

## Applications of waste date stones as a source of versatile activated carbons

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### ABSTRACT

Date pits or stones are becoming an increasingly available renewable biomass resource. Activated carbons for removal of pollutants from both the liquid and gas phase present a potential value-added use of such waste material. Date stones have a high elemental carbon content in the range of 42%–47% and accordingly the yield of activated carbon is still attractive after physical or chemical activation. The limited number of studies, reporting the conversion of date stones to various types of activated carbons, demonstrates that these carbons can remove phenolic organic compounds, dye-stuffs, heavy metal ions, and various gases. This article reviews the research undertaken on the production and application of date stone derived activated carbons in terms of activation conditions and adsorption capacities for different pollutants. In certain studies, significantly high adsorption capacities are reported indicating the future prospects for these carbons are highly attractive.

*Keywords:* Date pit; Activated carbons; Activation conditions; Adsorption capacities; Pollutant removal

### 1. Introduction

This review presents a detailed analysis of the current studies undertaken on the preparation of activated carbons from waste date stones and the applications of these date stone derived carbons for the removal of several pollutants in water. In the Middle East and North African (MENA) countries over 5 million MT of date fruits are produced annually with over 10% w/w of this produce comprising date stones [1,2].

Date stones from most varieties have very low ash content (below 1–2 wt.%), high carbon (45–50 wt.%), oxygen (35–40 wt.%), hydrogen (5–7 wt.%) and almost zero sulphur levels, which is greatly beneficial to the properties of derived activated carbons. The mineral content is low, dependent on the date variety and comprises mostly potassium

followed by phosphorus and magnesium. The majority of date stones are now coming from date processing factories producing seedless dates, jams, drinks, and marmalades. This is of major benefit to any potential date stone based activated carbon industry since the precursor stones are in one centralized location. The composition of the stone is made up of 43.9% cellulose, 17.7% hemicellulose and 16.3% lignin with low amounts of nitrogen, sulphur, and metals [3].

Treatment techniques for large volumes of polluted water include coagulation–flocculation, membrane separation, reverse osmosis, and oxidation processes. However, these treatment technologies generate their own problems including, the associated high capital and operating cost, large volumes of sludge formation, the formation of harmful by-products and the subsequent disposal problems. Adsorption treatment plants have low capital and operating costs and utilizing a low-cost biomass raw material lowers the cost further [4]; they are relatively easy to

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operate and the main issue to overcome is that of regeneration. For volatile organics – these can be recovered for re-use by steam stripping; refractory organics – usually require thermal regeneration; and, single component heavy metals can be regenerated by an acid wash and even recovered by electrolysis or precipitated as a re-usable salt, such as the hydroxide [5].

## 2. Adsorbent sources

### 2.1. Traditional sources of activated carbons

Activated carbon describes a group of amorphous carbonaceous compounds having large surface areas and internal porosities. Increasingly strict emission and discharge standards globally has greatly increased the demand for activated carbons, which traditionally have been produced from coal, lignite, peat, wood and oil residue/petroleum coke [6,7]. Several types of activated carbon are produced with varying functionalities to remove organics, anions, and cations [8]. With the advent of sustainable development and the emphasis on developing uses for renewable resources, the sources of precursors for activated carbon are growing with an emphasis towards agricultural waste products. The search for natural biomass resource adsorbents began just over 30 y ago with peat [9], rice husk and silk waste [10] and bagasse pith [11,12]. In theory, nearly all organic materials with relatively high carbon content can serve as raw materials, ranging from conventional materials such as wood, coconut shell or coal to natural or synthetic polymers [13].

### 2.2. Biomass activated carbon precursors

Agricultural residues have emerged as a key source of precursors for activated carbons in recent years, in part due to their suitability and due to the environmental issues associated with their handling and disposal. The use of lignocellulosic materials for the preparation of activated carbon, include materials such as almond shells [14], apricot stones [15], bamboo [16–18], *mariscus* [19], coconut shell [20], corn cob [21,22], fruit and vegetable shells [23], hardwoods [24], hazelnut shell [25], hemp [26], macadamia nutshell [27], oil-palm shell [28], olive stones [29,30], palm kernel [31], peach stones [32], peanut hulls [33], petroleum coke [34], pine cone [35], plum stones [36], vegetable and fruit husks, for example, rice husk [37], and sugar cane bagasse [11,38] have received significant attention. Outcomes from these studies indicate that many lignocellulosic agricultural residues are suitable precursors for activated carbons, exhibiting large pore volume, high surface area, a wide pore size distribution, as well as suitable hardness and bulk density. The more successful conversion of the biomass resources is achieved using those with high lignocellulosic content and lower amounts of cellulose and hemicellulose [39]. Typically, the adsorption capacity of activated carbon is proportional to the pore volume, pore size distribution, internal surface area and surface chemistry [40].

### 2.3. Alternative adsorbents

There is a range of alternative adsorbents to activated carbons. These are usually more expensive due to the nature

of their raw material source and processing costs and hence are designed and used for specialist applications. Some common examples include silica gel, zeolites and activated alumina [41]. Further examples include seafood waste derived chitosan [42–45], bone char [46], waste plastic [47] and clays [48–50]. Various novel adsorbents have recently been studied such as MCM-41 derivatives [51,52], carbon nanotubes [53], aluminophosphate molecular sieves [54], aluminosilicates [55,56], MXenes [57] and graphenes [58]. These adsorbents have shown high capacities, but production costs are currently uneconomical.

## 3. Activation methodology

Activated carbons are produced by the physical, chemical, or physico-chemical treatment of a carbonaceous raw material. The physical treatment includes heating the precursor in an inert gas atmosphere but also includes heating in the presence of steam or carbon dioxide at temperatures from 550°C to 950°C. In the chemical activation process, heating in an inert gas, for example, nitrogen, is carried out over a similar temperature range as the physical treatment method but this time the carbonaceous raw material has been soaked in an activating chemical. Several activating chemicals have been used and the most frequently applied ones are: phosphoric acid [59], nitric acid [60], sulphuric acid [61], potassium hydroxide [62], potassium bicarbonate [63] and zinc chloride [64,65], which are added to the raw material before the thermal processing. A combination of the two treatment types is often applied and is described as physico-chemical treatment.

