



# Synthesis of activated carbon from food waste

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## Abstract

Activated carbon is a material for many adsorption applications, combining low-cost and high-quality properties. Many sources of activated carbon have been reported including fly ash, lignite, coal, petroleum pitch, coconut shell and rice husk. Lignocellulosic biomass gains more and more attention due to the fact that it is easily obtained from a wide range of agricultural products and their by-products. Here, we review lignocellulosic-based activated carbon with focus on synthesis, characterization and performance for water decontamination and industrial wastewater treatment; examples for gas phase pollutants are given. Furthermore, the effect of various parameters, such as lignocelluloses source and activation temperature on final properties, is discussed. Special attention is given to activated carbons based on some of agricultural wastes/by-products of the Mediterranean region.

**Keywords** Activated carbons · Green materials · Wastewaters · Adsorption · Pollutants · Dyes · Heavy metals

## Introduction

Activated carbon is a well-known material used in a large number of environmental applications; namely water and wastewater treatment, gas filters and green gases capturing are some of them. High surface area, a microporous structure, and a high degree of surface reactivity make activated carbon materials versatile adsorbents, particularly effective in the adsorption of organic and inorganic pollutants from aqueous media (Ruiz et al. 2017).

On the other hand, the growing environmental awareness of the society, along with the subsequent international directives on this topic, force scientific community to embrace “green” thinking, hence implement Green Technology. Green technology, also referred as environmental technology or clean technology, is an encompassing term; it deals with using science and technology in order to protect the environment. A lot of techniques fall under this term such as the use of green chemistry, environmental monitoring, and more. Specifically, green chemistry is defined as the design of chemical products and processes to reduce or eliminate the use and generation of hazardous substances (Sheldon

2008), governed by 12 principles. One of them is the usage of renewable feedstock for material synthesis (Anastas and Eghbali 2010). The major renewable feedstock on the planet, both for material and energy, is biomass, the material available from living organisms. This includes wood, crops, agricultural residues, food, etc. (Fornasiero and Graziani 2011; Kamm et al. 2000). According to Environmental and Energy Study Institute, a list of some of the most “common” biomass feedstock is comprised of (1) grains and starch crops (sugar cane, corn, wheat, sugar beets, industrial sweet potatoes), (2) agricultural residues (corn stover, wheat straw, rice straw, orchard pruning), (3) food waste (waste produce, food processing waste), (4) forestry materials (logging residues, forest thinning), (5) animal by-products (tallow, fish oil, manure), (6) energy crops (switch grass, hybrid poplar, willow, algae) and (7) urban and suburban wastes (municipal solid wastes, lawn wastes, wastewater treatment sludge, urban wood wastes, disaster debris, trap grease, yellow grease, waste cooking oil). Biomass derived from plants, the so-called lignocellulosic biomass, is the most abundant and bio-renewable biomass on earth (Isikgor and Becer 2015).

In recent years, scientific interest on lignocellulosic precursors for activated carbon production, and its utilization including storage of gases as well as catalytic reactor, has been increased (Fiuza et al. 2015; Ruiz et al. 2017), leading to the replacement of less cost-effective materials such as metal organic frameworks (Kuppler et al. 2009; Llewellyn

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et al. 2008; Sumida et al. 2012) or less eco-friendly (in sense of production of raw material or activation treatment) such as fly ash (Lu and Do 1991).

Activated carbon is the generic term used to describe a family of amorphous carbonaceous adsorbents with a highly crystalline form and a well-developed internal pore structure. Any organic material can be the starter material (precursor) of activated carbon after being subjected to carbonization and activation of its organic substances (Bansal and Goyal 2005). The major components of woody plants, as well as grasses and agricultural residues are three structural polymers; lignin (10–25%), hemicelluloses (20–30%) and cellulose (40–50%) (Pérez et al. 2002). Apart of these three components, which vary regarding the source, there are also some minor, non-structural components, such as proteins, chlorophylls, ash, waxes, tannins (in the case of wood) and pectin (in most of fibers). Among the three fractions of the lignocellulosic materials, lignin has been identified as the main component in lignocellulosic biomass responsible for the adsorption process (Mohamad Nor et al. 2013). Nowadays, it is possible to find numerous research papers devoted to the synthesis, characterization and applications of novel precursors to produce activated carbon. Except from the treatment conditions, the biomass source determines many of the properties that the final material demonstrates. In fact, although the lignin is considered to be the major contributor for activated carbons production, properties such as the mean pore size versus the specific porous volume are effected by all precursor's components (Cagnon et al. 2009).

