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REVIEW PAPER

A review on the physicochemical properties and utilization of date seeds in value-added engineering products

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Abstract

Date palm (*Phoenix dactylifera*) is an agricultural crop, which plays an important role as a source of nutrition in the day-to-day life of people. Date palm cultivation, processing industries, and consumption generate tons of wastes. One of these wastes is date seed, which represents 10% of the total weight of date fruit. The utilization of date seed waste is a research topic of interest for many applications such as cosmetic, nutritional, and engineering. In this review, the different methods used for preparing date seeds' powder and extracting its oil are surveyed. A comprehensive review of the physical and chemical properties of the date seed powder and oil is provided in addition to the employed characterization methods. This paper also reviews the utilization of date seed waste in the most common engineering applications including biofuels, composites, and adsorbent applications. The paper also highlights the research limitation and future research potentials of the utilization of date seed for several engineering applications.

Keywords Date seeds · Engineering applications · Recycling · Biofuel · Composites

Introduction

One of the oldest and most valuable plants known to man is the date palm (*Phoenix dactylifera* L.). Fossil of dates, referring to the Neolithic age, have been found in the Arab Mediterranean countries [1]. Historically, this indicates that the date palm tree can be traced back to 12,000 years ago. It has sustainable values comprising the economical, nutritional, ecological, social, health and religious aspects [2]. Palm tree has a great resistance of to both heat and drought stresses, it can tolerate desert severe weather. Hence, it helps stabilizing people's life in arid and semiarid areas,

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e.g., Egypt, Iran, Algeria, Saudi Arabia and Iraq [3]. The total production of date fruits in the world during the same year was 8,328,055 tons [3]. In comparison with other crops, date fruit production is only 1% of wheat production worldwide, and 40% of the production of olive during the same year. Since 1961, date fruits production increased by 340% from 1961 to 2017 while wheat and olive production increased only by 247% and 154%, respectively, during the same period [3]. According to D. Johnson, the palm tree branches to 183 genera and over 2400 species [4] and the variation in the species of the date palm tree is based on the area where it is planted. Soil type, irrigation facilities and weather conditions affect the growth of date palm trees. For example, there are about 400 species available in Saudi Arabia only [5].

In addition to the diversity and high nutritional value of its fruits, palm trees generate extensive amounts of recyclable waste which are a very important source of raw materials throughout the year [6]. For example, the leaves were utilized in the construction of fences and ceilings or to be woven into mats or baskets. Its trunk was used as supporting columns for ceilings. The fibers that are surrounding the stems were used as water or coffee filters. Single date palm tree turns out 20 kilos of fibers a year by renewing its leaves and bark, while seed within the date fruit represents 10% of the total weight of the fruit [7]. Reverting back to the previously mentioned statistics and considering only the world production of date fruit during the year 2019, this implicates that 10% of that production is seeds, that is 9,075,446 tons per year. Typically, most of those wastes are not recycled or used properly except for the limited purpose of planting new trees. An interesting review paper on the preservation of the date palm fruits is done by Sarraf et al. and has reviewed the commercially viable advance and updated techniques related to storage and quality such as nutritional, color, flavor, and texture [8]. Recently, a number of studies have been conducted to explore the possible applications that utilize the seeds and other parts of date palm tree. They are related to medical and cosmetic applications, food, animal feed and agriculture applications and engineering applications, such as biofuels, reinforcement materials, insulation materials and filtration materials [9–13].

Awad et al. [14] recently reviewed the application of date palm fibers as a reinforcement in bio-composites material. They surveyed the most recently published related research activities. Mohamed Nouri [15] reviewed the potentials and challenges of using date seeds as environmental cleanup systems on account of the different properties. He has systematically reviewed the potential of date seeds as adsorbent for diverse toxic contaminant kinds such as heavy metals, pesticides, dyes, phenol compounds, gases, and other pollutants. However, to the best of the authors knowledge there is a very limited number of review papers that addresses the engineering applications of waste date seeds [14, 15]. Therefore, the aim of this paper is to survey and summarize most of the date seed engineering applications studies. This review paper fills a gap in the literature by providing a full overview of most of the work that has been published in this regard. However, any non-engineering application is beyond the scope of this work.

This paper is organized as follows: Sections two and three provide a brief overview of the different methods followed by researchers to prepare the powder or extract the oil from the date seeds. The fourth section presents and compares the different thermal, and chemical properties reported in the literature for different species of date seeds. Before the conclusion, in section five most commonly used products derived from date seeds will be reviewed.

Date seeds powder preparation process

The dark brown colored date seeds or stone is a solid body, rectangular, pointed at the ends, and occupies the center of the date fruit. It weighs between 0.5 and 4 g, its length range between 12 and 20 mm, and width between 6 and 15 mm, usually the length of the seed is three times the width, and its weight ranges between 10 and 20% of the total weight of the fruit [16]. 1440 years ago, the Holy Quran has dissected the date seed and name its parts in an unprecedented and precise manner. Externally, the date seed is made up of two sides: dorsal side and ventral side. The dorsal side is convex, contains a small, round-shaped, low-click called Al-Naqir (Micro Pyle). The ventral side has a furrow or a groove that extends along with the seed. A very thin membrane encapsulates the date seed called Al-Qatmir. Internally, the seed consists of the seed coat, the embryo, the germ pore, and the endosperm. The endosperm represents the bulk of the seed, composed of a semitransparent, hemicellulose material [16]. Therefore, in order to make use of the date seed, first, the unwanted parts of the seed must be washed out. Then it must be dried to remove any moisture content gained through the washing process or of that contained inside the seed, knowing that the seed contains 5 to 10% moisture [17], finally, grinding the clean dry seed to form a homogeneous seed powder. Then the powder formed is sieved until sizes are achieved.

Of all the studies reviewed, some of these studies did not provide detailed information on how the date seeds powder was prepared. Other studies that provided enough details of the preparation method did not agree on a single preparation method. Table 1 summarizes the variation in the preparation method with respect to the cleaning, drying, and grinding process; the absence of a standard method is evident in all these studies. Even though most of the studies used either distilled or just tap water as cleaning agent, they did not agree on soaking duration. Four studies used H_2SO_4 as a cleaning agent to remove the surface layers [18–21]. Yet, three of these four studies used 50% concentrated solution while the fifth used 70% [21]. Some other limited number of studies used deionized water for better purification. Also, ultrasonic waves have been used to remove dust and dirt from the sample in a couple of studies [22, 23].

The reviewed studies also differed regarding the method of drying, some used just sun heat or ambient temperature while others used ovens at different temperatures ranging from 40 °C to 105 °C. The same applies to the drying period too. It varied mostly according to the source of heating used from one hour to a week. No specific pattern can be found among all the reviewed studies to determine a mathematical relationship between the used temperature and drying duration. For example, Kolawole et al. and Danladi et al. both used 70 °C oven temperature for drying, however, Kolawole et al. applied it for 4 h only while Danladi et al. left the seeds in the oven under that temperature overnight, although both studies worked on

Table 1 Date seeds powder preparation

Study		Cleaning		Drying		Grinding	
Author	Year	Cleaning agent	Soaking duration	Temperature °C	Duration	Particle size mm	Apparatus
Devshony et al. [26]	1992	Water	–	Sun–dried	–	–	Hammer mill
Hussein [21]	1998	Water	0	60	24 h	1	–
		70% H_2SO_4	30 min	60	24 h	1	–
Besbses et al. [27]	2004	Water	–	50	12	1–2	Heavy duty mill
Besbses et al. [28]	2004	Water	–	50	12	1–2	Heavy duty mill
Saafi et al. [29]	2008	Water	–	80	24	–	Hammer mill
Ghazanfari [30]	2008	Water	–	60	6	0.595	–
Boukouada et al. [31]	2009	Water	–	60	48	1–2	
Fatma et al. [32]	2009	Water	–	50	12	1–2	
Alsewailem and Binkhder [33]	2010	Water	–	Vacuum oven	24 h	0.15	IKA MF 10
Al-Ghouti et al. [34]	2010	Distilled water	–	105	3 h	0.125–0.3 0.3–0.5 0.5–0.71	
El-Naas et al. [35]	2010	Water	–	–	–	0.125 to 0.212	–
Hamma et al. [36]	2012	Water	0	Ambient	Several days	0.1	–
Amani et al. [37]	2013	Water	–	–	–	1.2	–
Habib et al. [38]	2013	Water	–	Ambient	–	–	IKA M 20
Mitta et al. [18]	2014	50% H_2SO_4	5 h	–	–	0.06	–
Alsewailem and Binkhder [39]	2014	Water	–	Vacuum oven	24 h	0.15	IKA MF 10
Danladi et al. [25]	2014	Water	–	–	–	0.25	–
Mittal et al. [19]	2015	50% H_2SO_4		70	Overnight	0.06	
Ibrahem [40]	2015	Water					
Kolawole [24]	2015	Water		70	4 h	0.15	Hammer mill

Table 1 (continued)

Study		Cleaning		Drying		Grinding	
Author	Year	Cleaning agent	Soaking duration	Temperature °C	Duration	Particle size mm	Apparatus
Ameh et al. [41]	2015	Deionized water		Ambient		0.5 2 2.8	–
Al.Haddabi et al. [42]	2015	Water	–	500	1 h	0.53–0. 2	–
Adewunmi et al. [43]	2015	water	1 day	–	–	–	–
Bouallegue et al. [44]	2015	Distilled water	–	40	12 h	0.2—1.4	–
Ali et al. [45]	2015	Water	–	Sun-dried	–	0.425 < 1.2 < 1	
Al-Muhtaseb et al. [46]	2016	Water		100	12 h	–	
Jamil et al. [47]	2016	Water		70	Overnight	0.25–0.3	–
Azeem et al. [48]	2016	Water	–	Sun-dried		1	
Sabzevari and Kabiri [49]	2016	water	–	50	–	1	–
El Messaoudi et al. [50]	2016	Water	–	105	24 h	0.05–0.1 0.1–0.315 0.315–0.5 0.5–1	–
Al-Saidi [51]	2016	Water		70	1 day	0.25	
Al-Zuhair et al. [52]	2017	Water	–	Sun-dried	2 days	2.36 0.5 0.35	AR1043 Moulinex
Marzouk et al. [53]	2017	Water	–	75	24 h	0.05	–
Fadhil et al. [54]	2017	Boiling water	5 h	50	24 h	0.42	–
Rawa Yousuf [55]	2017	water	3 h	60	Overnight	≤ 4	UMA Pharmae

Table 1 (continued)

Study		Cleaning		Drying		Grinding	
Author	Year	Cleaning agent	Soaking duration	Temperature °C	Duration	Particle size mm	Apparatus
Al-Ghouti et al. [56]	2017	Distilled water	–	65	2 h	0.125–0.25 0.25–0.5 0.5–1	
Ben-Youssef et al. [57]	2017	Water	–	50	12 h	1	Hammer mill
Yousuf. et al. [55]	2017	Water	–	60	Overnight	≤ 4	UMA PHARMA
Qadir et al. [58]	2018	Water	–	40	–	–	Heavy duty mill
Elnajjar et al. [59]	2018	Distilled water		80	12	0.1—0.3 0.3 –0.85 0.85 – 1.18 > 1.18	JK–G–250B2
Al-Mosawi1 et al. [23]	2018	Distilled water	–	Sun-dried	1 day	0.0005	–
Abdulkareem et al. [60]	2018	Water	–	Sun-dried	Week	0.6 0.5 0.42 0.3	–
Mohamed et al. [61]	2018	Water 4 °C	3 days	After 90 °C	–	–	–
Al-Mosawi1 et al. [22]	2018	Distilled water	–	Sun-dried	24 h	0.0005	Micro mill
Giwa et al. [62]	2018	Water	–	Sun-dried	1 h	1.7	–
Saryono et al. [63]	2018	Water	–	Sun-dried	1 day	fine	
Elkhouly et al. [20]	2019	50% H_2SO_4	5 h	70 °C	8 h	0.075	–

polymeric composites [24, 25]. The variation was not only in variables but also in sequence too, while most of the studies followed the regular sequence, i.e., cleaning, drying, and grinding, a couple of studies did more cleaning or drying after grinding. For example, Al-Mosawi et al. reported that the prepared powder was dried after grinding in a furnace at a temperature of 25 °C for 5 h to remove any moisture from the powder, although he also worked on polymeric composites [22, 23].

The conducted review clearly shows that there was no specific standard method followed by researchers while preparing the date seed powder in all studies included in this review paper and reported the preparation process details. In addition, it was noticed that there is a significant effect caused by the used method of preparation on the achieved results of the study [34, 50, 56, 59]. For example, the cleaning agent, the duration of soaking, the drying temperature, and the duration of drying affect the size of the grinded particles.

Date seeds oil extraction process

In comparison with other vegetable oils, date seed oil has an exceptionally intense yellow color [29, 64]. The observed yellow color is due to the presence of carotenoids [65]. Boukouada and Yousfi [31] conducted a study to determine physicochemical properties of three types of date seed powder and date seed oil, namely Deglet Nour, Ghars, and Tamdjouhert. The study highlighted that the color of the three types of date seed oils varies from greenish yellow to brownish yellow, and it was found to be in the semisolid state at 20 °C. The average of the three types of oils for refractive index is 1.4786, specific gravity is 0.9042, and total lipids content is 5.4433%. For the three studied types of oil, the acid value was in the range of 1.35–1.38 mg KOH/g, iodine values in the range of 67.22–74.8 g iodine/100 g, saponification values in the range of 204.84–215.87 mg KOH/g. Date seed oil has thermal resistance, high oxidative stability, antioxidant activity, protecting ability from cellular and oxidative stress damage, and low free fatty acid [17, 27, 28, 32, 64–66]. A number of studies and review articles investigated the different properties of several date seed oils [26, 38, 64, 66–68]. Due to its intrinsic properties, the date seed oil is being utilized in a variety of applications such as cosmetic, nutritional, medicine, and other different industrial applications.

