Waste-based alternative adsorbents for the remediation of pharmaceutical contaminated waters: has a step forward already been taken?

Carla Patrícia Silva[a]*, Guilaine Jaria[a], Marta Otero[b], Valdemar I. Esteves[a], Vânia Calisto[a]

[a]Department of Chemistry and CESAM (Centre for Environmental and Marine Studies), University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal

[b]Department of Environment and Planning and CESAM (Centre for Environmental and Marine Studies), University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal

Abstract (147 words)

When adsorption is considered for water treatment, commercial activated carbon is usually the chosen adsorbent for the removal of pollutants from the aqueous phase, particularly pharmaceuticals. In order to decrease costs and save natural resources, attempts have been made to use wastes as raw materials for the production of alternative carbon adsorbents. This approach intends to increase efficiency, cost-effectiveness, and also to propose an alternative and sustainable way for the valorization/management of residues.

This review aims to provide an overview on waste-based adsorbents used on pharmaceuticals' adsorption. Experimental facts related to the adsorption behaviour of each adsorbent/pharmaceutical pair and some key factors were addressed. Also, research gaps that subsist in this research area, as well as future needs, were identified. Simultaneously, this review aims to clarify the current status of the research on pharmaceuticals' adsorption by waste-based adsorbents in order to recognize if the right direction is being taken.

----

*Corresponding author: E-mail address: patricia.silva@ua.pt

1.   Introduction

1.1 Environmental occurrence of pharmaceuticals

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

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

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

2

important group of emerging contaminants and an impressive number of published

works have focused on their removal from wastewater, which constitutes a great

challenge for the scientific community. Technologies for the removal of

pharmaceuticals from water include physical processes (sorption, membrane filtration),

biological processes (bacteria, enzymes, algae) or advanced oxidation processes (AOPs

- photocatalysis, strong oxidizers, sonolysis) (Hokkanen et al., 2016; Silva et al., 2012).

These technologies differ both in effectiveness and cost and each of them has its own

advantages and limitations.

1.2 Adsorption as a technology for the removal of pharmaceuticals from the environment

Adsorption has been a well-researched process for the removal of

pharmaceuticals from waters (e.g. Akhtar et al., 2016; Cabrita et al., 2010; Mestre et al.,

2007), being considered an efficient and versatile method due to the low initial

investment, operational simplicity, non-selective nature and also for not resulting in the

formation of hazardous products (Akhtar et al., 2016; Rafatullah et al., 2013).

Activated carbon (AC) is widely used as adsorbent for the removal of both organic and

inorganic pollutants, and was already proven to be capable of eliminating selected

pharmaceuticals (e.g. diclofenac, caffeine, bezafibrate, clofibric acid, carbamazepine)

(Coimbra et al., 2016; Sotelo et al., 2014; Sotelo et al., 2012; Ternes et al., 2002). This

preference may be due to AC properties, which include: (i) high surface area (S_{BET};

typically larger than 400 m^2 g^{-1} (Álvarez-Torrellas et al., 2016)); (ii) easy availability in

the market; (iii) unique combination between a highly developed porous network and

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

3. Relation between adsorbents' performance and application costs

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

Consideration should also be given to the process of scale-up for manufacturing, 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_{BET} was in the range 750-800 m^2 g^{-1}.

170 Authors considered that these values were within those observed for commercial ACs

171 and found that higher product yield and S_{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_{BET} up to 800 m^2 g^{-1}. 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

7

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_{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_{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

