

NOVEL OLEOPHILIC ADSORBENT BASED ON OCTANYL CHITOSAN SCHIFF BASE FOR OIL SPILL REMOVAL

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Abstract - The present work investigates the preparation of novel oleophilic octanyl chitosan schiff base and its applicability for the adsorption of oil spills from water surface. The developed Schiff base was prepared by simple chemical reaction of chitosan (CH) with octanal (Oct), then crosslinked with glutaraldehyde. Evidences of schiff base formation as well as its chemical structure were verified by using FT-IR spectroscopy and ion exchange capacity (IEC), while both thermal properties and morphological changes were investigated using TGA/DSC and SEM characterization tools, respectively. Results showed that ion exchange capacity (IEC) value recorded 9.95 meq/g in case of native chitosan and decreased gradually to 1.47 meq/g with increasing octanal ratio in the feed mixture. In addition, water uptake and solubility of octanyl chitosan schiff base were decreased compared to native chitosan as a result of the generated hydrophobic/oleophilic characters of the developed schiff base derivative. The obtained results showed improving oil uptake of the developed schiff base compared to native chitosan where it increased with the following affinity order; mineral oil < Kerosene < Diesel < light crude oil < heavy crude oil. The gained results suggest that chitosan schiff base could be used as an oleophilic sorbent for oil spill clean-up.

Index Terms - Chitosan; Octanal; Schiff base; Oleophilic character; Oil spill removal.

I. INTRODUCTION

When the oil is explored, transported and stored and its derivatives are used, there is a risk for spillage with the potential to cause significant environmental impact [1]. Due to its destructive properties; the entire character of the area is damaged once an area has been contaminated with oil. In addition, when oil encounters something to cling to (e.g., beach, rocks, feathers of a duck or a bathers hair), it is difficult to remove [2]. Therefore, pollution from petroleum oils affects sea life, economy, tourism, and leisure activities due to the coating properties of these materials [1]. When the oil is spilled in water or on land, the physical and chemical properties of oil change progressively. The spilled oil contributes an undesirable taste and odor to drinking water and causes severe environmental damage [3]. Oil pollution from food production, catering industry, petroleum chemical and petroleum mining, etc. has drawn the extensive attention of many researchers in recent years. Many methods, such as mechanical extraction, in situ combustion and chemical degradation, have been used to the cleanup of oil from polluted areas. Owing to better economical and environmental benefits, the use of sorbent is considered as an

effective method to concentrate, transfer, and absorb spilled oil [4]. High-efficient oil sorbent is required to possess desirable characteristics, such as excellent hydrophobicity and oleophilicity, high uptake capacity, fast oil sorption rate, low cost, and high buoyancy. So far, various materials including natural materials such as seaweed, alginate, dead biomass, rice hulls, carrageenan, lignins, cellulose, chitin, chitosan [5], inorganic mineral materials [6], and organic synthetic fibers [7], have been used for oil sorption [8]. Chitosan, discovered by Rouget in 1859 [9], is a technologically important poly-saccharide biopolymer. Chemically, it is a high molecular weight linear poly-cationic hetero polysaccharide consisting of two monosaccharides, N-acetyl-D-glucosamine and D-glucosamine, linked together by β -(1 \rightarrow 4) glycosidic bonds. The relative amount of the two monosaccharides in chitosan may vary, giving samples of different degrees of deacetylation (75-99%), molecular weights (50 2,000 kDa), viscosities, pKa values, etc [10-12]. Therefore, the term chitosan does not refer to a uniquely defined compound; it merely refers to a family of copolymers with various fractions of acetylated units. Indeed, chitosan is becoming most popular in different applications due to its excellent unique properties such

as bio-degradability, non-toxicity, lower density, ease modification and has lower cost [15]. Furthermore, chitosan can undergo physicochemical modification for allowing the formation of functional derivatives with a highly hydrophilic and/or hydrophobic character such as coating, carboxyl methylation [16],[17], grafting, and amination [18],[19]. It was reported that chitosan has various functional groups like hydroxyl and amino groups which induced simple chemical transformation and modifications. Schiff base compounds containing an imine group are usually formed by the condensation of a primary amine with an active carbonyl.

