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Abstract

Highly efficient low cost carbon adsorbents were prepared from synthetic polymers mixture, such as polyethyleneterephthalate (PET) and polyacrylonitrile (PAN), by chemical activation, with potassium hydroxide or potassium carbonate, at 1073 K. Mixtures polymers carbon activation is more effective with KOH than with K₂CO₃, since the apparent surface area and the micropore volume were always higher on those prepared with KOH. The activated carbons (ACs) obtained presented a high thermal stability, a basic character and a very high apparent surface area (between 1206 and 2828 m² g⁻¹), micropore volume (between 0.35 and 1.38 cm³ g⁻¹), with mean pore sizes ranging the supermicropores region. These ACs were successfully tested on 2,4-dichlorophenoxyacetic acid (2,4-D) and 4-chloro-2-methylphenoxyacetic acid (MCPA) removals from the liquid phase. The results achieved are very promising, as the adsorption capacity of these AC is higher than that obtained with commercial AC used for this end.

Keywords	Synthetic polymers; Chemical activation; Pesticides; MCPA; 2,4-D
Taxonomy	Environmental Analysis, Environmental Chemistry, Environmental Issues, Environmental Technology, Pollution, Environmental Science
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Suggested reviewers	Silvia Román, Suhas Dr., soheil Valizadeh

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Data will be made available on request

Dear Dr. Gardinali

Editors-in-Chief of Environmental Nanotechnology Monitoring and Management Journal,

I'm writing to submit the attached revised manuscript, in agreement with the reviewer suggestion, entitled "**Pesticides abatement using activated carbon produced from a mixture of synthetic polymers by chemical activation with KOH and K₂CO₃**", for publication in Environmental Nanotechnology Monitoring and Management.

Reviewer #1:

1. The title of the paper is not clear, what does "high" means in the title, furthermore, since authors used both KOH as well as K₂CO₃ why authors are using word "or"

Concerning the reviewer suggestion, we changed the title – removing the term "high" and also substituting the term "or" by "and".

2. In keywords perhaps there is no need of "mixtures"

We agree with the reviewer and we removed "mixtures" from the keywords

3. The abbreviation used in keywords must be mentioned in the abstract too.

We included four abbreviation in the abstract. These are clearly identified in bold.

4. At maximum places authors used word such, it should be such as.

We check the writing of the manuscript, asking for help to a colleague of English origin

5. In experimental part subheading 2.1 Production of activated. It is not complete

The authors have completed this section

6. Subheading 2.1 Line The chemical activation was performed in a horizontal tubular furnace with a fixed ratio of activating agent / precursor of 2, is not clear.

The authors have clarified this section. The change made, in the experimental part, are clearly identified in bold.

7. In results and discussion authors wrote that "The ACs were analysed to achieve their elemental composition, concerning the nitrogen, carbon, hydrogen and sulphur content" however they discussed only carbon and hydrogen content. Please clarify.

The authors included the follow sentence in the discussion part. The change made, in this part, are clearly identified in bold.

“The hydrogen and sulphur contents determined in the various ACs were in the range of the detection limits of the apparatus, and therefore, were not presented or discussed.”

8. Authors are suggested to check figure numbers.

The authors have checked and corrected the figures numbers

9. Authors are suggested to correct grammatical and typographical errors.

We check the writing of the manuscript, asking for help to a colleague of English origin

Pesticides abatement using activated carbon produced from a mixture of synthetic polymers by chemical activation with KOH and K₂CO₃

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Abstract

Highly efficient low cost carbon adsorbents were prepared from synthetic polymers mixture, **such as** polyethyleneterephthalate (**PET**) and polyacrylonitrile (**PAN**), by chemical activation, with potassium hydroxide or potassium carbonate, at 1073 K. Mixtures polymers carbon activation is more effective with KOH than with K₂CO₃, since the apparent surface area and the micropore volume were always higher on those prepared with KOH.

The activated carbons (ACs) obtained presented a high thermal stability, a basic character and a very high apparent surface area (between 1206 and 2828 m² g⁻¹), micropore volume (between 0.35 and 1.38 cm³ g⁻¹), with mean pore sizes ranging the supermicropores region. These ACs were successfully tested on 2,4-dichlorophenoxyacetic acid (**2,4-D**) and 4-chloro-2-methylphenoxyacetic acid (**MCPA**) removals from the liquid phase. The results achieved are very promising, as the adsorption capacity of these AC is higher than that obtained with commercial AC used for this end.

Keywords: Synthetic polymers, Chemical activation, Pesticides, MCPA, 2,4-D

1 - Introduction

Pesticides are used worldwide to prevent agriculture from various kinds of damage, adjust the growth of plants and increase the yields of crops. It has been estimated that 2.5 million tons of pesticides are applied worldwide each year and the application rates steel increasing with time (Nascimento et al., 2017). Based on BCC Research, the market of global pesticide reached \$37.5 billion in 2011 and proximally \$65.3 billion in 2017 (www.bccresearch.com, 2017). To minimise the threat, to the ecosystems and human life, several treatment processes are available for the removal of these compounds from drinking waters and wastewaters. Among the wide range of processes, adsorption onto ACs is the most widespread method used to deal with water contaminated by pesticides, dyes and with a diversity of hazard substances like phenolic compounds (Belo et al. 2017, Cansado et al. 2012, Cansado et al. 2017, Cougnaud et al. 2005, ACs are effective adsorbent for a wide range of applications, in the most diverse areas, such it exhibited a developed microporous or mesoporous structures, a large specific surface area and a diversity of heterogeneous groups on their surface with a possibility to be chemically modified (Mourão et al. 2011), and moreover they can be regenerated and reused (Ledesma et al. 2014, Qimeng et al. 2015, Sivashankar et al. 2014). Commercially available ACs are still considered expensive due to the use of non-renewable and relatively expensive precursors such as coal. This has led to a growing research interest in the production of activated carbons from renewable and cheaper resources (Adibfar et al. 2014, Gupta et al. 2011, Hameed et al. 2009, Salman et al. 2010, Valizadehet al. 2016).

Within this line, the work presented in this manuscript report the production of ACs from a synthetic polymer mixture of polyethyleneterephthalate (PET) with polyacrylonitrile (PAN), on different ratio, by chemical activation with KOH or K_2CO_3 , at 1073 K, and the respective application on pesticides removals from aqueous medium.

The synthetic polymers used, in this work, are not from a renewable source, but PET remains a considerable portion of the plastic volume wastes produced across the world. In Europe, more than 25 million tonnes of plastic wastes are produced each year (European Commission press-release 2018). Moreover, the wastes polymers are frequently found mixed, and contaminated with organic compounds, in the urban wastes, which make their recycling difficult or impossible (George and Kurian, 2014). However, this tremendous increase in PET, result of the enormous consumption, cause the accumulation of an enormous quantity of waste, which the disposal become more complex day by day.

The solutions available to deal with plastics waste are essentially landfills and incineration. However, the decreasing space for landfills, the cost involved and the environmental concerns enhance the importance of news disposal options.

In this sense, the use of polymer wastes mixture as precursors for ACs production is a good opportunity to reduce and rethink plastic wastes. PET has already been employed as precursor for carbon adsorbents production and PAN is a widely used polymeric precursor for activated carbon fibers and carbon material production (Ali et al. 2011, Esfandiari et al. 2012, Sych et al., 2006, Nabais et al. 2004). However, with the exception to our previous work (Belo et al. 2017), concerning the use of a PET-PAN blend in the production of high ACs by physical activation with carbon dioxide, its use in a mixed way was reported only using coal or cellulose as a major component (Grzyb et al. 2009, Lorenc-Grabowska et al. 2014). Also, to our knowledge, the use of ACs prepared from a polymers synthetic blend, by chemical activation, on the adsorption of 2,4-dichlorophenoxyacetic acid (2,4-D) and 4-chloro-2-methylphenoxyacetic acid (MCPA), from the aqueous medium, was never studied before.

2 - Experimental

2.1. - Production of activated

PET and PAN polymers were used, separately or on a blend form, as a precursor for the ACs production by chemical activation with KOH or K_2CO_3 , at 1073 K, and by physical activation with CO_2 at 1073 K, using a procedure reported before (Belo et al. 2017). **The chemical activation was performed in a horizontal tubular furnace traversed by a nitrogen flux of $85\text{ cm}^3\text{ min}^{-1}$. The precursor composition included the follow ratio 1:0, 3:1, 1:1 and 1:3 of PET and PAN. A ratio of activating agent / precursor of 2 was used and the activation took place at 1073 K. The heating steps started with a rate of 5 K min^{-1} , followed by a dwell time of 1 h, at 573 K. This step allowed the materials stabilisation and promoted a complete physical mixing of the two polymers with the chemical activating agent. The second heating step was 10 K min^{-1} until 1073 K, staying at this temperature for 30 min. The samples were cooled to room temperature under a nitrogen atmosphere, before being removed from the furnace.** They were repeatedly washed with distilled water until the washing water had a pH around 7.0. The samples designations respect the follow sequence, for example: PET-PAN-1:1-KOH; PET and PAN - are the abbreviation for the precursor used; the 1:1 - refers to the ratio polymers used on the mixture; KOH – refers to the activating agent used.

2.2. - Characterisation of the activated carbon

The ACs were characterised by thermogravimetric analysis in a Perkin Elmer STA6000 analyzer, from Perkin Elmer. The samples were placed in a vertical furnace, left until the weight stabilizes, and then heated at a rate of 10 K min^{-1} until a final temperature of 1123 K, in a helium flow of $20\text{ cm}^3\text{ min}^{-1}$, allowing at this temperature for 30 min, and simultaneously, the mass loss was registered.

All ACs produced were textural characterised by nitrogen adsorption at 77 K, the corresponding isotherms being obtained on a Quadrasorb gas adsorption manometric equipment from Quantachrome Instruments, using nitrogen of 99.999 % purity, supplied by Air Liquide. Previously to the determination of the adsorption isotherms, the samples were outgassed on a Master Prep unit from Quantachrome Instruments, for the period of 5 h at 523 K, using a heating rate of 2 K min⁻¹. The acquired data were analysed by the Dubinin-Radushkevich (DR) equation and the Brunauer-Emmett-Teller (BET) and alfa-s (α_s) methods.

The chemical characterisation was achieved by elemental analysis using a Eurovector EuroEA elemental analyser, with each analysis been performed with three replicates, using a procedure previously detailed (Cansado et al. 2017).

The surface functional groups were characterised by FTIR analysis. FTIR spectra were recorded with a Perkin Elmer Spectrum Two FT-IR Spectrophotometer, using the KBr disc method (1:750 (w/w), AC:KBr), with a resolution of 4 cm⁻¹ and 20 scans, between 4000 and 450 cm⁻¹.

The pH at the point of zero charge (pHpzc) was determined using a modified version of a simple method proposed by Noh and Schwarz. A mass titration was achieved using 7 % (w/v%) suspensions of carbon material in a 0.1 mol dm⁻³ solution of sodium nitrate (NaNO₃, > 99.5 %, from Riedel). The suspensions were then placed in a thermostatic shaker bath, at 298 K, for a period of 48 h. After the equilibrium time, the suspensions were filtered, and the pH of the aqueous phase was evaluated.

2.3. - Liquid-phase adsorption of MCPA and 2,4 - D

The adsorptives used in the adsorption studies, from the aqueous phase, were two phenoxy acids, the 4-chloro-2-methylphenoxyacetic acid (MCPA) and the 2,4-dichlorophenoxyacetic acid (2,4-D), purchased from Sigma - Aldrich with a reported purity of HPLC-Grade higher than 97.4 % and used as received. In the present work, a fixed quantity of AC was added to aqueous solutions of known concentrations of pesticide. Before starting the adsorption experiments, some tests were completed to determine the minimum contact time required to achieve equilibrium adsorption conditions for MCPA and 2,4-D, on the different AC. The kinetics studies were carried out at 298 K and showed that the adsorption equilibrium state was reached after a contact period of 24 h. The MCPA and 2,4-D removal from the liquid phase was done one an acidic medium, to ensure a medium with pH around 3, the water used to prepare the suspensions was acidified first. Upon equilibration, the concentration of MCPA and 2,4-D remaining in the liquid phase was measured by UV / visible spectrophotometry, using a PerkinElmer Lambda 850 spectrophotometer, from Perkin Elmer, at a wavelength of 228.6 or 279 nm for MCPA and 230 or 284 nm for 2,4-D, and the quantity adsorbed on the ACs was calculated via mass balance. The data were investigated based on the most widely used equations for modelling equilibrium data, from experimental liquid phase adsorption, **such as** Langmuir and Freundlich equations.