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

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

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

4.1 Agricultural and vegetable residues: Adsorption of antibiotics

Antibiotics constitute one of the most studied classes of pharmaceuticals in terms of adsorption onto alternative adsorbents (Table 1). This may be due to the fact that these are considered very hazardous compounds whose presence in the environment may result in effects on non-target organisms, which include the concerning bacterial antibiotic resistance (Zheng et al., 2013). Within the class of antibiotics, studies about the adsorption of sulfonamides onto adsorbents produced from agricultural/vegetable wastes are easily found, most of them considering the effect of pH and metal ions on the adsorption patterns. This may be due to the facts that: (i) sulfonamides can be neutral, cationic or anionic, depending on pH, i.e. pH affects the speciation and thus, the π-electron donating aptitude, as well as hydrophobicity, of the adsorbate molecules; and (ii) sulfonamides contain several functional groups allowing a strong interaction between the adsorbate and metal ions present in the aqueous solution (Tan et al., 2015; Xie et al., 2014; Zheng et al., 2013). Very recently, Zhou et al. (2016) investigated the ability of spent mushroom substrate, without any thermal or chemical treatment, to remove sulfa-antibiotics (sulfamethyldiazine, sulfamethazine, sulfathiazole, sulfamethoxazole) from aqueous solution. Their findings indicated that the adsorption capacity of spent mushroom substrate decreased in the order: sulfathiazole > sulfamethoxazole > sulfamethyldiazine > sulfamethazine, which was related to the differences in the chemical structures and functional groups of the antibiotics. Authors evaluated the effect of adsorbent initial concentration and the effect of pH: adsorption capacity increased with the antibiotic initial concentration and decreased as pH increased from 3 to 11. The dependence on pH of the adsorption of sulfamethazine onto 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^{-1}), 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 π–π 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_{BET} of 1524 $m^2\ g^{-1}$ and an adsorption capacity of 455

306   mg g^{-1} (in comparison with 1839 $m^2\ g^{-1}$ and 309 mg g^{-1} for S_{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 mg L^{-1} tetracycline, a

311   concentration below 0.1 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 π-π 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_{BET} (1521

318    $m^2\ g^{-1}$ in comparison with 1102 $m^2\ g^{-1}$ 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 π-π

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 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^{2+}-co-contaminated water since sulfamethoxazole adsorption capacity in the

350 binary system (9 182.74 mg kg^{-1}) was much higher than in the single system (1 827.82

351 mg kg^{-1}). 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^{2+}, slightly improved

353 by Zn^{2+} and improved by Cu^{2+}.

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 ºC) 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 lebbeck* seed ponds 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 lebbeck* seed ponds 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 ºC for 1 h): microwave allowed for the production of an

398   adsorbent with a higher S_{BET} (1434 m^2 g^{-1} in comparison with 1220 m^2 g^{-1}), 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^{-1} in comparison with

401   538 mg g^{-1}).

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_2 (N-bio-adsorbent) and under 7%

415   O_2 + 93% N_2 (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^{-1}, for N-adsorbent and between 214

418   and 286 mg g^{-1}, 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_{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, 17α-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_{BET} (2 m^2 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_{BET} (not higher than 84 m^2 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_{BET} (514 m^2 g^{-1}) in comparison with the previously

464   addressed studies, but not high enough to favourably compare to adsorbents like carbon

465   black (1443 m^2 g^{-1}) or commercial AC (950 m^2 g^{-1}). The adsorption efficiency was

466   negatively correlated with temperature, decreasing with increasing temperature in the

467   range 20-50 ºC, and positively correlated with the adsorbent dose, increasing with

468   increasing dose of adsorbent in the range 25 and 100 mg L^{-1} (for concentrations of

469   adsorbate from 20 to 100 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 17α-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 17α-ethinylestradiol to show strong hydrophobic

512   interactions throughout a wide range of pH values. The low dependence of adsorption

21

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. 17α-

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 π-π 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 ºC. 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^{-1}) which showed a S_{BET} of 5 m^2 g^{-1}. Meanwhile, the commercial AC

537 used by the authors for comparison purposes, presented a higher S_{BET} (1324 m^2 g^{-1}) and

538 displayed a larger MS-222 adsorption capacity (349 mg g^{-1}). In any case, even though

539 S_{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 (pH > pK_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 H$_3$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_{BET} (932 m^2 g^{-1}) and

555 maximum adsorption capacities of 475 and 419 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_{BET} (101 *vs.* 34 m^2 g^{-1}) and a considerably higher pore volume (0.145 *vs.*

