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Development of low-cost chitosan derivatives based on marine waste sources as oil adsorptive materials: I. Preparation and characterization

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ABSTRACT

The present work was undertaken to prepare low-cost oil adsorptive materials based on chitosan and its derivatives. Chitosan was prepared from chitin which firstly extracted from shrimp shells. Nonanyl and aminated chitosan derivatives were also prepared and verified their structures, thermal stability and the morphological changes using FT-IR spectroscopy, TGA/DSC, and SEM respectively. Results showed maximum ion exchange capacity (IEC) value was recorded in case of aminated chitosan (7.6 meq/g), while lower IEC value was obtained for nonanyl chitosan schiffbase (2.5 meq/g). Furthermore, the contact angle data indicates that nonanyl chitosan schiffbase exhibit hydrophobic and oleophilic characters and recorded maximum values at 127°, 36° using water and crude oil droplet. The observed improvement in oil/organic solvent/ and water selectivity verified also the chemical medications in addition to the change of the physical properties of chitosan surface. Finally, from the oil adsorption study, it has noticed that the oil adsorption capacity increased from 0.2 g/g in the case of chitosan to 5.1 g/g in the case of nonanyl chitosan schiffbase using heavy crude oil. While, only 9% of water could be uptake by nonanyl chitosan compared to 250.7% and 360% using chitosan and aminated chitosan. The increment of oil adsorption capacity also associated with increasing the oil viscosity in the following order; gas oil < mobil oil < light crude oil < heavy crude oil. The successful modification processes and the cheapness of the prepared materials make them acts as promising adsorbents for oil spill removal technology.

Keywords: Shrimp shells; Chitosan derivatives; Oleophilic character, Oil spill removal

1. Introduction

During the last thirty years, petroleum oil pollution resultant from exploration, transportation, and storage, has become one of the most important environmental subjects [1]. Accidents of oil spills that produced from tankers and oil drilling are the primary sources of this pollution. Hence, about 31.5 billion gallons of crude oil are transported over the sea by ship every day, while 2.73 billion gallons are consumed each day; there is also estimative that 100 million gallons are spilled every year in marine environments [2]. In fact, pollution by petro-

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leum oil spills affects sea life, Fisheries and aquaculture, human health, economy, and tourism [3–5]. Many physicochemical and biological methods have been established for oil spill removal, including burning, oxidation/reduction, dispersants, booms, and skimmers in addition to biological agents [6–8]. However, the high cost is the main limitations of some of these methods [9,10]. Adsorbent materials such as Bentonite organically [11], activated carbon [12], silica aerogels [2], natural and synthetic polymers [13,14] have been recorded to be one of the highly efficient materials from the economic and ecologic point of view for removing oil spills on shorelines [15]. It was stated that the adsorption of oil occurs in three steps; diffusion of the oil molecules into the surface of the adsorbent materials, followed by entrapment of oil into the adsorbent material structures and finally the oil droplets agglomerated in porous and rough structures of the sorbent [16]. Moreover, the development of oil adsorbent made of natural organic waste materials was introduced to afford resources for marine oil spill response with less cost and environmental load [17]. Choi et al. [18] examined the replacement of synthetic sorbents by cotton-containing nonwovens for use in oil spill cleanup. They reported that this natural cotton has slightly greater oil sorption capacities than that of 100% polypropylene fibers. Their results show that cotton-containing sorbents are reusable after a simple mechanical compression to remove oil and can float on sea water for a long period. Nenkova et al. [19] conducted experiments to examine the possibility of eliminating oil pollution by using fibrous-wood sorbents. They found that the sorbents by technical hydrolysis lignin (THL) and wool shoddy have high sorption ability to oil pollution. Also, the tested fibrous-wood materials showed a high rate and degree of purification in static conditions of highly polluted waters. Cojocaru et al. [20] studied three types of peat-based sorbents to determine their potential for oil spill cleanup. The best peat sorbent PT-1 can sorb 12–16 times its weight from different oils. Experimentally they showed that the removal efficiency is 99.21% for the optimal conditions.

Many reviews have been addressed the subject of oil spill removal materials. M. A. Hubbe et al. [21] reviewed the cellulosic substrates as oil spill removal adsorbents. Rafeah Wahi et al. [22] reviewed the oil adsorption using natural fibrous materials. A. A. Al-Majed et al. [7] reviews the state-of-the-art oil spill control techniques, its chemicals, and their advantages and disadvantages. A suggestion on natural sorbent is also outlined.

It was reported that chitosan has various functional groups like hydroxyl and amino groups which induced simple chemical transformation and modifications. Amination of chitosan has been studied as a modification tool [23]. Schiff bases formation is one of these modifications that obtained by chemical reaction of free amino groups of chitosan with active carbonyl compounds such as ketones and aldehydes [24]. The obtained (–RC=N–) groups of chitosan schiff bases offer several potential environmental applications by enhancing their adsorption complexation properties for dyes, phenols, oils [25]. It was reported that chitosan had been used for the treatment of wastewater from phenolic compounds [26,27] using immobilization of bacteria on chitin and chitosan flaked which degrade hydrocarbons [28]. Additionally, chitosan showed high adsorption capacity when it applied as oil adsorbent material for removing oil spills [8]. Our present work focused on the development of two derivatives of renewable commercial chitosan, namely; aminated chitosan and nonanyl chitosan Schiff base. The obtained materials were characterized using different characterization tools. Additionally; their hydrophobic/hydrophilic and oleophilic characters were evaluated through studying their selectivity for oil, water, and organic solvents. The novelty of this work comes from the fact that it is the first time to use such chitosan Schiff base derivative for the oil spill removal application. The formed Schiff base works on two directions to adsorb oils through attraction to the formed positive charges and the hydrophobic moiety of the Nonanal hydrocarbon chain.

2. Experimental

2.1. Materials

Shrimp shells were collected from wastes of seafood restaurants in Alexandria (Egypt). p-benzoquinone PBQ (99%) and nonanal (95%) were obtained from Sigma-Aldrich (Germany). Sodium hydroxide (99%), ethanol (99%), hydrochloric acid (purity 37%), and acetic acid (98%) were brought from El-Nasr Company (Alexandria). Ethylenediamine EDA (99%) was purchased from Alfa Aesar (Germany). Sulfuric acid (purity 98%) purchased from Sigma-Aldrich (Germany). Gas oil and mobil oil purchased from Exxon Mobil Egypt, Cairo, 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. Density and viscosity characteristics of the used petroleum oil derivatives were investigated in Table 1.

2.2. Methods

2.2.1. Extraction of chitin from shrimp shells

According to the published procedure [29], the de-mineralization of shells was the main process for chitin prepa-

Table 1
Density and viscosity characteristics of different petroleum oil derivatives

Type of oil	Density (g/cm^3)	Viscosity (poise)
Heavy crude oil	0.92	489
Light crude oil	0.87	70
Gas oil	0.7	1.5
Mobil oil	0.8	21.9

ration. In this step, the shells were scattered in 5% (w/v) HCl at ambient temperature in the ratio of 1:14 (w/v) overnight. Then, the shells were quite squishy and rinsed using water to remove acid and calcium chloride. The de-mineralized shells were treated with 5% (w/v) NaOH at room temperature for 24 h in the ratio of 12:1 (v/w). The residues were collected and washed to neutrality many times in running tap water and then; distilled water to obtain pure chitin.

