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KINETICS AND THERMODYNAMICS
OF DISPERSED OIL SORPTION BY KAPOK FIBER

KINETYKA I TERMODYNAMIKA SORPCJI
ZDYSPERGOWANEGO OLEJU PRZEZ WŁÓKNO KAPOKA

Abstract: This work was aimed at evaluating the sorption of dispersed oil by kapok fiber. The physicochemical characteristics of kapok fiber were investigated using BET, SEM, FTIR, XRD, contact angle and elemental analysis. The oil droplet size distribution at different temperatures was analysed using a Coulter counter, and its relationship with sorption was investigated. The effects of dosage, hydraulic retention time and temperature, on the sorption performance were studied. The result indicates that the sorption of dispersed oil by kapok fiber is spontaneous, endothermic and agreed with the pseudo-first-order reaction kinetics. The amount of oil that could be removed is about 28.5 %, while that of water is less than 1 % of the original amount (0.5 dm^3). Kapok is a promising natural hydrophobic fiber for dispersed oil removal from oily wastewater.

Keywords: dispersed oil, hydrophobic, kapok fiber, kinetics of sorption, thermodynamics of sorption

Introduction

There has been an increasing concern over the presence of dispersed oil in oily wastewater [1]. Most of the earlier and related works are mainly concerned about the removal of floating oil from the surface of water, and to be more specific, in the remediation of marine oil spills caused by the accidental release of petroleum from tankers and drilling rigs. The usual steps are to employ boomers and skimmers, to contain and collect the oil, and then to apply dispersant on the remaining oil slick to break it up into small droplets that would dilute and travel to deeper parts of the ocean and away from the coastline [2]. However, chemically-dispersed crude oil and oil dispersants could also affect the reproductive ability of marine species [3].

The immediate negative impact of a major oil spill to the marine environment could be visibly seen by the massive amount of oil floating on the water surface, which coats the surrounding flora and fauna, and also that of the coastal areas. Besides creating a scenery that would be very unappealing from an aesthetic point of view, it brings a tremendous

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change in the marine ecosystem that would inevitably incur a huge loss of marine and coastal wildlife. Marine contamination alters the physical, chemical and biological characteristics of the oceans and coastal zones which threatens the ecosystems and biodiversity by affecting the quality and productivity of marine ecosystems [4]. Thus, it is understandable that such an issue would rightfully deserve the priority in research.

However, its counterpart which is dispersed oil that stays in the water and would not float to the surface, is no less detrimental to the environment though its effects are not as immediate. It has been found that a minute amount of 0.1 mg/dm^3 of dispersed oil in water can upset the reproductive cycle of fish in rivers [5]. In the long run, its cumulative effect would be responsible for the eventual loss of indigenous aquatic and coastal marine species [6]. Ironically, the dispersed oil if left untreated, would pose a greater problem than the oil spills in regard to the extinction of marine species due to its insidious nature. Therefore, current knowledge gaps are to be identified for further research needs in assessing the fate and impacts of oil spills and oil dispersants in the marine environment [7].

Obviously, due to its microscopic size and inability to float to the surface, dispersed oil presents a greater degree of difficulty in terms of remediation and removal from water [8]. Therefore, the present work was aimed at evaluating the removal of dispersed oil using a natural hydrophobic plant material, called kapok fiber. Kapok fiber is widely used as oil adsorbent as compared with cotton, kenaf, etc. due to the presence of hydrophobic wax layer that brings about a high removal of oil. It has been reported that kapok fiber has been extensively used for the removal of stable or floating oil and some dispersed oil [9-13]. However, the sorption studies with special emphasis on kinetics and thermodynamics for unstable oil (emulsion) using kapok fiber have not been fully explored and well established. Herein, the effects of hydraulic retention time, temperature and sorbent dosage, on the oil and water sorption capacity were interpreted with special emphasis on the kinetics, thermodynamics and mechanisms of dispersed oil sorption onto kapok fiber.

Materials and methods

Materials

Kapok fiber and cooking oil (palm oil, brand Labour) were purchased from a local market in Johor state of Malaysia. The surfactant, Tween 80, was supplied by Scharlau.

Characterization of sorbent

The surface morphology of kapok fiber was observed using a LV/VP SEM (JSM-6380LV, JEOL), while the crystallinity in the material was evaluated by an XRD (D8 Advance, Bruker). The surface functional groups and the surface area of kapok fiber were analysed using an FTIR analyser (Spectrum One, Perkin Elmer) and a Surfer analyser (Thermo Scientific, Italy), respectively. The elemental composition was obtained using a Vario Microcube (Elementar, Germany). The contact angle of kapok fiber was measured by a uEye OCA (DataPhysics, Germany), while the dispersed oil droplet size was gauged by a Zetasizer Nano S (Malvern, UK).

