mL} C_{eq} K_L}{1 + C_{eq} K_L} \quad (1)$$

where n_{mL} is the monolayer capacity and K_L the Langmuir constant and n_{ads} is the measured adsorption at a solute equilibrium concentration C_{eq} . From the plots (C_{eq}/n_{ads}) against C_{eq} , the parameters n_{mL} and K_L are obtained. This equation presents some limitations especially when the adsorption is not limited to a monolayer and the adsorbent surface is heterogeneous. For these situations, the Freundlich equation can provide a very acceptable description of non-linear adsorption isotherms and can be written in the form [7]:

$$n_{ads} = K_F (C_{eq})^{1/n_F} \quad (2)$$

where n_{ads} is the measured adsorption at a solute equilibrium concentration C_{eq} and the constant K_F and exponent n_F are adjustable parameters whose values depend on the system. A plot of $\ln(n_{ads})$ versus $\ln(C_{eq})$ gives the values of K_F and n_F . The applicability of this equation to systems involving heterogeneous surfaces and organic compounds, like phenol and phenol-derivates, was reported as very acceptable over a wide range of concentrations [8, 9].

The objectives of this work were the examination of the modification of activated carbon, obtained from waste PET, waste cork and activated carbon cloth, by using various methods, the investigation of

the modification effects on the pore structure and surface properties and its potential application for the removal of phenolic compounds for drinking water concentration range.

2. Experimental

2.1. The activated carbon sample was produced, by chemical activation with potassium hydroxide (KOH > 87.5%, Vaz Pereira) from a waste cork or from a waste granulated PET, kindly provided by Selenis, Portugal. During the chemical activation the raw materials were dry impregnated with KOH. After that mixing step, with an impregnant/precursor mass ratio of 2, all the mixture was submitted to pyrolysis, for 30 min. at a final temperature of 973 K, achieved using a heating rate of 10 Kmin⁻¹, in a horizontal tubular furnace in a flow of dry nitrogen with flow rate 85 cm³ min⁻¹. The samples were cooled below 323 K before removing from the furnace. The pyrolysed sample was washed, with distilled water, until complete removal of the chemical activating agent. The AC obtained from cork and PET was designated by C-K and P-K respectively. An activated carbon cloth was also used for comparison.

2.2. Post-modification treatment with sodium hydroxide (NaOH > 98,6%, Vaz Pereira) – 0.5 g of untreated AC was mixed with 100 cm³, of 1 moldm⁻³ NaOH solution, for 2 hours, at 363 K. After that, the sample was filtered and washed until the wash water attained the same pH value as the distilled water employed and oven dried at 378 K. The modified samples were designated as C-Na1, P-Na1 and TC-Na1.

2.3. Post-modification treatment with urea ((NH₂)₂CO > 99.5%, Riedel) – 0.5 g of untreated AC was mixed with 100 cm³ of aqueous solution containing 2.0 g of urea, for 5 hours, at 363 K. After that, the sample was dried and pyrolysed in a horizontal tubular furnace in a flow of dry nitrogen with flow rate 85 cm³min⁻¹ until a final temperature of 973 K. The sample was cooled below 323 K before removing from the furnace. The carbonised sample was washed, with 1 dm³ of distilled water and stirring at 353 K, during 1 hour. The sample was filtered and oven dried at 373 K. The samples obtained from cork, PET and activated carbon cloth, were designated by C-U1, P-U1 and TC-U1 respectively.

2.4. Physical characterisation - All the AC were characterised structurally via nitrogen adsorption at 77 K, the corresponding isotherms being measured on a Quadrasorb, gas adsorption manometric equipment, from Quantachrome, using nitrogen of 99.999% purity supplied Air Liquide. Prior to the determination of the adsorption isotherms, the samples were outgassed on a Master Prep unit from Quantachrome, for 5 hours at 523 K, achieved using a heating rate of 5 Kmin⁻¹.

3. Results and Discussion – All samples were characterised by nitrogen adsorption at 77 K in order to obtain their textural properties. The N₂ adsorption isotherms at 77 K determined on the initial and post-treated samples present type I character, according to the IUPAC classification, without significant hysteresis at low pressure, indicating the absence of constrictions at the micropore entrances. Some variation in terms of pore volume, external surface area, micropore volume and pore size were obtained. In Table 1, a summary of all these results is given. There was a clear difference between the AC obtained from the natural polymer, cork, from the synthetic polymer precursor and from the activated carbon cloth, when submitted to reduction post treatment.