The extraction process of oil from date seeds has been investigated, studied, and optimized. Table 2 summarizes several related studies, particularly highlighting different variables such as origin and species type of date seed, seed powder particle size, oil yield, extraction technique, employed solvent, and extraction process time. The Soxhlet extractor method is the most used technique to extract oil from date seeds as shown in Table 2. The other used techniques, to the best of authors' knowledge, have not been used in two different studies. When other techniques were used, mostly compared to the Soxhlet performance. Also, some of the reviewed studies have not reported the factors considered nor the oil yield.

For Soxhlet technique, an elaborated optimization study was developed by Jamil et al. [70]. In this study, the effects of several parameters of the Soxhlet extractor method (i.e. temperature, solvent-to-seed ratio, and process time) on the oil yield

Table 2 Date seeds oil extraction process

Study	Area	Tree type	Technique	Temperature (°C)	Solvent	Process time (h)	Particle size (mm)	Oil yield (wt %)
Jamil et al. [47]	Oman	NR	Soxhlet	50 60 70	Hexane	5 6 7	0.00025 – 0.0003	10.6 – 16.5
Fadhil et al. [54]	Iraq	NR	Soxhlet	60–80	Petroleum ether	10	0.42	10.5
Ala'a et al. [69]	Oman	NR	Soxhlet	NR	Hexane	7	NR	16.5
Yousuf and Winterburn [55]	Iraq	NR	Soxhlet	100–180	Petroleum ether	0.5–4	< 1 2–4	3 1.5
					Chloroform		< 1 2–4	NR NR
					Methanol mixture		< 1 2–4	9.5 5.2
					Hexane		< 1 2–4	5 2.8
Devshony et al. [26]	Israel	Dekel Noor Zahidi Medjool Halawy	Soxhlet	40–60	Petroleum ether	9	NR	8.4 8.13 7.98 8.10
Boukouada and Yousfi. [31]	Algeria	Deglet Nour Ghars Tamdjouhert	Soxhlet	NR	Hexane	6	1–2	5.2 5.05 6.08
Abdalla et al. [67]	Sudan	Albarakawi Algundeila	Soxhlet	NR	Hexane	4–6	NR	6.83 5.06
Al-Zuhair et al. [52]	UAE	Khalas	Soxhlet	80	Hexane	12	PS > 2.36 2.36 > PS > 0.5 0.5 > PS > 0.35	2.38 7.95 11.67
			Solvent mixture	Ambient	Methanol–chloroform	0.5	PS > 2.36 2.36 > PS > 0.5 0.5 > PS > 0.35	3.19 6.72 8.9

Table 2 (continued)

Study	Area	Tree type	Technique	Temperature (°C)	Solvent	Process time (h)	Particle size (mm)	Oil yield (wt %)
Elnajjar et al. [59]	UAE	Allig	Folch	NR	Chloroform and methanol mixture	0.5	Nano-Size	5.7
							0.1–0.3	9.7
							0.3–0.85	9
							0.85–1.18	6.2
							> 1.18	4.7
							Whole	0
			Soxhlet	80	Hexane	12	0.1–0.3	10.52
							0.3–0.85	9.7
							0.85–1.18	8.9
							> 1.18	8
							Whole	0
		Khalas	Folch	NR	Chloroform and methanol mixture	0.5	0.1–0.3	9
							0.3–0.85	8.6
							0.85–1.18	5.7
							> 1.18	3
							Whole	0
			Soxhlet	80	Hexane	12	0.1–0.3	10.36
							0.3–0.85	8.42
							0.85–1.18	7.62
							> 1.18	5.5
							Whole	0.1

Table 2 (continued)

Study	Area	Tree type	Technique	Temperature (°C)	Solvent	Process time (h)	Particle size (mm)	Oil yield (wt %)
Ben-Youssef et al. [57]	Tunisia	Deglet Nour	Soxhlet	NR	Hexane	8	1	7.24
					MeTHF			5.97
			Ultrasound	40	Hexane	0.5		6.18
					MeTHF			5.57
			Microwave	NA	Hexane			5.52
					MeTHF			4.74
			Maceration	40	Hexane			4.44
					MeTHF			4.04
		Allig	Soxhlet	NR	Hexane	8		4.44
					MeTHF			5.02
			Ultrasound	40	Hexane	0.5		NR
					MeTHF			NR
			Microwave	NA	Hexane			NR
					MeTHF			NR
			Maceration	40	Hexane			NR
					MeTHF			NR

Table 2 (continued)

Study	Area	Tree type	Technique	Temperature (°C)	Solvent	Process time (h)	Particle size (mm)	Oil yield (wt %)
		Belah	Soxhlet	NR	Hexane	8		4.78
					MeTHF			5.74
			Ultrasound	40	Hexane	0.5		NR
					MeTHF			NR
			Microwave	NA	Hexane			NR
					MeTHF			NR
			Maceration	40	Hexane			NR
					MeTHF			NR

were analyzed to allocate the optimum conditions that allow maximizing the amount of oil yield extracted from date seed powder. By using central composite design (CCD) and a response surface methodology (RSM) for the experimental data, the study found that 16.5 wt.% oil yield was achieved at a temperature of 70 °C, 4:1 solvent-to-seed ratio and after 7 h of extraction process time. By applying analysis of variance (ANOVA), the study highlighted that the three selected parameters were significant with no significance found for the interaction between the selected parameters nor the quadratic form of them except for the temperature. Therefore, temperature was the most significant parameter to affect oil yield.

Fadhila et al. [54] studied the potential of utilizing date seeds oil as new feedstock for liquid biofuels production. Using the Soxhlet extraction method, petroleum ether as a solvent, temperature ranging from 60 to 80 °C, particle size of 0.42 mm, and process duration of 10 h, they reported an oil yield of 10.5 wt.%. In comparison with the previously discussed study [42], the oil yield of this study is less than the minimum oil yield reported there. Perhaps the use of petroleum ether as a solvent and using a larger range of particle size negatively affected the yield of oil. Devshony et al. [22] used petroleum ether as a solvent at lower temperature range than both studies [42, 49] and reported less amount of oil yield for four types of date seeds. Al-Zuhair et al. [47] used the Soxhlet extraction method, a temperature of 80 °C, hexane as a solvent, duration of 12 h, and three different particle sizes. The reported results show that smaller particle size resulted in higher percentage of oil yield. It is worth mentioning that hexane was mostly used as a solvent in most of the reviewed studies that employed the Soxhlet extraction method. In comparison with the studies that considered other solvents than hexane, it can be drawn that hexane mostly increases the percentage of oil yield from date seeds, except for MeTHF solvent for Belah type with process time equal to 8 h [52] and Methanol mixture [50].

Among the reviewed literature, different types of date seeds were investigated, compared, and reported [22, 50, 52, 54, and 63]. However, there was no constancy in the procedure used and some studies did not report some of the extraction procedure variables. While using petroleum ether as a solvent, temperature range of 40–60, and process time of 9 h, Deglet Nour showed the highest oil yield among other date seed types investigated [22]. In the other study conducted by Boukouada and Yousfi [27], Deglet Nour yield less amount of oil, but the process time was 3 h less than the previously discussed study, where the particle size was not reported [22]. Inversely proportional relation between particle size and oil yield is observed in most of the Soxhlet extraction method studies. Elnajjar et al. [54] used another extraction method called Folch in addition to the Soxhlet method with two types of seed (Allig and Khalas). As shown in Table 2, they used different testing conditions for each method used. For both extraction methods used, the smaller the particle size, before reaching nano-size, yield a higher amount of oil for both types of date seed. While the Soxhlet extraction method gave better oil yield than Folch in all size range, the processing time for the Folch extraction method is less than that for the Soxhlet extraction method. Another study reported a comparison between the yield of oil extracted using n-hexane as a solvent and the oil extracted using methanol-chloroform solvent mixture [47]. The methanol–chloroform solvent mixture was found more effective with larger particle size.

Ben-Youssef et al. [52] compared four extraction methods (i.e. Soxhlet, maceration, ultrasound, and microwave) while using two different solvents (n-hexane and MeTHF). The aim of the study was to evaluate the possibility of replacing the petroleum-based solvent by bio-based degradable solvent. The highest reported results of oil yield for the four-used method were for Deglet Nour. The Soxhlet extraction was more effective for both utilized solvents. Ultrasound and microwaves extraction results were slightly lower than that of the Soxhlet extraction method. However, the Soxhlet extraction method processing time was much longer than the processing time for other extraction methods.

Bouallegue et al. [65] studied the oil yield from date seed powders with different particle sizes ranging from 1.4 to 0.2 mm. Accelerated solvent extraction (ASE) and dynamic maceration (DM) were used with and without instant controlled pressure drop (DIC). Using DIC as texturing pretreatment increased seed oil yield from 4.57% to 10.49% ± 0.05% dry–dry basis (ddb) for DM and increased yields from 11.35% to 14.15% ± 0.05% ddb for ASE. Similar to the previously reported studies the effect of reducing particle size of seed powder was positive and increased oil yield. The reported studies show that the Soxhlet extraction method was intensively evaluated by researchers, and it was more effective in comparison with other extraction methods. The developed optimized extraction method, by Boullague et al. [65], shows unique and potential extraction method. However, no further or follow up studies were reported to reproduce, revaluate, or enhance the technique. It is noticeable that there is variation in the testing conditions for each study, some of which significantly affect the achieved results, such as date seed type, particle size, processing temperature, solvent type, and processing time. There is a pressing need for further research efforts to comprehensively evaluate, optimize, and standardize the proposed extraction method and testing conditions. Yahya et al. [71] did a techno-economic analysis on the oil extraction from date palm waste, char, and burnable gases recently. The economic analysis considering the various parameters has suggested that a net saving of USD 556.8 per ton of the date palm waste in the pyrolysis unit which can also lead to USD 44.77 million per annum to Saudi Arabia. Oil extracted from date seeds can be utilized as precursor for the preparation of nanoparticle of various sizes and large efforts are being done in this direction recently. Silver nanoparticles [72, 73], nanostructured carbon [74–76], micro- and nano-cellulose [77–81], zinc oxide nanoparticles [13], and cobalt oxide nanoparticles [82] were synthesized using date palm extracts very recently. Oil extracts from date seeds and date seed wastes are becoming an economical and green synthesis precursor and can lead to promising results in the near future itself.

Thermal and chemical properties

The physical and chemical properties of date seeds are important for any application or conversion to useful products. Thermal properties of raw date seeds powder believed to alter the thermal characteristics of the composites based on their filler percentage in it. As stated previously, there are a wide variety of date palm tree species. Hence, it is essential to know the thermal properties of the different species in order to properly select the perfect species for a certain application. Different thermal properties have been reported in literature, e.g. thermal conductivity, specific heat, endothermic effects, exothermic effects, and degradation temperature. However, these properties are dependent on the number of variables including the used sample species, moisture content, heating rate, and powder preparation method or oil extraction method. Hence, the reported results did not allow the comparison of different thermal properties of different species of date seeds. Hobani and Al-Askar investigated the thermal properties of both Khudary and Sufri dates. They determined the effective thermal conductivity, thermal diffusivity, and specific heat as a function of moisture at 50 and 70 °C at different moisture contents. They found that all the investigated thermal properties were linearly dependent on moisture content [83].

Besbes et al. studied the chemical composition and characteristic profiles of both Deglet Nour and Allig date seed oil. Using the differential scanning calorimeter (DSC) they investigated the melting peak, melting enthalpy, and onset temperature for both species. They reported a slight difference among the selected species and justified that by the different fatty acid composition. In their study, the moisture content of Deglet Nour and Allig date seed was 9.4 and 8.6%, respectively, and the prepared powder particle size was between 1 and 2 mm. The DSC thermograms were obtained at heating rate of 15 °C/min. The seed oil was extracted with petroleum ether at 40–60 °C [17]. They also highlighted that the thermal profile of date seed oil was affected by the heat treatment applied to the date seed, and the melting enthalpy decreased with respect to the time of heat treatment increased [28]. Rahman et al. confirmed that the endothermic events were dependent on the moisture content of the sample. They studied the thermal transition of roasted, unroasted, and defatted date seeds powder of unspecified date species. The particle size was 500 µm, and samples were scanned from − 90 °C to 60 or 80 °C at a rate of 5 °C/min for DSC and 3 °C/min for MDSC [84].

Nehdi et al. [65] used 1 mm particle size of the *P. canariensis* date seed powder with 10.20% moisture content to investigate its oil characteristics and chemical composition. They reported melting point of 3.71 °C and melting enthalpy of 62.08 J/g. These values are in range with those for Deglet Nour and Allig date seed oil as reported by Besbes et al. [17]. Suresh et al. studied the thermal properties of Khalas date seed with particle size ranging from 132 to 400 µm [85]. They examined the effect of moisture content as well as heating rate and they concluded that melting enthalpy increases with increasing moisture content, while the heat rate was found to affect the melting enthalpy based on the moisture content in the sample. A similar conclusion was drawn by Guizani et al. who studied the thermal characteristics of freeze-dried Khalas date seed [86].

The degradation profiles of six different species of date seeds were analyzed in a study conducted by Babiker et al., the species considered were Deglet Nour, Piarom, Safawi, Mabroom, Aliya, and Suffry. The experiments were conducted using thermogravimetric analyzer (TGA) under non-isothermal conditions and at a heating rate of 20 °C/min, the particle size reported was 250 mm and 355 mm. The results showed that Deglet Nour has the highest value among other species, even though there were only slight differences between all the different species, the values were ranging from 18.226 to 18.548 kJ/kg which as they claimed considered to be among the high-quality biological feedstock regarding energy recovery and recycling [87]. Nasser et al. investigated the fuel characteristics for eight different parts of the Sukkari date palm tree including its seed. Using particle size ranging from 420 to 850 µm, four fuel characteristics were determined for all eight samples including heating value [37] and fuel value index (FVI). The reported results showed that the most significant results of the date palm wastes for energy production with heating value of about 20 MJ/kg and fuel value index of 2078 which is almost double the value of tortilis [88]. Thermal stability was investigated in a study by Nehdi et al. [89] in which they examined the seed oil of six different species cultivated in Saudi Arabia, namely Barhi, Khalas, Manifi, Ruzeiz, Sulaj, and Sukkari. All studied species showed peak temperature above 340 °C which indicates high thermal stability. These encouraging thermal specifications have motivated researchers around the world to search for applications and value-added products to utilize the wasted large quantities of date seeds.