Oil sorption

A 0.5 dm^3 volume of distilled water was placed in a 1 dm^3 beaker containing 2 g of palm oil and 0.08 g of Tween 80 surfactant. A 5 cm magnetic stir bar was used to emulsify the mixture into dispersed oil at 600 rpm for 2 h. The concentration of dispersed oil was

fixed at 4 g/dm^3. A desired weight of kapok fiber was added into the dispersed oil with stirring maintained at 600 rpm for a required duration. Next, the wet sample was transferred to a Petri dish, weighed and left in the oven overnight at 378 K. The amounts of water and oil were determined by mass balance.

Results and discussion

Physicochemical characteristics of kapok fiber

Kapok fiber is made up of cellulose, lignin and polysaccharide. Its texture is glossy and yellowish with smooth wax layer. A small amount of plant wax that covers the kapok surface making it hydrophobic. Kapok fiber has received considerable interest as an oil sorbent because of its distinctive hollow lumen and hydrophobic properties [9]. The morphology and contact angle measurement of kapok fiber is shown in Figure 1.
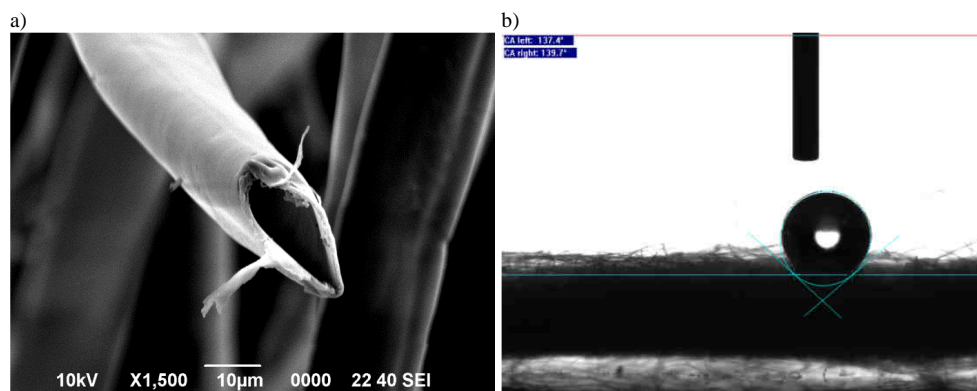
a)

b)

Fig. 1. a) SEM image and b) water contact angle of kapok fiber

From Figure 1a, the surface of kapok fiber is smooth with a layer of wax, and the cross-section is oval to round with a large lumen and thin wall (ca. 8-10 μm in diameter, and ca. 0.8-1.0 μm in thickness) [10]. The smooth wax layer is responsible for its hydrophobicity, and the large lumen greatly contributes to its sorption capacity. It is this hollow structure which separates kapok fiber from other natural fibers, endowing it a porosity of more than 80 % [11]. Kapok fiber is one of the few natural fibers that possesses large lumen with a coating of wax. The gaps between the circular fibrils could afford space for sorption, and the sorption volume can also be made available when the crystallinity in kapok fiber is disrupted to form more amorphous material. This structural change can be enhanced by stirring which has been proven to improve the oil sorption [12]. The contact angle of kapok fiber was observed to be 138.6° that is comparable as reported elsewhere [13]. The value is more than adequate to show that kapok fiber is very hydrophobic. Nevertheless, the contact angle may vary according to the place of origin. For instance, Dong et al. reported a contact angle of 151.2° which demonstrates the superhydrophobicity of kapok fiber from Java, Indonesia [14].

Figure 2 shows the FTIR spectrum of kapok fiber. Several primary peaks were detected in the FTIR spectrum. The broadest peak at 3333 cm^{-1} is linked to the non-free O—H stretching vibration [15]. The peak at about 2900 cm^{-1} could be assigned to the

