



## 33 1. Introduction

### 34 1.1 Environmental occurrence of pharmaceuticals

35 Consumption of pharmaceuticals has been increasing in the last few decades,  
36 existing more than 3 000 active substances commercially available and a continuous  
37 input of new molecules entering the market every year (aus der Beek et al., 2016;  
38 Calisto and Esteves, 2009), mainly due to the growth in the health-care sector  
39 investment, the increase of the world population, the advances in science and research,  
40 the high prevalence of chronic diseases and the rise of life expectancy (Akhtar et al.,  
41 2016; aus der Beek et al., 2016; Calisto et al., 2017).

42 The usual pathway of pharmaceuticals into the environment is their release into  
43 raw sewage, through excretion by humans and animals, followed by the often-  
44 inefficient treatment in sewage treatment plants (STPs) and consequent discharge into  
45 receiving waters. The efficiency of STPs in the elimination of these compounds is  
46 different for each pharmaceutical and greatly dependent on the type of treatment and  
47 operational conditions applied in these facilities, with removal rates varying from <10%  
48 to >90% (Kasprzyk-Hordern et al., 2009; Tran and Gin, 2017; Zhang et al., 2008). Due  
49 to the continuous input of pharmaceuticals into the aquatic environment together with  
50 their usual persistence, these compounds pose a long-term risk to the aquatic organisms  
51 (Akhtar et al., 2016; Silva et al., 2012). In order to avoid potential risks, the removal of  
52 pharmaceuticals at STPs before final release into receiving waters is utterly imperative.

53 The first reports explicitly referring the incomplete removal of pharmaceuticals  
54 in STPs were published in the 60s and 70s (Calisto and Esteves, 2009). However, it was  
55 only in the 90s that the ability of pharmaceuticals to interfere with the ecosystem was  
56 established (Silva et al., 2015). Since then, pharmaceuticals are considered as an

57 important group of emerging contaminants and an impressive number of published  
58 works have focused on their removal from wastewater, which constitutes a great  
59 challenge for the scientific community. Technologies for the removal of  
60 pharmaceuticals from water include physical processes (sorption, membrane filtration),  
61 biological processes (bacteria, enzymes, algae) or advanced oxidation processes (AOPs  
62 - photocatalysis, strong oxidizers, sonolysis) (Hokkanen et al., 2016; Silva et al., 2012).  
63 These technologies differ both in effectiveness and cost and each of them has its own  
64 advantages and limitations.

65

## 66 **1.2 Adsorption as a technology for the removal of pharmaceuticals from the** 67 **environment**

68 Adsorption has been a well-researched process for the removal of  
69 pharmaceuticals from waters (e.g. Akhtar et al., 2016; Cabrita et al., 2010; Mestre et al.,  
70 2007), being considered an efficient and versatile method due to the low initial  
71 investment, operational simplicity, non-selective nature and also for not resulting in the  
72 formation of hazardous products (Akhtar et al., 2016; Rafatullah et al., 2013).

73 Activated carbon (AC) is widely used as adsorbent for the removal of both organic and  
74 inorganic pollutants, and was already proven to be capable of eliminating selected  
75 pharmaceuticals (e.g. diclofenac, caffeine, bezafibrate, clofibrac acid, carbamazepine)  
76 (Coimbra et al., 2016; Sotelo et al., 2014; Sotelo et al., 2012; Ternes et al., 2002). This  
77 preference may be due to AC properties, which include: (i) high surface area ( $S_{BET}$ ;  
78 typically larger than  $400 \text{ m}^2 \text{ g}^{-1}$  (Álvarez-Torrellas et al., 2016)); (ii) easy availability in  
79 the market; (iii) unique combination between a highly developed porous network and  
80 the ability to react with heteroatoms creating a diversity of functionalities on the surface

81 and within the structural framework (Akhtar et al., 2016; Cabrita et al., 2010; Hokkanen  
82 et al., 2016; Mohan et al., 2014; Rafatullah et al., 2013; Silva et al., 2012); (iv) high  
83 removal efficiency with no harmful by-products' generation (Hokkanen et al., 2016;  
84 Nielsen et al., 2014). AC can be produced from a wide variety of raw materials (being  
85 coal the most commonly used) which should present characteristics such as high carbon  
86 content and low inorganic content together with low degradation by aging (Dias et al.,  
87 2007). For the production of ACs, two key activation methods are usually applied –  
88 physical and chemical activation. One of the physical activation distinctive features is  
89 avoiding the incorporation of additives/impurities coming from the activating agents,  
90 while chemical activation needs lower temperature and shorter activation time.  
91 Microporous, as well as ultramicroporous carbons, are usually generated by physical  
92 activation whereas carbons obtained by chemical activation generally have wider  
93 micropores and higher pore volumes (Suhas et al., 2016). Despite its prolific application  
94 in adsorption procedures, the main drawbacks of ACs produced from conventional  
95 precursors are their high production and regeneration costs, which limit their  
96 implementation on a large/industrial scale (Alsbaiee et al., 2016; Cabrita et al., 2010;  
97 Hokkanen et al., 2016; Mestre et al., 2009; Mestre et al., 2014; Mohan et al., 2014;  
98 Rafatullah et al., 2013). These facts have motivated, in recent years, the search for eco-  
99 friendly and low-cost materials including waste- and/or bio-based adsorbents. Research  
100 concerning the so-called alternative adsorbents for the removal of pharmaceuticals from  
101 water has been continuously increasing; still, it is scarce in comparison with that on the  
102 application of these adsorbents for the removal of metals and dyes.

103           Given the actual and growing number of studies on the adsorption of pharmaceuticals  
104 onto alternative adsorbents, this review aims to summarize information on this topic in a  
105 systematic way. Important parameters such as the adsorption capacity of each adsorbent, factors

106 affecting adsorption and adsorbent properties and the relation with the residues' valorization  
107 policy were analysed. Additionally, since this type of adsorbents is claimed to be cost-effective  
108 in comparison to traditional carbon adsorbents, it was also aimed to assess if the use of these  
109 adsorbents constitutes, in fact, a valid option for water treatment in what respects both cost- and  
110 adsorption-effectiveness. Then, the final goal is to highlight the research needs for this field of  
111 study.

112

## 113 **2. The valorization of residues as part of the Circular Economy concept**

114 Presently, there is an urgent need to implement sustainable waste management  
115 procedures in order to reduce waste and improve environmental health (Liguori and  
116 Faraco, 2016). Also, most wastes are still valuable resources with unexploited economic  
117 value. In this context, the transition from the Linear Economy (implying the production,  
118 utilization and elimination of residues) to the Circular Economy concept (that implies  
119 the materials' recycling and their return to the industry or market) has been gaining  
120 acceptance worldwide. The Circular Economy concept, which arose from the 3 R's Rule  
121 (Reduce, Reuse and Recycle), gives great emphasis to the zero-waste approach and the  
122 exploitation of renewable resources (Liguori and Faraco, 2016). Therefore, in what  
123 concerns the production of adsorbents, research has been conducted towards the  
124 utilization of precursors that are renewable, inexpensive and profusely available such as  
125 waste materials. The conversion of these materials into adsorbents can, therefore, be  
126 considered a "win-win" approach for both improving waste management and  
127 protecting the environment.

128

129

130

### 131 **3. Relation between adsorbents' performance and application costs**

132 Adsorption capacity is defined as the maximum amount of solute adsorbed onto  
133 an adsorbent under equilibrium conditions and is considered the key-point of each  
134 adsorbent material. It is influenced by factors like  $S_{\text{BET}}$  and the molecular and structural  
135 properties of the adsorbent which, in turn, depend on the precursor material (Akhtar et  
136 al., 2016; Cabrita et al., 2010; Xie et al., 2015). The adsorbate also plays an important  
137 role on the process, being the interaction between adsorbent and adsorbate likely  
138 dependent on the chemical and structural properties of the latter (Calisto et al., 2015;  
139 Inyang and Dickenson, 2015). According to Baccar et al. (2012), the characteristics of  
140 the adsorbate that influence the adsorption process are: (i) the molecular size  
141 (controlling the accessibility to the carbon pores); (ii) solubility in water (conditioned  
142 by the octanol/water partition coefficient,  $K_{\text{ow}}$ , and determinant for the hydrophobic  
143 interactions); (iii)  $pK_{\text{a}}$  (ruling the protonation state); and (iv) the nature of the  
144 substituents in benzene rings, when present. Still, adsorption capacity is also dependent  
145 on experimental conditions as the solution pH, adsorbate initial concentration, adsorbent  
146 dose, contact time, agitation speed, temperature, ionic strength, competition between  
147 compounds in the matrix, or the method to be used (batch or continuous mode) (Akhtar  
148 et al., 2016; Kyzas et al., 2015). Despite all these assumptions, no universal relationship  
149 has been established, so far, that allows to predict the performance of an adsorbent for a  
150 specific target adsorbate (e.g. pharmaceuticals, dyes, metals) (Qian et al., 2015).  
151 Consequently, the multiple factors taking part in the adsorption process must be  
152 assessed for each case.

153 Consideration should also be given to the process of scale-up for manufacturing,  
154 which will implies higher initial capital investment, but allows product costs to be more

155 realistically estimated and therefore will help to determine the economic feasibility of  
156 the adsorbent and its ultimate marketability (Kearns et al., 2014; Mestre et al., 2009; Ng  
157 et al., 2003). Even though adsorption capacity and economic feasibility are inter-related  
158 and dependent on each other, the adsorbent cost will depend on various other factors,  
159 such as the need to perform modification/activation, the availability of the raw material,  
160 or the reutilization and lifetime (Hokkanen et al., 2016; Inyang and Dickenson, 2015).

161         Using a waste as raw material is often empathised as a way to considerably  
162 decrease the production costs (in comparison with conventional precursors) and the  
163 resulting adsorbents are frequently claimed to be low-cost materials. However, a careful  
164 economic analysis is rarely presented. Stavropoulos and Zabaniotou (2009), Ng et al.  
165 (2003), Choy et al (2005), Lima et al. (2008) and Reza et al. (2014) studies are some  
166 important exceptions. Ng et al. (2003) have compared manufacturing costs of AC  
167 production from pecan shell, either by physical and chemical activation in order to  
168 estimate a fixed capital investment and an annual production cost for each process. The  
169 yield of activation was calculated to be 18% and  $S_{\text{BET}}$  was in the range 750-800 m<sup>2</sup> g<sup>-1</sup>.  
170 Authors considered that these values were within those observed for commercial ACs  
171 and found that higher product yield and  $S_{\text{BET}}$  resulted in a lower production cost,  
172 contradicting the idea that the best performance materials are always more expensive.  
173 Choy et al (2005) evaluated economic indices using KOH-chemically activated bamboo  
174 as precursor. The yield of carbonization was 22% and the prepared adsorbents presented  
175  $S_{\text{BET}}$  up to 800 m<sup>2</sup> g<sup>-1</sup>. The cash flow of the project was concluded to be sensitive to the  
176 chemical activation agent cost, the production capacity and the product selling price.  
177 Lima et al. (2008), who used broiler manure to manufacture AC through pyrolysis and  
178 activation (yield of 21.6%), concluded that the equipment for combined

179 pyrolysis/activation constituted the major contributor to the production cost. However,  
180 this cost was also dependent on the size of the manufacturing plant and the local  
181 environmental regulations. Additional savings can be provided by strategies as synthesis  
182 gas recovery and reuse as energy source. In the work by Stavropoulos and Zabaniotou  
183 (2009) numerous types of precursors were studied (used tires, wood, pet coke, carbon  
184 black, charcoal and lignite) and the final decision for the selection of a production  
185 scheme was based on economic criteria. Using physically activated carbons, the lower  
186 production cost was observed for pet coke, which presented a substantial margin from  
187 the selling price of commercially available ACs. Precursors with the highest production  
188 costs were used tires, wood and lignite wood. Also, some precursors improved their  
189 viability in the economic evaluation when  $S_{\text{BET}}$  was high enough to compensate lower  
190 product yields. As for the chemical activation, the costs were generally lower, mainly  
191 due to the higher production yield. Carbon black presented the lowest production cost  
192 while wood and used tires presented the highest, which was due to low product yields.  
193 The negative impact of a raw material with high management associated costs was also  
194 shown to be preferable to making use of a low-cost or free of charge waste material.

195       Even though the studies that perform an economic evaluation usually specify the  
196 yield of production and  $S_{\text{BET}}$ , it has to be highlighted that an exhaustive characterization  
197 of the adsorbents is never performed, which is an important gap found in literature, as  
198 well as the practical application of the adsorbents to better assess the cost-efficiency  
199 relation.

200

201

202



#### 203 4. Types of precursors and their application in the adsorption of pharmaceuticals

204 Research on the use of waste-based adsorbents for remediation of water  
205 contaminated with pharmaceuticals has been growing during the last twenty years.  
206 Tables 1 to 3 aim to summarize the literature related to this topic, presenting, for each  
207 study, the precursors and treatments for the production of adsorbents, the adsorbate(s)  
208 and experimental conditions. Also, Fig. 1 gives an overview on the percentage of  
209 studies dealing with a specific pharmaceutical, precursor and type of treatment, aiming a  
210 better visualization of the studies' distribution.

211 Generally, wastes used as adsorbent precursors in the context of  
212 pharmaceuticals' adsorption are of one of two types: agricultural or industrial.  
213 Therefore, this classification will be used in this section. As for the agricultural wastes,  
214 since these are easily and plentifully available, the production cost of the carbons  
215 prepared from these wastes is predictably low, constituting a potentially low-cost option  
216 in comparison with the commercially available adsorbents produced from sources that  
217 are not non-renewable (Ioannidou and Zabaniotou, 2007). Also, this type of residue is  
218 considered a good precursor for the production of adsorbents due to a good level of  
219 hardness and a low ash content (Dias et al., 2007). Adsorbents obtained from  
220 agricultural wastes are also reported to be much better in terms of  $S_{\text{BET}}$  ( $S_{\text{BET}}$  up to 2410  
221  $\text{m}^2 \text{g}^{-1}$ ) than those produced by other types of abundant wastes, as used tires ( $S_{\text{BET}}$  up to  
222  $1260 \text{m}^2 \text{g}^{-1}$ ) (Ioannidou and Zabaniotou, 2007). In what concerns municipal and  
223 industrial wastes (usually destined to incineration or landfilling), their accumulation is a  
224 result of modern society and industrial activities that have gradually created a pattern of  
225 massive production, consumption and disposal (Dias et al., 2007). Pulp and paper  
226 industry, for instance, is a well-developed and profitable industry in Europe, highly

227 contributing for economic growth. Nevertheless, it is also a very demanding activity in  
228 terms of energy and water, and also one of the most polluting industries in the world  
229 (Coimbra et al., 2015). As for the large water requirements, large volumes of  
230 wastewater are generated, which treatment unavoidably results in the generation of  
231 sludge. Worldwide, production of paper is estimated to be around 400 million tons  
232 being expected to reach up to 550 million tons by 2050. This increase may represent a  
233 growth in the pulp and paper mill sludge production of 48-86% (Faubert et al., 2016). It  
234 is then clear that this industry faces important challenges in what concerns the  
235 management of sludge, which constitutes an ideal candidate for the residues'  
236 valorization policy. Sludge generated at STPs (municipal wastes) has also the potential  
237 to be used as precursor in the production of adsorbents. Its treatment embodies an  
238 economical burden for STPs and hence its valorization as adsorbent may offer a cost-  
239 effective management option.