In the context of the present review, as agricultural wastes, residues of agricultural products and by-products (i.e., peels, stems and fruit core) are considered. The following sections describe the treatment and activation processes of carbonaceous materials of various lignocellulosic precursors. Furthermore, a comparison of activated carbon's final properties due to treatment conditions as well as the source is provided too. Related industrial applications are discussed briefly.

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## Lignocellulosic biomass for activated carbon preparation

The production of activated carbons from lignocellulosic sources is a two-phase process; it involves carbonization at low temperatures (700–800 K), in the absence of oxygen, to eliminate volatile materials, and subsequent activation at higher temperatures (1100–1300 K) to increase the porosity and the surface area of the solid. The process of activation

can be carried out in three ways: (1) with chemical agents (e.g., KOH, H<sub>3</sub>PO<sub>4</sub>, ZnCl<sub>2</sub>), known as chemical activation; (2) with CO<sub>2</sub>, air or water vapor for physical or thermal activation or; (3) these two methods combined (Marsh and Rodríguez-Reinoso 2006). Although physical activation is a low-cost process with a lower environmental impact, chemical activation is rather preferred because of porosity improvement (adsorption capacity) of the final material (Rodríguez-Reinoso and Molina-Sabio 1992).

Recent studies have shown that extraction of valuable solutions from agricultural by-product could also act as reagents of biochar activation, minimizing further the cost and the impact to the environment (Treviño-Cordero et al. 2013). To this end, the pre-treatment process of biomass should follow (among others) the following criteria: (1) affordable with low energy and resource consumption, (2) low water and chemical consumption in order to minimize or even eliminate liquid waste stream, (3) low operation risk and safe to operate as well as (4) low cost of the construction materials in order to be considered cost effective and eco-friendly. It is worth to mention that the challenge is to develop adsorbents which are not only cost effective and environmentally friendly, but also possess high efficiency, selectivity, regeneration rate and cycles (Ince 2014). There is massive literature upon the effect of preparation conditions on the physicochemical properties of the produced material, e.g., surface area, pore size distribution. Another critical factor is the physicochemical properties of the precursors itself; depending on weather conditions, harvesting methods and even on the season that it is collected, agricultural precursors' properties such as initial moisture, oxygen content, and derived components fraction of cellulose, hemicellulose, lignin may vary (Balan 2014; Huggins et al. 2011).

## Synthesis route

Activated carbons have a highly developed porosity and an extended interparticulate surface area. As it was already mentioned, preparation involves two main steps: the carbonization of the carbonaceous raw material at temperatures below 800 °C in an inert atmosphere and the activation of the carbonized product. Thus, all carbonaceous materials can be converted into activated carbon, although the properties of the final product will be different, depending on the nature of the raw material used, the nature of the activating agent, and the conditions of the carbonization and activation processes.

From the economical aspect, biomaterials are promising precursors for adsorbents because of their abundance. To preserve their cost-effective treatment, especially regarding large-scale applications, the source should be taken into account. For instance, although some agricultural wastes [i.e., coconut shells (Nandeshwar et al. 2016; Shrestha et al.

2013), hazelnut husk (Imamoglu and Tekir 2008; Kwiatkowski and Broniek 2017; Milenković et al. 2009), rice husk (Foo and Hameed 2011; Menya et al. 2018; Rwiza et al. 2018) and others] are acknowledged as highly efficient precursor, in many cases it has to be imported, resulting in an increase of cost. Therefore, agricultural/household residuals, including fruit and vegetable peels, are considered as good alternatives. Moreover, regions such as Mediterranean can take advantage of residuals produced from regional commodities like olive or peach stones. Properties of such agricultural wastes are collected from recent studies. Table 1 presents some indicative cases of the most investigated agricultural wastes as activated carbon precursors regarding only the obtained surface area; properties such as pore size and contaminant uptake are omitted because they depend mostly on synthesis process conditions. Effect of process conditions will be discussed in a following section.

### Carbonization process

Carbonization of biomass has a number of advantages over common biological treatments regarding time and required equipment. Also, high process temperatures can destroy pathogens and such potential organic contaminants as pharmaceutically active compounds that could be present (Libra et al. 2011). On the other hand, the preparation of activated carbon is usually conducted at relatively high temperatures; consequently, there is also a considerable risk of overheating, leading to complete combustion of the carbon (Foo and Hameed 2011). Besides of pyrolysis in furnaces, there have been developed other carbonization methods such as hydrothermal carbonization and microwave heating. When compared to fermentation and anaerobic digestion, hydrothermal carbonization is referred to as the most exothermic and efficient process for carbon fixation. In addition, some feed stocks are toxic and cannot be converted biochemically. Microwave technology is gaining importance as a promising technology for research and industrial applications. Microwave heating offers a potential means of cost reduction as it is capable of reducing the heating period, energy and gas consumption. Additionally, microwave irradiation may

promote rapid and precise temperature control and compact equipment size. However, application of microwave technology for carbonization process has not been implemented until recently; hence, there are very few studies that report its use for preparation of activated carbon (Foo and Hameed 2011; Thue et al. 2016).