2.2.2. Preparation of chitosan from chitin

Preparation of chitosan is naturally deacetylation of chitin in alkaline medium [30]. Removal of acetyl groups from the chitin was achieved using 50% (w/v) NaOH with a solid to solution ratio of 1:50 (w/v) at 100–120°C for 12 h. The resultant chitosan washed to neutrality with distilled water.

2.2.3. Chitosan purification

According to the previous method [30], chitosan sample was dissolved in 2% (w/v) acetic acid and was left overnight. Then, the chitosan solution was filtrated using cheese cloth to remove contaminants and undissolved particles. Finally, chitosan was precipitated with 5% (w/v) NaOH, collected and washed with distilled water to remove the excess of alkali.

2.2.4. Preparation of aminated chitosan

The preparation of aminated chitosan was performed according to Authors previous work [23,31] through three steps. Briefly, 4 g of chitin were dispersed in 50 ml of p-benzoquinone (PBQ) of known concentration at preferred pH and selected temperature with continuous stirring for 6 h. The resulted PBQ-conjugated chitin was estranged and washed with distilled water to get rid of the excess un-reacted PBQ. Secondly, 50 ml of EDA of known concentration was used for the dispersion of PBQ-conjugated chitin at a specific temperature; the solution was stirred for 6 h followed by separation and washing of the aminated modified chitin using distilled water to eliminate unreacted EDA. In the third step, deacetylation was carried out through simple treatment of the aminated modified chitin with an aqueous solution of 50% NaOH at 120–150°C for 6 h. The resulted aminated chitosan was then separated and washed with distilled water to take away the excess NaOH.

2.2.5. Preparation of nonanyl chitosan Schiff base

One gram of chitosan was dissolved in 50 ml of 2% (w/v) acetic acid and stirred at room temperature for 6 h. Ten ml of ethanol contains (1.86 mM) of Nonanal were added dropwise to the solution. The mixture was maintained under stirring for 6 h at 50°C. The formation of a deep yellow color was referred due to the formation of the chitosan Schiff base. The resultant Nonanyl chitosan was precipitated in a solution of 5% sodium hydroxide followed by filtration and wash with water and ethanol several times to remove unreacted aldehyde. Lastly, the products were filtered again and dried in a vacuum oven at 60°C overnight.

The schematic diagram describes the proposed mechanistic pathway for synthesis of (A) chitosan, (B) aminated chitosan, and (C) nonanyl chitosan Schiff bases are presented in Fig. 1.

2.3. Physico-chemical characterization

2.3.1. UV-Visible spectroscopic analysis

The electronic absorbance of the prepared chitosan and its derivatives were investigated using spectrophotometer scanned from 200 to 900 nm.

2.3.2. Infrared spectroscopic analysis (FT-IR)

The structures of the chitosan and chitosan derivatives were investigated by FT-IR spectroscopic analyses using Fourier Transform Infrared Spectrophotometer (Shimadzu FTIR – 8400 S, Japan). Samples (2–10 mg) were mixed thoroughly with KBr, and the absorbance of samples was scanned from 500–4000 cm^{-1}.

2.3.3. Thermogravimetric analysis (TGA)

TGA Analysis of chitosan and chitosan derivatives were carried out using Thermogravimetric Analyzer (Shimadzu TGA –50, Japan).

2.3.4. Scanning electron microscope (SEM)

The surface morphology of chitosan and chitosan derivatives were observed with the help of a scanning electron microscopy (Joel Jsm 6360LA, Japan) at an accelerated voltage of 10 kV. The fracture surfaces were vacuum coated with gold for scanning electron microscope (SEM).

2.3.5. Differential scanning calorimeter (DSC)

Differential scanning calorimeter (Shimadzu DSC–60-A, Japan) was used to evaluate the thermal stability of chitosan and its developed derivatives. Measurements have occurred at a heating rate of 30°C/min with continuous flow of N2 up to 400°C. Finally, the tested sample was encapsulated in an aluminum pan with one hole in the top.

2.3.6. Contact angle measurement

By using Contact angle measurement (Rame-hart instrument Co. Model 500-F1, UK), it's easy to study the oleophilic and hydrophobic characters for the prepared chitosan and its derivatives. The contact angle is defined as the angle between the solid surface and a tangent, drawn on the drop-surface, passing through the triple-point atmosphere – liquid (light crude oil and distilled water) – solid.

