# Development of chitosan beads as an oil adsorbent and its application in household grease traps

Rawinipa Srimoon<sup>a,\*</sup>, Jakkapan Potipat<sup>b</sup>

- <sup>a</sup> Department of Applied Science and Biotechnology, Faculty of Agro-Industrial Technology, Rajamangala University of Technology Tawan-Ok, Chanthaburi Campus, Chanthaburi 22210 Thailand
- <sup>b</sup> Department of Environmental Science, Faculty of Science and Technology, Rambhaibarni Rajabhat University, Chanthaburi 22000 Thailand

\*Corresponding author, e-mail: rawinipa.srimoon@gmail.com

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ABSTRACT: The purpose of this research was to develop chitosan beads as an oil adsorbent in household grease traps. The results showed that chitosan beads, synthesized from 3% w/v chitosan flakes in 5% v/v acetic acid and formed the beads in 2.0 M NaOH, provided the best characteristics. The white colored beads were slightly hard with maximum average weight and maximum diameter of  $0.0925 \pm 0.0101$  g and  $0.67 \pm 0.06$  cm. respectively. SEM images revealed that the beads had spherical shapes and homogenously distributed pores. The maximum adsorption capacity was  $1667.93 \pm 39.61 \text{ mg/g}$  ( $83.40 \pm 1.98\%$ ) at the optimum adsorbent dosage of 10 g/l, initial oil concentration 20 g/l, pH 5 and 303 K with 25 min of contact time. The adsorption was fitted to the Langmuir adsorption isotherm. Our results indicated that the adsorption was monolayer and chemisorption, and C<sub>m</sub> increased with increasing temperature. The kinetic study was correlated with the pseudo-second order, and the intraparticle diffusion was the rate controlling step. The adsorption of oil in the household grease trap showed a significant decrease in Fat, Oil & Grease (FOG), Biochemical Oxygen Demand (BOD), and Chemical Oxygen Demand (COD) (p < 0.05), while the pH did not change. Also, oil removal in real wastewater was lower than synthetic oil-in-water due to the competition for the biding sites between oil and other compositions presented in wastewater and the formation of stable micelle droplets by the surfactant. Nevertheless, the values of oil concentration in the household wastewater were lower than the standard limit of domestic discharge in Thailand, whereas the values in the treated wastewater from a noodle shop were over the standard value.

KEYWORDS: chitosan beads, oil removal, grease trap

# INTRODUCTION

Fat, oil, and grease (FOG) are a group of pollutants in water which have a very low affinity to water, but they are soluble in organic solvents. FOG originates from household and restaurants, as well as from food industries [1], and can be found in wastewater. It composed of both biological and mineral oils, i.e. fatty acids, triglycerides, lubricants, diesel oils, petroleum refineries, and other hydrocarbons, with low biodegradability [2]. FOG concentration normally reaches 500 mg/l, or an estimated 10% of organic pollutants found in household wastewater in Thailand; while FOG concentration collected from local restaurant wastewater is usually 1500 mg/l in average [3, 4]. Obviously, FOG in municipal wastewater is in the form of used cooking oil, of which the free fatty acid content is less than 15% of the total oil concentration [5]. In developed countries, FOG in the form of used cooking oil released to the environment is estimated at 2.5 l/per person/day, which is higher than in developing countries [6, 7]. FOG in water may have an impact in many ways ranging from clogging pipes to damaging the environment. The thin-film of oil-in-water surface limits the light penetration to the water column and the gas exchange between air-water boundary, decreasing the photosynthetic rate and dissolved oxygen in the water. The contamination of FOG also results in bioconcentration and biomagnification through the food chains. Moreover, FOG can affect wastewater treatments by forming the 'fatberg' and blocking of sewer systems [5, 8].