asymmetric and symmetric aliphatic CH_2 and CH_3 stretching vibrations. This is linked to the presence of plant wax, which typically consists of long-chain alkanes, aldehydes, fatty acids, esters, ketones and alcohols [16]. The three bands at 1735, 1370, and 1240 cm^{-1} correspond to the C=O stretching vibration of ketones, esters and carboxylic groups in lignin and acetyl ester groups in xylan [15]. The other pronounced band at 1424 cm^{-1} could be assigned to the C—O stretching in lignin [17]. It signifies that kapok fiber is a lignocellulosic fiber with a considerable waxy coating. The peak at 2900 cm^{-1} could be attributed to the presence of plant wax [14]. The natural coating of plant wax contributes to the buoyancy, hydrophobicity and oleophilicity of kapok fiber - the promising traits of dispersed oil sorbent. The amount of wax present would be inversely related to the intensity at 2918 cm^{-1}.
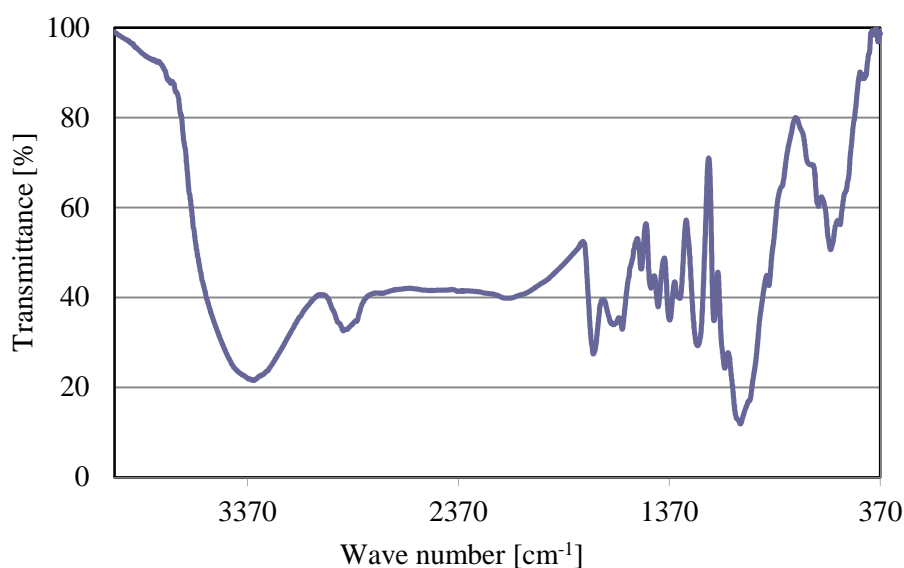

Fig. 2. FTIR spectrum of kapok fiber

Figure 3 shows the XRD spectrum of kapok fiber. The crystallinity and amorphous region present in kapok fiber are 63.2 % and 36.8 %, respectively. It can be observed that the major diffraction peaks appear in the position of 2-Theta at the angles of 5.9°, 12.3° and 22.4°, where the peaks of cellulose are centred at 12.3° and 22.4°. The high crystallinity of kapok fiber could be disrupted to form more amorphous region for oil sorption by simple treatment in water for a period of time. Wang and co-workers reported a better sorption performance of water-treated kapok fiber although the change in surface morphology is minimal [13]. An increase in amorphous region could also be brought about by the stirring method that could dramatically increase the oil sorption to as high as 200 times the amount of sorbent used [12].
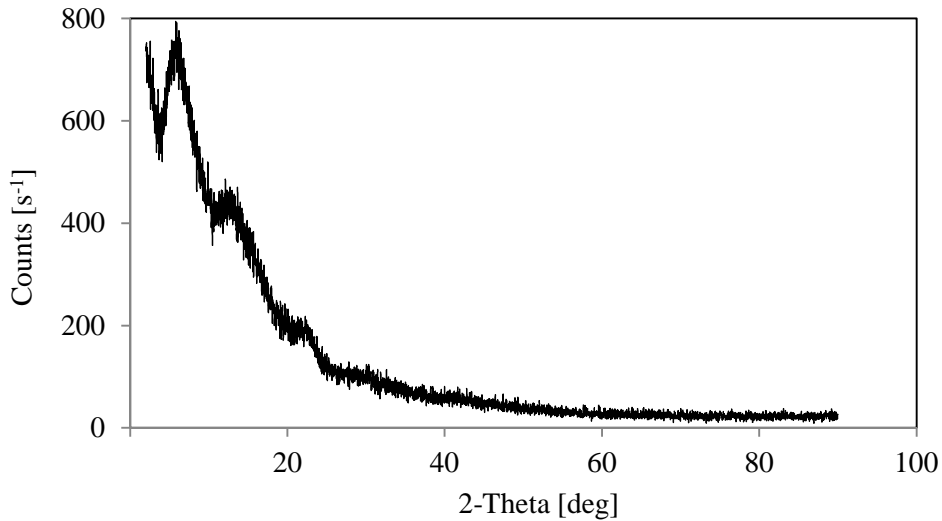
Fig. 3. XRD spectrum of kapok fiber