240         The production of adsorbents from wastes is mostly performed by the pyrolysis  
241 and chemical activation of precursors. Microwave is also used in an interesting  
242 percentage of studies, especially considering that it is a more recent approach for the  
243 treatment of precursors. For this reason, a sub-chapter dedicated to microwave will be  
244 presented for each type of precursor (agricultural or industrial). In what concerns the  
245 adsorbates, researchers have explored the adsorption patterns mainly of antibiotics and  
246 non-steroidal anti-inflammatory drugs (NSAIDs). Adsorption of other classes of  
247 pharmaceuticals (e.g. analgesics, anticonvulsants, antidepressants) was more rarely  
248 described (Fig. 1).

249

250

#### 251 **4.1 Agricultural and vegetable residues: Adsorption of antibiotics**

252           Antibiotics constitute one of the most studied classes of pharmaceuticals in  
253 terms of adsorption onto alternative adsorbents (Table 1). This may be due to the fact  
254 that these are considered very hazardous compounds whose presence in the environment  
255 may result in effects on non-target organisms, which include the concerning bacterial  
256 antibiotic resistance (Zheng et al., 2013). Within the class of antibiotics, studies about  
257 the adsorption of sulfonamides onto adsorbents produced from agricultural/vegetable  
258 wastes are easily found, most of them considering the effect of pH and metal ions on the  
259 adsorption patterns. This may be due to the facts that: (i) sulfonamides can be neutral,  
260 cationic or anionic, depending on pH, i.e. pH affects the speciation and thus, the  $\pi$ -  
261 electron donating aptitude, as well as hydrophobicity, of the adsorbate molecules; and  
262 (ii) sulfonamides contain several functional groups allowing a strong interaction  
263 between the adsorbate and metal ions present in the aqueous solution (Tan et al., 2015;  
264 Xie et al., 2014; Zheng et al., 2013). Very recently, Zhou et al. (2016) investigated the  
265 ability of spent mushroom substrate, without any thermal or chemical treatment, to  
266 remove sulfa-antibiotics (sulfamethyldiazine, sulfamethazine, sulfathiazole,  
267 sulfamethoxazole) from aqueous solution. Their findings indicated that the adsorption  
268 capacity of spent mushroom substrate decreased in the order: sulfathiazole >  
269 sulfamethoxazole > sulfamethyldiazine > sulfamethazine, which was related to the  
270 differences in the chemical structures and functional groups of the antibiotics. Authors  
271 evaluated the effect of adsorbent initial concentration and the effect of pH: adsorption  
272 capacity increased with the antibiotic initial concentration and decreased as pH  
273 increased from 3 to 11. The dependence on pH of the adsorption of sulfamethazine onto  
274 pyrolysed and activated tea waste was also observed by Rajapaksha et al. (2014);

275 however, contrarily to the previous case, the highest adsorption was verified under low  
276 pH conditions. Tzeng et al. (2016) tested the carbonization of cow manure for its use as  
277 an adsorbent for the removal of sulfamethazine from water. A high removal efficiency,  
278 up to 88% (for an adsorbent dose of 1 g L<sup>-1</sup>), was verified for the produced adsorbents.  
279 Once again, pH was considered to have an important role: at pH 3, sulfamethazine was  
280 considered to adsorb strongly through  $\pi$ - $\pi$  interactions, while at pH 10 the interaction  
281 between sulfamethazine and the adsorbent decreased due to electrostatic repulsion  
282 between anionic sulfamethazine and negatively charged adsorbent surface. Adsorption  
283 of sulfamethoxazole is also affected by pH, as stated by Zheng et al. (2013), Teixeira et  
284 al. (2012) or Jung et al. (2013). For adsorbents prepared from the perennial herb giant  
285 reed (by slow pyrolysis under nitrogen flow) (Zheng et al., 2013), adsorption increased  
286 with increasing pH from 1 to 4 and at pH > 6, as negatively charged sulfamethoxazole  
287 was dominant, electrostatic repulsion occurred between it and the negatively charged  
288 adsorbents. Same conclusions were stated by Teixeira et al. (2012) in the case of walnut  
289 shell adsorbents. The high dependence of antibiotics' adsorption on pH was also  
290 observed in the case of the competitive sorption of sulfamethazine, sulfamethoxazole,  
291 sulfathiazole and chloramphenicol with maximum sorption occurring around pH 4.0  
292 (Ahmed et al., 2017).

293         The adsorption of sulfamethoxazole onto agricultural/vegetable residues  
294 (bamboo, Brazilian pepper wood, sugarcane bagasse and hickory wood) was also  
295 studied with an unusual aim: to develop a new adsorbent that, when amended in soils  
296 irrigated with reclaimed water, would adsorb pharmaceutical contaminants present in  
297 water (protecting both soils and groundwater) (Yao et al., 2012). The adsorbents that  
298 presented higher performance, sugarcane bagasse and bamboo, were used in column

299 experiments: about 60% of sulfamethoxazole from reclaimed water was transported  
300 through soils not amended with the developed adsorbents, while only 2–14% was found  
301 in the leachate of the adsorbents-amended soils.

302         Considering tetracycline, the study of Martins et al. (2015) showed that NaOH-  
303 activated macadamia nut shells-adsorbents had potential for its adsorption in  
304 comparison with multi-walled carbon nanotubes (Zhang et al., 2011). Macadamia nut  
305 shells-adsorbents presented an  $S_{\text{BET}}$  of  $1524 \text{ m}^2 \text{ g}^{-1}$  and an adsorption capacity of  $455$   
306  $\text{mg g}^{-1}$  (in comparison with  $1839 \text{ m}^2 \text{ g}^{-1}$  and  $309 \text{ mg g}^{-1}$  for  $S_{\text{BET}}$  and adsorption capacity,  
307 respectively, for carbon nanotubes). Still considering tetracycline, Jing et al. (2014)  
308 performed a study where a rice husk-based adsorbent was modified with methanol.  
309 Aiming to evaluate this adsorbent potential for practical applicability, fixed-bed  
310 experiments were conducted: from an influent solution of  $5.0 \text{ mg L}^{-1}$  tetracycline, a  
311 concentration below  $0.1 \text{ mg L}^{-1}$  was measured in the effluent from the fixed-bed  
312 experiment. However, the use of methanol in the treatment of the precursor may be  
313 questionable from an environmental point of view. Álvarez-Torrellas et al. (2016) used  
314 both rice husk and peach stones as precursors for tetracycline adsorption high removal  
315 rates were observed, which were associated to the  $\pi$ - $\pi$  interactions and the formation of  
316 H-, -COOH and C=O bonds. The peach stones-based adsorbent was favourably  
317 compared with the commercial granular activated carbon (GAC) in terms of  $S_{\text{BET}}$  ( $1521$   
318  $\text{m}^2 \text{ g}^{-1}$  in comparison with  $1102 \text{ m}^2 \text{ g}^{-1}$  for GAC), showing its suitability as an alternative  
319 adsorbent. Torres-Pérez et al. (2012) converted the agricultural residues beet pulp and  
320 peanut hulls into adsorbents and also studied their adsorption capacity for tetracycline.  
321 Unlike the great majority of studies, the work by these authors presented adsorption  
322 results from real spring waters, where a slight decrease of the maximum adsorption

323 capacity was observed when comparing with the synthetic matrix. However, a more  
324 noticeable decrease (one third) occurred when using a commercial GAC.

325 For oxytetracycline (whose sorption mechanisms onto a maize straw adsorbent  
326 were concluded to be cation exchange and surface complexation through  $\pi$ - $\pi$   
327 interactions (Jia et al., 2013)) the pH-dependence was also verified, with sorption  
328 increasing until pH 5.5.

329 Yi et al. (2016) studied the potential of rice husk and wood chip adsorbents to  
330 adsorb levofloxacin from aqueous solution, concluding that wood chips presented  
331 greater potential for the adsorption of this antibiotic. Adsorption process was considered  
332 complex, consisting of both surface adsorption and pore diffusion. For ciprofloxacin  
333 and norfloxacin adsorption, date palm leaflets (El-Shafey et al., 2012) and *Trapa natans*  
334 husk (Xie et al., 2011) adsorbents were used. Both ciprofloxacin and norfloxacin  
335 adsorption was highly dependent on the solution pH and electrostatic interactions were  
336 proposed to be the main mechanism governing the adsorption (El-Shafey et al., 2012;  
337 Xie et al., 2011). Using lotus stalk-based adsorbents, the strong pH-dependent  
338 behaviour of norfloxacin and cephalexin was also observed by Liu W. et al. (2011) and  
339 Liu et al. (2011), respectively.

340 The effect of the presence of ions in solution on the adsorption capacity of the  
341 adsorbents is especially important since in real water systems, matrix effects and  
342 competition must be expected. Xie et al. (2014) determined that both sulfamethoxazole  
343 and sulfapyridine adsorption onto an adsorbent prepared from pine wood suffered a  
344 significant inhibition in the presence of  $\text{Cu}^{2+}$ . For sulfamethoxazole, the adsorption  
345 suppression was even greater than for sulfapyridine, which was thought to be consistent  
346 with the fact that sulfamethoxazole was more anionized under the tested pH inducing

347 stronger charge-assisted H-bonds than sulfapyridine. Contrarily, Han et al. (2013) found  
348 that a rice straw-based adsorbent was promising for the removal of sulfamethoxazole  
349 from a Cd<sup>2+</sup>-co-contaminated water since sulfamethoxazole adsorption capacity in the  
350 binary system (9 182.74 mg kg<sup>-1</sup>) was much higher than in the single system (1 827.82  
351 mg kg<sup>-1</sup>). In the study by Jia et al. (2013), sorption of oxytetracycline was found to be  
352 dependent on heavy metals presence being slightly inhibited by Pb<sup>2+</sup>, slightly improved  
353 by Zn<sup>2+</sup> and improved by Cu<sup>2+</sup>.

354         Despite the high scarcity of studies dealing with this specific topic, another  
355 factor known to affect the adsorbent performance when considering its application to  
356 the treatment of real waters is organic matter. Xie et al. (2014) studied the effects of  
357 dissolved humic acid on the adsorption of sulfamethoxazole and sulfapyridine on a rice  
358 straw-based adsorbent and observed that it was inhibited due to the competition for the  
359 adsorption sites between adsorbate and organic matter and/or to the blocking of pores  
360 by organic matter.

#### 361 *4.1.1 Adsorption of antibiotics onto microwave produced adsorbents*

362         More recently, microwave-assisted techniques have been gaining relevance as  
363 adsorbents' production method. In the conventional thermal processing methods  
364 (usually pyrolysis), the generated heat is transferred to the particles by convection,  
365 conduction and radiation mechanisms and the sample's surface is heated first in  
366 comparison with the internal zones, which results in a temperature gradient from the  
367 surface to the interior of each particle. Also, conventional heating methods usually  
368 imply using high temperatures (up to 900 °C) and consequently they have high energy  
369 requirements. Microwave radiation methods allow for a volumetric heating and may  
370 contribute to reduce the costs of AC preparation as for their relative low energy

371 consumption, short preparation time and high production yields (Hesas et al., 2013).  
372 Some works have already tested the application of this technique in the production of  
373 waste-based adsorbents for the adsorption of antibiotics (Ahmed and Theydan, 2012;  
374 Ahmed and Theydan, 2013a; Ahmed and Theydan, 2013b; Ahmed and Theydan, 2014;  
375 Huang et al., 2011; Reza et al., 2014; Saucier et al., 2015).

376 The adsorption of metronidazole onto an adsorbent prepared from *Siris* seed  
377 pods using microwave assisted activation with  $K_2CO_3$  (Ahmed and Theydan, 2013a)  
378 and with KOH (Ahmed and Theydan, 2013b) was already subject of attention.  
379 Adsorbents with excellent  $S_{BET}$  were obtained: 1676.16 and 1824.88  $m^2 g^{-1}$ , by  $K_2CO_3$   
380 and KOH activation, respectively. *Albizia lebbbeck* seed pods were also used for the  
381 production (by microwave-assisted KOH activation) of an adsorbent for the removal of  
382 ciprofloxacin and norfloxacin (Ahmed and Theydan, 2014). These authors (Ahmed and  
383 Theydan, 2014) shown also the potential of microwave-assisted activation for the  
384 production of an adsorbent with excellent surface properties ( $S_{BET}$ , micropores volume,  
385 and mesopores volume of 1824.88  $m^2 g^{-1}$ , 0.645  $cm^3 g^{-1}$  and 0.137  $cm^3 g^{-1}$ , respectively).  
386 The effect of pH was evaluated and it was observed that pH values of 9 and 5 were the  
387 best values to attain a maximum removal of ciprofloxacin and norfloxacin, respectively.  
388 This behaviour was also explained by Sun et al. (2012) and Liu et al. (2011) for  
389 ciprofloxacin (using *Cyperus alternifolius* as precursor) and norfloxacin (lotus stalk-  
390 based adsorbents), respectively. An *Albizia lebbbeck* seed pods adsorbent produced  
391 through both KOH and  $K_2CO_3$  microwave-assisted activation was also proven to be a  
392 good choice to adsorb cephalosporin (Ahmed and Theydan, 2012), with adsorption  
393 capacities in the range 118-137  $mg g^{-1}$ .