Table 1. Textural parameters of carbon samples obtained by analysis of the nitrogen adsorption isotherms

Activated Carbon	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]
P-K	1418	134	0.54	0.30	1.10
P-Na1	1127	91	0.46	0.24	1.04
P-U1	1388	155	0.52	0.27	1.32
C-K	986	86	0.38	0.22	0.99
C-Na1	1090	91	0.43	0.25	0.99
C-U1	1070	122	0.42	0.40	1.02
TC	740	15	0.30	0.18	0.86
TC-Na1	755	12	0.30	0.18	0.97
TC-U1	955	12	0.40	0.22	0.90

^aA – specific surface area, V – specific pore volume, L₀ - mean pore width; BET, S and 0 subscripts correspond to BET, α_S and DR methods, respectively.

The initial AC prepared, by chemical activation with KOH, from PET, (P-K), exhibits a pore volume of $0.54 \text{ cm}^3 \text{ g}^{-1}$ and a mean pore size of 1.1 nm. When submitted to a reduction post treatment with urea (P-U1) a small reduction in the pore volume and a broadening of pore size were observed. Regarding the AC submitted to a basic post treatment with NaOH (P-Na1), a clear reduction in the pore volume and a narrowing of the mean pore size took place.

Concerning the AC prepared, by chemical activation with KOH, from waste cork, the initial AC (C-K) exhibits a pore volume of $0.38 \text{ cm}^3 \text{ g}^{-1}$ and a mean pore size of 0.99 nm. When submitted to a reduction post treatment with urea (C-U1) an increase in the pore volume and a broadening of pore size were observed. Regarding the AC submitted to a basic post treatment with NaOH (C-Na1), an increase in the pore volume took place.

The untreated activated carbon cloth (TC) exhibits a pore volume of $0.30 \text{ cm}^3 \text{ g}^{-1}$ and a mean pore size of 0.86 nm. When submitted to a reduction post treatment with urea (TC-U1) an increase in the pore volume and a broadening of pore size were observed. However, when submitted to a basic post treatment with NaOH (TC-Na1), just a broadening of the mean pore size was observed.

Based on previous work and according to published results [3-5], the phenolic compound removals experiments were made in acidic medium, expecting an increase of the adsorption capacity of AC when the pH solution decreases. In the case of phenol adsorption from aqueous solutions, it has been reported, that there is a decrease in the surface coverage of the AC when their surface acidity increases. For this reason we have submitted the initial activated carbon (P-K, C-K and TC) to various reduction post treatments to improve the phenolic compounds adsorption. The basic character of the modified AC was confirmed by an increase in the point of zero charge and by the FTIR results, not show here.

All the activated carbon samples present a good behaviour in relation to the adsorption of the phenolic compounds tested in this work. As an example, in Figures 1 and 2, we show the *p*-nitrophenol experimental isotherms in liquid phase for two sets of samples. The activated carbon samples modified by treatment with sodium hydroxide show a distinct behaviour. While the carbons prepared from PET and cork precursors present high adsorption capacity, around 2.1 and 2.3 mmol/g respectively, the modified sample prepared from the activated carbon cloth present a lower maximum adsorption capacity, 1.9 mmol/g. Nevertheless, for the first two samples a plateau is achieved in the range of equilibrium concentrations studied, while for the cloth sample the maximum amount adsorption capacity does not seem to be achieved in this range. Based on the structural characteristics, a higher pore volume, in particular the micropore volume, of the cork and PET samples can justify the high adsorption capacity in liquid phase.

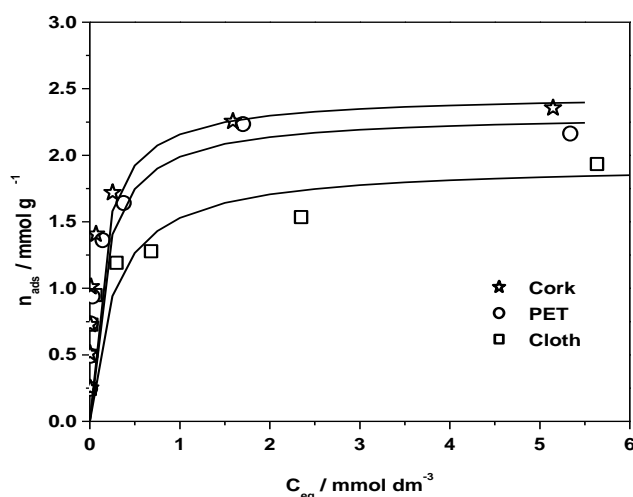


Fig. 1 Experimental adsorption isotherms of *p*-nitrophenol obtained at 298 K, on the activated carbon samples modified with NaOH.

