| 1 | Carbonaceous adsorbents from single and mixed rubber and |
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| 2 | plastic wastes. Adsorption of methylene blue |
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12 ABSTRACT

From rubber of used tires (TR), plastic bottle(PET) and automobile industry EPDM/PP 13 rubber/plastic (VR) both separately and as 1:1 binary and 6:1:1 ternary mixtures, 14 carbonaceous adsorbents (CAs) were first prepared by heat treatment at 900 °C in N₂ or 15 at 850 °C in steam, then characterized by the adsorption of N₂ at -196 °C and mercury 16 17 porosimetry, and eventually tested as adsorbents of methylene blue (MB) in aqueous solution. Yield is markedly higher with TR and similar with PET and VR, ranging 18 19 between 40.1% and 11.1%. Using mixtures instead of the individual components in the 20 preparation of CAs, significant mass changes occur, this proving that the starting 21 materials interacted with each other during the preparation of CAs. In the case of PET 22 and VR, it causes a substantial mass loss. As far as porosity is concerned, the trend is to 23 an increase in macroporosity with VR, mesoporosity with TR and macro-, meso- and 24 microporosity with mixed PET. Adsorption data for MB fit better to a pseudo-secondorder kinetics than to a pseudo-first-order kinetics and to the Langmuir equation than to 25

the Freundlich equation. Adsorption is markedly faster and higher for CAs prepared from PET and VR containing mixtures. The simultaneous use of physically mixed various waste materials is a very simple method of preparing CAs with a controlled porous structure and adsorption behaviour.

Keywords: Rubber and plastic waste materials, steam activation, carbonaceous
adsorbents, characterization, methylene blue adsorption.

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36 **1. Introduction**

During the last decades, the consumption of polymers has increased steadily 37 38 worldwide because of the population increase together with the trend of people to progressively improve their living conditions [1]. Polymeric materials of great 39 40 commercial importance are rubbers and plastics. Rubber is largely used in the manufacture of vehicle tires (TR). From a plastic as polyethylene terephthalate (PET), 41 specifically, synthetic fibers clothing (>60%) and plastic bottles (\approx 30%) are mainly 42 diene 43 produced [2]. Rubber/plastic ethylene propylene monomer 44 (EPDM)/polypropylene (PP) blends (VR) have applications in household appliances, automobiles, buildings and constructions, and so on [3]. After end-of-life, TR, PET and 45 VR are discarded and this results in the generation of large amounts of waste materials 46 47 that, as rubbers and plastics are resistant against microbial attack [4,5], accumulate in environment and have a strong detrimental impact (e.g., plastics are the greatest thread 48 49 for oceans and seas) and harmful effects on human health. The disposal of such amounts of waste materials represents a major environmental issue worldwide, mostly because 50

for the reduction of polymeric wastes the development of environmentally acceptable, 51 52 that are further cost-effective, technologies is a difficult challenge due to complexities inherent in the reuse of polymers [6]. For this purpose, recycling was encouraged as the 53 54 best alternative a few years ago [7-10]. TR, PET and VR may be valorised by conversion into value-added carbonaceous adsorbents (CAs) [11-13]. In fact, the 55 56 development of CAs from scrap tires or PET has been studied before [14-21]. Here, using TR (rubber), PET (plastic) and VR (rubber/plastic) in systems of one, two and 57 three components, CAs are prepared by thermal methods and characterized texturally as 58 well as tested as adsorbents of methylene blue (MB) in aqueous solution. MB [7-59 60 (dimethylamino)phenothiazin-3-ylidene]-dimethylazanium chloride]), an organic cationic dye with chemical formula C₁₆H₁₈N₃SCl.3H₂O, was chosen as adsorptive 61 62 because coloured organic effluents are produced in a number of industries including 63 rubber and plastic. The discharge of dyes in the environment is a matter of growing concern for both toxicological and esthetical reasons [22]. Dyes can cause allergic 64 65 dermatitis and skin irritation [23]. They can also have acute/or chronic effects on aquatic organisms, depending on their concentration and length of exposure [24]. Of 66 MB is known its strong adsorption on solids [25], including carbons [26]. In fact, it is 67 68 used as a test in the estimation of the properties of activated carbons [27], such as 69 mesopores (20-30 Å) [28]. Also, MB often serves as a model compound for removing organic contaminants from aqueous solutions [25]. The overall objective of this study 70 was to investigate the setting up of experimental methods for the simultaneous disposal 71 72 and valorisation of rubber and plastic polymeric solid waste pollutants by preparation of porous materials with feasible applications in water purification treatments. 73

74 2. Materials and methods

75 2.1. Raw materials

76 As furnished kindly by Recipneu (Sines, Portugal), TR was made up of truck and car rubbers in the ratio of 5:95. As received, TR was already wire-freed, shredded, 77 78 cryogenically size-reduced and sized, the fraction of particle sizes between 1 and 3 mm being selected for subsequent studies. As a source of post consumed PET, bottles of 79 80 mineral water for human consumption were employed. VR was provided by Catelsa 81 Cáceres, S.A. Using scissors, PET and VR were progressively size-reduced until pieces 82 smaller than 5 mm were obtained. Data of the elemental analysis (C, H, N, S, Odiff.) and proximate analysis (ash content) determined for TR, PET and VR are given in Table 1. 83

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2.2. Carbonaceous adsorbents

