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ORIGINAL ARTICLE

Moisture sorption isotherms of whole and fractionated date-pits: Measurement and theoretical modelling

Maha Al-Khalili, Nasser Al-Habsi *, **Rahman shafiur Mohammad**

Department of Food Science and Nutrition, College of Agricultural and Marine Sciences, Sultan Qaboos University, P. O. Box 34-123, Al-Khod 123, Oman

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Abstract Moisture sorption properties of whole date-pits (WDP) and three fractionated date-pits; defatted date-pits (DDP), residue (REP) and supernatant (SUP) fractions were studied. Sorption isotherms were measured using Differential Thermal and Humidity chamber at different temperatures (10, 30, 50, 70 and 90 °C) and relative humidity ranged from 0.05 to 0.9. Crossovers of isotherm curves were observed for all fractions between different temperatures. At 30 °C, BET-monolayers of WDP, DDP, REP and SUP were 4.9, 4.2, 3.8 and 3.2 g/100 g ds, respectively. The complete isotherms (i.e. 0.05–0.90 water activity) were modelled by GAB with high coefficient of determination (i.e. 0.944 to 0.999). In the cases of WDP and DDP, the isosteric heat plots showed increasing trends with the decreased moisture and peaks at moisture 0.025 and 0.040 g/100 g ds. Unlike all fractions, DDP isokinetic temperatures T_{is} (i.e. 97.4 °C) was lower than isobound temperatures T_{ib} (i.e. 145.0 °C) indicating complete removal of bound water occurred at higher temperature as compared to the temperature when all reactions reached at the same. The moisture sorption isotherm characteristics could be used in determining the end point of drying and storage stability as well as packaging design of the date-pits and their fractions.

1. Introduction

Date-pits are waste from date fruit processing factory, and its utilization or valorization could bring economic gain, reduce environmental waste, and enhance food security, circular economy and sustainability. Date-pits are generally used as animal feeds for livestock and poultry (Vandepopuliere et al., 1995). It is a lignocellulose material mainly composed of cellulose, hemicellulose and lignin. The chemical composition of these seeds determines their proper utilization (Shi et al., 2014). Date-pits are a valuable source of fibers (60 to 80 g/100 g), oil (3.9 to 13.8 g/100 g), protein (4.8 and 12.5 g/100 g) and contain a significant antioxidant potency due to their high compositions of

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* Corresponding author.
E-mail address: habsin@squ.edu.om (N. Al-Habsi).

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flavonoids and other active components (Metoui et al., 2019; Habib et al., 2017; Hamada et al., 2002; Habib and Ibrahim, 2009; Alyileili et al., 2020; Al-Khalili et al., 2021a; Nehdi et al., 2018; Besbes et al., 2009). Their components, such as polysaccharides, and oil (i.e. biofuel and cooking oil) could also be developed.

Date-pits have been used as an additive for different types of food products (Alamri et al., 2014, Almana and Mahmoud, 1994, Bouaziz et al., 2020, Ahmed et al., 2017, Anusree and Kousalya, 1998). Al-Khalili et al. (2023) reviewed the application of date-pits in coffee and other beverages, bakery goods, meat products, dairy products, desserts, spreads, and condiments. They indicated that desired functionality (i.e. sensory acceptability) could not be achieved with a high level of date-pits in food products. Therefore, it is important to measure the physico-chemical and sorption characteristics of date-pits. Other applications are to produce activated carbon for purifying water by removing different types of pollutants, such as heavy metals, boron, and pesticides. It can also be used as an ingredients for bio composed, biomass and fermentation processes (Hossain et al., 2014).

It was observed that bread containing 10 % coarse WDP powder showed a higher dietary fibre and produced similar characteristics as compared with wheat bran. However, fine WDP powder showed uniformity with overall sensory acceptability (Habibi Najafi et al., 2016). It was documented that acid and alkaline treatment of defatted date-pits increased body weight, feed intake and *in-vitro* digestibility when used as a chicken feed (Hussein et al., 1998). This was due to the increased solubilisation or swelling of fibres. Hydrochloric acid treatment at 100 °C for 12 h was used for DDP before its use as an ingredient for biomass fermentation (Nancib et al., 1997). Three types of date-pits fractions were developed by treating DDP with alkali at 30 °C (Al-Mawali et al., 2021, Al-Khalili et al., 2021a). The first fraction was the residue fibres after treatment with pH 13, second one was the precipitated fraction from supernatant at pH 5.5, and third one was the precipitated fraction at pH 1.5. They measured proton mobility, glass transition and solids melting-decomposition and they pointed that type 1 could be used in crackers, and type 2 could be used in bread, noodles and cookies, while type 3 could be used in edible coating and food emulsion formulation. Al-Khalili et al. (2021a) studied the hygroscopicity, solubility, morphology, structural characteristics and crystallinity of these fractions. They found that the fractionated date-pits could be used as a reinforcing bioplastic and bio-concrete (i.e. filler matrix), toxicant adsorption in the human digestive track, and as a food ingredient for breads, biscuits and rusks. In addition, they showed that there is a potential to use the alkaline digested date-pits as bioplastics or composites. Date-pits was used in other applications in different domains as well, such as biomass production (Elnajjar et al., 2021, Nancib et al., 1997, Nouri, 2021, El Hanandeh et al., 2021, El-Azazy et al., 2021), and bio-composite (Ruggiero et al., 2016, Alsewailem and Binkhder, 2010, Ejiogu et al., 2020). All of these findings supported that date-pits could be used more efficiently when treated to produce fractions with specific desired properties. Therefore, it is important to determine the properties of treated date-pits before identifying their proper applications.

Over 200 different equations were used in literature to predict the sorption isotherms at different temperatures (Van den Berg and Bruin, 1978; Al-Khalili et al., 2021b). These models are either theoretical based or rely on empirical basis (Weatherwax, 1974; Goula et al., 2008; Peng et al., 2007). The most used prediction models for determining food sample sorption isotherms are BET (Brunauer, Emett and Teller) and GAB (Guggenheim–Anderson–de Boer). This was due to their simplicity and theoretical basis (Alamri et al., 2018; Timmermann et al., 2001; Al-Khalili et al. 2021b). GAB model can be used to predict the isotherms over the complete range of water activity (i.e. 0.05 to 0.9), while the BET model is unable to predict sorption isotherms beyond 0.45 water activity (Labuza et al., 1985). Bell and Labuza (2000) indicated that an increase of 0.1 in water activity above the monolayer value could consequently decrease the materials shelf life by two to three times.

Al-Khalili et al. (2022), measured the physico-chemical, thermal, structural, and morphological characteristics of pressure cooked date-pits while soaked in 50 % water-alcohol solvent. However, it is also important to determine the water sorption properties of these treated date-pits when used in foods, biomass production and bio-composite. Moisture sorption isotherm could be used to determine date-pits shelf life, packaging and stability during storage (Fabra et al., 2009). In addition, the end point of drying could be determined from its moisture sorption isotherm. The binding nature (i.e. energy) of water could give an indication on its behaviour when date-pits are used in multicomponent formulations.

