

Adsorption characteristics of residual oil on amphiphilic chitosan derivative

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ABSTRACT

In this study, a novel chitosan-based polymeric surfactant, H-Oleoyl-Carboxymethyl chitosan was used as a coagulation agent for cleaning residual oil. The characteristics of H-Oleoyl-Carboxymethyl chitosan were investigated by FTIR and XRD. And the adsorption capacities of chitosan and H-O-CMCS for removing the residue oil from the wastewater of oil extraction have been investigated. H-O-CMCS exhibited a greater rate than chitosan in cleaning the residual oil from the wastewater of oil extraction at the optimum conditions. Equilibrium study, Langmuir/Freundlich adsorption models and the pseudo first- and second-order kinetic models were applied to describe the mechanism of adsorption experiments. The experimental data fitted well with the Langmuir model and the second-order kinetic model. Regeneration studies, using by the roasting and rinsing method, were undergone for three successive adsorption/desorption processes. H-O-CMCS still retained the residual oil removal capacity after regeneration.

Key words | adsorption, chitosan, H-O-CMCS, regeneration, residual oil

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NOMENCLATURE

C_e	residue oil concentration at equilibrium, mg/l	R^2	correlation coefficient
C_0	initial concentration of residue oil, mg/l	R_L	separation factor, dimensionless constant
k_1	rate constant of pseudo first-order adsorption, mg/g min	t	time taken for adsorption, min
k_2	rate constant of pseudo second-order adsorption, min^{-1}	V	sample volume, l
K_f	Freundlich constant related to adsorption capacity	W	mass of adsorbent, g
K_L	Langmuir constant relate to energy of adsorption		
n	Freundlich constant related to adsorption intensity		
q_e	adsorption density at equilibrium solute concentration, C_e , mg/g		
q_0	maximum amount of adsorption corresponding to complete monolayer coverage, mg/g		
q_t	amount of adsorption at time t , min		

INTRODUCTION

Over the recent years there has been an increasing concern for environmental risk of industrial activities associated with extraction, hydrocarbons, food processing, transportations and refining. These industries have increased the threat of oil pollution to the environment and their discharges into the natural environment create a major ecological problem throughout the world. Treatment and disposal of oily wastewater, such as the wastewater of oil extraction (WWOE), is presently one of the serious

environmental problems contributors (Arcadio & Gregoria 2003). The major difficulty in disposing the oily water is cleaning up the emulsified oil droplets (Zouboulis & Avranas 2000). Emulsified oil in wastewater can lead to severe problems in the different treatment stages. Oil in wastewaters has to be removed in order to: (1) prevent interfaces in water treatment units; (2) reduce fouling in process equipment; (3) avoid problems in biological treatment stages; and (4) comply with water discharge requirements. Hence the removal of residue oil from process or waste effluent becomes environmentally important (Ahmad *et al.* 2005a). Various processes have been developed to remove emulsified oil from contaminated areas (Choi *et al.* 1993). Coagulation method is widely used in the treatment of water and wastewater and well known for its capability of destabilizing and aggregating colloids (Wei *et al.* 2005). In conventional wastewater treatment systems, a number of natural sorbents have been studied for cleaning up oily wastewater, e.g. chitosan, bentonite and activated carbon (Feng *et al.* 2000).

Chitosan (CS) has the high affinity with the residual oil and the excellent properties such as biodegradability, hydrophilicity, biocompatibility, adsorption property, flocculating ability, polyelectrolyticity, antibacterial property and its capacity of regeneration in many applications (Majeti 2000). It has been used as non-toxic floccules in treatment of organically polluted wastewater (An *et al.* 2001). However, the excellent flocculating ability for the residual oil of chitosan has only been exhibited at acid condition (Ahmad *et al.* 2006). Thus, it is necessary to develop an efficient, environmental friendly chitosan derivative for removing the residual oil in a broader pH range. And in our previous study, H-O-CMCS had been prepared, which showed an enhancement for the effective adsorption for the residue oil from WWOE (Sun *et al.* 2008a).

The objective of this paper is to investigate the mechanism of H-O-CMCS as a coagulation agent to flocculate the residual oil. Several of the physicochemical parameters of the adsorption were evaluated at the dynamic equilibrium conditions. The isotherm and kinetic models were used to describe the experimental data of H-O-CMCS. Regeneration experiments were also investigated in this study. This information will be useful for further application in treatments of practical oily waste effluents.

MATERIALS AND METHODS

Materials

Chitosan was made from crab shell and obtained from Biotech Co. (Mokpo, Korea), degree of deacetylation 83.7%, molecular weight 66 kDa, white powder, less than 120 mesh in size. Chloroacetic acid, oleoyl chloride, chloroform, tetrachloromethane etc were purchased from Sigma Chemicals Co. (USA).

Samples of raw WWOE were collected from the system of typical WWOE treatment process in Shengli Oil Field of China, at the temperature ranging from 40 to 50°C. The samples were cooled to room temperature before experiment. The raw wastewater of oil extraction is colloidal suspension, which contains 100 mg/l–200 mg/l of the emulsified oil and 800 mg/l–1,000 mg/l of suspended solids. It is light brown liquid and discharged at temperature between 40 and 50°C. It is alkaline with ranging pH from 7.0 to 7.5. Table 1 shows the characteristics of raw WWOE. The oil droplets of raw WWOE can be found in two phases. One is suspended in the supernatant as emulsions; the other is floating as oil droplets on the upper layer of the suspension (Ahmad *et al.* 2005b). The residual oil in raw WWOE belongs to the first section which we are going to study.