85 2.2.1. Preparation

From each starting material separately and from mixtures of two and three 86 components at the mass ratio of 1:1 and 6:1:1, respectively, CAs were prepared by first 87 heating from ambient temperature to 900 °C in N2 or to 850 °C in steam and by then 88 soaking at maximum heat treatment temperature (MHTT) for 2 h in horizontal 89 cylindrical electrical furnaces. The heating rate in both temperature ranges and 90 atmospheres was 10 °C min⁻¹. For the steam activation experiments two furnaces placed 91 92 in series were used. One of them served as the steam generation system and the other 93 one as the activation system. The flow rate of liquid water (8 mLmin⁻¹) entering the vapour generation system was controlled with a peristaltic pump and steam was carried 94 by a N₂ stream (flow rate = 100 mLmin⁻¹) to the activation system. The carbonization 95 96 and activation conditions used in the preparation of the CAs are summarized in Table 2, which also lists yield values and sample codes. 97

98 2.2.2. Textural characterization

The textural characterization of the samples was carried out by N₂ adsorption at -99 196 °C and by mercury porosimetry. Routinely, the samples were first oven-dried at 120 100 101 °C overnight, allowed to cool down to room temperature in a CaCl₂ containing 102 desiccator, and weighed. Then, the isotherms of gas adsorption were determined in a Quantachrome apparatus (Autosorb-1). Approximately, 10 mg of sample was placed in 103 a glass holder and degassed at 250 °C for 12 h, prior to adsorption. The experiments of 104 105 mercury intrusion were performed in a Pore Master 60-Quantachrome porosimeter, 106 using ~ 0.3 g of sample. Textural data obtained from the N_2 isotherms or from the curves of mercury intrusion are given in Table 3. 107

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2.3. Adsorption of methylene blue

109 In the study of the adsorption process of MB (Panreac, reagent grade) experiments were carried out by the batch procedure, using a 10⁻³ mol L⁻¹ aqueous solution. First, the 110 UV-visible spectrum was recorded on a Shimadzu spectrophotometer (Model UV-1800) 111 112 and from it the wavelength corresponding to the absorbance maximum at 664 nm was 113 chosen. Second, it was checked that MB is stable in aqueous solution as a function of 114 time (i.e., after more than 10 days had elapsed no colour and absorbance changes was 115 observed in the MB solution) and also that Beer's law is obeyed well for concentrations between 10⁻⁶mol L⁻¹ and 5x10⁻⁵mol L⁻¹. After that, either ≈ 0.10 g or between ≈ 0.002 116 117 and 0.30 g of adsorbent and 25 mL of MB solution were added to a suit of 25 mL test tubes, which were mounted at once in a Selecta (Unitronic-OR-C) thermostatic shaker 118 bath with water at 25 °C and an agitation of 50 oscillations min⁻¹ and maintained under 119 these conditions for 5 min-12 d or for an equilibration time, which was prefixed after 120 previously carrying out kinetic experiments. Finally, the residual liquid was separated 121 by filtration and eventually analysed at 664 nm. The adsorption of MB was quantified 122 using the following mass balance equation: 123

$$124 q_e = (C_i - C_f)V/W (1)$$

where q_e stands for the amount of MB adsorbed per unit weight of adsorbent, C_i and C_f are the initial and final concentrations of MB, V is the solution volume (L) and W is the adsorbent weight.

128 **3. Results and discussion**

129 3.1. Preparation of CAs. Process yield

130 The pyrolysis of rubbers and plastics entails the formation of a solid residue from the base polymer and from additives such as fillers, vulcanizing agents and activators, if 131 used as compounding ingredients in their preparation. In connection with the chemical 132 composition of such a residue, it was reported previously that for TR it has a high 133 134 carbon content because of the important presence of carbon black in the rubber and also 135 the main part of sulphur and zinc incorporated to the rubber (cross-linking and vulcanizing agents) [30]. For PET, the residue was a black glossy carbon of the equal 136 137 size to the milled PET feed. The carbon has porous structure and was brittle but very 138 hard [31]. With regard to the EPDM/PP (Santoprene) blend it was also detected the presence of a carbonaceous residue, representing approximately 10% of the initial 139 weight of sample, after heating up to 550 °C in a dynamic TG run [32], in spite of the 140 141 fact that the thermal degradation of pure PP and EPDM separately at 550 or 700 °C did not result in any char residue [32, 33]. In general, the amount of resulting residue 142 143 depends on a number of factors such the number the starting material, reactor type, heating conditions and atmosphere. In Table 2 the yield values obtained in this study for 144 145 the process of preparation of the samples are presented. As a guide, yield is 40.1% for T900, 24.1% for TS, 22.7 wt% for M7, and 20.4 wt% for M2. Therefore, as expected, 146 147 yield is markedly higher when heating in steam because the mass loss in this