394 Lotus stalk-based carbon adsorbents were also produced by microwave process  
395 and used on the adsorption of oxytetracycline (Huang et al., 2011) and its performance  
396 was compared to lotus stalk-based carbon adsorbents produced by conventional heating  
397 methods (carbonization at 450 °C for 1 h): microwave allowed for the production of an  
398 adsorbent with a higher  $S_{\text{BET}}$  (1434 m<sup>2</sup> g<sup>-1</sup> in comparison with 1220 m<sup>2</sup> g<sup>-1</sup>), higher  
399 percentage of mesopores, smaller acidic oxygen functionalities, a more ordered stacking  
400 of layers and a higher maximum adsorption capacity (565 mg g<sup>-1</sup> in comparison with  
401 538 mg g<sup>-1</sup>).

402

#### 403 **4.2 Agricultural and vegetable residues: Adsorption of non-steroidal anti-** 404 **inflammatory drugs (NSAIDs)**

405 NSAIDs are amongst the most prescribed pharmaceuticals worldwide and once  
406 in the environment, are known to induce toxic effects on invertebrates and algae (Baccar  
407 et al., 2012). Table 2 presents the studies concerning the adsorption of NSAIDs onto  
408 adsorbents produced from agricultural/vegetable residues. Jung et al. (2015) considered  
409 the conformational and chemical properties of both adsorbate and adsorbent and  
410 evaluated the interaction energies between NSAIDs (diclofenac, naproxen, and  
411 ibuprofen) and an adsorbent produced from loblolly pine chip. Molecular modelling  
412 studies aimed to characterize not only the strength of adsorption but also the  
413 contribution of the adsorbents' surface functional groups to the adsorption capacity.  
414 Two types of adsorbents were prepared (under pure N<sub>2</sub> (N-bio-adsorbent) and under 7%  
415 O<sub>2</sub> + 93% N<sub>2</sub> (O-bio-adsorbent)). Specific hydrophobic interactions were considered to  
416 be dominant in the NSAIDs adsorption. Adsorbents showed differences in the  
417 adsorption capacities (between 290 and 372 mg g<sup>-1</sup>, for N-adsorbent and between 214

418 and 286 mg g<sup>-1</sup>, for O-adsorbent) attributed to the carbonaceous structure formed  
419 through the pyrolytic treatment. Another added-value of this study is that authors  
420 addressed multi-component adsorption systems (diclofenac/naproxen,  
421 naproxen/ibuprofen, and ibuprofen/diclofenac), which is a rarely assessed topic in  
422 literature. Comparatively to single-experiments, diclofenac maximum adsorption  
423 capacity was 18-25% and 27-35% in presence of ibuprofen and naproxen, respectively;  
424 adsorption capacity of ibuprofen decreased in presence of diclofenac (58-62%), and  
425 adsorption capacity of naproxen decreased 27-35 and 27-38%, in presence of ibuprofen  
426 and diclofenac, respectively. In the multiple-component system, adsorption was similar  
427 but slightly lower than that of the binary system for both diclofenac and naproxen, while  
428 ibuprofen suffered a marked decrease in adsorption, which was related to the adsorption  
429 sites occupation by naproxen and diclofenac due to their lower molecular size.

430         Some observations of the adsorption patterns of diclofenac, naproxen, ibuprofen,  
431 and ketoprofen onto an adsorbent prepared from olive wastes were linked to  $pK_a$ ,  $K_{ow}$   
432 and to the structural properties of the pharmaceuticals' molecules (Baccar et al., 2012).  
433 For instance, diclofenac adsorbed better than naproxen and, since their  $pK_a$  are similar,  
434 that was correlated to their different hydrophobicities; ibuprofen performed poorly at  
435 pH 4.1 (contrarily to what would be expected since lowest electrostatic repulsive  
436 interaction should happen between its deprotonated form at this pH value and the  
437 negatively charged adsorbent) because of its chemical structure, which may aggregate  
438 by hydrophobic interactions, making it difficult to access the adsorbent; ketoprofen  
439 presented a higher affinity to the adsorbent than the other compounds possibly due to  
440 ketone and carboxylate groups.

441 Jung et al. (2013) used the loblolly pine wood precursor to produce the N-bio-  
442 and O-bio- adsorbents, comparing the adsorption of diclofenac and ibuprofen with that  
443 of a commercial powdered AC (PAC). Both produced adsorbents presented a higher  
444  $S_{\text{BET}}$  and a far lower ash content than the PAC used for comparison. Adsorption of  
445 diclofenac and ibuprofen was evaluated under competition with sulfamethoxazole,  
446 carbamazepine,  $17\alpha$ -ethinylestradiol, bisphenol A and atrazine, and occurred preferably  
447 onto the N-bioadsorbent, followed by the PAC and the O-bioadsorbent. Produced  
448 adsorbents performed favourably also in presence of organic matter, with diclofenac and  
449 ibuprofen adsorption suffering only a slight decrease, contrarily to the common  
450 assumption that the presence of organic matter might decrease the adsorption by  
451 competing for adsorption available sites and/or by blocking the adsorbent pores  
452 (Homem and Santos, 2011; Jung et al., 2013). Still, sisal-based activated carbons were  
453 proven to be effective in the adsorption of ibuprofen, presenting an uptake that  
454 compared favourably with one commercial sample (Mestre et al., 2011). Meanwhile, no  
455 treated Isabel grape bagasse (very low  $S_{\text{BET}}$  ( $2 \text{ m}^2 \text{ g}^{-1}$ )) did not perform well in the  
456 adsorption of diclofenac (and showed very low removal percentages (Antunes et al.,  
457 2012). Low  $S_{\text{BET}}$  (not higher than  $84 \text{ m}^2 \text{ g}^{-1}$ ) was also verified for an olive stones-based  
458 adsorbent that was used for the uptake of diclofenac (Larous and Meniai, 2016).  
459 Authors also concluded that pH 2 was the optimum value for adsorption, which is quite  
460 unrealistic considering the applicability of the adsorbent in a real wastewater system.  
461 *Terminalia catappa* (a large tropical tree) fruit shells were also used as AC precursor  
462 (using sulfuric acid as activating agent) for the adsorption of diclofenac (Sathishkumar  
463 et al., 2015), presenting a higher  $S_{\text{BET}}$  ( $514 \text{ m}^2 \text{ g}^{-1}$ ) in comparison with the previously  
464 addressed studies, but not high enough to favourably compare to adsorbents like carbon

465 black ( $1443 \text{ m}^2 \text{ g}^{-1}$ ) or commercial AC ( $950 \text{ m}^2 \text{ g}^{-1}$ ). The adsorption efficiency was  
466 negatively correlated with temperature, decreasing with increasing temperature in the  
467 range 20-50 °C, and positively correlated with the adsorbent dose, increasing with  
468 increasing dose of adsorbent in the range 25 and 100  $\text{mg L}^{-1}$  (for concentrations of  
469 adsorbate from 20 to 100  $\text{mg L}^{-1}$ ).

470 Most of the published studies on the adsorption of NSAIDs were carried out in a  
471 discontinuous mode under agitation. However, Álvarez-Torrellas et al. (2016) studied  
472 the behaviour of adsorbents produced from peach stones and rice husk in fixed-bed  
473 under dynamic operation and used a commercial AC for comparison purposes. Authors  
474 found a great influence of the textural characteristics of the adsorbents on the slope of  
475 the breakthrough curves and on the values of breakthrough and saturation times: the  
476 flattest profile and tailing was obtained for the microporous commercial AC (which was  
477 related to a non-ideal transport within the pores); the mesoporous adsorbent produced  
478 from peach stones presented the steepest breakthrough curve and total column  
479 saturation; and the meso-macroporous adsorbent produced from rice husk presented the  
480 sharpest breakthrough curve and shortest exhaustion and breakthrough times. In terms  
481 of the adsorbed compounds (tetracycline and ibuprofen), flatter breakthrough curves  
482 were obtained for tetracycline, which was attributed to the higher length of the  
483 tetracycline molecule compared to ibuprofen.

#### 484 *4.2.1 Adsorption of NSAIDs onto microwave produced adsorbents*

485 Reza et al. (2014) studied the adsorption of ibuprofen using adsorbents produced  
486 from bamboo wastes by microwave-assisted activation. Maximum adsorption was  
487 reached at pH 2-5, which can be related with the adsorbent surface functional groups, as  
488 well as the ionic state of ibuprofen in this pH range. Authors also compared their results

489 on the adsorption of ibuprofen with those obtained for other adsorbents, namely a  
490 commercial AC, a metal organic framework and other alternative adsorbents reported in  
491 literature. In general, the bamboo-derived material compared favourably with those  
492 adsorbents and was considered to be an effective solution for the removal of ibuprofen  
493 from the aqueous phase. An adsorbent produced from cocoa shell via microwaves was  
494 used for the adsorption of diclofenac and nimesulide (Saucier et al., 2015). Simulated  
495 hospital effluents (containing diclofenac, nimesulide, amoxicillin, acetylsalicylic acid,  
496 saccharose and glucose, urea, and various inorganic components usually found in  
497 wastewater; pH 8) were used to evaluate the performance of the referred adsorbent,  
498 which was proven to be capable of an efficient removal of both diclofenac and  
499 nimesulide despite the complexity of the matrix (Saucier et al., 2015).

500

#### 501 **4.3 Agricultural and vegetable residues: Adsorption of other pharmaceuticals**

502 Table 2 presents the studies concerning the adsorption of other classes of  
503 pharmaceuticals onto adsorbents produced from agricultural/vegetable residues.  
504 Villaescusa et al. (2011) studied the adsorption of acetaminophen by three vegetable  
505 wastes (grape stalk, yohimbe bark and cork bark) with no thermal treatment. Grape  
506 stalks were the most efficient in the removal of acetaminophen, although sorption  
507 capacity was modest. N-bioadsorbent and O-bioadsorbent produced from loblolly pine  
508 wood already referred (Jung et al., 2013; see section 4.1.2) were also tested for the  
509 adsorption of  $17\alpha$ -ethinylestradiol and carbamazepine. Since these compounds possess  
510 a relatively high  $pK_a$ , their adsorption capacity varied only slightly with pH. This minor  
511 variation allows carbamazepine and  $17\alpha$ -ethinylestradiol to show strong hydrophobic  
512 interactions throughout a wide range of pH values. The low dependence of adsorption

513 capacity on pH for carbamazepine was also observed by Liu et al. (2013): authors  
514 removed carbamazepine and clofibric acid using a rice straw-based adsorbent and found  
515 that, for carbamazepine, the removal efficiency was just dependent on the adsorbent  
516 dosage while for clofibric acid, pH was the most important factor for adsorption. 17 $\alpha$ -  
517 ethinylestradiol was also successfully adsorbed by adsorbents produced from poultry  
518 and animal manure (Sun et al., 2011). Even in multi-component systems, this estrogen  
519 was efficiently removed and capable of replacing the adsorbed diclofenac when beneath  
520 neutral and basic conditions (Jung et al., 2013).

521 Dorzolamide and pramipexole removal from water was studied using and  
522 adsorbent produced from potato peels (Kyzas and Deliyanni, 2015). Authors determined  
523 that strong  $\pi$ - $\pi$  electron coupling and/or stacking between both pollutants' molecules  
524 and aromatic rings of the carbon were the prevalent adsorption mechanisms. Maximum  
525 removal occurred at pH 2 and 65 °C. The effect of pH was also evaluated for desorption  
526 (regeneration of the adsorbent) and it was found that, contrarily to adsorption, basic pH  
527 favoured desorption (optimum pH being pH 10) because the bonds between  
528 pharmaceuticals' molecules and the carbon surface become weaker.

529 Ferreira et al. (2015) prepared adsorbents using several agricultural wastes,  
530 namely *Eucalyptus* bark, peanut shells, walnut shells, peach stones, grape seeds and  
531 olive waste, as raw materials for the adsorption of MS-222, a fish anaesthetic widely  
532 used in aquaculture. Both the raw materials and the adsorbents (produced by pyrolysis)  
533 were fully physico-chemically characterized. All the adsorbents produced in this study  
534 were able to adsorb MS-222, even though this anaesthetic has a great affinity for the  
535 aqueous phase. The best adsorption capacity was attained by the peanut shells-based  
536 adsorbent (34 mg g<sup>-1</sup>) which showed a  $S_{BET}$  of 5 m<sup>2</sup> g<sup>-1</sup>. Meanwhile, the commercial AC

537 used by the authors for comparison purposes, presented a higher  $S_{\text{BET}}$  ( $1324 \text{ m}^2 \text{ g}^{-1}$ ) and  
538 displayed a larger MS-222 adsorption capacity ( $349 \text{ mg g}^{-1}$ ). In any case, even though  
539  $S_{\text{BET}}$  of the peanut shells-based adsorbent was three orders of magnitude lower than that  
540 of the AC, the adsorption capacity was only ten times lower.

#### 541 *4.3.1 Adsorption of other pharmaceuticals onto microwave produced adsorbents*

542 Reza et al. (2014) studied the adsorption of clofibric acid using bamboo wastes'  
543 adsorbents produced by microwave-assisted activation. These authors observed an  
544 adsorption capacity decrease with the alkalinity of the medium ( $\text{pH} > \text{p}K_{\text{a}}$ ) due to higher  
545 electrostatic repulsions was observed. Bamboo-based adsorbents compared well with  
546 commercial adsorbents and were considered as effective for the removal of clofibric  
547 acid from contaminated waters.

548

#### 549 **4.4 Municipal and industrial residues: Adsorption of antibiotics**

550 In Table 3, studies on the application of adsorbents produced from  
551 municipal/industrial residues for the adsorption of antibiotics are presented.

552 Adsorption of tetracycline and ciprofloxacin onto a  $\text{H}_3\text{PO}_4$  chemically activated  
553 adsorbent prepared from lignin was investigated by Huang et al. (2014). This lignin-  
554 based adsorbent presented a porous structure with a quite large  $S_{\text{BET}}$  ( $932 \text{ m}^2 \text{ g}^{-1}$ ) and  
555 maximum adsorption capacities of  $475$  and  $419 \text{ mg g}^{-1}$ , for tetracycline and  
556 ciprofloxacin, respectively. The extent of adsorption increased with temperature for  
557 tetracycline, while for ciprofloxacin, the adsorption capacity dropped slightly with  
558 increasing temperature. The adsorption of sulfamethoxazole, and six other  
559 pharmaceuticals, onto a primary paper mill sludge-adsorbent was studied by Calisto et  
560 al. (2015). This pyrolysed, non-activated adsorbent was shown to provide fast kinetics

561 (15-30 min) for the antibiotic; however, it was the pollutant with the lowest affinity for  
562 the adsorbent (see also section 4.2.2). That was explained considering the chemical  
563 structure of the antibiotic and the basic nature of the adsorbent surface. Adsorption  
564 coefficients followed the order cations > neutrals > anions, pointing to the role of  
565 electrostatic interactions on the adsorption process. Nielsen and Bandosz (2016) also  
566 studied the adsorption of sulfamethoxazole onto sewage sludge and fish waste and, in  
567 order to simulate the real and complex STPs' influents, studies were conducted for a  
568 mixture solution containing also carbamazepine and trimethoprim. Comparatively to the  
569 adsorbent prepared from fish waste, the sewage sludge-based adsorbent presented a  
570 thrice higher  $S_{\text{BET}}$  (101 vs. 34  $\text{m}^2 \text{g}^{-1}$ ) and a considerably higher pore volume (0.145 vs.  
571 to 0.098  $\text{cm}^3 \text{g}^{-1}$ ). The adsorption capacity was inversely correlated with the polarity of  
572 the pharmaceuticals, i.e. the most polar (sulfamethoxazole) was the least adsorbed, and  
573 was affected by competitive effects (sulfamethoxazole and trimethoprim were the most  
574 and the least sensitive, respectively, to competition by other drugs).