571   to 0.098 cm^3 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

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

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

Coimbra et al. (2015) evaluated the adsorption capacity of adsorbents produced by pyrolysis of paper mill sludge in two different matrices – ultrapure water and a STP secondary effluent – and found that this had no impact in the adsorption kinetics, equilibrium being reached quickly (within 200 min) in both matrices for all the tested pharmaceuticals (salicylic acid, diclofenac, ibuprofen and acetaminophen). With the same type of precursor, Jaria et al. (2015) tested different chemical activation agents (KOH, NaOH and $ZnCl_2$) and fluoxetine as adsorbate. Even though highest S_{BET} was observed for the $ZnCl_2$-AC, S_{BET} was not considered to be the key factor in the adsorption process since all the produced materials compared favourably with a commercial AC in terms of adsorption capacities. The same type of precursor (paper mill sludge) but with no chemical or physical activation was also applied on the adsorption of another antidepressant – citalopram (Calisto et al., 2014). Both primary and biological sludge were pyrolysed at different temperatures and residence times (best results for primary sludge pyrolysed at 800 ºC for 150 min) and even though this material did not present an adsorption capacity as high as the AC used for comparison, adsorption was relevant considering that it was a non-activated material. The rapid kinetics and the possible valorization of such a residue were also pointed out by authors as important advantages. The best adsorbent was latter on used to understand the 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_{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 K_2CO_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_{BET} up to 950 m^2 g^{-1}) and physical (S_{BET} up

633 to 750 m^2 g^{-1}) activation. These adsorbents were used for the adsorption of ibuprofen,

634 acetaminophen, acetylsalicylic acid, clofibric 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_{BET} of

645 the produced adsorbents was 891 and 866 m^2 g^{-1} for the cork powder and the peach

646 stones-based adsorbent, respectively, which were slightly lower than the S_{BET}

647 determined for the commercial ACs (1033-1120 m^2 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

5. Critical aspects

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

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

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

6. Conclusions

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

References

1. Ahmed, M.B., Zhou, J.L., Ngo, H.H., Guo, W., Johir, A.H., Belhaj, D., 2017. Competitive sorption affinity of sulfonamides and chloramphenicol antibiotics toward functionalized biochar for water and wastewater treatment. Bioresour. Technol. 238, 306–312

2. Ahmed, M.J., Theydan, S.K., 2012. Adsorption of cephalexin onto activated carbons from Albizia lebbeck seed pods by microwave-induced {KOH} and {K2CO3} activations. Chem. Eng. J. 211–212, 200–207.

3. Ahmed, M.J., Theydan, S.K., 2013a. Microwave assisted preparation of microporous activated carbon from Siris seed pods for adsorption of metronidazole antibiotic. Chem. Eng. J. 214, 310–318.

4. Ahmed, M.J., Theydan, S.K., 2013b. Microporous activated carbon from Siris seed pods by microwave-induced KOH activation for metronidazole adsorption. J. Anal. Appl. Pyrolysis 99, 101–109.

5. Ahmed, M.J., Theydan, S.K., 2014. Fluoroquinolones antibiotics adsorption onto microporous activated carbon from lignocellulosic biomass by microwave pyrolysis. J. Taiwan Inst. Chem. Eng. 45, 219–226.

6. Akhtar, J., Amin, N.A.S., Shahzad, K., 2016. A review on removal of pharmaceuticals from water by adsorption. Desalin. Water Treat. 57, 12842–12860.

7. Alsbaiee, A., Smith, B.J., Xiao, L., Ling, Y., Helbling, W.R.D., 2016. Rapid removal of organic micropollutants from water by a porous β-cyclodextrin polymer. Nature 529, 190–194.

8. Álvarez-Torrellas, S., Rodríguez, A., Ovejero, G., García, J., 2016. Comparative adsorption performance of ibuprofen and tetracycline from aqueous solution by carbonaceous materials. Chem. Eng. J. 283, 936–947.

9. Antunes, M., Esteves, V.I., Guégan, R., Crespo, J.S., Fernandes, A.N., Giovanela, 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 K2CO3: 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 H3PO4
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 cephalexin
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 K2CO3: 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., Esmaieli, 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, 17α-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_3PO_4 and $H_4P_2O_7$
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 π–π 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

1027   Fig. 1: Percentage of studies among those published on the adsorptive removal of

1028   pharmaceuticals by alternative adsorbents dealing with specified pharmaceuticals, type

1029   of treatment and type of precursor. Presented data refers to a population of 63 articles

1030   with publication date in the range 2003-2016.