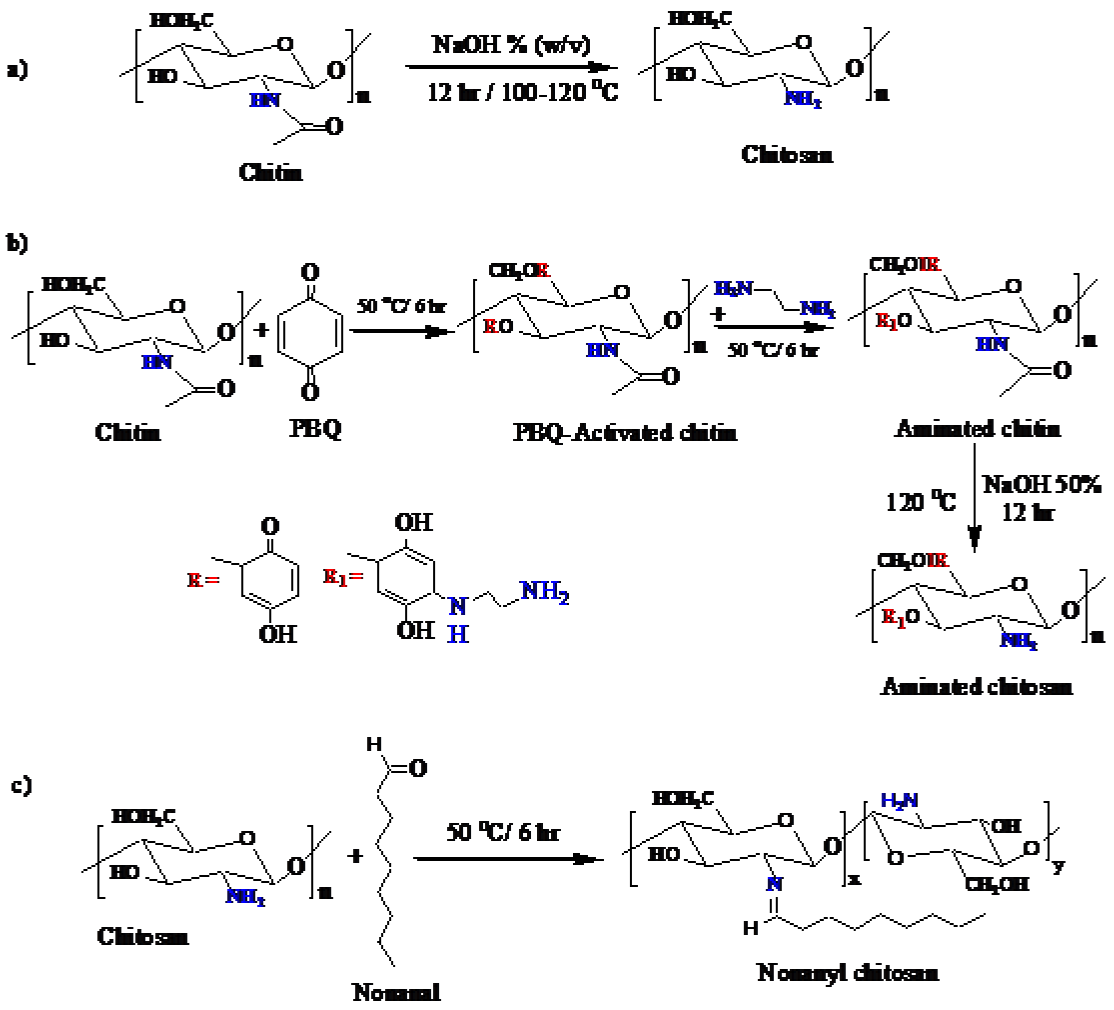

Fig. 1. Schematic representative pathway for synthesis of (a) chitosan, (b) aminated chitosan, and (c) nonanyl chitosan Schiff base.

2.3.7. Moisture measurement

The prepared samples were placed in humidity chambers with humidity ratio 80% overnight and then weighed before and after drying in an oven at 105°C for 3 h. Water content was calculated as follows equation.

$$\text{Moisture content } \% = \frac{(M - M_0)}{M_0} \times 100 \quad (1)$$

where M is the weight of the sample before drying, and M_0 is the weight of the dry sample.

2.3.8. Ion exchange capacity measurement (IEC)

A known weight of chitosan or chitosan derivatives were added to a known volume of 0.1 M H_2SO_4 solution and the mixture was kept in shaking for 3 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 (IEC) of chitosan samples were calculated using according to the following equation [32].

$$\text{IEC (meq/g)} = [(V_2 - V_1) \times A] / W \quad (2)$$

where V_2 and V_1 are the volumes of NaOH required for complete neutralization of H_2SO_4 in the absence and presence of polymer, respectively, and A, is the Normality of NaOH, and W, is the weight of sample taken for analysis.

2.3.9. Water / organic solvent uptake measurements

Usually, liquid uptake (water, organic solvent) can be defined as the maximum amount that may be absorbed by the specific material under certain operating condition. Briefly, liquid uptakes can be calculated by immersing 0.1 g of each sample into a beaker containing 25 ml of liquid under constant shaking rate (100 rpm) for constant time (2 h). The samples were separated gently and the excess of adherent liquid was removed using filter paper, weighed immediately in a closed balance. The used organic solvents were (methanol, ethanol, 1-pentanol, and 1-octanol).

The following equation can express the liquid uptake:

$$\text{Liquid uptake}(\%) = \frac{W_t - W_0}{W_0} \quad (3)$$

where W_t is the weight of the swollen sample after certain time, and W_0 is the initial dry weight.

2.3.10. Batch oil adsorption experiment

The method developed for the measurement of different oil adsorption capacity of the sorbent was based on the Standard Test Method for Sorbent performance of adsorbents (ASTM F726-99) [33]. The used oil derivatives were (light crude oil, heavy crude oil, Mobil oil, and gas oil).

All of the sorption experiments were performed in water–oil system with the constant initial weight of oil. In water–oil system test, 5 ml of oil was poured into a 500 ml beaker containing 400 ml of artificial seawater with salinity 3.5% NaCl. Then, a known weight of the prepared samples was added to the system with shaking at 100 rpm for a constant adsorption time (2 h). Then, samples were removed gently and weighted accurately using the balance to determine the total weight of adsorbed oil and water. Finally, the oil adsorption capacity was calculated using the following equations:

$$\text{Oil adsorption capacity}(g/g) = (W_s - W_w - W_0)/W_0 \quad (4)$$

where W_s is the weight of saturated sorbent (water + oil + sorbent), W_w is the weight of adsorbed water, and W_0 is the initial dry weight of adsorbent.

3. Results and discussion

3.1. Electronic spectrum

Electronic spectrum of chitosan and its two derivatives as performed from 200 to 1000 nm were investigated in Fig. 2. Chitosan was showing absorption band around 300 nm, that attributed to n-σ* of amine groups [34]. Attachment