3 - Results and Discussion

Production and Characterisation of Activated Carbon

A series of ACs samples were prepared from PET, PAN and from its physical mixture, using different ratios of each one, **such as** 1:1, 1:3 and 3:1 w/w, by chemical activation with K_2CO_3 or KOH, at 1073 K. The use of K_2CO_3 , as activating agent, allows to obtain a yield higher than 21.6%, independent of the precursor used. The use of KOH allows to a slightly lower yield, as presented in table 2 and 3.

In order to assess the thermal stability of different ACs, thermogravimetric analysis (TGA) were done and the results are presented in figure 1. At temperatures less than 373 K, all ACs presented a slight mass loss, that can be attributed to the water desorption from their own surface. A first observation allows state that, ACs prepared from PAN, chemical activated with KOH or K_2CO_3 , presented a great thermal stability, when compared with those prepared from PET. At 573 K, the AC prepared from PAN or from a mixture 1:1 of PET and PAN, the mass loss was less than 5 % and at 773 K the mass loss still inferior to 10 %. It is also remarkable, that keeping the same experimental conditions, the ACs prepared with K_2CO_3 exhibited a high thermal stability than those activated with KOH.

At 1073 K, all ACs lost less than 45% of their initial weight. The thermal stability increases with the PAN content, and the ACs prepared only from PAN lost less than 15 % of their initial weight. These achievements allow to state, that ACs prepared from PET, by chemical activation with KOH or K_2CO_3 , can be successfully used, on different applications, at moderate temperature. Though, it must be highlighted that, as the PAN content increase, the AC produced can be successfully used at higher temperatures and regenerated, for use on repeated cycles or furthers applications.

The ACs were analysed to achieve their elemental composition, concerning the nitrogen, carbon, hydrogen and sulphur content. Those prepared from PET presented a lower carbon and nitrogen content and their increment appears related to the PAN content on the precursor, regardless of the activating agent used (table 1 and 2). **The hydrogen and sulphur contents determined in the ACs were in the range of the detection limit of the apparatus, and therefore, were not presented or discussed.** Furthermore, the ACs prepared with K_2CO_3 exhibited a high carbon content when compared with those prepared with KOH, using the same precursor and experimental conditions. Concerning the nitrogen content, the difference was less significate.

The determination of the pH at the point of the zero charge (pHpzc) allows the net surface charge of the AC in solution. Selected samples were tested, and the results indicated an increase on the pHpzc values as the PAN content increases, independently of the activating agent used. The PET-KOH showed an essentially neutral character, confirmed by a pHpzc of 7.19, and PAN-KOH presented a basic nature with a pHpzc of 9.32. The same trend was observed with the AC prepared

with K_2CO_3 , with a pH_{pzc} varying from 8.21 on PET- K_2CO_3 to 8.77 on PAN- K_2CO_3 . The most pronounced basic character presented by the ACs prepared from PAN was attributed to the presence of surface functional groups containing nitrogen.

In order to compare the surface chemistry of the ACs resulting from the activation with K_2CO_3 and KOH, a FTIR characterisation was done and the spectra are shown in figure 2 and 3. A first look allows to remark the similitude between the spectra of the ACs produced from the same precursor, with both activating agents, such as these were almost overlapping. In this sense, the spectra were analysed simultaneously and only the obvious differences were assigned.

Regarding the spectra, the principal bands and peaks, presented in figure 2 and 3, are related to alkyl groups, namely CH_3 , CH_2 and CH , more precisely, with antisymmetric and symmetric stretching, in the range 2800 - 3000 cm^{-1} . Also, CH_2 and CH groups, in antisymmetric and the symmetric deformation mode, in the range 1365 - 1425 cm^{-1} can explain the IR profile. The peaks around 2357 cm^{-1} , present on all ACs, are justified by the presence of CO_2 . The presence of the OH group is identified through the large band around 3450 cm^{-1} , and in the range 1680 - 1820 cm^{-1} , in the stretching mode. The interferences around 1420 cm^{-1} also reflect the contribution of OH in deformation mode.

The presence of C=O group is reflected by a small band in the range between 1680 - 1725 cm^{-1} in the stretching mode. The small bands at lower wavelength could be related to C=O and C=C bindings or to C-O, and the out of plane C-H and O-H, bindings.

The presence of these bands, predominant on the ACs prepared from PET, confirms the presence of acidic groups on the surface. The C-O group influence is reflected in the narrow band at 1210 cm^{-1} , characteristic of the stretching mode. The intense band between 910 and 1350 cm^{-1} correspond to the presence of the bond C-O and C with a hybridization sp or sp^2 . These bands are less pronounced on the ACs containing PAN on the precursor, in agreement with the more basic character exhibited.

The ACs prepared from PAN fibers presented an IR spectrum with fewer peaks and bands with less intensity when compared with those prepared from PET. The chemical structure of the polymer, for instance, the absence of aromatic rings on PAN, contributes to this feature. However, the existence of some nitrogen in the composition of PAN polymer is reflected by the stretching and deformation modes of NH bond in the range 1420 - 1680 cm^{-1} . The stretching mode associated with C-N, C=N, can contribute to the profile of the IR spectrum around 1170 cm^{-1} , 1660 - 1770 cm^{-1} and 3300 - 3620 cm^{-1} . The nitro group was also identified through the bands between 1300 and 1380 cm^{-1} .

Finally, the dissimilitude of the spectra meets the characteristics obtained by elemental composition, particularly, the presence of nitrogen groups in agreement with the high nitrogen content and pH_{pzc}, reflecting the basic nature of the adsorbents, as presented in table 1.

All ACs were texturally characterised by nitrogen adsorption, at 77 K, and gave essentially type I isotherms, as presented in figure 4 and 5. All isotherms presented a well-defined knee, characteristic of adsorbents with narrow microporosity. It is noteworthy, the curvature extends successively, as the PAN content in precursor increases. The results of the isotherm analysis using the BET, DR and alfa-s methods are presented on table 1 and 2.

The AC surface area depends on three different parameters, namely the pyrolysis temperature, the raw material used and mass ratio of precursor with activating agent (KOH or K_2CO_3). At first, the data presented on table 1 and 2 allows to state that, AC with very high surface area (from 1206 to 2828 $m^2 g^{-1}$) could be obtained from waste synthetic polymers, used separately or in mixed way, using KOH or K_2CO_3 as activating agent.

As the PAN content increase in the precursor, the micropore volume and the apparent surface area (A_{BET}) rise, approaching the value obtained on the AC prepared only from PAN, independently of the activating agent used. Conversely, when the precursor had a low PAN content, the ACs present a micropore volume and surface area almost like the one obtained, only from PET.

Based on the same precursor composition, the AC activated with KOH presented a larger mean pore size, a similar or higher pore volume and apparent surface area, when compared with those activated with K_2CO_3 .

With our conditions, the activation with KOH seems more powerful and the enlargement of the pore size was evidenced by a more rounded isotherm as presented in **figure 4**. It should be further highlighted that, in the chemical activation, K_2CO_3 could be formed through the reaction between KOH and carbon, as well as metallic K and H_2 . The K_2CO_3 reaction with carbon gives rise to K_2O and CO, which will continue with the activation reaction, extending the entire process of chemical activation. Concerning the two activating agents, the related mechanism founded in the literature, for temperature higher than 973 K, allows to the production of K_2O or metal potassium. At higher temperature this species can be removed from the carbon matrix by evaporation (the point boiling point of potassium is 1035 K) or can be intercalated promoting the opening of the blocked pores (Valizadeh, et al. 2016). The ratio of activating agent / precursor used was constant but was expressed as a mass ratio. When expressed as a molar ratio of K/precursor, this was higher with KOH (K/precursor = 0.072 mol/g) than with K_2CO_3 (K/precursor = 0.060 mol/g). These results highlight the need to evaluate the effect activating agent/precursor ratio, especially in the case of K_2CO_3 .

For comparatives proposals, the results concerning the production of ACs from PET-PAN blend with different ratios, prepared by physical activation, with carbon dioxide, at 1073 K with different activating times were also included on table 3. As the activation time increase, the burn off increase and the textural characteristics, **such as** superficial area, pore volume and mean pore size increase. The ACs prepared from PET and PAN (1:1) by physical activation, with CO_2 at

1073 K, table 3, presented a high nitrogen content, reflected on a higher pH_{pzc}, higher than 10, when compared with those chemically activated with KOH or K₂CO₃.

Using the same precursor, the ACs produced by physical activation with CO₂ presented, always, lower apparent surface area, micropore volume and mean pore size, when compared with those chemicals activated with K₂CO₃ or KOH. In this sense, chemical activation, with both activating agents, allows obtaining ACs with textural properties considerably developed and physical activation allows obtaining narrow micropores ACs.

MCPA and 2,4-D removals from aqueous phase

The adsorption of MCPA and 2,4-D on selected AC was achieved after an equilibrium time of 24 h. The isotherms were acquired at optimal conditions previous defined in our group (pH = 3.0 and T = 298 K). The data for the MCPA and 2,4-D adsorption, on some AC prepared from different mixtures of synthetic polymers are presented in table 4 and 5 and figures 6 to 9. The uptake ($Q_{\text{ads}} / \text{mmol g}^{-1}$) of the adsorbate, at equilibrium concentration, ($C_{\text{eq}} / \text{mmol dm}^{-3}$), was calculated, based on equation 1, where C_0 is the initial concentration of adsorptive (mol dm^{-3}) in solution, V is the volume of solution used and m is the mass of AC.

$$Q_{\text{ads}} = V \frac{C_0 - C_{\text{eq}}}{m} \quad (\text{Equation 1})$$

In liquid phase, the adsorption capacity of ACs for pesticides, that have in their structure an aromatic ring, depends on numerous factors, **such as** the physical nature of the adsorbent, like apparent surface area and pore volume, ash content, functional groups and from the nature of the adsorbate, such as its pK_a, the presence of functional groups, polarity, molecular weight and size, aqueous solubility and experimental conditions **such as** pH, ionic strength and adsorbate concentration.

The comparison of both pesticides adsorption studied, of aromatic character, on the same AC and using the same experimental conditions evince the differences between them, justified by their properties. Nonetheless MCPA present a higher water solubility and pK_a (825 g L⁻¹, at 293 K and pK_a = 3.0) than 2,4-D (680 g L⁻¹, at 293 K and pK_a = 3.0), the nature and position of substituent groups plays a decisive role on adsorption, such MCPA adsorption capacity was always higher than 2,4-D, as presented in figures 6 to 9.

The AC adsorption capacity concerning MCPA and 2,4-D increase as the apparent surface area and micropore volume increase. With the AC – systems studied; the adsorption of both pesticides increases also as the PAN content increase in the precursor.

The maximum MCPA and 2,4-D adsorption was expressed as a function of total pore volume and of narrow micropore volume, as shown in figure 10. This good correlation allows confirm that size pore exclusion are not a relevant factor in the adsorption systems studied. It was verified

before, that through MCPA and 2,4-D removals from the liquid phase, pore size exclusion effect take place only when the ACs average pore diameter was smaller than 1.5 to 1.7 times, the adsorptive second widest dimension, it means pores sizes lower than 1.05 nm for these adsorptives (Belo et al. 2017). The ACs evaluated presented a mean pore size higher than 1.09 nm (exception on PET-K₂CO₃), this allow to confirm that pore size exclusion effect is not a relevant factor, on MCPA or 2,4-D removals from the liquid phase, on the set of carbon samples prepared.