The overall production process from the starting material to the final product can be carried out using a 1-step, a 2-step or a 3-step process operation. In the 1-step method the activating agent is added to the raw material initially and then this mixture is placed in a furnace for thermal treatment at a predetermined activation temperature, all taking place in one operating cycle. In the 2-step production operation stage process, the raw precursor is first charred, usually at a temperature lower than the activating temperature, in the region 350°C to 500°C. The char is then cooled, yielding a carbonaceous char as the starting feedstock for the second step. Then in the second step, the activation compound is added to the char, which is then activated in the furnace as step-2. The 3-step procedure follows the 2-step methodology except for a preliminary step, which usually takes the form of a pre-treatment phase, such as the removal of certain impurities from the raw material. However, microwave activation can also be used for the same purpose and with much less time. Although there are some studies that compare conventional heating to microwave heating, there are some missing links that make the work inadequate; as far as we know, microwave treated activated carbons have not been tested on heavy metals.

## 4. Criteria for high-quality adsorbents

The selection of the adsorbent in the utilisation of the adsorption process is primarily dependent on the uptake capacity of the adsorbent to an individual substance as well as the contact system design. Ideally, the adsorbent should satisfy four requirements [40,66]:

- reasonably high surface area and/or micropore volume to achieve a high adsorption capacity;
- the pore diameter must be sufficiently large to be appropriate to the size of the adsorbate molecule to allow for diffusion through the pores;
- the appropriate surface functional groups to attract the adsorbate molecule (or the large surface area may become of secondary importance);
- relatively large porous network for 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 pores of sufficient pore diameter to achieve the removal of the adsorbate. In addition, a large and cheap source of a precursor is also required.

The definition of a high-quality activated carbon is relative, but it should possess a high removal capacity for the adsorbate or adsorbates required to be removed/adsorbed. The properties that need to be assessed to fulfil 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 the date stone listed in Table 1 demonstrating its suitability for activated carbon production. Examination of Tables 2–4 provides a good insight into the process conditions necessary to achieve a high surface area date stone activated carbon. For chemical activation in Table 2, both acid treatment (particularly phosphoric acid) and alkali treatment (particularly KOH and  $K_2CO_3$ ) produce very high surface areas in the region of 1,100 to 1,200  $m^2/g$  and greater. However, further inspection reveals that additional factors influence the surface area. The temperature-time dependence is important. For studies at 700°C the thermal reaction contact time should be 4 h or more and for studies at 800°C or above the thermal contact time should be 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. In general, 2:1 seems an optimum value for the impregnation ratio in terms of providing a high surface area while not increasing costs significantly through excessive use of activation chemicals. Higher chemical impregnation ratios may result in a

Table 1  
Dyes adsorption onto date stone derived carbons

Temp. (°C)/ Power (W)	Time (m)	Activating agent/ Method	Pore volume ( $cm^3/g$ )	Surface area ( $m^2/g$ )	Capacity (mg/g) <sup>a</sup> another unit	Adsorbate	Model	Reference
400°C	58	$H_3PO_4$	1.26	725.00	345.00	Methylene blue	Langmuir	[72]
971°C	56	$CO_2$	0.41	666.00	110.00	Methylene blue	Langmuir	[72]
800°C	240	$ZnCl_2 + CO_2$	1.01	1,587.00	194.73	Methylene blue	Langmuir	[73]
					35.21	Congo red		
800°C	–	$CO_2 + HNO_3$	0.53	1,160.00	216.40	Methylene blue	Langmuir	[74]
900°C	30	$CO_2 + H_2SO_4$	–	–	80.29	Methylene blue	Langmuir	[75]
800°C	240	$ZnCl_2 + CO_2$	1.02	1,587.00	78.09% <sup>a</sup>	Orange G	–	[73]
660 W	8	$K_2CO_3$	0.656	1,144.25	485.44	Methylene blue	Langmuir	[76]
600 W	8	KOH + HCL	–	856.00	316.11	Methylene blue	Langmuir	[63]
Not activated (Raw date pit)			–	–	277.80	Methylene blue	Langmuir	[77]
–	480	$NaHCO_3 + H_2SO_4$	–	–	515.46	Methylene blue	Langmuir	[78]
					543.47	Crystal violet		
400°C	90	$H_3PO_4$	–	781.40	1,000.00	Alizarin dye	Langmuir	[79]
					1,111.11	Fluorescein dye		
900°C	120	$H_3PO_4$	1.1255	1,225.54	196.08	Rhodamine B dye	Langmuir	[59]
Not activated (Raw date pit)			0.21	86	31.5	Malachite green	Langmuir- Freundlich	[80]
700°C	180	$H_3PO_4$	0.55	909	64.7		Langmuir- Freundlich	
750°C	180	–	0.46	669.3	58		Langmuir- Freundlich	
900 W	180	$H_3PO_4$	0.72	1,123	98	Malachite green	Redlich- Peterson	[81]

Table 2  
Phenolic compounds adsorption onto date stone derived carbons

Temp. (°C)/ Power (W)	Time (m)	Activating agent/Method	Pore volume (cm <sup>3</sup> /g)	Surface area (m <sup>2</sup> /g)	Capacity (mg/g)	Adsorbate	Model	Reference
600°C	120	ZnCl <sub>2</sub>	1.06	1,509.0	103.09	Phenol	Dubinin–Radushkevich	[103]
800°C	160	KOH	1.21	1,450.0	169.49	Phenol	Dubinin–Radushkevich	[103]
800°C	–	CO <sub>2</sub> + HNO <sub>3</sub>	0.53	1,160.0	161.80	Phenol	Langmuir	[74]
700°C	60	FeCl <sub>3</sub>	0.573	761.4	184.86	p-Nitrophenol	Sips	[110]
800°C	120	H <sub>3</sub> PO <sub>4</sub>	0.17	425.0	263.15	o-Chlorophenol	Langmuir	[111]
900°C	30	CO <sub>2</sub> + H <sub>2</sub> SO <sub>4</sub>	–	–	46.076	Phenol	Langmuir	[105]
700°C	120	H <sub>3</sub> PO <sub>4</sub>	0.545	945.0	166.00	Phenol	Langmuir	[102]