575 Most of studies show results obtained by adsorbents produced from the same  
576 batch of a precursor, i.e. the consistency of the precursor and of the production process  
577 is usually not assessed and only a few authors carried out relevant studies on this issue  
578 (Jaria et al., 2017; Yao et al., 2013). Yao et al. (2013), for instance, used STPs sludge as  
579 raw material and compared the adsorption of fluoroquinolones onto adsorbents from  
580 different sources (from three different municipal STPs and from a food industry STP).  
581 Authors found that the different properties of sludge from different STPs may lead to  
582 adsorbents with different properties and therefore to different adsorption rates.

583



584 **4.5 Municipal and industrial residues: Adsorption of NSAIDs, analgesics and other**  
585 **pharmaceuticals**

586 Table 3 presents the studies related to the application of adsorbents produced  
587 from municipal/industrial residues in the adsorption of NSAIDs, analgesics and other  
588 pharmaceuticals.

589 Coimbra et al. (2015) evaluated the adsorption capacity of adsorbents produced  
590 by pyrolysis of paper mill sludge in two different matrices – ultrapure water and a STP  
591 secondary effluent – and found that this had no impact in the adsorption kinetics,  
592 equilibrium being reached quickly (within 200 min) in both matrices for all the tested  
593 pharmaceuticals (salicylic acid, diclofenac, ibuprofen and acetaminophen). With the  
594 same type of precursor, Jaria et al. (2015) tested different chemical activation agents  
595 (KOH, NaOH and ZnCl<sub>2</sub>) and fluoxetine as adsorbate. Even though highest  $S_{BET}$  was  
596 observed for the ZnCl<sub>2</sub>-AC,  $S_{BET}$  was not considered to be the key factor in the  
597 adsorption process since all the produced materials compared favourably with a  
598 commercial AC in terms of adsorption capacities. The same type of precursor (paper  
599 mill sludge) but with no chemical or physical activation was also applied on the  
600 adsorption of another antidepressant – citalopram (Calisto et al., 2014). Both primary  
601 and biological sludge were pyrolysed at different temperatures and residence times (best  
602 results for primary sludge pyrolysed at 800 °C for 150 min) and even though this  
603 material did not present an adsorption capacity as high as the AC used for comparison,  
604 adsorption was relevant considering that it was a non-activated material. The rapid  
605 kinetics and the possible valorization of such a residue were also pointed out by authors  
606 as important advantages. The best adsorbent was latter on used to understand the  
607 adsorption patterns of a multitude of compounds: carbamazepine, oxazepam, piroxicam,

608 cetirizine, venlafaxine and paroxetine (Calisto et al., 2015). Again, results for the  
609 produced adsorbent were compared to results for a commercially available AC and it  
610 was concluded that even though the adsorption effectiveness of the former was lower,  
611 the adsorption kinetics was faster. Adsorption coefficients following the order  
612 paroxetine > carbamazepine > oxazepam > cetirizine > venlafaxine > piroxicam,  
613 which was associated to the correlation between the compounds' structures and the  
614 surface chemistry of the adsorbent. Interestingly, the tendency was not the same on the  
615 commercial AC, which points out to the fact that, for this adsorbent, the high  $S_{\text{BET}}$  and  
616 the porous structure play a more important role than the surface chemistry (Calisto et  
617 al., 2015).

618         The most important by-product in the cork industry is cork powder. Mestre et al.  
619 (2007) studied the potential of adsorbents produced from this waste, prepared by both  
620 chemical activation (with  $\text{K}_2\text{CO}_3$ ) and a two-step activation methodology (chemical  
621 activation followed by steam activation), in order to remove ibuprofen from the liquid  
622 phase. Production methods led to different surface chemistry properties, which affected  
623 the adsorption capacity: the one produced by two-step activation presented higher  
624 ibuprofen adsorption capacity than the chemically activated, possibly due to a more  
625 developed supermicroporous structure of the two-step activated adsorbent. Adsorption  
626 of ibuprofen using this residue as precursor was further investigated by Mestre et al.  
627 (2009) and it was concluded that these alternative carbons performed better in  
628 adsorption capacity comparatively to commercial adsorbents used for comparison due to  
629 a unique combination of the basic nature of surface groups and the micropores size.  
630 Later on, these authors (Mestre et al., 2014) used a so far unexplored cork by-product –  
631 expanded corkboard granules – from which adsorbents with well-developed pore

632 structures were obtained by both chemical ( $S_{\text{BET}}$  up to  $950 \text{ m}^2 \text{ g}^{-1}$ ) and physical ( $S_{\text{BET}}$  up  
633 to  $750 \text{ m}^2 \text{ g}^{-1}$ ) activation. These adsorbents were used for the adsorption of ibuprofen,  
634 acetaminophen, acetylsalicylic acid, clofibrilic acid, caffeine and iopamidol and their  
635 removal efficiencies were comparable (or even higher) to those obtained with  
636 commercial carbons usually used for water treatment. Textural properties of the  
637 adsorbents played a role in the removal performance: chemically activated AC  
638 presented removal efficiencies up to 100% for smaller molecules, owing to their well-  
639 developed micropore structure; physically activated ones, with a mesopore structure and  
640 higher volume of supermicropores, removed preferentially bulky molecules (removal up  
641 to ~90%). Also, produced adsorbents presented lower ash, similar carbon and higher  
642 oxygen contents than the commercial ACs used for comparison. Cabrita et al. (2010)  
643 also used cork powder as well as peach stones from the fruit beverage industry for the  
644 production of adsorbents that were used for the adsorption of acetaminophen.  $S_{\text{BET}}$  of  
645 the produced adsorbents was 891 and  $866 \text{ m}^2 \text{ g}^{-1}$  for the cork powder and the peach  
646 stones-based adsorbent, respectively, which were slightly lower than the  $S_{\text{BET}}$   
647 determined for the commercial ACs ( $1033\text{-}1120 \text{ m}^2 \text{ g}^{-1}$ ). However, acetaminophen  
648 uptake and adsorption capacity by the adsorbent produced from cork residues were  
649 analogous to those obtained by commercial adsorbents used for comparison. The good  
650 performance of low-cost, alternative, lab-made adsorbents in the uptake of  
651 acetaminophen was also shown by Galhetas et al. (2014), who produced pine-based  
652 adsorbents with an identical/better performance than commercial carbons.

653

654

655

656 **5. Critical aspects**

657           Despite the well-reported advantages of commercial ACs, there is an undeniable  
658 need to produce low-cost and locally generated adsorbents, especially when the former  
659 are logistically not feasible or prohibitively expensive. Financial issues always gain  
660 more importance in times of economic recession: for instance, the 2000s' economic  
661 crisis managed research to be focused in more cost-effective approaches. This may  
662 explain the increased interest about alternative adsorbent materials with minor cost that  
663 occurred in the past few years (which can be observed by the very recent dates of the  
664 papers appearing in literature). Along with the low-cost and adsorption properties, the  
665 environmental-friendly nature of each adsorbent is also an important factor.

666           Fig. 2 aims to depict the percentage of studies dealing with a specific topic in  
667 order to better visualize the points that will be addressed next. Despite the remarkable  
668 effort and advances that have been taken in the area, some critical aspects related to the  
669 production of alternative waste-based adsorbents for pharmaceuticals' removal are to be  
670 pointed out: (i) Most of the works focus on batch operation mode under agitation; the  
671 lack of column-, pilot-, and full-scale studies, is evident, which makes it difficult to  
672 better estimate the potential applications of the adsorbents; (ii) Clearly the great  
673 majority of studies give attention to antibiotics, followed by NSAIDs. Even though the  
674 importance of studying these pharmaceuticals is clear, other classes should be  
675 addressed, whether more profoundly or for the first time; (iii) The adsorbate  
676 experimental concentrations used in the adsorption studies are usually not  
677 environmentally relevant but one or more orders of magnitude above. This fact can  
678 generate unrealistic adsorption parameters and should be object of improvements in  
679 future studies; (iv) Pharmaceutical solutions used are mainly synthetic in nature and

680 studies concerning the removal efficiency of the produced adsorbents in real water  
681 samples are lacking. Also, typical components of contaminated water systems, such as  
682 salts, surfactants, organic matter, etc., are scarcely taken into account even though these  
683 parameters strongly influence the adsorption processes; (v) Another gap in literature is  
684 the lack of multi-component studies. Since multiple pollutants are simultaneously  
685 present in real water matrices, it is important to produce adsorbents either with a wide  
686 range of affinities or with high selectivity. In any case, multi-component studies are  
687 imperative; (vi) It is confirmed in literature that adsorption properties improve with  
688 activation and modifications; however, the downside of such processing steps is  
689 invariably not mentioned and activation vs. non-activation should be better addressed  
690 and understood, especially in what concerns environmental and economic impacts; (vii)  
691 “Low-cost” is an often-used term to classify alternative adsorbents but critical  
692 discussion about the effective costs and related economical evaluations are very scarce  
693 in the literature reviewed. Consequently, it is difficult to predict if the production and  
694 application of such adsorbents is, indeed, a profitable approach. Along with that, studies  
695 are limited to the production costs and do not cover the application of the studied  
696 adsorbent. Contrarily, the application studies lack the cost analysis. Increased efforts for  
697 detailed economic and market analyses should be done; (viii) Regeneration may be an  
698 aspect that impacts the final costs of the process since regeneration of the adsorbent may  
699 increase the operating costs directly and/or by causing secondary pollution. However,  
700 when the adsorbent performance is not lost, it can be seen as a strategy to decrease the  
701 adsorbent application costs. Either way, reports on regeneration are also usually  
702 narrowly addressed; (ix) More understanding about the 3D aspects of adsorbents  
703 adsorption is also needed to explain phenomena as adsorbents presenting low  $S_{\text{BET}}$  but

704 large capacities (or the other way around) or how different types of adsorbates distribute  
705 onto the adsorbents (on all dimensional levels: pore, inside and below pore surfaces,  
706 throughout the solid material); (x) pH is vastly addressed and even though it is a key  
707 parameter to be studied, extreme values contemplated in some studies are unrealistic  
708 (e.g. for most wastewater treatment applications, pH 2, is not a realistic value to be  
709 considered for the optimization of adsorption); (xi) Comparison of adsorbents'  
710 performance is difficult due to a lack of experimental consistency, i.e. sorption  
711 capacities are reported for different values of pH, temperature, adsorbate concentration,  
712 adsorbent dose, particle size and  $S_{BET}$ ; similarly, adsorbents are produced under  
713 different thermal processing temperatures, residence times, atmosphere, etc; (xii) The  
714 comparison of the produced adsorbents with commercial ACs is scarce and, when  
715 performed, it is usually carried out only in terms of adsorptive performance but not in  
716 terms of cost-effectiveness.

717

## 718 **6. Conclusions**

719 As shown above, various alternative waste-based adsorbents have been  
720 investigated successfully in order to attain specific objectives, such as: (i) minimizing  
721 the usage of costly AC, (ii) avoiding the use of other treatment technologies that would  
722 be expensive and/or result in the generation of complex and/or toxic by-products, or (iii)  
723 valorizing residues that otherwise would be difficult and environmentally problematic  
724 to handle. However, it is reasonable to infer that much is yet to be done and that the  
725 production of alternative adsorbents capable to compete with the commercially  
726 available carbons is still an emerging field of research requiring further exploitation.

727

728 **Supplementary Material**

729 E-supplementary data of this work can be found in the online version of the paper.

730

731 **Acknowledgments**

732 This work was funded by FEDER through COMPETE 2020 and by national funds  
733 through FCT by the research project PTDC/AAG-TEC/1762/2014. Vânia Calisto and  
734 Marta Otero also thank FCT for a postdoctoral grant (SFRH/BPD/78645/2011) and  
735 support by the FCT Investigator Program (IF/00314/2015), respectively. Thanks are  
736 also due for the financial support to CESAM (UID/AMB/50017/2013), to FCT/MEC  
737 through national funds, and the co-funding by the FEDER, within the PT2020  
738 Partnership Agreement and Compete 2020.

739

740 **References**

- 741 1. Ahmed, M.B., Zhou, J.L., Ngo, H.H., Guo, W., Johir, A.H., Belhaj, D., 2017.  
742 Competitive sorption affinity of sulfonamides and chloramphenicol antibiotics toward  
743 functionalized biochar for water and wastewater treatment. *Bioresour. Technol.* 238,  
744 306–312
- 745 2. Ahmed, M.J., Theydan, S.K., 2012. Adsorption of cephalexin onto activated carbons  
746 from *Albizia lebbek* seed pods by microwave-induced {KOH} and {K<sub>2</sub>CO<sub>3</sub>}  
747 activations. *Chem. Eng. J.* 211–212, 200–207.
- 748 3. Ahmed, M.J., Theydan, S.K., 2013a. Microwave assisted preparation of microporous  
749 activated carbon from *Siris* seed pods for adsorption of metronidazole antibiotic. *Chem.*  
750 *Eng. J.* 214, 310–318.
- 751 4. Ahmed, M.J., Theydan, S.K., 2013b. Microporous activated carbon from *Siris* seed  
752 pods by microwave-induced KOH activation for metronidazole adsorption. *J. Anal.*  
753 *Appl. Pyrolysis* 99, 101–109.
- 754 5. Ahmed, M.J., Theydan, S.K., 2014. Fluoroquinolones antibiotics adsorption onto  
755 microporous activated carbon from lignocellulosic biomass by microwave pyrolysis. *J.*  
756 *Taiwan Inst. Chem. Eng.* 45, 219–226.
- 757 6. Akhtar, J., Amin, N.A.S., Shahzad, K., 2016. A review on removal of  
758 pharmaceuticals from water by adsorption. *Desalin. Water Treat.* 57, 12842–12860.
- 759 7. Alsbaiee, A., Smith, B.J., Xiao, L., Ling, Y., Helbling, W.R.D., 2016. Rapid removal  
760 of organic micropollutants from water by a porous  $\beta$ -cyclodextrin polymer. *Nature* 529,  
761 190–194.
- 762 8. Álvarez-Torrellas, S., Rodríguez, A., Ovejero, G., García, J., 2016. Comparative  
763 adsorption performance of ibuprofen and tetracycline from aqueous solution by  
764 carbonaceous materials. *Chem. Eng. J.* 283, 936–947.
- 765 9. Antunes, M., Esteves, V.I., Guégan, R., Crespo, J.S., Fernandes, A.N., Giovanela,  
766 M., 2012. Removal of diclofenac sodium from aqueous solution by Isabel grape

767 bagasse. *Chem. Eng. J.* 192, 114–121.