Synthesis of H-Oleoyl-Carboxymethyl chitosan (H-O-CMCS)

H-Oleoyl-Carboxymethyl chitosan was synthesized in the laboratory by the method of Sun *et al.* (2008b). First, Na-carboxymethyl chitosan (Na-CMCS) was prepared by

Table 1 | Characteristics of raw WWOE

Parameter	Concentration (mg/l)	Ion	Concentration (mg/l)
Total Oil and grease	200–1,500	Na ⁺ and K ⁺	2,000–6,000
Emulsified oil	100–200	Ca ²⁺	100–300
Chemical oxygen demand	60–524	Fe ³⁺	0.1–1.0
Demand	321–890	Mg ²⁺	10–140
Suspended solids	200–2,500	Cl ⁻	3,000–8,500
SRB		HCO ₃ ⁻	700–1,700

the method of Liu *et al.* (2001). Second, Na-O-CMCS was synthesized by reaction of Na-CMCS with oleoyl chloride. Finally, Na-O-CMCS (1 g) was suspended in 80% ethyl alcohol aqueous solution (100 ml), hydrochloric acid (10 ml, 37%) was added and stirred for 30 min (Sakairi *et al.* 1998). The solid was filtered and rinsed in 70–90% ethyl alcohol to neutral, vacuum dried. The products were the powder of H-O-CMCS (Liu *et al.* 2001; Chen & Park 2003).

Characterization methods

The IR spectrums of H-O-CMCS and CS were recorded on an FT/IR-430 Fourier Transform Infrared Spectrometer (Jasco Co. Tokyo, Japan) at room temperature based on the method of Shigemasa *et al.* (1996). A pellet was formed from 2 mg sample and 100 mg of KBr. Data analysis was carried out using Omnic-7.0 (Windows xp). X-ray diffraction (XRD) was carried out on Iodebeylex 2002 Xray powder diffractometer. Scanning electron microscopy (SEM) was done on EDAX, FEI Quanta 200 machine.

Adsorption experiments

At first, raw WWOE was laid for 2 h and separated. After separation, the floated oil was taken out and we could get the pre-WWOE. Then the residual oil content as emulsions in pre-WWOE was analyzed for the following experiment (Meyssami & Kasaeian 2005). A conventional beaker (100 ml) was used to coagulate the residual oil from the pre-WWOE with the adsorbents for quantitative analysis. The beakers were filled with 50 ml of pre-WWOE for each test run and stirred simultaneously at a defined speed (500 rpm) with six-spindle of steel paddles. After adding the adsorbents into the pre-WWOE, the beakers were rapidly mixed at various mixing time for different doses of adsorbents (Ahmad *et al.* 2003). Then we separated the floccules and analyzed the residual oil content in the system after the experiment. The samples were analyzed with different dosages of H-O-CMCS. Functions such as effect of contact time; effect of the pH; effect of the temperature and effect of initial concentration of oil were also analyzed. The reproducibility of the experimental data was tested by

triple-repeated experiment. The variance of the each data was within $\pm 5\%$.

The optimum conditions obtained from this preliminary analysis were then applied to test the equilibrium and rate adsorption experiment for H-O-CMCS at various initial oil concentrations.

The percentage adsorption of residue oil was calculated according to:

$$\text{Percentage Adsorption} = (C_0 - C_e) \times \frac{100}{C_0} \quad (1)$$

Adsorption equilibrium studies were conducted using the optimized contact time, the initial pH of pre-WWOE and the room temperature for H-O-CMCS. Isotherm studies were conducted with a constant H-O-CMCS powder weight dosage and varying the initial concentration of residue oil in pre-WWOE, which was collected from the different area. The amount of adsorption at equilibrium q_e was by the following mass balance equation:

$$q_e = (C_0 - C_e) \times \frac{V}{W} \quad (2)$$

where, q_e (mg/g) and C_e (mg/l) are, respectively, the adsorbent phase residue oil concentration and sample phase residue oil concentration at equilibrium; C_0 (mg/l), the initial residue oil concentration; V (l), the sample volume, and W (g), is the mass of adsorbent.

Regeneration studies

To study regeneration, we carried out two methods (roasting method & rinsing method) to recycle the adsorption capacity of H-O-CMCS. Regenerative experiments were carried out in 3 consecutive cycles. For each cycle, the residual oil in 500 ml pre-WWOE was adsorbed by 50 mg H-O-CMCS for 60 min. Then the floccule was disposed by roasting at certain temperature or rinsing with CCl_4 for 24 h. The adsorption capability of the H-O-CMCS powder (disposed) was tested by the method outlined in the section above on adsorption experiments. After each cycle of adsorption–desorption, the H-O-CMCS powder (disposed) was washed thoroughly with ultrapure water to neutrality and remeasured the adsorption capacity for residual oil in the succeeding cycle.