Belarbi et al. (2000) studied the moisture sorption isotherms of date-pits (Deglet-Nour variety) at 25 °C. Similarly, Suresh et al. (2017) studied the isotherm of freeze dried date-pits at room temperature (20 °C). Alyousef et al. (2020b) examined the isotherms of date-pits at three temperatures (30, 40 and 50 °C) and determined the binding nature of water. On the other hand, Ajibola et al. (2005) studied the isotherm of date-pits at temperature ranged from 40 to 60 °C within the relative humidity from 13.0 to 53.5 %. In the literature, limited research was presented on the moisture sorption isotherm of date-pits at a wider range of temperature and relative humidity. In addition, moisture sorption isotherms of fractionated date-pits were not reported earlier. Therefore, the objective of this work was to measure the moisture sorption isotherm of whole date-pits (WDP) and their pressure cooked fractions at a wider range of temperature (i.e. 10–90 °C) and relative humidity or water activity range (i.e. 0.05–0.9). The defatted date-pits (DDP) powder was fractionated by pressure cooking in a solvent of 50 % (v/v) water and alcohol mixture. The treatment provided two fractions, one as residue (REP) and another one as supernatant (SUP). Dynamic temperature and humidity (DTH) controlled chamber was used to measure their isotherms, which showed its capability to measure isotherm within a wide range of temperature at any range of relative humidity value (Al-Khalili et al., 2021b).

2. Materials and methods

2.1. Sample preparation and extraction method

Whole date-pits from khalas variety were purchased from a local market in Oman. These were cleaned by washing with hot water to remove any adhered date flesh. Whole date-pits were then dried in the oven (Gallenkamp, UK; model: 300 plus series) at 60 °C for 72 h. The dried whole date-pits were ground by a hammer mill (Model NO Cemotec 1090, Foss, Hoganas, Sweden). The whole date-pits powder was kept in a container, labelled as WDP and stored at ambient temperature for further treatment. WDP powder was defatted by petroleum ether at a ratio 1:50 (w:v) in the Soxhlet apparatus for 8 h. The defatted date-pits powder was dried in an oven for 18 h at 60 °C and considered as DDP. The DDP powder was soaked in 50 % ethanol at a ratio 1:50 (date-pits powder: solvent, w:v) with steering for 48 h. The mixture was further treated by pressure-cooking (model GPC307-6L, Geepas, Romania) at 100 °C until three blows were achieved (i.e.15 min). The mixture was left to cool for about 15 min at 20 °C. The precipitated residue was isolated manually by draining the supernatant. The residue was dried in the oven at 60 °C for 18 h and was considered as REP. The left supernatant was kept at 4 °C for 48 h and the precipitate was collected by isolating the supernatant manually. The sediment was dried in oven at 60 °C for 18 h and was considered as SUP.

2.2. Moisture content

Moisture content was measured according to the (AOAC, 2000) method. In this method, date-pits and their fractions (i.e. in triplicates) were placed in a vacuum oven (VD 23, Binder, Germany), at 70 °C for 18 h at a pressure of 10 kPa.

2.3. Sorption isotherm measurement

Moisture sorption isotherm was measured by Dynamic Thermal Humidity (DTH) controlled chamber method as recently developed by Al-Khalili et al. (2021b). This chamber utilized Advanced Preheating Technology-line™ technology, which maintains homogeneous climate conditions inside the chamber and ensured fast recovery of the humidity and temperature after opening and closing while measuring samples weight. Temperature and humidity ranged could be maintained at any incremental level between −15 to 100° C and 0 to 98 %, respectively (Al-Khalili et al. 2021b). The accuracy of the maintaining temperature (5 and 90 °C) and relative humidity (0.10–0.90) were checked by measuring temperature by a digital temperature and relative humidity meter.

Considering 0.2 g sample, initial conditioning and equilibrium time for each measurement (i.e. at specific relative humidity) was 30 min as recommended earlier by Al-Khalili et al. (2021b) considering no significant change in weight of the sample. In this procedure, date-pits and their fractions (0.2 g) were placed uniformly in a glass dish in triplicates. Dishes containing samp. les were incubated in the DTH Chamber. The chamber was set at 10 °C and 5 % relative humidity and sample weight was recorded after 30 min. The relative humidity was then changed to 10 % from 5 % and continued to increase up to 90 % with a 10 % step change. At each humidity, equilibrium time was considered as 30 min (Al-Khalili et al. (2021b). The same procedure was repeated for other temperatures (i.e. 30, 50, 70 and 90 °C) with relative humidity ranged between 5 and 90 % for each temperature.

2.4. Isotherm modelling

Moisture adsorption isotherms were commonly modelled by BET and GAB equations and it can be expressed as the following (Brunauer et al., 1938):

$$M_e = \frac{M_b B a_w}{[(1-a_w)(1+(B-1)a_w)]} \tag{1}$$

where M_e is the equilibrium moisture and M_b is the BET monolayer moisture contents (i.e. dry basis: g water/100 g dry solids), a_w is the water activity, and B is a constant that is related to the net heat of sorption (J/g-mole). BET isotherm is considered valid up to $a_w = 0.45$, and this can predict M_b and B (Labuza, 1968). BET parameters were predicted graphically by plotting $[a_w/(1-a_w)M_w]$ *versus* a_w up to 0.45. B value and M_b were estimated from the slope $[(B-1)/M_bB]$and the intercept $[1/M_bB]$ of the best fitted line. The BET-monolayer (M_b) value indicated the strongly bound water with the solids matrix and these are the most inert (i.e. not reactive). In addition, the energy state of this fraction of water is low. The value of B indicates the energy required to desorop the strongly bound water (i.e. bound water below water activity 0.45). The model parameters can be plotted as a function of temperature by using regression equation, thus the effect of temperature on the isotherm could be predicted.

GAB model (Anderson, 1946, DeBoer, 1953, Guggenheim, 1966) as shown in Equation (2) was used to fit the isotherm data within 0.05 to 0.95 water activity.

$$M_e = \frac{M_g C K a_w}{[(1-Ka_w)(1-Ka_w+CKa_w)]} \tag{2}$$

where, M_g is the GAB monolayer moisture content (i.e. dry basis, g/100 g dry solids) and C is a constant correlated to the monolayer heat sorption (J/g-mole), and K is a factor related to the multilayer heat of sorption. The GAB-monolayer is the strongly bound water considering the isotherm up to water activity 0.9 and adjusting the water sorption isotherm by adding the heat of sorption by multi-layer water. In the GAB model adsopted energies of monolayer and multilayer and separated, while BET model only considered the monolayer. The value of K is incorporated to include the effects of multilayer heat of sorption.

2.5. Isosteric heat

The isosteric heat was calculated using Clausius-Clapeyron equation and it could be expressed as:

$$\frac{d([ln(a_w)])}{d(\frac{1}{T})} = -\left(\frac{Q_s}{T}\right) \tag{3}$$

where Q_s is the net isosteric heat of sorption (kJ/kg), and can be defined as the energy needed to remove a unit mass of adsorbed water at a specific temperature (Aviara et al., 2002) and T is the temperature (K). The net isosteric heat of sorption (Q_s) was determined from the slope of ln (a_w) *versus* $1/T$ plots at a specific moisture content (Arslan-Tontul, 2021). The net isosteric heat indicated that how much energy is involved at a specific moisture over the temperature of the measured isotherm.

