



Efficient eco-friendly crude oil adsorptive chitosan derivatives: kinetics, equilibrium and thermodynamic studies

R.E. Khalifa^{a,*}, A.M. Omer^a, T.M. Tamer^a, A.A. Ali^b, Y.A. Ammar^c, M.S. Mohy Eldin^{a,*}

^aPolymer materials research department, Advanced Technologies and New Materials Research Institute (ATNMRI), City of Scientific Research and Technological Applications (SRTA-City), New Borg El-Arab City, P.O. Box: 21934 Alexandria, Egypt, email: randaghonim@gmail.com (R.E. Khalifa), mohyeldinmohamed@gmail.com (M.S. Mohyeldin)

^bEgyptian General Petroleum Corporation (EGPC), Egypt

^cChemistry Department, Faculty of Science, Al-Azhar University, Egypt

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ABSTRACT

In the present study, low-cost oil adsorptive materials based on chitosan (CS) and its functionalized derivatives (aminated chitosan (AmCS) and nonanyl chitosan schiffbase (NCS) were undertaken. The chemical structure of the CS sorbents, as well as its surface morphologies, was confirmed by Fourier infrared (FT-IR) spectroscopy and scanning electron microscope (SEM). Parameters affecting the sorption capacity such as reaction time, crude oil concentration, adsorbent dose, and temperatures were studied. Equilibrium studies of the oil sorption data have been analysed using the linear forms of Langmuir, Freundlich, Temkin, and Dubin-Radushkevich (D-R) isotherm models. The sorption kinetics was investigated by the pseudo-first and the pseudo-second-order, the Elovich, the intra particle diffusion kinetic, and the Boyd models. The equilibrium data were found to fit adequately with the Langmuir with maximum mono layer sorption capacities 32.154, 45.045, and 59.172 g/g for CS, AmCS, and NCS respectively. The kinetics of the oil sorption process onto chitosan derivatives could be described as pseudo-second-order and a film diffusion controlled mechanism. Besides, thermodynamic parameters computed from Van't Hoff plot confirmed the process to be endothermic, favourable and spontaneous.

Keywords: Oil spill; Chitosan derivatives; Kinetics; Isotherms; Thermodynamics

1. Introduction

Oil is one of the essential energy sources for human beings living in the developing world [1]. The unintentional discharge of oil in an aquatic ecosystem in the form of frequent oil spill often occur during oil utilisation process (exploration, routine shipping, processing, dumping, and run-offs from industry) [2] has a significant challenge on a global scale [3]. Oil Spills have been a matter of great concern for ecologists and environmental scientists since crude oil are one of the utmost critical organic pollutants in marine environments [4]. From environmental concern, oil leakage has to become a severe problem affecting the marine

life survival, shore life, and vegetation, i.e. seabirds, marine animals, terrestrial animals and other creatures. Further disruptions in the food chain [5] may occur as it can upset organisms by both physical and toxicological processes [6]. Also, such spilt oils also affect humans through the skin, eye irritation, and inhalation. In addition to ecological anxieties, spills in coastlines may have the economic matter in tourism, recreational areas, and fisheries industry as well as energy loss [7,8]. Oil spill treatment methods [9,10] classified as physical [11]/mechanical [12,13], chemical, and biological [13]. Until now, sorption technique [14] (mechanical recovery) has fascinated increasing academic and industrialised interests as one of the most simple, inexpensive, and effectual technologies, not only for the probability of

*Corresponding author.

whole oil cleanup but also for the opportune post-treatment of the oil-loaded sorbent with a solid or semisolid phase physical restraint [15]. Subsequently, ideal sorbents for oil spill cleanup should be characterised by oleophilicity-hydrophobicity, buoyancy, high sorption capacity, and higher absorption rate. Currently, various materials can be used as sorbents for spill sorption including low costs natural renewable materials [16–18] as sawdust, milkweed floss, cotton, wool, kenaf, sisal and kapok. On the other hand, several hydrophobic/oleophilic materials suffered from confines such as being readily fouled by oil or being blocked up due to the intrinsic oleophilicity [19,20]. As seen, an eco-friendly and effective alternate is requisite for the cleaning up of the oil spill.

Chitosan is a poly-glucosamine biopolymer and N-deacetylated chitin [21,22] derivative though this N-deacetylation is almost never complete [8]. Crustacean's shells, particularly of shrimp, lobster, cuttlefish, squid and crab are the primary commercial sources of chitin, and it is also found in molluscs, fungal cell wall and insects [23,24]. Besides, chitosan is a valuable biodegradable, biocompatible and nontoxic natural heteropolymer [25].

Further, chitosan has an excellent chelating influence related to the abundant free amino and hydroxyl groups along its backbone which prompted modifications and chemical transformation as Schiff bases formation via chemical reaction of the free amino groups with the active carbonyl group in ketones and aldehydes. Thus, it can be used efficiently in an extensive range of applications covering the areas of biomedicine, hydrogels, drug delivery, food packaging, and wastewater treatment [26,27]. Also, the obtained $-RC=N-$ groups in chitosan Schiff bases improving their adsorption complexation properties towards heavy metals, dyes, phenols, and oils. To the best of our knowledge, few types of research have stated the applicability of chitosan Schiff bases as natural sorbent materials for oil spills [28]. Inspired by this observation, we developed functional sorbent materials based on chitosan (CS).

The aim of the present work is to study the applicability of the sorption of the crude oil spills by two chitosan derivatives compared with the native chitosan biopolymer. The ability of different isotherms for modelling the equilibrium adsorption data of crude oil was established. Moreover, the kinetic studies have also been conducted to determine the rate of oil sorption and to suggest probable oil sorption mechanisms. Finally, the results were compared with the performance of other published data of different oil sorbents.

2. Experimental

2.1. Materials

Shrimp shells were collected from seafood restaurants in (Alexandria-Egypt). P-benzoquinone (PBQ, 99%), nonanal (95%), and sulfuric acid (98%) were obtained from Sigma-Aldrich (Germany). Sodium hydroxide (99%), ethanol (99%), hydrochloric acid (37%), and acetic acid (98%) were purchased from El-Nasr Company (Alexandria-Egypt). Ethylenediamine (EDA, 99%) was brought from Alfa Aesar (Germany). Heavy Land Egyptian crude oil was supplied from Belayem Petroleum Company (Egypt).

2.2. Preparation of chitosan derivatives

Chitosan was synthesised using methodology previously designated [29,30]. In this approach typically, chitin was extracted firstly from shrimp shells via simple demineralisation of shells in 5% (w/v) HCl solution, followed by rinsing the shells with distilled water, afterwards treated with 5% (w/v) NaOH. 50% (w/v) of an aqueous NaOH solution was used for the elimination of acetyl groups of the resultant chitin to produce CS. Thereafter, CS was washed several times till neutrality, purified by dissolving in 2% (w/v) acetic acid overnight, followed by rinsing with distilled water after precipitation using 5% (w/v) NaOH.

