Production and applications of activated carbons as adsorbents from olive stones

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Abstract

Olive stones have been widely used as a renewable energy biowaste source. As they are rich in elemental carbon (40–45 wt%), much research focussed on effectively converting olive stones, as precursors, into activated carbon adsorbents. However, only a few studies have concentrated on summarising the various techniques used to produce activated carbon from olive stone. This article reviews the research undertaken on the production and application of activated carbon as an adsorbent from olive stones for wastewater treatment. Various physical, chemical and physico-chemical treatments to remove heavy metals, organics and dyes are discussed, and the resultant adsorption capacities are reported. In several cases, very high adsorption capacities are recorded. Finally, the future prospects of these materials as adsorbents are discussed, and after further development work, olive stone-derived activated carbons have great potential especially in the area of organic polluted wastewaters.

Abbreviations

AC   Activated carbon
AOP   Advanced oxidation processes
MB   Methylene blue

1 Introduction

The term 'activated carbon' or AC defines a category of amorphous carbonaceous materials with high porosity and internal surface area. Activated carbon can be produced from any carbonaceous material, and until recently, anthracite and bituminous coals have been the major sources. Activated carbons are the most widely used adsorbents for the treatment of wastewaters and emissions.

Environmental awareness has also shaped the manufacturing of activated carbons by introducing the concept that normal everyday waste materials, such as agricultural by-products and old tyres [1], are potential precursor sources of

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activated carbon. Nowadays, the sources of activated carbon are extensive and are ever expanding. Any low-cost material with a high carbon content and low in inorganics content can be used as precursors to produce activated carbon [2–5]. Most of the literature refers to the production of active carbons from coal [6], bamboo [7–10] and other lignocellulosic materials [11–14]. Activated carbon is the most widely used adsorbent because of its low cost, exceptionally high porosity, tuneable pore size and high adsorptive capacities [15, 16]. The raw materials widely used initially for the production of commercial activated carbon are coal, bone char, peat, petroleum coke, lignite, wood and other biomass sources.

However, today the range of precursor materials is diverse and widespread. Nearly all organic materials with relatively high carbon content may serve as raw materials, ranging from conventional materials such as wood, coconut shell or coal to natural or synthetic polymers. For commercial grade carbons, the values of surface areas typically vary in the range between 500 and 1500 m^2/g or even as high as 3000 m^2/g [13]. They can be further separated into two sub-categories in accordance with their applications, namely, gas phase and liquid phase, in which the former is usually microporous (pore diameter < 2 nm) in granular form (2.36–0.833 mm, or 8/20 in mesh size) and the latter is mesoporous (pore diameter lies between 2 and 50 nm) in powdered form (0.150–0.043 mm, or 100/325). Both granular and powdered activated carbons have been

shown to be effective in wastewater treatment in which activated carbons play an important role in decolorising, odour removal, and metal recovery as well as organics adsorption.

Alternatively, adsorption, as a flexible, simple and inexpensive approach, can be used for process wastewater treatment, thus reducing the concerns over high operating and capital costs, efficiency and the need for secondary treatment [17–19]. A wide range of adsorbent materials have been developed and tested over the years and applied for the efficient treatment of various effluents, such as dye removal, heavy metals, pharmaceuticals, pesticides and a wide range of organic compounds. The intensive search for naturally occurring adsorbents began around 40 years ago using peat [20, 21], wood ([22, 23]) plant residues such as *Jatropha curcas* [24], mineral zeolites [25], textile wastes [26] and agricultural wastes [27, 28] Recently, adsorption onto activated carbon prepared from a wide range of low-cost biomass precursors has been reported ([29–31]). All these studies have found that the produced carbons have comparable and higher adsorption capacities than commercially available varieties. However, economic feasibility and locality of supply have limited their commercial production.

In addition to the naturally occurring adsorbent materials, many biomass wastes have been the subject of investigation:

Shells and husks from nuts and other agricultural products
Fruit stone waste
Adsorbents from other wastes such as vehicle tyres, waste plastics and seafood shell waste

These categories of wastes are presented in Section 2 of this review and some of the adsorption performance data are compared with the results of the olive stone-derived activated carbons for similar compounds in Section 3.5 of this study.

These results from these biomass waste studies indicate that some of these materials are suitable precursors for the production of activated carbons possessing high surface areas and pore volumes, a range of pore size distribution, appropriate hardness and bulk density. The criteria used when choosing a carbonaceous raw material include the potential for obtaining high-quality activated carbon with a low inorganic content, volume and cost of the raw material, workability of the raw material, minimum environmental impact and storage life of the raw material. As waste materials represent the feedstock to the activated carbon plant, then the raw material has a very low cost.

Olive stone is an essential by-product generated in the olive oil extraction industries. In terms of production scale, olive stones are produced by far on the largest scale, and a vast market includes the sale of stoneless olive products. It represents roughly 10% by weight of olive fruit and the amount of fixed and elemental carbon content within olive stone are

around 16 and 47 wt%, respectively [30], which is considered as one of the highest values of carbon among various stone fruits.

To date over one hundred research articles have been published on the production of activated carbon from olive stones. However, only a few review articles [32–37], mostly 5–10 years old, have been published in the last 15 years covering the area of olive stone, and none of them presents the detailed study of the production of activated carbon from olive stones. Consequently, this review covers the available studies on the production and application of olive stones to produce activated carbons.

2 Adsorption technology

2.1 Adsorption

Adsorption has long been used as a purification and separation process on an industrial scale. Highly porous adsorbents with good selectivity such as activated carbon have shown excellent ability in the removal of organic compounds such as dyestuffs, phenolics, endocrine-disrupting compounds, pesticides, pharmaceuticals and several metal ions [28, 38–40].

The phenomenon of adsorption follows one of three general types, namely, diffusion, surface chemical reaction including ion exchange and surface complexation. Diffusion processes are described in terms of pore diffusion, surface diffusion or a combination model of the two mechanisms; frequently, an external boundary layer film resistance is incorporated into these models. For chemical surface reactions, several kinetic models are available depending on the adsorbate–adsorbent functional group order of reaction; examples include pseudo-first-order, pseudo-second-order, Elovich, Avrami and Bangham models [41–44]. Surface complexation mechanisms have been proposed for many adsorption processes and especially in the case of heavy metal removal from wastewater. This process includes the coordination of the heavy metal ion with a number of functional surface groups and takes place via lone pair electron donation or hydrogen bonding [45]. The type of adsorption mechanism therefore depends on the nature of the adsorbate and the properties of the adsorbent.

Adsorption of dye onto adsorbents is a physical phenomenon in which dye molecules attach onto the adsorbent surface under the influence of van der Waals forces and hydrogen bonding. In a continuous contact system, each contact point is equivalent to an equilibrium stage or theoretical plate, offering adsorption as a unique advantage because it is possible to achieve complete separation within a short fixed-bed column. Adsorption can help significantly [26] with the serious issues of coloured/dye, pharmaceutical or metal ion containing effluents being discharged due to the toxicity, high

chemical stability and the presence of colour in water inhibiting the natural photosynthetic processes.

2.2 Advantages of adsorption in wastewater treatment

Several technologies are available for removing pollutants from wastewater and can be broadly divided into three categories, namely, physical (including adsorption), chemical and biological processes. These treatment techniques, including coagulation–flocculation, membrane separation, chemical oxidation, reverse osmosis and solvent extraction, have been used to process problematic polluted wastewaters [7, 46].

However, several of these treatment technologies generate their own problems including the associated high cost, large volumes of sludge formation and the subsequent disposal problems. To further understand the advantages and disadvantages of adsorption, it is essential to review the other available wastewater treatment technologies and their disadvantages.

Membrane filtration, such as ultrafiltration and reverse osmosis, involves the physical separation of dissolved dye molecules from effluent through permeable membranes under pressure and exhibit a good ability in separating solutes from wastewater. The major disadvantages of this process are the cost of the filter media and the occurrence of clogging, that most likely occurs in the case of build-up of a concentrated dye layer, which gradually reduces the overall removal efficiency with a lower flux rate [47]. Other physical separation options include irradiation [48] and electrokinetic coagulation [49]. They both exhibited good removal efficiency for certain dye species but were less effective in others [19], and further in-depth studies are needed.

Most chemical techniques such as chlorination, ozonation, wet air oxidation (WAO) and advanced oxidation process (AOP) [9, 10, 50] for organic and dye wastewater treatment aim to break down the complex chemical molecules into relatively simple and less toxic substances such as carbon dioxide or water via a series of oxidative reactions. However, dye molecules, in particular, usually possess good structural integrity, making them highly resistant to biodegradation or oxidation. Consequently, there is the additional generation of certain potentially toxic side products requiring further attention [51, 52].

WAO operates at high temperature and pressure, involving high operational costs, in order to convert diluted organic pollutants [53–55] to acetic acid, carbon dioxide and other resistant by-products [56]. As an alternative, AOP using Fenton's reagents, titanium oxides or ferrous ions as catalysts has been adopted in the degradation of organic pollutants, such as dye and phenolic compounds [7, 12, 14]. High removal efficiencies have been reported [57], but a ferrous sludge is generated and requires disposal [58].

Coagulation with the addition of flocculants has been applied to organic loaded wastewaters but removal efficiencies are only 80 to 90%; also, very careful pH control and sludge treatment after the process are disadvantages for organics [59] and heavy metals [60].

The major drawback in using electrochemical destruction [61] is the cost. Conventional aerobic methods such as activated sludge have been successfully applied in domestic wastewater treatment, but it depends on the pollutant affinity to the biomass [62]. The toxic nature of many organics and their strong molecular structure in the case of dyes and pharmaceuticals enables them to be highly resistant to microbial degradation [63–65]. Anaerobic digestion results in the generation of methane and hydrogen sulphide in the absence of oxygen which is acceptable for azo, diazo and reactive dye decolouration, but toxic aromatic amines in wastewater remained non-sensitive to the treatment [66].