The chemical composition of date seeds is also very important to propose applications. There were several attempts to find out the contents in date seeds in recent years. Metoui et al. [90] recently analyzed the chemical composition of two variants of Tunisian date seeds. The seeds were separated from the fruits, washed with distilled water, air-dried, and powdered. The 12 cultivar powders were conserved at − 20 °C for further analyses. Protein, fat, moisture, dietary fiber, sugar, ash, sodium, phosphorous, potassium, polyphenol, flavonoids, and anthocyanin were systematically analyzed. Among the minerals, potassium was present in the highest concentration, followed by phosphorus and sodium. The phenolic content in these varieties was higher than the other variants of date seeds and the authors have proposed the use in functional foods, pharmaceuticals, cosmetics, and food additives. Sawaya et al. [91] studied two date cultivars from Ruzeiz and Sifri grown in Saudi Arabia on account of chemical composition and nutritional quality in 1984. Both the seeds contained an average of 6.5% protein, 10.4% fat, 22.0% fiber, 1.1% ash, and around 60.0% of carbohydrates. The mineral analysis showed that K is having a higher concentration followed by P, Mg, Ca, and Na. Fe, Mn, Zn, and Cu were present in both variants in micro-quantities. They found out the chemicals present in the oil and protein efficiency values too. Besbes et al. [17] and his coworkers studied the chemical composition of seeds for two variants of date palm (*Phoenix dactylifera* L.) cultivars, Deglet Nour and Allig, from the Degache region, Tunisia.

The reviewed studies clearly indicate that the chemical composition of date seeds is very important for suggesting the products from these materials. Tafti and Panahi [92] analyzed two different Iranian date cultivars recently. The chemical composition of the date seeds is as follows: protein 4.84%, fat 12.22%, fiber 27.58%, carbohydrates 80.76%, ash 1.18%, and moisture 1.72%. They also contained minerals in which Fe was in high concentration while others such as Ca, Cu, Na, Zn, and Mn were less in content. The seeds also had a high amount of phenolics. Another interesting study from Elnajjar et al. [93] reported the morphological characteristics and chemical composition of DS powder of a local date palm cultivar from the UAE, Allig, before and after oil extraction. It was concluded that DS oil is an economically feasible oil source because of its high oil content. In order to measure the chemical composition Allig DS powder samples composed of particles ranging in size from 0.1 mm to 0.3 mm were prepared using the Soxhlet, Folch, and CO_2 supercritical extraction methods. Different characterization methods such as TGA, EDS, SEM, XRF analysis, ICP analysis, and fatty acid composition analysis using GC were employed to report the chemical composition before and after oil extraction. It was found that there is no significant change in the chemical composition before and after oil extraction. The most abundant elements were K and Na; however, P and Cr did not move to the oil extract. The DSs were found mainly to contain carbohydrates (81%), followed by fat (12%) and moisture (10%). The EDS analysis revealed C as the main constituent of the biomass, and its content was decreased by 21% following oil extraction. Analysis of the changes in the metal contents between before and after oil extraction revealed increases in P and S in the biomass after oil extraction, which is favorable for biodiesel production. Interesting results on stearic acid are also reported in the article. Nehdi et al. [65] conducted studies on properties of seeds and oil extracted from fully ripened *P. canariensis* date seeds. The percentage composition of the *P. canariensis* seeds found is as follows: 1.18% ash, 10.36% oil, 5.67% protein content, 72.59% total carbohydrate, and 10.20% moisture. Potassium (255.43), magnesium (62.78), calcium (48.56), and phosphorus (41.33) were the major nutrients (mg/100 g of oil). Mrabet et al. [94] recently reviewed the date seeds applications and cited the chemical composition works in it. They mainly focused on fatty acids and other useful chemicals from different sources and reviewed the applications of date seed oil.

Products derived from date seeds

According to the latest crop statistical data from the Food and Agriculture Organization [3], the total production of date worldwide has increased more than 40% from 2000 to 2019, as shown in Fig. 1 [3]. As a result, large quantities of date waste are generated annually, which is a serious concern for the date industry.

Date palm residues are abundant in environment and have a very low cost compared to other commonly used plants as reinforcement as shown in Fig. 2 [95]. Mostly, if this waste was utilized, it is used only in animal feed as in KSA or in road base gravel as in the USA [96]. However, it is reported that date palm fibers include a significant amount of cellulose which could be used to produce cellulose-based raw materials such as micro- or nano-cellulose in economic ways [95].

At the research level, a considerable amount of literature has been published on the utilization of date palm tree wastes medical, cosmetic, food, and nutrition related applications, also a number of review papers for such studies have been published [6, 97–101]. However, none of which focused specifically on the date seed waste nor the engineering applications. In 2014, Hossain et al. have published a review paper in the Journal of Food and Nutrition, covering the potential of date seed for developing value added products. They addressed the use of date seed as a water filtration medium where they cited seven studies. Other than that, they reported nine other applications for date seeds concerning health, food, animal feed, and agriculture

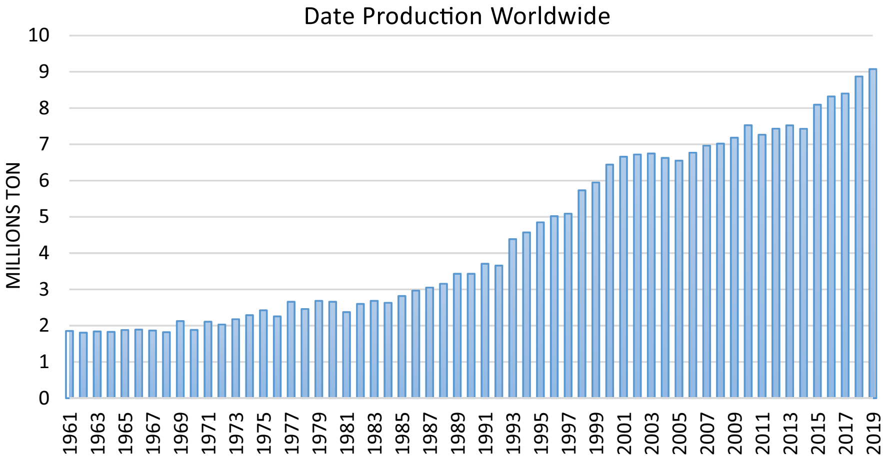

Fig. 1 Date Production Worldwide reproduced from [3]

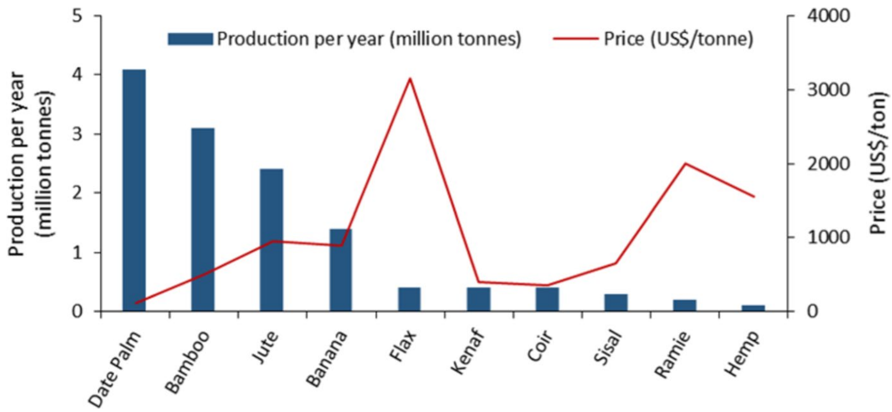

Fig. 2 Production per year and price of date palm against other plants [95]

[102]. Therefore, in the following part of this review, the focus will be towards the utilization of date seed specifically in engineering applications only.

Biofuel

In the light of global energy issues including increased consumption and depletion rate of fossil fuel resources, and global warming issues, researchers around the world are seeking alternative and renewable sources of energy. Biofuel is one of these solutions, which have been developed and produced on a large commercial scale [103, 104]. Date seed is an agricultural waste classified as renewable organic biomass feedstock that can be utilized through thermochemical or biochemical processes to produce bio-energy [105]. One of the oldest and most common thermochemical techniques used to harvest the energy from biomass is direct burning, which specifically suits dry-biomass with moisture content less than 50% such as date seed. Circulated fluidized bed burners are one of the thermochemical technologies that enhance combustion efficiency and limit its environmental impact [106].

In a simulation study, Alshwawra and Alasfar [107] investigated the combustion of date seed in a fluidized bed combustion unit using ANSYS/Fluent software and reported an adiabatic flame temperature of 839 K and maximum temperature in the burner of 761 K, at a fuel flow rate of 0.01 kg/s and air velocity of 2 m/s. The study results exhibited that the date seed has a good potential to be used as a solid fuel through direct burning in boilers. These results were validated experimentally later in a study by Al Asfar et al. [70], where they used a combustion burner unit. They reported minor variances between the theoretical and experimental results which were justified by the presence of a certain percentage of excess air and the adiabatic process assumption in the theoretical study. The study recommended the use of date seed as solid fuel in power plant for electricity generation and calculated 40% saving in fuel cost and less environmental impact due to the fact that the used biomass diminished the risk of sulfur SO_x and carbon oxides CO_x.

Pyrolysis is another thermochemical technology used to convert biomass through decomposition of its organic components in the absence of oxygen and at a temperature ranging from 400 to 500 °C into bio-oil, charcoal, and fuel gas. In 2009, Nurul Islam et al. [108] designed and fabricated fixed bed pyrolysis to convert date seed biomass into liquid fuel, char and gas. They used nitrogen as the carrier gas and investigated the effect of the reactor bed temperature, running time, and feed particle size on the product yield. They achieved the maximum liquid yield of 50 wt.% at a reactor bed temperature of 500 °C, feed size volume of 0.11–0.20 cm^3, and 120 min of running time. The results showed that higher heating value (HHV) of 28.636 MJ/kg, flash point of 126 °C, viscosity of 6.63 cSt at 26 °C. In 2012, Joardder et al. [109] reported similar results. Both studies were limited with the use of one species and didn't specify the used species.

Furthermore, Sait et al. [110] examined the combustion and pyrolysis characteristics of the date palm different wastes using a thermogravimetric analyzer (TGA). The study included date seeds, leaf, and leaf stems of unspecified species of date palm tree. They concluded that the date seed and leaf showed almost similar pyrolysis and combustion characteristics and have the potential to be converted into biofuels. A similar approach was followed by Babiker et al. [111] to evaluate the pyrolysis behavior for six different cultivars of date seeds: Deglet Nour, Piarom, Suffry, Safawi, Mabroom, and Aliya. The results showed that there are three different types of pyrolysis zones depending on the main constituents of every cultivar. The results showed that Mabroom has the highest activation energy regarding H_2 (63.21 kJ/mol) and CO (74.32 kJ/mol). Later in 2014, Hussain et al. [112] designed and fabricated a novel fluidized bed test rig to understand the pyrolysis behavior of the selected sample and to perform the pyrolysis. They studied three palm tree wastes: seed, leaf, and stem, and found that seed and leaf are a good source of energy due to their high volatile content.

Fadhil et al. [54] investigated the potential of date seeds as new feedstock for liquid biofuels production. Using a laboratory-scale fixed bed reactor heated by an electric furnace to conduct pyrolysis experiments under atmospheric pressure and with a flow of N_2 gas, they reported a calorific value of 37.38 MJ kg^{-1}, pour point of 2 °C, and flash point of 87 °C. The study also examined the influence of pyrolysis temperature, time, and particle size on product yield and found out that the maximum yield of (52.67% ± 1.50) was achieved at a pyrolysis temperature of 500 °C, pyrolysis time of 60 min, and 0.25 mm particle size. Finally, the study concluded that date seeds are a potential feedstock for producing alternative fuels.

Few published studies have experimentally analyzed the use of date seed as a solid biofuel in biomass boilers, in 2019. Cruz-Lovera et al. [113] published a study that analyzed the properties of date seeds in a biomass boiler system to evaluate their suitability and viability as a new solid biofuel. They investigated the feasibility of replacing an existing gas boiler in a university building in the south of Spain with a system of biomass boilers. The study results showed that the date seed biomass boilers effectively provided the building heating demand at a thermal efficiency of 80%. The proposed system also successfully reduced the total CO_2 emissions by 95 tons per year and achieved a reduction in the annual cost by more than 66% compared to the old natural gas boiler system. In comparison with other biomass feedstock such as olive seeds, date seed has higher moisture content and lower heating value (HHV) by 42% and 13.3%, respectively [114, 115] which indicates that olive seed would perform better than date seed as biomass. Despite that, the results of this study are still significant especially in arid and semiarid areas where the cultivation of date palm trees surpasses the cultivation of olive trees due to their outstanding drought resistance [101].