Regarding our previous work [31], AmCS derivative was prepared as follows; 4 g of chitin was dispersed in 50 mL of 6.9 mM PBQ solution and the pH was adjusted to 10 with 1 molar NaOH under continuous stirring at 30°C for 6 h. The obtained PBQ-conjugated chitin was then washed and discrete in 50 mL of 6.9 mM EDA solution with continuous stirring for a further 6 h at 30°C. The unreacted EDA was removed by washing. Next, the resultant aminated modified chitin was simply treated with 50% NaOH aqueous solution for 6 h at 120–150°C to obtain AmCS. The later was separated and washed with distilled water to get rid of the excess NaOH. On the other hand, NCS Schiff base was prepared as mentioned in our previous work [26] by dissolving 1 g of the prepared chitosan in 50 mL of 2% (w/v) acetic acid at 25°C for 6 h. Then, 1.86 mM Nonanal in 10 mL ethanol was dropped slowly to CS solution while keep stirring at 50°C for extra 6 h. A deep yellow coloured NCS Schiff base was formed after precipitation with 5% NaOH, followed by filtration, repetitive washing with water/ethanol, and finally drying for 24 h in a vacuum oven at 60°C.

2.3. Characterization

The chemical characteristics of the synthesised CS and its derivatives were investigated by Fourier-transform infrared (FT-IR) spectroscopy (Shimadzu FTIR-8400 S-Japan). In addition, investigation of the morphological properties was carried out using scanning electron microscopy (SEM, Joel Jsm 6360LA-Japan).

2.4. Kinetic and equilibrium studies

In order to describe the equilibrium and the kinetics of the oil sorption process onto the chitosan and its modified forms, the batch technique was employed to monitor the effect of the contact time (10–240 min), the initial crude oil concentration (8.33–50 g/L), the adsorbent dose (0.1–1 g), and the reaction temperature (25–40°C). A constant weight of the sorbent (0.1 g) was spread over the surface of 500 mL beaker holding 300 mL of artificial seawater composed from distilled water contains 3.5% NaCl. The sorbent materials were shaken with polluted seawater at 100 rpm for altered intervals at particular temperatures. Then, samples were removed gently and weighted perfectly using the balance to determine the total weight of adsorbed oil and water. Based on the standard test method for sorbent performance of adsorbents (ASTM F726-99) [32], the oil adsorption capacity at any time, q_t (g/g) was calculated using the following equation:

$$\text{Oil adsorption capacity} \left(\frac{\text{g}}{\text{g}} \right) = \frac{(W_s - W_w - W_0)}{W_0} \quad (1)$$

where W_s (g), is the weight of the saturated sorbent (water + oil + adsorbent), W_w is the weight of the adsorbed water, and W_0 is the initial dry weight of the adsorbent. The extraction separation using n-hexane as the solvent was used to determine the water content in the adsorbent sample.

2.5. Kinetics model fittings

Adsorption kinetics describes the rate of the solute uptake at the solid-solution interface and provides valuable information about the reaction pathways and mechanisms. The kinetics of crude oil sorption on chitosan and its derivatives were analysed using a simulation of kinetic models. The correlation coefficients (R^2) expresses the identification between experimental data and the model calculated values.

2.5.1. The pseudo-first-order kinetic model

This model suggests that the uptake rate of crude oil with time is directly related to the available amount of the active surface sites. The equation that describes the pseudo-first-order linear kinetic model was [33]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

where q_t and q_e (g/g) are the amounts of oil adsorbed on the adsorbent at time t and at equilibrium. k_1 is the first-order reaction rate constant (min^{-1}).

2.5.2. The pseudo-second-order kinetic model

The pseudo-second-order kinetic model [34] assumes that the chemical adsorption involving valence forces through exchange or sharing of electrons between sorbate and sorbent and could be the rate-limiting stage. The equation that describes this model was:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where k_2 (g/g·min) is the constant rate parameter of the pseudo-second sorption.

The initial adsorption rate, h (mol/g·min) is expressed as:

$$h = k_2 q_e^2 \quad (4)$$

2.5.3. The Elovich model

The simple Elovich model is one of the best suitable models for describing the kinetics of chemisorption whereby active sites are heterogeneous and therefore exhibit different activation energies for chemisorption [35]. A plot of q_t vs $\ln t$ should present a linear relationship for the applicability of simple Elovich kinetic according to the following equation:

$$q_t = \beta \ln(\alpha \beta) + \beta \ln t \quad (5)$$

where β is revealing the number of available adsorptive sites and α is the adsorption quantity [34].

2.5.4. The intra particle diffusion model

The effect of intra-particle diffusion is estimated by the evaluation of the initial adsorption rate. During a solid/liquid adsorption process, the adsorbate transported from the bulk solution phase to the internal active sites is usually controlled by liquid phase external mass transfer (boundary-layer diffusion), or mass transfer through pores (intra particle mass diffusion), or both [36]. The slowest step, which might be either pore or film diffusion, would be the overall rate-governing step of the adsorption process [37]. Weber–Morris noticed that in many adsorption cases, solute uptake varies almost proportionally with $t^{0.5}$ rather than with the contact time t according to [38]:

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

where k_p (g/g·min) is the intra-particle diffusion rate constant, C is an intercept that gives an idea about the boundary layer thickness. If the intra particle diffusion occurs, then q_t vs $t^{0.5}$ will be linear, and if the plot passes through the origin, then the rate controlling process merely is due to the intra particle diffusion. Otherwise, some other mechanisms in consort with intra particle diffusion are also convoluted.

2.5.6. Boyd model

Boyd model is widely used to determines the actual slowest step in the sorption process; whether it is the primary resistance to mass transfer in the thin film (boundary layer) surrounding the adsorbent particle, or the resistance to diffusion inside the pores. The kinetic data were analysed by [39]:

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 Bt) \quad (7)$$

where F is the fraction of solute adsorbed at any time and is calculated from $F = q_t/q_e$.

The following approximations are used to calculate the values of Bt for each fraction adsorbed:

$$\text{For } F < 0.85 \quad Bt = \left(\sqrt{\pi} - \sqrt{\pi - \left(\frac{\pi^2 F}{3} \right)} \right)^2 \quad \text{For } F < 0.8 \quad (8)$$

$$\text{For } F > 0.85 \quad Bt = -0.498 - \ln(1 - F) \quad \text{For } F > 0.85 \quad (9)$$

The linearity test of Bt vs t was used to distinguish between the film and particle-diffusion controlled adsorption. If the plot is a straight line passing through the origin, the adsorption rate was governed by particle diffusion; otherwise, it was administrated by the film diffusion. In contrast, the slow diffusion of oil molecules leads to slow solvation, indicating that the equilibrium would take a long time [35,40].