The effective treatment of FOG in wastewater is by reduction of FOG at its origins. Physical treatment, separation of the remaining FOG using equipment or certain methodologies such as grease traps, sedimentation tanks, dissolved air flotation, filtration, ultrafiltration, electroflotation, and electrocoagulation, has been employed [8]. Grease traps are oil separation equipment used in treatment of wastewater discharged from household and restaurant kitchens. FOG in influent water is raised to the surface of the first compartment of the grease trap and, then, swept out. The efficiency of grease trap can reach 60% removal rates [3]. Chemical treatments are usually performed after the primary treatment by adding coagulants and reagents (commonly iron and aluminum salts, polymers, and acids) into the water to emulsify or flocculate the oil-in-water [9-11]. Biological treatments, especially the activated sludge (AS), biological filters, and other biological reactors, are the most common methods used to remove the oil-in-water [12, 13]. Among the aforementioned methods, the adsorption process is widely used in the removal of oil-in-water. The main advantages of oil adsorption by adsorbents are: its effectiveness, low cost, easy to set up systems, and no sludge produced. Several materials have been reported as oil adsorbents: polystyrene resin [14], bentonite clay [15, 16], activated carbon [14, 17], zeolite [18], chitosan powder, and agricultural waste materials (such as walnut shell and dead biomass) [19], palm shell [20], and rice husk [21].

Chitosan is a natural polymer of polysaccharide derived from the alkaline-deacetvlation reaction of chitin, which is extracted from crustaceans, i.e. crabs and shrimps. Sub-units of chitosan are D-glucosamine and N-acetyl-D-glucosamine linked with  $\beta$ -(1,4)-glycosidic bonds [22, 23]. The deacetylation of chitin is performed in an alkaline solution (commonly >40% NaOH) at high temperatures. Chitosan is safe and biodegradable, so it is used in many applications: food industries, cosmetics, paper making industries, fertilizers, biomedical applications, and wastewater treatments [24]. Because of the presence of high porous structures and pH dependent amino and hydroxyl groups on the surface, chitosan has biding capacities; and it is the most common utilized adsorbent [25-27]. For examples, chitosan beads and flakes were used in the adsorption of heavy metals [28, 29], biodiesel [30], phosphate [31], and dyes [32, 33]. There are many morphologies of chitosan: powders, films, flakes, gels, fibers, membranes, capsules, and beads [34]. Conventional powders or flakes are not reliable due to their low stability, low density, and very fine particles. They are hard to separate or filter from the aqueous matrix [35]. Thus, chitosan beads, membranes, and other non-conventional or modified forms are more favorable.

Although the removal of oil-in-water using chitosan beads has been studied by many researchers over the years, most of them used complicated and high-cost methods. Hence, the objective of this research was to develop chitosan beads as an oil adsorbent by simple neutralization method. Moreover, this research is the first one to show that low-cost synthetic chitosan beads were able to be practically implemented to household grease traps. Therefore, the results will be useful in the development of commercial adsorbents in domestic oil-in-water treatment systems.

#### MATERIALS AND METHODS

#### Preparation of chitosan beads

Chitosan beads were prepared by the neutralization method modified from Igberase and Osifo [29] and Bekçi et al [32]. Chitosan flakes were dissolved in 5% v/v acetic acid at various concentrations (1, 2, 3, and 4% w/v) and shaken at 400 rpm over night to be completely dissolved. The chitosan solution was carefully dropped, using a dropper, into a NaOH solution at various concentrations (0.1, 0.5, 1.0 and 2.0 M) and left overnight. The coagulating chitosan beads were formed, filtered, rinsed withdistilled water, and dried at room temperature.

# SEM analysis

The morphology and surface of synthetic chitosan beads were further analyzed using a Scanning electron microscope (SEM LEO 1450VP), 15 kV at different magnifications ( $13 \times to 20 \times$ ). The sphericity factor (SF), to indicate the sphericity of the beads, was calculated from (1) [36].

$$SF = \frac{d_i}{d_c},\tag{1}$$

where  $d_i$  is the diameter of the maximum circular containing in the beads, and  $d_c$  is the diameter of the minimum circular rounding the beads.

#### Batch adsorption experiments

Batch adsorption experiments were performed in erlenmeyer flasks using chitosan beads that were synthesized from 3% w/v chitosan flakes in 5% v/v acetic acid and formed the beads in 2.0 M NaOH. The 50 ml of palm oil-in-water sample were used, and the solutions were agitated at 400 rpm. The effect of adsorbent dosages (5, 10, 20, and 30 g/l) and initial oil concentrations (10, 20, 50, and 100 g/l) on oil adsorption were conducted. The influence of contact time (in the range of 0–120 min) and the pH

values (varied from 3 to 11, adjusted with 0.1 M HCl or 0.1 M NaOH) were performed. The concentration of oil was determined by solvent extraction method in a separatory funnel with hexane as a solvent. The percentage of oil removal was also calculated.