atmosphere occurred surely not only by pyrolysis as in N₂ but also by gasification 148 149 processes. Furthermore, it can be observed that yield is higher with TR than with PET and VR and rather similar with PET and VR and also thereby when a mixture with a 150 151 greater proportion of TR was used. The calculated average yield is 25.1% and $\approx 16.7\%$ for all samples heated either in N₂ or in steam. As to the $\approx 16.7\%$ yield it is also worth 152 153 noting that this same value is obtained for the three sets of samples separately, i.e., for 154 TS, PS and VS, M1-3 and M7-9. Of course, from these results it is apparent that the 155 physically mixed starting materials did not interact with each other while being heated in the preparation of the samples. Nevertheless, some other factors with influence on the 156 157 mass changes produced during the process of preparation of the sample may be at play here. Thus, yield is significantly lower for M3 than for PS and VS and also for M8 than 158 159 for PS. In fact, as compared to the yields assessed from those obtained for TS, PS and 160 VS by taking into account the mass used for each starting material, it is found that yield is substantially lower for M3 and M8, i.e., -16.7 and -12.2 %, respectively. Surprisingly, 161 162 these results are compatible with the occurrence of chemical interaction between starting materials. If so, in view of the melting point of 147.0 °C for PP, 144.7 °C for 163 EPDM/PP thermoplastic vulcanize [34] and 255 °C for PET; TR polymers cannot melt 164 165 because of cross-linking, it seems feasible that during heat treatment the EPDM/PP 166 blend (i.e., EPDM particles closely dispersed in a PP matrix) melted at lower temperature and impregnated in part at least small PET pieces, making it possible the 167 chemical interaction between components of initial mixtures. Furthermore, the 168 169 impregnation and chemical processes could be promoted in the presence of a high content of PET (i.e., 50%, M3; 75%, M8) and under heating conditions above 255 °C 170 171 with both VR and PET in molten state. As a final comment it should be pointed out that for samples other than M3 and M8 the mass either increased for M2 (11.0%), M7 172

(6.11%) and M9 (4.3%) and slightly decreased for M1 (-1.07%). This almost negligible
mass change indicates that TR and PET did not interact chemically when they were
mixed together and heated in steam atmosphere.

176 3.2. Textural characterization of CAs

177 3.2.1. By N₂ adsorption at -196 °C

The adsorption isotherms of N₂ measured for the CAs are shown in Figs.1 and 2. By 178 their shape, in general, they are composite isotherms of types I or II and IV isotherms of 179 180 the well-known BDDT classification system. These isotherm shapes have been associated in their turn with a micropore filling, monalayer-multilayer, and monolayer-181 182 multilayer-capillary condensation adsorption mechanism followed by adsorption 183 systems made up of $N_2(g)$ as adsorptive and microporous, non-porous, and mesoporous solids as adsorbents [35]. The derived values of S_{BET} and pore volumes, which are listed 184 in Table 3, show that SBET and Woaresmall for T900 and V900 (i.e., V900 was non-185 186 amenable to the N₂-adsorption analysis) and that they increase slightly for TS, PS, VS, M2 and M9, more significantly for M1 and M7, and mostly for M3 and M8. Since W₀ is 187 $0.14 \text{ cm}^3 \text{g}^{-1}$ for PS and 0.07 cm³ g⁻¹ for VS, on the one side, and 0.39 cm³ g⁻¹ for M3 and 188 0.34 cm³ g⁻¹ for M8, on the other side, it is evident that the use of PET and VR 189 containing mixtures enhanced the development of microporosity, as compared to singly 190 191 PET and VR. The effect on the porous texture of the samples must originate as a result 192 of the mass loss produced during their preparation because of the presumable chemical interaction between VR and PET. However, W₀ is noticeably small not only for M8 than 193 194 for M3, in spite of the fact that the PET content in the starting mixture was higher for 195 M8 (75%) than for M3 (50%), and therefore it appears that the beneficial effect on 196 porosity was somehow mitigated by the presence of TR together with PET and VR in such a mixture. Accordingly, TR would dilute the action of VR on PET in respect of the 197

development of microporosity in the samples. In connection with V_{mi} and V_{me} it should be noted that V_{mi} is significantly smaller than W_0 and V_{me} is usually low for the CAs. Nevertheless, V_{me} is higher for TS (0.23 cm³ g⁻¹), M1 (0.17 cm³ g⁻¹) and M7 (0.20 cm³ g⁻¹), which demonstrates the favourable influence of TR on mesoporosity of the samples.

202 3.2.2. By mercury porosimetry

203 Figs. 3 and 4 depict the graphical plots obtained from porosimetry data concerning 204 the regions of meso- and mcropores of the samples. From these figures it follows that most of the CAs prepared in the present study are essentially macroporous materials, in 205 particular V900, VS, M3 and M9 which are CAs with a predominant presence of pores 206 207 with a radius between approximately 5000 and 250 Å.T900, TS, M1, M2 and M7, 208 besides mainly macropores, also contain a significant fraction of wide mesopores with pore radii of \approx 250-150 Å. Not only for TS but also for P900, PS, M1,M3 and M8 the 209 210 mesopore-size distribution is even wider, embracing pores of varying radius in the range of 150-20 Å. According to the slope of the curves of mercury intrusion, TS is the CA 211 that possesses the most heterogeneous porosity in the regions of macro- and mesopores. 212 213 It is also worth noting that, of all samples prepared in the present study, M3 is the only 214 CA with a higher content of different size narrowest mesopores. In brief, from these 215 results it becomes apparent that the general trend is to an increased content of meso- and 216 macropores with TR, macropores with VR and thereby meso- and macropores with PET containing mixtures. Notice that meso-and macroporosity are very poorly developed in 217 218 P900 and PS. The values of pore volumes collected in Table 3 show first that the highest values of V_{me-p} are by far 0.35 cm³ g⁻¹ for T900, 0.32 cm³ g⁻¹ for TS and 0.31 219 $\text{cm}^3 \text{g}^{-1}$ for M7. Furthermore, $V_{\text{ma-p}}$ is 1.24 $\text{cm}^3 \text{g}^{-1}$ for VS and 1.26 $\text{cm}^3 \text{g}^{-1}$ for M9. For 220 T900 and TS V_{ma-p} is 0.37 and 0.73 cm³ g⁻¹, respectively; i.e., also high, though much 221 less than for V900 and VS. Secondly, V_{me-p} is 0.02 cm³ g⁻¹ for PS and 0.31 cm³ g⁻¹ for 222