2.6. Equilibrium isotherms

Several models are always employed to interpret the equilibrium data. In this research, the Langmuir, Freundlich, Temkin, and Dubin-Radushkevich (D-R) models were utilised to explain the experimental data [41].

2.6.1. Langmuir isotherm

The basic assumption of the Langmuir is the formation of mono layer adsorption with homogeneous adsorption energy [41]. Also, it has been conventionally used to give an idea about the maximum adsorption capacity [42]. The following equation represents the generalised linear form of the Langmuir isotherm:

$$\frac{C_e}{q_e} = \frac{1}{(q_{max}K_L)} + \frac{C_e}{q_{max}} \quad (10)$$

where C_e (g/L) is the liquid phase sorbate concentration at equilibrium, q_e (g/g) is the amount of adsorbate adsorbed per unit mass of adsorbent. q_{max} (g/g) is the maximum adsorption capacity. K_L (L/g) is the Langmuir constant that is referred to as the empathy of binding sites and is related to the energy of sorption.

The essential characteristics and the feasibility of a Langmuir isotherm can be expressed regarding a dimensionless constant separation factor R_L as follows [43]:

$$R_L = \frac{1}{1 + K_L C_0} \quad (11)$$

where C_0 (g/L) is the initial crude oil concentration. R_L values specify the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable if $R_L > 1$.

2.6.2. Freundlich isotherm

This model assumes that the adsorption occurs on a multilayer heterogeneous surface with non-identical sites with non-uniform distributions of the heat of adsorption over the surface [43]. The equation that describes the Freundlich isotherm model is given in the following linear form:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (12)$$

where $1/n$ and K_f are the Freundlich constants related to adsorption intensity and adsorption capacity.

2.6.3. Temkin isotherm

This model describes the effects of indirect adsorbent/adsorbate interactions on the adsorption process. It predicted that the heat of adsorption in the adsorbent layer decreases linearly with the surface coverage owing to the adsorbent-adsorbate interaction and this drop is expected to be linear rather than logarithmic. Moreover, this model assumed the uniform distribution of the binding energies, up to maximum binding energy [42]. The linear equation expressed as:

$$q_e = B \ln KT + B \ln C_e \quad (13)$$

where B (J/mol) is the heat of adsorption, and K_T (L/g) is the maximum binding energy of adsorbent and adsorbate.

2.6.4. Dubin-Radushkevich (D-R) isotherm

This model is commonly used to describe the sorption isotherms of single solute systems [20]. The D-R isotherm, apart from being an analogue of the Langmuir isotherm, is more general than the Langmuir isotherm because it rejects the homogeneous surface or constant adsorption potential [44]. According to the linear form of the D-R isotherm model:

$$\ln q_e = \ln q_{D-R} - K_{ad} \epsilon^2 \quad (14)$$

The constant K_{ad} gives the mean free energy (E) of sorption per molecule of the sorbate when it is transferred to the surface of the solid from infinity in the solution. This energy can be figured with the following relationship:

$$E = \frac{1}{\sqrt{2K_{ad}}} \quad (15)$$

2.7. Thermodynamics

Various thermodynamic parameters such as Enthalpy (ΔH), Entropy (ΔS), and Gibbs free energy (ΔG) were obtained by the isothermal studies [45].

ΔG can be denoted by the van't Hoff equation:

$$\Delta G = -RT \ln K \quad (16)$$

where K_0 can be calculated by the subsequent equation:

$$K_D = \frac{Q_e}{C_e} \quad (17)$$

The Enthalpy (ΔH) and Entropy (ΔS) are calculated using the following equation:

$$\ln K_D = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (18)$$

where ΔG and ΔH are in (kJ/mol), ΔS is in (J/mol-K), T is the adsorption temperature in (K), and R is the universal gas constant (8.314 J/mol).

3. Results and discussion

3.1. Adsorbent characterization

3.1.1. FT-IR

The FT-IR spectra of CS and its functionalized forms were described in Fig. 1. The chart explains the systematic bands of CS i.e.; a broadband appears at 3425 cm^{-1} related to the stretching vibration of OH and NH_2 groups. Also, the bending O-H at 1394 cm^{-1} specifies the presence of OH groups [46]. Methyl and methylene groups were identified by the weak absorption peak (C-H stretch) at 2895 cm^{-1} .

The typical peak at 1624 cm^{-1} refers to the C=O stretching [47] and at 1070 cm^{-1} assigned to the C–O–C bridge [48] in the CS structure. On the other hand, the spectrum of AmCS, illustrate a broad band at 3441 cm^{-1} as a result of the stretching vibration of OH and NH₂ functions. While the shoulder appears at 1406 cm^{-1} may be due to the formation of hydroquinone produced during the reaction of chitin with PBQ [49]. Alternatively, the NCS, clarifies major differences in the wide peaks at 3425 cm^{-1} for CS and at 3419 cm^{-1} for NCS which regarded to consumption of the CS amine groups in the NCS Schiff base formation. Likewise, bands at 2910 cm^{-1} corresponding to –CH stretching, whereas the strong peaks located at 1589 cm^{-1} ascribed to the C=N stretching which formed between the CS and the aldehyde group.

3.1.2. SEM

Morphological investigation of CS and its Schiff bases is shown in Fig. 2. It is noticeable that the amination process

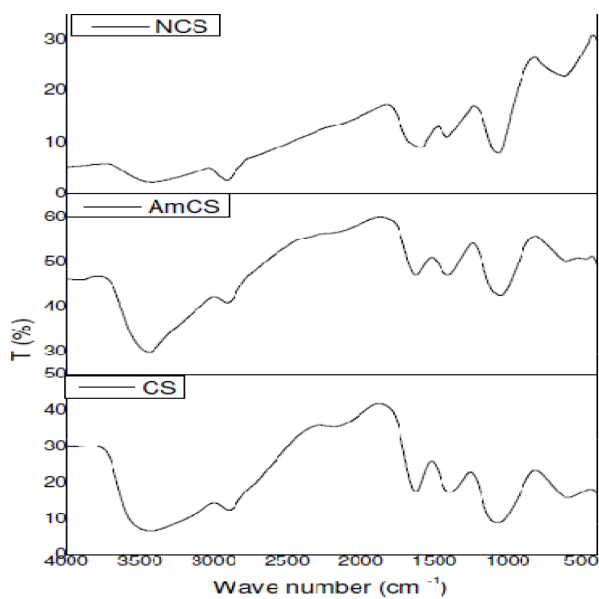


Fig. 1. FT-IR spectra of (a) CS, (b) AMCS, and (c) NCS Schiff base.

increases the surface roughness. Moreover, the coupling of Nonanal with the amine groups was observed by the pore formation on the NCS surface which referred to the capability of the internal structure of the polymer to distort.