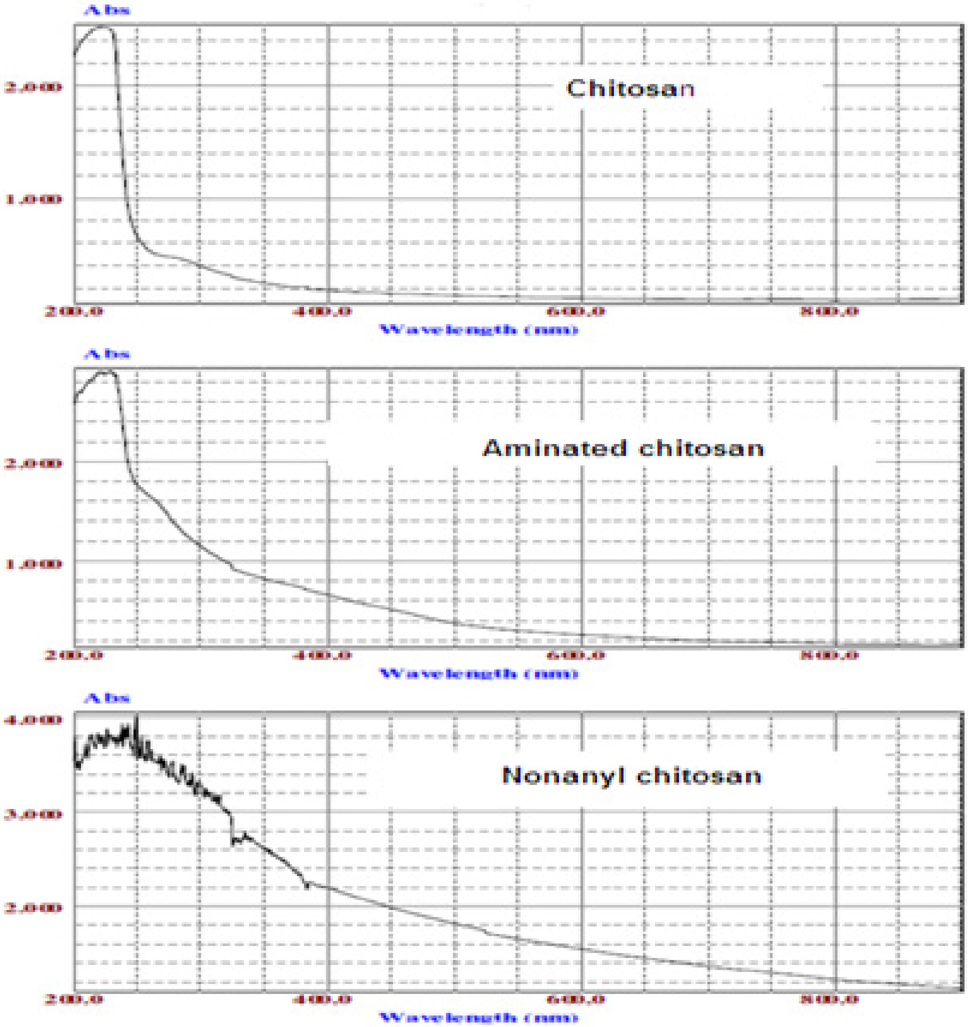

Fig. 2. Electronic spectrum of chitosan, aminated chitosan and nonanyl chitosan Schiff base.

of extra amine group to chitosan backbone illustrates the increase of peak intensity. Coupling of nonanal with chitosan amine groups generated a new type of transition n-π* that reflected on increasing the peak intensity and shifted it to higher wavelength [35].

3.2. FT-IR

The FT-IR spectra of chitosan, aminated chitosan and nonanyl chitosan were represented as shown in Fig. 3 (A–C). The FT-IR chart illustrates the regular bands of chitosan function groups; it can recognize a broad band around 3425 cm^{-1} corresponding to the stretching vibration of NH_2 and OH groups and O–H bending at 1394 cm^{-1} which indicates the presence of hydroxyl groups [36]. 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 [37]. Band at 1070 cm^{-1} ascribed to the stretching of the C-O-C bridge [38]. Additionally, for aminated chitosan spectrum (Fig. 3B), broad bands in the region 3441 cm^{-1} due to the stretching vibration of NH_2, OH functions. The shoulder at about 1406 cm^{-1} could be due to hydroquinone structures that produced from the reaction of aminated chitosan with PBQ [39,40], while, this shoulder was absent in the case of native chitosan. On the other hand, in the case of nonanyl chitosan derivative (Fig. 3C), the major differences are in the wide peaks at 3425 cm^{-1} for chitosan and at 3419 cm^{-1} for nonanyl chitosan that can be attributed to consumption of chitosan amine groups in Schiff base formation process. Also, absorption bands at 2910 cm^{-1} due to –CH stretching, the spectrum displays a strong absorption peak at 1589 cm^{-1} corresponding to the C=N stretching which formed between the aldehyde group and chitosan, On the other hand, there is no evidence of the characteristic band related to free aromatic aldehyde group near 1665 cm^{-1}.

3.3. TGA

Thermal gravimetric analysis (TGA) of chitosan and its two derivatives, aminated and nonanyl chitosan were presented in Fig. 4, and some detailed data are shown in Table 2. The first weight loss that starts from ambient temperature to about 150°C was attributed to the loss of moisture molecules that interrupted in polymer chain [40]. The increase of moisture content from 11.16% in chitosan to 12.31% in aminated chitosan can be referring to increase polymer hydrophilicity via amination process. In the other hand, limitation of moisture content in nonanyl chitosan to 8.61% may be attributed to the immobilized nonanyl group along polymer chain.

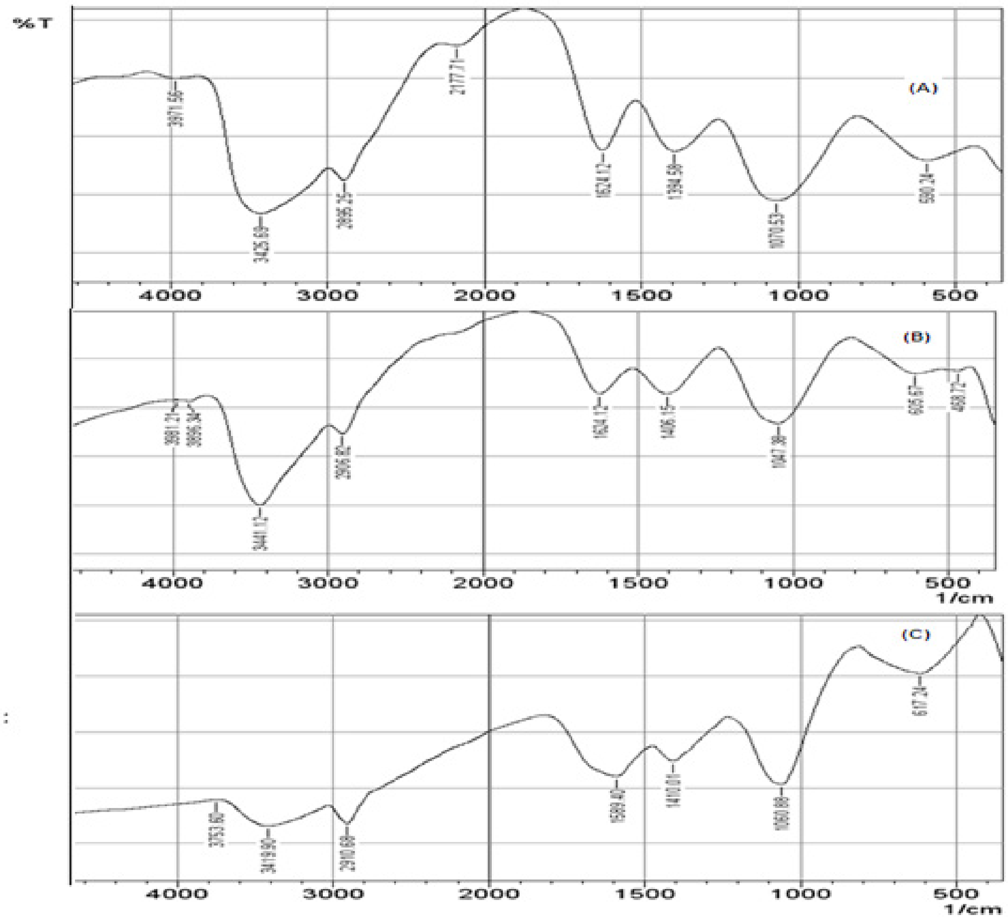

Fig. 3. FT-IR spectrum of (A) chitosan, (B) aminated chitosan, and (C) nonanyl chitosan Schiff base.

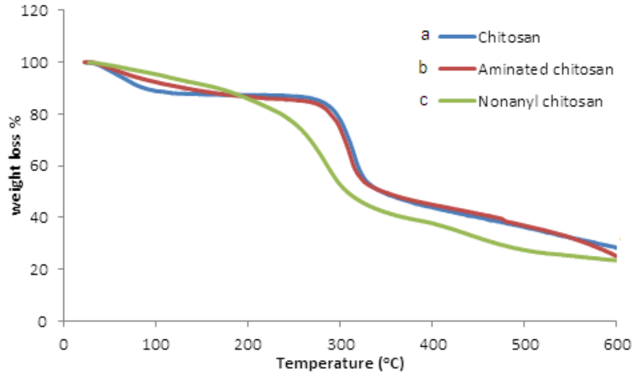

Fig. 4. TGA of (a) chitosan, (b) aminated chitosan, and (c) nonanyl chitosan Schiff base.

