

# Chapter 12

## Date Palm Based Activated Carbon for the Efficient Removal of Organic Dyes from Aqueous Environment



**Shamik Chowdhury, Sharadwata Pan, Rajasekhar Balasubramanian,  
and Papita Das**

**Abstract** Dyes are an important class of recalcitrant organic compounds, with a broad range of applications in the textiles and clothing industry. It is estimated that almost 2% of the dyes produced annually are discharged directly onto aqueous effluents through manufacturing and processing operations, and nearly 10% is subsequently lost during the coloration process. The presence of dyes in industrial wastewaters can create a host of environmental problems because of their potential cytotoxic, carcinogenic, and mutagenic effects on human health, as well as on general flora and fauna. Amongst the various physical, chemical, and biological techniques that are currently explored by the scientific community for the removal of dyes from aqueous medium, adsorption on activated carbon (AC) is widely considered as the most effective and promising option. However, commercially available ACs are fairly expensive and are often produced from non-renewable coal based resources, which make them economically undesirable and environmentally unsustainable. Consequently, there is a growing interest to synthesize ACs from renewable agricultural waste, which is conceived to be sufficiently abundant. Particularly, attributing to their high lignocellulosic composition and low ash content, date palm residues (such as fibers, seeds, rachis, fronds, etc.) as low cost precursors for manufacturing ACs are being intensively investigated in recent years. Compared to the commercial AC, the ACs derived from date palm byproducts exhibit superior textural characteristics, and, subsequently, greater adsorption capacity toward a plethora of dyes. Clearly, solicitations of date palm biomass, as a base feedstock for the mass production of AC, can not only solve the waste disposal crisis in date

---

S. Chowdhury (✉) · R. Balasubramanian  
Department of Civil & Environmental Engineering, National University of Singapore,  
Singapore, Singapore  
e-mail: [shamikchowdhury04@gmail.com](mailto:shamikchowdhury04@gmail.com)

S. Pan  
School of Life Sciences Weihenstephan, Technical University of Munich, Freising, Germany

P. Das  
Department of Chemical Engineering, Jadavpur University, Kolkata, India

palm growing countries, with a beneficial and enhanced revenue potential, but may also contribute in regulation of the unsustainable management of the waste byproduct. This chapter targets this aspect amongst others, with an objective to provide a systematic overview of the recent progress in the development and application of date palm based ACs for decolorizing textile effluents. Furthermore, it attempts to segregate and identify the key gaps in the specific domain knowledge, and lays out novel strategic research guidelines, for making further advances in this promising approach, to a hitherto sustainable development.

**Keywords** Dyes · Adsorption · Adsorbents · Activated carbon · Date palm

## 12.1 Introduction

It all started with a vivid purple dye, discovered serendipitously on April 28, 1856 during the Easter holidays. William H. Perkin (18) stumbled upon a technique to synthetically manufacture purple color, while attempting synthesizing the antimalarial drug ‘quinine’ from coal tar, which he promptly patented as ‘mauveine’. Until then, pigments extracted from natural resources, i.e., plants, insects, animals, mineral deposits, and even semi-precious stones, prevailed as the only coloring technology (Merdan et al. 2017). Attributing to their lasting color pay-off, reproducibility in shades, and overall cost factor, synthetic colorants soon ostracized the solicitations of natural dyes (Shahid-ul-Islam and Mohammad 2017).

Today, more than 100,000 synthetic dye variants, for instance acid dyes, azoic dyes, basic dyes, chrome dyes, diazo dyes, direct dyes, disperse dyes, reactive dyes, sulfur dyes, and vat dyes, commercially exist with an annual global market in excess of  $7 \times 10^5$  tons (Chowdhury and Saha 2010; Chowdhury et al. 2011). It is estimated that ~2% of the fabricated dyestuffs are discharged directly onto aqueous effluents, during manufacturing and subsequent processing operations (Singh and Arora 2011). Of the remaining 98%, approximately two thirds are employed by the textile industry, to dye natural and synthetic fiber or fabrics; about one sixth are utilized for coloring paper; and the rest are engaged predominantly in the production of organic pigments, and in the dyeing of leather and plastic. As the entire cohort of dye molecules do not bind to the substrate, an additional 10% is concomitantly lost during the dyeing process (Kausar et al. 2018). Depending on the type of dye, its loss in both the dyeing baths and the residual effluents, could vary from 2% for the basic dyes to as high as 50% for the reactive dyes (Singh et al. 2015). All these eventually manifest severe contaminations of surface and ground waters, in the vicinity of the dyeing industries.

Dyes, in general, are stable organic pollutants that persist in the environment due to their complex aromatic structures (Kodam and Kolekar 2015). The thin layer of discharged dyes, formed on the surface of the receiving water streams, can compromise the photosynthetic activity of aquatic flora by restricting sunlight penetration (Pereira and Alves 2012). This in turn decreases the dissolved oxygen levels, ultimately affecting the aquatic fauna (Sharma et al. 2015; Pathania et al. 2016a).

Furthermore, since synthetic dyes are derived from petrochemical sources, a vast majority of them act as toxic mutagens, potential carcinogens, and eye irritants (Merdan et al. 2017; Pathania et al. 2016b). The release of colored wastewaters into the ecosystem is, therefore, both unsafe and aesthetically unacceptable.

Consequently, a wide array of strategies have been extensively adopted and rigorously evaluated over the years, for the removal of color from textile wastewaters. These range from physical (adsorption, sedimentation, flotation, flocculation, coagulation, ultrafiltration, photoionization, incineration, and membrane separation) and chemical processes (neutralization, reduction, oxidation, electrolysis, ion-exchange, wet-air oxidation), to biological treatment methods (stabilization ponds, aerated lagoons, trickling filters, activated sludge, anaerobic digestion, and various types of microbial strains) (Crini 2006; Singh and Arora 2011). Amongst these, adsorption on solid media have garnered maximum scientific attention, attributing to its low capital investment as well as a multitude of competitive advantages: (i) flexibility and simplicity of design, (ii) ease of operation, (iii) insensitivity to toxic pollutants, (iv) lower sensitivity to diurnal variation, and (v) comprehensive removal of contaminants even from dilute solutions (Pereira and Alves 2012; Rafatullah et al. 2013; Yaqub et al. 2014). Additionally, adsorption cannot be linked with manifestation of objectionable and/or harmful byproducts (Rafatullah et al. 2013; Yaqub et al. 2014).