Figure 4 shows the N_2 adsorption-desorption isotherms of kapok fiber. The surface area of kapok fiber was measured as 79.8 m^2/g, while the pore volume at a relative pressure of 0.95 is 0.0101 dm^3/kg. The isotherm follows a type III without the knee, hence there is no detectable monolayer formation. It signifies that kapok fiber is a macroporous material as a result of weak interactions between nitrogen molecules and surface texture.
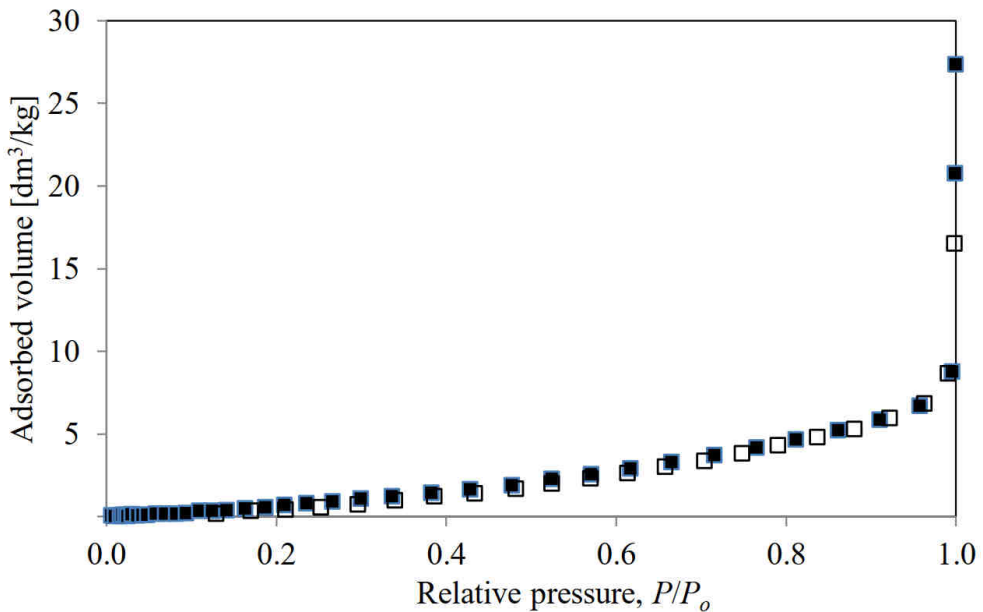

Fig. 4. N_2 adsorption-desorption isotherms of kapok fiber

The elements in kapok fiber are 0.338 % N, 45.2 % C, 6.26 % H, 0.105 % S and 48.1 % O. It is equivalent to the molecular formula of cellulose which is $(C_6H_{10}O_5)_n$. It signifies that kapok fiber is mainly composed of cellulose. Although cellulose is hydrophilic, kapok fiber is known for its hydrophobic character due to the surface wax [9, 10]. The presence of large amount of lignin and wax content would naturally protect it from mold, and also acts as an inherent pesticide. Little fractions of S and N in the composition reflect the plant protein components or amino acids.

Sorption kinetics

The rate of sorption of dispersed oil and water onto kapok fiber are shown in Figures 5 and 6, respectively. With an increase of contact time, the oil sorption capacity increases to a point of equilibrium. Oil may be retained in the internal voids of fiber trough van der Waals forces and hydrophobic interaction afforded by the wax layer [18]. The smooth wax layer also facilitates the diffusion of oil towards the internal lumen of fiber. In addition, the intermolecular forces responsible for cohesion and adhesion contribute to the capillary action especially for the large lumen. Thus, the removal mechanisms would likely include hydrophobic interaction, van der Waals forces, diffusion and capillary action.
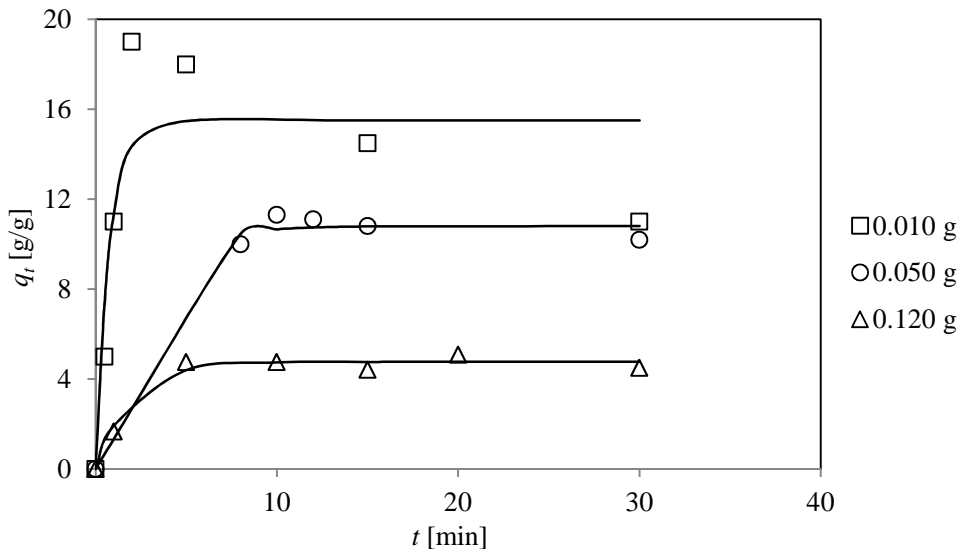

Fig. 5. Sorption of emulsified oil by different masses of kapok fiber (lines were predicted by pseudo-first-order model)