2.6. Isokinetic temperature

The isokinetic temperature (i.e. T_{is}), which is the temperature when all the reactions occur at a constant rate, and it was determined from the linear plot of enthalpies (ΔH) and entropies (ΔS) (Exner, 1970). The enthalpies ($\Delta H/R$) and entropies ($\Delta S/R$) were estimated from the slopes and intercepts of the linear plots between a_w and $1/T$, and it is demonstrated by Equation (4) (Telis-Romero et al., 2005):

$$lna_w = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \tag{4}$$

The isokinetic temperature was then determined from the slope of the plot between the enthalpy ($\Delta H/R$) and entropy ($\Delta S/R$) (Exner, 1970, Telis-Romero et al., 2005). At the isokinetic temperature, the rates of all reactions or changes occur at a same rate (i.e. reactions are independent of temperature).

2.7. Isobound temperature

The isobound temperature (T_{ib}) was determined by plotting temperature as a function of BET-monolayer solids at equilibrium temperature and it was considered as the intercept when water reached to zero (i.e. dry solids)(Rahman and Al-Saidi, 2017). This is the temperature when all water (i.e. bound and free) is desorbed.

2.8. Statistical analysis

Average and standard deviations were determined for each humidity equilibration. Standard experimental uncertainties were determined for each sample considering 0.95 level of confidence. The BET model parameters were estimated by regression of linearized isotherm Equation (1). Non-linear regression was implemented to predict the parameters of GAB model using the NLREG software (Sherrod, 1991). Coefficient of determination (R^2) were determined to validate the accuracy of the models.

3. Results and discussion

3.1. Moisture sorption isotherm

The standard uncertainties of the measured equilibrium moisture for all samples were varied from ± 0.07 to ± 0.08 g water/100 g ds (considering 95 % confidence level). Fig. 1 shows sigmoid shape (i.e., type II according to the International Union of Pure and Applied Chemistry, IUPAC) isotherms of the whole and date-pits fractions as a function of temperature (Brunauer, Deming, Deming, & Troller, 1940; Alothman, 2012; Zheng et al., 2018). Similar sigmoid shape was observed for the freeze dried date-pits isotherm (Suresh et al., 2013, Belarbi et al., 2000). The sigmoidal sorption isotherm was also commonly observed for foods, plant products and different types of plant leaves and biomaterials (Mulet et al., 1999, Rahman and Al-Belushi, 2006, Siripatrawan and Jantawat, 2006, Peng et al., 2007, Staudt et al., 2013, Alamri et al., 2018; Arslan & Togrul, 2006; Sinija & Mishra, 2008; Bahloul et al., 2008; Mohamed et al., 2005; Argyropoulos et al., 2012; López-Vidaña et al., 2021; López-Vidaña et al., 2016). Date-pits are mainly a lignocellulosic biomaterial that contain significant amount of cellulose, hemicellulose and lignin. Al-Khalili et al. (2021b) also observed similar shape of isotherm for commercial cellulose and lignin.

In general, isotherms shifted downward as temperature increased. This was due to the escaping tendency of the water at higher temperature (Kapsalis, 2017, Siripatrawan and Jantawat, 2006). The elevated temperature was found to decrease the number of molecules linked to the polar sites and cohesive pressure of the solid matrix (Alyousef et al., 2020b). Similarly, date-pits isotherms at temperatures 30, 40 and 60 °C showed similar behavior (Alyousef et al., 2020b) as well as starchy foods (Rohvein et al., 2004, Barreiro et al., 2003, Jorge, 1982) and fibers such as cellulose and lignin (Al-Khalili et al., 2021b). Kapsalis (2017) mentioned that at higher temperature, water molecules mobility enhanced the dynamic equilibrium between water vapor and adsorbed phases. The temperature effect on sorption behavior of constant moisture content of packed products is particularly important with different ambient temperature in different countries. High ambient temperature makes these products susceptible to increased water activity and thus the stability of the product will be affected negatively (Alam and Islam, 2015).

However, crossovers of the isotherms were observed at selected temperatures. The crossovers were observed at water activity of 0.50 (i.e. between 10 and 30 °C) and above 0.80 (i.e. between 70 and 90 °C) in the case of WDP. In the case of DDP, only one crossover was observed at water activity 0.50 (i.e. between 30 and 50 °C). REP showed three crossovers of the isotherm curves, first one at water activity 0.30 (i.e. between 10 and 30 °C), second ones at 0.85 (i.e. between 50 and 90 °C) and third ones at 0.50 (i.e. between 70 and

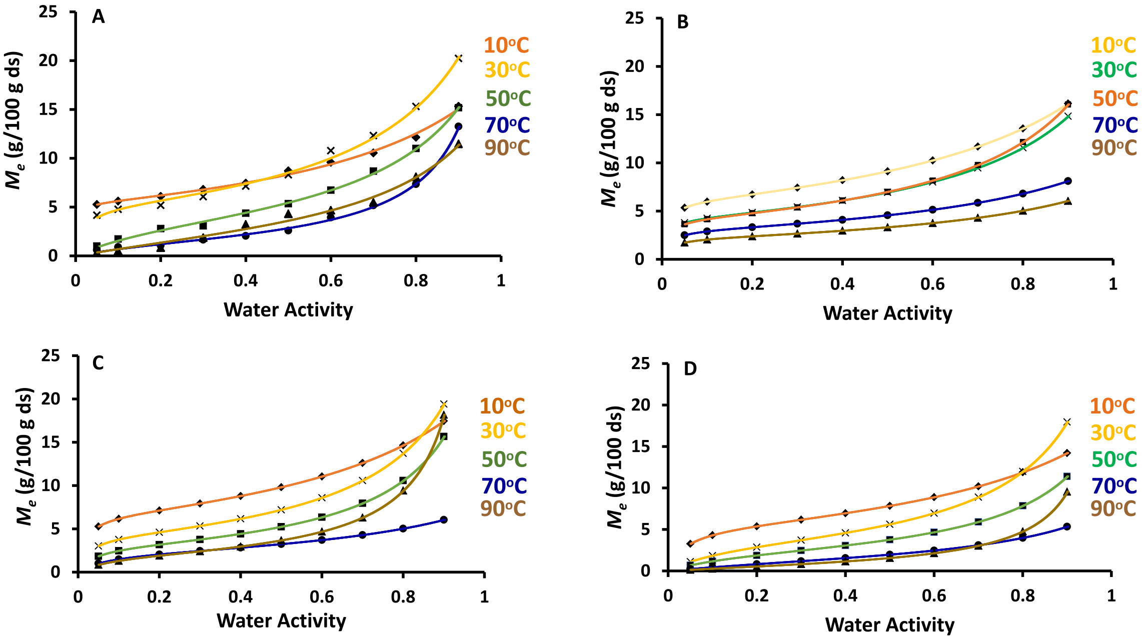

Fig. 1 Adsorption isotherm curves of A; WDP (CV: 0.07 g/100 g ds), B; DDP (CV: 0.08 g/100 g ds), C: REP (CV: 0.07 g/100 g ds) and D; SUP (CV: 0.08 g/100 g ds) for the temperatures from 10 to 90 °C.