M7. Likewise, V_{ma-p} is 0.02 cm³ g⁻¹ for PS and as high as 1.06 cm³g⁻¹ for M3. On the other hand, as expected in view of the V_{ma-p} values and estimate method, V_T is 1.32 cm³ g⁻¹ for VS, 1.69 cm³ g⁻¹ for M3 and 1.51 cm³ g⁻¹ for M9, and therefore also higher for CAs prepared using VR alone and mixed with other starting materials.

227 The values of V_{me-p} and V_{ma-p} in Table 3 provide further valuable insight into the influence on meso- and macroporosity of the starting material/mixture and the method 228 used in the preparation of the samples. Thus, the somewhat higher V_{me-p} for T900 than 229 230 for TS reveals that mesopores largely originated as a result of the pyrolysis of TR, 231 whereas the macropores should arise from the partial gasification of VR and TR in steam atmosphere. The chemical interaction between PET and VR should result in a 232 significant development of mesoporosity, as proved especially by the values of V_{me-p} 233 234 obtained for M3 and M8-9 as compared to those for PS and VS. As far as macroporosity is concerned, the only somewhat lower V_{ma-p} for M3 (1.06 cm³ g⁻¹) than for VS (1.24 235 $\text{cm}^3 \text{g}^{-1}$) together with the very small $V_{\text{ma-p}}$ for P900 (0.04 cm $^3\text{g}^{-1}$) and PS (0.02 cm $^3\text{g}^{-1}$) 236 argues for a favourable influence of the chemical interaction between VR and PET on 237 the creation of macropores. It is further consistent with the very high V_{ma-p} for M9 (1.26) 238 cm³ g⁻¹). By contrast, the values of V_{ma-p} for M1 (0.35 cm³ g⁻¹) and M2 (0.66 cm³ g⁻¹) 239 point out that TR and PET did not interacted with each other and that in the case of TR 240 241 and VR the interaction unfavourably influenced macroporosity. However, the opposite applies to VR as long as it was in a large excess with respect to TR and PET in the 242 243 starting mixture, as in the preparation of M9. Finally, it should be mentioned that for a larger number of samples V_{me-p} is higher than V_{me} , which is in line with the application 244 245 of controlled external pressure for mercury intrusion in pores of a porous solid dispersed in mercury. 246

247 3.2.3. Comparison of textural properties

Comparison of the apparent surface area and pore volumes for CAs with those 248 249 obtained previously for CAs prepared from TR and PET separately by steam activation 250 as well (see Table 4, [36-56]) (i.e., as far as to our knowledge, EPDM/PP has not been 251 used before in the preparation of CAs) reveals that they are frequently similar. Textural property discrepancies depending on the source as rule can be accounted for if one takes 252 into account that the preparation of CAs by steam activation is greatly influenced not 253 only by the starting material but also by the steam flow and heating conditions, as 254 255 illustrated by the S_{BET} values obtained previously for PET-derived CAs, which vary in the ranges of 705-1215 m² g⁻¹ with steam flows of 1.95-11.6 mL min⁻¹ and of 4-1235 m² 256 g^{-1} and 1163-1202 m² g⁻¹ by heat-treating at 600-900 °C and for 0.25-2 h, respectively 257 [56]. Furthermore, the development of porosity was also likely influenced by the 258 259 method of a single heat treatment in steam used in the preparation of CAs, because of 260 the simultaneous thermal degradation (pyrolysis) and activation processes of the starting 261 materials. Moreover, it should be pointed out that such a method has economic 262 advantages over the usual method of two successive carbonization and activation stages.

263 3.3. Adsorption process of MB

264 3.3.1. Adsorption kinetics

The data of concentration of the MB solution (C) as a function of time (t) obtained in the study of the adsorption kinetics of MB on the CAs are plotted in Figs. 5 and 6. At a simple glance, from these figures it follows that kinetics as a rule was faster with the CAs prepared from mixed components than from the single ones. The kinetic data were fitted to the pseudo-first order rate equation of Lagergren [57] and to the pseudo-second order rate equation of Ho and Mckay [58]. The former rearranged to a linear form is usually written as:

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$$log(q_e - q_t) = logq_e - \frac{K_1}{2.303}t$$
 (2)

with q_e and q_e being the adsorption capacities at equilibrium and at time t, respectively, and k_1 is the rate constant of first order adsorption. Therefore, the plot of log $(q_e - q_t)$

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versus t should be a straight line with slope log q_e and intercept $-k_1/2.303$.

By assuming that the adsorption capacity is proportional to the number of active sites occupied on the surface of the adsorbent, the Ho and Mckay equation [58] in the integrated rate law for the pseudo-second order reaction is:

279
$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$$
(3)

280 with
$$h = k_2 q_e^2$$
 (4)

where q_e and q_t are the amounts of MB adsorbed on the surface of the adsorbent at equilibrium and at any time t, respectively, and k_2 is the rate constant of second order adsorption and h is the initial adsorption rate. Here, the plot of t/qt against t should give a linear relationship, from which q_e and k_2 can be obtained.