The presence of amine groups in the polymeric chain leads to the possibility of a several chemical modifications, including the preparation of Schiff bases ($-RC=N-$) by reaction with aldehydes and ketones [21],[22]. Its attractiveness as analytical reagent rises from the fact that they enable simple and inexpensive determinations of various organic and inorganic substances [23]. It was reported that chitosan has been used for the treatment of wastewater from phenolic compounds [23],[24] using immobilization of bacteria on chitin and chitosan flaked which degrade hydrocarbons. Additionally, chitosan showed high adsorption capacity when it applied as oil adsorbent material for removing oil spills [12].

In this work study, novel chitosan/octanal Schiff base was prepared and characterized using different characterization tools. Moreover; their hydrophobic/hydrophilic and oleophilic characters were evaluated through studying performance on oil uptake capacity.

II. MATERIALS AND METHODS

2.1. Materials

Shrimp shells were collected from wastes of seafood restaurants in Alexandria (Egypt). Glutaraldehyde (99%), Acetic acid (98%), Mineral oil and Octanal (95%) were obtained from Sigma-Aldrich (Germany). Sodium hydroxide (99%), Ethanol (99%), hydrochloric acid (purity 37%), from El-Nasr Company (Alexandria), Sulfuric acid (Purity 95-97%) was Purchased from El-Gomhouria Co., (Egypt), Diesel oil and Kerosene oil Supplied from local gas station, (Egypt).

Crude oil samples: Two Egyptian crude oils, namely Marine (MB) and Land Belayem (LB) were supplied from Belayem Petroleum Company, (Egypt). Land Belayem crude oil is evidently heavier and more viscous than the Marine crude oil. Besides it contains higher asphaltenes (6 times larger) and sulfur.

2.2. Methods

2.2.1. Preparation step

2.2.1.1. Extraction of chitin and preparation of chitosan

Crushed shells were first treated with 10 % hydrochloric acid for 6 hr under mechanical stirring to remove associated minerals such as calcium and magnesium salts, then filtrated and washed with fresh water before treated with 10% sodium hydroxide to remove protein and lipid residue and extract chitin. The obtained was dried at 50 °C and kept for overnight. Chitin thus obtained can be hydrolyzed using 50% sodium hydroxide at a high temperature (100-150 °C) to provide chitosan [25],[26]. Finally, drying chitosan obtained at 50°C and kept for overnight [27].

2.2.1.2. Chitosan purification

Chitosan sample was dissolved in 2% acetic acid and left overnight. The solution was then filtrated through cheesecloth to remove contaminants and undissolved particles. Chitosan was then re-precipitated with 5 % sodium hydroxide, collected and washed with distilled water to remove the excess of alkali [25].

2.2.1.3. Preparation of chitosan / octanal Schiff base

Previously purified chitosan (0.4g) was dissolved in 20 ml of 2% acetic acid and stirred at room temperature for 6 hr. 10 ml ethanol of ethanol was added carefully to the viscous solution under stirring at room temperature then 5 ml of ethanol containing definite amount of octanal was added to solution under stirring to have homogenous solution. The temperature was raised to 80 °C under stirring for next 6 h. The obtained gel structure refers to the formation of the chitosan Schiff base. The reaction was stopped by precipitate gel in excess of 0.1M sodium hydroxide solution. The precipitate was filtered and washed with distilled water and ethanol several times to remove un-reacted octanal, then dried in oven at 60 °C overnight **"Fig.1"**.

Six different molar ratios of chitosan/octanal were prepared 1:0.5, 1:1, 1:2, 1:3, 1:4, and 1:5 and coded as CH-Oct0.5, CH-Oct1, CH-Oct2, CH-Oct3, CH-Oct4, and CH-Oct5 respectively in addition to the neat chitosan (CH- Oct0).

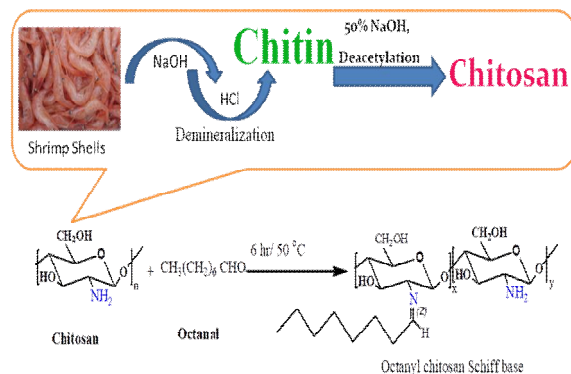


Fig.1: Schematic preparation of Octanyl chitosan schiff base.

2.2.2. Material characterization

2.2.2.1. Infrared spectrophotometric analysis (FTIR)

Chemical structure of chitosan and its schiff base forms were investigated using Fourier transform infrared spectrophotometer (Shimadzu FTIR-8400 S, Japan).