768 10. aus der Beek, T., Weber, F.-A., Bergmann, A., Hickmann, S., Ebert, I., Hein, A.,  
769 Küster, A., 2016. Pharmaceuticals in the environment--Global occurrences and  
770 perspectives. *Environ. Toxicol. Chem.* 35, 823–35.

771 11. Baccar, R., Sarrà, M., Bouzid, J., Feki, M., Blánquez, P., 2012. Removal of  
772 pharmaceutical compounds by activated carbon prepared from agricultural by-product.  
773 *Chem. Eng. J.* 211–212, 310–317.

774 12. Cabrita, I., Ruiz, B., Mestre, A.S., Fonseca, I.M., Carvalho, A.P., Ania, C.O., 2010.  
775 Removal of an analgesic using activated carbons prepared from urban and industrial  
776 residues. *Chem. Eng. J.* 163, 249–255.

777 13. Calisto, V., Esteves, V.I., 2009. Psychiatric pharmaceuticals in the environment.  
778 *Chemosphere* 77, 1257–1274.

779 14. Calisto, V., Ferreira, C.I.A., Santos, S.M., Gil, M.V., Otero, M., Esteves, V.I., 2014.  
780 Production of adsorbents by pyrolysis of paper mill sludge and application on the  
781 removal of citalopram from water. *Bioresour. Technol.* 166, 335–344.

782 15. Calisto, V., Ferreira, C.I.A., Oliveira, J.A.B.P., Otero, M., Esteves, V.I., 2015.  
783 Adsorptive removal of pharmaceuticals from water by commercial and waste-based  
784 carbons. *J. Environ. Manage.* 152, 83–90.

785 16. Calisto, V., Jaria, G., Silva, C.P., Ferreira, C.I.A., Otero, M., Esteves, V.I., 2017.  
786 Single and multi-component adsorption of psychiatric pharmaceuticals onto alternative  
787 and commercial carbons. *J. Environ. Manage.* 192, 15–24.

788 17. Choy, K.K.H., Barford, J.P., McKay, G., 2005. Production of activated carbon from  
789 bamboo scaffolding waste—process design, evaluation and sensitivity analysis. *Chem.*  
790 *Eng. J.* 109, 147–165.

791 18. Coimbra, R.N., Calisto, V., Ferreira, C.I.A., Esteves, V.I., Otero, M., 2015.  
792 Removal of pharmaceuticals from municipal wastewater by adsorption onto pyrolyzed  
793 pulp mill sludge. *Arab. J. Chem.*

794 19. Coimbra, R.N., Escapa, C., Paniagua, S., Otero, M., 2016. Adsorptive removal of  
795 diclofenac from ultrapure and wastewater: a comparative assessment on the  
796 performance of a polymeric resin and activated carbons. *Desalin. Water Treat.* 57,  
797 27914–27923.

798 20. Dias, J.M., Alvim-Ferraz, M.C.M., Almeida, M.F., Rivera-Utrilla, J., Sánchez-Polo,  
799 M., 2007. Waste materials for activated carbon preparation and its use in aqueous-phase  
800 treatment: A review. *J. Environ. Manage.* 85, 833–846.

801 21. Dubey, S.P., Dwivedi, A.D., Sillanpää, M., Gopal, K., 2010. Artemisia vulgaris-  
802 derived mesoporous honeycomb-shaped activated carbon for ibuprofen adsorption.  
803 *Chem. Eng. J.* 165, 537–544.

804 22. El-Shafey, E.-S.I., Al-Lawati, H., Al-Sumri, A.S., 2012. Ciprofloxacin adsorption  
805 from aqueous solution onto chemically prepared carbon from date palm leaflets. *J.*  
806 *Environ. Sci.* 24, 1579–1586.

807 23. Faubert, P., Barnabé, S., Bouchard, S., Côté, R., Villeneuve, C., 2016. Pulp and  
808 paper mill sludge management practices: What are the challenges to assess the impacts  
809 on greenhouse gas emissions? *Resour. Conserv. Recycl.* 108, 107–133.

810 24. Ferreira, C.I.A., Calisto, V., Santos, S.M., Cuerda-Correa, E.M., Otero, M., Nadais,  
811 H., Esteves, V.I., 2015. Application of pyrolysed agricultural biowastes as adsorbents  
812 for fish anaesthetic (MS-222) removal from water. *J. Anal. Appl. Pyrolysis* 112, 313–  
813 324.

814 25. Galhetas, M., Mestre, A.S., Pinto, M.L., Gulyurtlu, I., Lopes, H., Carvalho, A.P.,



815 2014. Chars from gasification of coal and pine activated with K<sub>2</sub>CO<sub>3</sub>: Acetaminophen  
 816 and caffeine adsorption from aqueous solutions. *J. Colloid Interface Sci.* 433, 94–103.  
 817 26. Han, X., Liang, C., Li, T., Wang, K., Huang, H., Yang, X., 2013. Simultaneous  
 818 removal of cadmium and sulfamethoxazole from aqueous solution by rice straw  
 819 biochar. *J. Zhejiang Univ. Sci. B* 14, 640–649.  
 820 27. Hesas, R.H., Daud, W.M.A.W., Sahu, J.N., Arami-Niya, A., 2013. The effects of a  
 821 microwave heating method on the production of activated carbon from agricultural  
 822 waste: A review. *J. Anal. Appl. Pyrolysis* 100, 1–11.  
 823 28. Hokkanen, S., Bhatnagar, A., Sillanpää, M., 2016. A review on modification  
 824 methods to cellulose-based adsorbents to improve adsorption capacity. *Water Res.* 91,  
 825 156–173.  
 826 29. Homem, V., Santos, L., 2011. Degradation and removal methods of antibiotics from  
 827 aqueous matrices – A review. *J. Environ. Manage.* 92, 2304–2347.  
 828 30. Homem, V., Alves, A., Santos, L.S., 2015. Alternative approaches for amoxicillin  
 829 removal from waters - Fentons oxidation versus sorption by almond shell ashes.  
 830 *Environ. Eng. Manag. J.* 14, 2399–2407.  
 831 31. Huang, L., Sun, Y., Wang, W., Yue, Q., Yang, T., 2011. Comparative study on  
 832 characterization of activated carbons prepared by microwave and conventional heating  
 833 methods and application in removal of oxytetracycline (OTC). *Chem. Eng. J.* 171,  
 834 1446–1453.  
 835 32. Huang, L., Wang, M., Shi, C., Huang, J., Zhang, B., 2014. Adsorption of  
 836 tetracycline and ciprofloxacin on activated carbon prepared from lignin with H<sub>3</sub>PO<sub>4</sub>  
 837 activation. *Desalin. Water Treat.* 52, 2678–2687.  
 838 33. Inyang, M., Dickenson, E., 2015. The potential role of biochar in the removal of  
 839 organic and microbial contaminants from potable and reuse water: A review.  
 840 *Chemosphere* 134, 232–240.  
 841 34. Ioannidou, O., Zabaniotou, A., 2007. Agricultural residues as precursors for  
 842 activated carbon production—A review. *Renew. Sustain. Energy Rev.* 11, 1966–2005.  
 843 35. Jaria, G., Calisto, V., Gil, M.V., Otero, M., Esteves, V.I., 2015. Removal of  
 844 fluoxetine from water by adsorbent materials produced from paper mill sludge. *J.*  
 845 *Colloid Interface Sci.* 448, 32–40.  
 846 36. Jaria, G., Silva, C.P., Ferreira, C.I.A., Otero, M., Calisto, V., 2017. Sludge from  
 847 paper mill effluent treatment as raw material to produce carbon adsorbents: An  
 848 alternative waste management strategy. *J. Environ. Manage.* 188, 203–211.  
 849 37. Jia, M., Wang, F., Bian, Y., Jin, X., Song, Y., Kengara, F.O., Xu, R., Jiang, X.,  
 850 2013. Effects of pH and metal ions on oxytetracycline sorption to maize-straw-derived  
 851 biochar. *Bioresour. Technol.* 136, 87–93.  
 852 38. Jing, X.-R., Wang, Y.-Y., Liu, W.-J., Wang, Y.-K., Jiang, H., 2014. Enhanced  
 853 adsorption performance of tetracycline in aqueous solutions by methanol-modified  
 854 biochar. *Chem. Eng. J.* 248, 168–174.  
 855 39. Jung, C., Park, J., Lim, K.H., Park, S., Heo, J., Her, N., Oh, J., Yun, S., Yoon, Y.,  
 856 2013. Adsorption of selected endocrine disrupting compounds and pharmaceuticals on  
 857 activated biochars. *J. Hazard. Mater.* 263, Part, 702–710.  
 858 40. Jung, C., Boateng, L.K., Flora, J.R.V., Oh, J., Braswell, M.C., Son, A., Yoon, Y.,  
 859 2015. Competitive adsorption of selected non-steroidal anti-inflammatory drugs on  
 860 activated biochars: Experimental and molecular modeling study. *Chem. Eng. J.* 264, 1–  
 861 9.  
 862 41. Kasprzyk-Hordern, B., Dinsdale, R.M., Guwy, A.J., 2009. The removal of

863 pharmaceuticals, personal care products, endocrine disruptors and illicit drugs during  
864 wastewater treatment and its impact on the quality of receiving waters. *Water Res.* 43,  
865 363–380.

866 42. Kearns, J.P., Wellborn, L.S., Summers, R.S., Knappe, D.R.U., 2014. 2,4-D  
867 adsorption to biochars: Effect of preparation conditions on equilibrium adsorption  
868 capacity and comparison with commercial activated carbon literature data. *Water Res.*  
869 62, 20–28.

870 43. Kyzas, G.Z., Deliyanni, E.A., 2015. Modified activated carbons from potato peels as  
871 green environmental-friendly adsorbents for the treatment of pharmaceutical effluents.  
872 *Chem. Eng. Res. Des.* 97, 135–144.

873 44. Kyzas, G.Z., Fu, J., Lazaridis, N.K., Bikiaris, D.N., Matis, K.A., 2015. New  
874 approaches on the removal of pharmaceuticals from wastewaters with adsorbent  
875 materials. *J. Mol. Liq.* 209, 87–93.

876 45. Larous, S., Meniai, A.-H., 2016. Adsorption of Diclofenac from aqueous solution  
877 using activated carbon prepared from olive stones. *Int. J. Hydrogen Energy* 41, 10380–  
878 10390.

879 46. Liguori, R., Faraco, V., 2016. Biological processes for advancing lignocellulosic  
880 waste biorefinery by advocating circular economy. *Bioresour. Technol.* 215, 13–20.

881 47. Lima, I.M., McAloon, A., Boateng, A.A., 2008. Activated carbon from broiler litter:  
882 Process description and cost of production. *Biomass and Bioenergy* 32, 568–572.

883 48. Liu, H., Liu, W., Zhang, J., Zhang, C., Ren, L., Li, Y., 2011. Removal of cephalixin  
884 from aqueous solutions by original and Cu(II)/Fe(III) impregnated activated carbons  
885 developed from lotus stalks Kinetics and equilibrium studies. *J. Hazard. Mater.* 185,  
886 1528–1535.

887 49. Liu, P., Liu, W.-J., Jiang, H., Chen, J.-J., Li, W.-W., Yu, H.-Q., 2012. Modification  
888 of bio-char derived from fast pyrolysis of biomass and its application in removal of  
889 tetracycline from aqueous solution. *Bioresour. Technol.* 121, 235–240.

890 50. Liu, W., Zhang, J., Zhang, C., Ren, L., 2011. Sorption of norfloxacin by lotus stalk-  
891 based activated carbon and iron-doped activated alumina: Mechanisms, isotherms and  
892 kinetics. *Chem. Eng. J.* 171, 431–438.

893 51. Liu, Z., Zhou, X., Chen, X., Dai, C., Zhang, J., Zhang, Y., 2013. Biosorption of  
894 clofibric acid and carbamazepine in aqueous solution by agricultural waste rice straw. *J.*  
895 *Environ. Sci.* 25, 2384–2395.

896 52. Martins, A.C., Pezoti, O., Cazetta, A.L., Bedin, K.C., Yamazaki, D.A.S., Bandoch,  
897 G.F.G., Asefa, T., Visentainer, J. V, Almeida, V.C., 2015. Removal of tetracycline by  
898 NaOH-activated carbon produced from macadamia nut shells: Kinetic and equilibrium  
899 studies. *Chem. Eng. J.* 260, 291–299.

900 53. Mestre, A.S., Pires, J., Nogueira, J.M.F., Carvalho, A.P., 2007. Activated carbons  
901 for the adsorption of ibuprofen. *Carbon* 45, 1979–1988.

902 54. Mestre, A.S., Pires, J., Nogueira, J.M.F., Parra, J.B., Carvalho, A.P., Ania, C.O.,  
903 2009. Waste-derived activated carbons for removal of ibuprofen from solution: Role of  
904 surface chemistry and pore structure. *Bioresour. Technol.* 100, 1720–1726.

905 55. Mestre, A.S., Bexiga, A.S., Proença, M., Andrade, M., Pinto, M.L., Matos, I.,  
906 Fonseca, I.M., Carvalho, A.P., 2011. Activated carbons from sisal waste by chemical  
907 activation with K<sub>2</sub>CO<sub>3</sub>: Kinetics of paracetamol and ibuprofen removal from aqueous  
908 solution. *Bioresour. Technol.* 102, 8253–8260

909 56. Mestre, A.S., Pires, R.A., Aroso, I., Fernandes, E.M., Pinto, M.L., Reis, R.L.,  
910 Andrade, M.A., Pires, J., Silva, S.P., Carvalho, A.P., 2014. Activated carbons prepared

911 from industrial pre-treated cork: Sustainable adsorbents for pharmaceutical compounds  
 912 removal. *Chem. Eng. J.* 253, 408–417.