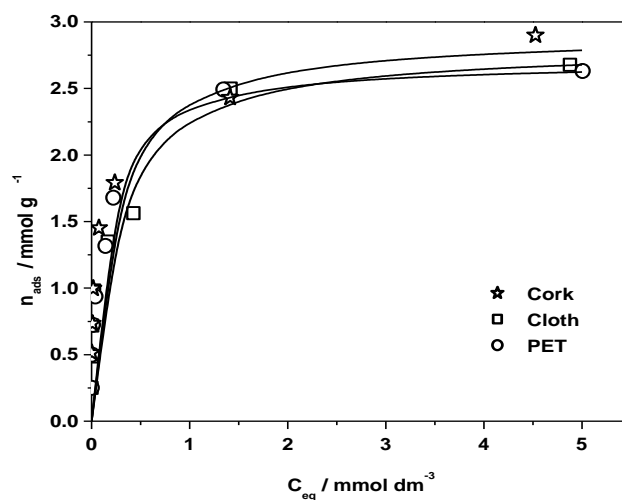


Fig. 2 Experimental adsorption isotherms of *p*-nitrophenol obtained at 298 K, on the activated carbon samples modified with $(\text{NH}_2)_2\text{CO}$.

In the case of adsorption of *p*-nitrophenol by the three samples post modified with $(\text{NH}_2)_2\text{CO}$, the behaviour is very similar. There are only small differences in the range of high equilibrium concentrations. However, the performances of these samples are superior to those prepared by modification with NaOH. The high adsorption capacities for *p*-nitrophenol of all the samples can't be explained by the different structural characteristics but only by the successful treatment with urea. The surface groups developed with this post-modification lead to an improvement of favourable interactions of the phenolic compound with those adsorbents.

4. Conclusions – The basic nature of the AC submitted to a reduction post treatment was confirmed by the higher point of zero charge. As expected, and based on the previous results, the AC modification with NaOH or with urea allowed us to increase the phenolic compounds removal.

All the activated carbon samples tested in the adsorption of phenolic compounds present a good adsorption capacity. The results in this phase can be explained in terms of structural characteristics and surface chemistry of the different adsorbents.

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References

- [1] I.P.P. Cansado, C. Galacho, Â.S. Nunes, M.M.L. Ribeiro Carrott and P.J.M. Carrott, Adsorption Science and Technology - in Press.
- [2] A. Baçaoui, A. Dahbi, A. Yaacoubi, F.J. Maldonado-Hódar, J. Rivera-Utrilla, F. Carrasco-Marín, and C. Moreno-Castilla, *Env. Sci. Technol.*, 36(19), (2002) 3844-3849.
- [3] P.A.M. Mourão, I.P.P. Cansado, P.J.M. Carrott and M.M.L. Ribeiro Carrott, *Materials Science Forum*, 636-637 (2010) 1404-1409.
- [4] K. László and A. Szucs, *Carbon*, 39 (2001) 1945-1953.
- [5] I.P.P. Cansado, M.M.L. Ribeiro Carrott, P.J.M. Carrott and P.A.M. Mourão, *Materials Science Forum*, 587 (2008) 753-757.
- [6] P.A.M. Mourão, P.J.M. Carrott and M.M.L. Ribeiro Carrott, *Carbon*, 44 (2006) 2422-2429.
- [7] P.J.M. Carrott, P.A.M. Mourão, M.M.L. Ribeiro Carrott and E.M. Gonçalves, *Langmuir*, 21 (2005) 11863-11869.
- [8] B. Ozkaya, *Journal of Hazardous Materials*, B129 (2006) 158–163.
- [9] G.G. Stavropoulos, P. Samaras and G.P. Sakellariopoulos, *Journal of Hazardous Materials*, 151 (2008) 414–421.