As stated previously, converting biomass into bio-energy can be done either by thermochemical or biochemical processes. So far most of the recent publications in the three common thermochemical processes were reviewed, i.e. combustion, gasification, and pyrolysis. Transesterification and esterification are biochemical processes used to convert biomass into biodiesel. Transesterification is a reversible chemical reaction in which the organic group R″ of an ester (fatty acids in biomass) is exchanged with the organic group R′ of alcohol which in turn transform the triglyceride into monoester and glycerin [116]. Different catalysts are used to improve the rate of reaction and the yield, among the most used catalysts are the alkalis, acids, and enzymes [116]. The most common commercially used catalysts are sodium hydroxide (NaOH) and potassium hydroxide (KOH) [48, 116]. Esterification is a chemical process between acid and alcohol in which carboxylic acid (biomass) is transformed into ester [117]. The main purpose of transesterification processes is to reduce the biomass oil viscosity while maintaining its heat value and increasing the cetane number which is an index used to define the combustion quality of diesel fuel [37, 116, 118–120]. The selection of process depends on the free fatty acid (FFA) content in biomass, if it was more than 3%, the process should start with esterification reaction followed by transesterification. The high percentage of FFA in a transesterification reaction produces soap that deactivates the catalyst. If the FFA content in biomass is less than 3% transesterification reaction can be used alone [117].

Biodiesel fuel as a commercial product must be tested according to the national standardized tests and all its analysis results must comply with the limit set by the same standard. Biodiesel standards identify the quality of biodiesel through a number of parameters that mainly focuses on the completion of the reaction. The most commonly used standards are the American Society for Testing and Materials (ASTM D 6751) and the European Standards (EN 14214) [116, 121–125].

Table 3 lists both standards' tests codes and limits, in comparison with ASTM standards defines a smaller number of parameters (15 against 23 in Europe) which provides more flexibility in utilizing a wider range of raw materials for production. EN standards are stricter than ASTM in the specification for sulfur content obviously for environmental reasons [116, 126].

A limited number of studies were published in the current decade investigating the utilization of date seeds in biodiesel production. Table 4 summarizes all the articles reviewed in this study concerning date seeds as a feedstock for biodiesel production. As the date seeds FFA percentage is less than 3% all the reviewed studies used transesterification process for biodiesel production. Hence, the table lists most of the important parameters for each study as well as the thermal and physical properties that are relevant to the scope of this study. It can be seen that 40% of the reviewed work include optimization of some or most of the variables in the transesterification process. Different types of catalysis were used with great focus on both sodium hydroxide (NaOH) and potassium hydroxide (KOH). The alcohol used was mainly either methanol or ethanol.

Azeem et al. [48] published a comprehensive optimization study in which they investigated the validity of producing biodiesel from three different cultivation of date seeds, namely Zahidi, Basra, and Khazravi date seeds. They used four different catalysts, three different catalyst concentrations for each catalyst, different molar ratio, and different process's temperature and time for each date type. The study's results showed that maximum yield of biodiesel was achieved with the immobilized KOH and lipase for all the three tested types of date seeds. The produced biodiesel was found to meet the ASTM and EN biodiesel standard, with high cetane number, low viscosity, and low flash point. The Basra date seed was found to have a low cloud point up to − 4.7 °C, which enables it to be used in colder regions of the world. The studies concluded that the yield of biodiesel production is inversely proportional to the concentration of catalyst. Nonetheless, the results showed that using mixed catalysis provided better biodiesel yields and required lower acid concentrations which minimized the environmental issue of downstream. Even though Azeem et al. [48] study included most of the process's parameters, they ignored the effect of date seed oil extraction process, i.e. solvent type, solvent ratio, temperature, time, and powder particle size on the biodiesel production. Jamil et al. [47] analyzed the effects of date seeds oil extraction process parameters including temperature, solvent-to-seed ratio, and time on the extraction of oils and then on the biodiesel production. The first part of the study regarding the optimization of the oil extraction process was reported in detail previously in the oil extraction topic. However, in the second part of the study, they did not report that effect on the produced biodiesel, instead, they just used one sample of the extracted oil to produce biodiesel and then they analyzed it without reporting the yield of production. As shown in

Table 3 The American society for testing and materials (ASTM D 6751) and the European standards (EN 14,214)

Property	ASTM D6751		Unit	EN 14,214	
	Method	Limits		Limits	Method
Cloud point	D2500	Report	°C		
Distillation T90 AET	D1160	360 max	°C		
Sulfur (S 15 Grade)	D5453	0.0015 max	ppm		
Sulfur (S 500 Grade)	D5453	0.05 max	ppm		
Water and sediment	D2709	0.050 max	% vol		
Flash point	D93	130.0 min	°C	101.0 min	EN ISO 2719/3679
Kinematic viscosity at 40 °C	D445	1.9–6.0	mm^2/s	3.5–5.0	EN ISO 3104
Cetane number	D613	47 min	–	51 min	EN ISO 5165
Sulfated ash content	D874	0.020 max	% (m/m)	0.02 max	ISO 3987
Copper strip corrosion	D130	No. 3 max	Rating	Class 1	EN ISO 2160
Acid value	D664	0.50 max	mg KOH/g	0.5 max	EN 14,104
Free glycerol	D6584	0.020 max	% (m/m)	0.02 max	EN 14,105/EN 14,106
Total glycerol	D6584	0.020 max	% (m/m)	0.25 max	EN 14,105
Phosphorous content	D4951	0.001 max	% (m/m)	0.00001	EN 14,107
Carbon residue	D4530	0.050 max (100%)	% mass	0.3 max (10%)	EN ISO 10370
Sulfur content			mg/kg	10 max	EN ISO 20846/20,884
Density at 15 °C			kg/m^3	860–900	EN SIO 3675/12,185
Water content			mg/kg	500 max	EN ISO 12937
Total contamination			mg/kg	24 max	EN 12,662
Oxidation stability at 110 °C			h	8 min	EN 14,112
Iodine value			–	120 max	EN 14,111
Linolenic acid methyl ester			% (m/m)	12 max	EN 14,103
Ester content			% (m/m)	96.5 min	EN 14,103
Methanol content			% (m/m)	0.2 max	EN 141,101
Monoglyceride content			% (m/m)	0.7 max	EN 14,105
Diglyceride content			% (m/m)	0.2 max	EN 14,105
Triglyceride content			% (m/m)	0.2 max	EN 14,105
Alkaline metals (Na + K)			mg/kg	5 max	EN 14,108

Table 3, all the reported results for the produced biodiesel agreed with the international standard for biodiesel.

Table 4 Biodiesel reviewed studies

Study	Transesterification									Properties						
Author	Year	Catalyst	Catalyst Conc. wt %	Alcohol	Molar ratio	Temperature °C	Time h	Particle size mm	Yield %	Cetane number	Cloud point (°C)	Pour point (°C)	Flash point (°C)	HHV MJ/kg	Viscosity mm^2/s	Density (g/m^3)
Amania et al. [37]	2013	NaOH	0.6	Methanol	1:4.5	60–65	2	1.2	98	60.3	4	− 1	140	39.55	3.8	0.877
Jamil et al. [47]	2016	KOH	1	Methanol	1:6	65	1	0.25–0.3	–	58.23	4	− 1	137	44.1	3.97	0.87
Fadhil et al. [54]	2017	KOH	1	Methanol Ethanol Mix of both	1:6	60 70 65	1	0.42	95.88	59.75	3	− 1	141	39.52	3.91	0.878
Azeem et al. [48]	2016	HCL KOH Lipase HCL + Lipase KOH + Lipase	Vary	Methanol	Vary	Vary	Vary	1	87 max	55–60.3	− 4.7 to 6.9	− 8.3 min	135 -140	–	–	Vary
Abu-Jrai et al. [127]	2017	KOH	6	Methanol	1:9	65	1	–	91.6	60.31	3.9	− 1.4	141	43.24	4.24	0.881
Al-Muhtaseb et al. [46]	2018	CaO Carbon	4	Methanol	1:12	70	2	–	98.2	59.31	3.6	− 2.1	145	44.19	3.98	0.892
Farooq et al. [128]	2019	Egg Shells	5	Methanol	1:12	70	1.5	–	93.5	56	–	–	155	–	3.21	0.872
Al-Zuhair et al. [52]	2017	NaOH Eversa Novozym	10	Methanol	1:5	40	6	2.36 0.5 0.35	30	–	–	–	–	–	–	–
Hellier et al. [129]	2019	KOH 1		Methanol	1:6	65	1	0.25–0.3	–	58.23	4 − 1	137	44.1		3.97	0.87

Similarly, Al-Zuhair et al. [52] investigated two different oil extraction techniques and then used the sample produced from one of them for biodiesel production. Three different types of catalysts were used but the only result reported was the yield of production which was very low in comparison with other studies [37, 46–48, 54, 127, 128]. The only reviewed study that investigated the combustion and emission characteristics of date seed biodiesel in a single cylinder direct injection diesel engine was published recently by Hellier et al. [129]. The date seed biodiesel used was prepared according to the early reported study [47], the results were compared with fossil diesel and soybean and rapeseed biodiesel. Among the significant results reported in this study, the lowest level of NO_x emissions was recorded for the date seeds biodiesel. Also, the levels of exhaust particulate matter were lower for the date seeds biodiesel.

In spite of the high production rate of date fruit in the MENA region and despite the increasing demand for alternative fuel, the number of studies that investigating new feedstock for biofuel or biodiesel production is limited. Moreover, a very limited number of date tree species have been tested for biodiesel production, and neither date seed powder preparation nor oil extraction process parameters were considered in all reviewed optimization studies.

Adsorbents

Adsorption is a surface phenomenon in which atoms, ions, molecules of dissolved gas, liquid, or steel (adsorbates) adhere to a surface (adsorbent). 3750 BC Egyptians and Sumerians used carbon in form of wood chars (charcoal) for the reduction of ores in the manufacturing of bronze [130]. Many other applications emerged over the centuries. However, it was not until 1822, when the first activated carbon was produced through thermal and chemical processes [131]. Activated carbon is charcoal processed to be extremely porous, hence a larger surface area for better adsorption capacity [132]. Currently, one of the best available technologies on an industrial scale in purification and separation processes is activated carbon [97]. Activated carbon plays an important role in many applications such as potable water treatment, decolorizing, metal ore processing, air treatment, effluent treatment, solvent recovery, and many other domestic and industrial applications. Generally, activated carbon is made of different types of precursors which may be of mineral origin, polymeric materials, or botanical origins like wood, coconut shells, and fruit seeds. Botanical origin precursors dominate almost 50% of the activated carbons industry [133]. Date seed is considered as a waste material that easily decomposes in nature, thus it’s an eco-friendly biomass feedstock. Given that, date seed is a suitable botanical precursor for making activated carbon adsorbents.

The processes of producing activated carbon can be mainly categorized into two main process types, namely physical and chemical processes. The physical process is a two-step process, at the first step the precursors are carbonized in an inert atmosphere and at elevated temperature in the range of 600–900 °C. In the second step, the carbonized materials are activated or oxidized at a temperature in the range of 600–1200 °C and in an oxidizing atmosphere that contains gases such as CO_2 or steam [134, 135]. The chemical process is a single-step process as both the activation and carbonization are done simultaneously. In the chemical process, the precursors are impregnated with a dehydrating agent such as H_3PO_4, KOH, NaOH, and $ZnCl_2$ at a temperature ranging from 400 to 800 °C to activate the carbon. The chemical process is favorable over the physical process for its lower temperature, shorter time, and higher yields. However, most of the chemical agents used for activation are classified as hazardous for the environment hence their use might be limited [134, 136]. Both physical and chemical activations (physicochemical) can be executed instantaneously after the carbonization step to improve the surface properties [137].

A considerable amount of literature has been published on the utilization of date seed as an adsorbent. These studies dealt with both purification and separation applications and handled a variety of pollutants, contaminants. The first review paper using date palm-based adsorbents was published in 2011 [97]. They presented an intensive summarization for most of the literature work on date palm-based adsorbent as well as its applications. In 2016, another review paper on the preparation of activated carbon from date seed was published [135]. In that review paper, the effect of preparation variables on pore structures and yields of date seeds carbons was addressed. Also, the adsorption application for the removal of dyes, phenols, pesticides, and heavy metals was summarized. It covered the effects of temperature, time, impregnation ratio, and type of activation agents on pore characteristics and yield. The third paper was published by Daniel et al. [134] but was focused only on three activation techniques for date seeds. Herein, we summarize some studies that utilized date seeds as adsorbents with a special focus on the preparation methodology as well as the concentration, type of contaminate or pollutants, and main adsorption capacity achieved.

Two studies out of the reviewed studies used the date seed as raw material without activation. Al-Ghouti et al. [34] used the raw date seeds for the removal of methylene blue (MB), copper ion (Cu^{2+}), and cadmium ion (Cd^{2+}) from aqueous solutions. In this study, experimental parameters such as pH, particle size, and initial solute concentration were investigated to understand the adsorption mechanism involved. For the considered contaminants, the maximum adsorption capacities were obtained after 72 h and the effect of particle size of raw date seeds was minor at low initial solute concentrations but at higher concentrations, it was observed significantly. For Cu^{2+} and Cd^{2+}, the behavior of adsorption processes was almost linear and consequently as described by the authors, and The Langmuir isotherms were not used to evaluate the results as they did not match the typical Langmuir model. The study highlighted that the adsorption characteristics of the three contaminants is influenced by surface functional groups on the raw date seeds surface. Also, four different mechanisms were observed for the considered contaminants such as hydrogen bonding, binding two cellulose/lignin units. Likewise, Mahmoodi et al. [138] tested the raw date seeds as adsorbent for dyes acid green 25 (AG25), acid black 26 (AB26), and acid blue 7 (AB7) onto date stones (DS) from single and ternary systems. To evaluate the adsorption capacity of date seeds in the mentioned systems, parameters such as dye concentration, adsorbent dosage, and pH were considered and kinetic, isotherm, and thermodynamic studies were conducted. The study concluded that date seeds could be used as eco-friendly adsorbents for textile dye removal from the considered two systems. For the adsorption kinetics of dyes on date seeds, the pseudo-second-order model was followed at different dye concentrations. Unlike the previous discussed study [34], the Langmuir and the extended Langmuir isotherm models were successfully applied and showed reasonable correlation compared to other used models. The presence of barrier in the adsorption and endothermic process was indicated through thermodynamics studies. While both papers highlighted the potential of using raw date seeds as eco-friendly adsorbent, researches considering raw date seeds as adsorbent for more contaminates are limited.