913 57. Mohan, D., Sarswat, A., Ok, Y.S., Pittman, C.U., 2014. Organic and inorganic  
 914 contaminants removal from water with biochar, a renewable, low cost and sustainable  
 915 adsorbent – A critical review. *Bioresour. Technol.* 160, 191–202.

916 58. Mondal, S., Sinha, K., Aikat, K., Halder, G., 2015. Adsorption thermodynamics and  
 917 kinetics of ranitidine hydrochloride onto superheated steam activated carbon derived  
 918 from mung bean husk. *J. Environ. Chem. Eng.* 3, 187–195.

919 59. Nazari, G., Abolghasemi, H., Esmaili, M., 2016. Batch adsorption of cephalexin  
 920 antibiotic from aqueous solution by walnut shell-based activated carbon. *J. Taiwan Inst.*  
 921 *Chem. Eng.* 58, 357–365.

922 60. Ng, C., Marshall, W.E., Rao, R.M., Bansode, R.R., Losso, J.N., 2003. Activated  
 923 carbon from pecan shell: process description and economic analysis. *Ind. Crops Prod.*  
 924 17, 209–217.

925 61. Nielsen, L., Biggs, M.J., Skinner, W., Bandosz, T.J., 2014. The effects of activated  
 926 carbon surface features on the reactive adsorption of carbamazepine and  
 927 sulfamethoxazole. *Carbon N. Y.* 80, 419–432.

928 62. Nielsen, L., Bandosz, T.J., 2016. Analysis of the competitive adsorption of  
 929 pharmaceuticals on waste derived materials. *Chem. Eng. J.* 287, 139–147.

930 63. Qian, K., Kumar, A., Zhang, H., Bellmer, D., Huhnke, R., 2015. Recent advances in  
 931 utilization of biochar. *Renew. Sustain. Energy Rev.* 42, 1055–1064.

932 64. Rafatullah, M., Ahmad, T., Ghazali, A., Sulaiman, O., Danish, M., 2013. Oil Palm  
 933 Biomass as a Precursor of Activated Carbons: A Review. *Crit. Rev. Environ. Sci.*  
 934 *Technol.* 43, 1117–11661.

935 65. Rajapaksha, A.U., Vithanage, M., Zhang, M., Ahmad, M., Mohan, D., Chang, S.X.,  
 936 Ok, Y.S., 2014. Pyrolysis condition affected sulfamethazine sorption by tea waste  
 937 biochars. *Bioresour. Technol.* 166, 303–308.

938 66. Reza, R.A., Ahmaruzzaman, M., Sil, A.K., Gupta, V.K., 2014. Comparative  
 939 Adsorption Behavior of Ibuprofen and Clofibric Acid onto Microwave Assisted  
 940 Activated Bamboo Waste. *Ind. Eng. Chem. Res.* 53, 9331–9339.

941 67. Rovani, S., Censi, M.T., Pedrotti Jr, S.L., Lima, É.C., Cataluña, R., Fernandes,  
 942 A.N., 2014. Development of a new adsorbent from agro-industrial waste and its  
 943 potential use in endocrine disruptor compound removal. *J. Hazard. Mater.* 271, 311–  
 944 320.

945 68. Sathishkumar, P., Arulkumar, M., Ashokkumar, V., Mohd Yusoff, A.R.,  
 946 Murugesan, K., Palvannan, T., Salam, Z., Ani, F.N., Hadibarata, T., 2015. Modified  
 947 phyto-waste *Terminalia catappa* fruit shells: a reusable adsorbent for the removal of  
 948 micropollutant diclofenac. *RSC Adv.* 5, 30950–30962.

949 69. Saucier, C., Adebayo, M.A., Lima, E.C., Cataluña, R., Thue, P.S., Prola, L.D.T.,  
 950 Puchana-Rosero, M.J., Machado, F.M., Pavan, F.A., Dotto, G.L., 2015. Microwave-  
 951 assisted activated carbon from cocoa shell as adsorbent for removal of sodium  
 952 diclofenac and nimesulide from aqueous effluents. *J. Hazard. Mater.* 289, 18–27.

953 70. Silva, C.P., Otero, M., Esteves, V., 2012. Processes for the elimination of estrogenic  
 954 steroid hormones from water: A review, in: *Environ. Pollut.* 165, 38–58.

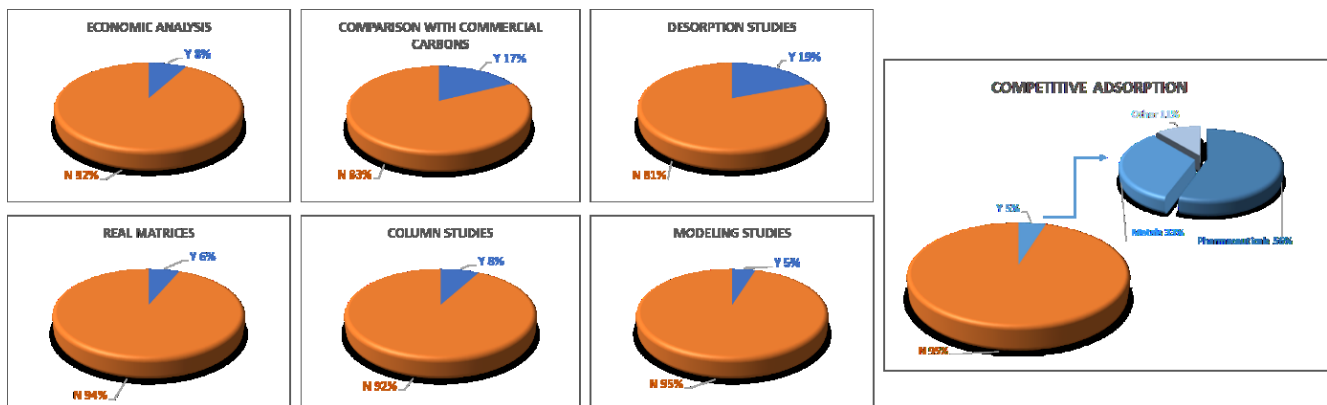
955 71. Silva, B., Costa, F., Neves, I.C., Tavares, T., 2015. Pharmaceuticals in the  
 956 Environment: Case Study of Psychiatric Drugs, in: Sharma, S.K. (Ed.), *Psychiatric*  
 957 *Pharmaceuticals as Emerging Contaminants in Wastewater*, Springer International  
 958 Publishing, London, pp. 19–46.

959 72. Sotelo, J.L., Rodríguez, A., Álvarez, S., García, J., 2012. Removal of caffeine and  
960 diclofenac on activated carbon in fixed bed column. *Chem. Eng. Res. Des.* 7, 967-974  
961 73. Sotelo, J.L., Ovejero, G., Rodríguez, A., Álvarez, S., Galán, J., García, J., 2014.  
962 Competitive adsorption studies of caffeine and diclofenac aqueous solutions by  
963 activated carbon. *Chem. Eng. J.* 240, 443–453.  
964 74. Stavropoulos, G.G., Zabaniotou, A.A., 2009. Minimizing activated carbons  
965 production cost. *Fuel Process. Technol.* 90, 952–957.  
966 75. Suhas, Gupta, V.K., Carrott, P.J.M., Singh, R., Chaudhary, M., Kushwaha, S., 2016.  
967 Cellulose: A review as natural, modified and activated carbon adsorbent. *Bioresour.*  
968 *Technol.* 216, 1066–1076.  
969 76. Sun, K., Ro, K., Guo, M., Novak, J., Mashayekhi, H., Xing, B., 2011. Sorption of  
970 bisphenol A, 17 $\alpha$ -ethinyl estradiol and phenanthrene on thermally and hydrothermally  
971 produced biochars. *Bioresour. Technol.* 102, 5757–5763.  
972 77. Sun, Y., Yue, Q., Gao, B., Huang, L., Xu, X., Li, Q., 2012. Comparative study on  
973 characterization and adsorption properties of activated carbons with H<sub>3</sub>PO<sub>4</sub> and H<sub>4</sub>P<sub>2</sub>O<sub>7</sub>  
974 activation employing *Cyperus alternifolius* as precursor. *Chem. Eng. J.* 181, 790-797  
975 78. Tan, X., Liu, Y., Zeng, G., Wang, X., Hu, X., Gu, Y., Yang, Z., 2015. Application  
976 of biochar for the removal of pollutants from aqueous solutions. *Chemosphere* 125, 70–  
977 85.  
978 79. Teixeira, S., Delerue-Matos, C., Santos, L., 2012. Removal of sulfamethoxazole  
979 from solution by raw and chemically treated walnut shells. *Environ. Sci. Pollut. Res.* 19,  
980 3096–3106.  
981 80. Ternes, T.A., Meisenheimer, M., McDowell, D., Sacher, F., Brauch, H.-J., Haist-  
982 Gulde, B., Preuss, G., Wilme, U., Zulei-Seibert, N., 2002. Removal of Pharmaceuticals  
983 during Drinking Water Treatment. *Environ. Sci. Technol.* 36, 3855–3863.  
984 81. Torres-Pérez, J., Gérente, C., Andrès, Y., 2012. Sustainable Activated Carbons from  
985 Agricultural Residues Dedicated to Antibiotic Removal by Adsorption. *Chinese J.*  
986 *Chem. Eng.* 20, 524–529.  
987 82. Tran, N.H., Gin, K.Y.-H., 2017. Occurrence and removal of pharmaceuticals,  
988 hormones, personal care products, and endocrine disrupters in a full-scale water  
989 reclamation plant. *Sci. Total Environ.* 599–600, 1503–1516.  
990 83. Tzeng, T.-W., Liu, Y.-T., Deng, Y., Hsieh, Y.-C., Tan, C.-C., Wang, S.-L., Huang,  
991 S.-T., Tzou, Y.-M., 2016. Removal of sulfamethazine antibiotics using cow manure-  
992 based carbon adsorbents. *Int. J. Environ. Sci. Technol.* 13, 973–984.  
993 84. Villaescusa, I., Fiol, N., Poch, J., Bianchi, A., Bazzicalupi, C., 2011. Mechanism of  
994 paracetamol removal by vegetable wastes: The contribution of  $\pi$ - $\pi$  interactions,  
995 hydrogen bonding and hydrophobic effect. *Desalination* 270, 135–142.  
996 85. Xie, H., Liu, W., Zhang, J., Zhang, C., Ren, L., 2011. Sorption of norfloxacin from  
997 aqueous solutions by activated carbon developed from *Trapa natans* husk. *Sci. China*  
998 *Chem.* 54, 835–843.  
999 86. Xie, M., Chen, W., Xu, Z., Zheng, S., Zhu, D., 2014. Adsorption of sulfonamides to  
1000 demineralized pine wood biochars prepared under different thermochemical conditions.  
1001 *Environ. Pollut.* 186, 187–194.  
1002 87. Xie, T., Reddy, K.R., Wang, C., Yargicoglu, E., Spokas, K., 2015. Characteristics  
1003 and Applications of Biochar for Environmental Remediation: A Review. *Crit. Rev.*  
1004 *Environ. Sci. Technol.* 45, 939–969.  
1005 88. Yao, Y., Gao, B., Chen, H., Jiang, L., Inyang, M., Zimmerman, A.R., Cao, X.,  
1006 Yang, L., Xue, Y., Li, H., 2012. Adsorption of sulfamethoxazole on biochar and its

1007 impact on reclaimed water irrigation. *J. Hazard. Mater.* 209–210, 408–413.  
1008 89. Yao, H., Lu, J., Wu, J., Lu, Z., Wilson, P.C., Shen, Y., 2013. Adsorption of  
1009 Fluoroquinolone Antibiotics by Wastewater Sludge Biochar: Role of the Sludge Source.  
1010 *Water, Air, & Soil Pollut.* 224, 1–9.  
1011 90. Yi, S., Gao, B., Sun, Y., Wu, J., Shi, X., Wu, B., Hu, X., 2016. Removal of  
1012 levofloxacin from aqueous solution using rice-husk and wood-chip biochars.  
1013 *Chemosphere* 150, 694–701.  
1014 91. Zhang, L., Song, X., Liu, X., Yang, L., Pan, F., Lv, J., 2011. Studies on the removal  
1015 of tetracycline by multi-walled carbon nanotubes. *Chem. Eng. J.* 178, 26–33.  
1016 92. Zhang, Y., Geißen, S.-U., Gal, C., 2008. Carbamazepine and diclofenac: Removal in  
1017 wastewater treatment plants and occurrence in water bodies. *Chemosphere* 73, 1151–  
1018 1161.  
1019 93. Zheng, H., Wang, Z., Zhao, J., Herbert, S., Xing, B., 2013. Sorption of antibiotic  
1020 sulfamethoxazole varies with biochars produced at different temperatures. *Environ.*  
1021 *Pollut.* 181, 60–67.  
1022 94. Zhou, A., Zhang, Y., Li, R., Su, X., Zhang, L., 2016. Adsorptive removal of sulfa  
1023 antibiotics from water using spent mushroom substrate, an agricultural waste. *Desalin.*  
1024 *Water Treat.* 57, 388–397.  
1025  
1026



1035 Fig. 2: Percentage of studies within the literature reviewed dealing with the following  
 1036 topics: economic analysis; comparison with commercial carbons; desorption studies;  
 1037 use of real matrices; column studies; modelling studies; and competitive adsorption.  
 1038 Note: Y – Yes; N – No. Presented data refers to a population of 63 articles with publication  
 1039 date in the range 2003-2016.  
 1040