In the case of applying adsorption technology for wastewater treatment, the first step is to target the most appropriate adsorbent for the pollutant in terms of capacity, the rate of uptake and the specific adsorbent cost. Furthermore, in a well-designed adsorption system, the pollutant can be totally removed for large volumes of wastewater treated before breakthrough occurs. These properties are interrelated with the adsorbent cost and the ability, or not, to regenerate the adsorbent with respect to the regeneration operating costs. The capital investment and installation costs for a commercial-scale adsorption system, usually fixed-bed columns containing granular activated carbons, are not high and the operational costs, mostly for the pumping process, are also reasonable as the pressure drops through granular carbons are relatively low and often downflow gravitational force can reduce this cost even more. Consequently, most of the criticism with regard to adsorption systems is with regard to regenerating the adsorbent. However, depending on the adsorbate–adsorbent, selecting the optimum regeneration approach can overcome much of the criticism. If the adsorbate is a highly toxic material, e.g. arsenate, arsenite, chromate, mercury, cadmium, etc., which cannot be regenerated for re-use therefore requiring in situ disposal, a very low-cost high capacity adsorbent should be selected; this can be stabilised or vitrified and sent to a hazardous waste landfill. Volatile solvents can be steam stripped off or hot gas stripped off the adsorbent in situ and then condensed for recovery and re-use. Heavy metals can be regenerated in the same manner as ion exchange columns; solvent stripping can be applied to various adsorbed species. A novel method is to pass a microbial broth through the spent adsorption column, containing a species of micro-organisms that will biodegrade the adsorbate—similar in principle to biosorption processes. For the more refractory stable organics, such as dyestuffs, the more expensive process of thermal regeneration is required and this usually requires transport offsite to a thermal

regeneration facility and the loss of approximately 10% of the adsorbent.

2.3 Adsorbent types and characteristics

2.3.1 Characteristics of adsorbents

The selection of the adsorbent in the utilisation of adsorption process is primarily dependent on the uptake capacity of the adsorbent for an individual substance as well as the contacting system design. Ideally, the adsorbent should satisfy four requirements [67, 68]:

- Reasonably high surface area or micropore volume to achieve a high adsorption capacity.
- The pore diameter must be sufficiently large appropriate to the size of the adsorbate molecule.
- The appropriate surface functional groups to attract the adsorbate molecule (or the large surface area may become of secondary importance).
- A relatively large porous network providing access to the internal surface area by diffusion.

For the first aspect, the number of active sites is proportional to the surface area, or more precisely, the micropore volume due to its dominant contribution to the surface area; therefore, a larger surface area adsorbent is apparently advantageous in adsorption. The functionality of the surface groups will create a positively, neutral or negatively charged surface capable of attracting the adsorbing species. The reasonably large porous network also plays a significant role as it allows a higher diffusion rate that is critical to adsorption kinetics and process design. It is important to determine the molecular dimensions of the pollutant adsorbate and ensure that the activated carbon produced has sufficient pores of sufficient pore diameter to achieve the removal of the adsorbate. In addition, a large and cheap source of precursor is also required.

There are numerous adsorbents in commercial or laboratory use, and some common examples are activated carbons [69], zeolites [70], silica [71] and activated alumina [72]. Other examples include bone char ([73–76]); agricultural wastes or by-products, for example, wood meals, bagasse, nutshells, rice husks, fruit stones or maize cobs ([77, 78]); inorganic minerals, for example, bentonite, Fuller's earth or clay ([79]); lignite ([80]); coconut shell ([81]); plastic wastes ([82–84]); chitin/chitosan [85, 86]; and aluminophosphate molecular sieves [87]. In recent years, some novel adsorbents such as carbon nanotubes or related structures are also being tested in adsorption applications [88, 89]. More details are presented in the following sections.

2.3.2 Naturally occurring resources

The early studies on the application of biomass resources as both adsorbents and precursors for the production of activated carbons were in the application of naturally occurring biomass resources, and some of these are currently used for commercial scale production of activated carbons. There is increasing pressure on these applications to be limited, as they represent a consumption of very slowly replaceable natural resources. Such materials that have been used as precursors include peat ([20, 21, 90]); lignite ([80]); various wood types, for example, *Eucalyptus* tree [22, 91], spruce wood [23, 92], sawdust [93], compressed wood [46], fir wood [94], oil palm wood [95], olive tree wood [96], tamarind wood [97], bamboo [98–100], *Jatropha curcas* [24] and wood biochar [101]; and sugarcane bagasse ([27, 28, 102]; McKay 1998; [68, 103]).

Other common naturally occurring and widely used adsorbents are the zeolites [25, 104], which have an aluminosilicate structure and come in various forms, and some are quartz, clinoptilolite, mordinite, chabazite and calcite.

2.3.3 Shells and husks

Waste by-products from the food crop sector have become one important source of activated carbon precursors in recent years. This has been associated with the environmental issues caused by large quantities of agricultural wastes. Much work has been done in the study and preparation of activated carbons from these cellulosic materials such as rice husk ([26]; [66]; [30, 31, 105]), almond shells [106–109], chickpea husk [110], coconut shell [9, 81, 111, 112], durian shell [53], oil palm shells [40, 54, 113], peanut hulls [107, 114, 115], pistachio nut shell [67], hazelnut shell [106, 116], *Eucalyptus globulus* [22, 117], macadamia nutshell [118, 119] and pine cone [110].

2.3.4 Fruit stone wastes

Across the world, stone fruit markets have been developed particularly for olives, dates and fig seeds. The stones of these products are hard and contain significant percentages of lignin, thus making them ideal as precursors for activated carbons. Among various stone fruits, olive stones have been widely studied as a precursor for activated carbon production mainly due to the high quality of activated carbon and the presence of high percentage of elemental carbon (40–45 wt%). But these studies have focussed on the production of the AC followed by testing for one or sometimes two pollutants, rather than selecting a pollutant compound first and then trying to tailor-make an olive stone-derived carbon with the most suitable adsorbent characteristics for that specific pollutant.

The canned fruit industry has been producing stoneless products for many years with the majority of these extracted fruit stones being discarded as wastes. In recent years, several of these stones have been used as precursors for the production of activated carbons. The fruit stones are rich in lignocellulose which provides a suitable base structure for the production of activated carbons. The range of fruit stones and related materials studied include apricot stones [120], date stones [121], plum stones [122–124], peach stones [125–127], cherry stones [128–130], olive stones [131], Macore fruit [132] and corn cob [118, 133–135].

2.3.5 Adsorbents from other wastes

Several studies have been undertaken to convert carbonaceous and other wastes into activated carbons or other adsorbing materials. The carbon containing wastes include vehicle tyres [136–138], plastic wastes [139, 140] and textiles, for example, silk waste [26].

Other waste materials have been used as precursors to produce effective adsorbents, for example, printed circuit board (pcb) e-waste has been treated with potassium hydroxide at 200 °C producing a cation exchange resin [141–147]. Another widely investigated adsorbent is chitosan produced by decarbonation followed by the deacetylation of seafood crustacea shells [85, 86, 148].

2.4 Advantages of activated carbons as adsorbents

In general, the adsorption capacity of activated carbon is proportional to the internal surface area, pore volume, pore size distribution and especially the surface chemistry. There are numerous reports of more organic adsorption in pores that are barely large enough to admit the adsorbate molecule; for example, it has been pointed out [149] that dyes and humic acids have dimensions (1.5–3.0 nm) that favour their adsorption in mesopores. Hence, the difference in pore size distribution affects the adsorption capacity for molecules of different sizes and shapes. The removal efficiency can be further enhanced by the electric force between the carbon surface and the adsorbate. In some cases, adsorption depends upon dissociation of particular functional groups—which in turn depend on the activating chemical and the conditions of application.

2.5 Activation methodology

The activation process to produce an activated carbon involves treating the carbonaceous precursor with a physical process such as heating in the presence of an inert gas or carbon dioxide or steam at temperatures in the range 500 to 1000 °C. An alternative process is the chemical activation method whereby a chemical is added to the precursor prior to the thermal treatment in the same temperature range.

Combinations termed physico-chemical treatment may also be used. The overall process may be carried out as a one-stage, two-stage or three-stage process. The one-stage process involves adding the activating chemical to the precursor material at the beginning of the process and placing this mixture in a furnace to be heated up to the preset activation temperature in one cycle. The two-stage process involves the charring of the precursor material in stage 1 at a temperature in the range 400 to 550 °C, followed by cooling to produce a high carbon content char as the raw material for stage 2. Stage 2 involves the addition of the activating chemical to the char followed by the furnace activation stage 2. The three-stage process is the same as the two-stage process except for an initial stage 1 pretreatment step which, for example, could be the solvent extraction of some impurities in the precursor.
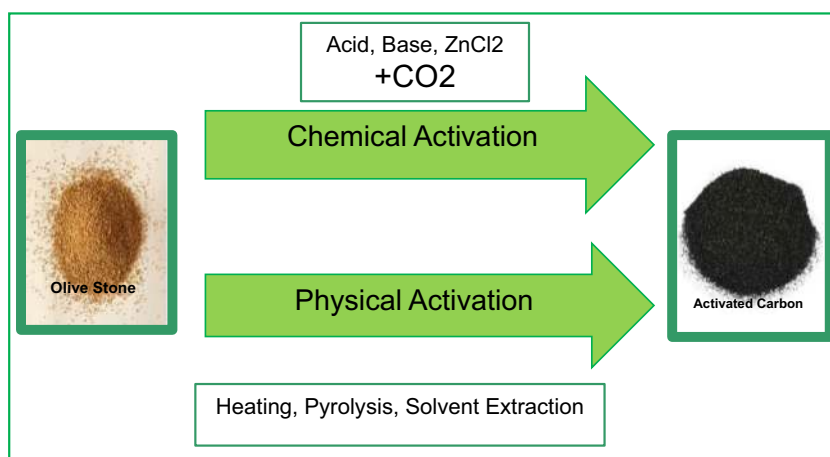
3 Olive stones

The main components of olive stones are presented in Table 1 [30, 35, 150] which include ultimate, proximate and lignocellulose analysis. It represents roughly 10% by weight of olive fruit [36]. The high percentage of carbon makes olive stone an attractive precursor for activated carbon production. Furthermore, there is a large industry in the production of seedless/stoneless olives, and this industry provides a significant, continuous supply of waste olive stones. Figure 1 depicts activation process of olive stone. In practice, these technologies may be used solely or in a cocktail mix in order to obtain optimal balance between economic benefit and technical efficiency during the course of water pollutant removal.