Table 3  
Pesticides, herbicides and medicinal drugs adsorption onto date stone derived carbons

Temp. (°C)/ Power (W)	Time (m)	Activating agent/Method	Pore volume (cm <sup>3</sup> /g)	Surface area (m <sup>2</sup> /g)	Capacity (mg/g)	Adsorbate	Model	Reference
850°C	217	KOH + CO <sub>2</sub>	0.46	880.18	6.47–13.03	Benzaton – Carbofuran	Freundlich	[119]
850°C	120	KOH + CO <sub>2</sub>	0.424	763.4	238.1	Pesticides	Langmuir	[39]
600°C	120	KOH	0.55	1,209	188.3	L-phenylalanine	Langmuir	[121]
800°C	120	ZnCl <sub>2</sub>	0.63	1,235	133.3	L-phenylalanine	Langmuir	[121]
620 W	8	KOH + HCl	0.638	817	100.38	Levofloxacin	Langmuir	[122]
700°C	120	CO <sub>2</sub>	–	1,295.2	60.5	Tiemonium methylsulfate (pharmaceutical)	Sips	[123]

loss in the 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, temperatures greater than 800°C are required and there is usually less surface functionality.

## 5. Date stones – a resource for activated carbons

### 5.1. Adsorption of dyes

Date pit derived carbons have been used to adsorb several dyestuffs. The different parameters used in the preparation of these activated carbons and the dye capacities are presented in Table 1. The annual production of dyestuffs worldwide is in the range of 1.8 to 1.9 million metric tonnes [67], comprising more than 10,000 dyes and pigments, which are mainly used in the textiles, paper, food, leather, cosmetics, and plastics industries. The textile industry consumes approximately 60% of these dyes with an estimated 10% to 20% of the dyes used lost in the dyeing process in effluent liquors [68], which are frequently discharged to the environment. Due to the large volumes of water involved and the relatively low dye concentrations, adsorption offers an attractive method for colour removal, providing the appropriate adsorbent materials are available at an attractive cost and have a high adsorption capacity for the dyes concerned [66].

Dye containing effluents are notorious because they are not only aesthetically unacceptable but are also ecotoxicological. These coloured effluents reduce the sunlight

penetration into the water and hence reduce the photosynthetic activity in the natural environment. In addition, many of the dyes are non-biodegradable and are therefore persistent pollutants, while biodegradable dyes reduce the dissolved oxygen in the water damaging the aquatic ecosystem [69]. Examples of the risk of dyes include benzidine dyes and certain cationic dyes, which the America Dye Manufacturers Institute reported as being very toxic to fish [70]; and Malachite green dye which is listed as a Class II health hazard and mutagen causing liver tumour formation [71].

Several dyes have been studied using date derived carbon adsorbents as shown in Table 1. The majority of these studies are based on using Methylene blue (MB) dye, which forms a useful basis for comparing and assessing the best process production conditions for a date pit derived carbon for this application. Also, the Methylene blue Number is a widely used standard for adsorbent quality gradings. The range of MB dye capacities varies from 80 to 515 mg/g in the studies listed in Table 1; this very wide range of values indicates the importance and influence of the process conditions.

Comparing the parameters in Table 1, there is little correlation between capacity and surface area or pore volume; although a number of the studies failed to report these two important parameters. In terms of the three process conditions of time, temperature and activating agent, there appears to be a trend towards high MB adsorption capacities >300 mg/g, with a long activation period, high temperatures, and the use of basic activating agents, such as, K<sub>2</sub>CO<sub>3</sub>, KOH and NaHCO<sub>3</sub> [63,76,78]. The activation of the date pits with these basic components generates

Table 4  
Adsorption of heavy metal ions onto date stone derived activated carbons

Temp. (°C)/Power (W)	Time (m)	Activating agent/ Method	Pore volume (cm <sup>3</sup> /g)	Surface area (m <sup>2</sup> /g)	Capacity (mg/g)	Adsorbate	Model	Reference
800°C	60	Pure steam	0.321	702.00	1,594.00	Zinc ions	Langmuir	[126]
					1,317.00	Copper ions		
					1,261.00	Lead ions		
900°C	180	CO <sub>2</sub>	0.312	690.00	1,555.00	Iron ions	Langmuir	[127]
					5.83	Aluminium		
Not activated (Raw date pit)			–	–	35.90	Copper ions	Langmuir	[82]
650°C	120	H <sub>3</sub> PO <sub>4</sub>	0.460	826.00	39.50	Cadmium ions	Langmuir	[128]
					31.25	Copper ions		
650°C	120	H <sub>3</sub> PO <sub>4</sub>	0.460	826.00	24.40	Nickel ions	Langmuir	[129]
					21.70	Zinc ions		
450°C Not activated (Raw date pit)			0.020	1.20	70.00	Lead ions	Langmuir	[130]
450°C	–	H <sub>3</sub> PO <sub>4</sub>	0.010	54.93	4.29	Chromium ions	Langmuir	[130]
Not activated (Raw date pit)			–	–	6.50	Cadmium ions	Freundlich	[131]
500°C	30	CO <sub>2</sub>	–	–	3.00	Cadmium ions	Langmuir	[86]
900°C	30	CO <sub>2</sub>	–	–	1.80			
650°C	30	H <sub>2</sub> SO <sub>4</sub>	–	307.80	19.64	Lead ions	Langmuir	[132]
					10.41	Zinc ions		