Residual-oil analysis

The residual-oil content was measured using the oil and grease method recommended by APHA, AWWA and WPCF (1992) Standard Method of Examination of Water and Wastewater, with tetrachloromethane being used as the oil-extraction solvent. The oil and grease content in the suspension was determined for each sample of pre-WWOE and post-WWOE. Three replicates of each test run were undertaken with the mean value obtained for residual-oil content being calculated from the replicates.

RESULTS AND DISCUSSION

The structure and characteristics of H-O-CMCS

The chemical structure of H-O-CMCS was represented in Figure 1. The data of FTIR had been shown in the previous study (Sun *et al.* 2008a). X-ray diffraction profiles of chitosan (A) and H-O-CMCS (B) are shown in Figure 2. The strongest reflection appear at $2\theta = 15^\circ$ and 22° , which correspond to crystal forms II (Dung *et al.* 1994). Compared with chitosan, H-O-CMCS shows less intense peaks at 2θ . For H-O-CMCS, peaks further broaden showing a decrease in the crystallinity of the substituted chitosan. Introduction of substituents into polysaccharide structures should disrupt the crystalline structure of chitosan, especially by the loss of

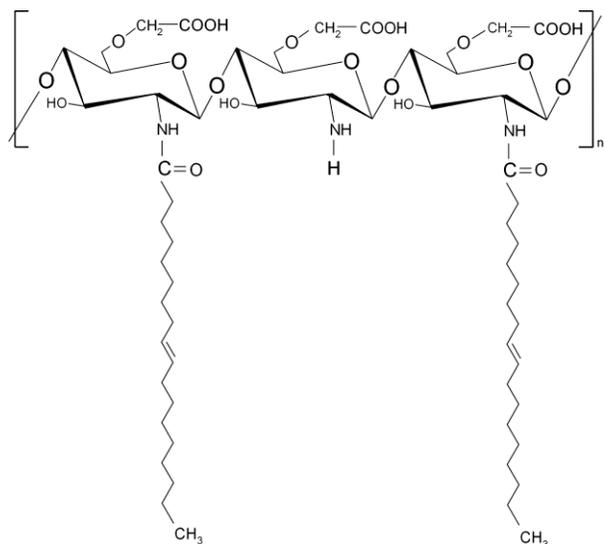


Figure 1 | The structure of H-oleoyl-carboxymethyl-chitosan (H-O-CMCS).

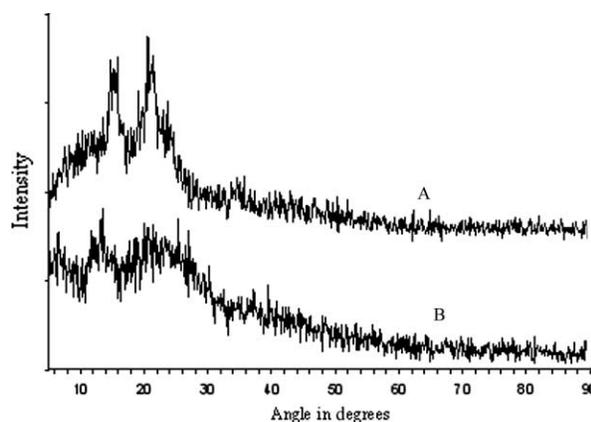


Figure 2 | The XRD spectrum of chitosan and the chitosan derivative A: chitosan, B: H-O-CMCS.

the hydrogen bonding. The crystallinity of chitosan polymer could play a restrictive role on adsorption capacity. The crystallinity parameter is a key-parameter in the accessibility to internal sites for adsorption. Many studies have shown that decreasing the crystallinity results in an improvement in adsorption capability (Kurita *et al.* 1979; Nalini & Rashmi 2006).

Effect of adsorbent dosage

The effects of adsorbent dosage of H-O-CMCS and chitosan for removing the residual oil were shown in Figure 3 with the mixing time of 30 min, a mixing rate of 500 rpm, sedimentation time of 60 min, the original pH (pH 7.0–7.5) and the residual oil concentration of 106.1 mg/l. H-O-CMCS and chitosan could wash up about 99% and 87% of residual oil from pre-WWOE when the adsorbents dosages were 10 mg/50 ml (0.2 g/l).

It was observed that H-O-CMCS had the best adsorption capacity for removing residual oil from pre-WWOE (pH 7.0–7.5), i.e., 99%, when the dosages of adsorbents were 0.2 g/l. The adsorption capacity of H-O-CMCS for the residual oil had a great increase between 5 mg and 10 mg (per 50 ml pre-WWOE) and when weight dosage 2 mg–5 mg (per 50 ml pre-WWOE) or weight dosage 10 mg–20 mg (per 50 ml pre-WWOE), the trend of H-O-CMCS adsorption capacity for the residual oil tended to balance. H-O-CMCS had high charge functional groups (oleoyl groups), therefore it required only a little quality of H-O-CMCS to destabilize the residue oil droplets.