The equilibration time (t_e, h) together with the values of q_e , $k_{1,2}$ and R^2 obtained 285 for the various CAs-BM adsorption systems by using equations (2) and (3) are given in 286 287 Table 5. First, it is worth noting that t_e varies in the wide range of 12-168 h. The t_e values indicate that the kinetics of the overall adsorption process is faster by the order 288 P900 = V900 > M3 >> M2 >> the rest of CAs. On the other, from the R² values it 289 290 becomes clear that the kinetic data fit better to the pseudo second order adsorption than to the pseudo first order adsorption. Furthermore, k_2 (g mol⁻¹ h⁻¹) varies by P900 > 291 292 V900 >> M3 > other samples. The so fast kinetics with P900 and V900, the adsorption to a large extent being almost an instantaneous process, can be accounted for by the 293 majority presence of large size pores in these CAs (see data in Table 5), which would 294

295 make easy the access of MB to surface adsorption sites. In the case of M3, which is a 296 CA possessing well developed porosity in the regions of not only meso- and macropores but also micropores (see Figs. 2 and 4 and Table 3), it is likely however that the 297 298 diffusion of such a large size adsorptive as the BM molecule was somehow hindered, this decelerating the adsorption process. In this connection it is worth mentioning that 299 the in dilute solution in water MB is present mostly as a monomer, the approximate 300 molecular dimensions being 12.5 to 16.0 Å long by 5.7 to 8.4 Å wide with a thickness 301 302 of about 5 Å [59], 13.82 Å in length and with 5.91 Å wide [60], and 17.0 x 7.6 x 3.3 Å[61]. Therefore, it can be foreseen that the fact that MB is a long tridimensional 303 304 molecule was the main factor with influence on its diffusion in micropores of the 305 adsorbent. The adsorption in micropores with M3 as the adsorbent is further proved by the high q_e (1.96 x 10⁻⁴ mol g⁻¹) obtained for this sample, as in micropore walls 306 307 concentrates most surface area of porous solids. It also applies to PS, M7 and M8, which as a rule are CAs with high W_0 . By contrast to P900, V900 and M3, k_2 is 308 309 markedly smaller for M1, T900, M2 and TS, all these samples having been prepared 310 from TS. In brief, it may be stated that by using the stating materials separately or mixed with each other in the preparation of CAs, the kinetics of the adsorption process 311 312 of MB in aqueous solution is faster and slower for the CAs prepared with PET and VS and with TR, respectively. 313

314 3.3.2. Adsorption isotherms

The isotherms measured for the adsorption of MB in aqueous solution on the CAs are plotted in Figs. 7 and 8. According to the system of classification of solution adsorption isotherms for organic solutes put forward by Giles et al. [62] more than fifty years ago, the aforesaid isotherms belong to the class L, which is the normal or "Langmuir" isotherm, usually indicative of molecules adsorbed flat on adsorbent

surface. A flat, rather than end-on, MB adsorption in micropores is compatible with the 320 big size of the MB, which is 12.5-17.0 Å long [59, 61], and therefore not too much 321 shorter than the greater microropore width of 20 Å. Accordingly, because of steric 322 323 hindrance, the MB could adopt a flat orientation on adsorbent surface. The occurrence of π - π dispersive interactions between aromatic rings of the MB molecule and adsorbent 324 surface, as reported in previous studies [60 and refs. therein], could also contribute to 325 326 the flat adsorption of the MB molecule. For that, as MB is a 17.0 x 7.6 x 3.3 Å three dimensional molecule [61], it would be necessary that MB suffered structural distortion, 327 328 perhaps involving the dimethylamino groups because of their supposedly distorted trigonal pyramidal geometrical shape. The reported projected area of the MB molecule 329 ranges between 130-135 Å [61]. On the other hand, the adsorption isotherms obtained 330 for the CAs-MB systems as a rule display a marked adsorption rise up to $C/C_0 \approx 0.1$ and 331 a long plateau above this C/C_0 . The former isotherm feature argues for a high affinity of 332 333 MB for the adsorbent. The latter feature means that a high energy barrier has to be overcome before additional adsorption can occur on new sites, after the surface has been 334 saturated to the first degree. Also, the solute has high affinity for the solvent, but low 335 336 affinity for the layer of solute molecules already adsorbed [62] Furthermore, the isotherms of T900 (Fig. 1) and M1 show a significant adsorption increase beyond the 337 plateau, at C/C₀ above about \geq 0.6, which was connected previously with the adsorption 338 339 on a fresh surface, i.e., the exposed parts of the layer already present, new surface or part of the original surface [62]. 340

341 The adsorption of MB under equilibrium conditions was analysed by the342 Langmuir isotherm that in the linear form is:

343
$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0}$$
 (5)

here q_e is the specific adsorption of MB, C_e is the equilibrium concentration, Q^0 is the monolayer adsorption capacity and b is the constant related to free energy or net enthalpy of adsorption (b $\propto e^{-\Delta H/RT}$). In Table 6 the values of Q^0 and b obtained from the slope and intercept of the plots of $C_e/q_e = f(C_e)$ are presented.