# pH<sub>zpc</sub> determination

The pHs at the point of zero charge  $(pH_{pzc})$  of chitosan beads were investigated according to Elanchezhiyan, Sivasurian, and Meenakshi [2]. Chitosan beads (0.5 g) were added to an aliquot of 50 ml of 0.01 M NaCl, and the pH values were adjusted (in the range of 2–12) using 0.1 M HCl or 0.1 M NaOH. The initial pHs (pH<sub>initial</sub>) of the solutions were recorded. Then, the solutions were shaken at 400 rpm for 48 h, and the final pHs (pH<sub>final</sub>) of the solutions were measured. The differences of the pH<sub>initial</sub> and pH<sub>final</sub> ( $\Delta$ pH) were calculated and plotted against the pH<sub>initial</sub>. The pH<sub>zpc</sub> of chitosan beads was found at the intersection of the curves at  $\Delta$ pH = 0.

#### Adsorption isotherm

The adsorption isotherms were analyzed using the batch adsorption experiment, i.e. chitosan beads were synthesized from 3% w/v of chitosan flakes in 5% v/v acetic acid and formed the beads in 2.0 M NaOH. 0.5 g chitosan beads were added into 50 ml of pH 5 oil-in-water solutions of various initial concentrations (10, 20, 50, and 100 g/l) and different temperatures (303, 323, and 333 K). The solutions were shaken at 400 rpm for 25 min. The oil concentration at the equilibrium was then determined. The Langmuir adsorption isotherm (2) and Freundlich adsorption isotherm (3) were calculated according to Bekçi et al [32].

$$\frac{C_e}{C_s} = \frac{1}{C_m L} + \frac{C_e}{C_m},\tag{2}$$

$$\ln C_s = \ln K_f + n_f \ln C_e, \qquad (3)$$

where  $C_e$  is the concentration of oil at the equilibrium (mg/l),  $C_s$  is the concentration of oil adsorbed onto the adsorbent (mg/g),  $C_m$  is the maximum adsorption capacity of the monolayer of the Langmuir adsorption (mg/g), L is the Langmuir constant or adsorption energy (l/mg),  $K_f$  is the relative adsorption capacity (mg/g), and  $n_f$  is the adsorption intensity for heterogeneity factor of the Freundlich isotherm.

#### Adsorption kinetics

The adsorption kinetics was also studied using the batch adsorption experiment. 0.5 g of chitosan

beads was added into 50 ml of 20 g/l oil-in-water samples at different temperatures (303, 323 and 333 K) and pH 5. The solutions were shaken at 400 rpm over time in a range of 0–120 min. The oil concentration at the equilibrium was then determined. The adsorption kinetics was performed with respect to the pseudo-first order (4), pseudosecond order (5), and intraparticle diffusion model (6) as described by Bekçi et al [32].

$$\frac{1}{q_t} = \left(\frac{k_1}{q_1}\right) \left(\frac{1}{t}\right) + \frac{1}{q_1},\tag{4}$$

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_t^2}\right) + \left(\frac{1}{q_2}\right)t,\tag{5}$$

$$q_t = k_p t^{0.5} + C, (6)$$

where  $q_t$  is the amount of oil adsorbed on the adsorbent (mg/g) at time t (min),  $q_1$  is the maximum adsorption capacity for pseudo-first order (mg/g),  $k_1$  is the pseudo-first order rate constant (min<sup>-1</sup>),  $q_2$  is the maximum adsorption capacity for pseudosecond order (mg/g),  $k_2$  is the pseudo-second order rate constant (g/mg min<sup>-1</sup>),  $k_p$  is the intraparticle diffusion rate constant (mg/g min<sup>-0.5</sup>), and *C* is the intraparticle diffusion intercept (mg/g).