The results across different studies cannot be easily compared due to the lack of standards, for either preparation or testing procedures. Banat et al. [139] studied copper and zinc ion removal using activated and non-activated date seeds. Unexpectedly, the reported results indicate that the raw date seeds showed higher Zn^{2+} and Cu^{2+} ion uptake than activated date seeds, which is justified by the homogenous high surface area and average pore size [140]. In addition to studying the copper and zinc ion removal, the effect of operating parameters such as contact time and temperature was studied. It was highlighted in the study that pH, the temperature, and initial metal ion concentration affects the uptake of metal ions. For both metal ions, the Freundlich isotherm model was fitted to the adsorption data with a higher than 99% of the regression coefficient. The study concluded that date seeds without any physical or chemical activation form could be used as an effective adsorbent for the treatment of waters containing heavy metal ions such as Zn^{2+} and Cu^{2+}.

A number of variables are considerably high in both preparation and testing, including particle size of date seed powder, powder preparation procedure, activation technique, time and temperature applied for both carbonization and activation, concentration range, pH value, and the chemical agents used. Hence, most of the reviewed studies performed partial optimizations study to monitor the effect of some above-mentioned variables on the adsorption capacity. Nevertheless, none of them investigated the adsorption performance of different types of date seed species, even though it was shown that the mechanical and thermal properties of different species differ from one species to another [17, 87].

For example, the effect of date seed powder's particle size on the adsorption capacity was investigated by El Bakouri et al. [141], where they used three particle sizes (63–100, 100–150 and 150–200 lm) at different concentrations (from 0.5 to 10 mg/l). They found that the adsorption capacity of the thermochemical treatment of date seeds increases when sorbent particle size decreases and justified that by the significant increase in surface area. Likewise, Awwad et al. [142] confirmed similar findings where they found that the removal of Zn [60], Co [60], Pb [60] and Fe(III) increased by 39% as the sorbents particle size decreased from 200 to 30 mesh size. Other studies also confirmed similar findings [56, 143–147]. It is worth to be mentioned that the results showed that the pseudo-second-order model and the Freundlich isotherm model were best described the adsorption of drin pesticides of acid-treated date seeds and adsorption process, respectively.

The conditions of preparation influence on porosity characteristics were also investigated in number of studies. Girgis and El-Hendawy [148] studied the effect of heat treatment temperature and impregnation agent concentration on the development of porosity of date seeds chemically activated carbon. They achieved their best result of the activated carbon porosity at a heat treatment temperature of 700 °C and the best adsorbing carbons were found at impregnation agent concentration at the range of 50–60 wt.%. Concerning the impregnation agent concentration, the results revealed that increasing the concentration generates more porosity but also it was a function of the heat treatment temperature. On the contrary, a number of other studies that were using similar impregnation agent but with different precursors agreed on much lower heat treatment temperature in the range of 300 to 450 °C [149–152].

Table 5 summarizes all reviewed studies including preparation methodology, concentration, and type of contaminate or pollutants and main results achieved.

One of the most comprehensive reviews was conducted by Awwad et al. [142], they did not specify the date seed species used but they produced three types of adsorbents out of the same raw material. The first was physically activated with pure steam for one hour at a temperature of 800 °C. The second was also physically activated but with steam and flow of nitrogen gas for one hour and at a temperature of 700 °C. The third was chemically activated by impregnation of 10% calcium acetate ($C_4H_6O_4Ca$) for one hour and at 700 °C. They tested the adsorption capacity of those three adsorbents for cobalt (II), iron (III) oxide, lead (II), and zinc (II) that existed in six samples of surface and groundwater collected from different locations in The Aseer area, Saudi Arabia. Both Freundlich and Langmuir adsorption isotherms were presented in the study, also kinetics of sorption was studied, and the adsorption capacity was evaluated. The authors highlighted the importance of establishing the most appropriate correlation for the equilibrium curve to optimize the design of sorption system for the removal of metal ions from a water sample. Freundlich and Langmuir showed high values of correlation; however, Langmuir has higher correlation coefficients. For the approximation of sorption reaction, pseudo-second-order kinetic model showed a more reliable description of the kinetics. Moreover, the study investigated the effect of contact time on the adsorption of metal ions, the effect of carbon particle size on the removal efficiency and the effect of carbon doses on removal of metal ion. Finally, complete the removal of contaminating metal ions was achieved, and they concluded that activated carbon prepared from date seeds is a potential adsorbent material for metal ions with high sorption capacity.

Likewise, El-Hendawy et al. [161] investigated the capabilities of four adsorbent samples on the removal of Pb^{2+} and Cd^{2+} metal ions as shown in Table 5. The results revealed that all obtained isotherms agreed with the Langmuir equation. Also, the results related the increase of adsorption capacity of both lead and cadmium ions to the increase of the pH of solutions as well as to the nitric acid surface treatment. Lead has lower solubility and lower pH for complexation or deposition; therefore, it removed slightly higher amounts than cadmium. The adsorbent texture characteristics were found not to be as crucial as the solution pH and the surface chemistry on the adsorption capacity.

Other technology that grant low-cost adsorbent for the removal of toxic pollutants from water was presented in the literature where date seed is used as a solid adsorbent [148]. Al-Ghouti et al. [145] presented the application of micro-emulsion-modified raw date seeds for removing methylene blue (MB), copper ion (Cu^{2+}),

Table 5 Adsorbent reviewed studies

Study		Adsorbent				Adsorbates		Adsorption		
Author	Year	Carbonization		Activation		*Contaminant*	*Concentration*	Capacity	Time	Temp
		Method	Temp	Agent	Temp		mg/l	mg/g	Hour	°C
Shahad et al. [153]	1998	Thermal	450–700	–	–	CO	4	62%	–	185
						CO_2	9.5	59%	–	
Abdulkarim et al. [154]	2002	Thermal	600	CO_2	950	MB	0–1000	590	48	25
						Phenol	0–1600	165		
Girgis and ElHendawy [148]	2002	Chemical	300–700	H_3PO_4	–	Iodine	10–50	528	24	Room temp
						Phenol		166		
						MB		240		
Banat et al. [139]	2002	Thermal	700	CO_2	700	Zn_2^+	20–100	0.15	24	25, 40, 50
						Cu_2^+	10–50	0.09		
Banat et al. [133]	2003	Thermal	700	CO_2	500, 900	MB	20–400	0.275	24	25. 45, 50
Banat et al. [155]	2004	Thermal	700	CO_2	900	Phenol	20–200	46.076	24	25–55
Abdulkarim and Al-Rub [156]	2004	Thermal	215	Air	300–350	Pb [60]	25–300	30.7	24	25
		Chemical	215	C_9H_7NO	300–350			30.6		
El-Sharkawy et al. [157]	2007	Thermal	–	Steam	900	MB	2000	0.579	36	25, 45
		Chemical	600	$ZnCl_2$	–	MB		0.396	36	25, 45
Al-Muhtaseb et al. [158]	2008	Thermal	900	CO_2	900	Al	5–50	0.305	24	22
Marzogui and Addoun [159]	2008	Chemical	600	N_2		Phenol	–	169.49	120	25
			800	KOH		C_7H_8O	–	322.58		
			600	$ZnCl_2$		C_6H_5ClO	–	208.33		

Table 5 (continued)

Study		Adsorbent				Adsorbates		Adsorption		
Author	Year	Carbonization		Activation		*Contaminant*	*Concentration*	Capacity	Time	Temp
		Method	Temp	Agent	Temp		mg/l	mg/g	Hour	°C
El Nemr et al. [160]	2008	Chemical	120	H_2SO_4		Cr(VI)	5–150	120.48	3	25
Abdel-Nasser El-Hendawy [161]	2009	Chemical	300–700	H_3PO_4	–	Pb_2^+, Cd_2^+	25–250	162, 160	24	25
		Thermal	500	Steam	850			169, 160		
		Chemical	700	KOH	–			182, 169		
		Thermal	600–700	Steam	–			139, 131		
El Bakouri et al. [141]	2009	Chemical	300	HCl	25	Aldrin	0.5–12.5	15.71	0.15–14	10–40
						Dieldrin		14.05		
						Endrin		11.69		
Al-Ghouti et al. [34]	2010	Raw				MB	50–900	277.8	72	20
						Cu_2^+	1–50	35.9		
						Cd_2^+		39.5		
El-Naas et al. [162]	2010	Thermal	600	CO_2	900	COD	950, 1662, 3490	31.37	24	25, 40, 60
El-Naas et al. [35]	2010	Thermal	600	CO_2	900	Phenol (Aqueous)	100 -300	262.3	72	25
						Phenol (Refinery)	88, 46	56.9		
Mouni et al. [163]	2010	Chemical	650	H_2SO_4	–	Pb[60]	20	19.64	1	20

Table 5 (continued)

Study		Adsorbent				Adsorbates		Adsorption		
Author	Year	Carbonization		Activation		*Contaminant*	*Concentration*	Capacity	Time	Temp
		Method	Temp	Agent	Temp		mg/l	mg/g	Hour	°C
Mahmoodi et al. [138]	2010	Raw				AG25	50	36.496	0.5	25–65
						AB26		39.526		
						AB7		33.784		
Danish et al. [164]	2011	Chemical	300	$ZnCl_2$	–	Cu[60]	50–200	37.3	3	20–40
						Ni[60]		29.9		
Reddy et al. [165]	2012	Thermal	800	CO_2	800–1000	–	–	–	–	–
Bouchelta et al. [132]	2012	Thermal	500–800	Steam + N_2	700	Cu_2^+	10	652.3	0.16	18
						Fe_3^+		552.9		
Awwad et al. [142]	2013	Chemical	700	$C_4H_6O_4Ca$	700	Co[60]	0.045–0.05	33	1	25
		Thermal	350	Steam + N2	700	Fe(III)	0.05–0.5	44		
		Thermal	350	Steam	800	Pb[60]	0.036–0.05	23.5		
						Zn[60])	0.241–0.5	120.5		
Belhachemi et al. [166]	2014	Thermal	825	CO_2	825	NO_2	500 ppm	129	0–6.67	25
		Chemical	550	$ZnCl_2$	–			124		
Al.Haddab et al. [42]	2014	Thermal	500	–	–	Boron	7	31.7	2–24	25–50
Al-Zuhair et al. [167]	2015	Thermal	600	CO_2	900	sulfur	20–100 ppm	7.2	0.66–1.5	250
Al-Saidi [51]	2016	Thermal	650	H_2O_2	–	Gold(III)	1000	78	0.016–3	25
El Messaoudi et al. [50]	2016	Chemical	–	H_2SO_4	–	MB	100	515.46	0.083–3	20–50
						CV		543.47		

Table 5 (continued)

Study		Adsorbent					Adsorbates		Adsorption		
Author	Year	Carbonization		Activation			*Contaminant*	*Concentration*	Capacity	Time	Temp
		Method	Temp	Agent	Temp			mg/l	mg/g	Hour	°C
Al-Ghouti et al. [56]	2017	Thermal	130	–	–		Br-	10–150	185.2	72	Room Temp
Ogungbenro [168]	2018	Thermal	600–900	CO_2	600–900		CO_2	–	141.14	5	20
Krishnamoorthy et al. [169]	2019	Chemical	650	H_3PO_4	–		Pb II	5–50	10.35	0.016–2	30–60
Hassana et al. [140]	2019	Thermal	130	Roasted			Profenofos	100 ppm	14.49	24	45
				KOH	500				4.380		
				–	–				370.4		
Mangwand et al. [170]	2020	Chemical	40	DETA		65	Cr(VI)	1	53.31	6.6	20–50
Bahamon et al. [171]	2020	Thermal	600–900	CO_2	600–900		CO_2	–	2.5	5	25
Alsulaili and Fahim [172]	2020	Chemical	300	H_3PO_4	85		Oil	9.5–13	0.012	3	20
Hasanzadeh et al. [173]	2020	Thermal	500	NaOH	700		Cefixime (CFX)	50–800	557.9	4	25
				KOH					571.5		
Muhammad Vohra [174]	2020	Chemical	500	KH_2PO_4	500		Gaseous ammonia	2.5–7.5 ppm	–	–	–
Mitra et al. [175]	2020	Thermal	400	KOH	–		Methyl orange	2–20	80.64	0.16–0.92	30–75

and cadmium ion (Cd^{2+}). The studied adsorbent was found more efficient with all pollutants. They concluded that this low-cost adsorbent was successful in removing both organic and inorganic pollutants. Also, other conclusions were drawn such as the importance of adsorption parameters for understanding adsorption mechanism, the percentage of the removal of Cu^{2+} and Cd^{2+} decreased when increasing pH at specific level of pH, and Freundlich model describes the isotherm with regression coefficient higher than 0.97. These results were in confirmation with the previous study's results [144]. Other recent studies related to the utilization of date palm seed biochar as adsorbent are Imen Ben Salem et al. [176], Sizirici et al. [177], Reza, Mahdi [178], Rambabu et al. [179], Benyoucef et al. [180] etc.

Although the number of studies in this research field is more than any of the other engineering applications that are considered in the current review, there are many that points need to be taken into consideration [97, 135]. There are many mineral pollutants, multi-component mixtures, and other contaminants that have not been addressed yet while using date seeds as adsorbents. Optimization studies are recommended since many variables are affecting the process of adsorption. The effect of using the physicochemical activation for date seed needs to be further investigated, studying the possibility of recycling the used adsorbents for further treatment process. Last, techno-economic studies are necessary to explore the possibility of industrializing the date seeds adsorbents.

Drilling fluids

Drilling fluids are water-based or oil-based fluid that consists of a variety compounds. The fundamental functions of drilling fluid are to lubricate, clean, fluid loss control, and stabilize the borehole by forming an effective filter cake to block the inflow of fluids from surrounding soil [181–185]. To fulfill these multiple functions, drilling is typically reinforced by a variety of synthetic or natural polymeric additives.