348 The Freundlich equation was also used:

$$349 logq_e = logK_F + \frac{1}{n}logC_e (6)$$

where K_f and n are the Freundlich constants which correspond to adsorption capacity 350 and adsorption intensity, respectively. Therefore, the plots of log qe against log Ce 351 352 should therefore be a straight line with slope $\log K_F$ and intercept 1/n. The resulting 353 values of K_F and 1/n for the CAs-MB adsorption systems under study are given in Table 354 6. The n value indicates the degree of nonlinearity between solution concentration and 355 adsorption, as follows: if n = 1, then adsorption is linear; if n < 1, then adsorption is a chemical process; if n > 1, then adsorption is a physical process. Since the values of n 356 357 obtained here, which are omitted for the sake of brevity, are in the range 0.02-10, it 358 indicates physical adsorption of MB on the CAs. It further represents good BM adsorption [63 and ref. therein]. 359

From the values of \mathbb{R}^2 listed in Table 6 it follows that the equilibrium experimental 360 data as a rule fit very well to the Langmuir equation (i.e., R² is higher than 0.990 for a 361 large number of adsorption systems) and considerably better to such an equation than to 362 the Freundlich equation. Furthermore, Q^0 (mol L⁻¹) varies in the range between 0.00 for 363 P900 and 0.92 10^{-3} for M8. Q⁰ is also as high as 0.85 x 10^{-3} mol L⁻¹ for M3. Therefore, 364 the higher Q⁰ values for these two CAs, which were prepared from PET and VS 365 containing mixtures, are consistent with the larger degree of microporosity development 366 in this couple of samples. For comparison purposes it is interesting to point out that Q^0 367

is = 0.72×10^{-3} for PS and 0.52×10^{-3} for VS and from these results it becomes also evident therefore that the use of mixed PET and VR, both together and also with TR, benefits the adsorption process of MB from the equilibrium standpoint. The favorable influence on adsorption was greater as the content of PET in the starting mixture increased, which was 75 % for M9, 50% for M3, 12.5 % M9 (Q⁰, 0.50 x 10⁻³) and 0.0% for M2 (Q⁰, 0.42 x 10⁻³).

374

4. Conclusions

375 From the above results, it may be concluded that the use of TR, PET and VR mixed with each other rather than separately in the preparation of CAs by heat treatment at 376 377 high temperature in N₂ or steam atmosphere entails the interaction between starting 378 materials, as evidenced not only from mass changes but also by textural effects and behaviour of CAs in the adsorption of MB in aqueous solution. The mass of sample 379 either increases or decreases depending on whether TR or VR is a main component of 380 the starting mixture. At most, it is +11.0 % for M2 and -16.7 % for M3. Regarding 381 porosity, the general trend is to an increase in macroporosity with VR, mesoporosity 382 with TR, and macro-, meso- and microporosity with mixed PET. For M3 (i.e., the CA 383 prepared from the 1:1 PET and VR mixture) S_{BET} is 675 m² g⁻¹ and the micro-, meso-, 384 macro- and total pore volumes are 0.39, 0.15, 1.06 and 1.60 cm³ g⁻¹, whereas for PS (i.e., 385 the CA prepared using PET only) S_{BET} is 248 m² g⁻¹ and the pore volumes are in turn 386 0.14, 0.02, 0.02 and 0.18 cm³ g⁻¹. M3 is the only CA with a higher content of different 387 388 size narrowest mesopores. Adsorption data obtained for MB fit better to a pseudosecond-order kinetics than to a pseudo-first-order kinetics and to the Langmuir equation 389 than to the Freundlich equation. Adsorption is markedly faster for CAs prepared from 390 391 PET and VR containing mixtures. The adsorption capacity was larger with the increase of the PET content in the starting mixture. The simultaneous use of physically mixed 392

various waste materials is a very simple method to prepare ACs with tailored properties
and behaviours, simply by controlling the composition of the starting heterogeneous
mixture.

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| 600 | |
| 601 | |
| 602 | |
| 603 | |

| Material | С | Н | N | S | O _{diff.} | Ashes |
|----------|------|-------|------|------|--------------------|-------|
| TR | 85.1 | 7.41 | 0.33 | 1.81 | 5.4 | 7.10 |
| PET | 62.9 | 4.27 | 0.00 | 0.00 | 32.8 | 0.00 |
| VR | 88.0 | 11.82 | 0.00 | 0.37 | 0.00 | 0.93 |
| | | | | | | |

605 Chemical analyses of TR, PET and VR (wt%).

| Starting | Detie | A | MHTT/ | Soaking | X ² = 1 = 1 / ==== + 0 / | Cala |
|------------------|-------|-----------------|-------|---------|--|------|
| material/mixture | Katio | Kauo Aunosphere | | time/h | Y leid/ wt% | Code |
| TR | | N_2 | 900 | 2 | 40.1 | T900 |
| PET | | N_2 | 900 | 2 | 17.1 | P900 |
| VR | | N_2 | 900 | 2 | 18.1 | V900 |
| TR | | $H_2O(v)$ | 850 | 2 | 24.1 | TS |
| PET | | $H_2O(v)$ | 850 | 2 | 13.7 | PS |
| VR | | $H_2O(v)$ | 850 | 2 | 12.2 | VS |
| TR/PET | 1:1 | $H_2O(v)$ | 850 | 2 | 18.7 | M1 |
| TR/VR | 1:1 | $H_2O(v)$ | 850 | 2 | 20.4 | M2 |
| PET/VR | 1:1 | $H_2O(v)$ | 850 | 2 | 11.1 | M3 |
| TR/PET/VR | 6:1:1 | $H_2O(v)$ | 850 | 2 | 22.7 | M7 |
| PET/TR/VR | 6:1:1 | $H_2O(v)$ | 850 | 2 | 13.2 | M8 |
| VR/TR/PET | 6:1:1 | $H_2O(v)$ | 850 | 2 | 14.5 | M9 |