**Table 1:** Adsorption of antibiotics onto agricultural/vegetable waste-based alternative adsorbents.

Type of waste	Adsorbed pharmaceutical	Adsorbent production	Adsorption conditions	Adsorption parameters and modelling	$S_{BET}^a$ ( $m^2 g^{-1}$ )	Reference
<i>Albizia lebbek</i>	Cephalexin	Microwave-assisted KOH and $K_2CO_3$ activation	T = 30-50 °C; $C_{adsorbate} = 20-100 mg L^{-1}$ ; $C_{adsorbent} = 0.5 g L^{-1}$ ; pH = 7; SS = 200 rpm	KM: PSO; IM: Langmuir; $Q_{max} = 118.08-137.02 mg g^{-1}$	1825	(Ahmed and Theydan, 2012)
<i>Siris</i>	Metronidazole	Microwave-assisted $K_2CO_3$ activation	T = 30-50 °C; $C_{adsorbate} = 20-100 mg L^{-1}$ ; $C_{adsorbent} = 0.5 g L^{-1}$ ; pH = 3-9; SS = 200 rpm	KM: PSO; IM: Langmuir; $Q_{max} = 180.74 mg g^{-1}$	1676	(Ahmed and Theydan, 2013a)
<i>Siris</i>	Metronidazole	Microwave-assisted KOH activation	T = 30-50 °C; $C_{adsorbate} = 20-100 mg L^{-1}$ ; $C_{adsorbent} = 0.5 g L^{-1}$ ; pH = 7; SS = 200 rpm	KM: PSO; IM: Langmuir; $Q_{max} = 196.31 mg g^{-1}$	1825	(Ahmed and Theydan, 2013b)
<i>Albizia lebbek</i>	Ciprofloxacin and norfloxacin	Microwave-assisted KOH activation	T = 30-50 °C; $C_{adsorbate} = 20-100 mg L^{-1}$ ; $C_{adsorbent} = 0.25-1.25 g L^{-1}$ ; pH = 2-12; SS = 200 rpm	KM: PSO; IM: Langmuir; $Q_{max} = 131.14 mg g^{-1}$ (ciprofloxacin); 166.99 $mg g^{-1}$ (norfloxacin)	1825	(Ahmed and Theydan, 2014)
Rice husk and peach stones	Tetracycline	Impregnation: 12 mol $L^{-1}$ $H_3PO_4$ , 85 °C, 6h. Heating: 400 °C (5 °C $min^{-1}$ ), 4 h, air flow (50 mL $min^{-1}$ )	T = 30 °C; $C_{adsorbate} = 100 mg L^{-1}$ ; $C_{adsorbent} = 0.3-20 g L^{-1}$ SS = 250 rpm	KM: PSO; IM: Langmuir; $Q_{max} = 845.9 mg g^{-1}$	1521	(Álvarez-Torrellas et al., 2016)
Date palm leaflets	Ciprofloxacin	Carbonization: $H_2SO_4$ treatment (40 g of clean dry palm leaflets + 12 mol $L^{-1}$ $H_2SO_4$ ); 160 °C, 25 min	T = 25-45 °C; $C_{adsorbate} = 100 mg L^{-1}$ ; $C_{adsorbent} = 2 g L^{-1}$ ; pH = 6; SS = 100 rpm	KM: PSO; IM: Langmuir; $Q_{max} = 125.0-133.3 mg g^{-1}$	24	(El-Shafey et al., 2012)
Lotus stalk	Oxytetracycline	Immersion in 40 wt.% $H_3PO_4$ 1:2 divided equally: (i) production through microwave, 700 W, 15 min; (ii) production by carbonization, 450 °C, 1 h	T = 20 °C; $C_{adsorbate} = 400 mg L^{-1}$ ; $C_{adsorbent} = 1 g L^{-1}$ ; pH = 2-11; SS = 125 rpm	KM: PSO; IM: Langmuir; $Q_{max} = 537.63-564.97 mg g^{-1}$	1434	(Huang et al., 2011)
Lignin	Tetracycline Ciprofloxacin	Carbonization at 450 °C for 1h, after impregnation with 40 wt.% $H_3PO_4$ solution 1:2 (g raw material/g $H_3PO_4$ ) for 12 h	T = 20 °C; $C_{adsorbate} = 180-600 mg L^{-1}$ ; $C_{adsorbent} = 1 g L^{-1}$ ; pH = 2-11; SS = 150 rpm	KM: PSO; IM: Langmuir; $Q_{max} = 475.48 mg g^{-1}$ (tetracycline); 418.60 $mg g^{-1}$ (ciprofloxacin)	931.53	(Huang et al., 2014)
Rice straw	Sulfamethoxazole	Production at 400 °C. Sieving for diameters <150, 150–250, and 250–425 $\mu m$ .	T = 25 °C; $C_{adsorbate} = 5-200 mg L^{-1}$ ; $C_{adsorbent} = 1 g L^{-1}$ ; pH = 3-7.5; SS = 150 rpm	IM: Langmuir; $Q_{max} = 1.83-9.18 mg g^{-1}$	3.58	(Han et al., 2013)
Almond shell	Amoxicillin	Burning: furnace with an oxygen-poor atmosphere (700 °C, 2 h)	T = 30 °C; $C_{adsorbate} = 0.8-10 g L^{-1}$ ; $C_{adsorbent} = 5 g L^{-1}$ ; SS = 120 rpm	KM: PSO; IM: Langmuir; $Q_{max} = 2.5 mg g^{-1}$	78.5	(Homem et al., 2015)
Rice husk	Tetracycline	MeOH-modification	T = 29 °C; $C_{adsorbate} = 100 mg L^{-1}$ ; $C_{adsorbent} = 1 g L^{-1}$ ; SS = 150 rpm	KM: PSO; IM: Langmuir; $Q_{max} = 10.25-18.53 mg g^{-1}$	66	(Jing et al., 2014)
Lotus stalk	Cephalexin	Soaking: $H_3PO_4$ (40 wt.% $H_3PO_4$ ; $H_3PO_4$ :raw material ratio of 2:1 (w/w)). Irradiation: ultrasound, 20 min. Heating: 450 °C. Modification: Fe(III) and Cu(II)	T = 20 °C; $C_{adsorbate} = 4-16 mg L^{-1}$ ; $C_{adsorbent} = 0.4 g L^{-1}$ ; pH = 2.5-10.5; SS = 350 rpm	KM: PSO; IM: Freundlich; $K_F = 14.73 mg g^{-1} (L mg^{-1})^{1/n}$	1031.8	(H. Liu et al., 2011)
Rice husk	Tetracycline	Fast pyrolysis: 723–773 K. Acidic or alkali treatment: 20 g crude material + 200 mL 10% $H_2SO_4$ (v/v) or 3 mol $L^{-1}$ KOH solution, 1 h.	T = 30 °C; $C_{adsorbate} = 50-1000 mg L^{-1}$ ; $C_{adsorbent} = 5 g L^{-1}$ ; pH = 5-9	KM: PSO; IM: Langmuir; $Q_{max} = 16.95-58.8 mg g^{-1}$	118	(Liu et al., 2012)



Macadamia nut shell	Tetracycline	NaOH-activation; impregnation ratio 3:1 (NaOH:bioadsorbent) ( <i>w/w</i> )	$C_{\text{adsorbate}} = 600 \text{ mg L}^{-1}$ ; $C_{\text{adsorbent}} = 1.0 \text{ g L}^{-1}$ ; $\text{pH} = 3\text{-}10$ ; $\text{SS} = 220 \text{ rpm}$	KM: PSO; IM: Temkin; $K_T = 5.87 \times 10^{-5} \text{ L g}^{-1}$	1524	(Martins et al., 2015)
Walnut shells	Cephalexin	Sieving: 251-354 nm. Chemical activation: $\text{ZnCl}_2$ , 6 h. Drying: 24 h, 105 °C, $\text{N}_2$ (300 $\text{cm}^3 \text{ min}^{-1}$ ), 450 °C (5 °C $\text{min}^{-1}$ ), 1 h. Washing: 0.05 M HCl	$T = 30 \text{ °C}$ ; $C_{\text{adsorbate}} = 100\text{-}200 \text{ mg L}^{-1}$ ; $C_{\text{adsorbent}} = 0.3 \text{ g L}^{-1}$ ; $\text{pH} = 6.5$ ; $\text{SS} = 200 \text{ rpm}$	KM: PSO; IM: Freundlich; $K_F = 155.2 \text{ mg g}^{-1} (\text{L mg}^{-1})^{1/n}$	1452	(Nazari et al., 2016)
Tea waste	Sulfamethazine	Pyrolysis: 300 and 700 °C (7 °C $\text{min}^{-1}$ , $\text{N}_2$ (5 mL $\text{min}^{-1}$ ). Steam activation: 5 mL $\text{min}^{-1}$ of steam, 45 min	$T = 25 \text{ °C}$ ; $C_{\text{adsorbate}} = 0\text{-}50 \text{ mg L}^{-1}$ ; $C_{\text{adsorbent}} = 1 \text{ g L}^{-1}$ ; $\text{pH} = 3\text{-}9$ ; $\text{SS} = 100 \text{ rpm}$	IM: Langmuir; $Q_{\text{max}} = 33.81 \text{ mg g}^{-1}$	576	(Rajapaksha et al., 2014)
Walnut shells	Sulfamethoxazole	Sieving: 250 $\mu\text{m}$ - 500 $\mu\text{m}$ . Washing: deionized water. Drying: 105 °C, 48 h. Treatment: ratio 1 g material/10 mL solution, with HCl (0.1 mol $\text{L}^{-1}$ ) or NaOH (3% <i>w/w</i> ), 24 and 1 h, respectively	$T = 20 \text{ °C}$ ; $C_{\text{adsorbate}} = 0.5 \text{ mg L}^{-1}$ ; $C_{\text{adsorbent}} = 10 \text{ g L}^{-1}$ ; $\text{pH} = 2\text{-}8$	IM: Freundlich; $K_F = 0.47 \text{ mg}^{1-1/n} \text{ g}^{-1} \text{ L}^{1/n}$	13	(Teixeira et al., 2012)
Sugar beet pulp and peanut hulls	Tetracycline	Pyrolysis: 850 °C (10 °C $\text{min}^{-1}$ ), $\text{N}_2$ (0.5 L $\text{min}^{-1}$ ). Introduction of steam: 857 °C (0.7 mL $\text{min}^{-1}$ , 80 min). Sieving: 0.25-0.5 mm. Washing: deionized water until pH constant. Drying: 110 °C	$T = 25 \text{ °C}$ ; $C_{\text{adsorbate}} = 50\text{-}300 \text{ mg L}^{-1}$ ; $C_{\text{adsorbent}} = 0.30\text{-}0.35 \text{ g L}^{-1}$ ; $\text{pH} = 3.4\text{-}4.2$ ; $\text{SS} = 300 \text{ rpm}$	IM: Langmuir; $Q_{\text{max}} = 288.0 \text{ mg g}^{-1}$	829	(Torres-Pérez et al., 2012)
Rice husk, Wood-chips	Levofloxacin	Pyrolysis: 300 and 600 °C	$T = 30 \text{ °C}$ ; $C_{\text{adsorbate}} = 100 \text{ mg L}^{-1}$ ; $C_{\text{adsorbent}} = 10 \text{ g L}^{-1}$ ; $\text{pH} = 2\text{-}9$	KM: PSO; IM: Langmuir; $Q_{\text{max}} = 1.49\text{-}7.72 \text{ mg g}^{-1}$	321	(Yi et al., 2016)
Spent mushroom substrate	Sulfamethyldiazine, sulfamethazine, sulfathiazole, sulfamethoxazole	Soaking with distilled water, 24 h. Drying: 35 °C, 4 h. Sieving: 100–300 $\mu\text{m}$	$C_{\text{adsorbate}} = 0.5\text{-}10 \text{ mg L}^{-1}$ ; $\text{pH} = 1\text{-}11$ ; $C_{\text{adsorbent}} = 2 \text{ g L}^{-1}$ ; $\text{SS} = 100 \text{ rpm}$	KM: PSO; IM: Langmuir; $Q_{\text{max}} = 2.1072 \text{ mg g}^{-1}$ (sulfamethyldiazine); 1.8103 $\text{mg g}^{-1}$ (sulfamethazine); 2.2991 $\text{mg g}^{-1}$ (sulfathiazole); 2.2133 $\text{mg g}^{-1}$ (sulfamethoxazole)	---	(Zhou et al., 2016)

<sup>a</sup> Whenever more than one adsorbent is produced, presented  $S_{\text{BET}}$  refers to the best/higher value obtained in each study. SS – Stirring Speed; KM – Kinetics Model; IM – Isotherm Model;  $C_{\text{adsorbate}}$  – Concentration of adsorbate;  $C_{\text{adsorbent}}$  – Concentration of adsorbent; FO – Fractionary order;  $K_F$  – Freundlich adsorption constant; PSO – Pseudo-second order;  $Q_{\text{max}}$  – Langmuir maximum adsorption capacity.

**Table 2:** Adsorption of non-steroidal anti-inflammatory drugs (NSAIDs) and other pharmaceuticals onto agricultural/vegetable waste-based alternative adsorbents.