The result indicates that the sorption of water is higher compared to that of oil for all masses of kapok fiber used. Although the surface wax layer is hydrophobic, the bulk of kapok fiber is inherently made up of cellulose (64 %) which is hydrophilic [19]. However, as compared to the high water sorption by cotton [20], kapok fiber would absorb water to a much lesser degree, due to the presence of wax layer. Furthermore, the maximum amount of water sorbed was less than 1 % of the total amount of water (0.5 dm^3) which would qualify kapok fiber as a hydrophobic material.
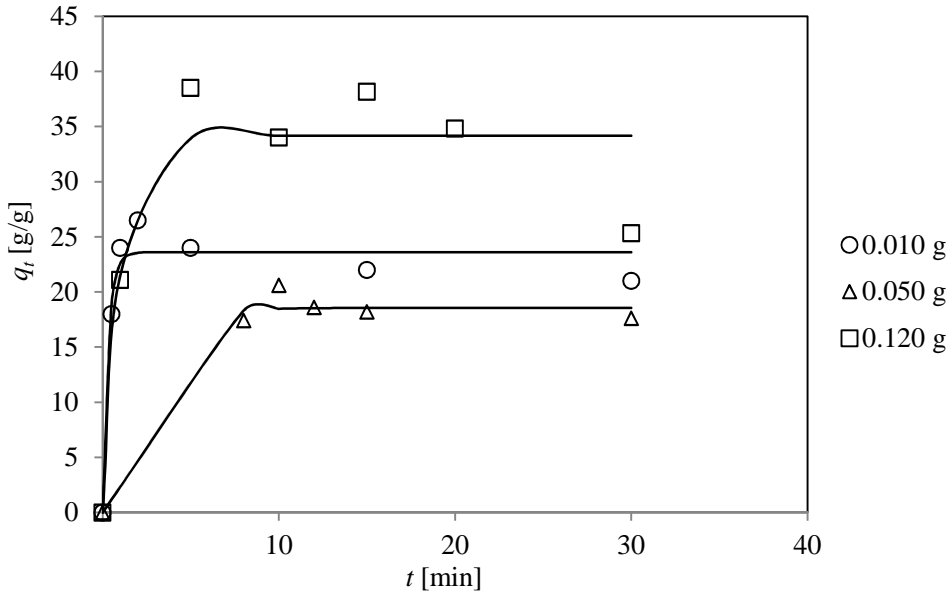
Fig. 6. Sorption of water by different masses of kapok fiber (lines were predicted by pseudo-first-order model)

To understand the sorption kinetics of dispersed oil by kapok fiber, the adsorption data were further analysed using pseudo-first-order and pseudo-second-order models, as follows [21, 22]:

$$q_t = q_e(1 - e^{-k_1 t}) \tag{1}$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{2}$$

where: q_e [g/g] and q_t [g/g] are the amount of oil sorbed at equilibrium and time t [min], respectively, and k_1 [min^{-1}] and k_2 [g/g · min] are the rate constants of the pseudo-first-order and pseudo-second-order equations, respectively.

Table 1 summarizes the kinetics constants of dispersed oil removal by kapok fiber. For different masses of sorbent, the theoretical values (q_e) by both models are quite close to the experimental values (q_{exp}). The pseudo-first-order model shows a better coefficient of determination (all R^2 values are closer to 0.999) and a lower sum of squared errors (*SSE*) than the pseudo-second-order model. The rate of sorption, k_1 decreases with increasing mass of sorbent indicates that the oil sorption is faster for smaller mass of sorbent. It signifies that the dominant mechanism is diffusion because a higher surface area exposure relative to volume for a smaller mass would facilitate a greater diffusion of oil droplets. Likewise, the rate of sorption for water decreases as mass of sorbent increases. The maximum amount of oil that could be removed was about 28.5 %. The applicability of pseudo-first-order model which suggests that the external diffusion is significant is also consistent with the sorption kinetics of crude oil from aqueous medium using hydrophobic corncobs [23].

Kinetics parameters for dispersed oil sorption by kapok fiber

Mass of kapok [g]	Sorbate	q_{exp} [g/g]	Removal [%]	Pseudo-first-order model				Pseudo-second-order model			
				q_e [g/g]	k_1 [min^{-1}]	R^2 [-]	SSE [-]	q_e [g/g]	k_2 [g/(g · min)]	R^2 [-]	SSE [-]
0.010	Oil	19.0	9.5	15.5	1.30	0.807	55.1	15.9	0.151	0.712	81.6
0.050		11.3	28.3	10.8	0.429	0.988	1.12	10.7	4.02	0.987	1.27
0.120		5.08	30.5	4.76	0.511	0.980	0.469	5.20	0.134	0.951	1.13
0.010	Water	26.5	0.053	23.6	3.15	0.957	20.6	23.7	0.512	0.930	33.8
0.050		20.6	0.206	18.6	0.539	0.978	6.40	18.5	9.36	0.978	6.54
0.120		38.5	0.924	34.2	0.994	0.898	116	35.2	0.0573	0.866	152

Sorption thermodynamics

An evaluation of thermodynamics is useful to understand the spontaneity of the sorption process. The change in free energy ($\Delta G°$) to reflect the spontaneity of the sorption process was calculated using the following equation.