Synthetic polymeric additives can be manufactured of different chemical compounds such as polyacrylate or polyacrylamide. However, these additives are non-eco-friendly and costly [186], and due to their sensitivity to divalent cations such as lime and seawater mud, their use is limited to fresh water [187]. Moreover, most of these synthetic additives require more adjustment to the drilling fluids as they increase their viscosity.

On the other hand, natural polymer additives comprise a wide range of renewable natural materials such as starch, guar gum, lignin, and cellulose. These natural additives outperform synthetic additives as they are abundantly available, hence cheaper, environmentally friendly, and compatible with different mud systems [187]. Yet some of these natural additives underperform at extreme operating conditions such as high temperatures and pressures.

Date seeds can be categorized as a multi-component natural polymer additive that consists of hemicellulose, lignin, and cellulose. To the best of the authors' knowledge, a total of eight studies have been published since 2014 investigating the use of date seeds as a natural additive to drilling fluids [187–194]. These studies were conducted by four different research teams from Saudi Arabia. Saudi Arabia is known to be one of the largest producers and consumers of dates, likewise, it is one of the leading countries in oil and gas production.

Wajeehuddin and Enamul Hossain [188] proposed and investigated three naturally available biopolymers additives to the drilling fluids. Driven by the need for new environmentally friendly and cost-effective drilling fluids, they used particle size distribution (PSD) to evaluate the potential use of the proposed additives, namely date seeds, grass, and grass ash. The three samples were sun-dried for one week, then a portion of the grass was burnt and grinded while the date seed and the other portion of the dried grass were directly grinded. Next, a Gilson sieve shaker was used to distribute the sum of the weights of particles accumulated on each sieve. Regarding the date seed sample, the obtained results showed that the date seeds sample has a good tendency to replace current commercial additives. At sieve size 300 μ the seed sample retained 82% of the total weight, and they argued that increasing particle size decreases the permeability of filter cake. Moreover, they compared their results with several patents and previous studies [195–199] and concluded that all samples, including date seeds, help to block the formation and prevent drilling fluid loss. However, this study is limited by the lack of information about the type of date seeds species utilized and grinding procedure followed. Nonetheless, the finding of this study might be affected by the absence of a cleaning procedure.

This study was part of a master thesis [189] in which the author extended the investigation to formulate new drilling fluid systems using the proposed additives and then evaluated the characteristics and behavior of these systems. In the second part of the study, XRF instrument was used to determine the elemental composition of the proposed samples. The results revealed that date seeds contained potassium, calcium, sulfur, silicon, iron, chlorine, phosphorous, and manganese and stated that all these elements are used to do different functions in the commercial drilling fluid. Then a set of tests were conducted on the formulated mud system including density, viscosity, filtration loss capacity, resistivity, and pH. For only three out of the five particle sizes studied previously, the rheological parameters were plotted and an optimum point for filtration loss per particle size was selected. Also, the study revealed that the addition of date seeds lower both pH and resistivity in the mud system. The comparison with the commercial mud system showed that the developed date seeds mud system performed better on the basis of plastic viscosity and filtration. Furthermore, the effect of high temperature on rheological parameters of the formulated mud system was investigated but at a limited temperature of 200 °F which was justified by the lake of high-temperature additives.

Amanullah [190] described the manufacturing process of a newly proposed date seed-based sized particulate loss control material which he coined as “ARC plug.” Followed that by a description of the physico-mechanical characteristics of the proposed ACR plug and evaluated its performance in different mud systems. Regarding the reported results, he stated that the date seeds have a high potential to replace the commercial loss control material imported from overseas. Amanullah et al. [191] tested the date seed powder for fluid loss additive in both fresh- and saltwater-based drilling mud systems. After describing the preparation and formulation process of six different mud systems, of which two included date seeds powder beside psyllium husk powder. The American Petroleum Institute [84] fluid loss behavior was evaluated for all six systems and then the best four systems were assessed for high-pressure high-temperature performance (HPHT). The results showed that adding the date seeds powder in the water-based and psyllium husk powder system reduced the filtration behavior of the system to 25% below the recommended API value. At HPHT the performance of the same formulation but with saltwater showed better fluid loss results than that with fresh water which came second. The effect of date seed powder on rheology properties was also investigated and the results revealed that there is a minimal influence of date seed powder on the rheology of the proposed formulated mud system. Amanullah et al. [192] patented this work under the title: Date seed powder as a fluid loss additive for drilling fluids, later in the same year. One of the limitations of this study was the use of a particle size less than 150 µm only [187]. Likewise, date seed concentration in the formulated mud system was not justified and the HPHT test was conducted at 100 °C and 500 psi which is considered moderate compared to other studies [187, 189, 193, 194].

Adewole and Najimu [187] considered the use of date seed as an additive in water-based drilling fluids and examined the effect of date seed fat, particle size, and concentration on the density, rheological properties, filtration properties, and thermal stability of the drilling fluids. The commercial bentonite was used as the base material to formulate the water-based mud system. Unlike the previous study, they utilized three different particle size ranges. Less than 75 µm, between 90 µm and 180 µm, and between 180 µm and 710 µm. The results highlighted the inversely proportional effect of date seed concentration on the fluid density. The effect of date seeds particle size and concentration were investigated to evaluate the shear thinning and gel strength and viscosity, which represent the rheology performance of the drilling formulation. It was reported that the addition of date seed to the drilling formulation reduces its shear thinning and gel viscosity and strength, while the particle size of date seed was reported to have an inversely proportional effect on both parameters. Based on the rheological studies results they suggested that date seed can be used as a rheological modifier for drilling fluids.

The other set of experiments aimed to evaluate the filtration properties and included the effect of date seeds oil content, particle size, distribution, and concentration on both fluid loss and filter cake. The results showed that removing oil from date seeds destroys the ester linkages that make date seeds more porous. Therefore, de-oiled date seed lowered both fluid loss and cake thickness; similar results were reported for the thermal stability as well. It was also reported that the smaller particle size of date seeds in drilling fluids, recorded lower fluid loss. On the other hand, higher date seed concentrations in the drilling fluids improved the fluid loss property, but for the residue thickness, the optimum concentration was reported to be between 15 and 20%.

To evaluate the thermal stability of the formulated drilling fluid thermogravimetric analysis was conducted to provide a reading of both percentage weight loss and derivative weight was recorded during an increase of temperature up to 600 °C. The results were plotted but it was not discussed in detail nor drawn a clear conclusion out of it, other than a negative effect of adding date seed to drilling fluid that was observed only at a temperature of about 250 and 300 °C.

AlAwad and Fattah [193] developed a test rig to simulate fractured formations based on using real core plugs with artificially induced fractures. The objective of the study was to test a new lost circulation control material formulated from crushed date seeds for fractures seal. Fresh water and 7% bentonite were used to formulate a water-based mud system, in addition to two different date seeds particle sizes which were tested separately and mixed: fine (from 0.25 mm to 1 mm) and coarse (from 1 to 3 mm). The effect of date seed concentration (5–10%), particle size (fine or coarse), temperature (25 to 90 °C) and pressure difference (200–600 psi) were investigated to validate the potential of using crushed date seeds as a seal fractured formations in the formulated drilling fluid. The reported results suggested that the optimum mud formulation was fresh water, 7% bentonite, 3.5% finely crushed date palm seeds, and 3.5% coarse crushed date palm seeds in weight bases. This study was further expanded to compare the previously reported results of date seed ability to seal an artificially made fracture with the newly formulated drilling fluid made of shredded waste car tires [194].

In conclusion, the limited number of studies reviewed in these topics clearly identifies the gap in the literature with regard to the utilization of date seeds as a loss control additive in drilling fluids. Furthermore, even existing reported studies share a number of limitations. For example, none of the reviewed studies reported specifically the used date seed species, nor the exact procedures employed during the process of cleaning, drying, and grinding of the used date seeds. It was proven previously that both issues have a major effect on the chemical, thermal, and mechanical characteristics of the resulted powder. Moreover, none of the reviewed studies tested the proposed formulation in a drilling plant, all studies carried out the investigation in a laboratory. Just one study investigated the performance of date seed additive in a saltwater-based drilling fluid system, while no one evaluated the performance of the proposed additive in an oil-based system. Several factors, such as date seed species, particle size, chemical composition, and concentration, might significantly affect the performance of the drilling fluid. Therefore, statistical analysis and optimization are recommended for identifying the significant factors of the date seed and their optimum conditions for the better performance of the drilling fluid. Also, the economic feasibility of utilizing date seed in drilling fluids has never been evaluated. Future work may also include the reinforcement of existing low-cost commercially available drilling fluids with the date seed additives.

Bio-composite

Composite materials are used widely in a growing number of engineering applications, such as thermal management, machine components, and biomedical devices. Composites allow engineers to overcome several challenges because of their unique characteristics, such as lightweight, resistance of creep, corrosion, and wear, and high-temperature exposure. Composite materials can be defined as a combination of two or more distinct materials (matrix and reinforcement), results in a new material with different properties from each component. In composites, the reinforcement or dispersed phase (particle, fiber, or structural) and the matrix or continuous phase (metal, ceramic, or polymer) bonded together not dissolved or blended in one another as it happens in metal alloys [200, 201]. Most of these high-performance composites are made of petroleum-based resources, which negatively affect the environment since they are difficult to be recycled [202, 203]. Therefore, using degradable, renewable, or sustainable materials (naturally derived from animals, plants, or minerals) instead of the petroleum-based ones is an eco-friendly choice and it is known as bio-composites.

Palm date seeds (PDS) become a promising choice as an enforcement material in a bio-composite structure. Researchers have started to study using PDS to enhance mechanical and thermal properties of the bio-composite, which lead to utilizing PDS in many engineering applications. There are several review articles focused on fabrication, properties, and application of using different kind of natural materials for bio-composites.

Sathishkumar et al. [204] reviewed the extraction process and characterization of natural reinforcement materials, preparation of bio-composites, mechanical, thermal, and machinability properties, and water absorption capability and its effect on mechanical properties. However, only powder preparation and preparation of bio-composites were discussed for the date seeds. Recently, Basim Abu-Jdayil et al. [205] published a review paper where the traditional, state-of-the-art, and natural thermal building insulation materials were discussed. As described by the authors, they focus more on the use of natural reinforcement for thermal building insulation materials. The authors discussed using date seed powder as a reinforcement of a thermoplastic composite to be used as a thermal insulator. Since the review considered a wide range of types of insulation materials and focused mainly on the thermal properties, the number of studies considered regarding the date seeds based bio-composites was limited and there was no consideration for reviewing the mechanical properties. Ghori et al. [206] published a review article where they focused on the origin, cultivation, and surface modification of date palm fibers, also, they covered the physical structure, chemical composition, and applications of date palm fibers-based bio-composite polymer. Although this review article considered date palm reinforcement and highlighted that the studies considering the thermal and mechanical properties in addition to modeling of date palm fibers are limited, date seed-based bio-composite was not included.

Certainly, there are many other review papers that reviewed the utilization of agricultural waste as a reinforcement for bio-composites but did not consider date palm seed. Azwa et al. [207] reviewed the degradation due to moisture, thermal effects, fire, and ultraviolet rays for polymer composites based on several natural reinforcements, date seeds were not included. Roy et al. [208] described their review as a brief outline of the research efforts and future work in the area of polymer bio-composite, however, date seeds were not considered at any part of this study. Similarly, date seeds were not discussed in the review papers that considered several types of plant reinforcement [202, 209]. This section of the review intended to include the recent research studies on the subject of date seed-based bio-composites, focusing more on fabrication and thermomechanical properties.

Research efforts toward developing date seed-based bio-composites are actively progressing. Researchers in this field investigate the use of date seeds as a reinforcement with the three types of matrices (polymer, metal, and ceramic matrix) to enhance some of the parameters of the developed composites. Their investigations focus on preparation methodology where factors such as crushing size, curing time, temperature, and additives are studied in addition to evaluating the properties of the developed date seed-based bio-composites. The preparation methodology of date seed powder has a similar procedure as described in the powder preparation section of this review. The produced date seed powder is then mixed with a matrix with considering factors such as using a coupling agent, the ratio between the matrix and the date seed powder, and manufacturing method used. Several manufacturing processes are used to fabricate the date seed-based bio-composite such as compression molding, injection molding, and extrusion.

To the best of authors knowledge, the first study evaluated the use of date seeds in bio-composites was published in 2005 by Ghazanfari et al. [210]. They evaluated using date seeds as a bio-filler by comparing to the bio-filler from pistachio shells when both were used for preparing thermoplastic composite. They prepared both date seed-based and pistachio-based bio-composite using polymer matrix, a 20% date seeds mixed with 80% and 79% high-density polyethylene (HDPE). For the 79% HDPE, a 1% flax fiber was used. Compression molding was used to fabricate the bio-composite with no variation considered for process temperature and pressure. They reported that stiffness of date seed-based bio-composite is lower than the pistachio shell-based bio-composite. In addition, improving the stiffness by using 1% flax fiber as a reinforcing agent for date seed-based bio-composite was highlighted. However, appearance, dispersion, bonding, and melt flow index of the date seed-based bio-composite were found to be better than pistachio shell-based bio-composite. For the superiority of MFI of the date seed-based bio-composite, they justified it by the higher content of oil and nutrient in the date seeds. It was concluded that date seed has a good potential to be used for producing bio-composite material.