Another perspective, that must be evaluated, is the influence of the ACs surface characteristics on the pesticides removals, that can be expressed as a relationship between the adsorption capacity and the respectively pH_{pzc}. Figure 11 show the maximum adsorption capacity as a function as the basicity character of the ACs. It is clear that surface chemistry nature influences the adsorption of both pesticides, such as the pH_{pzc} increase it is noteworthy that adsorption capacity removals increase, agreeing with published works.

The data were analysed based on the Langmuir (Eq.2) and Freundlich (Eq. 3) equations. In this equation, n_{mL} is the monolayer capacity and K_L is the Langmuir constant, K_F and n_F are Freundlich constants incorporating the factors affecting the adsorption capacity and the intensity of the adsorption process, respectively.

$$\frac{C_{eq}}{Q_{ads}} = \frac{1}{n_{mL}K_L} + \frac{1}{n_{mL}}C_{eq} \quad (\text{Equation 2})$$

$$\ln Q_{ads} = \ln K_F + \frac{1}{n_F} \ln C_{eq} \quad (\text{Equation 3})$$

The values of the parameters obtained by fitting the experimental data to the Langmuir and Freundlich equations are presented in table 4 and 5. In general, the fitting of the Langmuir equation present very good results, however, the n_{mL} values were higher on the ACs activated with KOH then the maximum adsorption capacity and the opposite was verified on the ACs prepared with K₂CO₃. Freundlich equation presents good results and the constant n_F ranges between 3.1 and 9.85 for the two adsorbates, indicating that their adsorption could be considered favourable and the adsorbent surface as heterogeneous.

The absolute values obtained for the n_{mL} and K_F parameters are presented in table 4 and 5. K_F values were determined for an equilibrium concentration equal to 1 mmol dm⁻³, yet as the values were similar or slight higher than the maximum adsorption capacity attained, meaning that equilibrium adsorption was reached. The K_F were closer to n_{max} with 2,4-D-AC systems, it is noteworthy that the Freundlich parameter n_F was higher, on the

isotherms for 2,4-D obtained on PET-KOH and PET-PAN-1:1-KOH, when the isotherms were more rectangular, corresponding to complete equilibrium adsorption. The values of $1/n_F$ obtained for the adsorption of MCPA and 2,4-D with all ACs samples were less than 1, indicating favourable adsorption, with the experimental conditions tested.

The ACs prepared from PET, PAN or from a mixture of these two polymers allow obtaining ACs with excellent textural characteristics. From table 4 and 5, the AC presented an MCPA adsorption capacity varying from 2.45 to 5.10 mmol g⁻¹. These values are very high when compared with those obtained on the AC prepared from the same precursor by physical activation, with carbon dioxide, as presented on table 6. Ours values were also higher than the maximum adsorption capacity obtained on AC commercially used for this purpose (around 0.78 mmol g⁻¹ or 160 mg g⁻¹) (Gimeno et al. 2003).

The results obtained enable us to establish, that an efficient pesticides removal, from the liquid media, is possible with these low-cost adsorbents prepared from a synthetic polymer mixture, which can partial simulate the plastic composition of urban waste solids residues. This approach allows obtaining a better quality of a low-cost AC for efficient removals of acidic pesticides from wastewaters.

4 - Conclusion

This work shows that mixed synthetic polymer can be used as precursor to produce activated carbon with a well-developed porosity using a stabilisation step by chemical activation with KOH or K₂CO₃. The ACs prepared from PET+PAN mixture presented excellent chemical and textural characteristics, such a moderate to basic character and high surface area and micropore volume. Mixtures polymers carbon activation is more effective with KOH than with K₂CO₃, since the apparent surface area and the micropore volume were always higher on those prepared with KOH.

The ACs tested for pesticides removals present a high adsorption capacity compared with those previous obtained with ACs prepared by physical activation, or even by a commercial AC prepared from precursors of same nature used for this intend. The experimental procedure comprise a way of valuing waste plastics and the results allow envisaging an assortment of potential applications for the activated carbons obtained.

Acknowledgements

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References

Adibfar, M., Kaghazchi, T., Asasian N. and Soleiman, M., (2014) Conversion of Poly (Ethylene Terephthalate) Waste into Activated Carbon: Chemical Activation and Characterization, *Chem. Eng. Technol.* 37, (6):979–986.

Ali, E., Tahereh, K. and Mansooreh, S. 2012. Preparation and evaluation of activated carbons obtained by physical activation of polyethyleneterephthalate (PET) wastes *Journal of the Taiwan Institute of Chemical Engineers* 43:631–637.

Belo, C.R., Cansado, I.P.P. and Mourão, P.A.M., 2017. Synthetic polymers blend used in the production of high activated carbon for pesticides removals from liquid phase, *Environ. Technol.*, 38:3, 285-296, DOI: 10.1080/09593330.2016.1190409.

Cansado, I.P.P., Belo, C.R. and Mourão, P.A.M., 2017. Valorisation of *Tectona Grandis* tree sawdust through the production of high activated carbon for environment applications, *Bioresource Technology* 249, 28-333.

Cansado, I.P.P., Mourão, P.A.M., Falcão, A.I., Ribeiro Carrott, M.M.L. and Carrott, P.J.M., 2012. The influence of the activated carbon post-treatment on the phenolic compounds removal. *Fuel Process. Technol.* 103, 64-70.

Cougnaud, A., Faur, C. and Le Cloirec, P., 2005. Removal of pesticides from aqueous solution: Quantitative relationship between activated carbon characteristics and adsorption properties. *Environ. Technol.* 26:8, 857-866.

Esfandiari, A., Kaghazchi, T., Soleimani, M., 2012. Preparation and evaluation of activated carbons obtained by physical activation of polyethyleneterephthalate (PET) wastes, *Journal of the Taiwan Institute of Chemical Engineers* 43:631–637.

George N. and Kurian, T., 2014. Recent Developments in the Chemical Recycling of postconsumer Poly (ethylene terephthalate) Waste *Ind. Eng. Chem. Res.* 2014, 53, 14185–14198.

Grzyb, B., Albiniak, A., Broniek, E., Furdin, G., Mareche, J.F. and Begin, D., 2009. SO₂ adsorptive properties of activated carbons prepared from polyacrylonitrile and its blends with coal-tar pitch, *Microporous and Mesoporous Materials* 118:163–168.

Gupta, V.K., Gupta, B., Rastogi, A., Agarwal, S. and Nayak, A., 2011. Pesticides removal from waste water by activated carbon prepared from waste rubber tire, *Water Res.* 45, 4047-4055.

Hameed, B.H., Salman, J.M. and Ahmad, A.L., 2009. Adsorption isotherm and kinetic modeling of 2,4-D pesticide on activated carbon derived from date stones, *Journal of Hazardous Materials* 163: 121–126.

http://europa.eu/rapid/press-release_IP-18-5_en.htm, 2018. Plastic Waste: a European strategy to protect the planet, defend our citizens and empower our industries, (Strasbourg, 16 January 2018), consulted 13/4/2018.

<https://www.bccresearch.com>, 2017, consulted 13/4/2018.

Ledesma, B., Román, S., Álvarez-Murillo, A., Sabio, E. and González, J.F., 2014. Cyclic adsorption/thermal regeneration of activated carbons, *Journal of Analytical and Applied Pyrolysis* 106:112–117.

Lorenc-Grabowska, E. and Wrocław, 2014. P.R. High basicity adsorbents from solid residue of cellulose and synthetic polymer co-pyrolysis for phenol removal: Kinetics and mechanism, *Applied Surface Science* 316:435–442.

Mourão, P.A.M., Laginhas, C., Custódio, F., Nabais, J.M.V., Carrott, P.J.M. and Ribeiro Carrott, M.M.L., 2011. Influence of oxidation process on the adsorption capacity of activated carbons from lignocellulosic precursors, *Fuel Processing Technology* 92:241-246.

Nabais, J.M.V., Carrott, P.J.M., Ribeiro Carrott, M.M.L. and Menéndez, J.A. 2004. Preparation and Modification of Activated Carbon Fibres by Microwave Heating, *Carbon* 42(7): 1315-1320.

Nascimento, M.M. Rocha, G.O. and Andrade, J.B., 2017. Pesticides in fine airborne particles: from a green analysis method to atmospheric characterization and risk assessment, *Scientific Reports*, 7: 2267, DOI:10.1038/s41598-017-02518-1.

Qimeng, L., Yanshan, Q. and Canzhu, G., 2015. Chemical regeneration of spent powdered activated carbon used in decolorization of sodium salicylate for the pharmaceutical industry, *Journal of Cleaner Production* 86:424-431.

Salman, J.M. and Hameed, B.H., 2010. Adsorption of 2,4-dichlorophenoxyacetic acid and carbofuran pesticides onto granular activated carbon. *Desalination*. 256, 129-135.

Sivashankar, R., Sathya, A.B., Vasantharaj, K. and Sivasubramanian, V. 2014. Magnetic composite an environmental super adsorbent for dye sequestration – A review. *Environmental Nanotechnology, Monitoring & Management* 1–2:36–49.

Sych, N.V., Kartel, N.T., Tsyba, N.N., Strelko, V.V., 2006. Effect of combined activation on the preparation of high porous active carbons from granulated post-consumer polyethyleneterephthalate. *Applied Surface Science* 252:8062–8066.

Valizadeh, S., Younesi, H. and Bahramifar, N., 2016. Highly mesoporous K₂CO₃ and KOH/activated carbon for SDBS removal from water samples: Batch and fixed-bed column adsorption process, *Environmental Nanotechnology, Monitoring & Management*, 6: 1-13.

Highlights:

- . First attempt to produce activated carbon from a mixture of synthetic polymers by chemical activation with KOH and K_2CO_3 .
- . The activation of the polymers mixtures is more effective with KOH than with K_2CO_3 .
- . Activated carbons with surface basic characteristics.
- . Activated carbon presenting excellent adsorption capacities concerning to the adsorption of acidic pesticides.

Pesticides abatement using activated carbon produced from a mixture of synthetic polymers by chemical activation with KOH and K₂CO₃

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Abstract

Highly efficient low cost carbon adsorbents were prepared from synthetic polymers mixture, such polyethyleneterephthalate (PET) and polyacrylonitrile (PAN), by chemical activation, with potassium hydroxide or potassium carbonate, at 1073 K. Mixtures polymers carbon activation is more effective with KOH than with K₂CO₃, such the apparent surface area and the micropore volume were always higher on those prepared with KOH.

The activated carbons (ACs) obtained presented a high thermal stability, a basic character and a very high apparent surface area (between 1206 and 2828 m² g⁻¹), micropore volume (between 0.35 and 1.38 cm³ g⁻¹), with mean pore sizes ranging the supermicropores region. These ACs were successfully tested on 2,4-dichlorophenoxyacetic acid (2,4-D) and 4-chloro-2-methylphenoxyacetic acid (MCPA) removals from the liquid phase. The results achieved are very promising, as the adsorption capacity of these AC is higher than that obtained with commercial AC used for this end.