$$\Delta G° = RT \ln K_d \qquad (3)$$

where: R = 8.314 J/(mol · K) is the gas constant, T [K] is the absolute temperature and K_d is the sorption equilibrium constant. The equilibrium constant, K_d was calculated as:

$$K_d = C_s/C_m \qquad (4)$$

where: C_s and C_m [g/g] are the equilibrium concentrations of oil molecules on the fiber and in the solution, respectively. The enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) can be obtained from the van't Hoff equation:

$$\ln K_d = \Delta S°/R - \Delta H°/RT \qquad (5)$$

Figure 7 shows the van't Hoff plot of dispersed oil sorption by kapok fiber at different temperatures, and the thermodynamics parameters are summarized in Table 2.
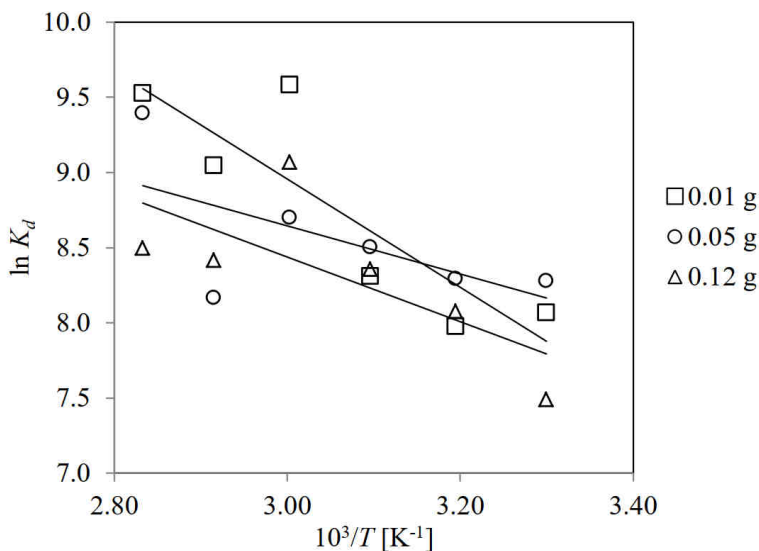

Fig. 7. van't Hoff plot of dispersed oil sorption by kapok fiber

Thermodynamic parameters for the sorption of dispersed oil by kapok fiber

Mass of kapok fiber [g]	T [K]	K_d	$\Delta G°$ [kJ/mol]	$\Delta H°$ [kJ/mol]	$\Delta S°$ [kJ/(mol · K)]
0.010	303	3.19	−19.8	29.9	0.164
	313	2.91	−21.5		
	323	4.05	−23.1		
	333	14.5	−24.8		
	343	8.48	−26.4		
	353	13.7	−28.1		
0.050	303	3.94	−20.6	13.4	0.112
	313	3.99	−21.7		
	323	4.93	−22.8		
	333	6.00	−23.9		
	343	3.51	−25.0		
	353	1.20	−26.2		
0.120	303	1.79	−19.6	17.8	0.124
	313	3.21	−20.9		
	323	4.25	−22.1		
	333	8.65	−23.3		
	343	4.51	−24.6		
	353	4.89	−25.8		

The free energy, $\Delta G°$ is negative at all temperatures, and decreases with the rise in temperature for the sorption of dispersed oil onto kapok fiber. This indicates that the sorption process is spontaneous in nature and that the degree of spontaneity increases with increasing temperature. The enthalpy, $\Delta H°$ is positive, indicating that the oil sorption is an endothermic process. In general, the absolute value of enthalpy is less than 40 kJ/mol for physisorption [24]. Therefore, the sorption of dispersed oil by kapok fiber can be categorized as physisorption. A positive $\Delta S°$ corresponds to a greater degree of disorder of the sorption system. Yet, there is a slight decrease of $\Delta S°$ with increasing mass of kapok sorbent, suggesting a less favourable sorption of dispersed oil at a higher dosage.

Droplet size distribution relative to sorption

The droplet size distribution was evaluated at different temperatures using a Coulter counter and its relationship with sorption capacities at different temperatures was investigated. The findings are shown in Figures 8 and 9.