Driven by the results of the previous study which highlighted the potential of date seed as a bio-filler, Ghazanfari et al. [30, 211] published two more comprehensive studies in which they used date seeds as a filling material in composition with HDPE and with four different levels of date seed powder concentrations. Flax fiber was not used in these studies, even though the advantage of using it for increasing the stiffness was discussed in the earlier study. The MFI of the composite decreased with the increase of date seed concentration. With the lowest value of 0.267 g/min for a concentration of 40%, they argued that it is still better than other organic-based fillers and that indicates better processability. The best onset melting point value of 111.26 °C was reported at date seeds concentration value of 10%, after which the MFI decreased as the concentration increased. On the other hand, the study revealed that due to the moisture content in date seed the thermal conductivity increased as the date seed concentration increased in the composite. Likewise, the specific heat value followed the same pattern but with more sensitivity to temperature changes than the values of thermal conductivity. For the mechanical properties, tensile strength (TS), tensile strain (ε), and flexural strain (ε_f) were improved only at date seed concentration of 10% after which all the values were negatively impacted. Flexural strength (FS), Young's modulus (E), and flexural modulus (E_f) were not improved at any amount of adding date seeds.

Alsewailem and Binkhader [33] studied the mechanical and thermal properties of date seed-based bio-composites. They considered two types of thermoplastic polymers, which are HDPE and polystyrene (PS). Two types of date seeds were used in this study, namely khalas (K) and sekari (S) with varied concentration (5–40 wt.%) and produced by injection molding. The results reported that neither mechanical nor thermal properties show an increase by adding date seeds except HDPE and only up to 10 wt.%. The results show that as the DPS filler increases the Izod impact strength (IIS) decreases. Just by adding 5 wt.% of DPS, the HDPE/DPS composite material's IS reduced by almost 80%, where it is only affected by 25% at 10 wt.% of DPS when PS100 polymer used, the sekari date seeds showed better results. The absence of an appropriate coupling agent system in this study was mentioned as a possible reason for the reduction in the mechanical properties, which may cause the coarse morphology of the composite. This justification was confirmed by the same authors on a later study when they used two types of coupling agents (diphenylmethane-4 4′ –diisocyanate and ethylene propylene grafted with maleic anhydride) which were able to show an improvement in the mechanical properties [39]. Similar findings were reported by Hamma et al. [36], the study mainly investigated various filler content ratios (10, 20, 30, and 40 wt.%) with and without using EBAGMA as a compatibilizer and emphasized on the enhancement of the morphology of PP/DSF when compatibilizer was used. The study shows that Young's modulus increased from 1400 to 1600 MPa by adding 30 wt.% of DPS to PP. whereas, E value reduced at the same filler ratio to 960 MPa when using EBAGMA with low Young's modulus added by 15 wt.% to the composite. The composite of PP/DPS has a reduction in IIS by 53% when adding 10 wt.% of DPS, whereas by adding EBAGMA adhesion to the composite, IIS improved by 14%.

Ejiogu et al. [212] investigated developing biodegradable hybrid composite based on both coconut shell and date seed powder as a reinforcement and waste high-density polyethylene (WHDPE). The preparation of the hybrid composite started with grinding and drying WHDPE, coconut shells, and date seeds. The particle sizes for the evaluated developed materials were fixed. Compression molding was the manufacturing process used to produce the bio-composite specimen with fixed process parameters. While manufacturing the composite the only factor varied was the ratio of coconut/date powder (5/25%, 10/20%, 15/15%, 20/10%, and 25/5%) also 100% WHDPE without any filler was used as a control sample. Authors found that mechanical properties were improved by introducing coconut/date seed powder and the highest value for mechanical properties were reported at 25/5%. The highest value for mechanical properties at 25/5% was justified by the more crystalline densified structure of the coconut powder compared to the date seed powder. The study shows the potential of using date seed for developing hybrid composite; however, no thermal properties were considered for this study.

Mittal et al. [18] studied mechanical, thermal, and degradation properties of a date seed-based bio-composite using bio-polyesters poly(butylene adipate-co-terephthalate) (PBAT) and poly-L-lactide (PLA). The study highlighted the thermal stability of DSP at the used processing temperatures. While the melting point in the PBAT date seed-based bio-composites was directly proportioned to the DSP content, no effect was observed for PLA date seeds bio-composite. Onset and peak crystallization temperatures both were directly proportional to the percentage of DSP. The results also show that as the wt.% of DPS increase, the stress at break decreased. So, when using PBAT as a polymer, at 10 wt.% filler ratio, the stress at break reduced by almost 30%, whereas with PLA polymer at the same ratio, the stress at break only suffers a 20% reduction. The addition of DPS was found to increase the stiffness that resulted in improving the stress. The usually reported reduction can be a result of poor interaction between the polymer and the filler or due to the bad distribution of the filler. Similar results were reported by Hamma et al. [36] they show that the composite of PP/DPS has a reduction in stress at break by 32% with adding 10 wt.% of DPS, whereas by adding EBAGMA adhesion to the composite, stress at break improved by 30%.

Yield strain and elongation is another way to see the effect of adding DPS to the composite on the mechanical properties. The results from Mittal et al. [213] study show that as the wt.% of DPS increases, the yield strain decreases. Therefore, when using PBAT as a polymer, at 40 wt.% filler ratio, the strain reduced from 13 to 6, which means more than 50% reduction, and the total deformation reduced at the ratio by almost 85%, whereas with PLA polymer at the same ratio, the strain suffers 90% reduction. The study also shows that when using PBAT as a polymer, at 10 wt.% filler ratio, E increased from 82.1 to 116.7 MPa, which means more than 40% increase, whereas with PLA polymer at the same ratio, E increased by 5% only. This significant difference in effect between the two polymers is due to the natural property of these polymers. Using PLA as a polymer, at 20 wt.% filler ratio, TS suffers by 35% from 70.3 to 44.9 MPa, whereas with PBAT polymer there is no significant change. So, with the stiff material the effect of adding DPS is considered whereas with low stiff material it is neglectable. The study revealed that the biodegradation was enhanced for the developed composites compared to the pure polymers. The same finding was highlighted in another study for the same research team where they focused on morphology and component migration [19]. These studies showed that some of the properties have different responses to the variation of DSP contents depending on the type of polymers used.

Mohamed et al. [56] studied the compatibility of date seeds with polylactic acid (PLA) and polycaprolactone (PCL) to produce a lightweight bio-composite to be used in applications such as construction. In this study, authors focused on specific mechanical energy (SME) and thermal degradation for four different levels of loading of date seeds and manufactured by using a twin-screw extruder. Also, wheat vital gluten (VG) was used as a filler with and without date seeds. In this study, eighteen blends with different component concentrations were prepared using an extruder. The study showed that SME decreased when introducing date seed to PLA up to 30% then it increased at 40% which was also the highest compared to PLA composites with VG and PLA composites with VG plus date seeds. This increase of SME at 40% DP was justified by the low plasticizing effect of DP compared to gluten. For PCL, SME increased when increasing DP up to 30% then at 40% decreased.

They concluded that DP has a significant effect on PLA and PCL thermal degradation kinetics.

Hesham Mostafa et al. [214] investigated the use of date seeds as a reinforcement and flame retardant bio-filler with a matrix of polyamide-6 (PA6) with and without adding a compatibilizer of maleic anhydride-grafted polypropylene (PP-g-MAH). No variation of particle size was considered in this study; however, the loading of date seeds was varied. The study revealed that 20 wt.% of the filler and 5 wt.% of the compatibilizer showed better compatibility and dispersion. The highest value of the storage modulus of this study was reported at 20 wt.% with compatibilizer. For tensile strength and impact strength, the result shows that using no compatibilizer is essential otherwise introducing the filler to the polymer decreases the impact strength. On the other hand, with using compatibilizer impact strength measurements increased at 10 wt.% and 20 wt.% but not at 30 wt.% which was justified by the filler aggregation and the insufficient amount of compatibilizer. The study reported no improvement for thermal stability property while using the date seed filler. In the presence of the compatibilizer, the weight percentage residue was enhanced. Increasing date seed filler was greatly enhancing the flame retardant properties.

Basim Abu-Jdayil et al. [215] filed a patent on thermal insulation bio-composite material based on date seeds and polyester resin. The described invention process for developing the thermal insulator is to mix ground date seeds with polyester resin, adding initiator compound, and allowing the mixture to cure. Basim Abu-Jdayil et al. [216] reported results for the thermomechanical properties for a composite made of unsaturated polyester and date seeds or date palm wood as filler. The results showed that using date seeds slightly increased thermal conductivity. While it was concluded that the date wood-based bio-composite showed better thermomechanical properties than that of date seeds, they also mentioned that both the date seeds and date wood are good option to manufacture stable and compatible composites. Recently, Basim Abu-Jadyil et al. [217] published a paper that aimed to develop thermoplastic date seed-based composites to be used as a thermal insulator. In this study, polystyrene was used as the matrix and date seed powder was used as the filler ranging from 0 to 50%. They reported that some degree of detachment between matrix and reinforcement and referred that to the poor compatibility between the filler and the matrix and the agglomeration of the filler which caused a remarkable water absorption capacity. There was also a slight increase in thermal conductivity, density, and thermal stability when date seeds powder percentage increased in the composite system. In addition, the study revealed that lower-bound models could be used to fit the thermal conductivity results. Finally, they emphasized on the advantage of using date seed powder to reduce the cost of the composite and to improve its biodegradability. In a book that focuses on fundamentals, design, fabrication, and applications of unsaturated polyester resins, Basim Abu-Jdayil [218] presented and discussed using date seeds as reinforcement fillers emphasizing on fabrication and methods of investigation of physical, thermal, and mechanical properties of unsaturated polyester resin composites. This chapter of the book shows the fundamentals and potential to consider the utilization of natural-based composite for eco-friendly impacts. While no optimum results were highlighted in these studies, the studies emphasized on using date seeds as a natural reinforcement because of cost reduction and its ability to improve biodegradability.

Alewo et al. [219] studied preparing a composite using an unsaturated polyester resin as a matrix and date palm seed particle as a natural reinforcement and investigated the mechanical and physical properties of the bio-composite. They indicate that at 25 wt.% of PDS and 2 mm particle size, the hardness increases almost double from 33 to 75 HRF. They justified this dramatic increase by the large size of PDS particle, but as the particle size decreases the effect on the hardness decrease. For tensile strength, the study showed that smaller particles size for date seed perform better than larger particles sizes. However, at 5 wt.% the tensile strength decreased which was justified by the poor particle distribution. The highest observed value for tensile strength and modulus of elasticity was at the smallest used size for date seed particles (0.5 mm) with 15 wt.% for tensile strength and 10 wt.% for modulus of elasticity. The study showed that as the particle size increases, *E* decreases. So, at 10 wt.% of DPS and particle size of 0.5 mm, *E* increased from 300 to 350 MPa. Whereas, at 2.0 and 2.8 mm, *E* decreased by 20 and 50%, respectively. On the other hand, the highest observed value for elongation and impact strength was at the largest used size for date seed particles (2.5 mm) with 10 wt.% for elongation and 5 wt.% for impact strengths. For hardness and flexural test, the highest value observed was at the mid used size for date seed particles (2 mm) with 25 wt.% for both tests. They found that as the DPS particle increases the IS of the composite decreases. They stated that at 25 wt.% of DPS to the polyester, the impact strength reduced from 4 to 2.8 kJ/m^2 when the particle size increases from 0.5 to 2.8 mm. It was observed that lower particle size resulted in lower water absorption. By using the micrographs, they highlighted that a good uniform distribution and bonding at 15 wt.% for all particle sizes. The study also investigated the unsaturated polyester (UP) with varying concentration (10, 20, 30, 40, 50 wt.%) for 150 μm particle size of date seeds showed that modulus and hardness increased by increasing the percentage of concentration and the opposite happened for the tensile strength and flexural strength. Moreover, Al-Mosawi et al. [23, 220] published two papers in 2018 where they investigated the use of date seed particles with UP. In these two studies, the comparison was made between a produced date seed-based bio-composite and calcium carbonate-based composite. Both date seed and calcium carbonate were tested at the same particle size (0.5 micro-meter). In both studies, authors highlighted the superiority of date seed-based composite over calcium carbonate-based composite. They applied several tests that showed the importance and effect of manufacturing factors on the obtained results and found that the tested composites behaved differently under some tests. Marzouk et al. [53] investigated adding date seeds as a reinforcement to low-density polyethylene (LDPE) to form a bio-composite. The thermal analysis of this study revealed that melting point and glass transition temperatures show no major effect for increasing the date seed particles. In addition, the crystallinity of the bio-composites has a slight increase with increasing the loading of date seeds. It was found that thermal degradation decreased while higher thermal stability was observed. The study highlighted that the *E* value increased from 7.7 to 8.2 MPa at 50 wt.% of DPS. However, the selection criteria of the compatibilizer can have a negative effect on some mechanical properties when added to a composite.

The study found that homogeneity was observed for the produced bio-composite even at the highest loading of date seed particles. The findings of this study show that date seed can be used as a reinforcement with LDPE, which enhance the properties of the produced bio-composite.

Ibrahem [40] studied the effect of several parameters on the tribological behavior of a composite consisting of polyester resin as the matrix and date seeds powder as the reinforcement. The study concluded that friction coefficient decreased with increasing the amount of date seed powder up to 10% under contact pressure and high sliding speed. Increasing date seed amount to 25% resulted in an increase of the friction coefficient under low contact pressure and high speed. The rate of wear of the proposed composite decreased with the increase in the amount of date seeds to 25% under medium sliding speed and low contact pressure. Ruggiero et al. [221] also studied wear in addition to adhesion and cohesion. The study considered the weight of percentage for date seed (0.5%, 1%, 2.5%, 5%, 7.5%, and 10%) with matrix of Glue Epoxy Rapid. For using date seed particles, the study concluded that homogeneous distribution for the composite was observed, no decreasing observed for the cohesion of the system at low concentration, increasing the adhesion of the steel adherent, the hardness, and the abrasive wear resistance. A number of studies that considered such parameters are limited and there is a need for further investigation for this type of application.