2.2.2.2. Thermal gravimetric analysis (TGA)

Thermal stability of chitosan and its schiff base forms was evaluated using thermo gravimetric analyzer (Shimadzu TGA-50, Japan). Measurements were carried out under a heating rate of 20°C/min under flow of N₂ up to 800°C. Then, all samples were encapsulated in a platinum pan with one hole in the top.

2.2.2.3. Scanning electron microscope (SEM)

The surface morphology of chitosan and its schiff base forms were followed by scanning electron microscopy (Joel Jsm 6360LA, Japan). The fracture surfaces were vacuum coated with gold for scanning electron microscope (SEM).

2.2.2.4. Determination of ion exchange capacity of chitosan and its Schiff bases

Chitosan is insoluble in sulfuric acid. A known weight of chitosan or chitosan derivatives were added to known volume of 0.1 M H₂SO₄ solution and the mixture was kept aside for 2 h. The mixture was filtered and an aliquot was titrated against standard solution of sodium hydroxide. Similarly control titration without the addition of chitosan was also run. From the difference in the volume of NaOH required for neutralization, ionic capacity of chitosan samples were calculated using following equation (1):

$$\text{Ion exchange capacity} = (V_2 - V_1) \times n / w \text{ (meq/g)} \quad (1)$$

Where V_2 and V_1 are the volumes of NaOH required for complete neutralization of H₂SO₄ in the absence and presence of chitosan, respectively, n is the normality of NaOH and w is the weight of sample taken for analysis [27].

2.2.2.5. Solubility test

Solubility test was performed by placing a weighed sampling in acetate buffer at certain pH and stirring well at room temperature for 6 hrs. The residue was then filtered, dried and weighed [28]. The solubility was determined by the following equation (2):

$$\text{Solubility\%} = 1 - \left[\frac{W_1}{W_0} \right] \times 100 \quad (2)$$

Where W_1 and W_0 are weight of insoluble part and Total weight of sample respectively

2.2.2.6. Water uptake

Water uptake estimation was performed by placing a weighed sample in 10 ml water. After 6 hr the sample

was then filtered off, carefully bolted with a filter paper and weighed. The water uptake was calculated by applying the following equation (3):

$$\text{Water uptake} = \frac{(M - M_0)}{M_0} \quad (3)$$

Where M is the weight of the swelled sample at time t and M_0 is the weight of the dry sample [25], [29].

2.2.2.7. Oil uptake

Oil Uptake was calculated by soaking a known weight of the samples (0.05grams) in 10 ml of oil (mineral oil, diesel oil, kerosene oil, light crude oil, heavy crude oil.) then placed in a closed glass containers for different time intervals., carefully bolted with a filter paper and weighed. weighed immediately in a closed balance [30],[31]. Oil uptake can be expressed by the following equation (4):

$$\text{Oil uptake} = \frac{(W_t - W_0)}{W_0} \quad (4)$$

Where; W_t is the weight of swollen sample after certain time and w_0 is the initial dry weight.

III. RESULTS AND DISCUSSION

3.1. Characterization

3.1.1. physic-chemical characterization

Fig.2 shows the ion exchange capacity of chitosan and its schiff base derivatives. The decline of curve from 9.9 of chitosan to 1.47 of CH-Oct5 refers to consumption of chitosan amine groups in the formation of schiff base bond. Same trend was observed when chitosan interact with aldehydes and ketons [32]. Fig.2 demonstrate water uptake of chitosan and its schiff base derivative. It was clear gradual decrease the water sorption capacity of chitosan (3.4 %) to 0 for CH-Oct5. The interaction of octanal with chitosan free amine groups could replace the hydrophilic group with an alternative hydrophobic aromatic group. Same results were observed by Mohyeldin et al [33].

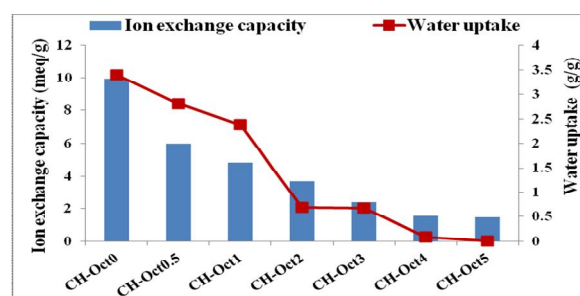


Fig.2: ion exchange capacity and water uptake of chitosan and its schiff base derivative.