Keywords: Synthetic polymers, Chemical activation, Pesticides, MCPA, 2,4-D

1 - Introduction

Pesticides are used worldwide to prevent agriculture from various kinds of damage, adjust the growth of plants and increase the yields of crops. It has been estimated that 2.5 million tons of pesticides are applied worldwide each year and the application rates steel increasing with time (Nascimento et al., 2017). Based on BCC Research, the market of global pesticide reached \$37.5 billion in 2011 and proximally \$65.3 billion in 2017 (www.bccresearch.com, 2017). To minimise the threat, to the ecosystems and human life, several treatment processes are available for the removal of such compounds from drinking waters and wastewaters. Among the wide range of processes, adsorption onto ACs is the most widespread method used to deal with water contaminated by pesticides, dyes and with a diversity of hazard substances like phenolic compounds (Belo et al. 2017, Cansado et al. 2012, Cansado et al. 2017, Cougnaud et al. 2005, ACs are effective adsorbent for a wide range of applications, in the most diverse areas, such it exhibited a developed microporous or mesoporous structures, a large specific surface area and a diversity of heterogeneous groups on their surface with a possibility to be chemically modified (Mourão et al. 2011), and moreover they can be regenerated and reused (Ledesma et al. 2014, Qimeng et al. 2015, Sivashankar et al. 2014). Commercially available ACs are still considered expensive due to the use of non-renewable and relatively expensive precursors such as coal. This has led to a growing research interest in the production of activated carbons from renewable and cheaper resources (Adibfar et al. 2014, Gupta et al. 2011, Hameed et al. 2009, Salman et al. 2010, Valizadehet al. 2016).

Within this line, the work presented in this manuscript report the production of ACs from a synthetic polymer mixture of polyethyleneterephthalate (PET) with polyacrylonitrile (PAN), on different ratio, by chemical activation with KOH or K_2CO_3 , at 1073 K, and the respective application on pesticides removals from aqueous medium.

The synthetic polymers used, in this work, are not from a renewable source, but in particular the PET remains a considerable portion of the plastic volume wastes produced across the world. In Europe, more than 25 million tonnes of plastic wastes are produced each year (European Commission press-release 2018). Moreover, the wastes polymers are frequently found mixed, and contaminated with organic compounds, in the urban wastes, which make their recycling difficult or impossible (George and Kurian, 2014). However, this tremendous increase in PET, result of the enormous consumption, cause the accumulation of an enormous quantity of waste, which the disposal become more complex day by day.

The solutions available to deal with plastics waste are essentially landfills and incineration. However the decreasing space for landfills, the cost involved and the environmental concerns enhance the importance of news disposal options.

In this sense, the use of polymer wastes mixture as precursors for ACs production is a good opportunity to reduce and rethink plastic wastes. PET has already been employed as precursor for carbon adsorbents production and PAN is a widely used polymeric precursor for activated carbon fibers and carbon material production (Ali et al. 2011, Esfandiari et al. 2012, Sych et al., 2006, Nabais et al. 2004). However, with the exception to our previous work (Belo et al. 2017), concerning the use of a PET-PAN blend in the production of high ACs by physical activation with carbon dioxide, its use in a mixed way was reported only using coal or cellulose as a major component (Grzyb et al. 2009, Lorenc-Grabowska et al. 2014). Also, to our knowledge, the use of ACs prepared from a polymers synthetic blend, by chemical activation, on the adsorption of 2,4-dichlorophenoxyacetic acid (2,4-D) and 4-chloro-2-methylphenoxyacetic acid (MCPA), from the aqueous medium, was never studied before.

2 - Experimental

2.1. - Production of activated

PET and PAN polymers were used, separately or on a blend form, as a precursor for the ACs production by chemical activation with KOH or K_2CO_3 , at 1073 K, and also by physical activation with CO_2 at 1073 K, using a procedure reported before (Belo et al. 2017). The chemical activation was performed in a horizontal tubular furnace with a fixed ratio of activating agent / precursor of 2, at 1073 K. The first step used a heating rate of 5 K min^{-1} followed by a dwell time of 1 h at 573 K, in order to stabilize the materials and to avoid a complete physical mixing of the two polymers with the chemical activating agent. The second heating step was 10 K min^{-1} until 1073 K, in a nitrogen flux of $85\text{ cm}^3\text{ min}^{-1}$, allowing at this temperature for 30 min. The samples were cooled to room temperature under a nitrogen atmosphere, before removing from the furnace. They were repeatedly washed with distilled water until the washing water had a pH around 7.0. The precursor composition included the follow ratio 1:0, 3:1, 1:1 and 1:3 of PET and PAN. The samples designations respect the follow sequence, for example: PET-PAN-1:1-KOH; PET and PAN - are the abbreviation for the precursor used; the 1:1 - refers to the ratio polymers on the mixture; KOH - was the activating agent used.

2.2. - Characterisation of the activated carbon

The ACs were characterised by thermogravimetric analysis in a Perkin Elmer STA6000 analyzer, from Perkin Elmer. The samples were placed in a vertical furnace, left until the weight stabilizes, and then heated at a rate of 10 K min^{-1} until a final temperature of 1123 K, in a helium flow of $20\text{ cm}^3\text{ min}^{-1}$, allowing at this temperature for 30 min, and simultaneously, the mass loss was registered.

All ACs produced were textural characterised by nitrogen adsorption at 77 K, the corresponding isotherms being obtained on a Quadrasorb gas adsorption manometric equipment from Quantachrome Instruments, using nitrogen of 99.999 % purity, supplied by Air Liquide. Previously to the determination of the adsorption isotherms, the samples were outgassed on a Master Prep unit from Quantachrome Instruments, for the period of 5 h at 523 K, using a heating rate of 2 K min⁻¹. The acquired data were analysed by the Dubinin-Radushkevich (DR) equation and the Brunauer-Emmett-Teller (BET) and α_s methods.

The chemical characterisation was achieved by elemental analysis using a Eurovector EuroEA elemental analyser, with each analysis been performed with three replicate, using a procedure previously detailed (Cansado et al. 2017).

The surface functional groups were characterised by FTIR analysis. FTIR spectra were recorded with a Perkin Elmer Spectrum Two FT-IR Spectrophotometer, using the KBr disc method (1:750 (w/w), AC:KBr), with a resolution of 4 cm⁻¹ and 20 scans, between 4000 and 450 cm⁻¹.

The pH at the point of zero charge (pH_{pzc}) was determined using a modified version of a simple method proposed by Noh and Schwarz. A mass titration was achieved using 7 % (w/v%) suspensions of carbon material in a 0.1 mol dm⁻³ solution of sodium nitrate (NaNO₃, > 99.5 %, from Riedel). The suspensions were then placed in a thermostated shaker bath, at 298 K, for a period of 48 h. After the equilibrium time, the suspensions were filtered and the pH of the aqueous phase was evaluated.

2.3. - Liquid-phase adsorption of MCPA and 2,4 - D

The adsorptives used in the adsorption studies, from the aqueous phase, were two phenolic acids, the 4-chloro-2-methylphenoxyacetic acid (MCPA) and the 2,4-dichlorophenoxyacetic acid (2,4-D), purchased from Sigma - Aldrich with a reported purity of HPLC-Grade higher than 97.4 % and used as received. In the present work, a fixed quantity of AC was added to aqueous solutions of known concentrations of pesticide. Before starting the adsorption experiments, some tests were completed to determine the minimum contact time required to achieve equilibrium adsorption conditions for MCPA and 2,4-D, on the different AC. The kinetics studies were carried out at 298 K and showed that the adsorption equilibrium state was reached after a contact period of 24 h. The MCPA and 2,4-D removal from the liquid phase was done one an acidic medium, to ensure a medium with pH around 3, the water used to prepare the suspensions was acidified first. Upon equilibration, the concentration of MCPA and 2,4-D remaining in the liquid phase was measured by UV / visible spectrophotometry, using a PerkinElmer Lambda 850 spectrophotometer, from Perkin Elmer, at a wavelength of 228.6 or 279 nm for MCPA and 230 or 284 nm for 2,4-D, and the quantity adsorbed on the ACs was calculated via mass balance. The data were investigated based on the most widely used equations for modelling equilibrium data, from experimental liquid phase adsorption, such Langmuir and Freundlich equations.

3 - Results and Discussion

Production and Characterisation of Activated Carbon

A series of ACs samples were prepared from PET, PAN and from its physical mixture, using different ratios of each one, such 1:1, 1:3 and 3:1 w/w, by chemical activation with K_2CO_3 or KOH, at 1073 K. The use of K_2CO_3 , as activating agent, allows to obtain a yield higher than 21.6%, independent of the precursor used. The use of KOH allows to a slightly lower yield, as presented in table 2 and 3.

In order to assess the thermal stability of different ACs, thermogravimetric analysis (TGA) were done and the results are presented in figure 1. At temperatures less than 373 K, all ACs presented a slight mass loss, that can be attributed to the water desorption from their own surface. A first observation allows state that, ACs prepared from PAN, chemical activated with KOH or K_2CO_3 , presented a great thermal stability, when compared with those prepared from PET. At 573 K, the AC prepared from PAN or from a mixture 1:1 of PET and PAN, the mass loss was less than 5 % and at 773 K the mass loss still inferior to 10 %. It is also remarkable, that keeping the same experimental conditions, the ACs prepared with K_2CO_3 exhibited a high thermal stability than those activated with KOH.

At 1073 K, all ACs lost less than 45% of their initial weight. The thermal stability increase with the PAN content, and the ACs prepared only from PAN lost less than 15 % of their initial weight. These achievements allows to state, that ACs prepared from PET, by chemical activation with KOH or K_2CO_3 , can be successfully used, on different applications, at moderate temperature. Though, it must be highlighted that, as the PAN content increase, the AC produced can be successfully used at higher temperatures and regenerated, for use on repeated cycles or furthers applications.

The ACs were analysed to achieve their elemental composition, concerning the nitrogen, carbon, hydrogen and sulphur content. Those prepared from PET presented a lower carbon and nitrogen content and their increment appears related to the PAN content on the precursor, regardless of the activating agent used (table 1 and 2). Furthermore, the ACs prepared with K_2CO_3 exhibited a high carbon content when compared with those prepared with KOH, using the same precursor and experimental conditions. Concerning the nitrogen content, the difference was less significate.

The determination of the pH at the point of the zero charge (pHpzc) allows the net surface charge of the AC in solution. Selected samples were tested and the results indicated an increase on the pHpzc values as the PAN content increases, independently of the activating agent used. The PET-KOH showed an essentially neutral character, confirmed by a pHpzc of 7.19, and PAN-KOH presented a basic nature with a pHpzc of 9.32. The same trend was observed with the AC prepared with K_2CO_3 , with a pHpzc varying from 8.21 on PET- K_2CO_3 to 8.77 on PAN- K_2CO_3 . The most

pronounced basic character presented by the ACs prepared from PAN was attributed to the presence of surface functional groups containing nitrogen.

In order to compare the surface chemistry of the ACs resulting from the activation with K_2CO_3 and KOH, a FTIR characterisation was done and the spectra are shown in figure 2 and 3. A first look allows to remark the similitude between the spectra of the ACs produced from the same precursor, with both activating agents, such as these were almost overlapping. In this sense, the spectra were analysed simultaneously and only the obvious differences were assigned.

Regarding the spectra, the principal bands and peaks, presented in figure 2 and 3, are related to alkyl groups, namely CH_3 , CH_2 and CH , in particular with antisymmetric and symmetric stretching, in the range $2800 - 3000\text{ cm}^{-1}$. Also, CH_2 and CH groups, in antisymmetric and the symmetric deformation mode, in the range $1365 - 1425\text{ cm}^{-1}$ can explain the IR profile. The peaks around 2357 cm^{-1} , present on all ACs, are justified by the presence of CO_2 . The presence of the OH group is identified through the large band around 3450 cm^{-1} , and in the range $1680 - 1820\text{ cm}^{-1}$, in the stretching mode. The interferences around 1420 cm^{-1} also reflect the contribution of OH in deformation mode.

The presence of C=O group is reflected by a small band in the range between $1680 - 1725\text{ cm}^{-1}$ in the stretching mode. The small bands at lower wavelength could be related to C=O and C=C bindings or to C-O, and the out of plane C-H and O-H, bindings.

The presence of these bands, predominant on the ACs prepared from PET, confirms the presence of acidic groups on the surface. The C-O group influence is reflected in the narrow band at 1210 cm^{-1} , characteristic of the stretching mode. The intense band between 910 and 1350 cm^{-1} correspond to the presence of the bond C-O and C with a hybridization sp or sp^2 . These bands are less pronounced on the ACs containing PAN on the precursor, in agreement with the more basic character exhibited.