Nagaraj et al. [222] investigated reinforcing vinyl ester by date seed filler (DSF-VE) focusing on mechanical and thermal properties. The study showed that mechanical and thermal properties were affected by the percentage of date seed filler loading. The study concluded that the optimum filler weight was 30% for thermal and mechanical properties. The noticed reduction in some properties was justified by the poor bonding between the filler and the matrix. The study also showed that DSF-VE composite is comparable to many composites with other fillers and fibers-based composites. Compared to the neat VE resin and for the optimum achieved value, using DSF improved the tensile strength by 64.49%, the impact strength by 43.96%, the flexural strength by 91%, the hardness by 93.67%, and thermal stability by 58.94%. In addition, a directly proportional relationship between water absorption and loading of the filler was reported. Various engineering products made of DSF-VE were demonstrated in the study. The study also showed the potential of DSF-VE composite; however, according to the author the study was the first in which DSF is used as a filler for VE matrix.

Elkhouly et al. [20] utilized date seed (DS) as a filler for a glass fiber (G-E) to enhance mechanical characteristics. As described in the study that date seed filler material of 75 micro-meter powder size was added to the base material (glass and epoxy resin) to enhance the mechanical properties of the composites. Rolling was used to manufacture the bio-composite. For comparison purpose, inorganic fillers (silicon carbide and aluminium oxide with a size of 15 micro-meter) was used. The authors reported that DS filler is a suitable reinforcement to improve the wear resistance of G-E fibers. Taguchi experimental design was considered for optimization purposes of the four factors considered (filler wt.%, type of filler, normal load (N), and abrasive size). According to the optimization performed, DS filler was better than aluminium oxide only and the wear rate was at 10 wt.% DS filler specimen was equal to that at 5 wt.% silicon carbide filler specimens. The 10 wt.% DS filled composite had wear rate reduced by 71% and toughness increased by 80% compared to the unfilled materials. In addition, the authors considered the economical comparison between DS and other fillers where they highlighted the economic benefit of using DS. While this study considered some mechanical tests, there are important mechanical tests to be considered to assist in identifying the possible applications.

Danladi et al. [25] used the natural rubber (NR) as a matrix with DPS reinforcement to form a bio-composite material and a rolling mill was used to fabricate the specimen. The results show that as the filler content increases the strain and elongation decreases. Both strain and elongation reduced by 10% when 10 wt % of DPS was added; however, the reduction increases to 25% at 20 wt.% with no significant changes up to 40 wt.%. The strain and elongation reduced by 70% when the DPS content reach 50 wt.%. On the other hand, they found that as the seed filler increases, the more the composite became rigid. As shown in Table 6, at 50% PDS and 0.2 mm particle size, the hardness was increased by almost 30% from 0.30 to 0.4 MPa. It was reported that the highest stress was recorded for the pure natural rubber, but it was observed that it decreased with increasing date seed up to 20% then an increase started after that till 40%. Because of this observation authors highlighted that 70/30 and 60/40 have better strength than the other tested samples. Young's modulus showed a direct proportion relationship with the date seed contents. These improvements on the stiffness, rigidity, strength, and Young's modulus were justified by the fact that adhesion occurred between the matrix and reinforcement. The study conducted a number of tests and commented on the improvement of the composite properties. However, research publications toward investigating the use of NR with DSP are still limited. In addition, several factors may need to be considered for further investigation such as studying the behavior of the composite when increasing the percentage of date seeds especially when there is a point where the response of specific parameters started to suddenly change.

For ceramics type of matrices, Alami [223] investigated the thermal and mechanical properties of a composite made of clay and date palm leaf, raw date seeds. The study focuses on the manufacturability of sheets made of clay-fronds-date seeds for the purpose of evaluating the potential of using the developed composite in thermal insulation. The used clay was crushed and sifted, the palm fronds dried and cut carefully into identical rectangular shapes, and the date seed was used as a filler with three arrangements (horizontal, vertical, and at 45). The specimens were donly tested by compression test and thermal conductivity test. The results showed that the mechanical properties were significantly improved, while thermal properties did not improve and were comparable to that of basic sand and clay. In addition, the same author published another study where he compared the same clay-fronds-crushed date seeds to clay-straw-olive husk [224]. Also, the thermomechanical tests were limited to compression and thermal conductivity. In this study, the author concluded that date seed-based bio-composite has better performance than olive husk-based bio-composite. Djafri and Chelouah [225] studied the effect of varying the particle size of ground date seeds (0–0.2, 0.2–0.25, 0.25–0.5, and 0.5–1 mm) when used with clay brick. They used five loading amounts (0, 5, 10, and 20 wt.%) for each particle size used. The study highlighted that increasing the diameter and content

Table 6 Bio-Composites reviewed studies

Study	Origin	Polymer	W%	Property												
				TS (MPa)	IS (Kj/m^2)	YS (%)	& (mm)	E (MPa)	S @ break (MPa)	T_m (°C)	T_g (°C)	ΔH_m (°C)	ΔH_c (°C)	Heat of fusion (j/g)	Hardness (HRF)	FS (MPa)
Alsewailem and Binkhder [33]	KSA	HDPE	10	16	210					135	86			170		
			20	16	180					135	82			140		
			30	17	150					135	75			120		
			40	15	130					135	70			–		
		PS100	10	34	28					135	85			180		
			20	28	20					135	80			160		
			30	22	25					135	75			150		
			40	18	6					135	68			110		
Hamma et al. [36]	Algeria	PP with EBAGMA	10		125.4			1194	20	164	116	101	95			
			20		103.2			1061	14.6	164	117	100	94			
			30		95.5			965	11.9	164	117	103	97			
			40		97			749	9.2	163	116	110	104			
		PP without EBAGMA	10		110			1474	20	164	115	99	94			
			20		80			1608	18	164	115	97	93			
			30		70			1608	15	164	116	93	94			
			40		50			1742	13	163	116	91	94			

Table 6 (continued)

Study	Origin	Polymer	W%	Property												
				TS (MPa)	IS (Kj/m^2)	YS (%)	& (mm)	E (MPa)	S @ break (MPa)	T_m (ºC)	T_g (ºC)	ΔH_m (ºC)	ΔH_c (ºC)	Heat of fusion (j/g)	Hardness (HRF)	FS (MPa)
Mittal et al. [18]	UAE	PBAT	10	9.0		14.1	83.4	116.7	14.8	120	84					
			20	9.7		9.7	50.9	149.0	11.8	119	86					
			30	9.3		7.4	22.5	197.1	8.5	119	87					
			40	10.7		5.9	13.3	256.7	8.2	115	90					
		PLA	10	53.5		2.2		3528	43.7	170	99					
			20	44.9		2.0		3508	28.1	170	102					
			30	7.3		0.3		2495	16.3	172	109					
			40	5.1		0.3		2216	18.8	172	111					
Alsewailem and Binkhder [39]	KSA	PS100 with DPMI	30	18	25											
		PS100 with EpP-g-MA	30	10	37											
Danladi et al. [25]	Nigeria	Natural Rubber	10	0.05		1.9	200	2.8							0.29	
			20	0.043		1.7	175	2.8							0.3	
			30	0.07		1.7	175	4.2							0.33	
			40	0.063		1.7	175	4.2							0.37	
			50	0.045		0.6	60	8.0							0.4	
Mittal et al. [19]	UAE	PBAT	40					246.3								

Table 6 (continued)

Study	Origin	Polymer	W%	Property												
				TS (MPa)	IS (Kj/m^2)	YS (%)	& (mm)	E (MPa)	S @ break (MPa)	T_m (°C)	T_g (°C)	ΔH_m (°C)	ΔH_c (°C)	Heat of fusion (j/g)	Hard-ness (HRF)	FS (MPa)
Ameh et al. [41]	Nigeria	PS (0.5 mm)	5	15	3.2			270							25	27
			10	16	3.3			350							30	23
			15	17	3.4			330							33	19
			20	17.5	3.8			330							38	15
			25	12	4.0			220							75	12
Kolawole et al. [226]	Nigeria	UPS	10	13	3.8			550							75	37
			20	7	4.4			500							75.4	40
			30	5	4.0			600							76	36
			40	5	3.2			900							76.2	22
			50	4	2.6			1700							78.6	20
Marzouk et al. [53]	Tunisia	LDPE	10					7.94		107		90.7	100.8			
			20					8.03		109		80.2	100.3			
			30					8.09		109		70.3	100.4			
			40					8.13		108		60.3	100.5			
			50					8.19		108		50.4	100.8			
Almosawi [220]	Iraq	PS	1		1.9											
			2		3.1											
			3		5.1											

Table 6 (continued)

Study	Origin	Polymer	W%	Property												
				TS (MPa)	IS (Kj/m^2)	YS (%)	& (mm)	E (MPa)	S @ break (MPa)	T_m (°C)	T_g (°C)	ΔH_m (°C)	ΔH_c (°C)	Heat of fusion (j/g)	Hard-ness (HRF)	FS (MPa)
Mohamed et al. [61]	KSA	PLA	10							140	130	20	15			
			20							138	128	24	20			
			30							140	126	22	25			
			40							144	126	18	20			
		PCL	10							58	36	60	76			
			20							60	40	58	68			
			30							58	38	64	62			
			40							64	48	52	50			
Almosawi et al. [23]	Iraq	UPS	1	30												
			2	36												
			3	50												

Table 6 (continued)

Study	Origin	Polymer	W%	Property												
				TS (MPa)	IS (Kj/m^2)	YS (%)	& (mm)	E (MPa)	S @ break (MPa)	T_m (ºC)	T_g (ºC)	ΔH_m (ºC)	ΔH_c (ºC)	Heat of fusion (j/g)	Hardness (HRF)	FS (MPa)
Abdulkareem et al. [60]	Nigeria	AL (0.3 mm)	5	78	74.4										41.5	
			10	73	73.8										43.5	
			15	71	72.5										44.2	
			20	63	72.2										44.8	
		AL (0.5 mm)	5	92	75										42.8	
			10	88	74.5										43.6	
			15	86	73.8										45.8	
			20	74	73.2										47	

of the grounded date seeds increase both the water content for plasticity and water absorption coefficient. On the other hand, they stated that increasing the particle size and content of date seeds decrease the compressive strength, apparent density and thermal conductivity. While these studies highlighted the potential of utilizing date seed to improve the thermomechanical properties of the composite, several factors and mechanical, thermal tests need to be considered for further investigation and optimization.

Abdulkareem et al. [60] investigated the use of date seed particles as a reinforcement for metal matrix (aluminium alloy). Authors reported that the larger the particle size the higher value of tensile strength of the composite was found, but that is not true for weight fraction higher than 10% which was reasoned by the wettability of the reinforcement with the matrix. The impact energy was decreasing while increasing the weight fraction of date seeds particles and larger particles showed higher impact energy; however, both sizes showed similar behavior while increasing the weight. Also, hardness showed higher values with increasing weight fraction and the larger particle size performed better. While the study highlighted the enhancement of tensile strength and hardness by introducing the date seed particles, the impact strength was not. Research work of metal matrix with date seed to produce bio-composites is limited. Further research studies are recommended to explore the advantage of developing metal date seed-based composite for aluminium or other possible metal.

In this section of the review, research works toward utilizing date seeds to fabricate bio-composites focused on thermal and mechanical properties was presented. The polymer, ceramic, and metal matrix were considered by researchers to be reinforced by date seeds. It was noticed that most of the studies used different sets of factors during the preparation and fabricating process of the bio-composite specimen. The percentage weight of date seeds in the composite was mostly the factor that was considered. Other factors such as the conditions of the manufacturing processes, date seed species, and coupling agent were not considered in many of the included studies. Therefore, future investigations of these factors in addition to considering the usage of date seed as reinforcement material and another type of natural materials are encouraged. For ceramics and metal matrix, the studies were limited with promising results as described by the authors. Therefore, studies for ceramics and metal types considering the manufacturing process and optimization are recommended. For all the types of matrices used, several thermal and mechanical parameters behaved differently while introducing the date seeds as a reinforcement and factors such as the weight percentage and particle size of the date seed shows an ability to enhance the properties up to some level. Optimization studies are encouraged to locate the optimum conditions for several considered factors focusing on the thermomechanical parameters based on the targeted engineering application.

Conclusion

Date seed is one of the agricultural waste biomasses, researchers have studied the possibility of utilizing date seeds in a variety of applications including medical, cosmetic, nutritional, and engineering. Several literature review papers implicitly reviewed the utilization of date seeds for different types of purposes, but none of which focused on the engineering type of applications. This review paper aims to survey the most common engineering application in which date seed was utilized.

In the first part of the study, the preparation methods of date seed powder were thoroughly reviewed. The preparation process included many variables such as the type of seeds used, washing methods, the liquids used for washing, the drying temperature and duration, the degree of grinding, and the size of the extracted particles. Lack of optimization studies was noticed, let alone the existence of an international approved standard. Likewise, methods for extracting date seed oil. However, it is noted that the Soxhlet extractor method was mostly used. A limited number of studies dealt with the thermal and mechanical properties of raw date seeds. It was noticeable that most of the reviewed studies neglected some properties and that a limited number of palm species were studied.

In the second part of the study, the most common viable applications of date seeds were reviewed. In the light of the increasing demand for alternative fuel, the utilization of date seeds in the production of biofuel and biodiesel is found to have a high potential as a new feedstock for biofuel or biodiesel production and meets both international testing standards of biodiesel. Also, a considerable amount of literature has been published on the utilization of date seed as an adsorbent. These studies dealt with both purification and separation applications and handled a variety of pollutants, contaminants. Date seed has also proven to be an economical eco-friendly feedstock as an adsorbent material. Moreover, date seeds can be categorized as a multi-component natural polymer additive that consists of hemicellulose, lignin, and cellulose; hence, it can work as an inexpensive eco-friendly drilling fluid. Even though a very limited number of studies investigated this type of application, date seed-based drilling fluid show a high potential to be an efficient replacement of the traditionally used expensive and hazardous fluids. Last, the thermal and mechanical properties of date seeds make it a good choice for the preparation of bio-composites materials. A comprehensive review was made of the latest published studies in this regard, which prove the feasibility of using date seeds for such applications in addition to the capabilities that have not yet been studied.

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