Table 2
Thermal gravimetric parameter chitosan, aminated chitosan and nonanyl Chitosan

Sample	Weight loss (%) ambient –150°C	T50 (°C)
Chitosan	11.16	346.85
Aminated chitosan	12.31	345.19
Nonanyl chitosan	8.61	307.12

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 [41]. There no significant difference in thermal stability between chitosan and aminated chitosan. Where, there is significant less stability of Schiff base derivatives that confirmed with published in the literature [42]. The third depuration that results from the decomposition which appears at high temperature may produce from the thermal degradation of a new crosslinked material formed by thermal crosslinking reactions occurring in the first stage of degradation process [43].

3.4. DSC

Fig. 5 demonstrates differential scanning calorimeter of chitosan, aminated chitosan and nonanyl chitosan. From the chart, it can observe the clear endothermic band around 100°C that attributed to evaporation of moisture content of samples, an increase in moisture content was found from chitosan to aminated chitosan and cinnamyl aminated chitosan. Chitosan as all polysaccharide has hydrophilic groups such as hydroxyl and amine groups, the ability of these groups to hold molecules of water – from surrounding or during preparation-increase with rising hydrophilic nature of polymer backbone. Aminated chitosan shows more hydrophilic character than chitosan itself that may be attributed to replacing amine groups with hydroxyl groups along polymer chains. As expected in nonanyl chitosan this peak almost neglected that may be attributed to increasing hydrophobic character of chitosan derivate by coupling with nonanal.

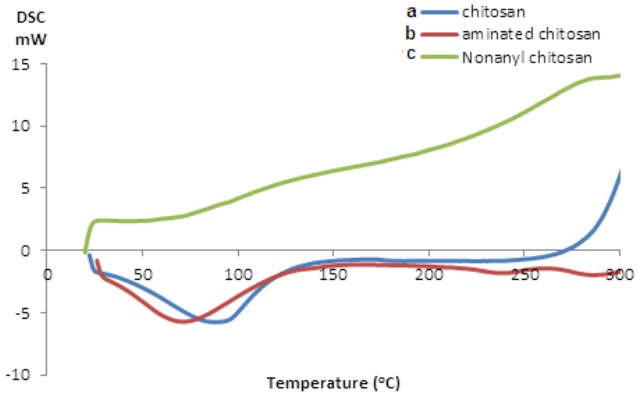

Fig. 5. DSC of (a) chitosan, (b) aminated chitosan, and (c) nonanyl chitosan Schiff base.

3.5. SEM

Morphological analysis of chitosan and its derivatives was performed with Scanning electron microscope as shown in Fig. 6. It is clear that there is an increasing in the surface roughness by amination process. Furthermore, pores were observed on the surface by coupling amine groups with nonanal, which may be referred to distortion of the internal structure of the polymer.

3.6. Wettability and moisture content

The wettability of a solid surface depends on two factors: the topographical microstructure and the surface chemical composition [44]. Contact angle measurements are used to investigate the oleophilic and hydrophobic characters for all the prepared chitosan and its derivatives using crude oil and water drops since it is very imperative to understand the wetting and adhesion properties that are essential for the sorbent materials that used in oil spill cleanup. According to Fig. 7 and Table 3, it was evident that the hydrophobic and oleophilic characters of nonanyl chitosan Schiff base were greatly improved and reached maximum values (127° and 36°) respectively compared to the native chitosan, which recorded (80° and 120°) using water and light crude oil droplets. These results could be attributed to the hydrophobic and oleophilic nature in addition to the long chains of nonanal which has the affinity to attach hydrocarbon compounds as oil. Furthermore, improvement of the hydrophilic characters of the aminated chitosan compared to the chitosan could be due to the presence of polar groups such as –OH and the extra hydrophilic –NH groups. On the other hand, the addition of the hydroquinone structures of aminated chitosan resultant from modification of chitin with p-benzoquinone (PBQ) molecules, where PBQ has the oleophilic nature. On the other hand, Table 3 also illustrates the relationship between the present functional groups and the capacity of the polymer to retain moisture molecules from enclosing atmosphere. The resultant jump in the hydrophilicity of aminated chitosan was responsible for raising its humidity due to the presence of excess free amino groups more than chitosan itself. On the other hand, the reducing of moisture content in case of nonanyl chitosan

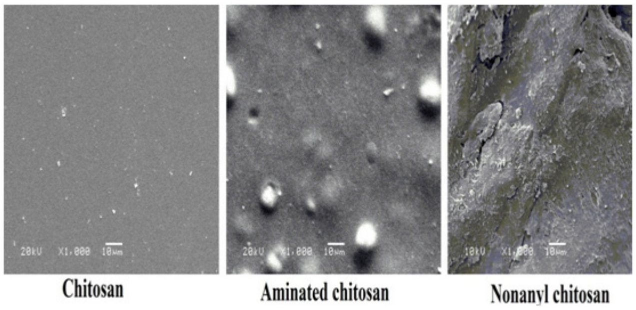
Chitosan Aminated chitosan Nonanyl chitosan

Fig. 6. SEM images of (A) chitosan, (B) aminated chitosan, and (C) nonanyl chitosan Schiff base.

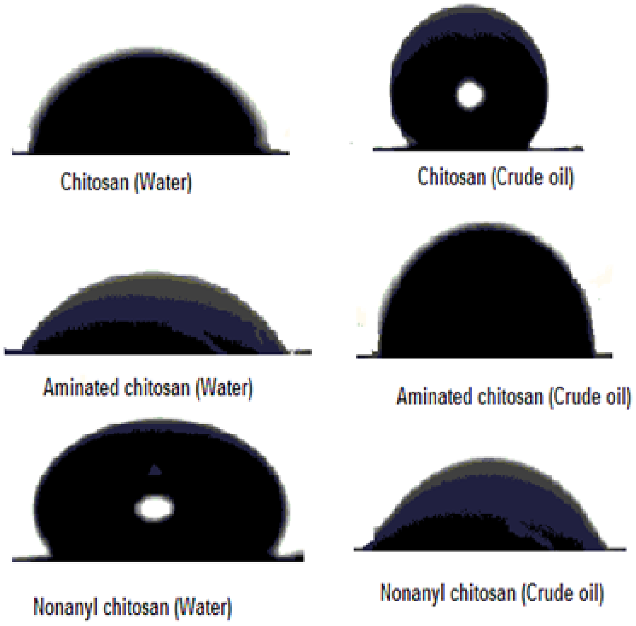
Chitosan (Water)
Chitosan (Crude oil)
Aminated chitosan (Water)
Aminated chitosan (Crude oil)
Nonanyl chitosan (Water)
Nonanyl chitosan (Crude oil)

Fig. 7. Contact angle images for chitosan, aminated chitosan, and nonanyl chitosan Schiff base using water and light crude oil droplets.