3.2. Factors affecting the adsorption performance of heavy crude oil

3.2.1. Effect of contact time

To establish the equilibrium time for the maximum oil uptake and to determine the kinetic behaviour of the adsorption process onto the prepared sorbents, the impact of the contact time was optimised. The effect of the contact time (10–240 min) for the sorption of oil on CS, AmCS, and NCS schiff base is depicted in Fig. 3. A significant influence of the adsorption time on the oil sorption capacity was noticed for all sorbent derivatives [6]. The sorption capacity was rapidly increased with time from the first 10 min until it reaches a maximum value after 180 min. The figure showed also an increase in the removing power of AmCS and NCS schiff base rather than the native CS with maximum sorption capacity of 17, 19, and 22 g/g for CS, AmCS, and NCS Schiff base respectively. These observations agreed with the published results by Sokker et al. [32] who attributed this behaviour to the hydrophobic interactions due to the

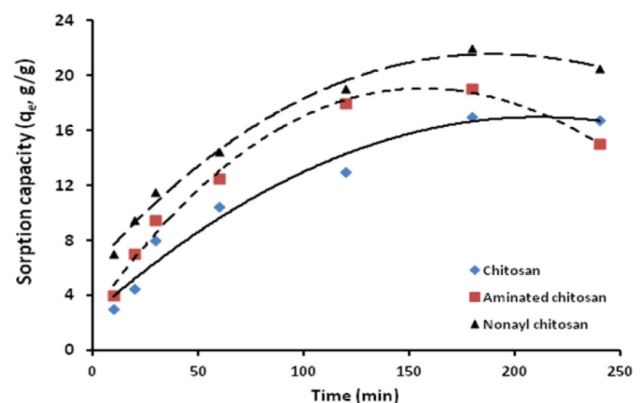


Fig. 3. Effect of the sorption time on the crude oil sorption capacity.

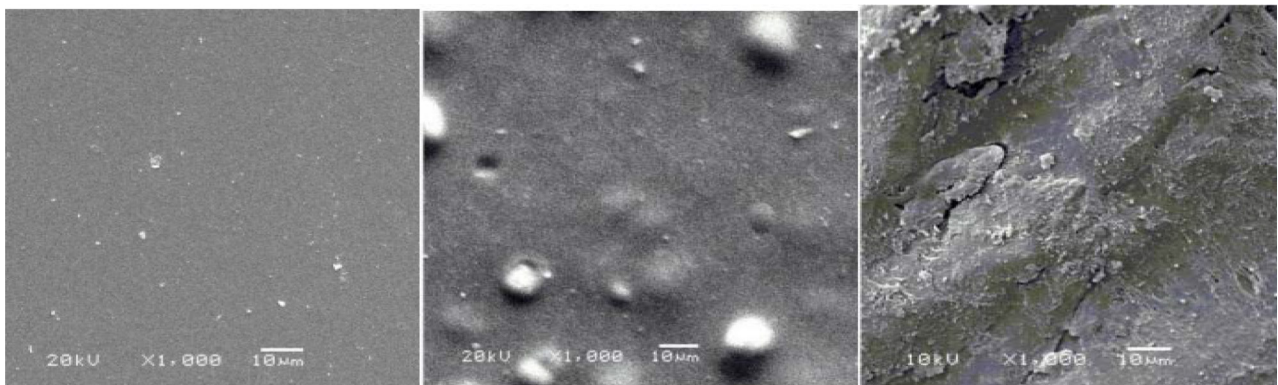


Fig. 2. SEM images of (a) CS, (b) AMCS and (c) NCS Schiff base.

methyl group of the acetamide function and the $-CH$ and $-CH_2$ groups of the glucose ring. Besides, the possibility of chain association through hydrogen bridges that usually generated by alcohol, amine, amide, and ether functions on the chitosan chain. This effect may be initially due to, the large concentration gradient between the liquid phase and the solid surface besides, more active sorptive sites are also available. Thus, the diffusion onto the external surface which is followed by pore diffusion into the intra particle matrix is faster up to attain the equilibrium at 180 min [8]. Eventually, when the time goes by, the adsorbed oil residue starts to block the sites near the outer surface so remainder oil can no longer diffuse to the active sites deep within the interior, solid surface [50].

3.2.2. Effect of initial crude oil concentration

The initial crude oil concentration study is remarkable because the oil residue in solute can strongly affect the adsorption kinetics and more specifically determine the equilibrium behaviour of the sorption process onto the prepared sorbents. Fig. 4 illustrates the oil sorption capacity as a function of the initial oil concentration at the equilibrium and at constant temperature. The plot shows that the adsorption of the oil increases with increasing the initial oil concentration from 8.33 to 50 g/L up to a specific value and then tends to reach a plateau. Indeed, at higher concentration, the gradient between the bulk solution and the centre of sorbent particle improves oil residue distribution through the film surrounding the particle and in the interior network of the prepared sorbents [51], as well, high adsorption rate and proper consumption of available vacant sites.

3.2.3. Effect of adsorbent amount

The mass of Chitosan adsorbents was varied from 0.1 to 1 g by keeping the initial oil concentration at 16.67 g/L. It was observed from Fig. 5 that with increasing the mass of adsorbents from 0.1 to 1 g, the oil sorption capacity decreased from 17 to 2.25, 18.99 to 3.3, and from 21.5 to 3.15 g/g for CS, AmCS, and NCS respectively. This sharp decrease in the adsorption capacity by the increase in the adsorbent

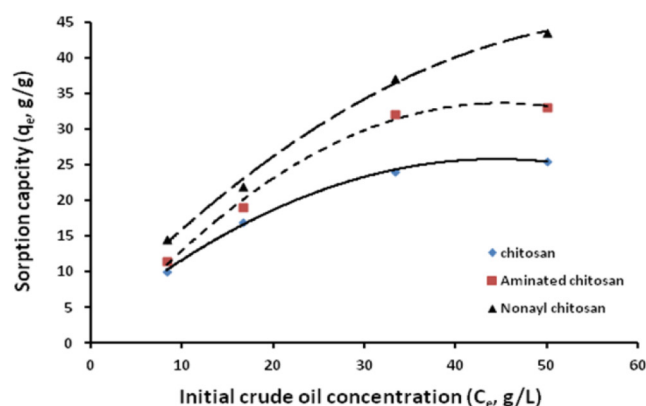


Fig. 4. Effect of the initial crude oil concentration on the sorption equilibrium.

amounts is mainly because of increasing the adsorbent dose attributable to the sites remaining unsaturated during the sorption process. This means that increasing the adsorbent dose at the same initial crude oil concentration decrease the amount of crude oil adsorbed per unit mass of chitosan adsorbents owing the availability of less amount of crude oil per unit mass of the adsorbent. This observation agreed with other relative publications [8,33].