90 °C). On the other hand, SUP fraction showed two intersections, first one at 0.70 (i.e. between 70 and 90 °C), and second one at 0.80 (i.e. between 10 and 30 °C). The crossover behavior of isotherm was identified earlier for starch and sugar based foods, such as beetroot (Iglesias et al., 1975), and barley mallet (Barreiro et al., 2003). In the case of sugar or carbohydrate-based products, they suggested that crossover could be due to the increased solubility (i.e. dissolution of sugars) of low molecular weight saccharides at a critical water activity (Balderrama and Cadima, 2014, Alhamdan and Hassan, 1999, Myhara et al., 1998). In the case of sugar based foods, crossover was explained by dissolution of sugars within water activity 0.45 and 0.55 (Alhamdan and Hassan, 1999, Myhara et al., 1998). The variations of the crossovers in the cases WDP and other treated fractions could be due to the variations of the swelling ability at critical water activity. It was expected to observe swelling variations of polysaccharides in whole date-pits and their function due to the removal of oils and pressure cooking in alcohol. In addition, in the case of starch, the creation of active sites and hygroscopicity was due to the variation of swelling above critical water activity, and this could result in the inversion of isotherm (Perdomo et al., 2009). However, Brett et al. (2009) pointed that the crossover could be correlated to the glass-rubber transition at a critical water activity.

3.2. BET isotherm model

Table 1 shows the BET model parameters for the WDP, DDP, REP and SUP at temperatures 10, 30, 50, 70 and 90 °C. The BET adsorption isotherm was fitted linearly up to water activity 0.40 and the coefficient of determination (R^2) varied from 0.885 to 0.999 (Table 1). At 10 °C the M_b values were 5.75 and 5.67 g/100 g for the DDP and REP, while WDP and SUP M_b values were 4.49 and 4.32, respectively. M_b value of freeze dried date-pits were estimated as 4.30 g/100 g ds at 20 °C (Suresh et al., 2013) and 4.27 g/100 g ds at 25 °C (Belarbi et al., 2000), while in this study it was observed as 4.49 g/100 g ds at 30 °C (Table 2). The BET-monolayer value indicated the active polar sites in the solid matrix. DDP and REP showed higher M_b values as compared to the WDP and SUP, this could indicate that former absorbs more water at same temperature and water activity (Alam and Islam, 2015). The BET monolayer values showed a general decreasing trend as the temperature increased for date-pits and fractionated fibers (Fig. 2). The reduction in M_b values could be due to the chemical and physical changes as affected by elevated temperature (McMinn and Magee, 2003). The decreasing trends of M_b with increasing temperature were also reported for many starchy food products (i.e. barley malt, rice, crackers and cookies) (Barreiro et al., 2003, Kim et al., 1998, Benado and Rizvi, 1985). Considering more than 40 foods, Iglesias and Chirife (1984) pointed that the effect of temperature on BET monolayer values varied differently depending on the types of foods and biomaterials. In this study, M_b values of WDP, DDP, REP and SUP decreased from 4.49 to 1.33 g/100 g ds, 5.75 to 2.40 g/100 g ds, 5.67 to 1.98 g/100 g ds, and 4.32 to 1.07 g/100 g ds, respectively when temperature increased from 10 to 90 °C.

The BET heat of sorption (i.e. B value) showed decreasing trends with the increase of temperature. At 10 °C, B values were 82.4, 173.0, 47.0 and 71.7 J/g-mol, in the cases of WDP, DDP, REP and SUP, respectively (Table 1 and Fig. 3). Belarbi et al. (2000) determined the B value of WDP (i.e. Deglet-Nour variety) as 52.2 at 25 °C, while in this study it was 65.0 at 30 °C (i.e. close to 25 °C).

Table 1 BET and GAB models' parameters for date-pits and fractionated date-pits fibers as a function of temperature.

Sample	BET Model Parameters				GAB Model Parameters				Thermodynamic Parameters	
	T (°C)	M_b g/100g ds	B	R^2	M_g g/100g ds	C	K	R^2	T_{is} (°C)	T_{ib} (°C)
WDP	10	4.49	82.44	0.997	5.38	426.73	0.71	0.995	111.6	102.8
	30	4.90	7.50	0.999	5.08	65.04	0.84	0.995		
	50	2.92	9.81	0.971	3.81	6.49	0.85	0.998		
	70	1.40	2.05	0.956	1.79	4.97	0.97	0.998		
	90	1.33	1.54	0.970	3.14	2.80	0.84	0.988		
DDP	10	5.75	173.00	0.994	6.00	170.00	0.70	0.988	97.4	145.0
	30	4.20	28.00	0.942	4.22	150.00	0.80	0.998		
	50	4.16	32.89	0.964	4.16	120.00	0.82	0.994		
	70	3.13	16.00	0.885	3.02	110.00	0.70	0.955		
	90	2.40	19.80	0.922	2.18	90.00	0.71	0.944		
REP	10	5.67	47.00	0.997	6.50	100.00	0.70	0.997	97.4	110.3
	30	3.81	72.86	0.985	4.16	50.00	0.87	0.999		
	50	2.79	34.78	0.981	3.00	30.00	0.90	0.999		
	70	1.84	23.81	0.968	2.30	20.00	0.70	0.997		
	90	1.98	13.10	0.989	2.00	13.00	0.99	0.999		
SUP	10	4.36	71.69	0.989	5.34	40.00	0.70	0.995	111.6	104.8
	30	3.20	9.60	0.992	3.50	9.34	0.90	0.999		
	50	2.20	8.30	0.988	2.45	8.00	0.88	0.999		
	70	1.29	4.04	0.968	1.65	3.80	0.80	0.997		
	90	1.07	2.69	0.999	1.09	2.68	0.99	0.999		

Table 2 BET and GAB models' parameters for whole date-pits in this study and in comparesion to literature.

Study	Variety/ Form	Temperatue (°C)	RHR* (%)	BET Model Parameters		GAB Model Parameters			Net Isostatic Heat (kJ/kg)
				M_b (g/100 g ds)	B	M_g (g/100 g ds)	C	K	
Current study	Khalasdate-pits powder	10	5.0–90.0	4.49	82.44	5.38	426.73	0.71	3450
		30		4.90	7.50	5.08	65.04	0.84	
		50		2.92	9.81	3.81	6.49	0.85	
		70		1.40	2.05	1.79	4.97	0.97	
		90		1.33	1.54	3.14	2.80	0.84	
Suresh et al. (2017)	Khalas freeze dried date-pits powder	20	11.5–84.3	4.30	–	4.1	–	–	–
Ajibola et al. (2005)	Whole date-pits powder	40	13.0–53.5	–	–	–	–	–	3250
		50		–	–	–	–	–	
		60		–	–	–	–	–	
		70		–	–	–	–	–	
		80		–	–	–	–	–	
Belarbi et al. (2000)	Deglet-Nour date-pits powder	25	11.0–90	4.27	52.2	4.89	3.75	0.93	–

*Relative Humidity Range.