Table 3
Wettability and moisture content of chitosan, aminated chitosan, and nonanyl chitosan Schiff base

Sample	Moisture content (%)	θ (Water)	θ (Light crude oil)
Chitosan	6.9	80	120
Aminated chitosan	10.8	52.5	82.5
Nonanyl chitosan	3.8	127	36

Schiff base could be related to the consumption of amine group of native chitosan through coupling with nonanal.

3.7. IEC measurement

Ion exchange capacity of chitosan and its derivatives was surveyed and investigated in Fig. 8. The rise of free amine content in aminated chitosan was the primary purposes for increasing its IEC value. On the contrary, a dramatic reduction in IEC of nonanyl chitosan was recorded, which associated with loss of free amine groups surface in the coupling process with nonanal.

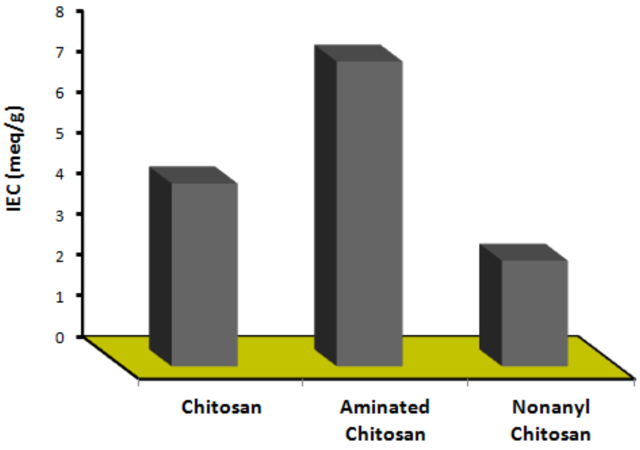

Fig. 8. Ion exchange capacity of chitosan, aminated chitosan and nonanyl chitosan Schiff base.

3.8. Water and organic solvent uptake behavior

Water and organic solvent uptake of the chitosan aminated chitosan and nonanyl chitosan were determined and summarized in Fig. 9. The obtained results display a remarkable increase in water uptake of the aminated derivative compared to chitosan and nonanyl chitosan. On the other hand, a sharp decline with nonanyl chitosan was recorded. Hydrophilic nature of chitosan was assigned to hydrophilic groups (i.e.; hydroxyl and amine groups) that spread along chain backbone, the addition of free amine groups in aminated chitosan support polymer hydrophilicity. Moreover, the coupling of amine groups with nonanal during nonanyl chitosan Schiff base formation could replace the hydrophilic groups with long aliphatic chains that effect on its polymer hydrophilicity. On the other hand, solvent uptake was carried out using various organic solvents namely; methanol, ethanol, 1-pentanol, and 1-octanol. It is important to note that the changes in the solvent uptake values may predominantly depend on the density of the organic solvents. Also, increasing the number of carbon chains results in a remarkable enhancement of solvent absorption, where solvent uptake amount grown in the order of methanol< ethanol < 1-pentanol < 1-octanol for the aminated and nonanyl chitosan derivatives. While, the previous arrangement reflected in the case of chitosan. Also, it was noticed that the organic solvent uptake amount in case of nonanyl chitosan was much more than chitosan and aminated chitosan. The presence of long hydrocarbon chains of nonanal in addition to the decrease in the free hydrophilic amine groups enhances the solubility of nonanyl chitosan in the organic solvent and then increasing its solvent uptake consequently. However, the presence of the quinone structure in aminated chitosan could support its uptake in the organic solvents compared to chitosan itself.

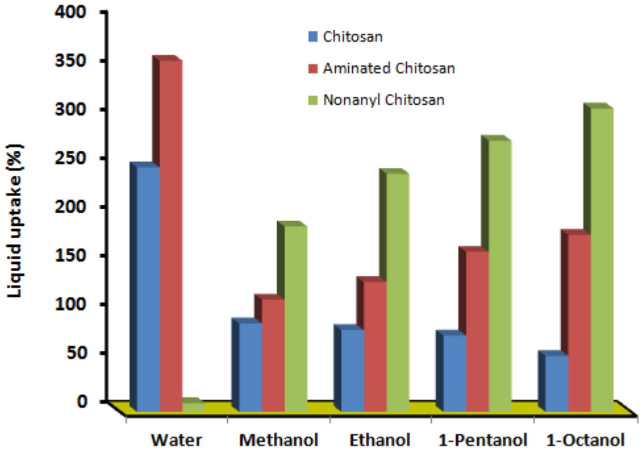

Fig. 9. Liquid uptake of chitosan, aminated chitosan, and nonanyl chitosan Schiff base.

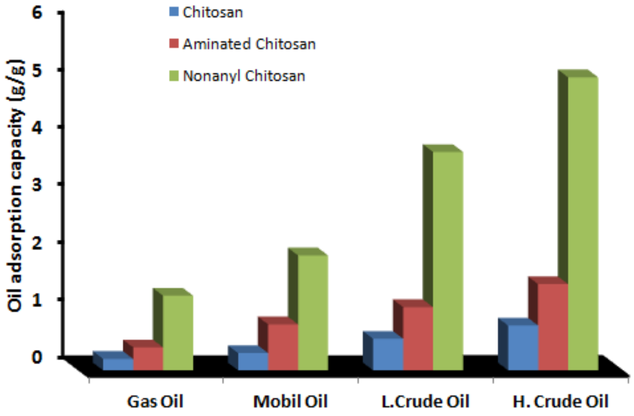

Fig. 10. Oil adsorption capacity for chitosan, aminated chitosan, and nonanyl chitosan derivatives, using gas oil, mobil oil, light and crude oil.

3.9. Oil adsorption behavior

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. Four types of oil specifically; gas oil, Mobil oil, light and crude oil were used to study the adsorption capacity behavior as shown in Fig. 10. 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 [45]:

- The attraction of opposite charges between chitosan/chitosan derivatives and oil.
- Tangle effect, in which chitosan acts as a network, getting involved around the drops of oil and catching them.