In light of the aforementioned merits, several diverse solid supports, such as zeolites, alumina, activated carbon, and silica gel, have been proposed and developed during recent years, to eliminate various categories of dyes from wastewaters (Gupta et al. 2009). Amongst them, activated carbon (AC) is the most widely studied adsorbent, because of its fundamental porous structure as well as many exciting properties: (i) high surface area ( $500\text{--}2000\text{ m}^2\text{ g}^{-1}$ ), (ii) controllable pore structure, (iii) admirable thermostability, (iv) low acid/base reactivity, and (v) good biocompatibility (Crini 2006; Gupta et al. 2009; Rafatullah et al. 2013; Suhas et al. 2016). Indeed, the enormous internal surface area, along with numerous cracks, crevices and voids between the carbon layers, permit and facilitate the accumulation of a large number of contaminant molecules, often in excess of the weight of the material. In addition, adsorption on AC is not usually selective, as it occurs through weak attraction forces, such as electrostatic or van der Waals forces (physisorption) (Gupta et al. 2009). This tendency can be leveraged to eliminate a wide range of colorants from textile effluents.

Despite their proven potential in adsorption processes, most commercial ACs are manufactured from expensive and nonrenewable fossil fuel based resources, for instance petroleum coke and coal (Gao et al. 2017; Rashidi and Yusup 2017), which seriously hinder their practical utility, especially at the industrial scale. This has paved way for a growing research interest in the production of AC from renewable, abundantly available, and low cost precursors (Crini 2006). In this context, date palm fruits processing products and byproducts are particularly attractive, because of their high cellulose (40–50%), hemicellulose, (40–50%), and lignin (15–35%)

content (Ahmad et al. 2012; Alrumman 2016) and low ash load (5%) (Ahmed 2016; Lattieff 2016). Further, the date palm is one of the most cultivated fruit-bearing flora in the arid and semi-arid regions of the world (El may et al. 2012; Elmay et al. 2014). It is estimated that the number of date palms worldwide is about 105 million (Elmay et al. 2013; Ahmed 2016). Date fruit production yields several crop residues, including date palm leaves (fronds), fruitstalk prunings, and seeds (also known as stones or pits) during date fruit harvesting; and trunks, rachis, and spines during replanting activities (El May et al. 2012). At present, over 3.7 million tons of date byproducts are being generated annually (Almi et al. 2015). Much of the waste is either illegally burnt (Chandrasekaran and Bahkali 2013; Usman et al. 2015; Arevalo-Gallegos et al. 2017), thereby contributing to air pollution, or simply left to decay in dedicated landfills (Bekheet and El-Sharabasy 2015; Nasser et al. 2016), emitting methane, a more potent greenhouse gas compared to carbon dioxide (CO<sub>2</sub>). Utilization of date palm byproducts, as a base feedstock for the mass production of AC, can mitigate the waste disposal crisis in date palm growing countries, with a potential revenue benefit option. Moreover, it may also assist in regulating unsustainable management of the waste byproduct. Compared to commercial AC, the AC prepared from date palm wastes, exhibit superior textural properties, and thus, greater adsorption capacity towards a multitude of dyes.

Therefore, the current chapter has been conceived to provide an overview of the latest development in valorization of date palm wastes for sustainable production of AC, including their potential as adsorbents for the removal of different types of synthetic colorants from wastewaters. Additionally, it makes an attempt to identify and segregate the fundamental lacunae in the domain, while laying out novel strategic research guidelines for making further advances in this promising waste valorization approach, with a clear mandate and focus on sustainable development.

## **12.2 Activated Carbon from Date Palm Residues for Dye Removal**

Over the past few years, a wide spectrum of date palm residues, including seeds, rachis, fronds and fibers, have been investigated, as a sustainable and renewable feedstock for preparation of AC (see Table 12.1). The yield, textural characteristics and surface chemistry of the ACs are largely dependent on both the lignocellulosic composition of the precursor, and the manufacturing process. In general, there are two fundamental steps for the production of AC: (1) the carbonization of raw materials below 800 °C in the absence of oxygen, and (2) the activation of the carbonized product, using either physical or chemical activation methods. More recently, alternative manufacturing protocols with energy and chemical stashes, such as microwave heating, have also been successfully developed for the preparation of AC from date palm biomass.

**Table 12.1** Carbonization and activation conditions of date palm residues, and the textural characteristics and dye adsorption capacities of the resulting activated carbons as reported in the literature

Raw Material	Carbonization condition	Activation condition	Activating agent	Remarks	$S_{BET}$ ( $m^2 g^{-1}$ ) <sup>a</sup>	$V_t$ ( $cm^3 g^{-1}$ ) <sup>b</sup>	Adsorbate	Conc. Range ( $mg L^{-1}$ )	Adsorption capacity ( $mg g^{-1}$ )	Reference
Date pits	600 °C/2 h	950 °C	CO <sub>2</sub>	–	–	–	Methylene blue	50–2000	590	Abdulkarim et al. (2002)
Date pits	700 °C/2 h	900 °C/30 min	CO <sub>2</sub>	–	–	–	Methylene blue	20–100	17.27	Banat et al. (2003a)
Date pits	600 °C/2 h	800 °C/1 h	CO <sub>2</sub>	Pretreatment with KOH	870	0.51	Methylene blue	–	123.1	Banat et al. (2003b)
Date pits	600 °C/6 h	–	ZnCl <sub>2</sub>	One step carbonization/activation	713	0.396	Methylene blue	–	127.3	El-Sharkawy et al. (2007)
Date pits	900 °C	–	Steam	One step carbonization/activation	1047	0.5797	Methylene blue	–	155.3	El-Sharkawy et al. (2007)
Date pits	600 °C/2 h	950 °C	Steam	–	1040	0.884	Methylene blue	10–100	244	Ashour (2010)
Date pits	600 °C/2 h	950 °C	Steam	–	1040	0.884	Remazol yellow	10–100	173	Ashour (2010)
Date pits	800 °C/1 h	971 °C/56 min	CO <sub>2</sub>	–	666	0.41	Methylene blue	400–1200	110	Reddy et al. (2012)
Date pits	800 °C/1 h	400 °C/58 min	H <sub>3</sub> PO <sub>4</sub>	–	725	1.26	Methylene blue	400–1200	345	Reddy et al. (2012)
Date pits	700 °C/1 h	–	FeCl <sub>3</sub>	One step carbonization/activation	780	0.573	Methylene blue	50–450	259.25	Theydan and Ahmed (2012)
Date pits	400 °C/2 h	–	ZnCl <sub>2</sub>	–	1380	0.91	Methylene blue	0–1000	434	Mahmoudi et al. (2015)