alkaline functional groups, such as hydroxyl groups, on the activated carbon surface. When applied to the dye solution at pH > 5.5, the hydroxyl hydrogens can diffuse into the water leaving a highly negative surface, which can attract the basic dye ions of MB and Crystal violet [78]. The MB adsorption capacities on the acid-treated date pits are still quite high (110 to 345 mg/g) in several cases [73,82–85], providing the adsorption solution pH is >5.5. The acid activation process places H<sup>+</sup> on the surface of the carbon, which will repel the positive basic dye ions; but in a high pH environment, the surface H<sup>+</sup> ions will diffuse into solution yielding some sites available with a surplus negative charge available to the positively charged basic dye ions. An exception appears to be the very low adsorption capacity of 80.3 mg/g reported by Banat et al. [86], but the short activation time of 30 min is probably responsible for this low capacity. There are several studies in the literature of MB dye adsorption onto different activated carbons, which provide a useful basis for comparing the adsorption performance of the date pit carbons. One of the highest reported capacities for MB on activated carbon was 969 mg MB/g on a Fox nutshell derived activated carbon, soaked in a zinc chloride solution for 24 h and then heated at 600°C for 60 min, resulting in a carbon with an exceptionally high surface area of 2,869 m<sup>2</sup>/g [87]. Narvekar et al. [88] prepared two glycerol-based carbons at 120°C and 350°C, assigned GBC-120 and GBC-350, respectively, using sulphuric acid as the activating agent. The GBC-120 sample had a surface area of only 21 m<sup>2</sup>/g but a capacity of 1,000 mg/g, while the GBC-350 sample had a surface area of 464 m<sup>2</sup>/g but had a much lower capacity of 130 mg/g. The SO<sub>3</sub>H functional group was driven off at the higher

temperature; this emphasizes the important role the activating agent can play in its relationship with the adsorbate molecule. A hydrothermal carbon was produced by Qian et al. [89] at 200°C for 24 h from bamboo and activated using sodium hydroxide. The surface area, 31.6 m<sup>2</sup>/g, was low, but the capacity of 656 mg MB/g carbon was very high. The date carbon had a similar high capacity to the last study, which represents a 50% (w/w) adsorption uptake; although the process conditions and the surface area were very different.

The capacity of Congo red dye is 35.2 mg/g, which is low even though the date pit derived carbon surface area is very high, 1,587 m<sup>2</sup>/g, but the dye molecular size is large with a molecular weight of 697 g/gmol [73,90]. This would restrict the number of pores accessible to this large dye molecule. In addition, Congo red dye is a direct dye and does not possess the same ionic characteristics as the previous dyes, although the coloured component has a predominantly positive charge. To further understand the reason for the low capacity it would have been useful if the paper had provided the pore size distribution and the initial and final solution pH values. Li et al. [91] produced a mesoporous activated carbon by a one-step microwave-phosphoric acid activation with a surface area of 1,600 m<sup>2</sup>/g and a mean pore diameter of 3.1 nm. The adsorption capacity was much higher than on the raw date pit (351 mg/g).

In another study using Congo red, Li et al. [92] produced 12 bamboo hydrochar samples at temperatures between 160°C and 180°C and reaction times from 30 to 360 min. The product surface areas were from 10 to 31 m<sup>2</sup>/g and the Congo red adsorption capacities were 30–97 mg/g; the highest adsorption capacities occurred on carbons prepared at

the two highest temperatures, namely, 240°C and 280°C, and the longest reaction times of 300 and 360 min. Abbas and Trari [93] produced activated carbon from apricot stones at a temperature of 250°C and a reaction time of 240 min, the resulting surface area was 88 m<sup>2</sup>/g and the Congo red adsorption capacity was 32.9 mg/g. The low temperature was probably responsible for the low surface area and in turn the low adsorption capacity. The last two studies had adsorption capacities in the same range as the date pit carbon, but the high capacity result of 351 mg/g suggests that more studies should be investigated using microwave carbonisation.

The adsorption of Orange G dye on date pit carbon was studied by Bouchemal et al. [73] using ZnCl<sub>2</sub> and CO<sub>2</sub> for the activation stage at 800°C and for 240 min. The surface area was 1,587 m<sup>2</sup>/g and the adsorption capacity was 25 mg/g. Not much information could be found on the adsorption of Orange G onto biomass derived activated carbons in the literature. However, Kundu et al. [94] produced a nanoporous carbon using phenol and formaldehyde as activating agents and hydrothermal reaction conditions in the presence of triblock co-polymer P123 at 130°C for 24 h. This was followed by calcination of the intermediate at 700°C for 3 h under nitrogen. The surface area was 814 m<sup>2</sup>/g but despite the high surface area the adsorption capacity was only 18.8 mg/g. In a further study by Arulkumar et al. [61] pods from the large tree, *Thespesia populnea*, were converted to carbon by activating with sulphuric acid for 60 min at 600°C. The low dye capacity was 9.1 mg/g and mainly due to the short reaction time and the relatively low chemical activating temperature. However, all three results indicate Orange G is a difficult dye to remove.

It was found that Alizarin blue adsorption has a very high capacity on date pit derived activated carbon due to two factors. Firstly, a very small molecular size (MW = 240 g/g mol), enabling the dye molecule to diffuse into most of the available pores. Secondly, the date carbon is positively charged so that it can attract the negatively charged Alizarin dye ions [79]. Fayazi et al. [95] studied the adsorption of Alizarin Red dye, a very similar basic dye from the same chemical family, but with a higher molecular weight. The iron oxide nanocomposite carbon had a surface area of 348 m<sup>2</sup>/g only and a slightly acidic surface. Consequently, the Alizarin dye capacity was relatively low at 109 mg/g. Both surface area and surface functionality are important for the adsorption of basic dyes.

The highest adsorption capacity in Table 1 of 1,111 mg/g is for the fluorescent dye, fluorescein, which is an organic molecule with a number of benzene rings [79]. The  $\pi$  bonds on the rings and the lone electron pairs on the oxygen atoms are attracted to the positive surface of the phosphoric acid activated date pit carbon. In addition, the molecular volume and molecular weight, MW = 332 g/gmol, are low, enabling access to many pores. For comparison, in a study by Pirillo et al. [96], goethite and magnetite were used as adsorbents to remove fluorescein and the adsorption capacities were 664 and 332 mg/g, respectively.