1031

1032

1033

1034
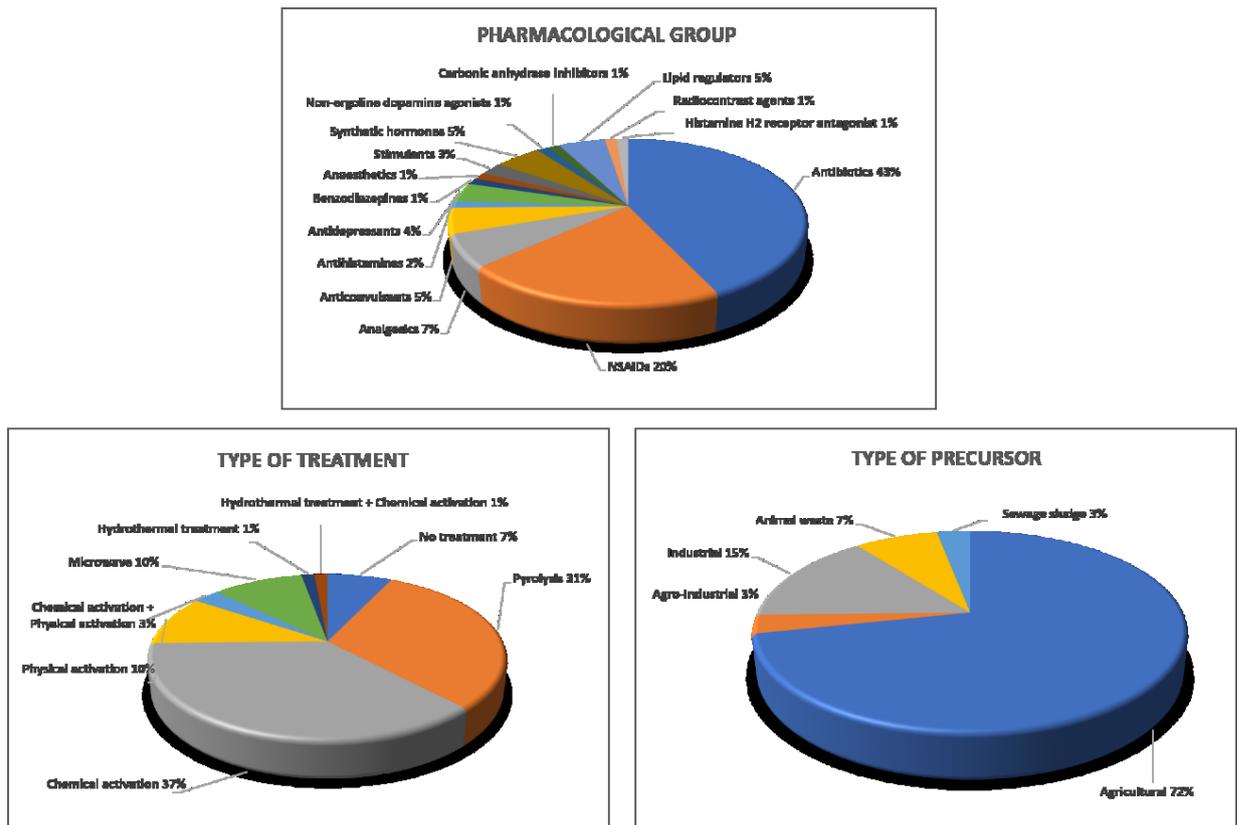
1035   Fig. 2: Percentage of studies within the literature reviewed dealing with the following