Table 1 Main components of olive stones

Analysis	%
Ultimate analysis	
C	46.5
H	6.4
N	0.4
S	0
Cl	0.34
Proximate analysis	
Fixed carbon	16.2
Volatile matter	72.7
Ashes	2.3
Moisture	8.8
Cellulose	28.1–40.4
Hemicellulose	18.5–32.2
Lignin	25.3–27.2
HHV* (MJ/kg)	19.4

* Higher heating value

Fig. 1 Activation process routes for olive stones

Most successful olive stone-derived activated carbons are based on the application of chemical, physical or physico-chemical as activation processes as presented in Tables 2, 3 and 4.

3.1 Chemical activation of olive stones

Table 2 shows the wide range of chemicals used for the activation of olive stones and include phosphoric acid, nitric acid, sulphuric acid, sodium hydroxide, potassium hydroxide, steam, potassium carbonate, zinc chloride, hydrochloric acid and hydrogen peroxide.

Activated carbons are excellent adsorbents due to their high surface area, microporous structure and high surface reactivity. Table 2 reflects the significance of chemical activation of olive stone. High surface reactivity, presence or absence of different functional groups especially oxygen groups, causes the phenomenon of ion adsorption on activated carbon as evident in the literature presented in Table 2 [153, 156]. Oxygen groups with acidic character are hydroxyl and carbonyl groups and they play an important role in the uptake capacity of adsorbent. Another important aspect of AC is their high surface area which can be increased with chemical activation, time and temperature as reported in Table 2 [154]. In a few cases, a combination of activating agents have been used, for example: sulphuric acid and ammonium thiosulphate, phosphoric acid and nitric acid, succinic acid and sodium bicarbonate, sulphuric acid and sodium hydroxide, zinc chloride and nitric acid, and hydrochloric acid and zinc chloride.

The data in Table 2 show the results of the chemical activation of olive stone and other olive industry-related products, such as olive pulp, olive pumice, olive cake and olive mill waste. The latter four materials are mainly comprised of olive fruit residues: all lacking the high carbon content and hardness of the olive stone.

The uptake of heavy metals onto chemically activated olive stones has been widely studied. In the case of cadmium removal [16], the capacity at pH = 5 was 24.83 mg/g but

dropped to 9.01 mg/g at pH = 2 due to the competition from hydrogen ions, and phosphoric acid was used to produce this activated carbon from olive stone with a 1169-m^2/g surface area. A zinc chloride-activated olive stone carbon only reported a capacity of 1.85 mg/g [158]; the surface area was 790 m^2/g but the pH was not provided—the positive charge on this carbon surface would repel the approaching cadmium ions. A complex chemical activation treatment using succinic acid and sodium bicarbonate [165] produced an activated carbon with a significant cadmium uptake capacity of 200 and 128 mg/g at pH = 4 and with a basic surface, but no surface area was provided. The capacity differences were due to the different activation times of 1.5 and 1.0 h, respectively; therefore, a knowledge of the surface areas would have been particularly interesting.

Another phosphoric acid (PA)-activated carbon [171] from olive stone also had a significant cadmium adsorption capacity of 51.1 mg/g and the surface area was 1194 m^2/g at pH = 5. The uptake of cobalt, nickel and copper on activated carbons obtained by treating olive stones with PA and PA + O_3 (ozone) provided capacities in the range 10 to 17.9 mg/g, but treatment with PA + HNO_3 (nitric acid) increased the nickel and copper capacities to 20.5 and 34.2 mg/g, respectively, by creating more oxidised sites in the form of surface carboxylic acid hydrogen ions for exchange with the metal ions [163]. In this study, the high capacity-activated carbon had the lowest surface area, 173 m^2/g, indicating the importance of surface functional groups on carbon for heavy metal ion adsorption–ion exchange. Two studies reported lead capacities of 148.8 and 147.5 mg/g using PA to activate the olive stone [168, 171], and time, temperature and pH were the same and the only difference was a small difference of the surface areas which were 1081 and 1194 m^2/g, respectively. In another study on lead removal, Blázquez et al. [172] treated olive stones separately with two acids, namely, sulphuric and nitric and sodium hydroxide, but the specific surface areas were extremely low as 0.51, 2.45 and 0.25 m^2/g, respectively, with correspondingly low lead capacities of 14.1, 15.3 and 16.2 mg/g, respectively.

Table 2 Adsorption capacities of various olive stone AC obtained via chemical activation

Precursor	Activation method	Pollutant	Adsorption capacity (mg/g)	Removal efficiency (%)	Time (h)	Temp (°C)	pH	Area (m²/g)	Ref.
Olive stone	Chemical (H_3PO_4)	Cadmium (II)	9.01	68.0	4	20	2	1169	[16]
			24.83	–	4	20	5		
Olive mill waste	Chemical (KOH) with carbonisation	Chromium (III)	0.61[a]	–	*	25	7	1641	[151]
		Bisphenol A	2.58[a]	–	*	25	7		
	Chemical (KOH) without carbonisation	Chromium (III)	0.47[a]	–	*	25	7		
		Bisphenol A	1.75[a]	–	*	25	7		
Olive stone	Chemical (KOH)	Toluene	720.00	–	–	–	–	883	[152]
Olive pulp	Chemical (H_2O)	Arsenic (III)	1.39	–	–	–	–	1030	[153]
Olive pulp	Chemical (K_2CO_3)		0.86	–	–	–	–	1850	
Olive stone	Chemical (K_2CO_3)		0.74	–	–	–	–	1610	
Olive pulp	Chemical (HNO_3)		0.21	–	–	–	–	732	
Olive seed	Chemical (KOH) (800/1 h)	Methylene blue	190.00	–	–	–	NA	367	[154]
	Chemical (KOH) (800/2 h)	Methylene blue	217.00	–	–	–		419	
	Chemical (KOH) (800/3 h)	Methylene blue	208.00	–	–	–		401	
	Chemical (KOH) (800/4 h)	Methylene blue	255.00	–	–	–		492	
	Chemical (KOH) (900/1 h)	Methylene blue	236.00	–	–	–		455	
	Chemical (KOH) (900/2 h)	Methylene blue	263.00	–	–	–		508	
	Chemical (KOH) (900/3 h)	Methylene blue	241.00	–	–	–		465	
	Chemical (KOH) (900/4 h)	Methylene blue	262.00	–	–	–		506	
Olive cake	Chemical (HCl)	Cadmium (II)	0.10	–	1	–	6.5	NA	[155]
		Chromium (III)	1.05	–	1	–	6.5		
		DBSNa	0.57	–	6	–	6.5		
		Phenol	0.40	–	16	–	6.5		
		Silver (I)	5.03	–	1	–	6.5		
		Methylene blue	0.40	–	16	–	6.5		
	Chemical (HNO_3)	Cadmium (II)	0.08	–	1	–	6.5		
		Chromium (III)	0.58	–	1	–	6.5		
		DBSNa	0.48	–	6	–	6.5		
		Phenol	0.25	–	16	–	6.5		
		Silver (I)	0.39	–	1	–	6.5		
		Methylene blue	0.42	–	16	–	6.5		
	Chemical (H_2SO_4)	Cadmium (II)	0.17	–	1	–	6.5		
		Chromium (III)	2.93	–	1	–	6.5		
		DBSNa	0.52	–	6	–	6.5		
		Phenol	0.13	–	16	–	6.5		
		Silver (I)	72.00	–	1	–	6.5		
		Methylene blue	0.31	–	16	–	6.5		
Solvent-extracted olive pulp	Chemical (H_2SO_4)	Iodine	494.00	–	–	–	6–7	NA	[156]
	Chemical (($NH_4)_2S_2O_8$ in H_2SO_4)	Iodine	270.00	–	–	–			
		Zinc (II)	4.61	98.0	–	–			
Olive stone	Chemical (H_2SO_4)	Iodine	570.00	–	–	–			
Olive seed	Chemical (H_3PO_4) (400 °C)	Methylene blue	110.00	–	–	–	–	NA	[157]
	Chemical (H_3PO_4) (600 °C)		112.50	–	–	–	–		
	Chemical (H_3PO_4) (800 °C)		115.00	–	–	–	–		
Olive stone	Chemical ($ZnCl_2$)	Cadmium (II)	1.85	–	–	20	–	790	[158]
Olive pomace	Chemical (H_3PO_4)	Copper (II)	0.50*		1.5	–	5	NA	[159]
		Cadmium (II)	0.10*		1.5	–	5		
	Chemical (H_2O_2)	Copper (II)	0.19*		1.5	–	5		
		Cadmium (II)	0.05*		1.5	–	5		
Olive stone	Chemical ($ZnCl_2$)	Remazol Red B						790	[131]
Olive tree pruning	Chemical (HNO_3)	Lead (II)	25.54	–	–	–	3–5	425	[160]
	Chemical (H_2SO_4)	Lead (II)	23.87	–	–	–	3–5	611	
	Chemical (NaOH)	Lead (II)	26.63	–	–	–	3–5	3526	
Olive stone	Chemical (H_3PO_4)	Amoxicillin	57.00	93.0	116	20	–	1174	[161]
Olive stone	Chemical (H_3PO_4)	Phenol	110.30	–	4	30	–	NA	[162]
Olive stone	Chemical (H_3PO_4)	Cobalt (II)	10.25	–	10	30	5	1194	[163]
		Nickel (II)	12.91	–	10	30	5		
		Copper (II)	14.16	–	10	30	5		
	Chemical (H_3PO_4) + O_3 post-treat	Cobalt (II)	16.20	–	10	30	5	798	
		Nickel (II)	12.44	–	10	30	5		
		Copper (II)	17.91	–	10	30	5		
	Chemical (H_3PO_4) + HNO_3 post-treat	Cobalt (II)	14.08	–	10	30	5	173	
		Nickel (II)	20.49	–	10	30	5		
		Copper (II)	34.16	–	10	30	5		
Olive stone	Chemical (H_3PO_4)	Phenol	32.36	–	–	–	6	1242	[164]
		Methylene blue	454.54	–	–	–	6.8		
	Chemical (H_3PO_4 + 2 M HNO_3)	Phenol	28.57	–	–	–	4.95	1163	