The ACs prepared from PAN fibers presented an IR spectrum with fewer peaks and bands with less intensity when compared with those prepared from PET. The chemical structure of the polymer, in particular the absence of aromatic rings on PAN, contributes to this feature. However, the existence of some nitrogen in the composition of PAN polymer is reflected by the stretching and deformation modes of NH bond in the range $1420 - 1680\text{ cm}^{-1}$. The stretching mode associated with C-N, C=N, can contribute to the profile of the IR spectrum around 1170 cm^{-1} , $1660 - 1770\text{ cm}^{-1}$ and $3300 - 3620\text{ cm}^{-1}$. The nitro group was also identified through the bands between 1300 and 1380 cm^{-1} .

Finally, the dissimilitude of the spectra meets the characteristics obtained by elemental composition, in particular the presence of nitrogen groups in agreement with the high nitrogen content and pH_{pzc}, reflecting the basic nature of the adsorbents, as presented in table 1.

All ACs were texturally characterised by nitrogen adsorption, at 77 K, and gave essentially type I isotherms, as presented in figure 4 and 5. All isotherms presented a well-defined knee, characteristic of adsorbents with narrow microporosity. It is noteworthy, the curvature extends successively, as the PAN content in precursor increases. The results of the isotherm analysis using the BET, DR and alfa-s methods are presented on table 1 and 2.

The AC surface area depends on three different parameters, namely the pyrolysis temperature, the raw material used and mass ratio of precursor with activating agent (KOH or K_2CO_3). At first, the data presented on table 1 and 2 allows to state that, AC with very high surface area (from 1206 to 2828 $m^2 g^{-1}$) could be obtained from waste synthetic polymers, used separately or in mixed way, using KOH or K_2CO_3 as activating agent.

As the PAN content increase in the precursor, the micropore volume and the apparent surface area (A_{BET}) rise, approaching the value obtained on the AC prepared only from PAN, independently of the activating agent used. Conversely, when the precursor had a low PAN content, the ACs present a micropore volume and surface area almost similar to the one obtained, only from PET. Based on the same precursor composition, the AC activated with KOH presented a larger mean pore size, a similar or higher pore volume and apparent surface area, when compared with those activated with K_2CO_3 .

With our conditions, the activation with KOH seems more powerful and the enlargement of the pore size was evidenced by a more rounded isotherm as presented in figure 1. It should be further highlighted that, in the chemical activation, K_2CO_3 could be formed through the reaction between KOH and carbon, as well as metallic K and H_2 . The K_2CO_3 reaction with carbon gives rise to K_2O and CO, which will continue with the activation reaction, extending the entire process of chemical activation. Concerning the two activating agent, the related mechanism founded in the literature, for temperature higher than 973 K, allows to the production of K_2O or metal potassium. At higher temperature this species can be removed from the carbon matrix by evaporation (the point boiling point of potassium is 1035 K) or can be intercalated promoting the opening of the blocked pores (Valizadeh, et al. 2016). The ratio of activating agent / precursor used was constant, but was expressed as a mass ratio. When expressed as a molar ratio of K/precursor, this was higher with KOH (K/precursor = 0.072 mol/g) than with K_2CO_3 (K/precursor = 0.060 mol/g). These results highlight the need to evaluate the effect activating agent/precursor ratio, especially in the case of K_2CO_3 .

For comparatives proposals, the results concerning the production of ACs from PET-PAN blend with different ratios, prepared by physical activation, with carbon dioxide, at 1073 K with different activating times were also included on table 3. As the activation time increase, the burn off increase and the textural characteristics, such superficial area, pore volume and mean pore size increase. The ACs prepared from PET and PAN (1:1) by physical activation, with CO_2 at

1073 K, table 3, presented a high nitrogen content, reflected on a higher pH_{pzc}, higher than 10, when compared with those chemically activated with KOH or K₂CO₃.

Using the same precursor, the ACs produced by physical activation with CO₂ presented, always, lower apparent surface area, micropore volume and mean pore size, when compared with those chemicals activated with K₂CO₃ or KOH. In this sense, chemical activation, with both activating agents, allows obtaining ACs with textural properties considerably developed and physical activation allows obtaining narrow micropores ACs.

MCPA and 2,4-D removals from aqueous phase

The adsorption of MCPA and 2,4-D on selected AC was achieved after an equilibrium time of 24 h. The isotherms were acquired at optimal conditions previous defined in our group (such pH = 3.0 and T = 298 K). The data for the MCPA and 2,4-D adsorption, on some AC prepared from different mixtures of synthetic polymers are presented in table 4 and 5 and figures 6 to 9. The uptake ($Q_{ads} / \text{mmol g}^{-1}$) of the adsorbate, at equilibrium concentration, ($C_{eq} / \text{mmol dm}^{-3}$), was calculated, based on equation 1, where C_0 is the initial concentration of adsorptive (mol dm^{-3}) in solution, V is the volume of solution used and m is the mass of AC.

$$Q_{ads} = V \frac{C_0 - C_{eq}}{m} \quad (\text{Equation 1})$$

In liquid phase, the adsorption capacity of ACs for pesticides, that have in their structure an aromatic ring, depends on numerous factors, such the physical nature of the adsorbent, like apparent surface area and pore volume, ash content, functional groups and from the nature of the adsorbate, such its pK_a, the presence of functional groups, polarity, molecular weight and size, aqueous solubility and experimental conditions such pH, ionic strength and adsorbate concentration.

The comparison of both pesticides adsorption studied, of aromatic character, on the same AC and using the same experimental conditions evince the differences between them, justified by their properties. Nonetheless MCPA present a higher water solubility and pK_a (825 g L⁻¹, at 293 K and pK_a = 3.0) than 2,4-D (680 g L⁻¹, at 293 K and pK_a = 3.0), the nature and position of substituent groups plays a decisive role on adsorption, such MCPA adsorption capacity was always higher than 2,4-D, as presented in figures 6 to 9.

The AC adsorption capacity concerning MCPA and 2,4-D increase as the apparent surface area and micropore volume increase. With the AC – systems studied, the adsorption of both pesticides increases also as the PAN content increase in the precursor.

The maximum MCPA and 2,4-D adsorption was expressed as a function of total pore volume and also of narrow micropore volume, as shown in figure 10. This good correlation allows

confirm that size pore exclusion are not a relevant factor in the adsorption systems studied. It was verified before, that through MCPA and 2,4-D removals from the liquid phase, pore size exclusion effect take place only when the ACs average pore diameter was smaller than 1.5 to 1.7 times, the adsorptive second widest dimension, it means pores sizes lower than 1.05 nm for these adsorptives (Belo et al. 2017). The ACs evaluated presented a mean pore size higher than 1.09 nm (exception on PET-K₂CO₃), this allow to confirm that pore size exclusion effect are not a relevant factor, on MCPA or 2,4-D removals from the liquid phase, on the set of carbon samples prepared.

Another perspective, that must be evaluated, is the influence of the ACs surface characteristics on the pesticides removals, that can be expressed as a relationship between the adsorption capacity and the respectively pH_{pzc}. Figure 11 show the maximum adsorption capacity as a function as the basicity character of the ACs. It is clear that surface chemistry nature influence the adsorption of both pesticides, such as the pH_{pzc} increase it is noteworthy that adsorption capacity removals increase, be in agreement with published works.

The data were analysed based on the Langmuir (Eq.2) and Freundlich (Eq. 3) equations. In these equation, n_{mL} is the monolayer capacity and K_L is the Langmuir constant, K_F and n_F are Freundlich constants incorporating the factors affecting the adsorption capacity and the intensity of the adsorption process, respectively.

$$\frac{C_{eq}}{Q_{ads}} = \frac{1}{n_{mL}K_L} + \frac{1}{n_{mL}}C_{eq} \quad (\text{Equation 2})$$

$$\ln Q_{ads} = \ln K_F + \frac{1}{n_F} \ln C_{eq} \quad (\text{Equation 3})$$

The values of the parameters obtained by fitting the experimental data to the Langmuir and Freundlich equations are presented in table 4 and 5. In general, the fitting of the Langmuir equation present very good results, however, the n_{mL} values were higher on the ACs activated with KOH then the maximum adsorption capacity and the opposite was verified on the ACs prepared with K₂CO₃. Freundlich equation presents good results and the constant n_F ranges between 3.1 and 9.85 for the two adsorbates, indicating that their adsorption could be considered favourable and the adsorbent surface as heterogeneous.

The absolute values obtained for the n_{mL} and K_F parameters are presented in table 4 and 5. K_F values were determined for an equilibrium concentration equal to 1 mmol dm^{-3} , yet as the values were similar or slight higher than the maximum adsorption capacity attained, meaning that equilibrium adsorption was reached. The K_F were closer to n_{max} with 2,4-D-AC systems, it is noteworthy that the Freundlich parameter n_F was higher, on the isotherms for 2,4-D obtained on PET-KOH and PET-PAN-1:1-KOH, when the isotherms were more rectangular, corresponding to complete equilibrium adsorption. The values of $1/n_F$ obtained for the adsorption of MCPA and 2,4-D with all ACs samples were less than 1, indicating favourable adsorption, with the experimental conditions tested.

The ACs prepared from PET, PAN or from a mixture of these two polymers allow obtaining ACs with excellent textural characteristics. From table 4 and 5, the AC presented an MCPA adsorption capacity varying from 2.45 to 5.10 mmol g^{-1} . These values are very high when compared with those obtained on the AC prepared from the same precursor by physical activation, with carbon dioxide, as presented on table 6. Ours values were also higher than the maximum adsorption capacity obtained on AC commercially used for this purpose (around 0.78 mmol g^{-1} or 160 mg g^{-1}) (Gimeno et al. 2003).

The results obtained enable us to establish that an efficient pesticides removals, from the liquid media, is possible with this low-cost adsorbents prepared from a synthetic polymer mixture, which can partial simulate the plastic composition of urban waste solids residues. This approach allows obtaining a better quality of a low-cost AC for efficient removals of acidic pesticides from wastewaters.

4 - Conclusion

This work shows that mixed synthetic polymer can be used as precursor to produce activated carbon with a well-developed porosity using a stabilisation step by chemical activation with KOH or K_2CO_3 . The ACs prepared from PET+PAN mixture presented excellent chemical and textural characteristics, such a moderate to basic character and high surface area and micropore volume. Mixtures polymers carbon activation is more effective with KOH than with K_2CO_3 , such the apparent surface area and the micropore volume were always higher on those prepared with KOH.

The ACs tested for pesticides removals present a high adsorption capacity compared with those previous obtained with ACs prepared by physical activation, or even by a commercial AC prepared from precursors of same nature used for this intend. The experimental procedure comprise a way of valuing waste plastics and the results allow envisaging an assortment of potential applications for the activated carbons obtained.