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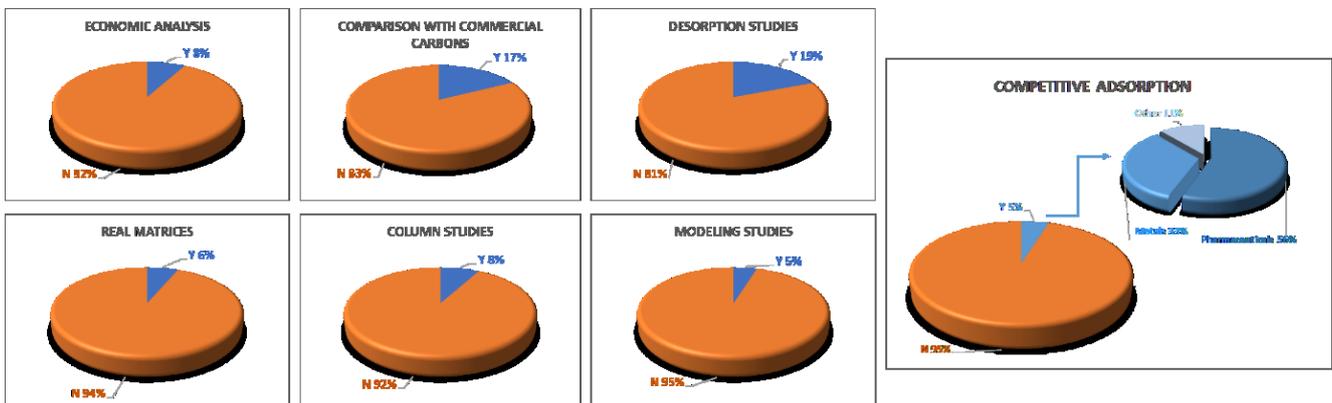
Table 1: Adsorption of antibiotics onto agricultural/vegetable waste-based alternative adsorbents.