### Activation process

Physical activation of carbonized material involves the implementation of hot gases or water vapor steams (Román et al. 2008; Vivo-Vilches et al. 2015; Zhang et al. 2014). This step generally is carried out in the presence of an inert gas to convert this organic precursor to primary carbon, which is a mixture of ash, tars, amorphous carbon, and crystalline carbon. Another approach is activation/oxidation where high temperature in the presence of carbon dioxide, steam is required. Undesirably, in the step of carbonization, some decomposition products or tars are deposited in the pores (Maciá-Agulló et al. 2004; Rodríguez-Reinoso and Molina-Sabio 1992).

Chemical activation, on the other hand, prohibits the formation of tar; in this way a carbonized product with a well-developed porosity may be obtained in a single operation (Kalderis et al. 2008; Lozano-Castelló et al. 2001). Chemical activation takes place prior to carbonization wherein the agricultural waste is impregnated with certain chemicals, which is typically an acid such as  $H_3PO_4$ , a strong base such as KOH, and NaOH or a salt such as  $ZnCl_2$ . Then, the agricultural precursor is carbonized at lower temperatures (450–900 °C). There are studies where the carbonization/activation step proceeds simultaneously with the chemical activation (Ludwinowicz and Jaroniec 2015; Milenković et al. 2009). It is also supported that the chemical incorporated to the interior of the precursor particles reacts with the products resulting from the thermal decomposition of the precursor, reducing the evolution of volatile matter and inhibiting the shrinking of the particle; in this way, the conversion of the precursor to carbon is high, and once the chemical is eliminated after heat treatment, a large amount of porosity is formed (Kumar and Jena 2016; Shamsuddin et al. 2016). Chemical activation is preferred over physical activation owing to the lower temperature and shorter time needed for activating the material. The chemical activation method presents many advantages over the physical activation method, and therefore, it has been employed in many studies when the preparation of activated carbon from agricultural wastes is concerned. In addition, activated carbon obtained by chemical activation exhibits a larger surface area and a better developed mesoporosity than physical activation (Aygün et al. 2003; Valix et al. 2004). On the other hand, from the economical as well as environmental point of view, chemical activation requires the use of agents that raises the

**Table 1** Surface area of various agricultural wastes abundant in Mediterranean region

Precursor	Surface area (m <sup>2</sup> /g)	References
Orange peels	1090	Fernandez et al. (2014)
Orange peels	1477	Xie et al. (2014)
Olive stones	1031.5	Román et al. (2008)
Olive stones	790.25	Kula et al. (2008)
Peach stones	608	Duranoğlu et al. (2010)
Potato peels	904–1041	Kyzas et al. (2016)

total cost of the production process (Dias et al. 2008; Zhang et al. 2004).

As it was mentioned in previous section, the suitability of an activated carbon for different applications is a matter of many parameters. Although carbonization/activation conditions play the most important role in adsorbent's efficiency, they are not the only contributors in the porous structure of activated carbon; the original nature and structure of the precursor is also significant. In order to determine and evaluate those factors, proximate and ultimate analyses of the precursor are routinely performed in the related literature (Jin et al. 2012; Koay et al. 2013).

## Characterization of activated carbon

In general, material characterization should be fit for purpose; that means that the selection of characterization methodology should be based upon what kind of information is important for the specific use of the subjected material. As it was mentioned, characterization of adsorbents derived from lignocellulosic-based materials should not only be conducted on the final product but on the precursor of the activated carbon as well. Analysis of raw material determining moisture, percentage of main polymeric structure as well as density and other compounds presence is required. Proximate analysis conducted prior to carbonization phase and ultimate analysis after that, provide important information about the properties of the final product (Fu et al. 2013; González and Pliego-Cuervo 2013; Kumar and Jena 2016; Wilkins et al. 2001).