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References

- Adibfar, M., Kaghazchi, T., Asasian N. and Soleiman, M., (2014) Conversion of Poly(Ethylene Terephthalate) Waste into Activated Carbon: Chemical Activation and Characterization, *Chem. Eng. Technol.* 37, (6):979–986.
- Ali, E., Tahereh, K. and Mansooreh, S. 2012. Preparation and evaluation of activated carbons obtained by physical activation of polyethyleneterephthalate (PET) wastes *Journal of the Taiwan Institute of Chemical Engineers* 43:631–637.
- Belo, C.R., Cansado, I.P.P. and Mourão, P.A.M., 2017. Synthetic polymers blend used in the production of high activated carbon for pesticides removals from liquid phase, *Environ. Technol.*, 38:3, 285-296, DOI: 10.1080/09593330.2016.1190409.
- Cansado, I.P.P., Belo, C.R. and Mourão, P.A.M., 2017. Valorisation of *Tectona Grandis* tree sawdust through the production of high activated carbon for environment applications, *Bioresource Technology* 249, 28-333.
- Cansado, I.P.P., Mourão, P.A.M., Falcão, A.I., Ribeiro Carrott, M.M.L. and Carrott, P.J.M., 2012. The influence of the activated carbon post-treatment on the phenolic compounds removal. *Fuel Process. Technol.* 103, 64-70.
- Cougnaud, A., Faur, C. and Le Cloirec, P., 2005. Removal of pesticides from aqueous solution: Quantitative relationship between activated carbon characteristics and adsorption properties. *Environ. Technol.* 26:8, 857-866.
- Esfandiari, A., Kaghazchi, T., Soleimani, M., 2012. Preparation and evaluation of activated carbons obtained by physical activation of polyethyleneterephthalate (PET) wastes, *Journal of the Taiwan Institute of Chemical Engineers* 43:631–637.
- George N. and Kurian, T., 2014. Recent Developments in the Chemical Recycling of postconsumer Poly(ethylene terephthalate) Waste *Ind. Eng. Chem. Res.* 2014, 53, 14185–14198.
- Grzyb, B., Albiniak, A., Broniek, E., Furdin, G., Mareche, J.F. and Begin, D., 2009. SO₂ adsorptive properties of activated carbons prepared from polyacrylonitrile and its blends with coal-tar pitch, *Microporous and Mesoporous Materials* 118:163–168.
- Gupta, V.K., Gupta, B., Rastogi, A., Agarwal, S. and Nayak, A., 2011. Pesticides removal from waste water by activated carbon prepared from waste rubber tire, *Water Res.* 45, 4047-4055.
- Hameed, B.H., Salman, J.M. and Ahmad, A.L., 2009. Adsorption isotherm and kinetic modeling of 2,4-D pesticide on activated carbon derived from date stones, *Journal of Hazardous Materials* 163: 121–126.
- http://europa.eu/rapid/press-release_IP-18-5_en.htm, 2018. Plastic Waste: a European strategy to protect the planet, defend our citizens and empower our industries, (Strasbourg, 16 January 2018), consulted 13/4/2018.
- <https://www.bccresearch.com>, 2017, consulted 13/4/2018.

- Ledesma, B., Román, S., Álvarez-Murillo, A., Sabio, E. and González, J.F., 2014. Cyclic adsorption/thermal regeneration of activated carbons, *Journal of Analytical and Applied Pyrolysis* 106:112–117.
- Lorenc-Grabowska, E. and Wrocław, 2014. P.R. High basicity adsorbents from solid residue of cellulose and synthetic polymer co-pyrolysis for phenol removal: Kinetics and mechanism, *Applied Surface Science* 316:435–442.
- Mourão, P.A.M., Laginhas, C., Custódio, F., Nabais, J.M.V., Carrott, P.J.M. and Ribeiro Carrott, M.M.L., 2011. Influence of oxidation process on the adsorption capacity of activated carbons from lignocellulosic precursors, *Fuel Processing Technology* 92:241-246.
- Nabais, J.M.V., Carrott, P.J.M., Ribeiro Carrott, M.M.L. and Menéndez, J.A. 2004. Preparation and Modification of Activated Carbon Fibres by Microwave Heating, *Carbon* 42(7): 1315-1320.
- Nascimento, M.M. Rocha, G.O. and Andrade, J.B., 2017. Pesticides in fine airborne particles: from a green analysis method to atmospheric characterization and risk assessment, *Scientific Reports*, 7: 2267, DOI:10.1038/s41598-017-02518-1.
- Qimeng, L., Yanshan, Q. and Canzhu, G., 2015. Chemical regeneration of spent powdered activated carbon used in decolorization of sodium salicylate for the pharmaceutical industry, *Journal of Cleaner Production* 86:424-431.
- Salman, J.M. and Hameed, B.H., 2010. Adsorption of 2,4-dichlorophenoxyacetic acid and carbofuran pesticides onto granular activated carbon. *Desalination*. 256, 129-135.
- Sivashankar, R., Sathya, A.B., Vasantharaj, K. and Sivasubramanian, V. 2014. Magnetic composite an environmental super adsorbent for dye sequestration – A review. *Environmental Nanotechnology, Monitoring & Management* 1–2:36–49.
- Sych, N.V., Kartel, N.T., Tsyba, N.N., Strelko, V.V., 2006. Effect of combined activation on the preparation of high porous active carbons from granulated post-consumer polyethyleneterephthalate. *Applied Surface Science* 252:8062-8066.
- Valizadeh, S., Younesi, H. and Bahramifar, N., 2016. Highly mesoporous K_2CO_3 and KOH/activated carbon for SDBS removal from water samples: Batch and fixed-bed column adsorption process, *Environmental Nanotechnology, Monitoring & Management*, 6: 1-13.

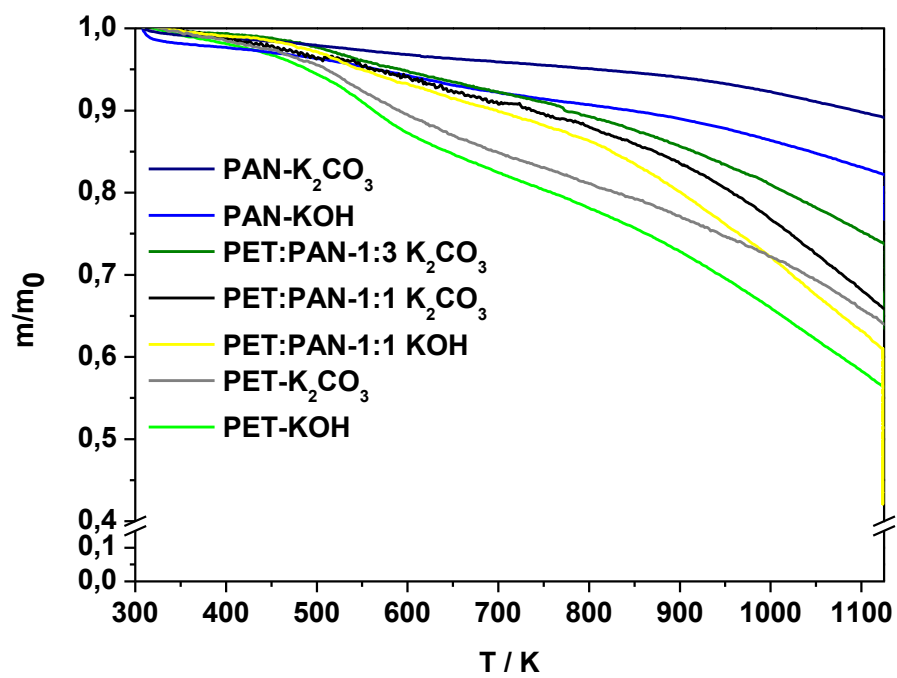


Figure 1 –

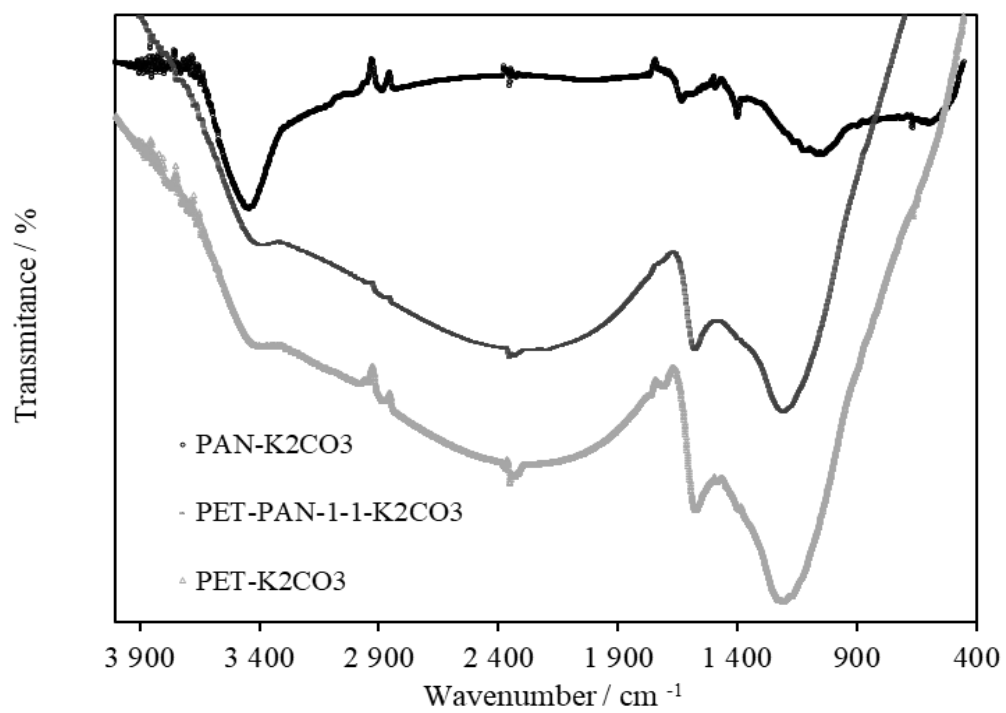


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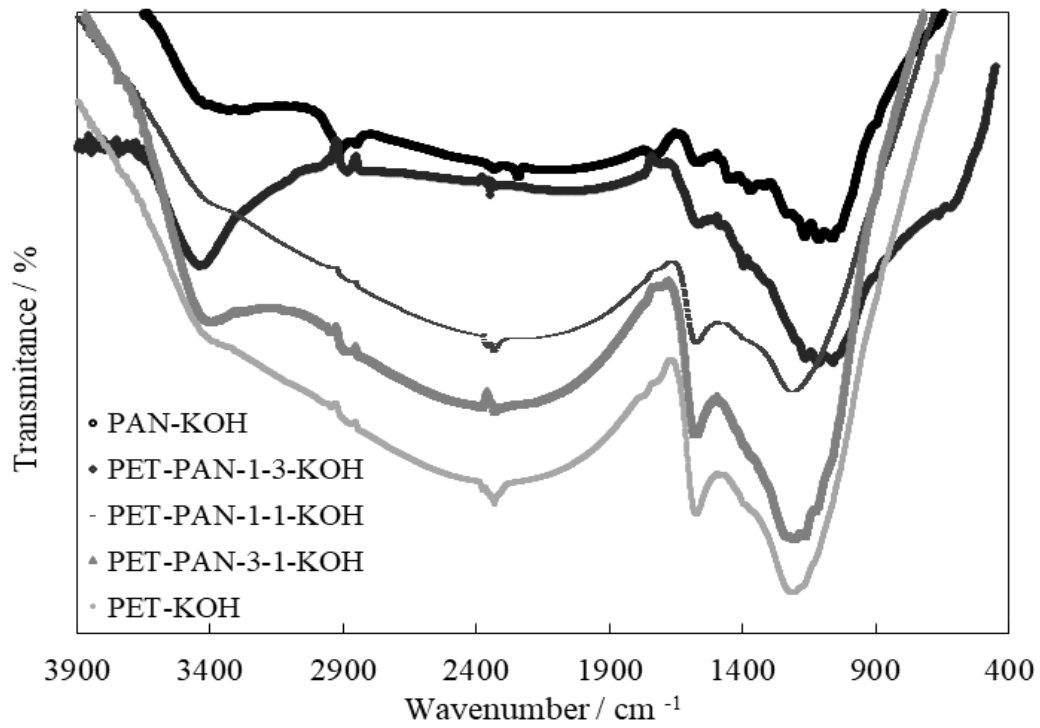