610 Preparation of CAs. Yield and notations.

614 Textural data of CAs.

| Sample | S _{BET} ^a / | $W_0^a/$ | $V_{mi}{}^{a}/$ | V _{me} ^a / | V _{me-p} ^b / | V _{ma-p} ^b / | V _T ^{a,b} / |
|--------|---------------------------------|--------------------------------|--------------------------------|--------------------------------|----------------------------------|----------------------------------|---------------------------------|
| Sumple | $m^2 g^{-1}$ | $\mathrm{cm}^3\mathrm{g}^{-1}$ | $\mathrm{cm}^3\mathrm{g}^{-1}$ | $\mathrm{cm}^3\mathrm{g}^{-1}$ | cm ³ g ⁻¹ | $\mathrm{cm}^3\mathrm{g}^{-1}$ | $\mathrm{cm}^3\mathrm{g}^{-1}$ |
| T900 | 64 | 0.05 | 0.01 | 0.04 | 0.35 | 0.37 | 0.77 |
| P900 | 0.0 | 0.00 | 0.00 | 0.00 | 0.07 | 0.04 | 0.11 |
| V900 | 28 | 0.02 | 0.01 | 0.07 | 0.05 | 0.70 | 0.77 |
| TS | 278 | 0.19 | 0.13 | 0.23 | 0.32 | 0.73 | 1.24 |
| PS | 248 | 0.14 | 0.03 | 0.12 | 0.02 | 0.02 | 0.18 |
| VS | 100 | 0.07 | 0.08 | 0.04 | 0.01 | 1.24 | 1.32 |
| M1 | 353 | 0.22 | 0.17 | 0.17 | 0.18 | 0.35 | 0.75 |
| M2 | 153 | 0.11 | 0.07 | 0.13 | 0.19 | 0.66 | 0.96 |
| M3 | 675 | 0.39 | 0.33 | 0.13 | 0.15 | 1.06 | 1.60 |
| M7 | 358 | 0.23 | 0.17 | 0.20 | 0.31 | 0.81 | 1.35 |
| M8 | 572 | 0.34 | 0.28 | 0.16 | 0.18 | 0.41 | 0.93 |
| M9 | 264 | 0.17 | 0.12 | 0.12 | 0.08 | 1.26 | 1.51 |

615a The N2 adsorption isotherm; SBET, BET surface area ($p/p^0 = 0.05 - 0.30$, am = 16.2 Å2); W0 micropore616volume (Dubinin-Radushkevich equation [29]); Vmi, micropore volume (Vad at $p/p^0 = 0.10$, Vad = volume617adsorbed); Vme, mesopore volume (Vad at $p/p^0 = 0.95$ at $p/p^0 = 0.10$). W0, Vmi and Vme are expressed as618liquid volumes. b Mercury porosimetry: Vme-p, mesopore volume; Vma-p macroporore volume. VT = W0 +619Vme-p + Vma-p.

625 Preparation of activated carbon from tire rubber and PET wastes. Results of steam

| 626 | activation from the literature. |
|-----|---------------------------------|
| | |

| | | | | | Volume | Volume | |
|----------|-----------------------------|------------|----------------|--|-----------------|-----------------|------------|
| Starting | Charring | Activation | Yield/ | Yield/ $S_{BET/}$ wt% m ² g ⁻¹ | of | of | Ð |
| material | conditions | conditions | wt% | | micropores | mesopores | References |
| | (°C, h, atm.) | (°C, h) | | | $/cm^{3}g^{-1}$ | $/cm^{3}g^{-1}$ | |
| Tire | | 700-900, | | 12.00 | | | |
| rubber | | 3 | 9 | 1260 | | | [36] |
| | | 850-900, | | 400 4004 | 0.10.0.00 | | |
| | $600, 0.75, N_2$ | 1-3 | | 420-1031 | 0.13-0.28 | | [37] |
| | | 935, | 25 | 610 | | | |
| | 450, 90, N_2 | 0.5-11.5 | 35 | 640 | | | [38] |
| | | 900, | 04 74 | 054 050 | | | 5003 |
| | $600, 4, N_2$ | 1-3 | 84-74 254, 272 | | | [39] | |
| | | 900 | | 238-602 | 22% | 78% | [40] |
| | 500, 1, N ₂ | 850 | 68-24 | 386-755 | 0.12-0.26 | 0.21-1.09 | [41] |
| | 500 1 N | 850, | | 770 | 0.20 | 0.66 | [10] |
| | 500, 1, N ₂ | 0.5-1.5 | | 770 | 0.30 | 0.66 | [42] |
| | 200 0 75 N | 970, | 40.25 | 122 | | | [40] |
| | $800, 0.75, N_2$ | 2-2.5 | 40-35 | 432 | | | [43] |
| | 500, N ₂ | 850 | 35 | 985 | 0.37 | 0.79 | [44] |
| | 500, N ₂ | 850, 900 | | >500 | | | [45] |
| | 1 200 N. | 750-900, | 01 12 | 05 1217 | 0.02.0.47 | 0 10 1 25 | [46] |
| | 1,800,102 | 1-3 | 91-15 | 83-1317 | 0.03-0.47 | 0.19-1.25 | [40] |
| | | | | | | | |
| | | 1000, | 0.5 | 518 | | | [47] |
| | | 3 | 9.5 | 540 | | | [47] |
| | | | | | | | |
| DET | 700 or 750 No | 900, | 50 | 1190-1443 | 0 42-0 65 | | [48-51] |
| 1 12 1 | 700 01 730, 1N ₂ | 1.5 | 50 | 1170-1443 | 0.72-0.03 | | [+0-J1] |
| | 500, 2, N ₂ | 500 | 17.1 | 359 | | | [52] |