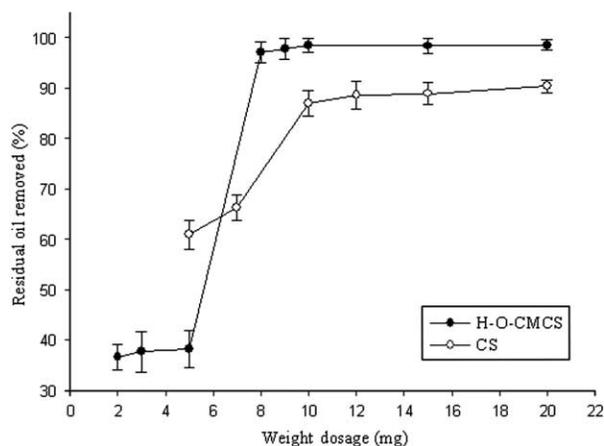


Figure 3 | Percentage of residual oil adsorption vs. dosage of H-O-CMCS and chitosan.

Chitosan is a well-known coagulation agent, with amine functional groups, which are very attracted to anionic ions, therefore, it could easily bind and bridge into flocs (Ahmad *et al.* 2003). At pH 7.0–7.5 (the initial pH of pre-WWOE), all the free ions were neutralized, which could not further adsorb the carbonyl ions of residual oil (Ahmad *et al.* 2005b). Thus, neutralization could influence the ability of chitosan in adsorbing the residual oil strongly (Sandhya & Tonni 2003). And H-O-CMCS had the better adsorption capability than chitosan in removing the residual oil from pre-WWOE at initial pH as shown in Figure 3.

When the dosage of adsorbents was 10 mg (per 50 ml pre-WWOE), two adsorbents achieved the preferable percentage of removing residual oil from pre-WWOE respectively. So we took 10 mg (per 50 ml pre-WWOE) as the experimental dosage in the following experiments.

Effect of mixing time

The effects of mixing time (0–180 min) for the residual oil adsorption were shown in Figure 4 using the fixed adsorbent dosage (10 mg/50 ml). The other experimental conditions were similar as the above section. It was observed that H-O-CMCS only needed 3 min to achieve maximum amount (99%). CS needed 30 min to achieve maximum percentage (87%) of residual oil. The results were demonstrated that H-O-CMCS could be faster to achieve the maximum percentage of residual oil adsorption compared with chitosan. H-O-CMCS and chitosan had

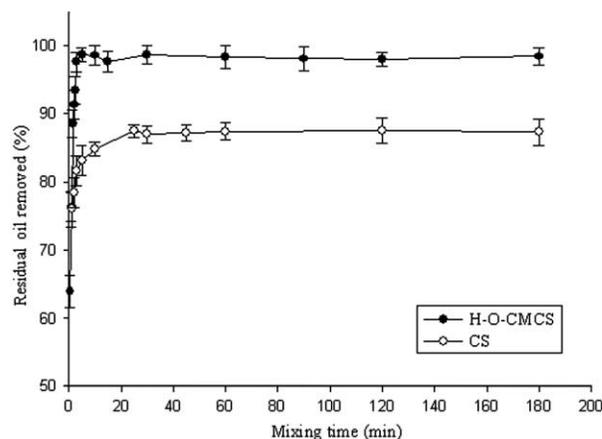


Figure 4 | Percentage of residual oil adsorption vs. mixing time for H-O-CMCS and chitosan.

the similar trend and there was no noticeable change in residue oil adsorption with mixing time prolonging as they achieved the maximum percentage of residual oil adsorption. In further research, when the mixing time was prolonged more than 24 h, the percentage of residual oil adsorption of H-O-CMCS and chitosan also achieved almost 99% and 87%. So the flocs which were formed by H-O-CMCS and chitosan were very stable. This was because that they not only agglomerated the suspended residue oil in the pre-WWOE but adsorbed the residue oil.

At a shorter mixing time, the percentage of residual oil adsorption was low for two adsorbents. For H-O-CMCS and chitosan, the percentage of residual oil adsorption had been increasing from 0–30 min, this was because that the breakage of the oil droplets were enhanced, thus reducing the diameter of the oil droplets (emulsification) which caused more interfacial area for the adsorption to happen and encouraged the adsorption of residue oil by adsorbents. Therefore, mixing time between the oil molecule and the adsorbents particles was important in adsorbing the residue oil.

Effect of pH

The effect of pH (0.5–7.5) of H-O-CMCS and chitosan for removing residual oil was shown in Figure 5. The other experimental conditions were similar as the above section. It was noticed that pH could influence the percentage of residual oil adsorption for two adsorbents. At pH 5–7,

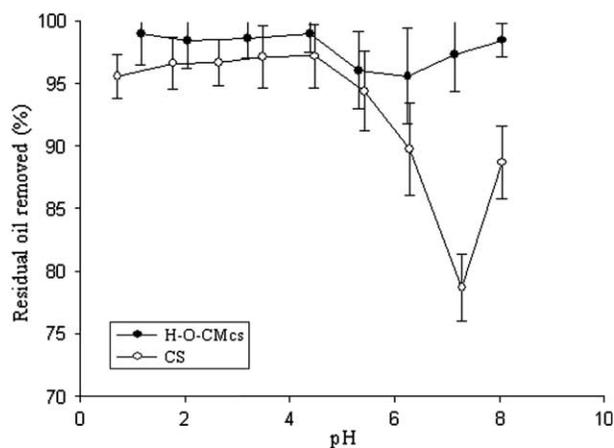


Figure 5 | Percentage of residual oil adsorption using H-O-CMCS and chitosan vs. different pH of pre-WWOE.

the adsorption capacity of chitosan for removing residual oil from pre-WWOE had the stronger decrease compared with H-O-CMCS.