Type of waste	Adsorbed pharmaceutical	Adsorbent production	Adsorption conditions	Adsorption parameters and modelling	S_{BET}[a] $(m^2\ g^{-1})$	Reference
Albizia lebbeck	Cephalexin	Microwave-assisted KOH and K_2CO_3 activation	T = 30-50 ºC; $C_{adsorbate}$ = 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)
Siris	Metronidazole	Microwave-assisted K_2CO_3 activation	T = 30-50 ºC; $C_{adsorbate}$ = 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)
Siris	Metronidazole	Microwave-assisted KOH activation	T = 30-50 ºC; $C_{adsorbate}$ = 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)
Albizia lebbeck	Ciprofloxacin and norfloxacin	Microwave-assisted KOH activation	T = 30-50 ºC; $C_{adsorbate}$ = 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 ºC, 6h. Heating: 400 ºC (5 ºC min^{-1}), 4 h, air flow (50 mL min^{-1})	T = 30 ºC; $C_{adsorbate}$ = 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 ºC, 1 h	T = 20 ºC; $C_{adsorbate}$ = 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 ºC 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 ºC; $C_{adsorbate}$ = 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 ºC. Sieving for diameters <150, 150–250, and 250–425 μm.	T = 25 ºC; $C_{adsorbate}$ = 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 ºC, 2 h)	T = 30 ºC; $C_{adsorbate}$ = 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 ºC; $C_{adsorbate}$ = 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 ºC. Modification: Fe(III) and Cu(II)	T = 20 ºC; $C_{adsorbate}$ = 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 ºC; $C_{adsorbate}$ = 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) (*wt:wt*)	$C_{adsorbate}$ = 600 mg L^{-1}; $C_{adsorbent}$ = 1.0 g L^{-1}; pH = 3-10; SS = 220 rpm	KM: PSO; IM: Temkin; K_T = 5.87×10^{-5} L g^{-1}	1524	(Martins et al., 2015)
Walnut shells	Cephalexin	Sieving: 251-354 nm. Chemical activation: ZnCl$_2$, 6 h. Drying: 24 h, 105 ºC, N$_2$ (300 cm^3 min^{-1}), 450 °C (5 °C min^{-1}), 1 h. Washing: 0.05 M HCl	T = 30 °C; $C_{adsorbate}$ = 100-200 mg L^{-1}; $C_{adsorbent}$ = 0.3 g L^{-1}; pH = 6.5; SS = 200 rpm	KM: PSO; IM: Freundlich; K_F = 155.2 mg g^{-1} (L mg^{-1})$^{1/n}$	1452	(Nazari et al., 2016)
Tea waste	Sulfamethazine	Pyrolysis: 300 and 700 ºC (7 ºC min^{-1}, N$_2$ (5 mL min^{-1}). Steam activation:5 mL min^{-1} of steam, 45 min	T = 25 °C; $C_{adsorbate}$ = 0-50 mg L^{-1}; $C_{adsorbent}$ = 1 g L^{-1}; pH = 3-9; SS = 100 rpm	IM: Langmuir; Q_{max} = 33.81 mg g^{-1}	576	(Rajapaksha et al., 2014)
Walnut shells	Sulfamethoxazole	Sieving: 250μm - 500 μm. Washing: deionized water. Drying: 105° C, 48 h. Treatment: ratio 1 g material/10 mL solution, with HCl (0.1 mol L^{-1}) or NaOH (3% *w/w*), 24 and 1 h, respectively	T = 20 °C; $C_{adsorbate}$ = 0.5 mg L^{-1}; $C_{adsorbent}$ = 10 g L^{-1}; pH = 2-8	IM: Freundlich; K_F = 0.47 mg$^{1-1/n}$ g^{-1} L$^{1/n}$)	13	(Teixeira et al., 2012)
Sugar beet pulp and peanut hulls	Tetracycline	Pyrolysis: 850 ºC (10 ºC min^{-1}), N$_2$ (0.5 L min^{-1}). Introduction of steam: 857 ºC (0.7 mL min^{-1}, 80 min). Sieving: 0.25-0.5 mm. Washing: deionized water until pH constant. Drying: 110 °C	T = 25 °C; $C_{adsorbate}$ = 50-300 mg L^{-1}; $C_{adsorbent}$ = 0.30-0.35 g L^{-1}; pH = 3.4-4.2; SS = 300 rpm	IM: Langmuir; Q_{max} = 288.0 mg g^{-1}	829	(Torres-Pérez et al., 2012)
Rice husk, Wood-chips	Levofloxacin	Pyrolysis: 300 and 600 ºC	T = 30 °C; $C_{adsorbate}$ = 100 mg L^{-1}; $C_{adsorbent}$ = 10 g L^{-1}; pH = 2-9	KM: PSO; IM: Langmuir; Q_{max} = 1.49-7.72 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 μm	$C_{adsorbate}$ = 0.5-10 mg L^{-1}; pH = 1−11; $C_{adsorbent}$ = 2 g L^{-1}; SS = 100 rpm	KM: PSO; IM: Langmuir; Q_{max} = 2.1072 mg g^{-1} (sulfamethyldiazine); 1.8103 mg g^{-1} (sulfamethazine); 2.2991 mg g^{-1} sulfathiazole); 2.2133 mg g^{-1} (sulfamethoxazole)	---	(Zhou et al., 2016)

[a] 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.