#### Oil removal efficiency in synthetic wastewater

The optimum conditions (adsorbent dosage, initial oil concentration, pH of the solution, temperature, and contact time) were used to study the efficiency of oil removal in synthetic oil-in water samples. The oil concentration was determined as FOG using the solvent extraction method. Biochemical oxygen demand (BOD) was analyzed using the dilution method. Chemical oxygen demand (COD) was determined using the open reflux method. The pH was measured by pH meter (Consort C3010).

#### Oil removal efficiency of household grease trap

Three different household wastewater samples, two from houses and the other from a noodle shop, were investigated using grease trap at the optimum conditions, except uncontrolled pH, temperature, and contact time. The grease trap was designed according to the Pollution Control Department [3] (Fig. S1). The outflow pipe of the kitchen sink was connected to a 17 l fiber glass grease trap, which contained chitosan beads (50 g) in the sieve. Wastewater containing fat, oil, and grease (FOG) was fed into the system with a consistent flow rate about 1 l/min and made contact with the chitosan beads. The treated water flew through the first



Fig. 1 The morphology and surface of synthetic chitosan beads (showing only the treatments that formed the beads: treatments = % chitosan/molar of NaOH).

barrier entering the second channel and the third channel, respectively. Finally, the treated wastewater flew out to a water container. The outlet water was collected for analysis of water quality parameters. The oil concentration was determined as FOG using the solvent extraction method. BOD was analyzed using the dilution method. COD was determined using the open reflux method. The pH was measured by pH meter.

#### Statistical analysis

All experiments were done in triplicates, and the results were presented as mean  $\pm$  SD. The statistical analysis was evaluated by one-way analysis of variance (ANOVA), followed by the Duncan multiple range test at *p* < 0.05 of significance.

#### **RESULTS AND DISCUSSION**

#### Characterizations of chitosan beads

Chitosan beads were synthesized by dissolving chitosan flakes (1, 2, 3, and 4% w/v) in 5% v/v acetic acid and neutralized by NaOH (0.1, 0.5, 1.0, and 2.0 M). The results showed that the beads were not formed when flakes' concentrations were 1% and 2% w/v, while the 3% w/v of chitosan flakes in 2.0 M NaOH (i.e. 3%/2.0 M treatment) gave the best bead characteristics. Under these conditions, the synthetic chitosan beads are quite hard, fine, and white in color with maximum average weight and maximum diameter of  $0.0925 \pm 0.0101$  g and  $0.67 \pm 0.06$  cm, respectively. The morphology and surface of chitosan beads were examined using the scanning electron microscope (SEM), and the results are shown in Fig. 1. It was demonstrated that the beads in 3%/2.0 M treatment also generated homogenously distributed pores. The sphericity factor (SF) was 0.8708 indicating that chitosan beads were likely circular (SF = 1 is the perfect sphere and SF < 1 is less).



**Fig. 2** The effect of (a) adsorbent dosages and initial oil concentrations, and (b) contact time on oil removal.

#### Adsorbent dosage and initial oil concentration

The effect of adsorbent dosages and initial oil concentrations on oil removal using chitosan beads are demonstrated in Table S1 and Fig. 2(a). The results showed that increasing the adsorbent dosage increased the percentage of oil removal significantly (p < 0.05) due to the availability of initial adsorption sites, and chitosan beads at 10 g/l gave the highest percentage of oil removal. However, the adsorption of oil on chitosan beads beyond the concentration of 10 g/l was significantly decreased (p < 0.05) because the vacant sites on the beads' surface adsorbed oil were almost fully occupied. Igberase and Osifo [29] also found that the adsorption of cadmium and lead on polyaniline grafted cross-linked chitosan beads did not change when the adsorbent dosage was over 4.5 g/l due to the full occupation of metals on the beads biding sites. The results also demonstrated that the percentage of oil removal significantly increased (p < 0.05) with increasing initial oil concentration and attained the maximum adsorption at the concentration of 20 g/l. It meant that, at this point onward, the number of oil molecules was higher than the biding



Fig. 3 The effect of (a) pH, and (b) the  $\ensuremath{\text{pH}_{\text{zpc}}}$  of chitosan beads on oil adsorption.

sites, and the adsorption was decreased. Hameed and El-Khaiary [37] similarly reported that the adsorption of malachite green using oil palm trunk fiber reached maximum adsorption at 25 mg/l of malachite green. Beyond this concentration, the adsorption was decreased. Therefore, the adsorption of oil on chitosan beads depends on the adsorbent dosage and initial oil concentration.