Chitosan could clean up about 97% of residual oil from pre-WWOE at lower pH ($\text{pH} < 4.5$). This is because chitosan has reached its saturation point at pH 4.5 (Ahmad *et al.* 2005a). In acidic condition chitosan provokes physicochemical effect, apparently serving to demulsify. More protons will be available to protonate amine groups of chitosan molecules to form $-\text{NH}_3^+$ groups (Ahmad *et al.* 2005a). This enhanced the ability of the amine group of chitosan to attack the carbonyl group of residual oil and led to an increase in the electrostatic attractions between the residual oil molecules and adsorption site of chitosan. Therefore, the electrostatic attractions indirectly enhanced the adsorption of residue oil onto chitosan. But at pH 4.5–7.0, the percentage of adsorption of chitosan decreased, compared with that at pH 4.5. This might be because the destabilization of chitosan under the condition of a weaker acid.

H-O-CMCS could flocculate almost 99% of the residual oil in a broader pH range. The percentage of residual oil adsorption had a light decrease at pH 5–7. This was due to not all amine groups of CMCS had been modified by oleoyl chloride in the procedure of synthesis H-O-CMCS. So H-O-CMCS also had some primary amine groups (NH_2) which would affect the adsorption capacity of H-O-CMCS for the residual oil by pH change. And another probable reason is when pH shifted from the light acidic agent to

neutral, the adsorption process itself was unstable due to the characteristics of pre-WWOE had changed.

When pH was more than 7.5 the percentage of residue oil adsorption was increasing and an identical trend could be seen for both chitosan and H-O-CMCS. It was known that the addition of excessive NaOH to a suspension with residue oil in order to increase the alkalinity could lead to saponification process (Ahmad *et al.* 2003). So the pH not only affected the degree of ionization and adsorption of residual oil for the adsorbents but also affected the oil/grease–water interfacial film to destabilize emulsion in pre-WWOE (Schulz *et al.* 1998; Bailey *et al.* 1999). The study on the effect of pH for the residual oil adsorption was essential to determine the optimum pH condition for H-O-CMCS.

Effect of temperature

The effect of temperature for the residual oil adsorption was conducted by the mixing time 30 min at 500 rpm of rotation speed (Figure 6). The other experimental conditions were similar with the above section Effect of adsorbent dosage. The adsorption capacity of H-O-CMCS for removing residual oil from pre-WWOE is instable with temperature rising. The adsorption capacity of chitosan had a little increase when the temperature was less than 50°C.

H-O-CMCS could clean up almost 99% of residual oil from pre-WWOE, when the temperature was lower than 45°C. But the percentage of residual oil adsorption

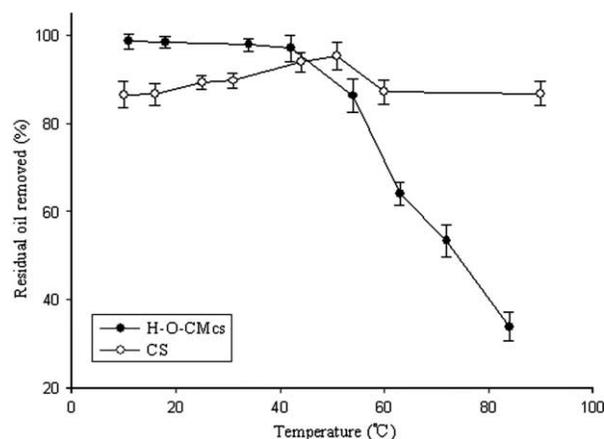


Figure 6 | Percentage of residual oil adsorption using H-O-CMCS and chitosan vs. different temperature of pre-WWOE.

had a large decrease if the temperature exceeded 45°C. When temperature achieved 84°C, the percentage of residual oil adsorption was only about 33%. This was might because the interaction force between the oil molecule and the adsorbents particles had destroyed with temperature rising. Thus the temperature was an important factor in removing the residual oil for H-O-CMCS. This phenomenon provided the recycling possibility of H-O-CMCS for removing the residual oil from pre-WWOE.

Chitosan achieved the maximum percentage of residual oil adsorption at the temperature rage from 40°C to 50°C. With the temperature rising (<50°C), the percentage of residual oil adsorption also increased. This was because that the chitosan particles and the emulsified oil droplets would be more active in higher temperature compared with in lower temperature, so the flocs could be formed easily. But when the temperature exceeded 50°C, destruction of crystalloid construction of chitosan could result in the changes of the adsorption capacity of residual oil. So the percentage of removal residual oil by chitosan from pre-WWOE would decrease if the temperature exceeded 50°C. Furthermore, the emulsification went stronger with the rising of temperature, and it will influence the

adsorption capability of two adsorbents for removal residual oil from pre-WWOE. Thus the system temperature was an important factor in removing the residual oil.

SEM

SEM was taken to prove the phenomena of residue oil adsorption by H-O-CMCS powder. Figure 7b and d is a magnified picture from Figure 7a and c, which help us more exactly to observe the powder of H-O-CMCS compared with Figure 7a and c.