Table 2 (continued)

Precursor	Activation method	Pollutant	Adsorption capacity (mg/g)	Removal efficiency (%)	Time (h)	Temp (°C)	pH	Area (m^2/g)	Ref.
		Methylene blue	625.00	–	–	–	4.45		
	Chemical (H_3PO_4 + 3 M HNO_3)	Phenol	24.39	–	–	–	4.35	614	
		Methylene blue	666.66	–	–	–	4.25		
	Chemical (H_3PO_4 + 4 M HNO_3)		666.66	–	–	–	4.05	222	
	Chemical (H_3PO_4 + 5 M HNO_3)		526.31	–	–	–	3.8	13	
Olive wood**	Washing (ethanol)	Phenol	1.09	67–84	72	20	7	78	[96]
		2-Chlorophenol	6.54						
		3-Chlorophenol	7.69						
		4-Chlorophenol	9.09						
		2-Nitrophenol	0.64						
		4-Nitrophenol	2.25						
		2,4-Di-nitrophenol	0.57						
	Washing (tetrahydrofuran)	Phenol	1.11	13–84	72	20	7	103	
		2-Chlorophenol	6.85						
		3-Chlorophenol	10.42						
		4-Chlorophenol	11.36						
		2-Nitrophenol	0.67						
		4-Nitrophenol	2.31						
		2,4-Di-nitrophenol	0.63						
	Washing (ether)	Phenol	1.05	17–81	72	20	7	135	
		2-Chlorophenol	7.19						
		3-Chlorophenol	9.71						
		4-Chlorophenol	10.87						
		2-Nitrophenol	0.62						
		4-Nitrophenol	2.36						
		2,4-Di-nitrophenol	0.57						
	Washing (dichloromethane)	Phenol	1.10	33–53	72	20	7	123	
		2-Chlorophenol	7.30						
		3-Chlorophenol	9.90						
		4-Chlorophenol	11.36						
		2-Nitrophenol	0.66						
		4-Nitrophenol	2.46						
		2,4-Di-nitrophenol	0.62						
	Washing (hexane)	Phenol	1.05	28–68	72	20	7	106	
		2-Chlorophenol	7.09						
		3-Chlorophenol	9.26						
		4-Chlorophenol	10.64						
		2-Nitrophenol	0.63						
		4-Nitrophenol	2.40						
		2,4-Di-nitrophenol	0.59						
Olive stones	Succinylation (succinic acid + NaHCO$_3$)	Cadmium (II)	200.00	–	1.5	20	4	NA	[165]
Olive stone	Chemical (H_2SO_4 + NaOH reflux)	Cadmium (II)	128.20	–	1	25	4	NA	[166]
		Safranin	526.30	–	1	25	6.8		
Olive stone	Physico-chemical ($ZnCl_2$ + CO_2)	Ethanol	73.70	–	–	–	–	1448	[167]
	Chemical ($ZnCl_2$ + HNO_3)		97.60	–	–	–	–	1264	
	Chemical ($ZnCl_2$ + HNO_3) (400 °C)		81.50	–	–	–	–	1319	
	Chemical ($ZnCl_2$ + HNO_3) (700 °C)		70.70	–	–	–	–	1444	
Olive stones	Chemical (H_3PO_4)	Copper (II)	17.78	62.0	10	30	5	1081	[168]
		Nickel (II)	24.07	78.0	10	30	5		
		Lead (II)	148.77	100.0	10	30	5		
Olive stones	Chemical (HCl + $ZnCl_2$ 0.5 g)	Phenol	78.74	40.4	48	25	7.5	834	[169]
	Chemical (HCl + $ZnCl_2$ 1 g)		84.03	41.9				1093	
	Chemical (HCl + $ZnCl_2$ 2 g)		85.47	44.8				1266	
Olive stones	Chemical (H_3PO_4)	Cyanide	57.35	–	5	20	10.9	680	[170]
Olive stones	Chemical (H_3PO_4)	Copper (II)	17.67	68.0	10	30	5	1194	[171]
		Cadmium (II)	57.10	23.0			5		
		Lead (II)	147.53	–			5		
Olive stones	Chemical (H_2SO_4)	Lead (II)	14.11		2	25	5	0.51	[172]
	Chemical (HNO_3)		15.33					2.45	
	Chemical (NaOH)		16.25					0.25	

[a] Millimoles per gram

*Till equilibrium was reached

**(l/g) reported instead of (mg/g)

Table 3 Adsorption capacities of various olive stone AC obtained via physical activation

Precursor	Activation method	Pollutant	Adsorption capacity (mg/g)	Removal efficiency (%)	Time (h)	Temp (°C)	pH	Area (m²/g)	Ref.
Olive stones	Conventional heating	Copper (II)	17.83	98.6*	3	–	4.5	883	[173]
		Iron (II)	57.47	99.3*	3	–	4.5		
		Lead (II)	22.37	98.8*	3	–	4.5		
Olive stone waste	Conventional heating	Cadmium (II)	7.80	95.0	*	30	5	886	[174]
		Nickel (II)	8.42	99.1	*	30	5		
		Zinc (II)	11.14	99.2	*	30	5		
Olive cake	Thermal	Cadmium (II)	0.14	22.5	1	–	6.5	NA	[155]
		Chromium (III)	2.09	90.4	1	–	6.5		
		DBSNa	0.67	34.5	6	–	6.5		
		Phenol	0.73	22.5	16	–	6.5		
		Silver (I)	6.72	82.7	1	–	6.5		
		Methylene blue	0.72	–	16	–	6.5		
Solvent-extracted olive pulp	Physical (H_2O/N_2)	Iodine	478.00	–	–	–	6–7	364	[156]
		Zinc (II)	32.68	68.6	–	–			
Olive stone	Physical (H_2O/N_2)	Iodine	550.00	–	–	–		474	
		Zinc (II)	16.08	–	–	–			
Olive mill waste	Thermal	Methylene blue	14.95	–	2	–	–		[175]
Olive waste cake	Physical (H_2O/N_2) (70 min/800 °C)	Methylene blue	373.00	–	4	20	NA	1201	[176]
		Iodine	1261.00	–	2				
	Physical (H_2O/N_2) (30 min/800 °C)	Methylene blue	115.00	–	4			514	
		Iodine	796.00	–	2				
	Physical (H_2O/N_2) (60 min/850 °C)	Methylene blue	490.00	–	4			1271	
		Iodine	1495.00	–	2				
	Physical (H_2O/N_2) (40 min/750 °C)	Methylene blue	121.00	–	4			687	
		Iodine	741.00	–	2				
	Physical (H_2O/N_2) (60 min/750 °C)	Methylene blue	197.00	–	4			700	
		Iodine	996.00	–	2				
	Physical (H_2O/N_2) (40 min/850 °C)	Methylene blue	364.00	–	4			1127	
		Iodine	1017.00	–	2				
	Physical (H_2O/N_2) (50 min/800 °C)	Methylene blue	285.00	–	4			1025	
		Iodine	930.00	–	2				
Olive pomace	Untreated	Copper (II)	0.18*		1.5	–	5	NA	[159]
		Cadmium (II)	0.03*		1.5	–	5		
Olive cake	Untreated	Cadmium (II)	65.36	66.0	24	28	6	NA	[177]
			60.61	61.0	24	35	6		
			44.44	50.0	24	45	6		
Olive pomace	Solvent extracted and incompletely combusted	Total phenols	11.40	90.0	24	–	4–10	NA	[178]

Table 3 (continued)

Precursor	Activation method	Pollutant	Adsorption capacity (mg/g)	Removal efficiency (%)	Time (h)	Temp (°C)	pH	Area (m²/g)	Ref.
Olive pomace	Solvent extraction, packed bed	Methylene blue	13.85	52.0	7	–	–	NA	[29]
Olive stone	Thermal (with CO_2 and steam)	–	–	–	–	–	–	1187	[179]
Olive stone	Plasma enhanced (N_2 plasma 30 min)	Phenol	635.20	–	4	30	–	988	[162]
	Plasma enhanced (N_2 plasma 10 min)		323.26	–	4	30	–	1055	
	Plasma enhanced (N_2 plasma 5 min)		226.35	–	4	30	–	1140	
Olive stone	No treatment	Alizarin Red S	16.10	–	72	20	7.2	0.16	[180]
		Methylene blue	13.20	–	72	20	7.2		
Olive stone	Physical (H_2O)	Nitrogen dioxide	131.00	–	–	–	–	807	[181]
Olive wood**	Pyrolysis (100 °C)	Phenol	0.80	13–87	72	20	7	110	[96]
		2-Chlorophenol	4.51						
		3-Chlorophenol	5.00						
		4-Chlorophenol	5.53						
		2-Nitrophenol	0.49						
		4-Nitrophenol	2.46						
		2,4-Di-nitrophenol	0.47						
	Pyrolysis (150 °C)	Phenol	0.78	12–77	72	20	7	9	
		2-Chlorophenol	4.05						
		3-Chlorophenol	4.93						
		4-Chlorophenol	5.38						
		2-Nitrophenol	0.48						
		4-Nitrophenol	2.38						
		2,4-Di-nitrophenol	0.45						
	Pyrolysis (200 °C)	Phenol	0.72	47–76	72	20	7	176	
		2-Chlorophenol	3.34						
		3-Chlorophenol	4.00						
		4-Chlorophenol	4.44						
		2-Nitrophenol	0.46						
		4-Nitrophenol	2.16						
		2,4-Di-nitrophenol	0.44						
	Pyrolysis (250 °C)	Phenol	0.76	22–75	72	20	7	26	
		2-Chlorophenol	3.66						
		3-Chlorophenol	4.35						
		4-Chlorophenol	4.76						
		2-Nitrophenol	0.48						
		4-Nitrophenol	2.34						
		2,4-Di-nitrophenol	0.45						

Table 3 (continued)