(continued)

Table 12.1 (continued)

Raw Material	Carbonization condition	Activation condition	Activating agent	Remarks	$S_{BET}$ ( $m^2 g^{-1}$ ) <sub>a</sub>	$V_t$ ( $cm^3 g^{-1}$ ) <sup>b</sup>	Adsorbate	Conc. Range ( $mg L^{-1}$ )	Adsorption capacity ( $mg g^{-1}$ )	Reference
				One step carbonization/activation						
Date pits	400 °C/2 h	–	ZnCl <sub>2</sub>	One step carbonization/activation	1380	0.91	Methyl Orange	0–1000	455	Mahmoudi et al. (2015)
Date stones	500 °C/0.5 h	–	ZnCl <sub>2</sub>	One step carbonization/activation	–	–	Methylene blue	–	286.3	Alhamed (2006)
Date stones	700 °C	600 W/8 min	KOH	Microwave-assisted activation	856	0.468	Methylene blue	50–500	316.11	Foo and Hameed (2011)
Date stones	500 °C/1.25 h	–	ZnCl <sub>2</sub>	One step carbonization/activation	1046	0.641	Methylene blue	50–450	381.79	Ahmed and Theydan (2012)
Date stones	700 °C/1.25 h	–	FeCl <sub>3</sub>	One step carbonization/activation	780	0.573	Methylene blue	50–450	255.32	Ahmed and Theydan (2012)
Date stones	500 °C/1 h	–	ZnCl <sub>2</sub>	One step carbonization/activation	1046	–	Methylene blue	50–450	398.19	Ahmed and Dhedan (2012)
Date palm seeds	200 °C/5 h	600 °C/1 h	NaOH	–	1282	0.66	Methylene blue	50–500	612.1	Islam et al. (2015)
Date palm seeds	700 °C/1 h	–	H <sub>3</sub> PO <sub>4</sub>	One step carbonization/activation	–	–	Methylene blue	–	199.4	Hussein et al. (2015)

Date palm rachis	800 °C/1 h	–	KOH	One step carbonization/activation	1160	0.583	BEZAKTIV red S-MAX	10–100	128.21	Daoud et al. (2017)
Date palm fronds	700 °C/1 h	–	H <sub>3</sub> PO <sub>4</sub>	One step carbonization/activation	–	–	Methylene blue		199.8	Hussein et al. (2015)
Date palm fibers	700 °C/1 h	–	H <sub>3</sub> PO <sub>4</sub>	One step carbonization/activation	–	–	Methylene blue		198.8	Hussein et al. (2015)

<sup>a</sup>Brunauer–Emmett–Teller specific surface area. Values are rounded off to the nearest whole number wherever applicable.

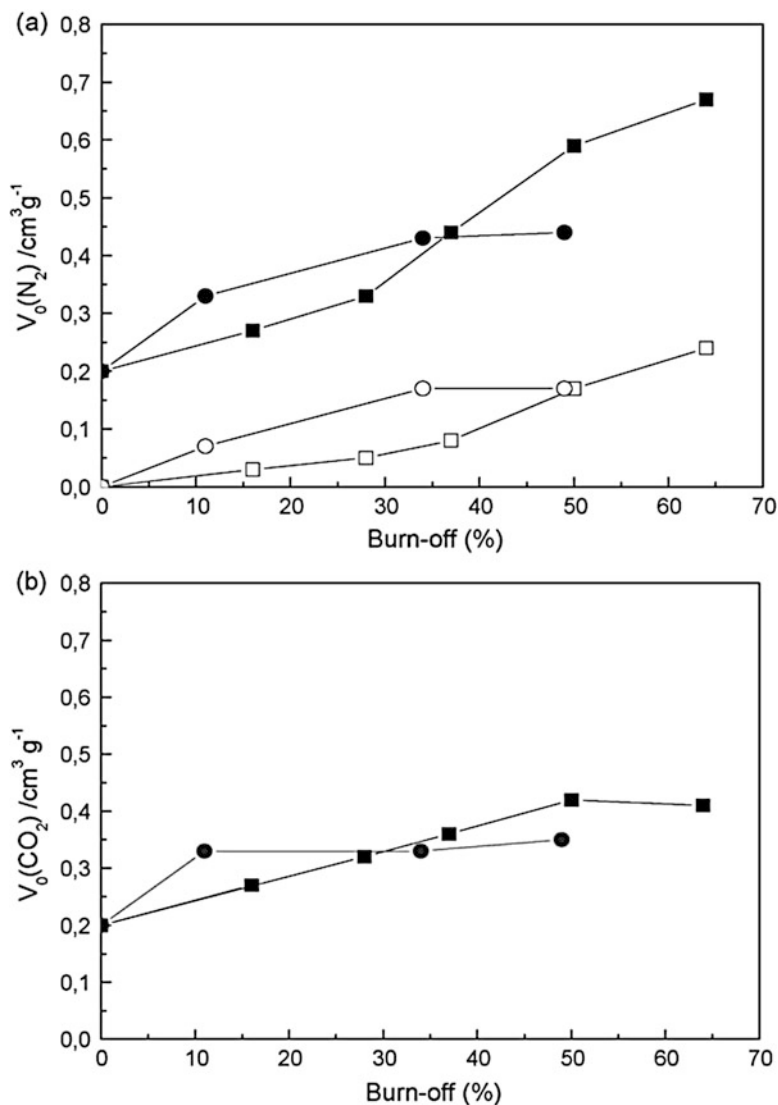
<sup>b</sup>Total pore volume.