## Effect of precursor

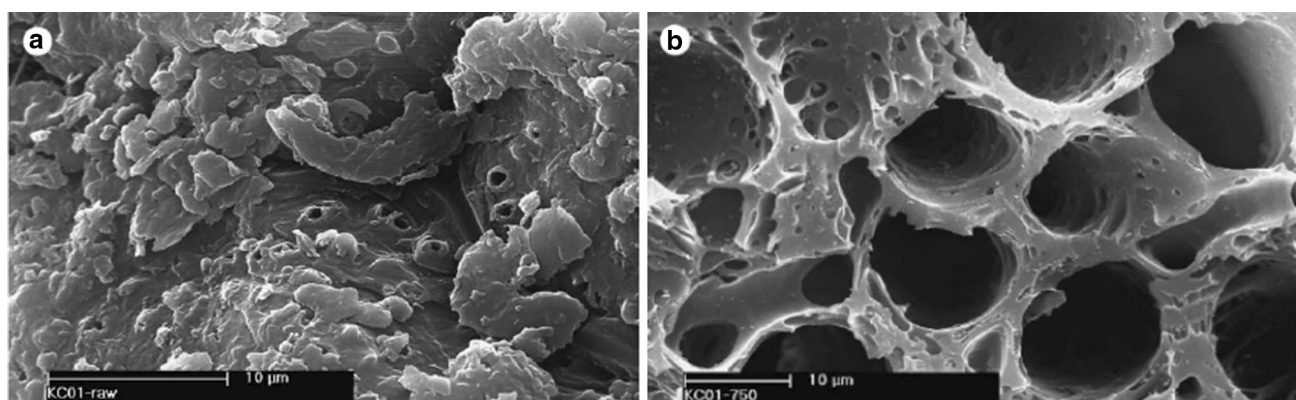
The initial content of volatile matter in the precursor is a key factor for the properties of the obtained activated carbon.

Although not very recent, the work of Şentorun and his associates (Şentorun-Shalaby et al. 2006) is a good example of the above statement. In this work, it was investigated whether and how the initial sulfur content of activated carbon precursor affects the obtained properties of the final material. In order to achieve different sulfur content for apricot stones from the same region, they dried the stones at two different environments prior activation process; sun-dried and SO<sub>2</sub>-dried apricot stones. Although activation conditions were kept the same for both cases, structural and adsorption properties differ. As it is illustrated in Figs. 1 and 2, the two pre-treatment methods resulted with very different materials regarding porosities and internal microstructure. The highest BET surface area (1092 m<sup>2</sup>/g) was obtained from the activated carbon derived from low sulfur content (0.04%) apricot stone with a particle size range of 1–3.35 mm at the activation conditions of 800 °C for 4 h.

## Effect of synthesis conditions

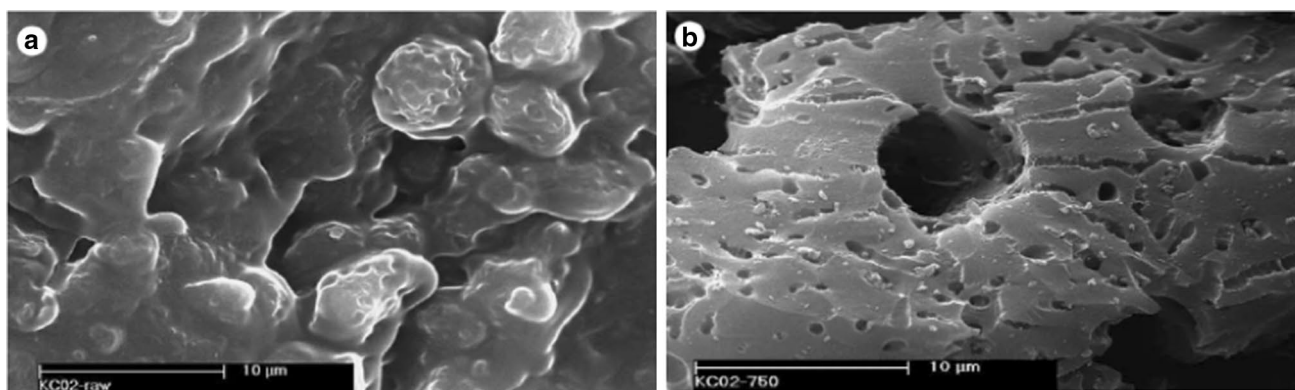
Temperature during carbonization phase plays also a significant role in the final material's properties. Biochar yield increases with a decrease in pyrolysis temperature, an increase in the residence time and a preferable low heating rate (Tripathi et al. 2016). In a recent study, Palanisamy et al. reported that biochar of *C. vulgaris* prepared at higher temperatures (450–600 °C) contained a higher proportion of organic matter (C, H and N) than those produced at lower temperatures.