The SEM photographs of H-O-CMCS powder before adsorption was shown in Figure 7a and b. Figure 7b is a magnified picture from Figure 7a, which help us more exactly to observe the powder of H-O-CMCS compared with Figure 7a. SEM observations (Figure 7a) of H-O-CMCS powder (particle size < 120 mesh) revealed its the irregular shapes, which also had the irregularly distributed pores in its interior (Figure 7b).

Figure 7c and d presented a significant change of the structure and appearance on H-O-CMCS powder after experiment. The SEM photographs revealed that most of the H-O-CMCS powder areas were covered with muddy-like

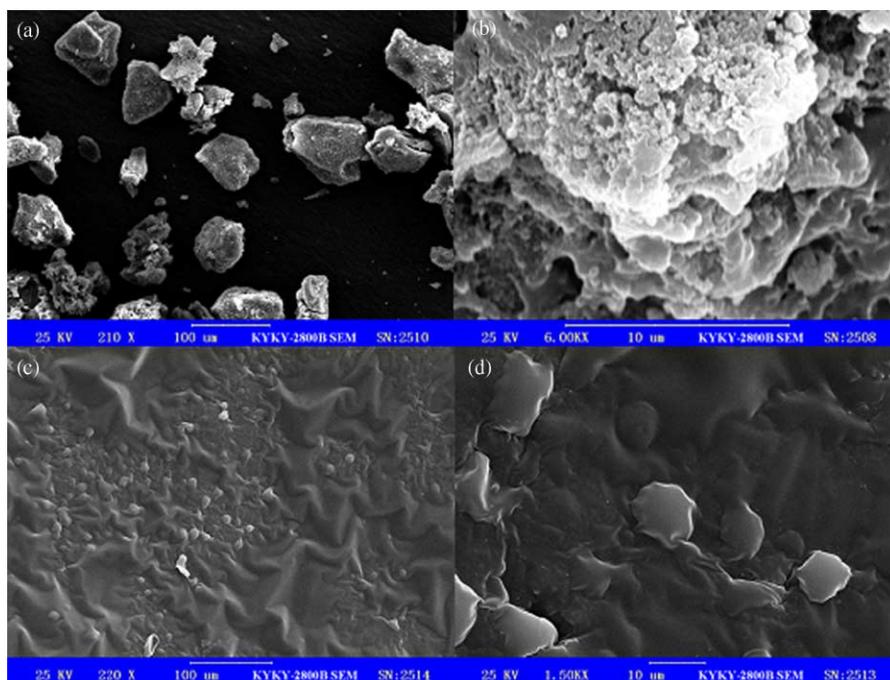


Figure 7 | Electron microscopic photographs of H-O-CMCS powder (a, b) before and (c, d) after residue oil adsorption.

substance and this is the adsorbed residue oil. Figure 7d showed that H-O-CMCS powder could integrate firmly with the residual oil particles for its groups. These images proved that H-O-CMCS could adsorb the residual oil from pre-WWOE and develop a layer of oily substance on the surface.

Adsorption equilibrium of H-O-CMCS for removing the residual oil

Analysis of equilibrium data is important for developing a model that can be used for the design of adsorption systems. The data of the equilibrium adsorption of residue oil at 10 mg weight dosage of H-O-CMCS powder and pre-WWOE solution adjusted to initial pH was shown in Figure 8. The adsorption capacity of H-O-CMCS for removing residual oil could not exhibit totally in the low oil concentration, so it caused the lower adsorption capacity of the residual oil firstly. And it achieved the adsorption equilibrium while the oil concentrations rising.

Adsorption isotherms of H-O-CMCS for removing the residual oil

Adsorption isotherm is important in describing how solutes interrelate with the adsorbent and so is critical in optimizing the use of adsorbents. Several isotherm equations have been used for equilibrium modeling of adsorption systems (Aksu & Akpınar 2000; Aksu & Tezer 2000; Antizar-Ladislao & Galil 2004). Two classical adsorption

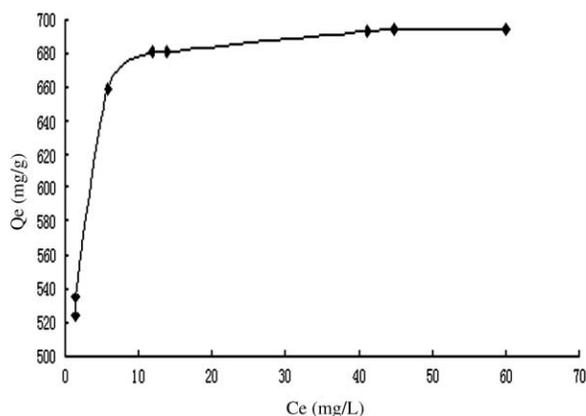


Figure 8 | Equilibrium adsorption of residue oil on the H-O-CMCS powder.

models, i.e., Langmuir and Freundlich isotherms, are most frequently employed. The Langmuir isotherm assumes monolayer coverage of adsorbate over a homogeneous adsorbent surface. While the Freundlich isotherm assumes a heterogeneous surface with a nonuniform distribution of heat of adsorption over the surface and a multilayer adsorption can be formed. In this work, the two models were used to describe the relationship between the amount of H-O-CMCS (10 mg) and its equilibrium concentration in solutions at different oil concentration.