3.2.4. Effect of temperature

The impact of temperature on the adsorption of crude oil was evaluated at a range of 25–40°C (Fig. 6). It was obvious that elevated temperatures had a positive consequence of promoting the adsorption process. As the temperature increase the adsorption rates and collisions between the oil and the adsorbent surface increase subsequently the adsorption quantity improved. Additionally, adsorption at comparatively high temperatures enhanced the adsorption rate without significant extra energy input owing to the activation of the adsorbate molecules. Moreover, this result demonstrated that the sorption process was an endothermic [52].

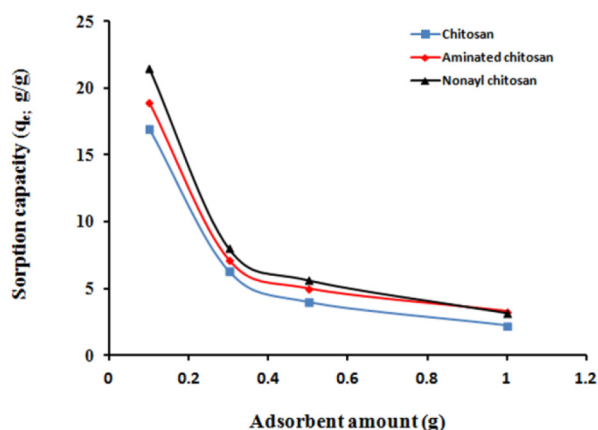


Fig. 5. Effect of the adsorbent amount on the crude oil sorption capacity.

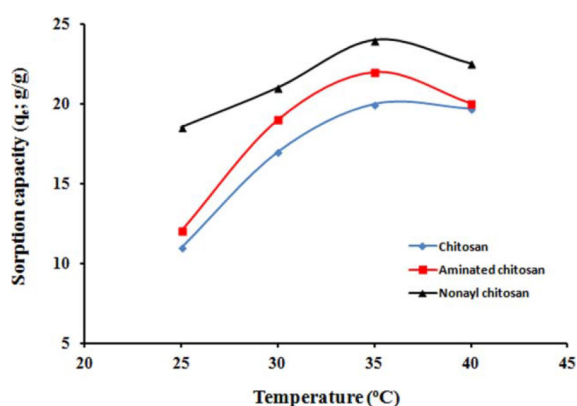


Fig. 6. Effect of the reaction temperature on the crude oil sorption capacity.

3.3. Adsorption kinetics

The linear plots $\ln(q_e - q_t)$ against t (Fig. 7a) allows the calculation of the values of K_1 and $q_{e,cal}$ from the slope and the intercept. The pseudo-first-order parameters are listed in Table 1, along with the corresponding R^2 values. Furthermore, Fig. 7b illustrates the linear plot of the pseudo-second-order equation. It was clear that the correlation coefficient, R^2 of the pseudo-second-order adsorption model (Table 1), is closer to 1 indicating that the pseudo-second-order model predominates the oil adsorption process.

Additionally, comparing the values of $q_{e,cal}$ obtained from the slope of the linear plot with that obtained

from the experimental data ($q_{e,exp}$) illustrate that the two values are closer to each other than the pseudo-first-order model. Therefore, this sorption system fitted the pseudo-second-order model well for all sorbents. As well, the initial sorption rate (h) was faster in case of NSC schiff base than in AmCS and CS. From our knowledge, the pseudo-first-order model and pseudo-second-order model are based on the hypothesis of physisorption and chemisorption process, respectively [36]. Thus, it can be concluded that the adsorption process of spilt oil molecules onto the prepared chitosan sorbents are the chemisorption. This investigation agrees with other publications [8,35,50].

