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Abstract

Outstanding adsorbents, presenting high potentialities for application in liquid phase adsorption, for pesticides removal, were obtained from granulated poly(ethyleneterephthalate) and cork waste.

In this work, a series of ACs was prepared by physical activation with CO₂ or chemical activation with KOH or KOH with urea. The urea addition promoted an increase on the surface area and micropore volume, a mean pore size broadening and a considerable increase in nitrogen content.

A selection of ACs was tested for pesticides removal in particular for MCPA and they reveal good adsorption capacities, particularly P-UD1 and C-UD5, whose MCPA quantities adsorbed are greater when compared with the results found in the literature.

Introduction

The widespread use of pesticides in agricultural and other activities increases the residue levels of these chemicals in soils and waters, thus becoming an important environmental problem. Pesticides are generally applied in higher amounts than those needed for pest control and they are swept away by transport processes such as leaching.

Liquid phase adsorption is one of the mechanisms which decrease solute mobility and thus could be suitable for assessing the capacity of materials to adsorb pollutants.

Among the methods currently employed to remove inorganic and organic pollutants (including herbicides) from the aqueous or gaseous phase, adsorption onto activated carbons (ACs) is often considered to be the most efficient and one of the most economical [1]. In particular, the concentration of compounds belonging to the phenoxyacid group has increased and a worrying fact is that these compounds are more often detected in both superficial and underground waters.

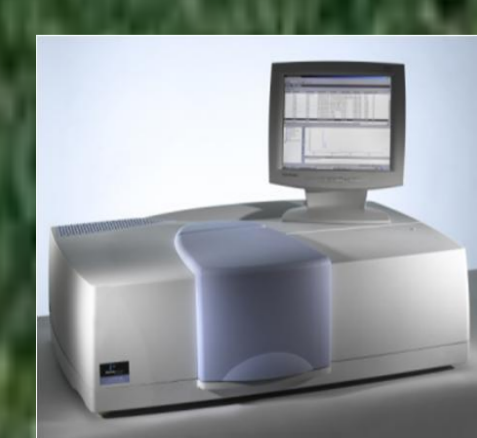
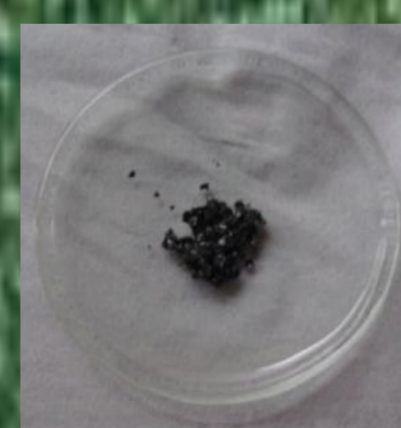
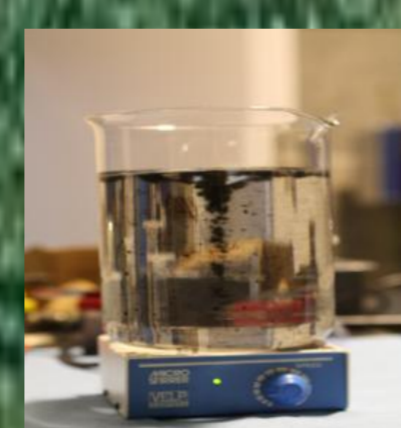
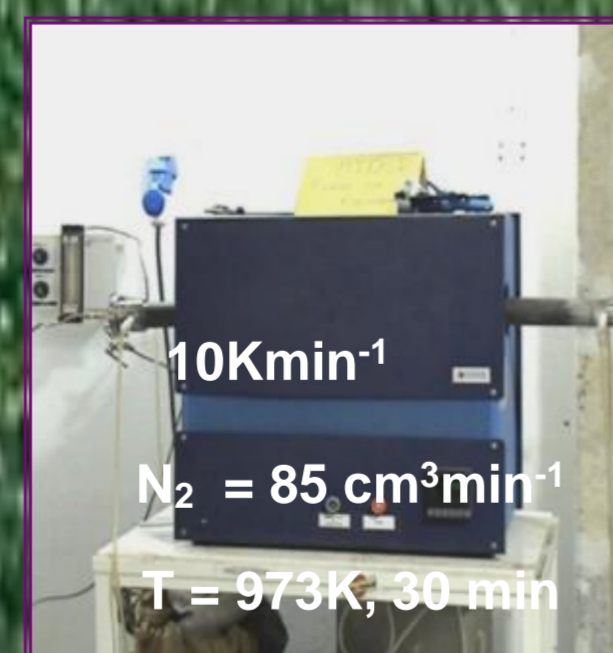
MCPA was selected because it is considered highly carcinogenic, its biological degradation is very slow and it has been detected in natural and drinking waters with contamination levels up to 0.4 µg/L [2]. In Portugal, for example, permitted levels have been decreased to only 0.1 µg/L for any one pesticide or a total of 0.5 µg/L for all [3].