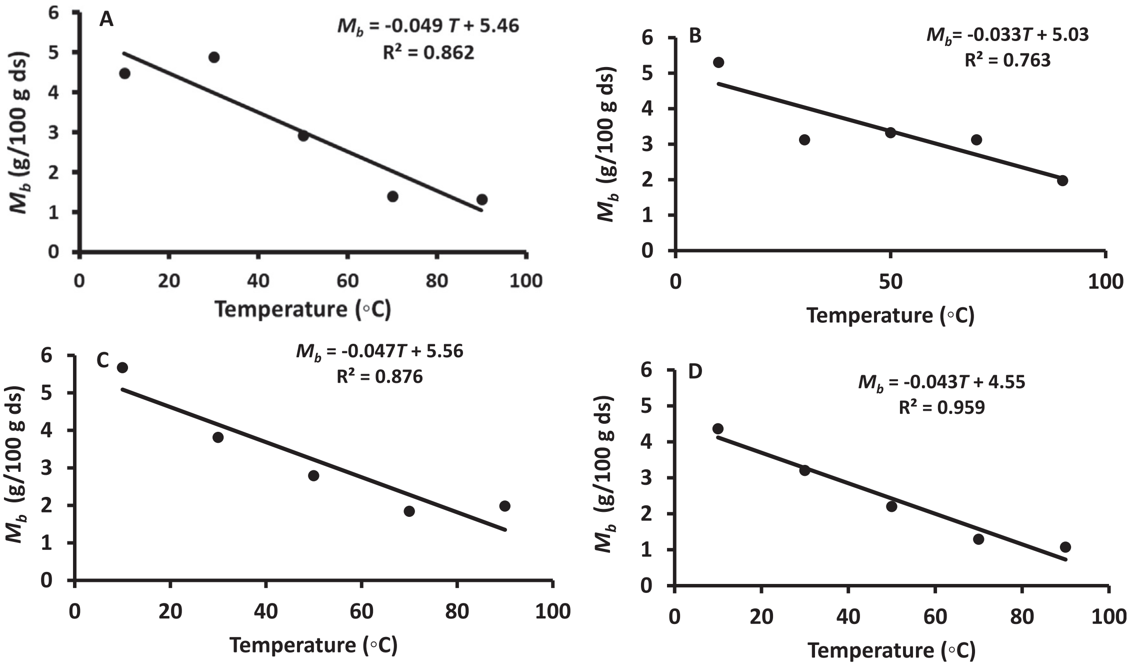

Fig. 2 BET (A: WDP, B: DDP, C: REP, D: SUP) monolayer values as a function of temperature.

3.3. GAB isotherm model

The GAB model parameters are presented in Table 1 and the coefficient of determination (R^2) varied from 0.944 to 0.999 for WDP and fractionated fibers (Table 1). At 10 °C, DDP and REP showed higher M_g values (i.e. 6.00 and 6.50 g/100 g ds, respectively) as compared to WDP and SUP (i.e. 5.38 and 5.34 g/100 g ds, respectively). In both cases (i.e. BET and GAB), monolayer moisture increased with the removal of oil, as this trend was also observed by De Jong et al. (1996) for whole and defatted foods. In the case of freeze dried date-pits, Suresh et al. (2013) estimated the M_g value as

4.1 g/100 g ds, while Belarbi et al. (2000) found M_g of Deleget-Nour date-pits as 4.89 g/100 g ds. In this study, the M_g values were higher as compared to the reported values. The variation in sorption capacity between different samples particularly at higher water activity values is attributed to differences in the structural integrity (Alam and Islam, 2015). Similar to BET model, the M_g values from GAB model followed a decreasing trend with the increase in temperature (Fig. 4). However, in the case of WDP (Fig. 4A), the variability was higher at the elevated temperature and it could be due to the different types of components reacting at higher temperature. Fig. 5 shows that moisture residual plots as a function of water activity. These figures show low errors (i.e. ± 0.008 g/g-dry-solids or ± 0.8 g/100 g ds) of the model from experimental data.

The C values (i.e., constant related to sorption energy difference between upper layers and monolayer) shows a decreas-

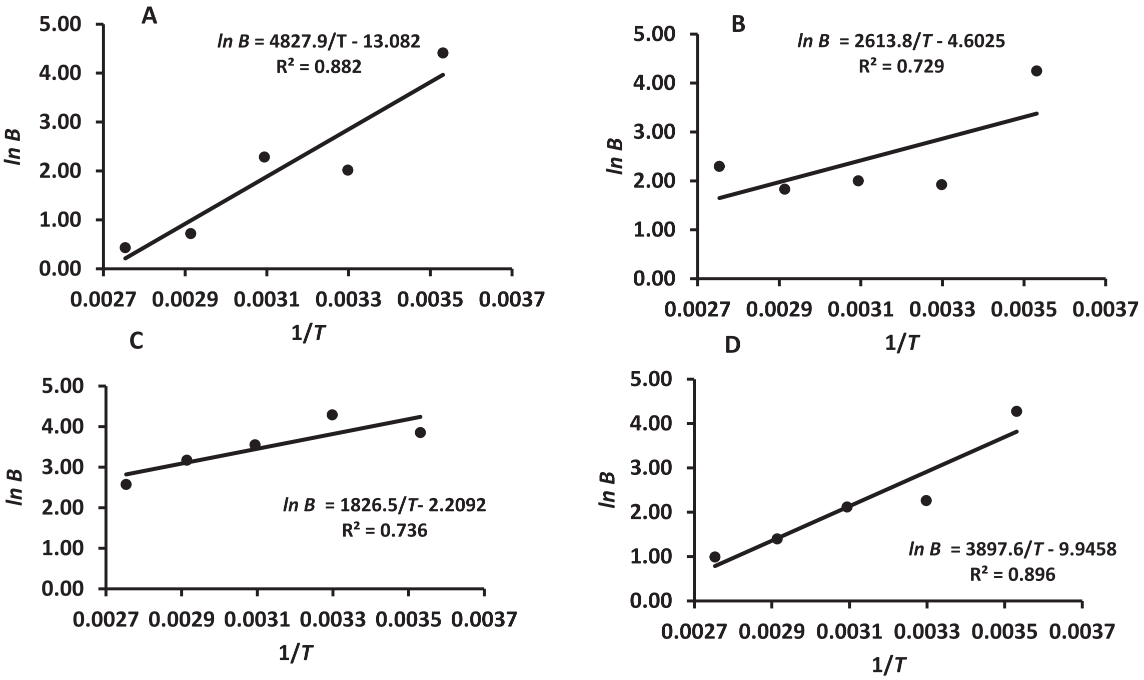

Fig. 3 BET model B-values (A: WDP, B: DDP, C: REP, D: SUP).