Langmuir isotherm is expressed as:

$$\frac{C_e}{q_e} = \left(\frac{1}{K_L q_0} \right) + \left(\frac{1}{q_0} \right) C_e \quad (3)$$

where q_0 (mg/g) is the maximum amount of adsorption corresponding to complete monolayer coverage and K_L is the Langmuir constant. A linearized plot of (C_e/q_e) vs. C_e gives K_L and q_0 .

The essential features of Langmuir isotherm can be expressed in terms of dimensionless constant separation factor, R_L , which is expressed by the following equation (Hall *et al.* 1966):

$$R_L = \frac{1}{(1 + K_L C_0)} \quad (4)$$

where C_0 (mg/l) is the initial concentration of residue oil, K_L is Langmuir constant. The parameters show the shapes of the isotherms according to Table 2 (Hall *et al.* 1966).

Freundlich isotherm is expressed as:

$$q_e = K_f \times C_e^{1/n} \quad (5)$$

Where, q_e is solid phase sorbate concentration in equilibrium (mg/g), C_e is liquid phase sorbate concentration in equilibrium (mg/l), K_f is Freundlich constant and $1/n$ is the

Table 2 | Effect of separation factor on isotherm shape

R_L value	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$R_L = 0$	Irreversible
$0 < R_L < 1$	Favorable

heterogeneity factor. Freundlich expression can be obtained in a linear form by taking logarithms of Equation (5).

$$\log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e \quad (6)$$

Therefore, a plot of linearized $\log q_e$ vs. $\log C_e$ enables the constant K_f and exponent $1/n$ to be determined.

Langmuir and Freundlich adsorption constants evaluated from the isotherms with the correlation coefficients were listed in Table 3. As it could be seen that the Langmuir isotherm gave better fit than the Freundlich isotherm for H-O-CMCS under the concentration range studied (correlation coefficient, R^2), which demonstrated that the adsorption on the biomass surface was a monolayer not a multilayer adsorption. According to the Langmuir equation, the maximum uptake capacity (q_0) of H-O-CMCS for the residual oil was $714.2857 \text{ mg g}^{-1}$. The values of R_L of H-O-CMCS are given in Table 4. The R_L values show that favorable adsorption of residue oil on H-O-CMCS takes place; therefore, H-O-CMCS is a favorable adsorbent.

Rate of adsorption of H-O-CMCS for removing the residual oil

In order to examine the mechanism of adsorption such as mass transfer and chemical reaction, several kinetic models are used to test experimental data. The rate of adsorption of residue oil by H-O-CMCS powder was determined using two simple kinetic analyses. The first one is;

Pseudo-first-order Lagergren's equation (Annadurai & Krishnan 1997);

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (7)$$

where q_t is the amount of adsorption at time t and k_1 is the rate constant of pseudo-first-order adsorption.

Table 3 | Comparison of Langmuir and Freundlich isotherms constants for H-O-CMCS

	Langmuir model			Freundlich model		
	K_L	q_0	R^2	K_f	n	R^2
H-O-CMCS	2.3333	714.2857	0.9999	537.5266	13.5870	0.8336

Table 4 | R_L Values of H-O-CMCS based on the Langmuir equation

Residue oil initial concentration (mg/l)	R_L Values of H-O-CMCS
106.1	0.004023
108.5	0.003934
137.6	0.003105
148.1	0.002885
150.1	0.002847
179.8	0.002378
183.5	0.002330
198.9	0.002150

After integration and applying the initial condition $q_t = 0$ at $t = 0$, Equation (7) becomes

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (8)$$

The pseudo-second-order equation was given by (Mckay *et al.* 1982):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (9)$$

where k_2 is the rate constant of pseudo-second-order adsorption. Integrating Equation (9) and applying the initial condition, Equation (9) becomes

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \quad (10)$$

or

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (11)$$

The equilibrium adsorption capacity q_e and the pseudo second-order rate constant k_2 can be experimentally determined from the slope and the intercept of the plot (t/q_t) against t . It is observed that, k_2 and q_e can be calculated from the intercept and slope of the plot (t/q_t) vs. t and there is no need to know any parameter in advance. Normally pseudo-first-order equation is expressed in the range of reaction only and does not fit well with the whole range of contact time and is generally applicable over the initial stage of the adsorption processes, although it has been effectively used to describe adsorption reactions.

Table 5 | Comparison of first- and second-order adsorption rate constants (k_1 , k_2), calculated and experimental q_e values and the initial adsorption rate (V_0) for H-O-CMCS

Residue oil initial concentration (mg/l)	First-order kinetic			Second-order kinetic				
	k_1	R^2	q_e (exp)	q_e (cal)	k_2	R^2	q_e (exp)	q_e (cal)
106.1	0.6665	0.6866	523.71	110.97	0.0181	0.9999	523.71	526.32
148.1	0.3694	0.6893	681.25	108.94	0.0075	0.9999	681.25	666.67
179.8	0.0168	0.2739	693.30	25.73	0.0049	0.9997	693.30	714.29

The adsorption kinetic data of the residual oil using H-O-CMCS at different initial oil concentration was shown in Table 5. It is observed that, the correlation coefficient (R^2) for the second-order kinetic model was close to 1.0, and the theoretical values of q_e also agreed well with the experimental data. On the other hand, the correlation coefficient for the pseudo first-order kinetic was lower than for the pseudo second-order one. In addition, the theoretical q_e value obtained from the first-order kinetic model did not give reasonable value with significant deviation from the experimental one. This suggests that the adsorption of residue oil onto H-O-CMCS powder is not a first-order reaction. While for pseudo-second-order equation, a two-step linear relationship is obtained. Whereby this equation is based on the adsorption capacity, it predicts the behavior over the whole range of studies supporting the validity and is in agreement with chemisorptions being the rate-controlling (Ahmad *et al.* 2005a). Therefore, the pseudo-second-order model could be used for the prediction of the kinetics of adsorption of residual oil on H-O-CMCS.