It was clear from results that there was a major increase in the oil adsorption capacity of nonanyl chitosan 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; gas oil < Mobil oil < light crude oil < heavy crude oil. Evidently, maximum adsorbent amounts were 0.78, 1.5, and 5.1 g/g, were recorded using heavy crude oil for chitosan, aminated chitosan, and nonanyl chitosan 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. Sokker et al. [14] reported the adsorption of crude oil (initial concentration 0.5–30 g/L) from aqueous solution using hydrogel of chitosan-based polyacrylamide (PAM) prepared by radiation-induced graft polymerization. The results obtained showed that the hydrogel prepared at the concentration of 40% acrylamide (AAm) and a radiation dose of 5 kGy has high removal efficiency of crude oil 2.3 g/g at pH 3. Barros et al. [26] presented study to evaluate the capacity of adsorption of crude oil spilled in seawater by chitin flakes, chitin powder, chitosan flakes, chitosan powder, and chitosan solution. The results showed that, although chitosan flakes had a better adsorption capacity by oil (0.379 ± 0.030 grams oil per gram of adsorbent), the biopolymer was sinking after adsorbing oil. Chitosan solution did not present such inconvenience, despite its lower adsorption capacity (0.013 ± 0.001 grams oil per gram of adsorbent). It was able to form a polymeric film on the oil slick, which allowed to restrain and to remove the oil from the samples of sea water. The study also suggests that chitosan solution 0.5% has greater efficiency against oil spills in the alkaline medium than acidic medium. Srinivasan and Viraraghavan [8] evaluate efficiencies of chitosan to remove oil from water. The oils used in the study were standard mineral oil, vegetable oil and cutting oil. The adsorption capacity of chitosan was found around 100 mg/g for all types of oils. Germ et al. [47] studied the removal of heavy oil using chitosan microspheres. The results obtained show that the chitosan microspheres used as natural polymeric resins perform well in removing heavy oil from produced water, with adsorption efficiency greater than 90% at the beginning of the test, i.e., over than 180 ppm of this oil was removed from the oily water for both flows used. Ummadisingu and Gupta [48] studied the kinetics for the removal of oil from oil–water solutions using chitosan. The effect of various influencing parameters such as contact time, pH, initial concentration, and mass of adsorbent were studied. The equilibrium time for adsorption of oil on chitosan was obtained as 6 min. The maximum capacity of chitosan to adsorb oil from oil–water solution was found to be 17.96 g/g of adsorbent. The removal efficiency was observed to be higher in the acidic medium. The adsorption properties of chitosan have been attributed mainly to its positive charge. The comparison between the results as mentioned above is not available since the conditions used in each study are entirely different. However, the high adsorption capacity obtained by Ummadisingu and Gupta is referred to the use of high concentration of oil-water solution; 185 g/L.

4. Conclusion

Two different chitosan derivatives named aminated and nonanyl chitosan Schiff base were prepared based on marine waste sources. FT-IR, TGA, DSC, and SEM characterization tools were applied to verify the physicochemical changes after modification of chitosan. The influence of chemical modification of chitosan on the hydrophilic/hydrophobic properties was investigated using wettability and liquid uptake experiments. High oil selectivity of nonanyl chitosan was substantially observed while higher water uptake was recorded by aminated chitosan. The effect of both type and viscosity of oil on the adsorption capacity of all prepared materials were optimized. The results showed that nonanyl chitosan Schiff base can adsorb 5.1 g/g of heavy crude oil while only 9% of water could be uptake. The results of this study provided an approach to fabricate hydrophobic/oleophilic adsorbents based on chitosan derivatives especially nonanyl chitosan Schiff base for removing highly viscous crude oil spills from the surface of the water.

References

[1] H. Sarkheil, J. Tavakoli, Oil-polluted water treatment using nano size bagasse optimized isotherm study, Eur. Online. J. Nat. Soc. Sci., 4 (2015) 392–400.

[2] M.O. Adebajo, R.L. Frost, J.T. Kloprogge, O. Carmody, S. Kokot, Porous materials for oil spill cleanup, a review of synthesis, J. Porous. Mater., 10 (2003) 159–170.

[3] H. Lee, Impacts of oil spills : ecological, human health and economic. Plan II Honors Program, The University of Texas at Austin (2011): pp. 1–70.

[4] C. Senanurakwarkul, M. Program, T. Chavarnakul, The study of factors influencing the decision to select the use of oil sorbent in Thailand, IJRMT, 2 (2012) 603–609.

[5] L. Wang, L. Zhuo, Y. He, Y. Zhao, W. Li, X. Wang, F. Lee, Oil spill identification, Guang Pu Xue Yu Guang Pu Fen Xi? 24 (2004) 1537–9.

[6] ITOPF, Technical Information Paper, Use of booms in oil pollution response (2013). Available from: http://www.itopf.com/knowledge-resources/documents-guides/document/tip-3-use-of-booms-in-oil-pollution-response.

[7] A.A. Al-Majed, A.R. Adebayo, M.E. Hossain, A novel technology for sustainable oil spills control, Environ. Eng. Manag. J., 13 (2014) 265–274.

[8] A. Srinivasan, T. Viraraghavan, Oil removal from water using biomaterials, Biores. Technol., 101 (2010) 6594–6600.

[9] A. Lewis, B.K. Trudel, R.C. Belore, J.V. Mullin, Large scale dispersant leaching and effectiveness experiments with oils on calm water. Mar. Pollut. Bull., 60 (2010) 244–254.

[10] M. Hussein, A.A. Amer, I.I. Sawsan, Heavy oil spill cleanup using law grade raw cotton fibers: Trial for practical application, J. Pet. Technol. Alter. Fuels., 2 (2011) 132–140.

[11] S. Panpanit, C. Visvanathan, The role of bentonite addition in UF flux enhancement mechanisms for oil/water emulsion, J. Membr. Sci., 184 (2001) 59–68.

[12] M. Inagaki, A. Kawahara, Y. Nishi, N. Iwashita, Heavy oil sorption and recovery by using carbon fiber felts, Carbon, 40 (2002) 1487–1492.

[13] H. Zhu, S. Qiu, W. Jiang, D. Wu, C. Zhang, Evaluation of electrospun polyvinyl chloride/polystyrene fibers as sorbent materials for oil spill cleanup, Environ. Sci. Technol., 45 (2011) 4527–4531.

[14] H.H. Sokker, N.M. El-Sawy, M.A. Hassan, B.E. El-Anadouli, Adsorption of crude oil from aqueous solution by hydrogel of chitosan based polyacrylamide prepared by radiation induced graft polymerization, J. Hazard. Mater., 190 (2011) 359–365.

[15] S.M. Sidik, A.A. Jalil, S. Triwahyono, S.H. Adam, M.A.H. Satar, B.H. Hameed, Modified oil palm leaves adsorbent with enhanced hydrophobicity for crude oil removal, Chem. Eng. J., 203 (2012) 9–18.

[16] B. Tansel, B. Pascual, Removal of emulsified fuel oils from brackish and pond water by dissolved air flotation with and without polyelectrolyte use: pilot-scale investigation for estuarine and near shore applications, Chemosphere, 85 (2011) 1182–1186.

[17] M. Saito, N. Ishii, S. Ogura, S. Maemura, H. Suzuki, Development and water tank tests of Sugi bark sorbent (SBS), Spill. Sci. Technol. B., 8 (2003) 475–482.

[18] H. Choi, H. Kwon, J.P. Moreau, Cotton nonwovens as oil spill cleanup sorbents, Textile Res. J., 63 (1993) 211–218.