There is a direct relationship between the droplet size distribution and sorption capacity, where the same trend is observed at different temperatures. As the sorption is endothermic, increasing the temperature would facilitate the sorption process. The increase in energy would also bring about more collision which would facilitate coalescence (demulsification), hence increasing the sorption [25]. The first peak (maximum sorption) occurred at 333 K, but an increase in temperature to 343 K was observed to have a negative effect on sorption. This could be explained by the fact that an excess of heat beyond that required for demulsification, could re-emulsify the mixture again and hinder the sorption process. However, a further increase in temperature to 353 K had a positive effect on the sorption process which could be resulted from the occurrence of phase separation in which the dispersed oil mixture would separate out as two immiscible liquids.
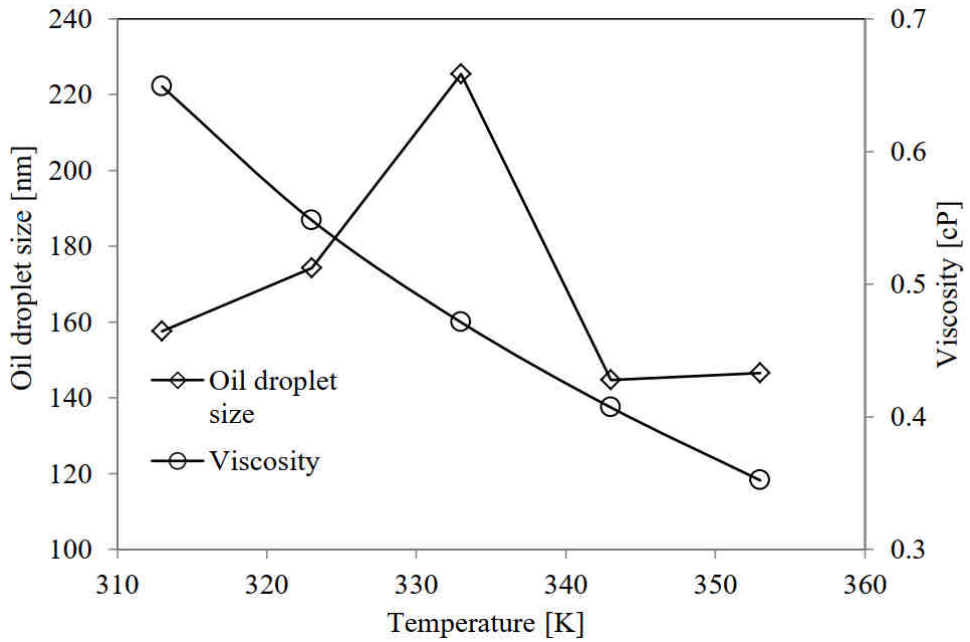
Fig. 8. Droplet size distribution and viscosity of dispersed oil at different temperatures
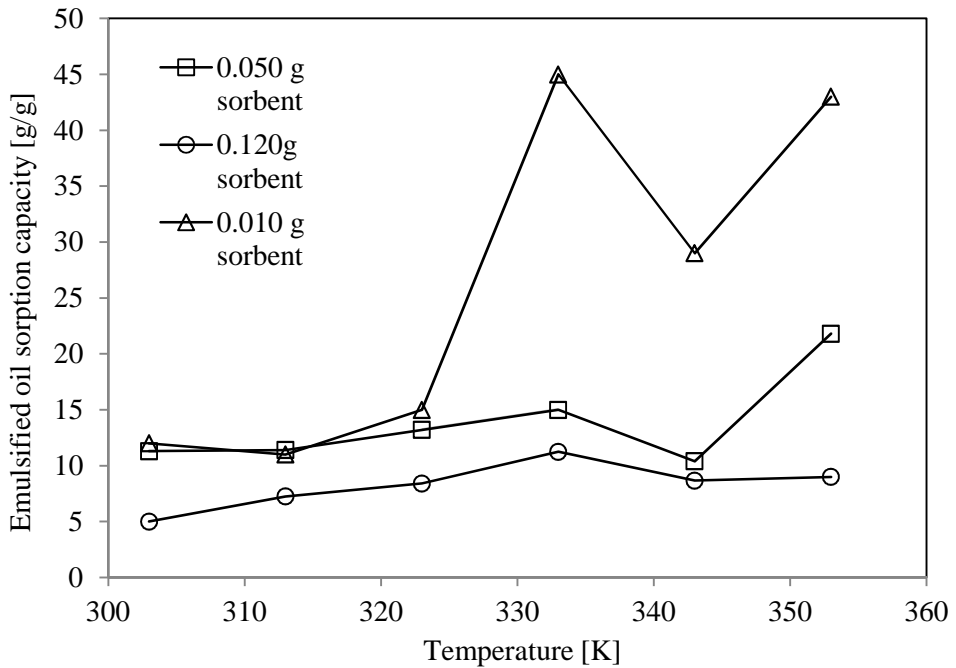

Fig. 9. Sorption capacities at different temperatures

The application of heat promotes the oil/water separation and accelerates the sorption process. An increase in temperature has the effects of reducing the oil viscosity (Fig. 8), increasing the mobility of oil molecules, increasing the collision of oil droplets and favouring coalescence [25]. Besides weakening the interfacial film (tension) between the oil droplets and water due to expansion, heat also increases the density difference of the two fluids to further improve the separation [26].

Comparison with other sorbents

This outcome from this work has been compared with other related studies on the removal of dispersed oil. Table 3 summarizes the performance of some sorbent materials for the removal of dispersed oil.