#### Contact time

To determine the effect of contact time on the adsorption of oil onto the chitosan beads, 10 g/l of chitosan beads and 20 g/l of oil concentration were used. The result is depicted in Fig. 2(b). It showed a sharp increase in the percentage of adsorption during the initial contact time and attained equilibrium at 25 min when the maximum adsorption was  $83.40 \pm 1.98\%$ . The adsorptions between 25– 30 min were not significantly different (p > 0.05), and percentage of adsorption was declined after 30 min. This phenomenon was due to the fully occupied adsorption sites by oil molecules on the beads surface [2, 29].

# pH and pH<sub>zpc</sub>

The influence of pH (ranged between 3 and 11) on the oil adsorption of chitosan beads was investigated at 10 g/l of adsorbent dosage, 20 g/l initial oil concentration, and for 25 min contact time. The results are shown in Fig. 3(a). The results of  $pH_{zpc}$  (using 0.01 M NaCl in the range of pH 2–12) are illustrated in Fig. 3(b).

As shown in Fig. 3(a), the results revealed that the oil adsorption of chitosan beads depended on the pH of the solution. The highest adsorption capacity was at pH 5 (82.67%). In addition, it was observed from Fig. 3(b) that the  $pH_{zpc}$  of the chitosan beads was 7.67. It can be explained that when the pH was lower than  $\ensuremath{\text{pH}_{\text{zpc}}}\xspace$  , the surface of the chitosan beads was positively charged due to the protonation of amino groups of chitosan (Fig. 4(a)). Thus, by electrostatic attraction, the positive bead surface favored the adsorption of negatively charged oil molecules (Fig. 4(b)). Nevertheless, the adsorption at pH < 5 was low because the dissolution of chitosan was favorable under acidic condition. The decrease in the adsorption at pH beyond the pH<sub>zpc</sub> came from the repulsive force between the negative charges on the surface of the beads and the charges of the oil molecules [37].

#### Adsorption isotherms

The most common isotherms, the Langmuir and the Freundlich, were used to describe the adsorption of oil onto chitosan beads. Fig. 5(a,b) show the plots in the Langmuir and the Freundlich adsorption isotherms at 303, 323, and 333 K, respectively. The isotherms constant values are shown in Table 1.

The results showed that the adsorption of oil onto the chitosan beads was fitted to the Langmuir isotherms, confirmed by the value of  $R^2$  of the Langmuir (0.9524–0.9927) at all temperatures compared with those of the Freundlich (0.3681– 0.4899). This implied that the oil adsorption was a monolayer on homogenous surface of the adsorbent [37, 38]. The maximum adsorption capacity ( $C_m$ ) increased with increasing temperature, indicating that the adsorption was endothermic in nature. The results were similar to the adsorption data of cadmium and lead onto chitosan beads, i.e. the adsorption was a monolayer type, and the maximum adsorption capacity increased when the temperature increased (from 298 to 318 K) [29].

The  $R_L$  value was the dimensionless constant separation factor or equilibrium parameter, expressing the feasibility of adsorption for the Langmuir isotherm. If the  $R_L$  value is between 0–1, the adsorption is favorable. If the  $R_L$  value is more than 1, the adsorption is unfavorable. When the  $R_L$ values are 1 and 0, the adsorptions are linear and irreversible, respectively [39]. The  $R_L$  value was



Fig. 4 (a) The protonation of amino groups of chitosan at  $pH < pH_{zpc}$  leads to the presence of positive charges on chitosan surface, and (b) the adsorption of oil molecules (negative charges) on chitosan surface (positive charges).



Fig. 5 (a) The Langmuir adsorption isotherms, and (b) the Freundlich adsorption isotherms.