Water solubility of chitosan and its schiff base derivative are shown in Table 1. From the obtained results, it can be seen that the water solubility of chitosan significantly ($p < 0.05$) decreased after interact with octanal and as the molar ratio increased from CH-Oct1 to CH-Oct5. The water solubility is an important property of water contact materials.

Chitosan amine groups have an essential role in chitosan solubility. The protonation of amine groups of chitosan in the acid medium enhance chitosan solubility. The decrease in chitosan solubility can be attributed to the chemical interaction of chitosan amine groups with octanal. Consumption of amine groups reduced the membranes solubility in acidic solution [34]-[36].

Table 1: solubility percent of chitosan and its schiff base derivative at different pH

	CH-Oct0	CH-Oct0.5	CH-Oct1	CH-Oct2	CH-Oct3	CH-Oct4	CH-Oct5
pH3	99.88	99.78	99.66	86.55	57.76	39.27	1.78
pH4	99.75	89.74	87.21	64.19	25.33	13.40	1.25
pH5	96.37	71.82	64.26	41.83	8.17	4.79	0.19
pH6	88.28	61.74	51.27	27.38	4.25	1.99	0
pH7	0	0	0	0	0	0	0
pH8	0	0	0	0	0	0	0

3.1.2. Fourier-transform infrared

The FT-IR spectra of chitosan, chitosan/Octanal Schiff base were represented as shown in "Fig.3". The FT-IR chart illustrates the regular bands of chitosan function groups; it can recognize a broadband around 3425 cm^{-1} corresponding to the stretching vibration of NH₂ and OH groups and O-H bending at 1394 cm^{-1} which indicates the presence of hydroxyl groups [37]. The weak absorption peak at 2895 cm^{-1} (C-H stretch) for methyl and methylene groups, the characteristic peak of chitosan at 1624 cm^{-1} assigned to the C=O stretching [38]. The band at 1070 cm^{-1} ascribed to the stretching of the C-O-C bridge [39]. Additionally, for chitosan/Octanal Schiff base "Fig.3" the major differences are in the wide peaks at 3425 cm^{-1} for chitosan and at 3444 cm^{-1} for chitosan/Octanal Schiff base that can be attributed to consumption of chitosan amine groups in Schiff base formation process. Also, absorption bands at 2937 cm^{-1} for chitosan/Octanal Schiff base due to -CH stretching, As the molar ratio chitosan/ Octanal was increased strong absorption peaks at 1566 cm^{-1} corresponding to the C=N stretching which formed between the aldehyde group and chitosan appeared. In the meantime, the peak at 1624 cm^{-1} was weakened. On the other hand, there is no evidence of the characteristic band related to free aromatic aldehyde group near 1665 cm^{-1} .

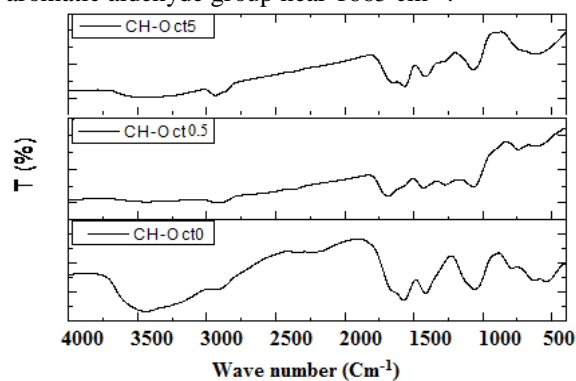


Fig.3: FT-IR of chitosan and Octanyl chitosan schiff base derivative.

3.1.3. Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis (TGA) of chitosan and the octanyl chitosan schiff base was presented in "Fig.4". The first weight loss that starts from ambient temperature to about 150 °C resulted from evaporation of moisture that attached from the atmosphere or during the reaction process. The increase of moisture content was attributed to the pseudo hydrophilic character that associated with porous materials [32]. The subsequent degradation that recognized from 220 °C to 320 °C was a result of oxidative decomposition of the chitosan backbone. In this stage, first depression was produced from destruction of amine groups to form cross linked fragments [40]. There no significant difference in thermal stability between chitosan, and chitosan/Octanal Schiff base due to the temperature required to lose their half weights (T50%) were ranged from 325 to 385 °C as represented in Table 2. Where there is significantly less stability of Schiff base derivative that confirmed with published in the literature [41]. The third depuration that results from the decomposition which appears at high temperature may produce from the thermal degradation of a new cross-linked material formed by thermal crosslinking reactions occurring in the first stage of the degradation process [42].