Another example is given by Kyzas et al. where metal ion removal by activated carbon from potato peels was investigated (Kyzas et al. 2016). In this work, potato peels were cleaned and dried for 24 h for moisture reduction. The activation agent used was H<sub>3</sub>PO<sub>4</sub>. All conditions kept same (amount of dried material, activation agent etc.) and three samples were produced at different heating temperature



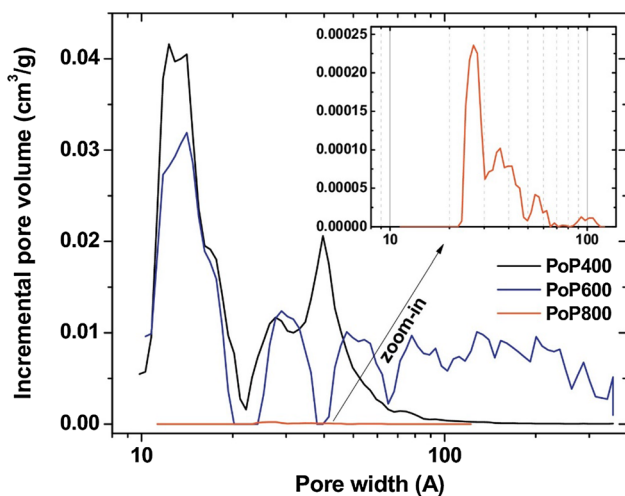
**Fig. 1** Scanning electron microscopy (SEM) micrograph of sun-dried apricot stone **a** prior activation, **b** after activation; prior activation the sun-dried raw material presents almost no porosity and a thick wall

structure while after activation a wide, well distributed porosity is observed. Reprinted with permission by Elsevier (Şentorun-Shalaby et al. 2006)



**Fig. 2** Scanning electron microscopy (SEM) micrographs of  $\text{SO}_2$ -dried apricot stone **a** prior activation, **b** after activation; high ash and sulfur content of the precursor leads to the appearance of a non-porous cloudy surface **a** while activated material does not pre-

sent a well-developed porous network compared to sun-dried material (Fig. 1). Reprinted with permission by Elsevier (Şentorun-Shalaby et al. 2006)



**Fig. 3** Pore size distribution curves of potato peels (denoted as PoP in the graph) carbons activated at 400, 600, and 800 °C. PoP400 is defined by micro–meso porosity while PoP600 curve shows a structure combined of all three groups of pores. Reprinted with permission by Elsevier (Kyzas et al. 2016)

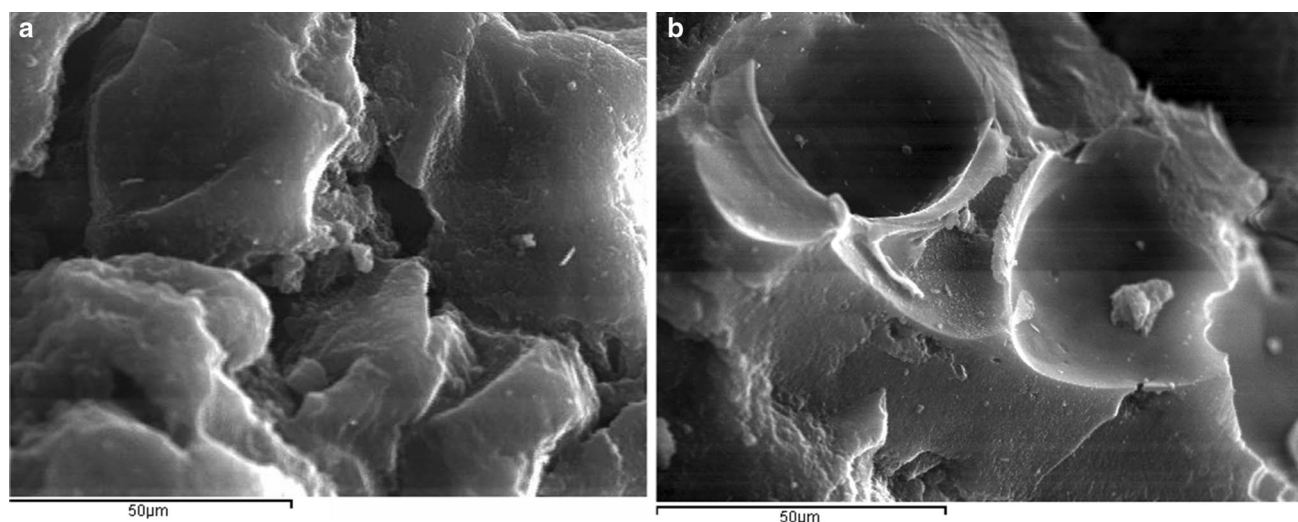
(400, 600, 800 °C). Comparison of the samples regarding, among others, the surface area of the material, revealed that the higher surface area resulted was for the sample treated at 600 °C, while at higher temperature the surface area of the sample was less than  $1 \text{ m}^2/\text{g}$ . Size distribution analysis confirms the aforementioned results as it is shown in Fig. 3. Low surface area of the sample treated at 800 °C is attributed to overheating of the sample, hence leading to precursor's combustion.