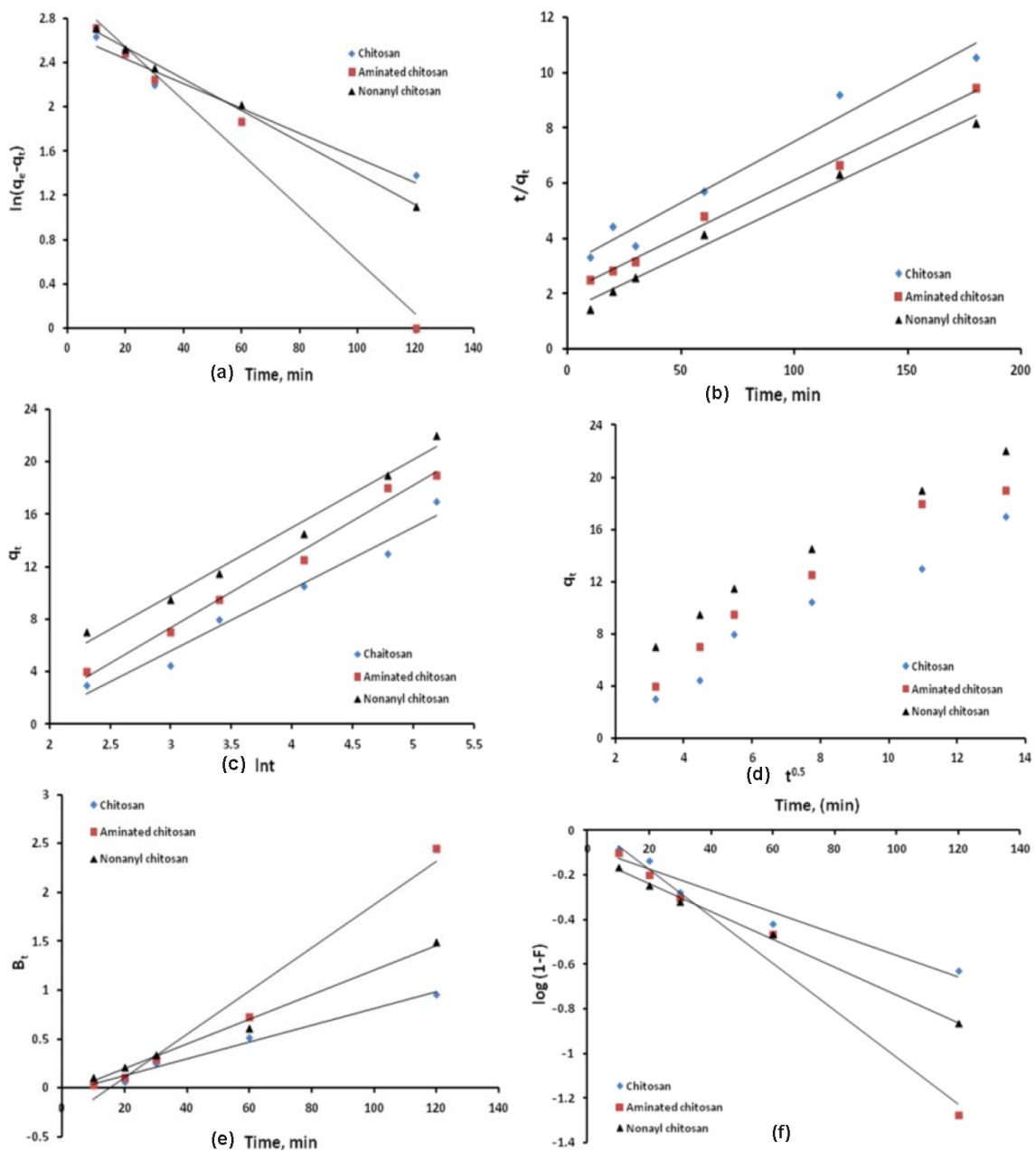


Fig. 7. Kinetics models for the sorption of the crude oil onto the prepared chitosan derivatives; (a) Pseudo-first, (b) Pseudo-second order model, (c) Simple Elovich, (d) intra-particle diffusion model, (e) Boyd, and (f) reconfirmation Boyd model.

However, the simple Elovich model is used widely in describing the kinetics of chemisorption. The Elovich parameters which determined from the slope and the intercept of the linearization of the Elovich equation (Fig. 7c) are tabularized in Table 1. The value of β is revealing the number of available adsorptive sites, whereas α is the adsorption quantity [34,53]. This value is supportive in considerate the first step adsorption behaviour. It was declared from the table that a good correlation among the experimental points and the theoretical lines is observed for CS, AmCS, and NCS Schiff base. It denotes that the Elovich equation fit the kinetic data over a short period.

Also, when the correlation between the sorption capacity and the constant is negative, it is accepted that the adsorbent does not retain the sorbate. The positive value of the constants contributes the confirmation for occurring of sorption. Consequently, the number of active sites available for sorption was reduced due to a large number of sorbate

molecules compared to the available active sites on the sorbent surface. The applicability of the Elovich equation for the present kinetic data specifies that the Elovich model was able to designate the initial kinetics of the crude oil sorption on the surface of the fabricated Chitosan sorbents properly. This observation is a covenant with many other published results [34].

On the other hand, the pseudo-first and the pseudo-second-order equations are based on the adsorption capacity. They only predict the behaviour over the whole range of studies supporting the validity that the chemisorption is the rate control. Thus, these findings remain uncertain about the adsorption mechanism. Therefore, the intra particle diffusion model was integrated. Fig. 7d illustrates a plot of q_t against $t^{0.5}$ for the sorption of crude oil onto the prepared Chitosan sorbents. The intra-particle diffusion plot confirms that the adsorption occurs in 3 steps. The first, sharper region, fastest step, the plot is linear due to mass transfer which is attributed to the diffusion of oil transported from the bulk solution to the external sorbent surface or the boundary layer diffusion of the solute molecules. In this part, the instantaneous adsorption is very fast because of the strong interaction between the oil molecules and the external surface of the chitosan derivatives [54]. After boundary-layer diffusion, the oil entered into the pores of the solid interior sorbent by intra-particle diffusion, as reflected by the second linear part of the plot. This stage describes the gradual adsorption region, where intra-particle diffusion is rate limited. The third stage is the diffusion through small pores and is followed by the establishment of final equilibrium during the intra-particle diffusion. The sorption started to slow down and became stagnant as the adsorbate molecules occupied all the active sites of the adsorbent, and the maximum adsorption was reached [55].

Table 2 listed the intra particle diffusion constants, k_p and C as well as the corresponding correlation coefficient, R^2 for the above three steps. Ultimately, it is seen that the first stage have a higher rate compared to the second and third stages. It was also noticed that R^2 values are high, suggesting that the intra particle diffusion model can follow the oil sorption process. Referring to Fig. 7d, although all of the intra-particle diffusion plots for chitosan derivatives exhibited a linear relationship, none of these line segments passed through the origin. Similarly, the straight lines of the second stages did not pass through the origin, and this deviation from the origin or near saturation may be due to the difference in the mass transfer rate at the initial and final stages of adsorption [56]. The non-zero intercepts of the

Table 1
Sorption parameters of pseudo first, pseudo-second-order, and Elovich kinetic models kinetic model

Kinetic model		CS	AMCS	NCS
Isotherm	Parameter	Value		
Pseudo-first-order	$q_{e,cal}$ (g/g)	7.24	8.22	7.68
	$q_{e,exp}$ (g/g)	17	19	22
	K_1 (min ⁻¹)	0.011	0.024	0.014
	R^2	0.951	0.976	0.997
Pseudo-second-order	$q_{e,cal}$ (g/g)	22.47	24.69	25.51
	$q_{e,exp}$ (g/g)	17	19	22
	K^2 (g/g·min)	0.0006	0.0007	0.0011
	h (mol/g·min)	0.327	0.483	0.723
	R^2	0.965	0.995	0.988
Elovich model	α (g/g·min)	1.047	0.824	0.582
	β (g/g)	4.719	5.425	5.189
	R^2	0.97	0.99	0.985

Table 2
Rate parameters of intra particle diffusion for the crude oil adsorption on the prepared chitosan derivatives

Sorbent type									
CS			AMCS			NCS			
Parameters values									
K_p 1–3 (g/g·min)	C	R^2	K_p 1–3 (g/g·min)	C	R^2	K_p 1–3 (g/g·min)	C	R^2	
1.145	0.618	1	2.371	3.529	0.999	2.371	3.529	0.999	
0.904	3.215	0.99	1.325	2.244	1	1.325	2.244	1	
0.12	18.614	1	0.407	13.545	1	0.407	13.545	1	

plots elucidate that the intra-particle diffusion is engaged in the adsorption process, but it is not the individual rate-controlling step for adsorption of oil onto chitosan materials.

Moreover, Fig. 7e displays the Boyd plot for the crude oil adsorption on all chitosan derivatives. The plots for all are linear, but they do not pass through the origin, indicating the film-diffusion-controlled mechanism. Further, $\log(1-F)$ vs time was plotted to reconfirm the above observation. The deviation of the straight lines from the origin for all plots shown in Fig. 7f, support the fact that the adsorption of crude oil onto chitosan sorbents occurs via the internal transport mechanism. Similar observations were also investigated by other studies [35,57,58].