The adsorption of Rhodamine B dye on acid treated date pit carbon is also moderate, 196 mg/g, following a similar pattern to Methylene blue but with a reasonably higher molecular volume, MW = 478 g/gmol [59]. In a further study,

Danish et al. [97] used *Acacia mangium* wood activated by phosphoric acid at 500°C for 120 min and obtained a surface area of 1,216 m<sup>2</sup>/g to adsorb Rhodamine B. Despite the large available surface area obtained, the acidic nature of the adsorbent surface only resulted in an adsorption capacity of 76.7 mg/g. Lacerda et al. [98] completed a detailed assessment on the production of activated carbons from three biomass sources: carnauba, macauba and pine nut wastes, and their subsequent application for Rhodamine B adsorption. The temperature was fixed at 500°C for 1 h and two activation agents were tested, namely, calcium chloride and phosphoric acid, resulting in six activated carbons being produced. The surface areas were from 260 to 430 m<sup>2</sup>/g and the capacities varied from 30 to 40 mg/g, the higher capacities being associated with the calcium chloride activated carbons and linked to the more basic nature of the adsorbent surface. The overall low surface areas and therefore the low capacities are due to the short reaction time and the low activation temperature.

The adsorption of Malachite green dye was investigated on raw date stones, thermally treated date stones, phosphoric acid treated date stones, and microwave treated date stones. The highest reported adsorption capacity was for microwave treated date stone at 98 mg/g due to its much higher surface area and pore volume than the rest of the adsorbents studied [99]. The maximum adsorption capacity of Malachite green (MG), dye onto *Luffa aegyptiaca* peel treated with sodium hydroxide was 78.8 mg/g [100], while that of thermally treated pomegranate peel was only 31.4 mg/g [101]. Thus, date pit derived activated carbons have competitive dye adsorption abilities compared to other biomass derived activated carbons. The adsorption mechanisms of large molecules like Malachite green containing benzene rings will adsorb via the ring  $\pi$ -electron clouds attaching themselves to any positive locations on the adsorbent surface by physisorption; consequently surface area will have a major effect on uptake capacity. Furthermore, after activation, the positive MG ions in solution will be attracted to any positive sites on the date carbon surface mainly by chemisorption.

## 5.2. Adsorption of phenolic compounds

The production of phenol in 2016 exceeded 10 million tonnes. The major uses of phenol are for the production of bisphenol A, phenolic resin and formaldehyde industries, cyclohexanol, pharmaceuticals, dyes and chlorophenols. Phenol is known to cause various health effects in humans following exposure through inhalation, oral and dermal contact. Phenol is an irritant and corrosive material, which makes the skin and mucous membranes susceptible to its toxic effects. Fatalities due to ingestion have occurred and a lethal oral dose, LD<sub>50</sub>, threshold in the region of 70 mg/kg has been established for adults. In addition, the liver and heart cardiovascular system have been proposed as potential targets for phenol toxicity. Three phenolic compounds have been tested, the majority of the studies using phenol itself and one study each using o-chlorophenol and p-nitrophenol, respectively.

In the case of the five phenol studies, the phenol adsorption capacities on the date derived chars are in the range

100–170 mg phenol/g date carbon [74,102–104] with one exception, that was 46 mg/g [105]. Unfortunately, no surface area or pore volume was reported in this paper but the activation time was only 30 min, and this very short reaction time was probably not sufficient to develop a comprehensive pore network and high surface area. Three phenol capacities are in the range of 160–170 mg/g and these values are characteristic of several literature phenol adsorption capacities on activated carbon studies. However, there seems to be little correlation between the process conditions, surface areas and adsorption capacities. In the case of the three phenol capacities in the range 160–170 mg/g the activation agents used were two with acid and one with alkali. The temperatures were similar, between 700°C and 800°C; two had similar reaction times (120 and 160 min), while one was not provided. However, the three surface areas are 1,450; 1,160 and 945 m<sup>2</sup>/g. Consequently, it is difficult to develop a successful formula of conditions to produce a date carbon with an optimum adsorption capacity for phenol. Therefore, it is important to compare the adsorption capacity values with those in the literature.

Studies by Al Doury and Ali [106], Hara and Jena [87], Prashanthakumar et al. [107] and Karri et al. [108] developed activated carbons from various biomasses with phenol adsorption capacities of 45, 100, 120 and 86 mg/g respectively; all below the 160–170 mg/g capacities of date stone activated carbons. McKay et al. using a commercial water treatment carbon with a surface area of 1,050 m<sup>2</sup>/g obtained a phenol capacity of 214 mg/g [109]. A summary of the research undertaken on phenols and phenolic compounds using date stone derived carbons is presented in Table 2.

### 5.2.1. Para-nitrophenol

Para-nitrophenol (or p-nitrophenol) is used in the production of a range of chemicals, including dyestuffs, pharmaceuticals, pesticides as well as in the manufacture of a variety of pharmaceuticals and in the leather processing industry. Exposure to p-nitrophenol causes cyanosis, drowsiness, nausea, skin allergies and headaches in humans.

A capacity of 186 mg/g of p-nitrophenol was obtained [110] on date pit carbon activated using ferric chloride at a temperature of 700°C for 60 min and a surface area of 761 m<sup>2</sup>/g. Other studies on biomass activated carbons have yielded similar adsorption capacities. Other carbons have been reported with capacities of 179, 195 and 234 mg/g respectively [15,112,113]. Further details of the activation conditions are presented in Table 2.

### 5.2.2. o-Chlorophenol

Chlorophenols are used in herbicides, insecticides, wood preservatives and intermediates in the manufacture of pharmaceuticals and dyestuffs [114]. The world production is over 100,000 tonnes per year. Due to its poor biodegradability, chlorophenols have a half-life in aerobic waters in excess of 3 months, making them a serious threat to the environment. At concentrations as low as 0.1 µg/L chlorophenols impart taste and odour problems to water. They are known to be both toxic and carcinogenic, and several phenolics and chlorophenolics have been listed as toxic pollutants [115].