Precursor	Activation method	Pollutant	Adsorption capacity (mg/g)	Removal efficiency (%)	Time (h)	Temp (°C)	pH	Area (m²/g)	Ref.
	Pyrolysis (300 °C)	Phenol	0.72	13–55	72	20	7	18	
		2-Chlorophenol	3.66						
		3-Chlorophenol	4.41						
		4-Chlorophenol	4.88						
		2-Nitrophenol	0.46						
		4-Nitrophenol	2.28						
		2,4-Di-nitrophenol	0.43						
Olive stone	Untreated	Cadmium (II)	4.90	45–82	2	25	7	NA	[182]
			5.71		2	40	7		
			6.00		2	60	7		
		Chromium (III)	6.96	86–90	2	25	4		
			6.99		2	40	4		
			7.03		2	60	4		
		Lead (II)	6.66	76–88	2	25	5		
			6.06		2	40	5		
			5.40		2	60	5		
Olive stone	Untreated	Chromium (III + VI)	2.17		5	25	2	NA	[183]
			2.45		5	60	2		
			3.67		5	80	2		
		Chromium (VI)	1.73		5	25	2		
			2.35		5	60	2		
			4.82		5	80	2		
Olive stones	Untreated	Cadmium (II)	0.93	96.0	1.3	25	7	0.38	[184]
			0.92		1.3	30	7		
			0.90		1.3	50	7		
			0.88		1.3	70	7		
			0.86		1.3	90	7		
	Physical (CO₂ 1 h)		78.74	44.8					
	Physical (CO₂ 1 h)		83.33	43.7					
	Physical (CO₂ 1 h)		156.25	61.5				NA	
Olive stones	Untreated	Iron (III)	1.50	90.0	–	20	–	0.6	[185]
Olive stones	Untreated	Lead (II)	4.57		2	25	5	0.16	[172]
Olive stones	Pyrolysis (500 °C)	Sulphonic compounds	570.00	–	2	25	–	760	[186]
		Phenolic compounds	500.00	–					
Olive stones	Physical (CO₂)	Methylene blue	2.66	–	300	25	–	760	[31]
			2.75			60			

Table 3 (continued)

Precursor	Activation method	Pollutant	Adsorption capacity (mg/g)	Removal efficiency (%)	Time (h)	Temp (°C)	pH	Area (m^2/g)	Ref.
80% OS/novolac resin/ hexamethylenetetramine mix			3.13			25			
60% OS/novolac resin/ hexamethylenetetramine mix			3.19			60			

Several studies are presented in Table 2 for the adsorption of phenol from water using olive stone-derived carbons. Soudani et al. [164] treated olive stones with PA only and PA with four different molar concentrations (2, 3, 4 and 5 M) of nitric acid and these five activated carbons had surface areas ranging from 1242 to 13 m^2/g from PA treatment only to PA + 5 M HNO$_3$ treatment. Three of these were tested for phenol adsorption— PA, PA + 2 M HNO$_3$, PA + 3 M HNO$_3$—with relatively low capacities of 32.4, 28.6 and 24.4 mg/g, respectively. The capacity trend follows the surface area trend but was not proportional to the large surface area change of 2:1; phenol can adsorb due to the negative polarity on its hydroxyl group but is more frequently considered as adsorbing via the π-electron cloud on the benzene ring. Therefore, the nitric acid treatment is adding some positive functionality to the olive stone-activated carbon. All five activated carbons were used for the adsorption of methylene blue with capacities of 454, 625, 667, 667 and 526 m^2/g, respectively. Again, the capacity trend is not proportional to surface area, although the pH for the PA-only-treated carbon was much higher than in the other four systems. For the three systems involving 2, 3 and 3 M HNO$_3$ sufficient, for example, carboxylic or OH for 3 exchange with H+, sites must have been generated to remove the very high amounts of the positively charged coloured ion of the methylene blue molecule. In the case of the 5-M HNO$_3$-treated carbon, the lower capacity, but still 526 mg/g, could be due to the surface area reduction—now only 12% of the 2-M nitric acid treated carbon.

Other dye adsorption studies have been reported for safranin yellow [166] and Remazol Red B [131], and both basic dyes have capacities of 526 and 9 mg/g. A single study for toluene adsorption on KOH-activated olive stone [152] produced a very high uptake of 720 mg/g, but no pH data was provided in this study. Iodine adsorption, a standard test for activated carbons on H$_2$SO$_4$-treated olive stone, yielded a high capacity of 570 mg/g, but the activated carbon surface area was not reported. Most of the remaining studies summarised in Table 2 relate to olive industry wastes not involving olive stones.

Bautista-Toledo et al. [151] treated olive mill waste with KOH and studied the adsorption of Cr(III) and bisphenol A; all the capacities were below 3 mg/g. Budinova et al. [153] treated olive pulp with KOH and K$_2$CO$_3$ for As(III) removal, but all capacities were less than 1.5 mg/g. Stavropoulos and Zabaniotou [154] treated olive seeds with KOH at various temperatures and contact times and obtained reasonable adsorption capacities for MB, in the range 190–263 mg/g.

Cimino et al. [155] treated olive cake samples by three methods—HCl, HNO$_3$ and H$_2$SO$_4^-$—and tested several adsorbates, namely, Cd(II), Cr(III), DBSNa, phenol, Ag(I) and MB, and in all cases, the capacities were less than 3 mg/g except the HCl-treated olive seed for Ag(I) which had a capacity of 72 mg/g. This could be attributed to the affinity of Ag(I) for the U-impregnated surface. Lafi [157] obtained MB

Table 4 Adsorption capacities of various olive stone AC obtained via physico-chemical activation

Precursor	Activation method	Pollutant	Adsorption capacity (mg/g)	Removal efficiency (%)	Time (h)	Temp (°C)	pH	Area (m²/g)	Ref.
Olive stone	Chemical (KOH) + microwave	Cadmium (II)	11.72	95.3				1281	[187]
		Copper (II)	22.73	98.6	The maximum capacities were determined via the Langmuir isotherm model by modelling of experimental data with various experimental factors and levels.				
		Iron (II)	62.50	99.3					
		Lead (II)	23.47	98.8					
		Nickel (II)	12.00	98.2					
		Zn (II)	15.08	98.4					
Olive stones	Microwave (KOH impregnated)	Copper (II)	22.73	98.6	3	–	4.5	1281	[173]
		Iron (II)	62.50	99.3	3	–	4.5		
		Lead (II)	23.47	98.8	3	–	4.5		
Olive waste cake	Physical (H₂O/N₂) (70 min/800 °C)	Methylene blue	373.00	–	4	20	–	1201	[176]
		Iodine	1261.00	–	2				
	Physical (H₂O/N₂) (30 min/800 °C)	Methylene blue	115.00	–	4			514	
		Iodine	796.00	–	2				
	Physical (H₂O/N₂) (60 min/850 °C)	Methylene blue	490.00	–	4			1271	
		Iodine	1495.00	–	2				
	Physical (H₂O/N₂) (40 min/750 °C)	Methylene blue	121.00	–	4			687	
		Iodine	741.00	–	2				
	Physical (H₂O/N₂) (60 min/750 °C)	Methylene blue	197.00	–	4			700	
		Iodine	996.00	–	2				
	Physical (H₂O/N₂) (40 min/850 °C)	Methylene blue	364.00	–	4			1127	
		Iodine	1017.00	–	2				
	Physical (H₂O/N₂) (50 min/800 °C)	Methylene blue	285.00	–	4			1025	
		Iodine	930.00	–	2				
Olive stone	Thermal	Methylene blue	38.00	–	–	–	9	368	[188]
		Iodine	238.00	–	–	–	9		
Olive pulp	Thermal	Methylene blue	46.00	–	–	–	9	396	
		Iodine	294.00	–	–	–	9		
Olive stone	Thermal + K₂CO₃	Methylene blue	394					1610	
		Iodine	1540						
Olive pulp	Thermal + K₂CO₃	Methylene blue	420					1850	
		Iodine	1720						
Olive stone	Thermal and chemical (KOH)	Lead (II)		100.0	6			1203	[189]
	Thermal and chemical (ZnCl₂)	Lead (II)		34.0	6			735	
Olive stone	Physico-chemical (ZnCl₂ + CO₂)	Ethanol	73.70	–	–	–	–	1448	[167]
Olive stones	Physico-chemical (HCl + ZnCl₂ 0.5 g + CO₂)	Phenol	126.58	67.4	48	25	7.5	985	[169]
	Physico-chemical (HCl + ZnCl₂ 1 g + CO₂)		147.06	68.5				1546	
	Physico-chemical (HCl + ZnCl₂ 2 g + CO₂)		158.73	73.0				1793	

capacities of 110–115 mg/g on PA-treated olive seed at various temperatures, but no surface areas were provided. PA- and H$_2$O$_2$-treated olive pace showed capacities lower than 0.5 mg/g for Cd and Cu adsorption [159]. Other treatments in Table 2, for example, the organic solvent washing of olive wood [96], showed low capacities, less than 12 mg/g, for a range of chlorophenols and nitrophenols. One interesting result is the adsorption of the pharmaceutical amoxicillin onto PA-treated olive stone [161] because of the recent awareness of the accumulation of pharmaceutical personal care products, PPCPs, in drinking water sources.

3.2 Physical activation of olive stones

For the physical activation processes in Table 3 direct thermal treatments such as pyrolysis, nitrogen and steam, carbon dioxide and steam, nitrogen with plasma heating and carbon dioxide alone are widely used. Ion exchange sites and functional groups sometimes become more important than surface area [180] especially for the removal of dyes. Also, some pollutants have affinity with particular elements which can enhance uptake capacity as it was reported that increase in phenol adsorption was highly dependent on nitrogen content [162]. Moreover, pyrolysis was also employed to increase the surface acidity and decrease the surface basicity. This is due to the release of volatile basic compounds attached to the surface of the material [96]. Pyrolysis at above 100 °C resulted in the increase of carbon content due to the loss of volatile components and water; hence, the recovery of phenol decreases mainly due to the loss of water. At high temperature (250 °C), recovery decreased due to the depolymerisation of lignocellulose material [96]. In addition, particle size plays an important role in increasing the surface area and uptake capacity of adsorbent as smaller particle size offers a larger surface area [178].