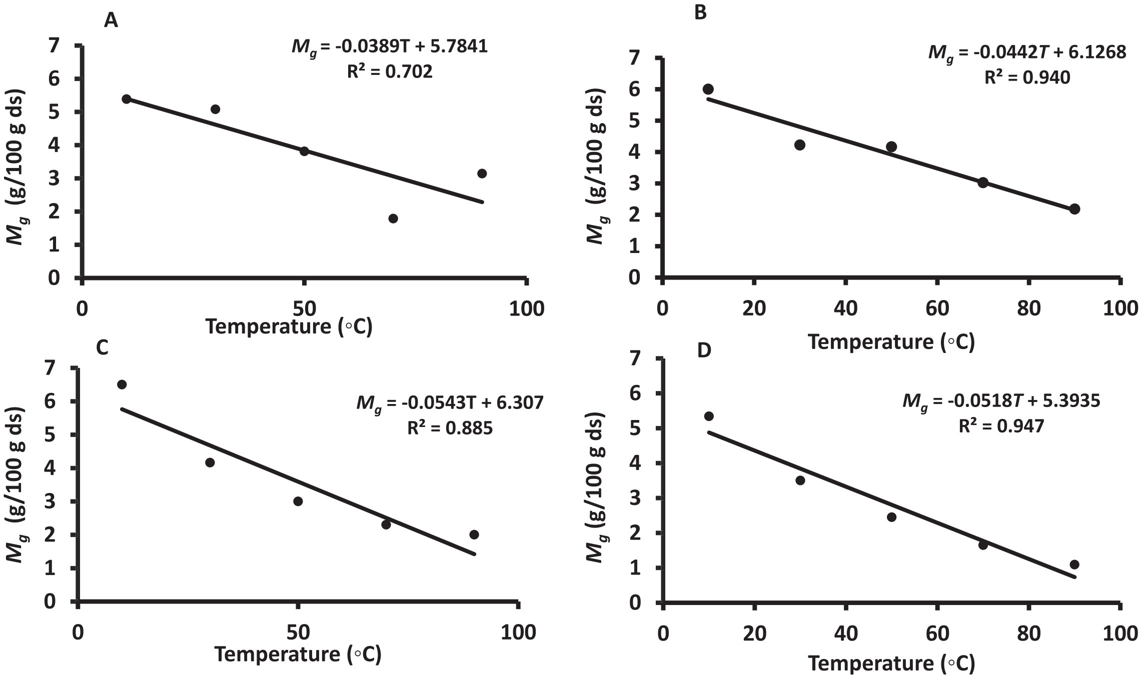

Fig. 4 GAB (A: WDP, B: DDP, C: REP, D: SUP) monolayer values as a function of temperature.

ing trend with the increase of temperature for all samples ($R^2 \geq 0.931$) (Fig. 6). The constant *C* of WDP dropped from 426.7 (i.e. at 10 °C) to 65.04, 6.49, 4.97 and 2.80, as the temperature increased to 30, 50, 70 and 90 °C, respectively (Table 1). At 25 °C, Belarbi et al. (2000) observed much lower value of *C* (i.e. 3.75) in the case of date-pits, while in this study it was observed as 65.04. The constant *K* was a positive value less than unity for WDP powder and the fractionated fibers in all isotherms (Table 1 and Fig. 7). The *K* values were similar to the values observed for date-pits (Belarbi et al., 2000), cellulose and lignin (Al-Khalili et al., 2021b). Theoretically, *K* values should be less than unity as observed in this study (Chirife et al., 1992, Rahman, 2009, Belarbi et al., 2000). In the case of SUP, the multilayer sorption energy (i.e. *K*-value) was

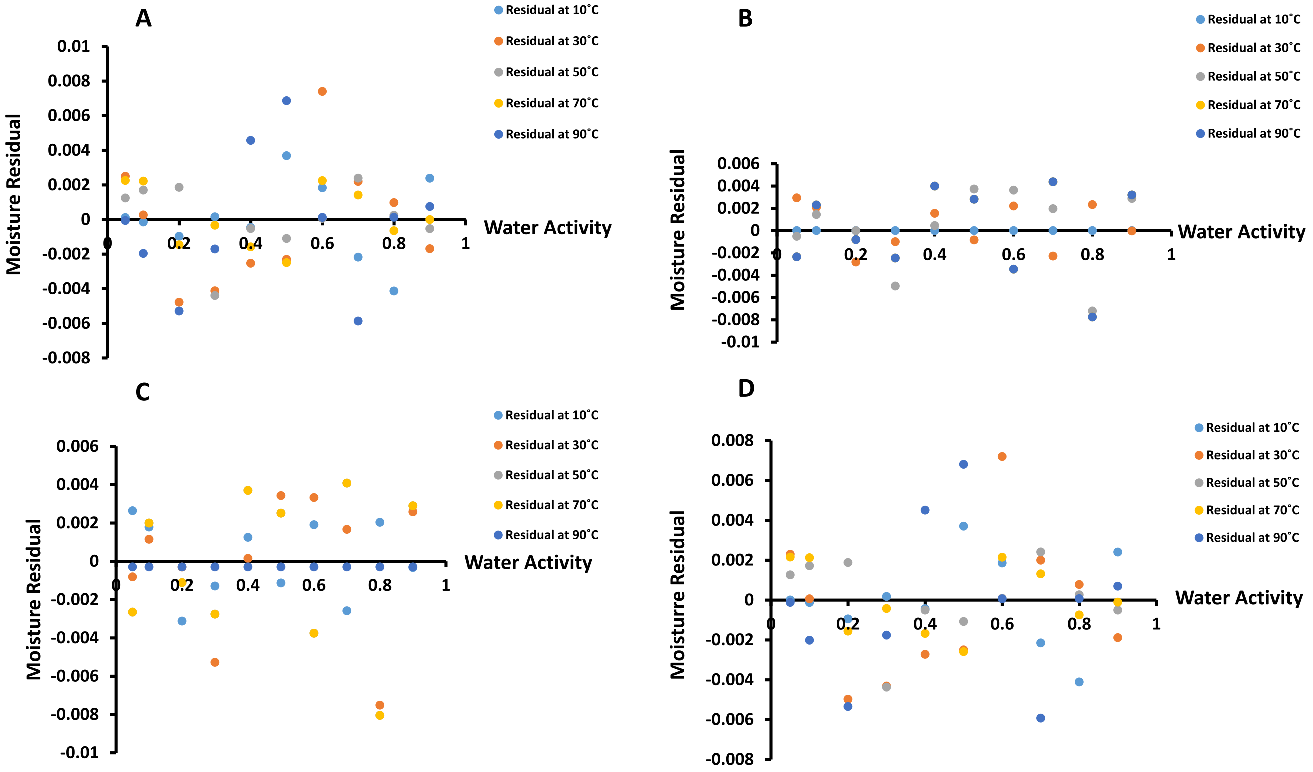

Fig. 5 Moisture residual plots of (A: WDP, B: DDP, C: REP, D: SUP) as water activity.

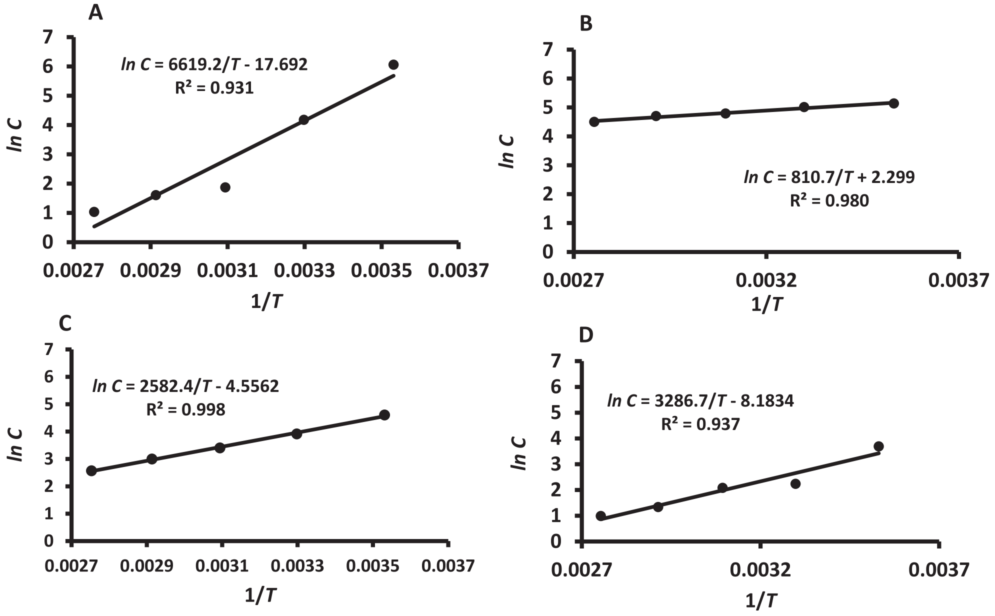

Fig. 6 GAB model *C*-values (A: WDP, B: DDP, C: REP, D: SUP) as a function of temperature.