Akhrib et al. [111] produced activated carbon from date pit at 800°C for 120 min using phosphoric as the activating agent. The surface area was only moderate at 425 m<sup>2</sup>/g but the adsorption capacity for chlorophenol was quite high at 263 mg/g. Several biomass carbons in the literature are much lower, ranging between 45 and 73 mg/g [20,106,116]. Higher results have also been reported on commercial activated carbons of 434 and 380 mg/g [114,117]. Since little data is available for the adsorption of phenolic compounds on date pit carbons as represented in Table 2, and no obvious trends are apparent linking process conditions to properties and capacities, further research in this area is required.

### 5.3. Adsorption of insecticides and pharmaceutical compounds

A limited number of studies have been performed using date pit derived activated carbons for the removal of certain insecticides and pharmaceutical drugs from the water. Both of these issues have created considerable concern amongst environmentalists and the public. These contaminants are transported from agricultural land where they are used into receiving waters, where they enter the aquatic and then human food chain [118]. The increased use of pharmaceutical medicines and antibiotics has also led to their steady accumulation in wastewaters, which following discharge into the environment can be abstracted back into the potable water system. These collective pharmaceuticals are called pharmaceutical personal care products (PPCPs). Several of the PPCPs are difficult to remove by filtration, biological treatment, advanced oxidation, and the relatively low concentrations of these pollutants makes flocculation/coagulation and settling uneconomic. Consequently, the application of suitable activated carbons for adsorption has great potential.

Only five studies relating to these applications could be found and the results are summarised in Table 3. Salman et al. [119] studied the removal of two insecticides, bentazon and carbofuran, using date pit derived active carbon at 850°C activated with carbon dioxide and potassium hydroxide. The date pit was activated for 217 min producing a carbon with a surface area of 880 m<sup>2</sup>/g and porosity 0.46 cm<sup>3</sup>/g. The adsorption capacity for bentazon (MW = 240 g/gmol) was 6.47 mg/g and for carbofuran (MW = 221 g/gmol) was 13.0 mg/g. In another study, the adsorption capacity for levofloxacin was 100 mg/g on date stone activated carbon by potassium hydroxide [120]. In a further study with pharmaceuticals, using phenylalanine and KOH activated date stones and zinc chloride activated date stones, adsorption capacities of 188 and 133 mg/g were achieved respectively [121].

In the literature, steam activated carbon from Lawsonia wood had a surface area of 584 m<sup>2</sup>/g and porosity of 0.44 cm<sup>3</sup>/g had an adsorption capacity of 169 mg bentazon/g for an initial concentration of 80 mg/L [124]. The pH was less than 6 resulting in a positively charged carbon surface which could attract the negatively charged bentazon species resulting in a large capacity. In another study, Salman and Mohammed [125] produced carbon from pomegranate tree branches and obtained a bentazon adsorption capacity of 80 mg/g with an initial concentration of 250 mg/L. The adsorption of 2,4-dichlorophenoxyacetic acid (2,4-D) resulted

in adsorption capacity of 238.1 mg/g with a date pit carbon prepared under similar conditions to the last set except for a shorter time which resulted in a lower surface area.

#### 5.4. Adsorption of heavy metals

Several heavy metals have been adsorbed onto date pit derived activated carbons and the different parameters used in the preparation of these activated carbons and the metal ion capacities are presented in Table 4.

Heavy metals are discharged into rivers, streams and receiving waters, normally in relatively low concentrations, from a wide range of large scale industries; including: microelectronics, electroplating, batteries, mining, coin manufacture, cable and wire, car, ship and aircraft manufacturers, wood preservatives, metal-based dyestuffs, the leather industry, etc., as well as through storm water runoff.

Most of the heavy metals from these industries, such as cadmium, chromium, copper, lead, mercury, nickel, zinc, etc. are carcinogens, toxic at low concentrations and pose a serious threat to both human and aquatic lives. Their hazardous properties imply non-biodegradability and the potential for accumulation in living tissues, thus entailing bio-magnification via the food chain. Due to the relatively low metal ion concentrations present in industrial effluents and storm water runoff, adsorption and ion exchange provide an attractive method for metal ion removal and the opportunity for water reuse [55].

Limited studies have focused on the removal of metallic ions from water using date derived carbons as shown in Table 4 and the wide range of values reported indicates the importance and influence of the process conditions. Comparing the parameters in Table 4, there is little correlation between capacity and surface area or pore volume; although a number of the studies failed to report these two important parameters. The activation of the date pits with these basic components provides the surface of the activated carbon with alkaline functional groups, such as hydroxyl groups. The acid activation process places  $H^+$  on the surface of the carbon, which will repel the positive metal ions; but in a high pH environment, the surface  $H^+$  ions will also diffuse into solution yielding some sites available with a surplus negative charge available to attract the positively charged metal ions. There are many studies in the literature for heavy metal adsorption onto various activated carbons which provide a useful basis for comparing the adsorption heavy metal removal capacity of the date pit carbons. The general mechanism for the heavy metal adsorption onto biomass activated carbons is the attraction of the metal cations to the negatively charged surface of the activated carbon and ion exchange with the acidic surface functional groups – the capacity is usually a maximum at pH values 5–6. In case of binary or ternary systems, the adsorption of lead ions was preferred, followed by copper then nickel. The adsorption capacity for date pit biochar decreased by 48% to 75% in a multi-component system due to the competitive behaviour of ions [133].

##### 5.4.1. Adsorption of copper

In Table 4, the capacities for copper ions in three studies are reported as 35.9 mg-Cu/g [77], 31.25 mg-Cu/g [128]

and 1,317 mg-Cu/g [126]. Some literature values for copper removal based on using other adsorbents are 43.5 mg-Cu/g on activated carbon from grape seed [134], 25.4 mg-Cu/g olive stone waste [135], 23.0 mg-Cu/g on biomass gasification residue [136], 22.9 mg-Cu/g on apricot stone [137], and 29.0 mg-Cu/g on rice husk activated carbon [138]. The adsorption capacities are almost all in the range of 20–45 mg-Cu/g and the date stone carbons are in the higher range of the values. The very high value of 1317 mg-Cu/g is unique, but all the conditions of this study are not included in the manuscript making it difficult to explain the reason why.