[19] S. Nenkova, R. Garvanska, S. Jelev, Fibrous-wood sorbent for eliminating oil pollution, Autex Res. J., 4 (2004) 157–163.

[20] C. Cojocaru, M. Macoveanu, I. Cretescu, Peat-based sorbents for the removal of oil spills from water surface: application of artificial neural network modeling, Colloids and Surfaces A: Physicochem. Eng. Aspects, 384 (2011) 675–684.

[21] M.A. Hubbe, O.J. Rogas, M. Fingas, B.S. Gupta, Cellulosic substrates for removal of pollutants from aqueous systems: 3. Spilled oil and emulsified organic liquids, Bioresources, 8 (2013) 3038–3097.

[22] R. Wahi, L.A. Chuah, T.S.Y. Choong, Z. Ngaini, M.M. Nourouzi, Oil removal from aqueous state by natural fibrous sorbent: an overview, Sep. Purif. Technol., 113 (2013) 51–63.

[23] M.S. Mohy Eldin, E.A. Soliman, A.I. Hashem, T.M. Tamer, Antimicrobial activity of novel aminated chitosan derivatives for biomedical applications, Adv. Polym. Technol., 31 (2012) 414–428.

[24] M.S. Mohy Eldin, A.I. Hashem, A.M. Omer, T.M. Tamer, Preparation, characterization and antimicrobial evaluation of novel cinnamyl chitosan Schiff base, Int. J. of Adv. Res., 3 (2015) 741–755.

[25] E.M. El-Sayed, T.M. Tamer, A.M. Omer, M.S. Mohy Eldin, Development of novel chitosan schiff base derivatives for cationic dye removal: methyl orange model, Desal. Water Treat., 57(47) (2016) 22632–22645

[26] F.C.D.F. Barros, L.C.G. Vasconcellos, T.V. Carvalho, R.F.D. Nascimento, Removal of petroleum spill in water by chitin and chitosan, Orbital: Electron. J. Chem., 6 (2014) 70–74.

[27] M.A.L. Milhome, D. Keukeleire, J.P. Ribeiro, R.F. Nascimento, T.V. Carvalho, D.C. Queiroz, Removal of phenol and conventional pollutants from aqueos effluent by chitosan and chitin, Quím. Nova 32 (2009) 2122–2127.

[28] A.R. Gentili, M.A. Cubitto, M.E. Ferrero, M.S. Rodriguéz, Bioremediation of crude oil polluted seawater by a hydrocarbon-degrading bacterial strain immobilized on chitin and chitosan flakes, Int. Biodeterior. Biodegrad., 57 (2006) 222–228.

[29] M.M. Islama, S.M. Masumb, M.M. Rahmana, M.A.I. Mollab, A.A. Shaikhc, S.K. Roya, Preparation of chitosan from shrimp shell and investigation of its properties, Int. J. Basic App. Sci. IJBAS-IJENS., 11 (2011) 77–80.

[30] G. Rigby, Substantially undegraded deacetylated chitin and processes for producing the same, patent. USA., 2 (1936) 040, 879.

[31] M.S. Mohy Eldin, E.A. Soliman, A.I. Hashem, T.M. Tamer, Antibacterial activity of chitosan chemically modified with new technique, Trends Biomater. Artif. Organs, 22 (2008) 121–133.

[32] S.P. Ramnani, S. Sabharwal, Adsorption behavior of Cr (VI) onto radiation crosslinked chitosan and its possible application for the treatment of waste water containing Cr (VI), React. Funct. Polym., 66 (2006) 902–909.

[33] B. Alireza, T. Jun, M. Gordon, Standardization of oil sorbent performance testing, J. Test. Eval., 43 (2015) 1–8.

[34] M.S. Mohy Eldin, A.I. Hashem, A.M. Omer, T.M. Tamer, Wound dressing membranes based on chitosan: Preparation, characterization and biomedical evaluation. Int. J. of Adv. Res., 3 (2015) 908–922.

[35] D.D. Perrin, W.L.F. Armarego, D.D. Perrin, Purification of laboratory chemicals, Pergamon Press. Second Edition, Oxford (1980): pp. 66–72.

[36] T. Sun, D. Zhou, J. Xie, F. Mao, Preparation of chitosan oligomers and their antioxidant activity, Eur. Food Res. Technol., 225 (2007) 451–456.

[37] J. Zhang, Q. Wang, A. Wang, Synthesis and characterization of chitosang-poly (acrylic acid)/attapuligate supersorbent composites, Carbohydr. Polym., 68 (2007) 367–374.

[38] G.A. Mun, Z.S. Nurkeeva, S.A. Dergunov, I.K. Nama, T.P. Maimakov, E.M. Shaikhutdinov, S.C. Lee, K. Park, Studies on graft copolymerization of 2-hydroxyethyl acrylate onto chitosan, React. Funct. Polym., 68 (2008) 389–395.

[39] S. Kumara, P.K. Duttab, J. Koh, A physico-chemical and biological study of novel chitosan–chloroquinoline derivative for biomedical applications, Int. J. Biol. Macromol., 49 (2011) 356–361.

[40] T.M. Tamer, A.M. Omer, M.A. Hassan, M.E. Hassan, M.M. Sabet, M.S. Mohy Eldin, Development of thermo-sensitive poly N-isopropyl acrylamide grafted chitosan derivatives, J. Appl. Pharm. Sci., 5 (2015) 001–006.

[41] A. Pawlak, M. Mucha, Thermogravimetric and FTIR studies of chitosan blends. Thermochim Acta., 396 (2003) 153–166.

[42] E.R. Kenawy, F.I. Abdel-Hay, M.S. Mohy Eldin, T.M. Tamer, E.M.A.E. Ibrahim, Novel aminated chitosan-aromatic aldehydes schiff bases: synthesis, characterization and bio-evaluation, Int. J. Adv. Res., 3 (2015) 563–572.

[43] J. Zawadzki, H. Kaczmarek, Thermal treatment of chitosan in various conditions, Carbohydr. Polym., 80 (2010) 394–400.

[44] X. Zhang, Z. Li, K. Liu, L. Jiang, Bioinspired multifunctional foam with self-cleaning and oil/water separation, Adv. Funct. Mater., 23 (2013) 2881–2886.

[45] R.A.A. Muzzarelli, Chitin, Pergamon Press, 1st Edition. (1977).

[46] A.K. Aboul-Gheit, F.H. Khalil, T. Abdel-Moghny, Adsorption of spilled oil from seawater by waste plastic, Oil. Gas. Sci. Technol. Rev. IFP., 61 (2006) 259–268.

[47] I.C.D.S. Grem, B.N.B. Lima, W.F. Carneiro, Y.G.D.C. Queirós, C.R.E. Mansur, Chitosan microspheres applied for removal of oil from produced water in the oil industry, Polímeros, 23 (2013) 705–711.

[48] A. Ummadisingu, S. Gupta, Characteristics and kinetic study of chitosan prepared from seafood industry waste for oil spills cleanup, Desal. Water Treat., 44 (2012) 44–51.