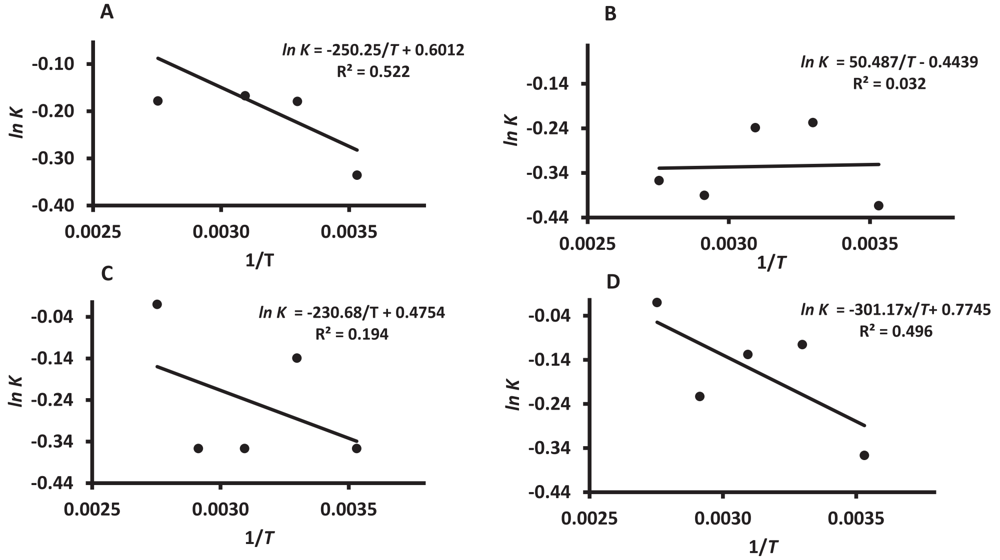

Fig. 7 GAB model *K*-values (A: WDP, B: DDP, C: REP, D: SUP) as a function of temperature.

highly affected by temperature, however WDP and RES showed lower effects. The DDP fraction showed the minimal effect by temperature. This could be due to the varitions of the compsotions in defferent fractions and their surface energy.

3.4. Isosteric heat of adsorption

Fig. 8 showed the isosteric heat of sorption in relation to the moisture content. In the case of WDP and DDP, the isosteric heat curves showed peaks at moisture 4.0 and 6.0 g/100 g ds, respectively. A sharp decrease was observed below the critical moisture. Similarly, Viollaz and Rovedo (1999) observed a sharp decrease at low moisture in the case of starch and gluten. The net isosteric heat of adsorption at 4.0 g/100 g ds (i.e. peak) was 4000 kJ/kg in the case of WDP, while DDP showed 2000 kJ/kg at critical moisture of 6.0 g/100 g ds. This indicated that the water binding energy was much higher in the case of WDP as compared to DDP (i.e. removal of oil reduced the water binding energy). Considering statistical models, Alyousef et al. (2020a) determined that water in date-pits was physically bound to the solids matrix. Therefore, removal of oil may change the surface characteristics of the matrix and allowed to spread the adsorbed water and caused lower energy of water binding. The WDP and DDP fractions possessed

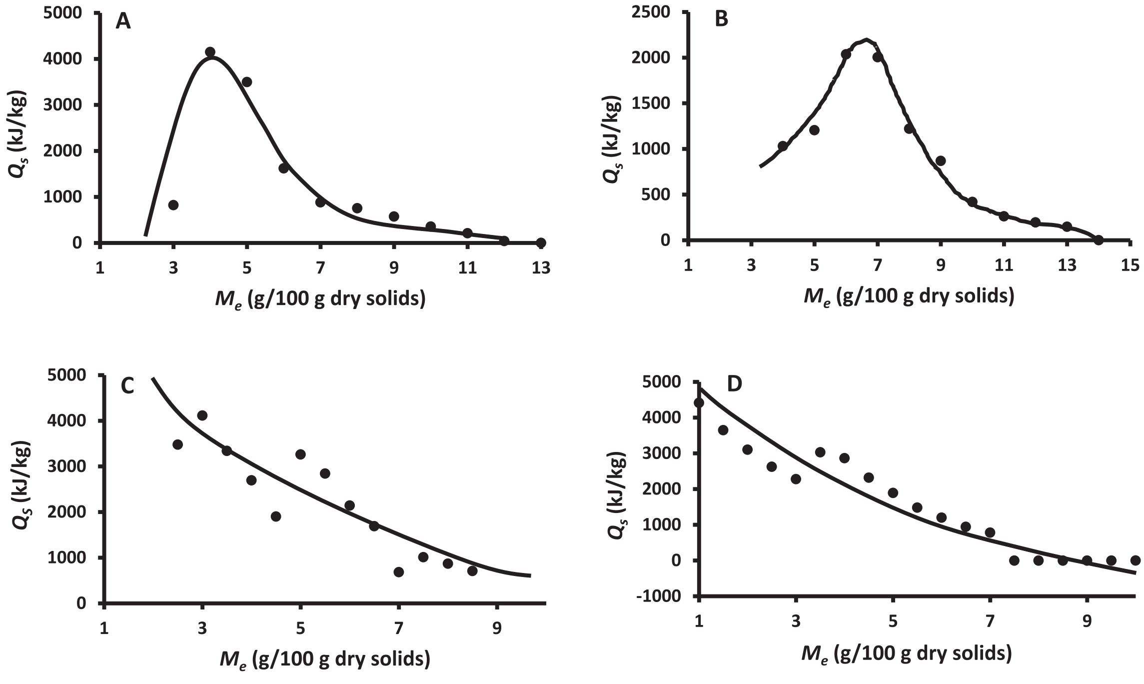

Fig. 8 Isosteric heat of adsorption as a function of moisture content (A: WDP, B: DDP, C: REP, D: SUP) (Line shows the trend).