Langmuir isotherm						
Temp. (K)	Slope	y-intercept	$R^2$	$C_m (mg/g)$	L (l/mg)	
303	0.0003017	1.2967059	0.9927	3314.551	0.000233	
323	0.0001881	1.8530300	0.9730	5316.321	0.000102	
333	0.0001587	1.8688436	0.9524	6301.197	0.000085	
		Freundlich	isotherm			
Temp. (K)	Slope	y-intercept	$R^2$	$n_f$	$K_f (mg/g)$	
303	0.3681	4.1430	0.3681	0.368	62.992	
323	0.4628	3.4645	0.4628	0.463	31.960	
333	0.4899	3.3046	0.4899	0.490	27.238	

 Table 1
 The Langmuir and the Freundlich isotherms' constants.



**Fig. 6** (a) The pseudo-first order model, (b) the pseudo-second order model, and (c) the intraparticle diffusion model.

calculated from (7).

$$R_L = \frac{1}{1 + LC_0},\tag{7}$$

where  $C_0$  is the initial oil concentration (mg/l) and *L* is the Langmuir constant (l/mg). The  $R_L$ values of the experiment were between 0 and 1 (0.1767, 0.3300, and 0.3706 at 303, 323 and 333 K, respectively), indicating that the adsorption of oil onto chitosan beads is favorable for the Langmuir isotherm. When compared with the adsorption of other negative charges onto chitosan surface, such as phosphate (PO<sub>4</sub><sup>3-</sup>), the data were also well fitted to the Langmuir isotherm with the  $R_L$  values between 0 and 1 [31].

# Adsorption kinetics

The pseudo-first order, pseudo-second order, and intraparticle diffusion models were used to investigate the adsorption kinetics of oil by chitosan beads. The fitted curves to the models are demonstrated in Fig. 6, and the constant values calculated from the model equations are presented in Table 2.

It was clear that the experimental data were fitted to the pseudo-second order model, which gave the highest values of  $R^2$  (0.9965–0.9985), indicating that the adsorption showed chemisorption behavior [40]; and the adsorption between oil molecules and the beads involved an electron sharing affinity. Thus, the pseudo-second order model could be used to predict the rate at which the oil molecules are adsorbed onto chitosan beads. The rate law of the reaction may be expressed as (8).

$$\frac{\mathrm{d}q_e}{\mathrm{d}t} = k_2 (q_e - q_t)^2, \tag{8}$$

where  $q_t$  is the amount of oil adsorbed onto the adsorbent (mg/g) at time t (min),  $q_e$  is the amount of oil adsorbed onto the adsorbent at the equilibrium (mg/g), and  $k_2$  is the pseudo-second order rate constant (g/mg min<sup>-1</sup>). The integration of (8) for the condition at t = 0,  $q_t = 0$  gave (9)

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \tag{9}$$

The maximum adsorption capacity  $(q_2)$  and the pseudo-second order rate constant  $(k_2)$  increased as the temperature increased from 303 to 333 K, which implied that the adsorption capacity was temperature-dependent. It correlated with the adsorption isotherm data that the adsorption of oil onto chitosan beads was an endothermic process. The adsorption kinetic data were similar to the adsorption data of malachite green onto chitosan beads [32] and oil palm trunk fiber [37], which were well described by the pseudo-second order model.

Adsorption using porous adsorbent is usually controlled by intraparticle diffusion process. As depicted in Fig. 6(c), the plots of the amount of oil adsorbed onto chitosan beads at time t ( $q_t$ ) against the square-root of time t ( $t^{0.5}$ ) provided two segment lines. The first line (t = 0-25 min) showed a sharp increase in adsorption rate and reached the maximum adsorption. It was suggested that the oil molecules were rapidly adsorbed onto the chitosan surface or diffused from the bulk solution to the biding sites on the adsorbent surface, attributed by the driving force from the concentration gradient of

The pseudo-first order							
Temp. (K)	Slope	y-intercept	$R^2$	$q_1 \text{ (mg/g)}$	$k_1 \; (\min^{-1})$		
303	0.002302	0.000555	0.8995	1801.801802	4.147747748		
323	0.001957	0.000547	0.8827	1828.153565	3.577696527		
333	0.001148	0.000532	0.8447	1879.699248	2.157894737		
The pseudo-second order							
Temp. (K)	Slope	y-intercept	$R^2$	$q_2 \ ({ m mg}/{ m g})$	$k_2$ (g/mg min <sup>-1</sup> )		
303	0.000588	0.001422	0.9984	1700.680272	0.000243139		
323	0.000589	0.000911	0.9985	1697.792869	0.000380813		
333	0.000569	0.000159	0.9965	1757.469244	0.002036233		
The intraparticle diffusion							
Temp. (K)	Slope	y-intercept	$R^2$	$k_p \ (\mathrm{mg/g}\ \mathrm{min}^{-0.5})$	<i>C</i> (mg/g)		
303	356.73	0	0.9671	356.73	0		
323	373.21	0	0.9445	373.21	0		
333	404.79	0	0.8531	404.79	0		