The data summarised in Table 3 are based on olive stones and related olive industry waste materials, which have been activated by thermal treatment only or other physical activation means. Alsaibi et al. applied thermal treatment to produce an activated carbon of surface area 883 m^2/g (Alslaibi et al. [187] and a second carbon of surface area 886 m^2/g [174]. The first AC was used to remove Cu (17.8 mg/g), Fe (57.5 mg/g) and Pb (22.4 mg/g), and the second AC was used to remove Cd (7.80 mg/g), Ni (8.42 mg/g) and Zn (11.1 mg/g). Although no activating agent is present, the presence of the major constituents—cellulose, hemicellulose and lignin—enables some surface active sites and porosity to be developed due to thermal treatment only. These metal adsorbing/ion exchanging functional groups –COOH, –OH enable the metal ions to be removed from the solution, but to a lesser extent than the chemical activation methods described in Table 2. The temperature for thermal treatment was not mentioned in many of these papers.

More conventional physical activation using steam/nitrogen was performed [156] by producing an AC with a surface area of 474 m^2/g. No temperature was provided and the loading capacity was high at 550 mg/g, but again the heavy metal uptake capacity, in this case zinc, was only 32.7 mg/g. High surface area olive stone applications were reported for this carbon [179]. An interesting study applying N$_2$ + plasma was performed [162] by using treatment times of 5, 10 and 30 min and produced ACs of surface areas 1140, 1055 and 988 m^2/g, respectively. The high phenol adsorption capacities for these three ACs were 226.4, 323.3 and 635.2 mg/g, respectively. Interestingly, the longer the treatment time, the lower the surface area, but the higher the phenol adsorption capacity. The prolonged treatment opened up micropores into mesopores causing the reduction in surface area with time and also changed the surface functionality, generating more nitrogen surface groups and decreasing the number of oxygen surface functional groups. Both of these effects favoured a high affinity for phenol adsorption.

Albadarin and Mangwandi [180] used olive stone directly without any activation treatment to adsorb two dyes, MB and Alizarin Red. Consequently, there are no significant surface groups available to adsorb the large positively charged basic dye coloured ions, and consequently, very low uptake capacities of 13.2 and 16.1 mg/g, respectively, were obtained. Ghouma et al. [181] used steam activation of olive stones to obtain an AC surface area of 807 m^2/g, which was found to have an adsorption capacity of 131 mg/g for nitrogen dioxide. Both basic and acidic functional groups on the AC surface allow the reduction of NO$_2$. Olive stones activated with CO$_2$ were used to remove Cd from water [184] under various conditions. Good capacities of 78.7, 83,3 and 156 mg/g were obtained due to the additional –COOH groups created by the CO$_2$ treatment, but no surface areas were provided.

Fewer studies used olive stones directly without pretreatment. Hernáinz et al. [182] performed three temperature isotherms for Cd removal at 25, 40 and 60 °C with low capacities of 4.90, 5.71 and 6.00 mg/g. Similar studies were undertaken for Cr(III) and Pb(II) and all the adsorption capacities were less than 7.5 mg/g [182]; all the experiments were conducted at pH = 7. Calero et al. [183] studied the removal of Cr(III) and Cr(VI) using untreated olive stones, Moubarik and Grimi [184] studied the removal of Cd (II) and Hodaifa et al. [185] studied Fe (III) removal and Blázquez et al. [172] studied Pb(II) removal—all these investigations used untreated olive stones but all these capacities were less than 5 mg/g.

Olive stones pyrolysed at 500 °C (SA of 760 m^2/g) demonstrated a high capacity for phenolic compounds, 500 mg/g, and sulphonic compounds, 570 mg/g, due to their ability to II-bond on the positive carbon surface [186]. Several other olive industry wastes have undergone physical treatment/activation. Cimino et al. [155] used the same pollutants they studied in Table 1, this time using thermally treated olive cake, but all

capacities were less than 6.75 mg/g. Baçaoui et al. [176] using steam/N_2-activated olive waste cake, prepared at various times and temperatures, studied the adsorption of MB and iodine. The surface areas generated were between 514 and 1271 m^2/g, and the very high iodine capacities reported were in the range 741 to 1495 mg/g and the high MB capacities ranged from 115 to 490 mg/g. Al-Anber and Matouq [177] obtained high capacities of 65.4, 60.6 and 50.0 mg/g for Cd adsorption at 28, 35 and 45 °C, respectively, for untreated olive cake. Solvent-extracted olive pumice had a capacity of 11.40 mg/g for mixed phenols [178] and 13.85 mg/g for MB [29].

A wide range of chlorophenols and nitrophenols were tested using pyrolysed olive wood at 50 °C temperature intervals from 100 to 300 °C, but all the capacities in Table 3 are less than 5.6 mg/g. The results in Tables 2 and 3 for the olive industry wastes excluding olive stones used as raw materials, namely, olive cake, olive wood, olive pomace, olive seed and olive pulp, in almost all cases, using relatively low temperature treatment, < 300 °C, had very low capacities. This suggests only a low concentration of surface functional groups has been created for both physical and chemical activation. Furthermore, for the heavy metals, some fraction of the adsorption uptake will occur by surface complexation, which is a widely recognised mechanism in biomass adsorption systems.

3.3 Physico-chemical activation treatment of olive stones

Table 4 presents the physico-chemical activation studies using olive stones. The processes include potassium hydroxide and microwave treatment steam and nitrogen mix, heat treatment with potassium carbonate/potassium hydroxide/zinc chloride and washing with selected organic solvents followed by pyrolysis of the resulting residue, zinc chloride and carbon dioxide, and zinc chloride with hydrochloric acid. The use of zinc chloride in activated carbon production has decreased in recent years due to its classification as a toxic heavy metal and its potential to leach out of the carbon into the treated water. Thermal–chemical activation led to the formation of more developed pore structure and larger surface area [188]. There are some results reported in Table 4 that show very low uptake capacity [96]. It is mainly due to the fact that olive woods do not fall under the category of AC and there is very little functionality and surface area.

Table 4 summarises the results of physico-chemical treatment studies using olive stones and olive industry wastes. These treatments mostly involve a chemical treatment coupled with a thermal or microwave treatment. Alslaibi et al. [187] produced an olive stone-derived activated carbon with a surface area of 1281 m^2/g using KOH and microwave treatment. The maximum capacities reported for this AC for six metal ions were determined based on the Langmuir model analysis of the experimental data as follows: 11.7, 22.7, 62.5, 23.5,

12.0 and 15.1 mg/g for Cd, Cu, Fe(II), Pb(II), Ni and Zn. Although these results are quite good, they are lower than the values obtained by Bohli et al. [168, 171] in Table 2 for Cd, Zn and Pb, although the Cu result is higher. The results are only slightly higher for Cu, Fe(II) and Pb(II) than the thermally treated date stones in Table 3 [187].

Petrov et al. [188] used K_2CO_3 treatment with thermal activation to produce carbon with MB and iodine capacities of 394 and 1540 mg/g compared to the thermal treatment only results in Table 3 of 38 and 238 mg/g for MB and iodine, respectively. Spahis et al. [189] studied the removal of Pb from water using olive stones treated as (i) thermal and KOH and (ii) thermal and $ZnCl_2$; the results were presented with respect to % removal of Pb with time and it was concluded that KOH-treated samples gave better capacities as compared with $ZnCl_2$. They did not present values in milligrams [96] and extended their studies on olive wood-chemical treatment only in Table 2 and thermal treatment only in Table 3 to include the two integrated techniques in Table 4. However, it can be seen from the results that all the capacities are less than 6.54 mg/g and are typically in between the two sets of results in Tables 2 and 3. Furthermore, all the surface areas for all three treated olive woods lie in the range 70–195 m^2/g. In these studies, the thermal treatment temperatures are too low to generate significant porosity, and normally, temperatures in excess of 600 °C are needed to develop high porosity. Also, the chemicals used are conventional solvent extraction chemicals rather than the normal activation chemicals.

Olive stones treated with $ZnCl_2$ and CO_2 yielded an AC with a high surface area of 1448 m^2/g and significant ethanol adsorption capacity of 73.7 mg/g [167]. Temdrara et al. [169] used a treatment of HCl + $ZnCl_2$ + CO_2 and obtained very good capacities of 126.6, 147.1 and 158.7 mg/g for phenol using various $ZnCl_2$ loadings.

3.4 Experimental details of the various treatment studies

Tables 5, 6 and 7 show the experimental conditions for the three previous ables 2, 3 and 4 respectively. Determining the most effective process conditions from an economic perspective depends on a number of interrelated factors:

1. Reaction temperature and time: The higher the temperature and the longer the reaction time, the more expensive the process.
2. Activating agent ratio to olive stone mass and the cost of the activating agent.
3. Product yield and surface area: A high activated carbon yield from the activation stage provides a large quantity of adsorbent; also, a high specific surface area is often an indication of a high adsorption capacity and this is directly enhanced by increased product yield. The high surface