##### 5.4.2. Adsorption of lead

Only a single study has reported the adsorption of lead ions on the date stone derived activated carbons [129], having a specific surface of 826 m<sup>2</sup>/g, pore volume of 0.46 cm<sup>3</sup>/g and a capacity of 38.5 mg-Pb/g at the optimum pH of 6. Above a pH of 6 soluble lead complexes form, while the adsorption capacity increases from pH 3 to pH 6 as the competition from hydrogen ions decreases and the surface charge becomes more negative due to the presence of more hydroxyls in solution. The adsorption of lead is due to the electron dense sites on the surface of the carbon and some ion exchange with the acidic surface functional sites. Other studies include the adsorption of lead on apricot stone activated carbon [139], sawdust [140], activated carbon from hazelnut husk [141] and activated carbon from municipal organic solid waste [142] with lead adsorption capacities of 21.4, 3.19, 13.5 and 90.0 mg-Pb/g respectively. The date derived activated carbon has a high capacity compared to the other biomass-derived adsorbents, only the municipal organic waste has a significantly higher capacity for the lead.

##### 5.4.3. Adsorption of zinc

The adsorption of zinc from water has been carried out using phosphoric activated date stones [129], having a surface area of 826 m<sup>2</sup>/g and pore volume 0.46 cm<sup>3</sup>/g, with a capacity of 21.7 mg-Zn/g. Activated carbons have been prepared under similar conditions from almond husk and the untreated carbon had a zinc capacity of 31.0 mg-Zn/g, while sulphuric acid treated almond husk carbon had a capacity of 35.0 mg-Zn/g [143]. Hydrolysed olive paste [144] and olive stone derived activated carbons [135,145] have zinc adsorption capacities of 12.2, 17.0 and 11.1 mg-Zn/g respectively. Even commercial activated carbon [146] only has a capacity of 20.5 mg-Zn/g. Consequently, the date stone derived carbon is a relatively good adsorber of zinc ions, but not as good as almond husk carbon, probably due to the higher carbon content of the raw almond husk.

##### 5.4.4. Adsorption of nickel

Nickel adsorption onto Tunisian date stone derived carbon was studied [129] and found to have an adsorption capacity of 24.4 mg-Ni/g. Activated carbons produced from olive stone waste [135] and palm kernel shell gasification [136] have capacities of 17.0 and 18.0 mg-Ni/g, respectively, slightly lower capacities than the date stone carbon.

Untreated and sulphuric acid treated almond husk carbons [147] again yielded higher nickel capacity products of 30.8 and 37.2 mg-Ni/g, respectively.

#### 5.4.5. Adsorption of cadmium

Cadmium is a highly toxic heavy metal strongly linked to the battery industry. Date stone derived carbon has shown a high capacity for cadmium in the order of 39.5 mg-Cd/g [77]. Acid-modified biomass carbons [148] and olive stone activated carbon [145] have shown lower capacities of 9.40 mg-Cd/mg and 7.80 mg-Cd/g respectively.

In the case of the nutshells, the almond husk carbon [149] and the walnut shell [150] also exhibited lower capacities, namely, 9.40 and 12.0 mg-Cd/g respectively, than the date stone carbon. Higher capacities for cadmium have been obtained on waste materials activated carbons including 61.0 mg-Cd/g on municipal organic solid waste [142] and also 115 mg-Cd/g on orange peel derived biochar [151]. The exceptional high capacity in the latter case was attributed to a high calcite concentration in the orange peel, enabling significant surface precipitation of  $\text{CaCd SO}_3$ .

#### 5.4.6. Adsorption of aluminium

The removal of aluminium from water has been investigated using date stone activated carbon [127] and has a capacity of 5.83 mg-Al/g. Other adsorbents tested for Al removal include: humin [152] and  $\text{FeCl}_3$  impregnated activated carbon [153] with capacities of 1.91 and 4.37 mg-Al/g respectively; higher capacities have been reported, such as 22.5 mg-Al/g for beach cast seaweed [154] and the highest capacity of 270 mg-Al/g using a more complex biomass-based adsorbent [155], namely, palm shell mesoporous activated carbon impregnated with La/Mg/Si.

#### 5.4.7. Adsorption of chromium

The adsorption capacity of Cr(VI) onto date stones could only be found on raw (water washed and dried) date stones, having a specific surface of 1.2 m<sup>2</sup>/g and pore volume 0.02 cm<sup>3</sup>/g. There was a considerable change in the Cr(VI) capacity with pH due to both the speciation characteristics of Cr(VI) in water and the surface charge on the powdered date stones with solution pH. The surface functional groups have been characterized [130] as mainly acidic comprising hydroxyl (-OH), carboxylic acid (-COOH) and carbonyl (-COO-). The highest adsorption capacity of 70.5 mg-Cr(VI) occurred at pH = 2. This is because the Cr(VI) species is predominantly the negatively charged  $\text{HCrO}_4^-$  and since the date surface is positive at pH < 5, making the conditions for adsorption favourable. Furthermore, it is considered that the abundance of hydrogen ions at a pH of 2 in solution helps to neutralize the negatively charged acidic species on the surface further enhancing this high adsorption capacity. The adsorption capacity decreases as the pH increases and at pH = 5.4 the surface charge is negative and the Cr(VI) species is mainly  $\text{Cr}_2\text{O}_7^{2-}$  and some  $\text{CrO}_4^{2-}$ , which can now ion exchange with the acidic functional groups. However, the increasing hydroxyl concentrations in the solution and the negative date stone surface charge act to repel the negative chromium species leading to a

decreasing adsorption capacity. The adsorption capacity in the pH range 5 to 6 was 18.4 mg-Cr(VI)/g.