### 12.2.1 *Physically Activated Carbon*

The typical synthesis route for the preparation of AC *via* physical activation involves two consecutive steps. The first step is ‘carbonization’ of the raw materials, where the precursor is pyrolyzed in the temperature range 400–700 °C in an inert atmosphere (usually nitrogen or argon) (Menya et al. 2018). During this phase, a vast majority of the non-carbon species, such as oxygen and hydrogen, are expelled as volatile gases (Gaspard et al. 2014), resulting in the formation of a fixed carbon mass (called ‘char’) that has a rudimentary pore structure (Rashidi and Yusup 2017), and hence manifests a minimal adsorption capacity (Menya et al. 2018). The second step in the preparation of AC, by physical activation, involves a controlled ‘gasification’ of the char at high temperatures (600–1000 °C) in the presence of a suitable oxidizing gas, such as air, CO<sub>2</sub>, steam, or their mixtures (Menya et al. 2018). When the carbonized raw material is subjected to partial gasification, majority of the reactive carbon atoms are selectively eliminated from the sample, thereby converting the char into a form that contains the utmost possible number of randomly distributed pores of various shapes and sizes (Gaspard et al. 2014). Indeed, the final activated carbon has a well-developed porosity and a correspondingly large surface area. A typical instance is that of Ashour (2010), who developed ACs with enormous specific surface area (1040 m<sup>2</sup> g<sup>-1</sup>), sufficiently large pore volume (0.884 cm<sup>3</sup> g<sup>-1</sup>), and a well-defined micro/mesoporous structure through steam activation of date pits. When tested as adsorbents employing a batch experimental set-up, the date pit-derived ACs showed remarkably high adsorption capacities towards both anionic (remazol yellow, 173 mg g<sup>-1</sup>) and cationic (methylene blue, 244 mg g<sup>-1</sup>) dyes, similar to commercial ACs.

The extent of pore formation and pore size distribution, and thus the adsorption potential, are, however, strongly dependent on the cellular structure of the original material, activation holding time, as well as the choice of the activation agent. For instance, Belhachemi et al. (2009) compared the influence of CO<sub>2</sub> and steam as activating agents, on the textural characteristics of ACs synthesized from date pits. It was found that, under analogous experimental conditions, the molecular size and reactivity of the activating agents played important roles in porosity development of the resulting ACs. Particularly, attributing to its smaller molecular size and faster diffusion rates, steam activation, in general, produced ACs with broader pore size distributions and greater surface area compared to CO<sub>2</sub> activation. However, additional improvement in porosity with increasing burn-off extent was more pronounced for CO<sub>2</sub> than steam (see Fig. 12.1). This trend can be ascribed to the way by which these agents react with the active sites of the pore structure. Precisely, steam attacks the active sites at the center and on the pore walls simultaneously. On the other hand, CO<sub>2</sub> primarily reacts with the active sites at the center of the pores (thus creating microporosity), and only attacks the pore walls when the activation time is too long. The latter results in significant broadening of the micropore diameter, ultimately yielding more mesoporous carbons (González et al. 2009). Despite the clear dissimilarities between the pore size distributions obtained using





**Fig. 12.1** Evolution of pore volume as a function of burn-off. (a) Micropore volume ( $V_0(N_2)$ ):  $\blacksquare$  –  $\text{CO}_2$  activated,  $\bullet$  – steam activated; Mesopore volume ( $V_{0,95} - V_0(N_2)$ ):  $\square$  –  $\text{CO}_2$  activated,  $\circ$  – steam activated. (b) Micropore volume ( $V_0(\text{CO}_2)$ ):  $\blacksquare$  –  $\text{CO}_2$  activated,  $\bullet$  – steam activated. Reproduced from Belhachemi et al. (2009), Copyright 2009, with permission of Elsevier

steam and  $\text{CO}_2$  as activation agents, both steam and  $\text{CO}_2$  have been widely used to produce ACs from date palm residues, with high adsorption capabilities towards several classes of dyes (Table 12.1).

In comparison to other activation approaches, several key merits of physical activation could be distinguished: (i) simplicity and ease of operation with no additional processing, such as washing of the end products; (ii) environmentally benign approach, since it avoids the use of toxic and harmful chemicals; (iii) scalability and low-cost (Ioannidou and Zabaniotou 2007; Sevilla and Mokaya 2014). Nevertheless, prolonged activation time associated with dual-stage processes, low carbon yield, and high power consumption, significantly limits the economic feasibility of the process (Rashidi and Yusup 2017).

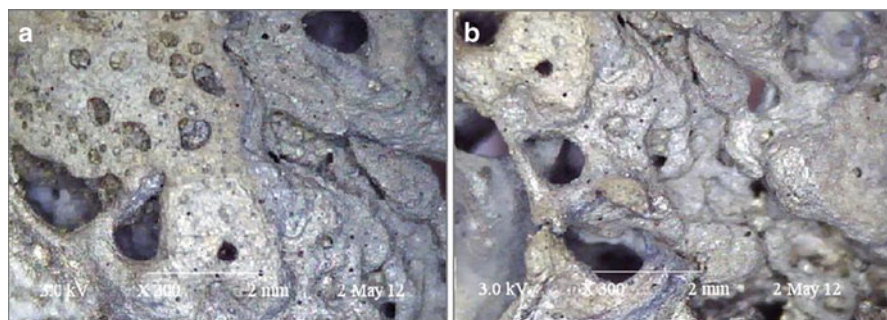
### **12.2.2 Chemically Activated Carbon**

As opposed to physical activation, chemical activation, in general, is a single stage process (Rashidi and Yusup 2017), implying that the transformation of the waste biomass into a carbonaceous residue and the generation of porosity take place concurrently. It usually involves impregnating the precursor with a chemical, followed by pyrolysis at relatively low temperatures of 400–700 °C (Menya et al. 2018). The most widely used chemical activating agents include alkalis such as potassium hydroxide (KOH) and sodium hydroxide (NaOH), acids such as phosphoric acid ( $\text{H}_3\text{PO}_4$ ), and transition metal salts like zinc chloride ( $\text{ZnCl}_2$ ) and ferric chloride ( $\text{FeCl}_3$ ) (Rashidi and Yusup 2017). These chemicals act both as dehydrating agents and as oxidants, so that carbonization and activation processes occur simultaneously in a single step (Hsi et al. 2011). For instance, when  $\text{H}_3\text{PO}_4$  is used as the chemical activating agent, it hydrolyses the glycosidic linkages in the polysaccharides (hemicellulose and cellulose) and cleaves the aryl ether bonds in lignin at low temperatures (Gaspard et al. 2014). This structural reconfiguration weakens the precursor structure and swells the carbon framework, allowing the cellulose microfibrils to separate. As the temperature increases, cyclisation and condensation reactions lead to aromatization of the carbon skeleton, and the altered microfibrils form an open porous structure (Gaspard et al. 2014). It is, therefore, conceivable that in the chemical activation process, the pore size distribution and the surface area are determined by the mass of chemical agent infused into the precursor and the impregnation duration (Rafatullah et al. 2013; Gaspard et al. 2014). Nevertheless, the flexibility to obtain different pore size distributions depends entirely on the reagent employed. Further, the carbon yield in chemical activation is usually higher compared to physical activation, since the chemical activating agents inhibit the formation of tar and curb the production of other volatile substances during pyrolysis, due to their inherent dehydrogenation properties (Gaspard et al. 2014). Consequentially, the chemical activation route has been more frequently exploited for the processing of date palm residues into ACs, for pollution control in the textile industry (Table 12.1), even though it requires meticulous washing to remove the residual chemicals, which may entail additional costs (Rashidi and Yusup 2017).