The two samples were further examined for their textural properties. Scanning Electron Microscopy (SEM) (Fig. 4) revealed that potato peels treated at 600 °C perform larger porous. Relevant studies including many

different lignocellulosic materials report the influence of treatment conditions on the produced activated carbons.

Köseoğlu and Akmil-Başar (2015) report the effect of treatment temperature on orange peel activation. Chemical activation using zinc chloride ( $\text{ZnCl}_2$ ) and potassium carbonate ( $\text{K}_2\text{CO}_3$ ) was performed. The activation temperatures and impregnation ratios were selected at the range of 500–1000 °C and 1:1, respectively. The carbon content of activated carbons resulted 70%, while BET surface area of activated carbons prepared with  $\text{K}_2\text{CO}_3$  and  $\text{ZnCl}_2$  activation is 1352 and  $1215 \text{ m}^2/\text{g}$ , respectively. An increase in the temperature for both  $\text{K}_2\text{CO}_3$  and  $\text{ZnCl}_2$  led to a decrease in the yields of the activated carbons. The overall yield of material estimated to be greater for activated carbons by  $\text{ZnCl}_2$  than those activated by  $\text{K}_2\text{CO}_3$ , although it does not play any role in performance.

Besides, the activation temperature, the time and heating rate are also important preparation variables for obtaining activated carbon with specific characteristics (Yorgun and Yildiz 2015). According to literature, chemically activated carbon materials can developed surface areas ranging from very poor surface area to as high as  $3000 \text{ m}^2/\text{g}$ , a broad range of pore size distribution from a few nm to a few micrometers and pore volume from 0.1 to  $2.5 \text{ cm}^3/\text{g}$ . From released scientific reviews, it is possible to note that activation with alkaline agents produces the highest surface area values. Secondly, treatment with acids and acid salts induce also the formation of high surface areas (Köseoğlu and Akmil-Başar 2015; Kumar and Jena 2016; Shamsuddin et al. 2016; Yorgun and Yıldız 2015). Additionally, depending on the activation agent, the carbon surface exhibits numerous functional groups, mainly acidic, which favor specific interactions allowing it to act as an ionic interchanger (Bharathi and Ramesh 2013; Toles et al. 2000).



**Fig. 4** Scanning electron microscopy (SEM) micrographs of surface morphology of potato peels samples; **a** potato peels treated at 400 °C, **b** potato peels treated at 600 °C. Comparing the two samples

the effect of treatment temperature is obvious; potato peels treated at 600 °C perform larger porous. Reprinted with permission taken by Elsevier (Kyzas et al. 2016)

At this point, it is possible to note that physically activated carbons have smaller surface area values than those obtained by chemical (i.e.,  $H_3PO_4$ , KOH, NaOH and  $ZnCl_2$ ) activation. However, there have been reported high surface area adsorbents from lignocellulosic precursors activated physically (Maciá-Agulló et al. 2004).

## Adsorption applications

### Liquid phase

Various industrial processes such as mineral processing, metal mining, tanning in the leather industry, dyeing in textile industry and pigment manufacture, contribute in the discharge of water pollutants which can be classified as inorganic (heavy metals, sulfates, nitrates), organic (dyes, phenols, pesticides) and biological (viruses, bacteria). There have been developed many technologies and processes utilized to remove chemical pollutants from various aqueous matrices. Drawbacks associated with some of the processes include: low removal efficiencies, high cost of regeneration, sludge deposition, high energy demand and high reagent requirements. Agricultural-based adsorbents are promising alternatives to the conventional decontamination materials mainly due to the high efficiency they present at almost zero cost concerning their synthesis.

### Dyes

Dyes are widely used in industries such as textiles, rubber, plastics, printing, leather, cosmetics etc., to color their

products. As a result, they generate a considerable amount of colored wastewater. Besides esthetic issues, dyes can have acute and/or chronic effects on exposed organisms depending on the exposure time and dye concentration.