3.4. Adsorption isotherm

The Langmuir isotherm declares that the adsorbents with the highest possible q_{max} and a high value of K_L are the most desirable. The linear plot of C_e/q_e vs C_e which has a slope of $1/q_{max}$ and the intercept of $1/q_{max} K_L$ is described in Fig. 8a. From the regression correlation coefficient (R^2) values which regarded as a measure of the goodness of fit of the experimental data on the isotherm's model (Table 3), it

Table 3

Parameters of the different isotherm models and correlation coefficients for the adsorption of the crude oil

Adsorbent type		CS	AMCS	NCS
Isotherm	Parameter	Value		
Langmuir	q_{max} (g/g)	32.154	45.045	59.172
	K_L (L/g)	0.0997	0.0787	0.0768
	R^2	0.995	0.977	0.977
Freundlich	K_f (g/g)	4.542	4.656	5.545
	$1/n$	0.445	0.517	0.494
	R^2	0.942	0.954	0.988
Temkin	K_T (L/g)	0.521	1.221	0.753
	B (J/mol)	7.523	10.82	12.99
	R^2	0.978	0.955	0.966
D-R	K_{ad} (mol ² /KJ ²)	5.369	4.932	2.93
	E (KJ/mol)	0.305	0.318	0.413
	R^2	0.956	0.885	0.786

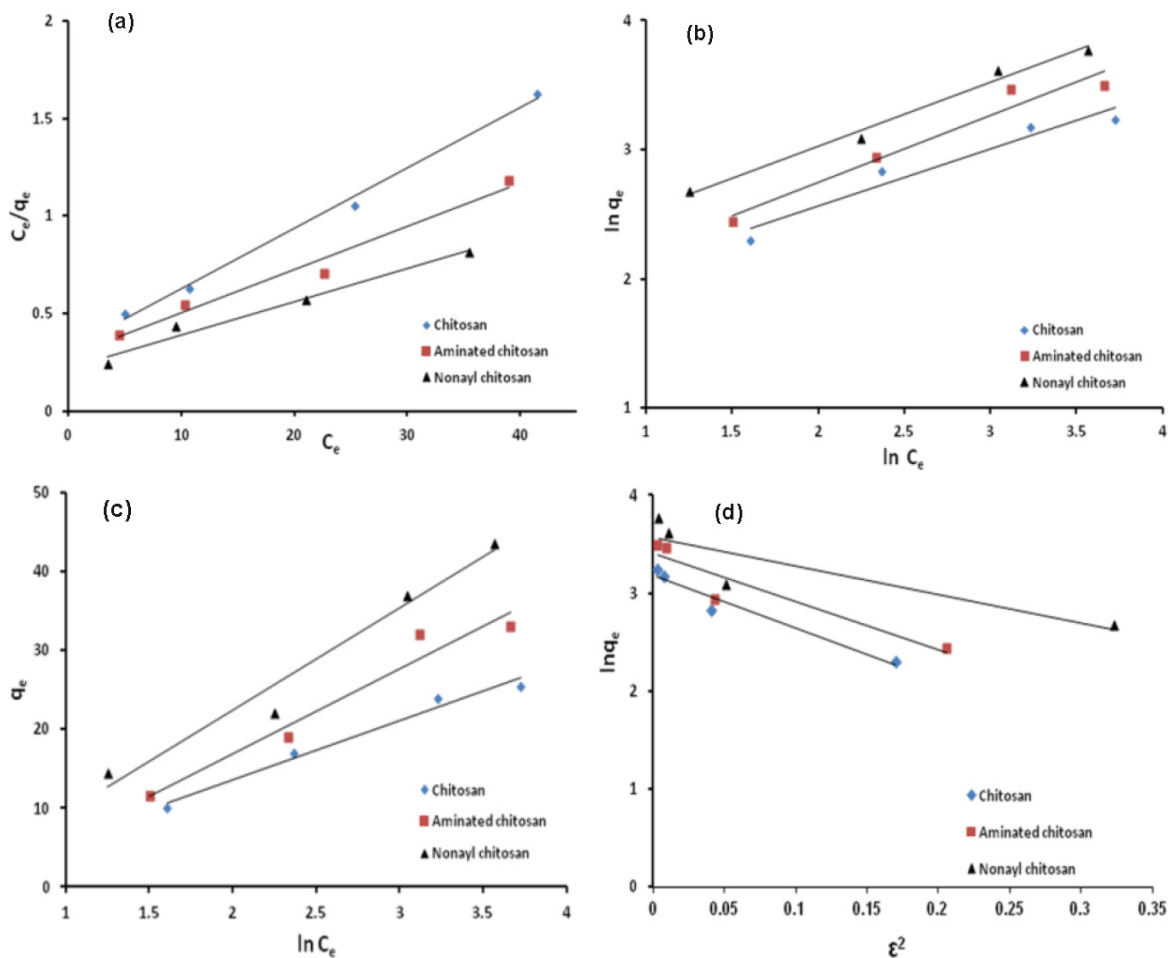


Fig. 8. Equilibrium isotherm for the sorption of the crude oil onto the prepared chitosan derivatives; (a) Langmuir (b) Freundlich isotherm, (c) Temkin and (d) Dubin-Radushkevich isotherm.

explains that the Langmuir can represent the adsorption of oil onto the surface of chitosan derivatives. Also, the high mono layer coverage of oil on the outer surface of chitosan sorbents occurs uniformly on the reactive sites via the strong electrostatic attraction between oil molecules and adsorbent bending sites onto chitosan derivatives rather than in pure chitosan [44,51]. In this study, all R_L values described in Table 4 are fall between zero and one, showing that the oil sorption process is favourable at the experimental conditions. The low values of R_L could explain the high adsorption of the spilled oil from the artificial seawater.

The Freundlich constants K_f and n are obtained from the respective slope and intercept of the plot $\ln q_e$ vs $\ln C_e$ (Fig. 8b). Smaller values of $1/n$ indicate the stronger interaction between the adsorbent and crude oil spill [22]. The adsorbents possess high adsorption capacity, and hence it can be employed as low-cost adsorbent for the removal of oil spills. The parameters of Freundlich isotherm are shown in Table 3. The correlation coefficient for NCS Schiff base ($R^2 = 0.988$) indicating that this model can describe well the sorption of the crude oil. The K_f constant is concerned with the ability of the adsorbent to adsorb, and n constant is concerned with the tendency of the adsorbate to be adsorbed. The slope $1/n$ measures the surface heterogeneity which becomes more predominant as $1/n$ gets closer to zero. When the values for $1/n$ are below 1 it confirms a standard Freundlich isotherm, while values above 1 are indicative of the cooperative sorption. Thus; the favorability of adsorption for the prepared chitosan derivatives under the concentration range studied is better onto NCS and AmCS than CS [59].