Other raw biomass materials have been used for Cr(VI) adsorption from water, including juniper sawdust and avocado kernel shells with capacities of 16.0 and 10.1 mg-Cr(VI)/g, respectively [156]; as well as almond [157] and sugarcane bagasse pith [158] with capacities of 3.40 and 5.75 mg-Cr(VI)/g, respectively. Hydrochloric acid and also phosphoric acid treated seaweed-derived activated carbons [159] have also been used with capacities of 12.8 and 11.0 mg-Cr(VI)/g, respectively. Choudhary and Paul [160] using a biochar obtained a Cr(VI) capacity of 21.3 mg-Cr(VI)/g. The Cr(VI) capacity of raw date stones powder is very competitive with all these values.

#### 5.5. Adsorption of gases and other studies

Only a limited number of studies have been performed using date pit derived activated carbons for the removal of gases. These include nitrogen dioxide, nitrogen, and the lower hydrocarbon gases. The results are shown in Table 5. The uptake of nitrogen dioxide onto adsorbents has been reviewed recently [161] Two studies are reported for the adsorption of nitrogen dioxide on date stone derived activated carbon with the following capacities: 2.70 and 2.80 mmol/g [84] and 2.32 mmol/g [162]. Literature capacities on similar materials include 1.44 mmol/g on KOH activated walnut shell [163], 1.46 mmol/g on KOH activated plum stone and 0.98 mmol/g on CO<sub>2</sub> activated pine sawdust [164]. Comparing these results and the properties of the various activated carbons there appears to be no individual activated carbon property that follows the NO<sub>2</sub> adsorption capacity. There is no trend with the surface area but there is a general moderate trend with total porosity and possibly some functionality.

The capacity of nitrogen on the date stone derived activated carbon is 0.902 mmol/g [165]. This is high compared with the capacity of the mineral clinoptilolite for nitrogen which is only 0.32 [169]. A coconut based activated carbon had a capacity of 0.7 mmol/g at 25°C and 100 kPa [170].

The methane capacity of the date stone carbon is 1.72 mmol/g [165] but the methane capacity on clinoptilolite was very much lower at 0.032 mmol/g [169]. However, a much higher methane adsorption capacity of 3.0 mmol/g was obtained on KOH activated bituminous coal derived activated carbon [171].

The adsorption capacities of ethane and ethylene on date stone carbon were found to be 2.76 and 1.42 mmol/g respectively [165]. Higher capacities for ethane and ethylene of 7.2 and 6.0 mmol/g were obtained using asphalt treated activated carbons [172] and 7.94 and 6.50 mmol/g for ethane and ethylene respectively using sucrose based activated carbons [173].

El Naas et al. [166] applied date activated carbon to chemical oxygen demand (COD) removal but the carbon only had a low uptake. Similar modest results were obtained using activated carbons for COD removal from landfill leachate achieving 80% COD removal and COD removal in wastewater from mineral processing. However, the percentage removal data on its own is insignificant as it depends on the initial COD concentrations.

Table 5  
Gases and others adsorption onto date stone derived carbons

Temp. (°C)/ Power (W)	Time (m)	Activating agent/Method	Pore volume (cm <sup>3</sup> /g)	Surface area (m <sup>2</sup> /g)	Capacity (mmol/g)	Adsorbate	Model	Reference
550°C	90	ZnCl <sub>2</sub> + HCl	0.480	1,172	2.700	Nitrogen dioxide	–	[84]
825°C	240	CO <sub>2</sub>	0.510	1,359	2.800	Nitrogen dioxide	–	
850°C	30	CO <sub>2</sub>	0.050	126	4.400 mg/g	Nitrogen dioxide	–	
850°C	60	CO <sub>2</sub>	0.190	421	70.800 mg/g	Nitrogen dioxide	–	[162]
850°C	120	CO <sub>2</sub>	0.290	655	106.900 mg/g	Nitrogen dioxide	–	
					0.902	Nitrogen	–	
900°C	180	CO <sub>2</sub>	0.287	645	1.720	Methane	Langmuir	[165]
					1.420	Ethylene	–	
					2.760	Ethane	–	
900°C	90	CO <sub>2</sub>	0.229	490	4.360 mg/g	COD reduction	Langmuir	[166]
800°C	60	H <sub>3</sub> PO <sub>4</sub>	–	–	375.000 mg/g	Iodine (Iodine number)	–	[167]
900°C	120	H <sub>3</sub> PO <sub>4</sub>	–	1,225	–	–	–	[59]
700°C	360	Physical	0.716	635	–	–	–	[168]
600°C	60	ZnCl <sub>2</sub>	0.610	1,061	–	–	–	[64]

An interesting observation in Table 5 relates to the two studies using zinc chloride as an activating agent [64,84]. Both products were activated at relatively low temperatures of 550°C and 600°C under relatively short activation times of 90 and 60 min respectively. Both developed similar average porosities of 0.48 and 0.61 cm<sup>3</sup>/g, respectively, while both also have a significant surface area of 1,172 and 1,061 m<sup>2</sup>/g respectively. Whilst these conditions are attractive, the significant cost of zinc chloride must be considered and the possibility of the carbon product containing zinc will restrict its usage in drinking water applications. Other results in Table 5 are for activated carbon production only; one using phosphoric acid and achieving a high surface area of 1,225 m<sup>2</sup>/g [59] and another study using physical activation [168] where only a moderate surface area of 635 m<sup>2</sup>/g was achieved. The low value is probably due to the temperature of 700°C which is low for physical activation.

## 6. Conclusion

The analysis of the adsorption capacities of activated carbons produced from date stones shows the adsorption capacities compare favourably with capacities of other biomass-based and commercial activated carbons for most types of pollutants. Therefore, further detailed research is justified into their utilization and optimization of activation procedures for specific pollutants, since this is an increasing biomass waste resource. To improve understanding, future studies should provide detailed activation conditions and biomass characterization, which are frequently not reported. In addition, studies focusing on various pollutants of a different nature will provide greater information on the effectiveness of specific activation methods.

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