Figure 3 -

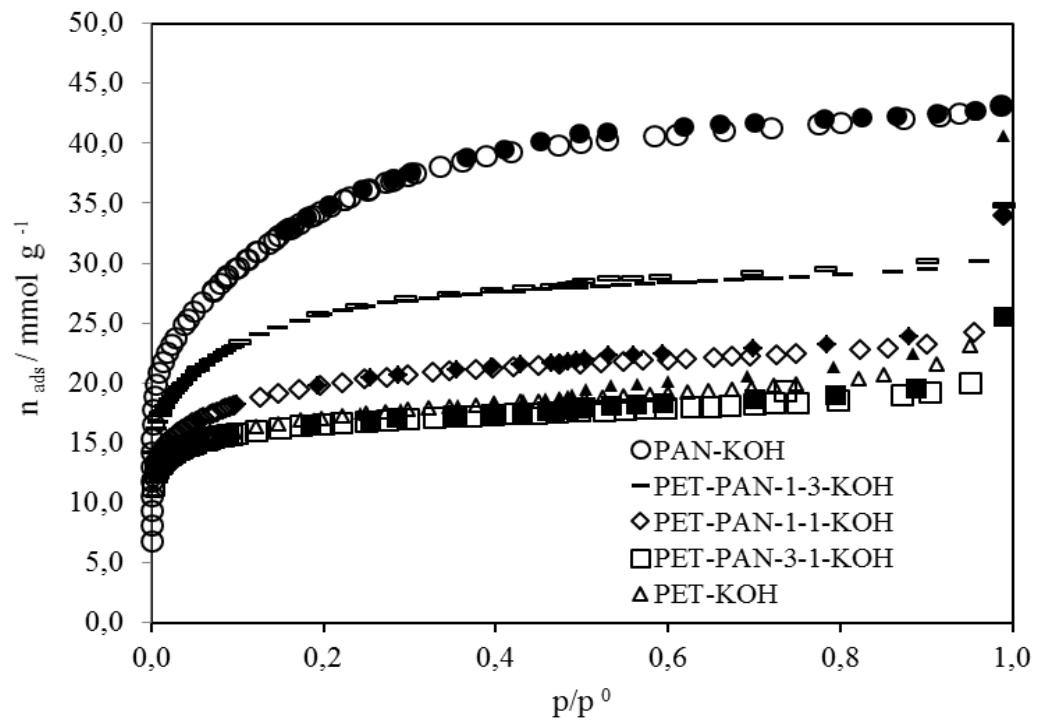


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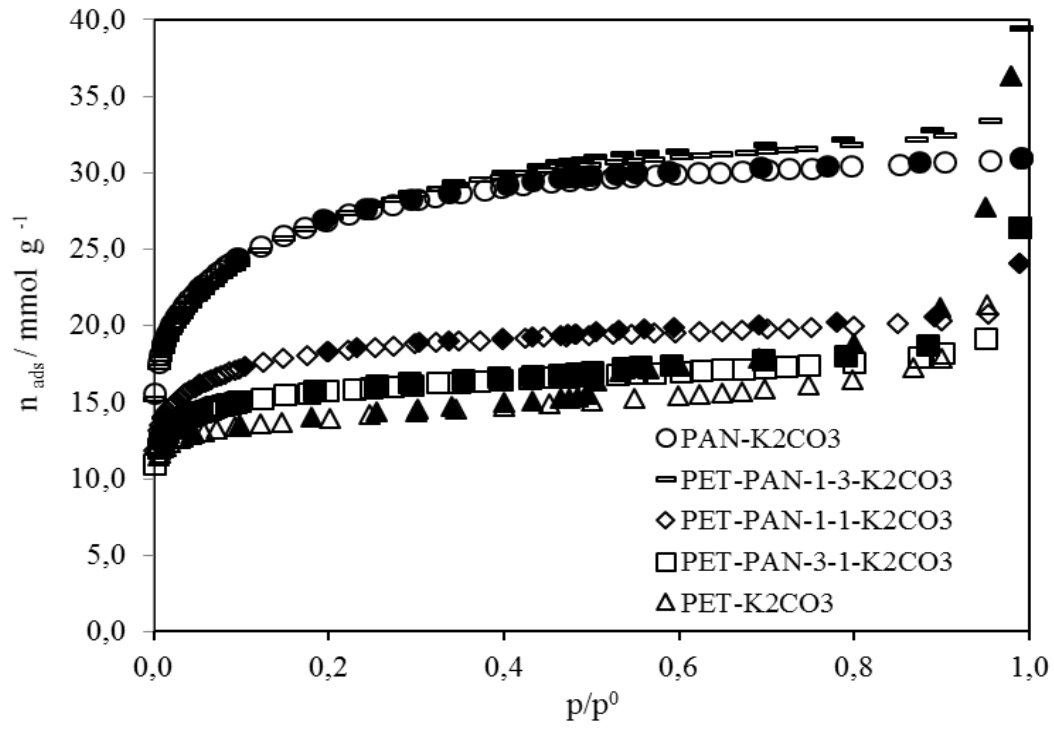


Figure 5 -

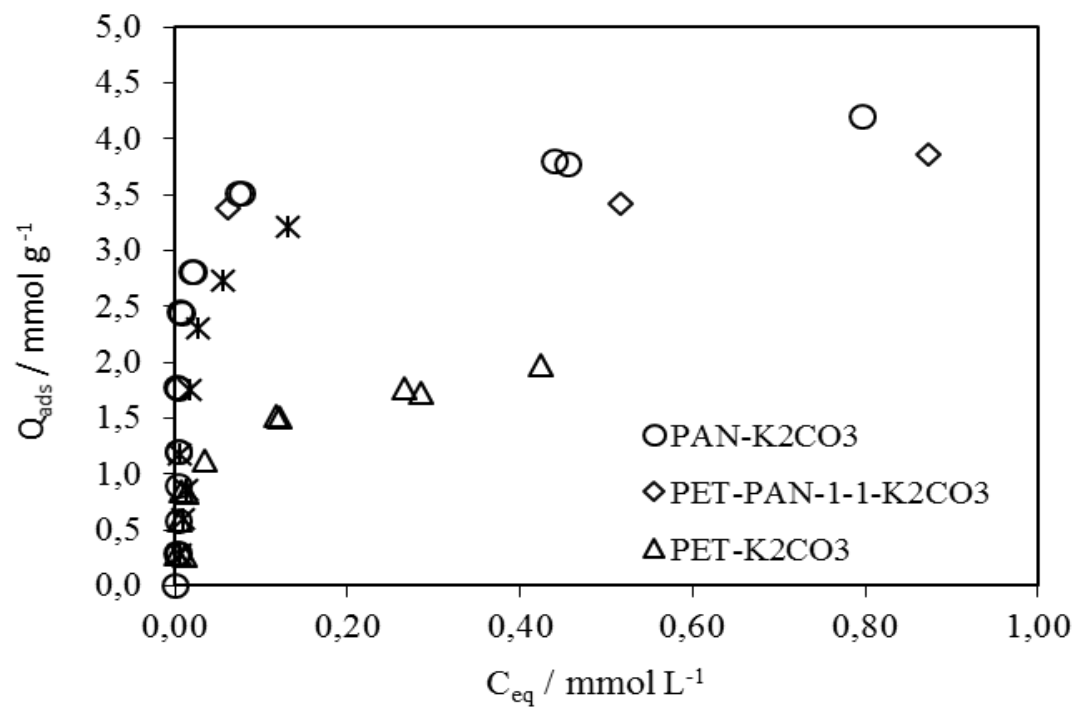


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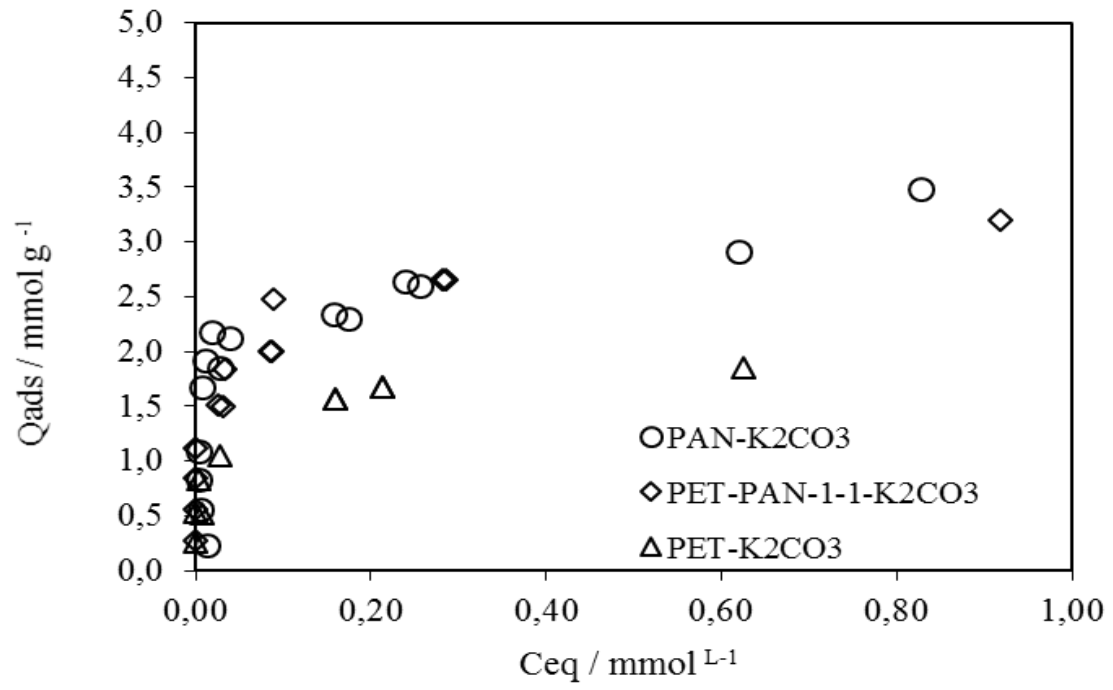


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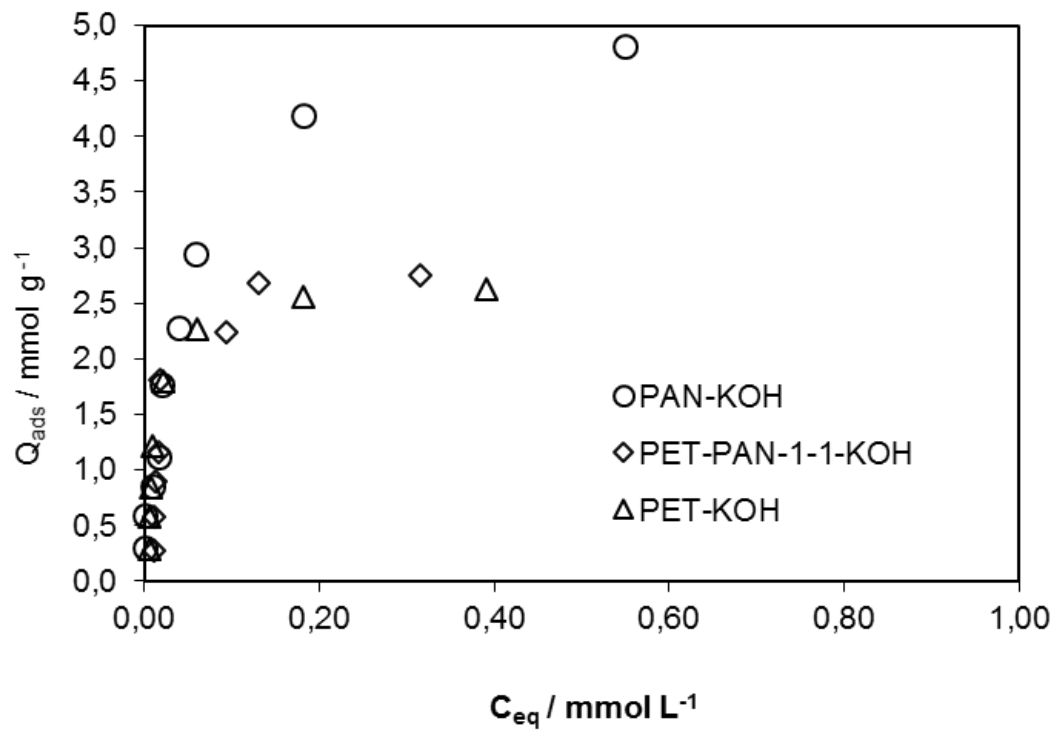