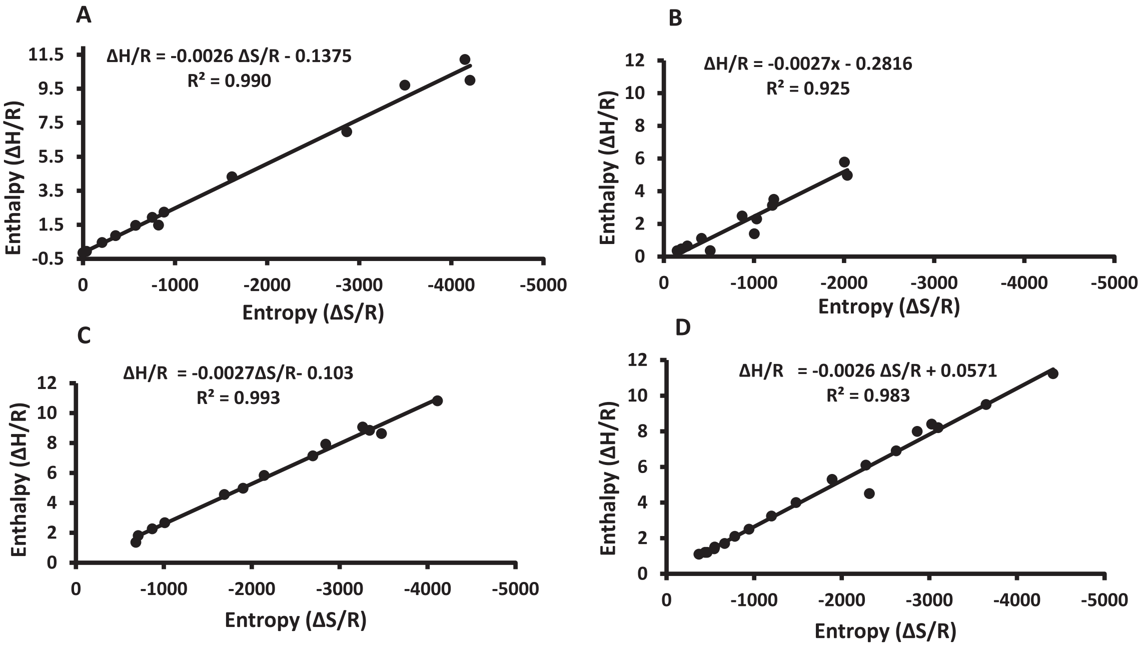

Fig. 9 Differential enthalpy ($\Delta H/R$) as a function of differential entropy ($\Delta S/R$) for A: WDP, B: DDP, C: REP and D: SUP.

complex structural matrix with varied polar sites and these could cause variations of water binding energy. In the case of whole date-pits, Ajibola et al. (2005) determined the net isostatic heat as 3250 kJ/kg at moisture content 5.0 g/100 g ds, while in this study it was 3450 kJ/kg (Table 2). However, they did not measure the isostatic heat below moisture 5.0 g/100 g ds. In the case of serum albumin, isosteric heat showed a sharp increase up to moisture 5.0 g/100 g ds and below 5.0 g/100 g ds it remained nearly constant. They identified this as step function with rounded corners and low moisture (e.g. monolayer or below) possessed lower energy similar to multi-layer water. These variations depended on the type of foods or biomaterials. They also mentioned that isotherm models (e.g. BET or GAB) did not provide nature of adsorbed water (i.e. binding nature), and real representation can be obtained from the variation of water activity with temperature at constant moisture using Eq. (3). In the case of cooked wheat, Turhan et al. (2003) also observed rounded corner below moisture 5.0 g/100 g ds. There was a sharp increase from 15.0 to 5.0 g/100 g ds, moisture content. They mentioned that below BET-monolayer the binding energy did not change.

REP and SUP fractions showed an increasing trend with the decreasing moisture content without any peak at low moisture. Similar, trends were observed in the case of caseins (27–80 °C) (Diamante, 1991), dried fruits (Lim et al., 1995), macadamia nuts (Palipane and Driscoll, 1993), fruits (Tsami, 1991, Ayranci et al., 1990, Hossain et al., 2001, Myhara et al., 1998), vegetables (Kiranoudis et al., 1993, Kaymak-Ertekin and Sultanoğlu, 2001), alfalfa (Fasina and Sokhansanj, 1993), and corn chips (Achoba et al., 1991). It is important to point that most of the cases the isosteric heat was reported up to moisture 5.0 g/100 g ds. This was due to the missing of isotherm at high temperature range (i.e. mainly above 60 °C). In the current study, water binding in whole date-pits and their fractions could be assessed at low moisture since the isotherm measurement was up to 90 °C.

3.5. Isokinetic temperature

Fig. 9 demonstrates the plotting of the differential enthalpy ($\Delta H/R$) as a function of differential entropy ($\Delta S/R$) for WDP and the fractionated date-pits fibres. A linear trend satisfied the enthalpy–entropy compensation theory. The linear correlations (R^2) were 0.990, 0.925, 0.993 and 0.983, respectively for WDP, DDP, REP and SUP. The isokinetic temperatures (T_{is}) were 111.6, 111.6 and 97.4 °C for WDP, REP and SUP, respectively (Table 1). These were close to the isobound temperature (T_{ib}) for WDP, REP and SUP (i.e. 102.8, 110.3 and 104.7 °C, respectively) (Table 1). Similar findings were also established for banana (Rahman and Al-Saidi, 2017) and mango (Telis-Romero et al., 2005). However, in the case of DDP, T_{is} (i.e. 97.39 °C) showed to be lower as compared to T_{ib} (i.e. 145.01 °C) (Table 1), which indicated that complete removal of bound water occurred after the temperature when all reactions were at the same rate.

Greater T_{is} values compared to the T_{ib} values for WDP and REP could corroborates to the enthalpy–entropy compensation theory, which indicated that their sorption processes are enthalpy-driven mechanisms. Similarly, the compensation theory was used to assess moisture sorption processes of different fruit seeds such as prickly pear seeds (Hassini et al., 2015) and jambolana seeds (De Araújo and Da Silva Pena, 2022). It was observed that these processes were also controlled by enthalpy. On the other hand, higher T_{ib} values of DDP and SUP fractions compared to their T_{is} values implied entropy-driven processes, which indicated greater freedom of the molecules within the matrix of these fibres (Spada et al., 2013).

4. Conclusion

Sorption isotherms of the WDP, and their fractions (i.e. DDP, REP and SUP) were measured and modeled by BET and GAB equations. At temperature 10 °C, BET-M_b and GAB-M_g were observed higher for DDP and REP as compared to WDP and SUP, which indicated higher level in the strongly bound water in the case of DDP and REP at the same conditions. WDP in this study showed higher values of BET monolayer at ambient temperature (20–30 °C) compared to whole date-pits presented in the literature. This could be due to the variety and maturity level as well as processing conditions. Isosteric heats of sorption was decreasing trends in the case of fractions REP and SUP, however WDP and DDP fractions showed peaks followed by a sharp decrease of the isosteric heat. This could be an indication of the variable binding nature (i.e. energy) with the types of treatments (i.e. petroleum ether and alcohol). Isokinetic temperature of WDP and SUP were observed higher as compared to the DDP and REP fractions. This indicated that all reactions reached at the same rate at much lower temperature (i.e. variability of the reactions in the WDP and SUP was higher). In the cases of WDP and their fractions, isokinetic temperatures were close to the isobound temperatures in all cases, except for DDP fraction. Over all, the treatments and composition of the extracted fractions affected the sorption characteristics of the fibers.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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