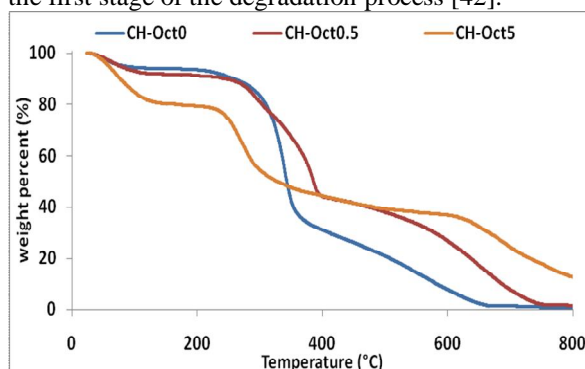


Fig.4: TGA of chitosan and Octanyl chitosan schiff base derivative.

Table 2 estimate that incase of chitosan/Octanal Schiff base the degradation starts earlier than chitosan because of loose networks or moisture present due to Schiff base incorporation process leading to porosity. Interestingly, chitosan/Octanal Schiff base has overall higher stability than chitosan because even at 600 °C , 36.46% of chitosan/Octanal Schiff base is not degraded, but in case of chitosan, only 8.43 % is not degraded [43].

Table2: Thermal gravimetric peaks of chitin, chitosan/ Octanal Schiff base with different molar ratio

Sample	Ambient- 150°C (%)	T25% °C	T50% °C	W% at 600	Residual%
CH-Oct0	6.02	319.34	342.81	91.57	8.43
CH-Oct0.5	8.24	323.48	385.49	74.14	25.86
CH-Oct5	19.86	246.61	325.74	63.54	36.46

3.1.4. Morphology Structure Characterization (SEM)

The surface morphological analysis of chitosan and Chitosan/Octanal Schiff base derivative with different molar ratio were studied using scanning electron microscope (SEM) and listed in "Fig.5". The SEM graphs show a remarkable increase in surface roughness as increase the modification. This is explicated by changing the internal structure of chitosan. Immobilization of Octanal molecules into chitosan backbone gives the polymer some hydrophobic nature [25]. This will stimulate a change in the internal forces between polymer chains and may also induce changes of solid-state crystalline [12]. Furthermore, pores were observed on the surface by coupling amine groups with Octanal, which could be referred to distortion of the internal structure of the polymer.

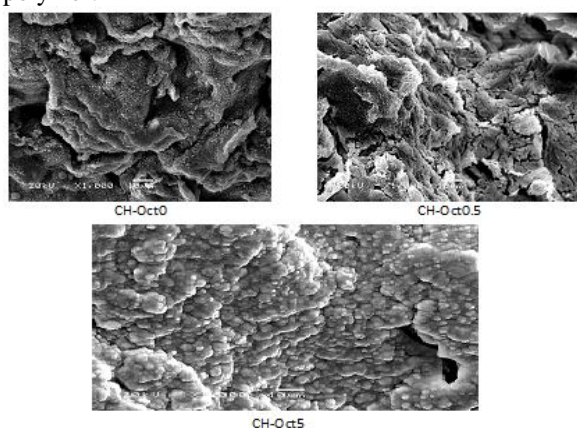


Fig.5: SEM images of chitosan and Octanyl chitosan schiff base derivative.

3.2. Adsorption process

3.2.1. Effect of different molar ratio in oil uptake

In fact, the determination of oil adsorption capacity of sorbents is a helpful method to verify the maximum amount adsorbed oil by the used adsorbent. When oil is poured over the water surface, it spreads as much as possible, and it tends to stick to any solid surface. Indeed, the process in which chitosan or its derivative materials adsorbs oils is not yet completely understood, but some studies stated two types of adsorption mechanisms based on experimental observations [44].

- (i) Attraction of opposite charges between chitosan/chitosan derivatives and oil.
- (ii) Tangle effect, in which chitosan acts as a network, getting involved around the drops of oil and catching them.

In order to know the maximum oil sorption capacity of chitosan and chitosan Schiff base, the oil sorption measurement was studied in pure oil without any water [45]. Therefore, five types of oil specifically; mineral, kerosene, diesel, light crude, and heavy crude oil were used to study the oil uptake behavior and the sorption capacity [31].