A notable example is that of Theydan and Ahmed (2012), who prepared ACs from date pits through chemical activation with  $\text{FeCl}_3$ . Textural parameters, evaluated from nitrogen ( $\text{N}_2$ ) adsorption/desorption isotherms, revealed that the as-made ACs were predominantly microporous ( $0.468 \text{ cm}^3 \text{ g}^{-1}$ ), with micropores accounting for nearly 82% of the total porosity. Moreover, the AC samples had fairly large surface areas ( $780 \text{ m}^2 \text{ g}^{-1}$ ), and could, therefore, adsorb huge amount of dyes from aqueous media. Indeed, a removal efficiency in excess of 90% was recorded for methylene blue, with the maximum adsorption capacity peaking around  $259 \text{ mg g}^{-1}$  at  $30^\circ \text{C}$ . A further improvement in the dye removal capacity ( $382 \text{ mg g}^{-1}$ ) was achieved upon activation with  $\text{ZnCl}_2$  (Ahmed and Theydan 2012). This observation was attributed to the better capability of  $\text{ZnCl}_2$  to eliminate volatile species from the precursor, as compared with  $\text{FeCl}_3$ , which resulted in ACs with increased surface areas ( $1046 \text{ m}^2 \text{ g}^{-1}$ ) and larger micropore volumes ( $0.512 \text{ cm}^3 \text{ g}^{-1}$ ) (Fig. 12.2) (Ahmed and Theydan 2012). Kinetic studies suggested that adsorption of methylene blue on the AC samples followed a pseudo-second-order rate equation, and the adsorption equilibrium data could be well represented by the Langmuir isotherm. Thermodynamic analysis indicated that the adsorption process was spontaneous and endothermic.

In another noteworthy study, Islam et al. (2015) devised a novel strategy to synthesize ACs from date seeds. Their approach involved hydrothermal carbonization of the waste biomass at  $200^\circ \text{C}$ , followed by impregnation with  $\text{NaOH}$ , and heating under a  $\text{N}_2$  flow at  $600^\circ \text{C}$  for 1 h. The resulting carbon materials displayed a relatively higher specific surface area and a total pore volume of  $1282 \text{ m}^2 \text{ g}^{-1}$  and  $0.66 \text{ cm}^3 \text{ g}^{-1}$ , respectively. Subsequently, they evaluated the adsorption potential of the date seed based ACs for methylene blue, by conducting batch adsorption tests. The adsorption equilibrium exhibited a perfect correlation with both the Langmuir and Freundlich isotherms with a monolayer uptake capacity of  $612 \text{ mg g}^{-1}$ , which is among the largest reported in the literature.

Impressively, employing  $\text{H}_3\text{PO}_4$  as the activating agent, Hussein et al. (2015) produced a series of ACs from an array of byproducts, derived from processing of



**Fig. 12.2** Scanning electron microscopy (SEM) images of activated carbon prepared from date pits through chemical activation with (a)  $\text{FeCl}_3$  and (b)  $\text{ZnCl}_2$ . Reproduced from Ahmed and Theydan (2012), Copyright 2012, with permission of Elsevier

the Iraqi Khestawy date palm: palm fronds (AC1), date palm seeds (AC2), and palm fiber (AC3). The sample AC1, due to its profound porosity, as inferred by estimating the moisture content, demonstrated the maximum adsorptive uptake of methylene blue compared with AC2 and AC3.

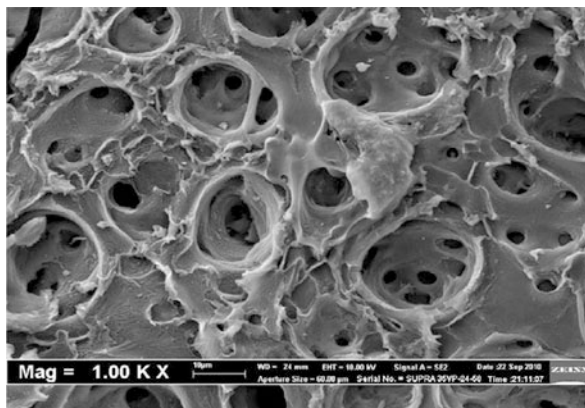
More recently, El-Shafey et al. (2016) explored Omani date palm leaflets as a precursor for AC *via* KOH activation. The as-prepared ACs were further oxidized and functionalized to produce basic and hydrophobic ACs. They were then tested for methylene blue adsorption from aqueous solutions. Depending on the surface chemistry, methylene blue interacted differently with the carbon sample under investigation. Interestingly, in spite of its relatively small surface area, the hydrophobic ACs showed the best dye removal performance.

### 12.2.3 *Physiochemically Activated Carbon*

It is evident from the breadth of aforementioned discussions that both physical and chemical activation methods are being actively pursued to obtain ACs from date palm biomass, for remediation of hazardous dye-bearing effluents. Nevertheless, in some cases, the activation step may involve longer processing times and require larger equipment. This results in highly non-uniform heating profiles, which in turn deteriorates the quality of the resulting ACs (Yuen and Hameed 2009). Additionally, there is a considerable risk of local overheating or even thermal runaway reaction, leading to the complete combustion of the char (Yuen and Hameed 2009). In an effort to overcome the aforementioned challenges, Foo and Hameed (2011) devised a rapid and facile physiochemical method for preparing ACs from date stone char, which involved KOH treatment and a short burst of direct microwave irradiation. The as-obtained ACs presented a well-developed and easily accessible porous structure (Fig. 12.3), with huge specific surface area ( $856 \text{ m}^2 \text{ g}^{-1}$ ) and large pore volume ( $0.468 \text{ cm}^3 \text{ g}^{-1}$ ). Consequently, these ACs could readily adsorb dyes from aqueous solutions, with a maximum monolayer uptake capacity of  $316 \text{ mg g}^{-1}$  for methylene blue.