 Table 2
 Kinetic parameters of oil adsorption onto chitosan beads at different temperatures.

oil and vacant sites on the surface of beads [27]. This indicated that the initial time of adsorption was controlled by the intraparticle diffusion process, i.e. the adsorption rate controlling step. Besides, the intraparticle diffusion constant ( $k_p$ ) increased with increasing temperature. On the contrary, the latter segment line (t > 25 min) showed constant adsorption, due to the lack of available sites on the adsorbent surface.

# Oil removal efficiency in synthetic wastewater

The optimum adsorption conditions (10 g/l of adsorbent, 20 g/l oil concentration, 25 min of contact time, at 303 K, and pH 5) were used in order to obtain efficiency in the oil removal in the synthetic oil-in-water sample. The result revealed that the maximum adsorption was  $83.40 \pm 1.98\%$  or  $1667.93 \pm 39.61$  mg/g.

# Oil removal efficiency in the household grease trap

Chitosan beads were practically applied to the household grease trap at different on-site household wastewater samples to determine oil removal at optimum conditions, except uncontrolled pH, temperature and contact time. Oil concentrations (in term of FOG, BOD, COD, and pH of the influent and effluent water were analyzed (Table S2). Oil concentration, BOD, and COD in effluent water decreased significantly (p < 0.05) when the influent water had passed through the grease trap using chitosan beads as the adsorbent. The percentage of oil

reduction of the 6-occupant household was the highest (71.01%), followed by the 2-occupant household (66.99%) and the noodle shop (54.19%). BOD and COD also decreased in the similar sequences. The pH of treated and untreated wastewater from the 2-occupant household and the noodle shop were significantly different (p < 0.05), whereas the pH of the 6-occupant household was not (p > 0.05). The results indicated that the efficiency of oil removal in real wastewater samples were lower than those of the synthetic oil-in-water samples. It might be due to the competition between oil molecules and other substances which can be adsorbed by chitosan beads. In addition, the emulsified oil by surfactants led to the formation of more stable oil droplets, hindering the adsorption of oil molecules onto the surface of chitosan. Pintor et al [8] reported that the surface-active agents influenced the stability of oil-in-water, the higher concentration of surfactants, the more stable oil-emulsion. Moreover, the adsorption of oil in synthetic water was performed in the batch experiment with 25 min of contact time, while the adsorption of oil in real wastewater in the grease trap was the continuous mode. Wastewater was fed to the grease trap with an uncontrolled flow rate (about 1 l/min in average), thus the adsorption could not attain the equilibrium as compared with the laboratory experiment. This occurrence made a considerable point for further research to improve the oil removal from household wastewater using grease traps. According to the reports of the Pollution Control Department of Thailand, the household grease trap can reduce fat, oil and grease by 60% [3]. The problems from FOG in domestic wastewater have generally been controlled because FOG is restricted from activities such as cleaning and cooking. In this research, oil concentration, as FOG and BOD, in the household effluent water were below the discharge limit of Type-d buildings (household) defined by Thai legislation (i.e. FOG < 20 mg/l and BOD < 50 mg/l), and the noodle shop's were over the discharge limit of Type-e buildings (restaurant) [41].