Table 5 Chemical activation methods and the variations used in literature

Carbonisation		Impregnation characteristics		Comments	Ref.
Temp (°C)	Time (min)	Chemical	Ratio (chemical:precursor)		
400/500/600	60	Phosphoric acid	0.75/1.0/1.5:1	–	[16]
500	120	Potassium hydroxide	2:1	After impregnation of KOH, mixture was heated to 300 °C for 1 h and then at 800 °C for 2 h	[151]
—	120	Potassium hydroxide	2:1		
840	60	Potassium hydroxide	1/2/4/5:1	Samples were pyrolysed at 300 °C for 3 h followed by 800 °C for 2 h in N_2 posterior to KOH impregnation	[152]
800	60	Potassium hydroxide	2:1		
800	10 + 120	Water vapour	—	Carbonisation of raw olive stone at 800 °C for 10 min, further activated with water vapour at 800 °C for 2 h	[153]
950	720 + 10	Potassium carbonate	1:1	Chemically activated olive pulp and olive stones are considered different	
800	10 + 120	Nitric acid	3:1	The carbonised raw olive stone was treated with HNO_3 for 1 h, then washed and dried	
700	60	Hydrochloric acid	1:1	Carbonisation was carried out at 700 °C for 60 min and activation carried out using 2 N HCl and HNO_3	[155]
700	60	Nitric acid	1:1		
700	60	Sulphuric acid	1.8:1	Air-dried olive cake was treated with conc. H_2SO_4 and then carbonised at 700 °C for 60 min	
600/900	60/60	Potassium hydroxide (75% w/w)	1:1	Carbonisation at 600 °C for 1 h followed by chemical activation with KOH, and further activation after drying at 900 °C for 1 h. The activated carbon was then washed and dried	[190]
		Potassium hydroxide (50% w/w)	1:1		
400/600/800	60	Phosphoric acid (85%)	0.2:1	The seeds were treated with 85% pure H_3PO_4 (for 1 l of seeds, 200 cm^3 of acid was added) for 2 days and then activated at 400/600/800 °C for 1 h	[157]
650	120	Zinc chloride	—	Olive stone samples were mixed with $ZnCl_2$ (10/20/30% conc.) and then carbonised in a muffle furnace at 650 °C for 2 h, subsequently washed and dried	[158]
—	1440*	Phosphoric acid (50%)	5:1	50 g of olive pomace was added to t1250 ml of chemical of varying concentrations. (* contact time for the chemical/olive pomace)	[159]
	180*	Hydrogen peroxide (1 M)	5:1		
170/380	30/150	Phosphoric acid	1:1	Impregnation with H_3PO_4 was carried out at 110 °C for 9 h, followed by carbonisation at 170 °C for 30 min and then at 380 °C for 150 min	[161]
170/410	30/150	Phosphoric acid	1:1	Impregnation with H_3PO_4 was carried out at 110 °C for 9 h, followed by carbonisation at 170 °C for 30 min and then at 380 °C for 150 min	[162]
500	120	Phosphoric acid	4.5/5.3/6:1	Impregnation was carried out at 85 °C for 4 h	[191]
410	150	Phosphoric acid	1:1	Impregnation with H_3PO_4 was carried out at 110 °C for 9 h, followed by carbonisation at 410 °C for 150 min. The AC were post-treated with ozone and HNO_3	[163]
25	240	Ozone treatment	—	AC was exposed to O_3 at room temperature for 4 h at 12 mg/l conc. in an air–ozone mixture, washed and dried after treatment	
100	600	Nitric acid	—	500 ml 2 M nitric acid was added to 50 g AC sample and then washed and dried after treatment	
170/380	30/150	Phosphoric acid/nitric acid	1:1	Impregnation with H_3PO_4 was carried out at 110 °C for 9 h, followed by carbonisation with steam and nitrogen at 170 °C for 30 min and then at 380 °C for 150 min. The samples were then further activated using 2/3/4/5 mol/l HNO_3	[164]
90	1440	Succinic anhydride + $NaHCO_3$	—	A suspension of olive stone and pyridine (30 ml) in toluene (200 ml) heated at 60 °C was added at once to succinic anhydride (20 g). The resulting mixture was stirred overnight at 90 °C. After cooling, the solid was filtered off and washed thoroughly and treated with $NaHCO_3$	[165]
400/500/600/700	60	Phosphoric acid	1/2/4:1		[192]
20	1440	Phosphoric acid	8:1		[166]

Table 5 (continued)

Carbonisation Temp (°C)	Time (min)	Impregnation characteristics Chemical	Ratio (chemical:precursor)	Comments	Ref.
		Sulphuric acid + NaOH reflux for 1 h		The olive stone was mixed with conc. H$_2$SO$_4$ at rtp for 24 h and then neutralised using NaOH and subsequently washed and dried	
500	180	Zinc chloride	–	Olive stones were impregnated in a ZnCl$_2$ solution at 85 °C for 7 h under constant stirring	[167]
500 + 400/700	180	Zinc chloride + HNO$_3$	–	Olive stone AC was further oxidised using 6 M HNO$_3$ for 1 h and heat treated at 400 and 700 °C under He	[168]
410	150	Phosphoric acid	1:1	Olive stones were impregnated in H$_3$PO$_4$ at 110 °C for 9 h, followed by carbonisation at 410 °C for 150 min	[169]
800	60	Zinc chloride + HCl	0.5/1/2:1	Olive stones and ZnCl$_2$ (0.5/1/2 g ratios) were both carbonised at 800 °C for 1 h followed by chemical treatment (reflux) with HCl for 3 h and washed and dried afterwards	[170]
300	60	Phosphoric acid	2:1	Olive stones are carbonised at 300 °C for 1 h followed by H$_3$PO$_4$ impregnation. Further activation is carried out at 700 °C for 2 h followed by washing and drying	[171]
380	150	Phosphoric acid	1:1	Raw milled olive stones were impregnated with a phosphoric acid solution (50% by weight) at 110 °C for 9 h, followed by thermal activation at 380 °C for 2.5 h	[172]
50	1440	Sulphuric acid / Nitric acid / Sodium hydroxide	2:1	OS was chemically treated by soaking and shaking in a 2-M H$_2$SO$_4$, HNO$_3$, or NaOH (Merck p.a.) solutions in a rotary shaker for 24 h, at 50 °C, followed by washing and drying	

area needs to be supported by the adsorbent having the correct functional groups for the specific pollutant adsorption and pores commensurate with the size of the pollutant molecule. Furthermore, solution pH influences the activated carbon surface charge.

4. Porosity and surface functionality: The properties of the adsorbate have a major effect on the uptake capacity, and based on the chemical nature of the adsorbate (e.g. anionic or cationic), the surface functionality of the activated carbon will play a significant role. The molecular size of the adsorbate molecule is important with respect to the pore size distribution/porosity of the adsorbate. A large adsorbate molecule, for example with a molecular diameter > 2 nm, will be best accommodated in a mesoporous adsorbent. For an adsorbate species with a molecular diameter around 0.5 nm, normally, we would be looking for a mainly microporous activated carbon, but it should also be accompanied with a large overall porosity and, hence, a large surface area.

A literature review offers an excellent opportunity to review the available studies, experimental conditions, characterisation data and adsorption results for the range of adsorbates studied. This enables researchers to decide which conditions or range of conditions are likely to lead to an optimum adsorption treatment system design; examples are as follows:

i. q_e versus temperature: However, temperature is not an independent variable and is strongly dependent on reaction time and activating agent (if any).

ii. q_e versus specific surface area: This relationship is a good indicator of the quality of the activated carbon itself but does not indicate whether the percentage product carbon is in the range of 10 or 50% of the original biomass olive stone raw material.

iii. q_e versus (specific surface area divided by fractional yield): This combined parameter relates the adsorption capacity to the original unit mass of raw olive stone feedstock. It is probably the best overall indicator of adsorption performance quality.

However, it should be noted that there are still omissions in relation to establishing the optimum economic value since reaction temperature, reaction time and the amount and cost of the activating agent are not included in these relationships. Furthermore, kinetic studies should be included in the appraisal for economic design. The more rapid is the approach to equilibrium, and hence, the maximum adsorption capacity is reached, then the more polluted water can be treated in a fixed amount of time. This means that the size of the treatment plant can be reduced with a subsequent saving on the capital investment cost of the treatment plant. Consequently, in the present review, a number of the most frequently studied adsorbates

Table 6 Physical activation methods and the variations used in literature

Carbonisation		Impregnation characteristics		Comments	Ref.
Temp (°C)	Time (min)	Chemical	Ratio (chemical:precursor)		
715	120	Potassium hydroxide	1.53:1	–	[173]
715	120	Potassium hydroxide	1.53:1	–	[174]
840	60	–	–	Samples were pyrolysed at 300 °C for 3 h followed by 800 °C for 2 h in N_2 posterior to KOH impregnation	[152]
700	60	–	–	No chemical activation for this olive cake carbon	[155]
850	90	Steam/nitrogen	–	Activation of carbon was carried under steam/nitrogen mixture at 800 °C for 0.66/1.5/2 h for different samples	[156]
150	Until colour changed from brown to black	–	–	–	[175]
400	60	Steam/nitrogen	–	Activation times were varied between 30 and 70 min and temperatures between 750 and 850 °C. Activated carbons were boiled in distilled water for 30 min, dried, ground and sifted	[176]
510–850	850	CO_2	–	Carbonisation carried initially at 510 °C at 1 °C/min, and further from room temperature to 850 °C/min, followed by CO_2 activation at 800 °C	[193]
600	60	Steam (70%) in N_2	–	Activation of the obtained char is realised at 750 °C under 70 vol% H_2O in N_2 during 360 min	[181]
100/150/200/250/300/400	60	–	–	Sample was placed in a furnace under N_2 flow and temperature raised to the desired set point and maintained for 1 h	[96]
800	60/120/180	Carbon dioxide	–	Olive stone powder was carbonised at 800 °C for various times (1/2/3 h) in CO_2 to obtain various activated carbons	[169]
800	60	Pyrolysed at 500 °C	–	OS was pyrolysed at 500 °C then activated at 800 °C for 1 h	[186]
1000	30	Carbon dioxide	–	OS/novolac/hexamethylenetetramine mix was formed into small cylinders and cured at 170 °C for 30 min, then was carbonised at 1000 °C. After the carbonisation, the samples were activated using CO_2 at 900 °C	[31]

have been tested using the above qe correlative relationships when the data is available in the open literature.

3.5 Comparison of olive stone AC with other adsorbents

A number of the highest olive stone-derived activated carbon adsorption capacities from Tables 2, 3 and 4, are compared with other adsorbents for the same chemical species adsorbate in Table 8. It must be emphasised that making comparisons of this nature is very difficult, since the range of capacities for any specific adsorbate varies by a factor from 10 to 100 depending on the AC production conditions (and therefore the specific olive stone AC properties) and, in particular, the adsorption contact conditions, including contact time, pH, initial concentration, temperature, adsorbent mass to solution volume/concentration ratio and adsorbent particle size.

The results in Table 8 show that olive stone can be a competitive precursor for the production of activated carbon. Although comparing the activation and adsorption conditions

is very difficult, a simple comparison of olive stone capacities shows that olive stone has the potential to surpass many other adsorbents, such as in the cases of the removal of safranin, iodine and phenol. E-waste adsorption capacities of heavy metals were higher than that of any other adsorbate. However, e-waste-derived adsorption applications are limited to a much shorter range of adsorbates than that of olive stones, but the e-waste sorbent is a cation exchanger and the mechanism follows metal ion exchange with potassium and calcium ions. Agricultural by-products are known for being potential sources for the production of activated carbons with high surface areas and adsorption capacities. Compared to other agricultural products in Table 8, olive stones outperformed all of the agricultural products in several studies reported and in many other literature studies. But it must be emphasised that the success of the adsorption capacity depends on the method and conditions of activation relative to the adsorbate. In the literature as a whole, there are few studies in which the biomass-derived activated carbon has been prepared with a specific adsorption duty in mind.