AbdurRahman et al. (2013) studied the removal of various dyes from textile wastewater by adsorption on orange peels. Obtained results indicate that the adsorption of dyes onto orange peels is influenced by pH values, amount of adsorbents and contact time. The adsorption of dyes onto orange peels follows the Langmuir isotherm model. Additionally, it is reported that for higher removal of dyes from textile effluents, adsorbent dose of 1.5 g was favorable. The uptake of the dye increased with increasing contact time and the optimum contact time was 2 h. Also, the adsorption was found to be higher for pH 7. Authors concluded that even though the removal efficiency of orange peels is not much higher than other bio-adsorbents, it is preferred for its availability.

Another work has been conducted for examining the removal of Methylene blue from aqueous solution (Amela et al. 2012) by biosorption on banana and orange peels. The maximum values of adsorption capacities for activated banana peel was 19.671 and 18.647 mg/g for natural banana peel for pH 4–8 at 20 °C. The suitability of the adsorbent was tested by fitting the adsorption data with four isotherms, namely Freundlich, Langmuir and Temkin. The characteristic parameters for each isotherm have been determined. The Freundlich equation represented the best fit of experimental data for activated banana peel than the other isotherm equations, and Langmuir equation described the adsorption of natural biosorbent.

Valorization of olive stones as an agricultural waste into an efficient granular activated carbon for the removal of methylene blue in batch and fixed bed modes from aqueous solutions was proposed by Benallou Benzekri et al. (2018). The activated carbon preparation was carried out in two steps: an impregnation with 50% phosphoric acid at 170 °C for 2.5 h followed by physical activation using steam at 750 °C. The synthesized activated carbon was compared to a commercial one. Volumetric method for surface area determination by N<sub>2</sub> adsorption at 77 K for both samples revealed a surface area of 1031.5 of the olive stone activated carbon and 1029.2 m<sup>2</sup>/g. of the commercial one. The Langmuir model was found to describe correctly the isothermal adsorption of Methylene blue for both adsorbents and resulted in adsorption capacities of 107 for the synthesized and 121 mg/g for the other.

Survey on the feasibility of the biosorption of two acid dyes (Acid blue 113 and Acid black 1) from aqueous solution using biomass prepared from potato peel waste was attempted by (Hoseinzadeh et al. 2014). Adsorption isotherms were constructed, and the kinetics of dye adsorption was studied. The maximum biosorption was observed at a pH of 2 and 3 for Acid blue 113 and Acid black 1, respectively. The biosorption of two dyes increased with increasing contact time, while equilibrium was reached approximately after 2 h. Pseudo-second-order kinetic and the Langmuir isotherm model was shown to have better fit for the adsorption of Acid blue 113 and Acid black 1 on used potato peel waste.

## Heavy metal ions

The release of heavy metals into our environment is still large. In certain areas of the world, it is even increasing. The pollution of water resources due to the disposal of heavy metals has been an increasing worldwide concern for the last few decades. It is well known that some metals can have poisonous or otherwise toxic to human beings and ecological environments, include chromium, antimony, copper, lead, mercury, cadmium, manganese. Studies on heavy metal adsorption by activated carbon from agricultural wastes have shown remarkable removal efficiency even compared to commercial ones (Babel and Kurniawan 2004; Kołodziejka et al. 2017). Among others, most common metals constituting in water pollution are arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), mercury (Hg) and their ions. Related studies are presented for heavy metals adsorption by activated carbons from various fruit and vegetable peels as well as stones that can be found abundant in Mediterranean region.

According to Khalfaoui and Meniai (2012), orange peels can efficiently remove copper ions from aqueous solutions. In fact the use of orange peels without any pretreatment leads at copper retention percentage of 75%,

whereas percentages over 99% could be achieved by means of chemical activations with sulfuric acid, caustic soda, methanol and acetic anhydride. Remarkably, results showed that saturation was reached after 10 and 5 min, for the cases of no pretreated and the chemical activated orange peels, respectively. The pH study indicated that a value between 4 and 6 seemed to be the most adequate. The results also show that the copper initial concentration value has an influence on the retention capacity for the natural solid support. The sorption kinetic study showed that the process could be considered of a pseudo-second order, whereas the obtained equilibrium data were best fitted to the Freundlich model.