| 500 Na | 850, | 22 1700 | | 0.93 | 0.15 | [53] |
|-------------------|-----------|-----------|----------|-----------|------------|------|
| 500, 112 | 0.5-4 | | 1700 | 0.75 | 0.15 | [33] |
| 500 1 N. | 850, | 00 m | 204 1740 | 0.21.0.02 | 0.04 0.15 | [54] |
| 500, 1, 102 | 0.08-4 | 00-22 | 394-1740 | 0.21-0.95 | 0.04 -0.13 | [34] |
| 500 1 N. | 850, | | 1200 | 0.55 | 0.21 | [42] |
| 500, 1, 102 | 0.5, 1.5 | | 1200 | 0.55 | 0.21 | [42] |
| U.SO. 1.24 | 500-800, | ~ 15 | 1020 | 0.36 | | [55] |
| Π_2 504, 1-24 | ≈0.05-0.5 | ~ 13 | 1050 | 0.30 | | [33] |
| | 600-900, | ~17 0 | 4 1025 | 0 0 74 | 0.0.25 | [56] |
| | 1 | ~1/-8 | 4-1233 | 0-0.74 | 0-0.55 | [30] |
| | | | | | | |

| | | pseudo-f | odel | pseudo-second-ordermodel | | | |
|--------|-------------------|---|---------------------------|--------------------------|-------------------------------|---|----------------|
| Sample | t _e /h | $\begin{array}{c} q_e {\cdot} 10^4 / \\ mol \ g^{-1} {\cdot} \end{array}$ | $k_1 \cdot 10^3 / h^{-1}$ | \mathbb{R}^2 | $q_e \cdot 10^4 / mol g^{-1}$ | $k_2 \cdot 10^{-3}/$ g mol ⁻¹ h ⁻¹ | \mathbb{R}^2 |
| T900 | 120 | 0.91 | 13.59 | 0.968 | 1.15 | 0.66 | 0.960 |
| P900 | 12 | 0.08 | 19.11 | 0.767 | 0.19 | 23.77 | 0.999 |
| V900 | 12 | 0.13 | 19.81 | 0.746 | 0.28 | 13.63 | 0.998 |
| TS | 168 | 1.19 | 16.35 | 0.854 | 1.74 | 0.76 | 0.976 |
| PS | 168 | 1.25 | 19.81 | 0.900 | 2.00 | 1.13 | 0.995 |
| VS | 168 | 1.05 | 19.58 | 0.959 | 1.78 | 1.14 | 0.995 |
| M1 | 168 | 1.25 | 12.67 | 0.938 | 1.57 | 0.42 | 0.943 |
| M2 | 120 | 1.18 | 15.20 | 0.964 | 1.81 | 0.69 | 0.984 |
| M3 | 24 | 0.80 | 21.88 | 0.785 | 1.96 | 2.69 | 0.999 |
| M7 | 168 | 1.02 | 17.27 | 0.923 | 1.96 | 1.10 | 0.991 |
| M8 | 168 | 1.09 | 16.81 | 0.888 | 1.87 | 1.04 | 0.990 |
| M9 | 168 | 1.05 | 20.04 | 0.944 | 1.78 | 1.17 | 0.994 |

| | | Langmuir | | | Freundlich | |
|--------|---|---|----------------|-------|---|----------------|
| Sample | Qo·10 ³ / mol g ⁻¹ | b·10 ⁻³ / L mol ⁻¹ | R ² | 1/n | $K_{\rm F}{\cdot}10^3/$ / (mol g-1)/(mol L-1)^1/n | R ² |
| T900 | 0.22 | 33.66 | 0.981 | 1.11 | 939.29 | 0.907 |
| P900 | 0.00 | -0.88 | 0.897 | 50.67 | ∞ | 0.679 |
| V900 | 0.02 | 1.93 | 0.790 | 11.44 | ∞ | 0.741 |
| TS | - | 19.77 | 0.980 | 0.25 | 4.10 | 0.844 |
| PS | 0.72 | 16.00 | 0.994 | 0.35 | 8.08 | 0.804 |
| VS | 0.52 | 74.41 | 0.999 | 0.10 | 1.06 | 0.984 |
| M1 | 0.80 | 53.74 | 0.997 | 0.26 | 6.05 | 0.944 |
| M2 | 0.41 | 17.57 | 0.990 | 0.26 | 2.6 | 0.906 |
| M3 | 0.85 | 10.13 | 0.988 | 0.34 | 8.34 | 0.987 |
| M7 | 0.61 | 7.12 | 0.987 | 0.26 | 3.24 | 0.972 |
| M8 | 0.92 | 17.41 | 0.991 | 0.29 | 7.06 | 0.968 |
| M9 | 0.50 | 13.00 | 0.994 | 0.27 | 3.04 | 0.991 |
| | | | | | | |

Fig. 1



647 Fig.2



Fig. 3



Fig. 4



Fig. 5







Fig. 7



Fig. 8