Meanwhile, Banat et al. (2003b) investigated the adsorption of methylene blue onto ACs derived from date seeds through physiochemical activation, with KOH and  $\text{CO}_2$  as the activating agents. The experimental equilibrium data conformed to the Langmuir isotherm, with maximum monolayer coverage of  $123 \text{ mg g}^{-1}$ . The latter could be attributed to the significantly high surface area ( $870 \text{ m}^2 \text{ g}^{-1}$ ) of the as-prepared AC samples.

**Fig. 12.3** SEM image of activated carbon derived from date stone char by microwave induced KOH activation. Reproduced from Foo and Hameed (2011), Copyright 2011, with permission of Elsevier



### 12.3 Summary and Outlook

It is apparent from the extensive literature review that exploiting date palm byproducts, as a base feedstock for the production of carbonaceous adsorbents, can resolve the waste disposal crisis in date palm growing countries, with a potential revenue benefit option. In addition, it may also aid in regulating the unsustainable management of the waste byproduct. Compared to commercial AC, the ACs prepared from date palm wastes exhibit superior textural properties, and thus, greater adsorption capacity towards a multitude of dyes. However, this field of investigation is still at a nascent stage. Several fundamental issues and technical bottlenecks need immediate attention, to make more significant advances in this exciting new research domain of topical interest. First, the assessment of the dye removal capability of date palm based ACs is strictly restricted to batch adsorption tests. There is hardly any report on the adsorption of dyes using fixed bed reactor set-up. Continuous column study is, therefore, highly recommended since it represents a more practical approach of exploring the actual process-level performance of an adsorbent. Second, the equilibrium adsorption data, without exception, have been empirically correlated with the conventional isotherm models (such as Langmuir, Freundlich, Temkin etc.). However, since these analytical isotherm models are incapable of predicting pH-dependent adsorption behavior in a consistent manner (Jeppu and Clement 2012), the well-established surface ionization/complexation model or the double layer retention model should be frequently applied to investigate the effect of pH or ionic strength on the adsorption process. Third, although the ease of regenerating the spent adsorbent dictates the techno-economic viability of an adsorption process, studies along this direction are currently unavailable and should be actively pursued in the immediate future. Last but not the least, since several different varieties of dyes could simultaneously co-exist in industrial effluents, future research efforts should, therefore, also focus on evaluating the adsorption potential of the date palm based ACs with simulated wastewater, in order to ascertain their practical use.

Beyond these considerations, a rigorous assessment of the engineering economics of the date palm derived carbonaceous adsorbents should be conducted, upon scaling up the materials, for large-scale industrial applications. Additionally, economic models must be identified to perform a life cycle assessment, in order to establish the feasibility and sustainability of the bulk production of ACs from different date palm residues.

## References

- Abdulkarim MA, Darwish NA, Magdy YM, Dwaidar A (2002) Adsorption of phenolic compounds and methylene blue onto activated carbon prepared from date fruit pits. *Eng Life Sci* 2:161–165. [https://doi.org/10.1002/1618-2863\(200206\)2:6<161::AID-ELSC161>3.0.CO;2-2](https://doi.org/10.1002/1618-2863(200206)2:6<161::AID-ELSC161>3.0.CO;2-2)
- Ahmad T, Danish M, Rafatullah M, Ghazali A, Sulaiman O, Hashim R, Ibrahim MNM (2012) The use of date palm as a potential adsorbent for wastewater treatment: a review. *Environ Sci Pollut Res* 19:1464–1484. <https://doi.org/10.1007/s11356-011-0709-8>
- Ahmed MJ (2016) Preparation of activated carbons from date (*Phoenix dactylifera* L.) palm stones and application for wastewater treatments: review. *Process Saf Environ Prot* 102:168–182. <https://doi.org/10.1016/j.psep.2016.03.010>
- Ahmed MJ, Dhedan SK (2012) Equilibrium isotherms and kinetics modeling of methylene blue adsorption on agricultural wastes-based activated carbons. *Fluid Phase Equilib* 317:9–14. <https://doi.org/10.1016/j.fluid.2011.12.026>
- Ahmed MJ, Theydan SK (2012) Physical and chemical characteristics of activated carbon prepared by pyrolysis of chemically treated date stones and its ability to adsorb organics. *Powder Technol* 229:237–245. <https://doi.org/10.1016/j.powtec.2012.06.043>
- Alhamed YA (2006) Activated carbon from dates' stone by ZnCl<sub>2</sub> activation. *J King Abdulaziz Univ Eng Sci* 17:75–100. <https://doi.org/10.4197/Eng.17-2.4>
- Almi K, Lakel S, Benchabane A, Kriker A (2015) Characterization of date palm wood used as composites reinforcement. *Acta Phys Pol A* 127:1072–1074. <https://doi.org/10.12693/APhysPolA.127.1072>
- Alrumman SA (2016) Enzymatic saccharification and fermentation of cellulosic date palm wastes to glucose and lactic acid. *Braz J Microbiol* 47:110–119. <https://doi.org/10.1016/j.bjm.2015.11.015>
- Arevalo-Gallegos A, Ahmad Z, Asgher M, Parra-Saldivar R, Iqbal HMN (2017) Lignocellulose: a sustainable material to produce value-added products with a zero waste approach – a review. *Int J Biol Macromol* 99:308–318. <https://doi.org/10.1016/j.ijbiomac.2017.02.097>
- Ashour SS (2010) Kinetic and equilibrium adsorption of methylene blue and remazol dyes onto steam-activated carbons developed from date pits. *J Saudi Chem Soc* 14:47–53. <https://doi.org/10.1016/j.jscs.2009.12.008>
- Banat F, Al-Asheh S, Al-Makhadmeh L (2003a) Evaluation of the use of raw and activated date pits as potential adsorbents for dye containing waters. *Process Chem* 39:193–202. [https://doi.org/10.1016/S0032-9592\(03\)00065-7](https://doi.org/10.1016/S0032-9592(03)00065-7)
- Banat F, Al-Asheh S, Al-Makhadmeh L (2003b) Preparation and examination of activated carbons from date pits impregnated with potassium hydroxide for the removal of methylene blue from aqueous solutions. *Adsorp Sci Technol* 21:597–606. <https://doi.org/10.1260/026361703771953613>
- Bekheet SA, El-Sharabasy SF (2015) Date palm status and perspective in Egypt. In: Al-Khayri J, Jain S, Johnson D (eds) *Date palm genetic resources and utilization*. Springer, Dordrecht, pp 75–123. [https://doi.org/10.1007/978-94-017-9694-1\\_3](https://doi.org/10.1007/978-94-017-9694-1_3)
- Belhachemi M, Rios RVRA, Addoun F, Silvestre-Albero J, Sepúlveda-Escribano A, Rodríguez-Reinoso F (2009) Preparation of activated carbon from date pits: effect of the activation agent and liquid phase oxidation. *J Anal Appl Pyrolysis* 86:168–172. <https://doi.org/10.1016/j.jaap.2009.05.004>