Type of waste	Adsorbed pharmaceutical	Adsorbent production	Adsorption conditions	Adsorption parameters and modelling	$S_{BET}^a$ ( $m^2 g^{-1}$ )	Reference
Rice husk and peach stones	Ibuprofen	Impregnation: 12 mol L <sup>-1</sup> H <sub>3</sub> PO <sub>4</sub> , 85 °C, 6h. Heating: 400 °C (5 °C min <sup>-1</sup> ), 4 h, air flow (50 mL min <sup>-1</sup> )	T = 30 °C; $C_{adsorbate} = 100$ mg L <sup>-1</sup> ; $C_{adsorbent} = 0.3$ -20 g L <sup>-1</sup> ; SS = 250 rpm	KM: PSO; IM: Guggenheim–Anderson–de Boer; $Q_{max} = 239.8$ mg g <sup>-1</sup>	1521	(Álvarez-Torrellas et al., 2016)
<i>Artemisia Vulgaris</i> leaves	Ibuprofen	Weed treatment: 60% (v/v) H <sub>2</sub> SO <sub>4</sub> , 8–12 h. Washing: water until pH 6–7, drying 120 °C, 6 h. Carbonization at 450 °C, 30 min, N <sub>2</sub> (3 °C min <sup>-1</sup> ).	T = 25-45 °C; $C_{adsorbate} = 10$ mg L <sup>-1</sup> ; $C_{adsorbent} = 0.2$ g L <sup>-1</sup> ; pH = 2-8; SS = 200 rpm	KM: PSO; IM: Langmuir; $Q_{max} = 16.945$ mg g <sup>-1</sup>	358	(Dubey et al., 2010)
Pine	Acetaminophen, caffeine	Gasification: pilot-scale fluidized bed reactor (height 3.7 m; square section 0.2 m). Activation: K <sub>2</sub> CO <sub>3</sub> (1:1 and 1:3 weight ratio of precursor: K <sub>2</sub> CO <sub>3</sub> ), N <sub>2</sub> flow (5 cm <sup>3</sup> s <sup>-1</sup> ), 700-900 °C (10 °C min <sup>-1</sup> ), 0.5-2 h	T = 30 °C; $C_{adsorbate} = 120$ mg L <sup>-1</sup> ; $C_{adsorbent} = 0.3$ g L <sup>-1</sup> ; SS = 700 rpm	KM: PSO; IM: Langmuir; $Q_{max} = 270.3$ -434.8 mg g <sup>-1</sup> (acetaminophen) 476.2-500.0 mg g <sup>-1</sup> (caffeine)	1500	(Galhetas et al., 2014)
Agricultural wastes	MS-222	Pyrolysis: 400 °C, 120 min; 500 °C, 120 min; or 500 °C, 10 min (10 C° min <sup>-1</sup> )	T = 25 °C; $C_{adsorbate} = 250$ mg L <sup>-1</sup> ; $C_{adsorbent} = 10$ -50 g L <sup>-1</sup> ; SS = 90 rpm	KM: Double exponential; IM: Langmuir-Freundlich; $Q_{max} = 4$ -34 mg g <sup>-1</sup>	11	(Ferreira et al., 2015)
Loblolly pine chip	Diclofenac, naproxen, and ibuprofen	Thermal treatment: 300 °C, 15 min, pure N <sub>2</sub> (N-bioadsorbent), 7% O <sub>2</sub> + 93% N <sub>2</sub> (O-bioadsorbent). Activation: 4 M NaOH, 2 h. Washing: 0.1 M HCl	$C_{adsorbate} = 20$ μM; $C_{adsorbent} = 2$ g L <sup>-1</sup> ; SS = 500 rpm	IM: Langmuir; $Q_{max} = 214$ -372 mg g <sup>-1</sup> (diclofenac); 228-290 mg g <sup>-1</sup> (naproxen); 286-311 mg g <sup>-1</sup> (ibuprofen)	1360	(Jung et al., 2015)
Potato peels	Dorzolamide Pramipexole	Activation: KOH. Heating: 600 °C (25 °C min <sup>-1</sup> ), nitrogen flow (500 mL min <sup>-1</sup> ), 2 h	T = 25, 45, 65 °C; $C_{adsorbate} = 0$ -200 mg L <sup>-1</sup> ; $C_{adsorbent} = 1$ g L <sup>-1</sup> ; pH = 2-12; SS = 160 rpm	KM: PSO; IM: Langmuir; $Q_{max} = 66$ mg g <sup>-1</sup> (pramipexole); 60 mg g <sup>-1</sup> (dorzolamide)	---	(Kyzas and Deliyanni, 2015)
Olive stones	Diclofenac	Impregnation: 10% H <sub>2</sub> SO <sub>4</sub> in the ratio 1:1, 24 h. Washing: distilled water. Drying: at room T (> 6 h), then at 110 °C (24 h). Carbonization: 550 °C in an oven, 1 h	T = 23 °C; $C_{adsorbate} = 20$ mg L <sup>-1</sup> ; $C_{adsorbent} = 5$ g L <sup>-1</sup> ; pH = 4.2; SS = 500 rpm	KM: PSO; IM: BET; $Q_{max} = 0.26$ mg g <sup>-1</sup>	84	(Larous and Meniai, 2016)
Rice straw	Clofibric acid Carbamazepine	No treatment other than sieving and drying	T = 28 °C; $C_{adsorbate} = 100$ mg L <sup>-1</sup> ; $C_{adsorbent} = 0.5$ -1.0 g L <sup>-1</sup> ; pH = 3.5-6.8; SS = 180 rpm	KM: PSO; IM: Freundlich; $K_F = 3.94 \times 10^{-2}$ mg g <sup>-1</sup> (L mg <sup>-1</sup> ) <sup>1/n</sup> (clofibric acid); $7.12 \times 10^{-2}$ mg g <sup>-1</sup> (L mg <sup>-1</sup> ) <sup>1/n</sup> (carbamazepine)	---	(Liu et al., 2013)
Mung bean husk	Ranitidine hydrochloride	Carbonization: 550 °C (55 °C/15 min), 1 h; increase of temperature to 650 °C and activation with steam, 1 h	T = 36 °C; $C_{adsorbate} = 100$ mg L <sup>-1</sup> ; $C_{adsorbent} = 0.1$ -10 g L <sup>-1</sup> ; pH = 2-12; SS = 40-220 rpm	KM: PSO; IM: Langmuir-Freundlich; $Q_{max} = 26.5$ mg g <sup>-1</sup>	405	(Mondal et al., 2015)
Bamboo waste	Ibuprofen and Clofibric acid	Impregnation: 5 M ZnCl <sub>2</sub> ; 1 h; 333 K. Microwave heating: 720 W, 15 min. Washing: deionized water until pH 6–7	T = 25 °C; $C_{adsorbate} = 0$ -50 mg L <sup>-1</sup> ; $C_{adsorbent} = 1$ g L <sup>-1</sup> ; pH = 3-9; SS = 100 rpm	KM: PSO; IM: Langmuir; $Q_{max} = 278.5$ mg g <sup>-1</sup> (ibuprofen); 229.3 mg g <sup>-1</sup> (clofibric acid)	722	(Reza et al., 2014)
Coffee, eucalyptus, soybean oil	17α-Ethinylestradiol	Carbonization: 800 °C (20 °C min <sup>-1</sup> ), 30 min, under argon	T = 25 °C; $C_{adsorbate} = 2$ mg L <sup>-1</sup> ; $C_{adsorbent} = 1.5$ g L <sup>-1</sup> ; pH = 2-12.5	KM: General order; IM: Langmuir-Freundlich; $Q_{max} = 7.88$ mg g <sup>-1</sup>	16.5	(Rovani et al., 2014)
<i>Terminalia catappa</i> shells	Diclofenac	Fruit shell powder with H <sub>2</sub> SO <sub>4</sub> (1:1 (w/v)); heating, 12 h, 400 °C	T = 20-50 °C; $C_{adsorbate} = 50$ mg L <sup>-1</sup> ; $C_{adsorbent} = 50$ mg L <sup>-1</sup> ; pH = 5-9; SS = 160 rpm	KM: PSO; IM: Langmuir; $Q_{max} = 78.5$ -96.1 mg g <sup>-1</sup>	514	(Sathishkumar et al., 2015)

Cocoa shell	Diclofenac Nimesulide	Microwave pyrolysis: nitrogen (200 mL min <sup>-1</sup> ). Acidification: 6 mol L <sup>-1</sup> HCl under reflux	T = 25-50 °C; C <sub>adsorbate</sub> = 10-300 mg L <sup>-1</sup> ; C <sub>adsorbent</sub> = 2.5 g L <sup>-1</sup> ; pH = 7-10; SS = 150 rpm	KM: General order; IM: Langmuir; Q <sub>max</sub> = 63.47 mg g <sup>-1</sup> (diclofenac); 74.81 mg g <sup>-1</sup> (nimesulide)	619	(Saucier et al., 2015)
Vegetable wastes	Acetaminophen	Drying: 110 °C until constant weight. Sieving: 0.63–0.75 mm	T = 5-30 °C; C <sub>adsorbate</sub> = 20 mg L <sup>-1</sup> ; C <sub>adsorbent</sub> = 6.67 g L <sup>-1</sup> ; pH = 1-6	KM: PSO; IM: Langmuir; Q <sub>max</sub> = 2.18 mg g <sup>-1</sup>	---	(Villaescusa et al., 2011)

<sup>a</sup> Whenever more than one adsorbent is produced, presented S<sub>BET</sub> refers to the best/higher value obtained in each study. SS – Stirring Speed; KM – Kinetics Model; IM – Isotherm Model; C<sub>adsorbate</sub> – Concentration of adsorbate; C<sub>adsorbent</sub> – Concentration of adsorbent; FO – Fractionary order; K<sub>F</sub> – Freundlich adsorption constant; PSO – Pseudo-second order; Q<sub>max</sub> – Langmuir maximum adsorption capacity.

**Table 3:** Adsorption of antibiotics, non-steroidal anti-inflammatory drugs (NSAIDs) and other pharmaceuticals onto industrial/municipal waste-based alternative adsorbents.

Type of waste	Adsorbed pharmaceutical	Adsorbent production	Adsorption conditions	Adsorption parameters and modelling	$S_{BET}^a$ ( $m^2 g^{-1}$ )	Reference
Industrial cork and peach stones	Acetaminophen	Chemical activation with $K_2CO_3$ (weight ratio 1:1), 700 °C, 1 h	T = 30 °C; $C_{adsorbate} = 120 mg L^{-1}$ ; $C_{adsorbent} = 0.15 g L^{-1}$ ; pH = 5.8; SS = 700 rpm	KM: PSO; IM: Langmuir; $Q_{max} = 200-204 mg g^{-1}$	891	(Cabrita et al., 2010)
Paper mill sludge	Citalopram	Pyrolysis: 10 °C $min^{-1}$ , $N_2$ atmosphere (0.5 $dm^3 min^{-1}$ ). Different combinations pyrolysis temperature/ residence time: 315 °C/150 min, 600 °C/10 min, 800 °C/10 min, 800 °C/150 min	T = 25 °C; $C_{adsorbate} = 5 mg L^{-1}$ ; $C_{adsorbent} = 0.1-2.5 g L^{-1}$ ; pH = 5; SS = 50 rpm	KM: PSO; IM: Freundlich; $K_F = 6.7 mg g^{-1} (mg L^{-1})^{-N}$	209	(Calisto et al., 2014)
Paper mill sludge	Carbamazepine, Oxazepam, Sulfamethoxazole, Piroxicam, Cetirizine, Venlafaxine, Paroxetine	Pyrolysis: 10 °C $min^{-1}$ , $N_2$ atmosphere (0.5 $dm^3 min^{-1}$ ), 800 °C, 150 min	T = 25 °C; $C_{adsorbate} = 5 mg L^{-1}$ ; $C_{adsorbent} = 0.02-0.12 g L^{-1}$ ; pH = 10.5; SS = 80 rpm	KM: PSO; IM: Langmuir; $Q_{max} = 7.8 mg g^{-1}$ (oxazepam); 5.82 $mg g^{-1}$ (piroxicam); 8.2 $mg g^{-1}$ (cetirizine); 8.5 $mg g^{-1}$ (venlafaxine); 12.6 $mg g^{-1}$ (carbamazepine); 1.69 $mg g^{-1}$ (sulfamethoxazole); 38 $mg g^{-1}$ (paroxetine)	209	(Calisto et al., 2015)
Paper mill sludge	Diclofenac, salicylic acid, ibuprofen, acetaminophen	Pyrolysis: 800 °C under $N_2$ (0.5 $dm^3 min^{-1}$ ), 150 min	T = 25 °C; $C_{adsorbate} = 100 mg L^{-1}$ ; $C_{adsorbent} = 0.1-2.5 g L^{-1}$ ; pH = 7.6; SS = 250 rpm	KM: PSO; IM: Langmuir-Freundlich; $Q_{max} = 23.4-26.7 mg g^{-1}$ (diclofenac); 12.1-15.1 $mg g^{-1}$ (salicylic acid); 12.7-12.9 $mg g^{-1}$ (ibuprofen); 12.3-15.5 $mg g^{-1}$ (acetaminophen)	209	(Coimbra et al., 2015)
Primary paper mill sludge	Fluoxetine	Activation: KOH, NaOH and $ZnCl_2$ , ratio 1:1 (w/w), 80 rpm, 24 h. Pyrolysis: nitrogen flow, 800 °C (10 °C $min^{-1}$ ), 10 min	T = 25 °C; $C_{adsorbate} = 10 mg L^{-1}$ ; $C_{adsorbent} = 0.025-0.900 g L^{-1}$ ; pH = 9.5; SS = 80 rpm	KM: PSO; IM: Langmuir-Freundlich; $Q_{max} = 28.4-191.6 mg g^{-1}$	592	(Jaria et al., 2015)
Cork powder	Ibuprofen	Chemical activation: $K_2CO_3$ , 1:1 weight proportion. Pyrolysis: 700 °C, 1 h. Physical activation: steam and $N_2$ as carrier flow, 750 °C, 1 h	T = 25-40 °C; $C_{adsorbate} = 20-120 mg L^{-1}$ ; $C_{adsorbent} = 0.67 g L^{-1}$ ; pH = 2-11; SS = 700 rpm	KM: PSO; IM: Langmuir; $Q_{max} = 378 mg g^{-1}$	1060	(Mestre et al., 2007)
Cork powder	Ibuprofen	Chemical activation: $K_2CO_3$ , 700 °C, 1 h. Further physical activation: steam, 750 °C, 1 h	T = 30 °C; $C_{adsorbate} = 90 mg L^{-1}$ ; $C_{adsorbent} = 0.67 g L^{-1}$ ; pH = 4; SS = 700 rpm	KM: PSO; IM: Langmuir; $Q_{max} = 378 mg g^{-1}$	1060	(Mestre et al., 2009)
Industrial pre-treated cork	Ibuprofen, acetaminophen, acetylsalicylic acid, clofibric acid, caffeine and iopamidol	Chemical activation: 1:1 and 1:2 for KOH (2 h) and $K_2CO_3$ (24 h). Physical activation: steam, 800 °C, 1 h	T = 30 °C; $C_{adsorbate} = 20-150 mg L^{-1}$ ; $C_{adsorbent} = 0.67 g L^{-1}$ ; pH = 3-5; SS = 700 rpm	KM: PSO; IM: Langmuir; $Q_{max} = 174.4 mg g^{-1}$	948	(Mestre et al., 2014)
STPs sludge	Gatifloxacin	Activation: $ZnCl_2$ , ratio 5 (sludge):3 ( $ZnCl_2$ ). Pyrolysis: 550 °C, 1 h. Washing: HCl	T = 25 °C; $C_{adsorbate} = 100 mg L^{-1}$ ; $C_{adsorbent} = 5 g L^{-1}$ ; SS = 170 rpm	IM: Langmuir; $Q_{max} = 19.80 mg g^{-1}$	297.5	(Yao et al., 2013)

<sup>a</sup> Whenever more than one adsorbent is produced, presented  $S_{BET}$  refers to the best/higher value obtained in each study. SS – Stirring Speed; KM – Kinetics Model; IM – Isotherm Model;  $C_{adsorbate}$  – Concentration of adsorbate;  $C_{adsorbent}$  – Concentration of adsorbent; FO – Fractionary order;  $K_F$  – Freundlich adsorption constant; PSO – Pseudo-second order;  $Q_{max}$  – Langmuir maximum adsorption capacity.