Experimental

The work presented here focuses on the adsorption of MCPA on a series of ACs prepared from recycled PET or cork waste via different activation methods as detailed previous [4, 5]. All ACs were prepared and characterised as follow:



2 g PET or Cork
+ CO₂
4 g KOH
4 g KOH + (x) g urea



λ = 228.6 or 279 nm

Equilíbrio time
2 days



pH = 3



Results and Discussion

All ACs prepared were characterised via N₂ adsorption at 77K and the textural characteristics, obtained from the application of the BET, DR and α_s methods, are presented in table 1.

Interesting results were observed with the ACs enriched with nitrogen, from urea, during the chemical carbonisation / activation step. These ACs presented very high values of specific surface area and micropore volume, improving largely the potential application for adsorption from liquid phase.

Concerning the MCPA removal, the isotherms obtained and the adsorbed quantities presented as a function of the micropore volume and surface area (fig. 1a and 1b), are very elucidative and clearly show the influence of the urea on the activation process. On the UD samples, which presented the highest micropore volume, the MCPA adsorbed achieved maxima amounts for an equilibrium concentration of 100ppm, around one and a half times those obtained with the other adsorbents and higher than those found in the literature.

Table 1. Textural and chemical parameters of carbon samples obtained by different techniques (A - surface area, V - pore volume, L₀ - mean pore width; BET, S and 0 subscripts correspond to BET, α_s and DR methods, respectively).

(X-CO₂- physical activation with CO₂, X-KOH chemical activation with KOH, X-UD1 - chemical activation with KOH and urea)

Activated Carbon	A _{BET} / m ² g ⁻¹	A _s / m ² g ⁻¹	V _s / cm ³ g ⁻¹	V _p / cm ³ g ⁻¹	L _p / nm	pH _{PZC}
C-CO ₂	787	20.4	0.33	0.31	1.18	10.1
C-KOH	986	86	0.38	0.32	0.82	7.14
C-UD5	2670	151	1.05	0.47	1.70	8.50
P-CO ₂	832	114	0.38	0.38	1.23	9.80
P-KOH	1418	134	0.53	0.30	1.07	7.21
P-UD1	2634	135	0.99	0.47	1.31	7.39

Conclusions

The present study shows that activated carbons prepared from PET or cork waste can be used successfully as adsorbents for the removal of MCPA from aqueous solutions. The ACs tested display very different textural and chemical properties, nevertheless we found that the micropore volume and the surface area seem to be the determinant factors influencing MCPA removal from the liquid phase.

The textural and chemical characteristics of the nitrogen enriched AC turn to light the influence of the urea on the pore volume development during the chemical activation step.

Finally, the MCPA removal was real improved when using the enriched nitrogen ACs, such as C-UD5 and P-UD1, as the maximum achieved, at the same concentration are considerable larger to those obtained with the others adsorbents.

References

- Gimeno, O.; Plucinski P.; Kolaczowski, S.T. *Ind. Eng. Chem. Res.* **2003**, *42*, 1076.
- Garcia-Segura, S.; Cesar Almeida, L.; Bocchi, N.; Brillas, E. *J. Hazard. Mater.* **2011**, *194*, 109.
- Decreto Lei nº 306/2007, *Diário da República*, 1.ª série ; N.º 164; 27 de Agosto de 2007.
- Cansado, I.; Galacho, C.; Nunes, A.; Ribeiro Carrott, M.; Carrott, P. *Adsorpt. Sci. Technol.* **2010**, *28*, 807.
- Cansado, I.; Mourão, P.; Falcão, A.; Ribeiro Carrott, M.; Carrott, P. *Fuel Processing Technology*, **2012**, *103*, 64.