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^{-1} H_3PO_4, 85 ºC, 6h. Heating: 400 ºC (5 ºC min^{-1}), 4 h, air flow (50 mL min^{-1})	T = 30 ºC; $C_{adsorbate}$ = 100 mg L^{-1}; $C_{adsorbent}$ = 0.3-20 g L^{-1}; SS = 250 rpm	KM: PSO; IM: Guggenheim–Anderson–de Boer; Q_{max} = 239.8 mg g^{-1}	1521	(Álvarez-Torrellas et al., 2016)
Artemisia Vulgaris leaves	Ibuprofen	Weed treatment: 60% (*v/v*) H_2SO_4, 8–12 h. Washing: water until pH 6–7, drying 120 ºC, 6 h. Carbonization at 450 ºC, 30 min, N_2 (3 ºC min^{-1}).	T = 25-45 ºC; $C_{adsorbate}$ = 10 mg L^{-1}; $C_{adsorbent}$ = 0.2 g L^{-1}; pH = 2-8; SS = 200 rpm	KM: PSO; IM: Langmuir; Q_{max} = 16.945 mg g^{-1}	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_2CO_3 (1:1 and 1:3 weight ratio of precursor: K_2CO_3), N_2 flow (5 $cm^3\ s^{-1}$), 700-900 ºC (10 ºC min^{-1}), 0.5-2 h	T = 30 ºC; $C_{adsorbate}$ = 120 mg L^{-1}; $C_{adsorbent}$ = 0.3 g L^{-1}; SS = 700 rpm	KM: PSO; IM: Langmuir; Q_{max} = 270.3-434.8 mg g^{-1} (acetaminophen) 476.2-500.0 mg g^{-1} (caffeine)	1500	(Galhetas et al., 2014)
Agricultural wastes	MS-222	Pyrolysis: 400 ºC, 120 min; 500 ºC, 120 min; or 500 ºC, 10 min (10 Cº min^{-1})	T = 25 ºC; $C_{adsorbate}$ = 250 mg L^{-1}; $C_{adsorbent}$ = 10-50 g L^{-1}; SS = 90 rpm	KM: Double exponential; IM: Langmuir-Freundlich; Q_{max} = 4-34 mg g^{-1}	11	(Ferreira et al., 2015)
Loblolly pine chip	Diclofenac, naproxen, and ibuprofen	Thermal treatment: 300 ºC, 15 min, pure N_2 (N-bioadsorbent), 7% O_2 + 93% N_2 (O-bioadsorbent). Activation: 4 M NaOH, 2 h. Washing: 0.1 M HCl	$C_{adsorbate}$ = 20 μM; $C_{adsorbent}$ = 2 g L^{-1}; SS = 500 rpm	IM: Langmuir; Q_{max} = 214-372 mg g^{-1} (diclofenac); 228-290 mg g^{-1} (naproxen); 286-311 mg g^{-1} (ibuprofen)	1360	(Jung et al., 2015)
Potato peels	Dorzolamide Pramipexole	Activation: KOH. Heating: 600 ºC (25 ºC min^{-1}), nitrogen flow (500 mL min^{-1}), 2 h	T = 25, 45, 65 ºC; $C_{adsorbate}$ = 0-200 mg L^{-1}; $C_{adsorbent}$ = 1 g L^{-1}; pH = 2-12; SS = 160 rpm	KM: PSO; IM: Langmuir; Q_{max} = 66 mg g^{-1} (pramipexole); 60 mg g^{-1} (dorzolamide)	---	(Kyzas and Deliyanni, 2015)
Olive stones	Diclofenac	Impregnation: 10% H_2SO_4 in the ratio 1:1, 24 h. Washing: distilled water. Drying: at room T (> 6 h), then at 110 ºC (24 h). Carbonization: 550 ºC in an oven, 1 h	T = 23 ºC; $C_{adsorbate}$ = 20 mg L^{-1}; $C_{adsorbent}$ = 5 g L^{-1}; pH = 4.2; SS = 500 rpm	KM: PSO; IM: BET; Q_{max} = 0.26 mg g^{-1}	84	(Larous and Meniai, 2016)
Rice straw	Clofibric acid Carbamazepine	No treatment other than sieving and drying	T = 28 ºC; $C_{adsorbate}$ = 100 mg L^{-1}; $C_{adsorbent}$ = 0.5-1.0 g L^{-1}; pH = 3.5-6.8; SS = 180 rpm	KM: PSO; IM: Freundlich; K_F = 3.94×10^{-2} mg g^{-1} (L mg^{-1})$^{1/n}$ (clofibric acid); 7.12×10^{-2} mg g^{-1} (L mg^{-1})$^{1/n}$ (carbamazepine)	---	(Liu et al., 2013)
Mung bean husk	Ranitidine hydrochloride	Carbonization: 550 ºC (55 ºC/15 min), 1 h; increase of temperature to 650 ºC and activation with steam, 1 h	T = 36 ºC; $C_{adsorbate}$ = 100 mg L^{-1}; $C_{adsorbent}$ = 0.1-10 g L^{-1}; pH = 2-12; SS = 40-220 rpm	KM: PSO; IM: Langmuir-Freundlich; Q_{max} = 26.5 mg g^{-1}	405	(Mondal et al., 2015)
Bamboo waste	Ibuprofen and Clofibric acid	Impregnation: 5 M $ZnCl_2$; 1 h; 333 K. Microwave heating: 720 W, 15 min. Washing: deionized water until pH 6−7	T = 25 ºC; $C_{adsorbate}$ = 0-50 mg L^{-1}; $C_{adsorbent}$ = 1 g L^{-1}; pH = 3-9; SS = 100 rpm	KM: PSO; IM: Langmuir; Q_{max} = 278.5 mg g^{-1} (ibuprofen); 229.3 mg g^{-1} (clofibric acid)	722	(Reza et al., 2014)
Coffee, eucalyptus, soybean oil	17α-Ethinylestradiol	Carbonization: 800 ºC (20 ºC min^{-1}), 30 min, under argon	T = 25 ºC; $C_{adsorbate}$ = 2 mg L^{-1}; $C_{adsorbent}$ = 1.5 g L^{-1}; pH = 2-12.5	KM: General order; IM: Langmuir-Freundlich; Q_{max} = 7.88 mg g^{-1}	16.5	(Rovani et al., 2014)
Terminalia catappa shells	Diclofenac	Fruit shell powder with H_2SO_4 (1:1 (*w/v*)); heating, 12 h, 400 ºC	T = 20-50 ºC; $C_{adsorbate}$ = 50 mg L^{-1}; $C_{adsorbent}$ = 50 mg L^{-1}; pH = 5-9; SS = 160 rpm	KM: PSO; IM: Langmuir; Q_{max} = 78.5-96.1mg g^{-1}	514	(Sathishkumar et al., 2015)