- Chandrasekaran M, Bahkali AH (2013) Valorization of date palm (*Phoenix dactylifera*) fruit processing by-products and wastes using bioprocess technology – review. Saudi J Biol Sci 20:105–120. <https://doi.org/10.1016/j.sjbs.2012.12.004>
- Chowdhury S, Saha P (2010) Sea shell powder as a new adsorbent to remove basic green 4 (malachite green) from aqueous solutions: equilibrium, kinetic and thermodynamic studies. Chem Eng J 164:168–177. <https://doi.org/10.1016/j.cej.2010.08.050>
- Chowdhury S, Mishra R, Saha P, Kushwaha P (2011) Adsorption thermodynamics, kinetics and isosteric heat of adsorption of malachite green onto chemically modified rice husk. Desalination 265:159–168. <https://doi.org/10.1016/j.desal.2010.07.047>
- Crini G (2006) Non-conventional low-cost adsorbents for dye removal: a review. Bioresour Technol 97:1061–1085. <https://doi.org/10.1016/j.biortech.2005.05.001>
- Daoud M, Benturki O, Kecira Z, Girods P, Donnot A (2017) Removal of reactive dye (BEZAKTIV red S-MAX) from aqueous solution by adsorption onto activated carbons prepared from date palm rachis and jujube stones. J Mol Liq 243:799–809. <https://doi.org/10.1016/j.molliq.2017.08.093>
- El May Y, Jeguirim M, Dorge S, Trouvé G, Said R (2012) Study on the thermal behavior of different date palm residues: characterization and devolatilization kinetics under inert and oxidative atmospheres. Energy 44:702–709. <https://doi.org/10.1016/j.energy.2012.05.022>
- Elmay Y, Trouvé G, Jeguirim M, Said R (2013) Energy recovery of date palm residues in a domestic pellet boiler. Fuel Process Technol 112:12–18. <https://doi.org/10.1016/j.fuproc.2013.02.015>
- Elmay Y, Jeguirim M, Dorge S, Trouvé G, Said R (2014) Evaluation of date palm residues combustion in fixed bed laboratory reactor: a comparison with sawdust behaviour. Renew Energ 62:209–215. <https://doi.org/10.1016/j.renene.2013.07.007>
- El-Shafey EI, Ali SNF, Al-Busafi S, Al-Lawati HAJ (2016) Preparation and characterization of surface functionalized activated carbons from date palm leaflets and application for methylene blue removal. J Environ Chem Eng 4:2713–2724. <https://doi.org/10.1016/j.jece.2016.05.015>
- El-Sharkawy EA, Soliman AY, Al-Amer KM (2007) Comparative study for the removal of methylene blue via adsorption and photocatalytic degradation. J Colloid Interface Sci 310:498–508. <https://doi.org/10.1016/j.jcis.2007.02.013>
- Foo KY, Hameed BH (2011) Preparation of activated carbon from date stones by microwave induced chemical activation: application for methylene blue adsorption. Chem Eng J 170:338–341. <https://doi.org/10.1016/j.cej.2011.02.068>
- Gao Z, Zhang Y, Song N, Li X (2017) Biomass-derived renewable carbon materials for electrochemical energy storage. Mater Res Lett 5:69–88. <https://doi.org/10.1080/21663831.2016.1250834>
- Gaspard S, Passé-Coutrin N, Durimel A, Cesaire T, Jeanne-Rose V (2014) Activated carbon from biomass for water treatment. In: Gaspard S, Ncibi MC (eds) Biomass for sustainable applications: pollution remediation and energy. RSC Publishing, London, pp 46–105. <https://doi.org/10.1039/9781849737142-00046>
- González JF, Román S, González-García CM, Valente Nabais JM, Ortiz AL (2009) Porosity development in activated carbons prepared from walnut shells by carbon dioxide or steam activation. Ind Eng Chem Res 48:7474–7481. <https://doi.org/10.1021/ie801848x>
- Gupta VK, Carrott PJM, Ribeiro Carrott MML, Suhas (2009) Low-cost adsorbents: growing approach to wastewater treatment – a review. Crit Rev Environ Sci Technol 39:783–842. <https://doi.org/10.1080/10643380801977610>
- Suhas, Gupta VK, Carrott PJM, Singh R, Chaudhary M, Kushwaha S (2016) Cellulose: a review as natural, modified and activated carbon adsorbent. Bioresour Technol 216:1066–1076. <https://doi.org/10.1016/j.biortech.2016.05.106>
- Hsi H-C, Horng RS, Pan T-A, Lee S-K (2011) Preparation of activated carbons from raw and biotreated agricultural residues for removal of volatile organic compounds. J Air Waste Manag Assoc 61:543–551. <https://doi.org/10.3155/1047-3289.61.5.543>