REGENERATION STUDIES

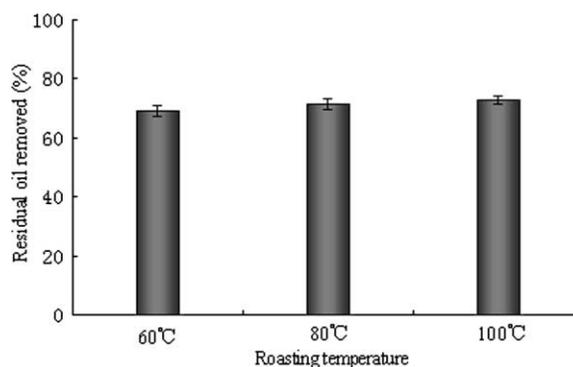
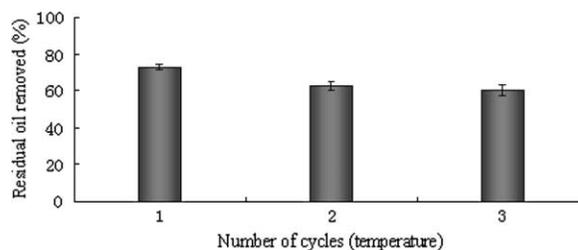
Roasting method

Since H-O-CMCS lost its adsorption capacity for residual oil at high temperature, regeneration of the adsorbent was possible to be reused. The regenerating effects on certain roasting temperatures (60°, 80° and 100°) of H-O-CMCS were shown in Figure 9. And the residual oil adsorption capacity of H-O-CMCS underwent three cycles at 100° was illustrated in Figure 10. The maximum percentage of residual oil adsorption in the roasting regenerative experiments was 73%. The regenerative adsorption capacity of H-O-CMCS was observed to increase with the rise of roasting temperature. The interaction force between the oil

molecule and the adsorbents particles was more easily destroyed in the high temperature (100°), compared with the low temperature. With the number of cycles going, the adsorption capacity tended to descend. After each cycle of adsorption/desorption, there still were residual oil particles existed both in the interior and the surface of H-O-CMCS. That's probably why the adsorption capacity of H-O-CMCS for residual oil could not be recovered to the initial potential completely.

Rinsing method

The effects of regeneration by rinsing method underwent three cycles were shown in Figure 11, the percentage of residual oil adsorption was 59%, 57% and 56%, respectively.

**Figure 9** | Regeneration studies of roasting method at three temperatures.**Figure 10** | Regeneration studies of roasting method after three cycles at 100°.

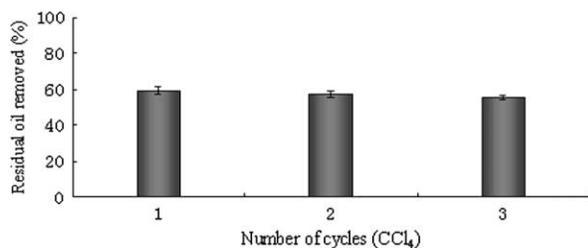


Figure 11 | Regeneration studies of rinsing method after three cycles.

It is observed that the residual oil adsorption capacity remained almost constant after three cycles. And the regenerating effect of roasting method (73%) was better than the rinsing method (59%). The phenomena is mainly attributed to rinsing with CCl₄ could wash the residual oil out of H-O-CMCS interior holes only.

The primary objective of regeneration is to restore the adsorption capacity of exhausted adsorbent while the secondary objective is to recover valuable components present in the adsorbed phase, which is essential for practical application of H-O-CMCS in the treatments of oily waste effluents.

CONCLUSIONS

The destabilization of oil-in-water is successfully performed by the application of H-O-CMCS and chitosan. H-O-CMCS powder shows the better performance as a coagulation agent for removing the residual oil from pre-WWOE, compared with chitosan powder. The optimum adsorption parameters of H-O-CMCS were found for the reduction of the residual-oil content from pre-WWOE. H-O-CMCS could flocculate 99% of the residual oil from the pre-WWOE. Isotherm data can be well fitted by the Langmuir equation. Adsorption kinetics of residue oil onto H-O-CMCS follows the pseudo-second-order kinetic model. The significant uptake of residue oil on H-O-CMCS was further proved by SEM micrographs. The regeneration studies demonstrated that the H-O-CMCS powder can be recovered by roasting and rinsing for the re-adsorption of the residual oil. It was proved that H-O-CMCS was a potential biomaterial as coagulation for removing the residual oil in this paper.

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