| Cocoa shell | Diclofenac Nimesulide | Microwave pyrolysis: nitrogen (200 mL min^{-1}). Acidification: 6 mol L^{-1} HCl under reflux | T = 25-50 °C; $C_{adsorbate}$ = 10-300 mg L^{-1}; $C_{adsorbent}$ = 2.5 g L^{-1}; pH = 7-10; SS = 150 rpm | KM: General order; IM: Langmuir; Q_{max} = 63.47 mg g^{-1} (diclofenac); 74.81 mg g^{-1} (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; $C_{adsorbate}$ = 20 mg L^{-1}; $C_{adsorbent}$ = 6.67 g L^{-1}; pH = 1-6 | KM: PSO; IM: Langmuir; Q_{max} = 2.18 mg g^{-1} | --- | (Villaescusa et al., 2011) |

[a] 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.

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 ºC, 1 h	T = 30 ºC; $C_{dsorbate}$ =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 ºC min^{-1}, N_2 atmosphere (0.5 dm^3 min^{-1}). Different combinations pyrolysis temperature/ residence time: 315 ºC/150 min, 600 ºC/10 min, 800 ºC/10 min, 800 ºC/150 min	T = 25 ºC; $C_{adsorbate}$ = 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 mil sludge	Carbamazepine, Oxazepam, Sulfamethoxazole, Piroxicam, Cetirizine, Venlafaxine, Paroxetine	Pyrolysis: 10 ºC min^{-1}, N_2 atmosphere (0.5 dm^3 min^{-1}), 800 ºC, 150 min	T = 25 ºC; $C_{adsorbate}$ = 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 ºC under N_2 (0.5 dm^3 min^{-1}), 150 min	T = 25 ºC; $C_{adsorbate}$ = 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 ºC (10 ºC min^{-1}), 10 min	T = 25 ºC; $C_{adsorbate}$ = 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 ºC, 1 h. Physical activation: steam and N_2 as carrier flow, 750 ºC, 1 h	T = 25-40 ºC; $C_{adsorbate}$ = 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 ºC, 1 h. Further physical activation: steam, 750 ºC, 1 h	T = 30 ºC; $C_{adsorbate}$ = 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 ºC, 1 h	T = 30 ºC; $C_{adsorbate}$ = 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 ºC, 1 h. Washing: HCl	T = 25 ºC; $C_{adsorbate}$ = 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)

[a] 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.