- Hussein FH, Halbus AF, Lafta AJ, Athab ZH (2015) Preparation and characterization of activated carbon from Iraqi Khestawy date palm. *J Chem*. <https://doi.org/10.1155/2015/295748>
- Ioannidou O, Zabaniotou A (2007) Agricultural residues as precursors for activated carbon production – a review. *Renew Sust Energ Rev* 11:1966–2005. <https://doi.org/10.1016/j.rser.2006.03.013>
- Islam M, Tan IAW, Benhouria A, Asif M, Hameed BH (2015) Mesoporous and adsorptive properties of palm date seed activated carbon prepared via sequential hydrothermal carbonization and sodium hydroxide activation. *Chem Eng J* 270:187–195. <https://doi.org/10.1016/j.cej.2015.01.058>
- Jeppu GP, Clement TP (2012) A modified langmuir-freundlich isotherm model for simulating pH-dependent adsorption effects. *J Contam Hydrol* 129–130:46–53. <https://doi.org/10.1016/j.jconhyd.2011.12.001>
- Kausar A, Iqbal M, Javed A, Aftab K, Nazli Z-i-H, Bhatti HN, Nouren S (2018) Dyes adsorption using clay and modified clay: a review. *J Mol Liq* 256:395–407. <https://doi.org/10.1016/j.molliq.2018.02.034>
- Kodam KM, Kolekar YM (2015) Bacterial degradation of textile dyes. In: Singh SN (ed) *Microbial degradation of synthetic dyes in wastewaters*. Springer, Cham, pp 243–266. [https://doi.org/10.1007/978-3-319-10942-8\\_11](https://doi.org/10.1007/978-3-319-10942-8_11)
- Lattief FA (2016) A study of biogas production from date palm fruit wastes. *J Clean Prod* 139:1191–1195. <https://doi.org/10.1016/j.jclepro.2016.08.139>
- Mahmoudi K, Hosni K, Hamdi N, Srasra E (2015) Kinetics and equilibrium studies on removal of methylene blue and methyl orange by adsorption onto activated carbon prepared from date pits – a comparative study. *Korean J Chem Eng* 32:274–283. <https://doi.org/10.1007/s11814-014-0216-y>
- Menya E, Olupot PW, Storz H, Lubwama M, Kiros Y (2018) Production and performance of activated carbon from rice husks for removal of natural organic matter from water: a review. *Chem Eng Res Des* 129:271–296. <https://doi.org/10.1016/j.chemd.2017.11.008>
- Merdan N, Eyupoglu S, Duman MN (2017) Ecological and sustainable natural dyes. In: Muthu SS (ed) *Textiles and clothing sustainability*. Springer, Singapore, pp 1–42. [https://doi.org/10.1007/978-981-10-2185-5\\_1](https://doi.org/10.1007/978-981-10-2185-5_1)
- Shahid-ul-Islam, Mohammad F (2017) Anthraquinone-based natural colourants from insects. In: Muthu SS (ed) *Textiles and clothing sustainability*. Springer, Singapore, pp 81–98. [https://doi.org/10.1007/978-981-10-2185-5\\_3](https://doi.org/10.1007/978-981-10-2185-5_3)
- Nasser RA, Salem MZM, Hiziroglu S, Al-Mefarrej HA, Mohareb AS, Alam M, Aref IM (2016) Chemical analysis of different parts of date palm (*Phoenix dactylifera* L.) using ultimate, proximate and thermo-gravimetric techniques for energy production. *Energies* 9:374. <https://doi.org/10.3390/en9050374>
- Pathania D, Gupta D, Al-Muhtaseb AH et al (2016a) Photocatalytic degradation of highly toxic dyes using chitosan-g-poly(acrylamide)/ZnS in presence of solar irradiation. *J Photochem Photobiol A Chem* 329:61–68. <https://doi.org/10.1016/j.jphotochem.2016.06.019>
- Pathania D, Katwal R, Sharma G, Naushad M (2016b) Novel guar gum / Al<sub>2</sub>O<sub>3</sub> nanocomposite as an effective photocatalyst for the degradation of malachite green dye. *Int J Biol Macromol* 87:366–374. <https://doi.org/10.1016/j.ijbiomac.2016.02.073>
- Pereira L, Alves M (2012) Dyes – environmental impact and remediation. In: Malik A, Grohmann E (eds) *Environmental protection strategies for sustainable development*. Springer, Dordrecht, pp 111–162. [https://doi.org/10.1007/978-94-007-1591-2\\_4](https://doi.org/10.1007/978-94-007-1591-2_4)
- Rafatullah M, Ahmad T, Ghazali A, Sulaiman O, Danish M, Hashim R (2013) Oil palm biomass as a precursor of activated carbons: a review. *Crit Rev Environ Sci Technol* 43:1117–1161. <https://doi.org/10.1080/10934529.2011.627039>
- Rashidi NA, Yusup S (2017) A review on recent technological advancement in the activated carbon production from oil palm wastes. *Chem Eng J* 314:277–290. <https://doi.org/10.1016/j.cej.2016.11.059>



- Reddy KSK, Al Shoaibi A, Srinivasakannan C (2012) A comparison of microstructure and adsorption characteristics of activated carbons by CO<sub>2</sub> and H<sub>3</sub>PO<sub>4</sub> activation from date palm pits. *New Carbon Mater* 27:344–351. [https://doi.org/10.1016/S1872-5805\(12\)60020-1](https://doi.org/10.1016/S1872-5805(12)60020-1)
- Sevilla M, Mokaya R (2014) Energy storage applications of activated carbons: supercapacitors and hydrogen storage. *Energy Environ Sci* 7:1250–1280. <https://doi.org/10.1039/C3EE43525C>
- Sharma G, Naushad M, Pathania D et al (2015) Modification of Hibiscus cannabinus fiber by graft copolymerization: application for dye removal. *Desalin Water Treat* 54:3114–3121. <https://doi.org/10.1080/19443994.2014.904822>
- Singh K, Arora S (2011) Removal of synthetic textile dyes from wastewaters: a critical review on present treatment technologies. *Crit Rev Environ Sci Technol* 41:807–878. <https://doi.org/10.1080/10643380903218376>
- Singh SN, Mishra S, Jauhari N (2015) Degradation of anthraquinone dyes stimulated by fungi. In: Singh SN (ed) *Microbial degradation of synthetic dyes in wastewaters*. Springer, Cham, pp 333–356. [https://doi.org/10.1007/978-3-319-10942-8\\_15](https://doi.org/10.1007/978-3-319-10942-8_15)
- Theydan SK, Ahmed MJ (2012) Adsorption of methylene blue onto biomass-based activated carbon by FeCl<sub>3</sub> activation: equilibrium, kinetics, and thermodynamic studies. *J Anal Appl Pyrolysis* 97:116–122. <https://doi.org/10.1016/j.jaap.2012.05.008>
- Usman ARA, Abduljabbar A, Vithanage M, Ok YS, Ahmad M, Ahmad M, Elfaki J, Abdulazeem SS, Al-Wabel MI (2015) Biochar production from date palm waste: charring temperature induced changes in composition and surface chemistry. *J Anal Appl Pyrolysis* 115:392–400. <https://doi.org/10.1016/j.jaap.2015.08.016>
- Yaqub MT, Sen TK, Afroz S, Ang HM (2014) Dye and its removal from aqueous solution by adsorption: a review. *Adv Colloid Interf Sci* 209:172–184. <https://doi.org/10.1016/j.cis.2014.04.002>
- Yuen FK, Hameed BH (2009) Recent developments in the preparation and regeneration of activated carbons by microwaves. *Adv Colloid Interf Sci* 149:19–27. <https://doi.org/10.1016/j.cis.2008.12.005>