Table 7 Physico-chemical activation methods and the variations used in literature

Method	Carbonisation		Impregnation characteristics		Comments	Ref.
	Temp (°C)	Time (min)	Chemical	Ratio (chemical:precursor)		
Microwave	600	–	Potassium hydroxide	0.5/1.25/2.0:1	Microwave with a frequency of 2.4 GHz at power levels from 264 to 616 W was used for 4/6/8 min for activation of impregnated char	[187]
Microwave	600	1440	Potassium hydroxide	1.87:1	Microwave with a frequency of 2.4 GHz at power levels from 565 W for 7 min was used for activation of impregnated char	[173]
Pyrolysis and chemical activation	800/900	60/120/ 180/240	Potassium hydroxide	4:1	Char created by pyrolysis at 800 °C and then activated by KOH and consequently washed and dried	[154]
Physico-chemical	850	90	Steam/nitrogen → sulphuric acid	10: 1	Further activation after the steam/nitrogen was carried out in 10% H_2SO_4 solution for 6 h at 25 °C	[156]
Physico-chemical			Steam/nitrogen → $(NH_4)_2S_2O_8$ in H_2SO_4	10: 1	Further activation after the steam/nitrogen was carried out in $(NH_4)_2S_2O_8$ in 1 M H_2SO_4 for 10 h at 25 °C	
Hydrothermal	160–240	60/120/240/ 360/480	Water	8: 1	One hydrochar was further carbonised under N_2 at 900 °C for 3 h	[194]
Succinylation	90	1440	Succinic anhydride + $NaHCO_3$	–	A suspension of olive stone and pyridine (30 ml) in toluene (200 ml) heated at 60 °C was added at once to succinic anhydride (20 g). The resulting mixture was stirred overnight at 90 °C. After cooling, the solid was filtered off and washed thoroughly and treated with $NaHCO_3$	[165]
Physico-chemical	825	20/40/60/ 72/80 (h)	Carbon dioxide	–	The chemically activated carbons were physically activated using CO_2 for different periods of time	[167]
Physico-chemical	800	60	Carbon dioxide + zinc chloride + HCl	0.5/1/2:1	Zinc chloride and olive stones were both carbonised together under CO_2 for 1 h using the same ratios as in the chemical method, followed by the same chemical treatment with HCl afterwards	[169]

4 Criteria for producing quality activated carbons from olive stones

The definition of a high-quality activated carbon is relative and should include the terminology: it has a high removal capacity for the adsorbate or adsorbates required to be removed/adsorbed. The properties that need to be assessed to fulfill this definition are surface functionality, surface charge, zeta potential and point of zero charge, surface area, pore diameter, pore size distribution, density, hardness and regenerability. Features of a suitable raw material source for activated carbon production should include a high carbon content; a low ash content; a low sulphur content; low content of other impurities, such as chloride and heavy metals; availability; and cheapness. The typical composition of olive stone listed in Table 1 demonstrates that it possesses a range of high-quality properties indicating its suitability for activated carbon production. To make an assessment of the process conditions to achieve a high surface area olive stone-activated carbon examination of Tables 2, 3 and 4 provides a good insight. For chemical activation in Table 2, both acid treatment, particularly phosphoric acid, and alkali treatment, particularly KOH and K_2CO_3, produce surface areas in the region of 1100 to 1200 m^2/g and even greater. However, further inspection reveals that additional factors influence surface area. Therefore, the temperature–time dependence is important: for studies at 700 °C, the thermal reaction contact time should be 4 h or more; for studies at 800 °C or above, the thermal contact time is over 2 h. The alkali reaction is complete in a slightly shorter time than the acid activation process. The other contributing factor is the activating chemical impregnation ratio. At a 1:1 ratio, there is often not enough activating chemical to complete the surface functionality and porosity development, and the surface areas are on the low side; consequently, the high surface areas reported for chemical activation use a ratio of 2:1 or greater. In general, 2:1 seems an optimum value for the impregnation ratio in terms of providing a high surface area and still remains relatively

Table 8 Comparison of olive stone AC adsorption capacities with other adsorbents

S. no.	Adsorbate	Capacity (mg/g)				
		Olive stone		Adsorbents		
			Reference			Reference
1	Safranin	526	[166]	*Spirulina* sp. algae	54	[195]
				Clay	18	[196]
				MgO on graphene	14	[197]
				Fe_3O_4 nanoparticles	92	[198]
2	Bisphenol A	2.7	[151]	*Ulva prolifera*	9	[199]
				Chitosan	35	[200]
				Vermiculite	93	(Liu et al. 2017)
				Montmorillonite	4	[201]
3	Cadmium	200	[165]	*Diplotaxis harra*	32	[202]
				Glebionis coronaria	58	[203]
				Pcb e-waste	236	[143]
				Furnace slag	19	[204]
				Montmorillonite	22	[205]
4	Copper	34	[163]	Orange peel	9	[206]
				Sludge	46	[207]
				Pcb e-waste	190	[141]
				Chitosan	188	(Kalra et al. 2018)
				Orange peel CNPs	17	[206]
				Sugarcane bagasse AC	13	[208]
5	Lead	149	[168]	Sludge	64	[207]
				Pcb e-waste	704	[141]
				Red mud	65	[209]
				Clinoptilolite	18	[210]
6	Nickel	24	[168]	Sludge	9.1	[207]
				Pcb e-waste	205	[143]
				Chitosan	105	[211]
				Brown algae AC	64	[212]
				Green algae AC	92	[212]
7	Methylene blue dye	667	[164]	Sludge	137	[207]
				Bamboo	454	[213]
				Fox nutshell	968	[214]
				Biochar	114	[215]
				Milled biochar	354	[216]
8	Chromium	7	[182]	Sludge	15	[207]
				Alga *Pterocladia*	66	[217]
				CNTs	113	[218]
				Magnetic biochar	8.4	[219]
				Amino-crab shell	41	[220]
				Biochar	21	[221]
9	Cobalt	16	[163]	Pcb e-waste	212	[143]
				Diplotaxis harra	26	[202]
				Glebionis coronaria	46	[203]
				Spirulina sp.	96	[222]
				Activated charcoal	50	[222]
10	Zinc	16	[156]	Bagasse pith	147	[223]
				Pcb e-waste	124	[143]
				Chitosan	104	[211]
				Furnace slag	18	[204]
				Zeolite	55	
11	Iodine	1540	[188]	Desert plant	1178	[224]
				Acorn shell	1209	[225]
12	Phenol	635	[162]	Fox nutshell	75	[214]
				Sludge	42	[207]
				Avocado kernel AC	90	[226]
				Bentonite	66	[227]
13	Chlorophenol	11	[96]	Filtrasorb AC	140	[228]
				Wheat husk biochar	9.3	[]
				Muscovite-CTAB	111	[]

cheap for the activation chemicals. Higher chemical impregnation ratios may result in a loss in surface area if the reaction contact time is too long as micropores are transformed into mesopores and mesopores are transformed into macropores. In the case of physical activation treatment only, higher temperatures, > 800 °C, are required and there is usually less surface functionality.

5 Conclusion

Olive stones have been proposed and studied as a suitable precursor for the production of activated carbons for wastewater treatment applications. Many adsorption applications have been reported including the treatment of wastewaters containing phenol, chlorophenol, nitrophenol, ethanol, iodine, methylene blue dye, remazol red B dye, safranin, amoxicillin and several heavy metals. Most researchers have focussed their attention on the method, conditions and characterisation of the derived activated carbons and their adsorption capacities for these various pollutants. Three of the classical standard activated carbon tests, using methylene blue, iodine and phenol, have generated excellent high adsorption capacities, namely, 667, 1495 and 635 mg/g, respectively. These represent some of the highest values ever reported for activated carbons. Another extremely high capacity has been recorded for safranin dye as 526 mg/g. Furthermore, some tests, for the removal of heavy metals, have also yielded very good capacities, namely, lead with 148 mg/g and cadmium with 200 mg/g, but in general, activated carbons do not have high uptake capacities for metal ions.

In terms of the olive stone activation experiments themselves, the following criticisms are made regarding the current literature:

- A lack of reporting of all the experimental details, for example, heating rate, activation temperature, activating agent concentrations, yields and inert gas flow rates.
- A lack of reporting or determining all the characterisation parameters; in most cases, the surface areas are provided, but frequently mean pore size, pore size distribution and porosity are omitted; these are very important to ensure that large pollutant molecules can diffuse and adsorb into the pores.
- More information on surface functionality and zeta potential needs to be provided, since adsorption capacity is more dependent on surface functionality than surface area.
- A major criticism is that the design of tailor-made adsorbents for specific pollutant removal applications needs to be explored and applied by optimisation techniques such as RSM, response surface methodology; for practical applications, the pollutant must be defined first and then decide what properties of the activated carbon are needed, then optimise and design the industrial-scale system.

The following areas are lacking in terms of pollution application studies:

- More detailed temperature studies to establish more thermodynamic parameters such as enthalpy, entropy, Gibbs free energy and activation energy.
- More experimental conditions need to be investigated in both equilibrium and kinetics, especially the effect of pH and, in particular, the reporting of the final pH, which has a major influence on metal adsorption capacity.
- More fixed-bed and regeneration studies are essential to enhance the development and application of olive stone-derived activated carbons on a commercial scale.
- It is also important to test more equilibrium, kinetic/mass transport and fixed-bed models to enable accurate simulation and design models to be developed.

In conclusion, most studies have focussed on equilibrium isotherm analyses and adsorption capacities, but beyond these studies, only a few investigators have reported batch kinetic studies. In order to take the development of olive stone-derived activated carbons to the next stage of development, more kinetic studies are required and more studies on a laboratory scale or small pilot plant scale fixed-bed columns are required with their associated regeneration studies. In addition, optimisation studies are required for targeted pollutants, and preliminary simulation process designs and cost estimates should be carried out.

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