It was clear from results that there was a major increase in the oil adsorption capacity of chitosan/octanal Schiff base compared to the original form of chitosan due to increasing its hydrophobic and oleophilic characters after schiff base formation. Positively, the adsorption capacity of all prepared adsorbents is increased in the following order; mineral oil < Kerosene < Diesel < light crude oil < heavy crude oil [12].

Evidently, maximum adsorbent amounts were 1.22 and 6 g/g, were recorded using heavy crude oil for chitosan, and chitosan/octanal Schiff base, respectively. Adsorbents work best on heavy, sticky, more viscous oils [46]. Fundamentally, high oil viscosity can induce adsorption properties by enhancing the adherence of oil onto the surface of the adsorbent material.

"Fig.6" shows time dependent curve of adsorption process of different oils using chitosan and its schiff base derivative. It was clear increase oil uptake by increase the substitution degree that can explain by increase hydrophobic character of polymer. As expected, the sorption capacity increased as the sorption time increased till reached to equilibrium at 3 hr.

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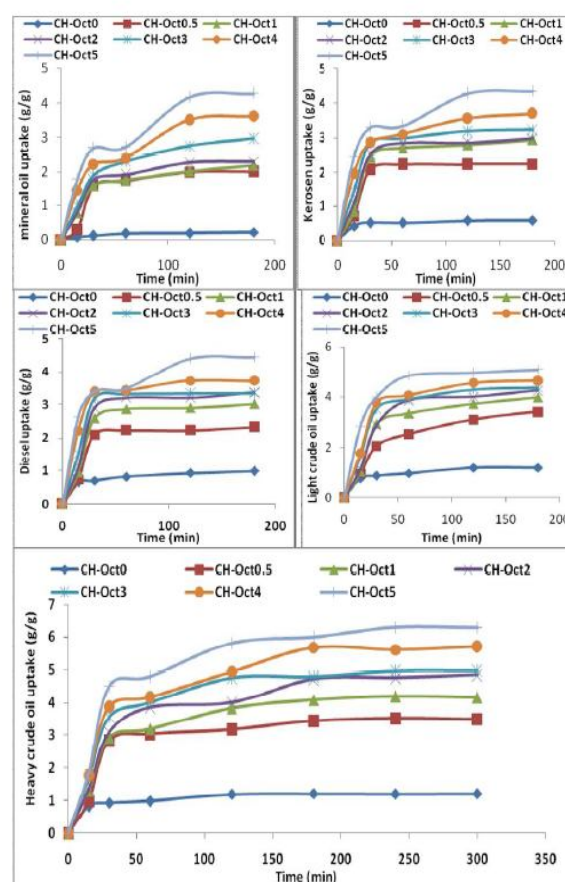


Fig. 6: Effect of different molar ratio chitosan/Octanal in different oil uptake.

Also, "Fig.6" illustrates that for CH-Oct5 the maximum heavy crude oil uptake (6 g/g) more than the maximum mineral oil uptake (4.27 g/g) achieved at 3hr. Furthermore, the oil uptake (g/g) was rapid within the first 30 min, then increased slowly and finally decreased. This is attributed to a large number of vacant surface adsorption sites are available for adsorption during the initial stage, and with the lapse of time the remaining vacant surface adsorption sites are difficult to be occupied due to repulsive forces between the oil adsorbed on the adsorbent [47]. In all of the studied time periods, the chitosan/octanal Schiff base adsorbed more oil than the chitosan. This indicates the affinity of Schiff base formation reaction between octanal and chitosan [48]. "Fig.6" shows that with increase the ratio of chitosan/octanal Schiff base, the oil uptake increased at the equilibrium time (3 hr).

CONCLUSION

The hydrophobic-oleophilic characters of low-cost commercial chitosan were greatly improved by the formation of chitosan/octanal Schiff base. The chitosan/octanal Schiff base was characterized FT-IR, TGA, and SEM. The influence of chemical modification of chitosan on the hydrophobic-oleophilic properties was examined using liquid uptake experiments indicated that the oil uptake using chitosan/octanal Schiff base was higher than chitosan, while higher water uptake was documented by chitosan. The effect of both type and viscosity of oil on the adsorption capacity of chitosan, chitosan/octanal Schiff base were optimized. The results illustrated that of this work can absorb 6 g/g of heavy crude oil while no water could be uptake. The results of this work improved an approach to fabricate hydrophobic/oleophilic adsorbents of chitosan/octanal Schiff base for removing highly viscous crude oil spills from the surface of seawater.

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