Table 3

Dispersed oil removal by various sorbents

Adsorbent	Method	Dosage	Emulsion concentration	Surfactant and quantity	Removal efficiency	References
Kenaf	Deep-bed filter medium; continuous flow; 0.0638 dm^3/min; 414 kPa	7.5 cm bed	5000 mg/dm^3	Triton; 250 mg/dm^3	99 %	[27]
Acylated cotton	Percolation through cotton bed; 0.095 dm^3/min	4 g; bed: 90 mm height, 30 mm diameter	10 % V_{oil}:V_{water}	Sodium dodecyl sulphate; 20 %	14.5 g/g	[28]
Acetylated micro-size sugarcane bagasse	Batch method	10 $g/0.1 dm^3$	200 mg/dm^3	Tween 80, 0.5 %	20 g/g (58 %)	[29]
Chitosan–TiO$_2$ composite membrane	Vacuum filtration; 0.09 MPa	Separation area 12.56 cm²	1.5 g/dm^3	Sodium dodecyl sulphate; 0.05 g	97 %	[30]
Kapok fiber in calcium stearate-treated cotton bag	Oil collector; batch stirring	0.3 g	10 % V_{oil}:V_{water}	None	98.9 %	[31]
Surfactant-modified barley straw	Batch shaking	1.0 $g /0.1 dm^3$	11.5 g/dm^3	Emulsifier; 12.5 g	576 mg/g	[32]
ZnO nanoneedles-coated kapok fiber	Batch agitation	0.1 g	10 % V_{oil}:V_{water}	None	68.5 g/g (86.4 %)	[33]
Lauric acid and ethanediol modified corn cob	Batch vibration	9.3 g/dm^3	185 mg/dm^3	Sodium dodecyl sulphate; 4 % (w/w)	16.5 mg/g (83.0 %)	[34]
Kapok fiber	Batch stirring	0.05 $g/0.5 dm^3$	2 $g/0.5 dm^3$	Tween 80; 0.08 g	11.3 g/g (28.3 %)	This study
Kapok fiber	Batch stirring	0.12 $g/0.5 dm^3$	2 $g/0.5 dm^3$	Tween 80; 0.08 g	5.08 g/g (30.5 %)	This study
Polyvinylpyrrolidone-coated magnetic nanoparticles	Demulsification	400 mg/dm^3 at pH 7.0	2.7 g/dm^3	Sodium dodecyl sulfate	> 99%	[35]
Amphipathic chitosan-based flocculant	Flocculation	500 mg/dm^3	1000 mg/dm^3	Sodium dodecyl sulfate	> 98%	[36]

Despite the development of sorbents derived from modified natural materials, the preparation of oil sorbent with excellent stability and recyclability through cheap and simple method, and most importantly, without the use of hazardous materials is highly desirable. ZnO [33] and ethanediol [34] are both hazardous substances with ethanediol being very toxic. From Table 3, most modified sorbents offer very good performance. However, a high removal of dispersed oil in [31] and [33] could be due to the absence of chemical surfactant (emulsifier). The resulting dispersed oil obtained by vigorously agitating the oil-water mixture would therefore be very unstable, and the oil droplets would coalesce readily and be easily sorbed by the sorbents. All natural sorbents are cost-effective, renewable and sustainable from an environmental point of view. Kapok fiber is comparable with some of the modified sorbents in terms of sorption capacity, and exhibits a better performance than [32] and [34]. Kenaf offers a superior oil removal performance even without modification [27]. This could be due to the method employed for oil removal and the inherent hydrophobic property of kenaf attributed to the presence of waxy substances. The contact angle of kenaf is 98.9° [37]. However, this value is lower in comparison with that of kapok fiber, that is 138.6°. Therefore, if the same method in [27] is employed using kapok fiber, a better performance would also be expected. In a previous work, the removal performance of kapok fibre for stable oil can reach as high as 200 g/g [12]. Very recently, PVP-coated Fe_3O_4 MNPs (magnetic nanoparticles) prepared via solvothermal method exhibited good demulsification performance where removal ratio exceeded 99 %, and is a facile and reliable technique for removing emulsified oil from aqueous environment at low and medium pH conditions [35]. Another very recent research also found that synthetic graft copolymer flocculants, poly(dimethyl acryloyloxyethyl benzyl ammonium chloride) (PDBC) grafted onto chitosan (CS) molecular chain, demonstrated both oil removal efficiency and turbidity removal ratio that exceeded 98.0 %, indicating that CS-g-PDBC was a class of green and promising flocculant for the treatment of emulsified oily wastewater [36].

Conclusions

Kapok fiber was used to remove dispersed oil, wherein the sorption kinetics and thermodynamics were evaluated. The oil sorption capacity increases with contact time, but decreases with dosage. A higher oil removal performance of 28.5 % was achieved using 0.05 g and 0.12 g of kapok fiber, with less than 1 % of water absorbed. The analysis on the kinetics conclusively proves that the sorption process would best be represented by the pseudo-first-order model. The experimental results show that an increase in temperature generally favours the sorption process. The sorption process by kapok fiber can be categorized as physisorption, where the degree of spontaneity would increase with increasing temperature. The range of parametric values from this work would facilitate the selection of favourable conditions to be employed for the dispersed oil sorption by kapok fiber.

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