Liu et al. (2013) have conducted experiments of cysteine-modified orange peel for the removal of Cu(II) from aqueous solutions compared to diethylenetriamine-modified orange peel. Both materials were systematically evaluated via their capabilities for adsorbing Cu(II), including the key influential parameters such as initial pH, contact time and initial Cu(II) concentration. This work suggests that the sorption of Cu(II) onto both materials fits well with the pseudo-second-order equation, and the corresponding sorption isotherm can be classified to a Langmuir. The maximum capacities of both materials for adsorbing Cu(II) were found to be 95.23 and 83.68 mg/g, respectively, about three times higher than that of unmodified orange peels. The sorption efficiency of cysteine-modified orange peel drops by merely about 3% after 5 cycles, implying a promising usage in the removal of Cu(II) from wastewater in practice.

The performance of a microporous activated carbon prepared chemically from olive stones for removing Cu(II), Cd(II) and Pb(II) from single and binary aqueous solutions was investigated by Bohli et al. (2015). Adsorption kinetic rates were found to be fast and kinetic experimental data fitted very well the pseudo-second-order equation. The adsorption isotherms fit the Redlich–Peterson model very well and maximum adsorption amounts of single metal ions solutions follow the trend Pb(II) > Cd(II) > Cu(II). In another work, Bohli and Ouederni (2016) modified surface structure of activated carbon from olive stones using ozone (O<sub>3</sub>) in the gaseous phase and in liquid phase using nitric acid (HNO<sub>3</sub>) were examined. The activated carbon exhibits a high surface area of 1194 m<sup>2</sup>/g and shows a predominantly microporous structure. They also revealed that acidic treatment lead to fixation of high amount of surface oxygen functional groups, thus making the carbon surface more hydrophilic. The obtained data from Co(II), Ni(II), and Cu(II) heavy metal ions removal were well fitted to the Redlich–Peterson and Langmuir equation. Further investigation of metal ions removal ability from binary systems presented an important maximum adsorbed amount as compared to single systems.

## Gas phase

Although there is a great amount of literature for lignocellulosic activated carbons used efficiently in aqueous solution, development of such adsorbents for gas phase applications is in immature level. The main drawback for gas phase applications of lignocellulosic-based activated carbon was considered the low surface area of produced material. Nowadays, research on surface modification of activated carbon from agricultural precursors has open the way for efficient application in air pollution control (Mohamad Nor et al. 2013). The potential use of those adsorbents as catalysts for flue gas, gas storage material of CH<sub>4</sub>, CO<sub>2</sub> and other has attracted scientists' interest for further study. The first reports for efficient CO adsorption (Grigor'ev et al. 2003), CO<sub>2</sub> capture (Fiuza et al. 2015) and other flue gas compounds (H<sub>2</sub>S, NO<sub>x</sub>) (Ghouma et al. 2017) by activated carbon have been already released.

Among the various harmful gases, nitrogen oxides (NO<sub>x</sub>) have a negative impact through the smog and acid rain formations as well as the decrease of the superior ozone layer (Blondeau et al. 2005; Wilkins et al. 2001). The most recent work for NO<sub>x</sub> adsorption from automotive gas exhaust was conducted by Ghouma et al. (2017). In this study, adsorption of NO<sub>2</sub> at room temperature and very low concentration was performed onto three different activated carbons. The importance of textural and surface properties was realized. The results obtained during the different experiments indicate that both of these properties are responsible of NO<sub>2</sub> uptake and reduction to NO. The reduction rate of NO<sub>2</sub> is found to be very high when the activated carbon is prepared by H<sub>3</sub>PO<sub>4</sub> activation. Adsorption capacity was found to be higher for one of the subjected activated carbons, attributing this fact to the presence of high amount of basic groups. According to the interpretation of NO<sub>2</sub> breakthrough curve, AC-H<sub>2</sub>O sample has a mesoporous domain, which enables a better diffusion of NO<sub>2</sub> inside the activated carbon particles. The particular study is considered to be the only that examines NO<sub>x</sub> adsorption onto lignocellulosic-based activated carbon.

## Conclusion

Available literature and studies upon lignocellulosic-based activated carbon was reviewed with emphasis on agricultural by-products mainly of Mediterranean region. Activation methods have been introduced, while advantages and disadvantages of each have been presented as well. Effects of various parameters on final material's properties have been presented and discussed. As it is reported, pH and initial pollutant concentration play important role in adsorption efficiency. Other parameters that influence the overall

performance are the origin of the precursors, pre-treatment and activation conditions as it were observed from the obtained results. This chapter focus on orange, banana and potato peels, olive and apricot stones; all important parameters of their efficiency are discussed and related results are shown. The majority of the cited studies concern activated carbon for dyes and metal pollutants removal, while there are a few researches upon applications for gas phase pollution. Although in some of the case physicochemical properties, and especially adsorption capacity, are not as high as that of the relevant commercial materials, agriculture by-products still seem to be the best alternative for adsorption processes.

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