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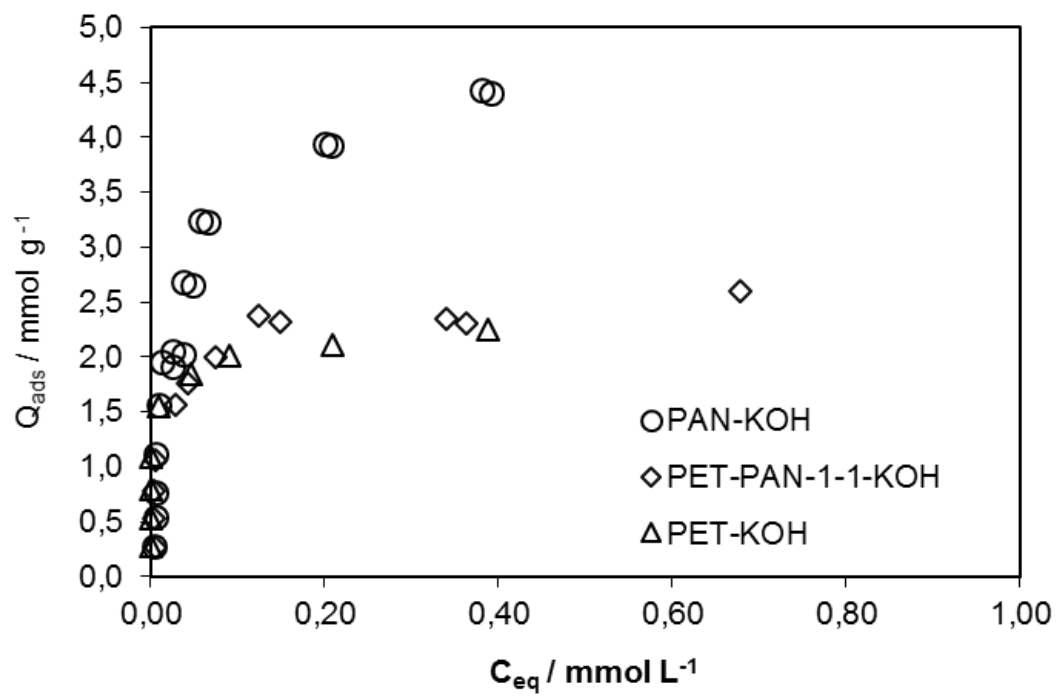


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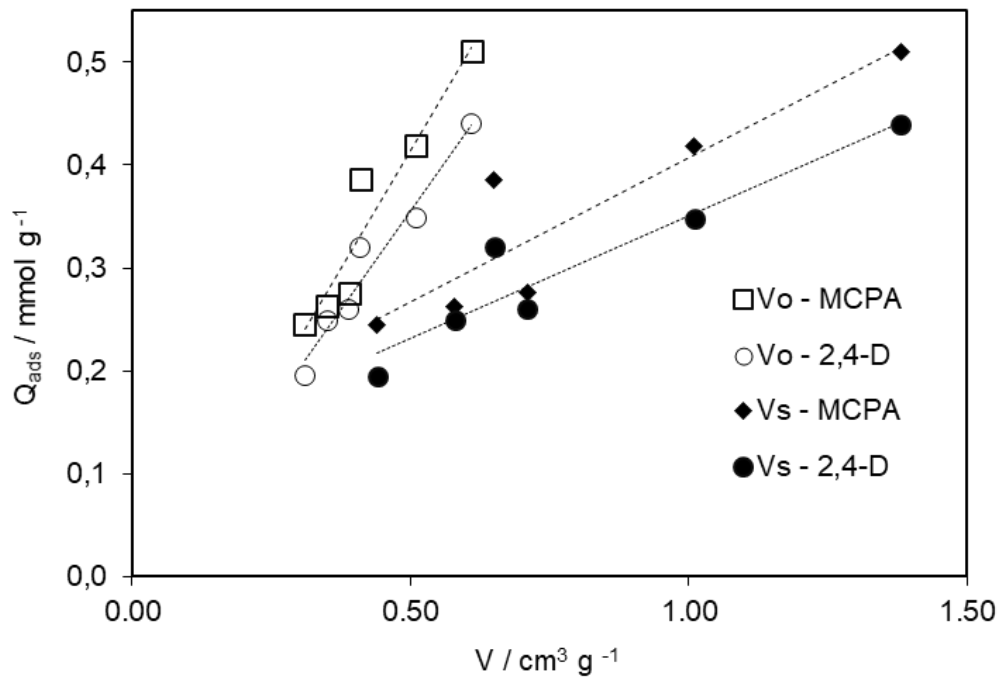


Figure 10 –

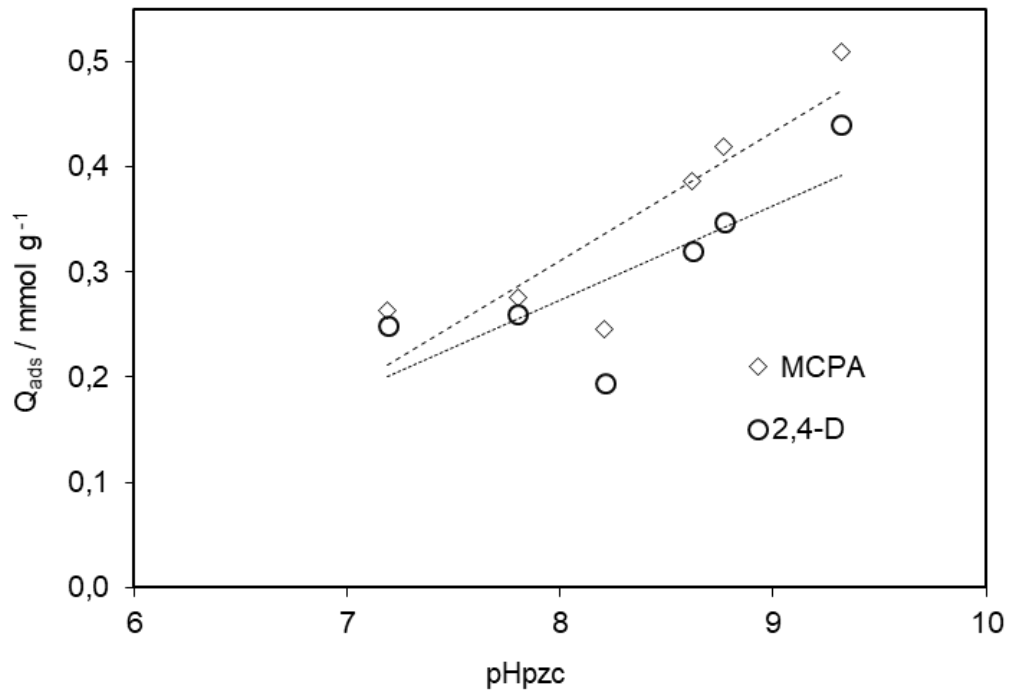


Figure 11-

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Table 1 -

Activated Carbon	Yield (%)	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	N/%	C/%	pH _{PZC}
PET-KOH	19.9	1439	140.8	0.58	0.35	1.17	0.46	69.2	7.19
PET-PAN-									
3-1-KOH	23.1	1417	76.3	0.58	0.36	1.01	0.92	69.8	7.80
PET-PAN-									
1-1-KOH	19.3	1651	85.8	0.71	0.39	1.20	1.04	62.8	---
PET-PAN-									
1-3-KOH	18.5	2139	68.2	0.94	0.48	1.27	1.25	75.1	8.63
PAN-KOH	17.9	2828	69.5	1.38	0.61	1.58	4.23	74.3	9.32

Table 2 -

Activated Carbon	Yield (%)	$A_{\text{BET}}/$ $\text{m}^2 \text{g}^{-1}$	$A_s/$ $\text{m}^2 \text{g}^{-1}$	$V_s/$ $\text{cm}^3 \text{g}^{-1}$	$V_0/$ $\text{cm}^3 \text{g}^{-1}$	$L_0/$ nm	N/ %	C/ %	pH_{PZC}
PET-									
K_2CO_3	21.6	1206	150	0.44	0.31	0.92	0.37	73.8	8.21
PET-PAN-									
3-1- K_2CO_3	22.5	1359	67	0.55	0.37	1.01	---		---
PET-PAN-									
1-1- K_2CO_3	24.5	1536	42.6	0.65	0.41	1.09	1.57	72.5	8.62
PET-PAN-									
1-3- K_2CO_3	21.9	2202	78.4	1.03	0.51	1.28	---	---	---
PAN-									
K_2CO_3	21.9	2217	32.4	1.01	0.51	1.21	2.16	83.1	8.77

Table 3 –

Activated Carbon	Yield (%)	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	N/%	C/%	pH _{PZC}
PET-PAN-3-1-240	25.1	557	24	0.22	0.14	0.84	---	---	---
PET-PAN-3-1-720	41.6	621	15	0.46	0.28	1.00	---	---	---
PET-PAN-3-1-1200	52.0	800	16	0.34	0.21	1.30	---	---	---
PET-PAN-1-1-240	22.6	587	13	0.25	0.15	0.86	7.8	78.6	10.5
PET-PAN-1-1-720	38.1	829	14	0.35	0.21	0.80	6.2	88.1	10.8
PET-PAN-1-1-1200	49.7	1117	13	0.50	0.28	0.97	---	---	---
PET-PAN-1-3-240	22.7	465	13	0.19	0.12	1.02	---	---	---
PET-PAN-1-3-720	49.0	854	19	0.35	0.22	1.01	---	---	---
PET-PAN-1-3-1200	59.1	1233	17	0.52	0.30	1.42	---	---	---

Table 4-

System	n_{max} /mmolg ⁻¹	n_{mL} /mmolg ⁻¹	K_L /dm ³ mmol ⁻¹	K_F /mmolg ⁻¹ (dm ³ mmol ⁻¹) ^{1/n_F}	n_F
PET-KOH	2.63	2.94	23.7	3.24	5.57
MCPA PET-PAN- 1:1-KOH	2.76	3.31	16.2	3.53	5.05
PAN-KOH	5.10	3.54	49.5	6.87	3.10
PET-KOH	2.49	2.46	42.3	2.45	9.56
2,4-D PET-PAN- 1:1-KOH	2.60	2.90	13.2	2.89	9.85
PAN-KOH	4.40	4.87	23.1	5.50	4.55

Table 5 –

System	n_{max} /mmolg ⁻¹	n_{mL} /mmolg ⁻¹	K_L /dm ³ mmol ⁻¹	K_F /mmolg ⁻¹ (dm ³ mmol ⁻¹) ^{1/n_F}	n_F
PET-K ₂ CO ₃	2.45	2.05	31.1	2.44	4.10
MCPA PET-PAN-1:1- K ₂ CO ₃	3.86	3.78	19.1	4.33	3.75
PAN- K ₂ CO ₃	4.19	4.17	85.6	4.72	6.66
PET- K ₂ CO ₃	1.95	1.99	28.9	2.12	4.66
2,4-D PET-PAN-1:1- K ₂ CO ₃	3.20	2.88	40.4	3.32	5.86
PAN- K ₂ CO ₃	3.48	2.91	27.7	3.33	5.74

Table 6 -

System		n_{\max}	n_{mL}	K_L	K_F	n_F
		/mmolg ⁻¹	/mmolg ⁻¹	/dm ³ mmol ⁻¹	/mmolg ⁻¹ (dm ³ mmol ⁻¹) ^{1/n_F}	
	PET-8300	1.7	1.67	78.8	1.83	7.5
MCPA	PAN-8960	1.2	1.18	11.9	1.13	3.7
	PET-PAN-81200	1.0	0.93	23.4	0.89	6.6

Pesticides abatement using high activated carbon produced from a mixture of synthetic polymers by chemical activation with KOH or K₂CO₃

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