# CONCLUSION

Development of chitosan beads as an oil adsorbent in household grease traps showed that the conducive conditions for bead synthesis were 3% w/v chitosan flakes in 5% v/v acetic acid and formed the beads in 2.0 M NaOH. The obtained beads were slightly hard and spherical in shapes with homogenously distributed pores. The maximum adsorption capacity was  $1667.93 \pm 39.61 \text{ mg/g}$  $(83.40 \pm 1.98\%)$  occurred at the adsorbent dosage = 10 g/l, initial oil concentration = 20 g/l, equilibrium time = 25 min, pH = 5, and 303 K. The adsorption was better described by the Langmuir isotherm, suggesting monolayer adsorption type. The adsorption kinetics was fitted very well with the pseudo-second order, and the rate controlling step was intraparticle diffusion. The adsorption of oil onto the chitosan beads in the household grease trap using real wastewater showed a significant decrease in FOG, BOD and COD (p < 0.05). However, the percentage of oil removal in real wastewater was significantly lower than in synthetic wastewater because of the competition between the oil and other substances in the real wastewater. Moreover, the formation of stable micelles by the surfactants reduced the adsorption of oil onto the adsorbent. Therefore, it is necessary to develop more methods and use them in couple with the adsorption method to improve the reduction of oily wastewater.

#### Appendix A. Supplementary data

Supplementary data associated with this article can be found at http://dx.doi.org/10.2306/ scienceasia1513-1874.2021.046.

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# Appendix A. Supplementary data

<b>Table S1</b> Percentage of oil removal at different adsorbent dosage and initial oil concentration $(n = 3)$ .
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Chitosan beads		Initial oil conce	entration (g/l)	
dosage (g/l)	10	20	50	100
5.0	$62.28 \pm 1.02^{a,1}$	$63.60 \pm 2.30^{b,1}$	$37.94 \pm 1.40^{c,1}$	$20.24 \pm 2.11^{d,1}$
10.0	$72.27 \pm 1.18^{a,2}$	$81.00 \pm 0.69^{b,2}$	$67.14 \pm 1.66^{c,2}$	$38.78 \pm 2.63^{d,2}$
20.0	$63.48 \pm 0.64^{a,3}$	$77.63 \pm 0.63^{b,3}$	$61.23 \pm 1.15^{c,3}$	$30.41 \pm 2.56^{d,3}$
30.0	$59.35 \pm 2.19^{a,4}$	$72.46 \pm 4.22^{b,4}$	$64.34 \pm 2.88^{c,4}$	$27.77 \pm 2.09^{d,4}$

The superscript letters (a,b,c,d) in each row show the significant differences (p < 0.05).

The superscript numbers (1,2,3,4) in each column show the significant differences (p < 0.05).

**Table S2** Removal of oil as FOG, BOD, COD, and pH in real wastewater using the grease trap with chitosan beads (n = 3).

Sample	Parameter	Before	After	%Removal
2-occupant household	FOG (mg/l)	$7.70 \pm 0.49^{a}$	$2.54 \pm 0.07^{b}$	66.99
-	BOD (mg/l)	$26.97 \pm 1.95^{a}$	$9.27 \pm 0.07^{\rm b}$	65.64
	COD (mg/l)	$110.17 \pm 11.12^{a}$	$37.78 \pm 0.92^{b}$	65.71
	pH	$6.12 \pm 0.05^{a}$	$6.34 \pm 0.06^{a}$	-3.54
6-occupant household	FOG (mg/l)	45.77±1.74 a	$13.27 \pm 0.65 \mathrm{b}$	71.01
	BOD (mg/l)	$135.24 \pm 4.08^{a}$	$37.34 \pm 1.54^{b}$	72.39
	COD (mg/l)	$543.19 \pm 20.59^{a}$	$152.23 \pm 15.08^{b}$	71.97
	pH	$7.02 \pm 0.18^{a}$	$7.06 \pm 0.17^{a}$	-0.62
a noodle shop	FOG (mg/l)	$3,598.06 \pm 315.85^{a}$	$1,648.40 \pm 182.05^{b}$	54.19
-	BOD (mg/l)	$25,062.04 \pm 3,132.19^{a}$	$12,116.24 \pm 1,465.34^{ m b}$	51.66
	COD (mg/l)	$54,819.97 \pm 3,451.98^{a}$	$26,276.73 \pm 1,133.67^{ m b}$	52.07
	pH	$7.74 \pm 0.26^{a}$	$7.05 \pm 0.75^{b}$	8.96

The superscript letters (a,b) in each row show the significant differences (p < 0.05).



Fig. S1 Diagram of the grease trap in the experiment.