The plot of q_e against $\ln C_e$ shown in Fig. 8c representing the Temkin model and provides a straight line with a slope of B which is positive for chitosan and its modified forms. When the intercept value is larger, this means that the adsorbent/adsorbate interaction is also larger [23]. The parameters of this model, as well as the corresponding R^2 values, are listed in Table 3. The correlation coefficients ($R^2 = 0.978, 0.96,$ and 0.97) in case of CS, AmCS, and NCS Schiff base indicating that this model is the best fit for the sorption equilibrium of crude oil onto the surface of these sorbents. This observation is in agreement with other published results [59].

However, the Langmuir, the Freundlich, and the Temkin isotherms are insufficient to explain the physical and chemical characteristics of adsorption. Thus, the D-R isotherm model was applied as the calculated energy (E) from the slope of the linear plot of $\ln q_e$ vs K_{ad} (Fig. 8d) gives information about the sorption mechanism. It is perceived as the

Table 4

R_L values based on the Langmuir equation of the oil adsorption onto the chitosan derivatives

Sorbent type	CS	AMCS	NCS
Initial concentration, g/L	RL values		
8.33	0.5465	0.6039	0.6098
16.67	0.3759	0.4326	0.4386
33.33	0.2415	0.2759	0.2809
50	0.1672	0.2026	0.2066

amount of energy required to transfer 1 mole of the adsorbate molecule from infinity in the bulk of the solution to the site of sorption [51]. The D-R correlation R^2 value equal to 0.95 for pure chitosan and this indicates that the isotherm models fit the experimental data in the following manner Langmuir > Temkin > D-R > Freundlich model. On the other hand, it obeying different behaviour in case of AmCS; Langmuir > Temkin > Freundlich > D-R model. For the NCS Schiff base, the isotherm fitting follows Freundlich > Langmuir > Temkin > D-R isotherm model. The adsorption energy ($E < 8$ kJ/mol) indicates that the oil sorption process could be considered as physisorption [50,51].

3.5. Thermodynamic

Fig. 9 and Table 5 lists the values for the thermodynamic parameters for the synthesised CS and its derivatives. The positive value for the ΔH designates that the adsorption is endothermic which describes the increase of oil adsorption capacity by raising the temperature. The positive value for the ΔS shows an increased in the disorder at the solid/liquid boundary during oil adsorption onto the CS sorbents. Further, the negative value of the ΔG indicates that the adsorption is spontaneity and does not require any external energy source [45,60].

3.6. Comparison of oil sorption capacity with various adsorbents

Performance comparison between the studied chitosan derivatives and some other published adsorbents for the removal and recovery of the crude oil under different operating conditions based on the maximum sorption capacity is shown in Table 6. There was a diversity of altered kind of modifications to natural sorbent materials reported in the literature, which enriched hydrophobicity and sorption capacity. Ideally, the minimal modification is preferred to retain the useful properties of the native material while improving weaker properties, i.e. enhancing buoyancy and oil sorption while not varying the affinity of the materials. It was observed that the derived chitosan from shrimp shells and its derivatives gave a remarkable high adsorption

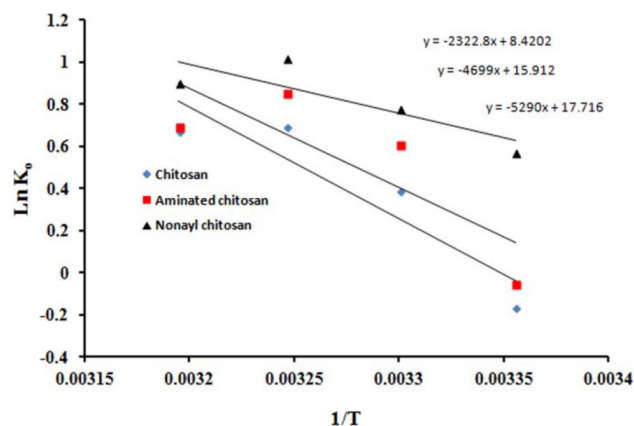


Fig. 9. Thermodynamics of the sorption of the crude oil onto the prepared chitosan derivatives.

Table 5
Thermodynamic parameters of the adsorption capacity for the crude oil by various chitosan adsorbents

Thermodynamic parameters									
CS			AMCS			NCS			
T (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol K)
298	-0.434	43.98	147.29	-0.356	39.067	132.29	-1.557	19.31	70
303	-1.179			-0.107			-1.906		
308	-1.925			-1.678			-2.256		
313	-2.679			-2.34			-2.607		

Table 6
A comparison of the maximum adsorption capacity for the crude oil by various chitosan adsorbents

Adsorbent	Sorption capacity/ Removal efficiency	Reference
Chitin flaks	0.258 g/g	[5]
Chitin powder	0.17 g/g	[5]
Chitosan flakes	0.379 g/g	[5]
Chitosan powder	0.281 g/g	[5]
Chitosan-based polyacrylamide hydrogel	2.3 g/g	[32]
Chitosan (prawn shells)	18.52 g/g	[8]
Chitosan-coated mesh	>99%	[24]
Chitosan based aerogel membrane	99%	[4]
Chitosan micro spheres	>90%	[10]
Acetylated corncobs	0.0768 mg/g	[61]
Lauric acid (LA) modified oil palm leaves	1.2 ± 0.12 mg/g	[35]
Carbonized rice husks (CRH)	6 g/g	[35]
Recycled wool-based non woven material	11.5	[35]
Butyl rubber	25 g/g	[62]
Non-woven polypropylene	15 g/g	[62]
Chitosan (shrimp shells)	32.15	This study
Aminated chitosan	45.05	This study
Nonanyl chitosan schiff base	59.17	This study

capacity compared to the other listed sorbents. However, this comparison is unfair owing to the diversity of the operating conditions.

4. Conclusion

Adsorption studies had been carried out for the removal of the crude oil spill by the chitosan and chitosan

Schiff base derivatives. The prepared sorbent was characterized by FTIR and SEM. The effect of numerous factors on the sorption capacity was also investigated. It was concluded that the oil sorption process on CS, AmCS and NCS Schiff base follow the pseudo-second-order model. Additionally, it was revealed that the sorption process is not only controlled by the intra particle diffusion but the film diffusion also played an essential role. Further, the extent of the film diffusion and the intra particle diffusion depended on the ionic state of the adsorbate. Adsorption of the spilt crude oil onto CS and AmCS followed the Langmuir isotherm, while fitting well to both Langmuir and Freundlich in case of NCS Schiff base with high monolayer coverage of the oil onto the AmCS and the NCS Schiff base than the native CS. The separation factor (R_L) of the Langmuir and the exponent (n) of the Freundlich indicated the favorability of adsorption of oil from artificial seawater. Furthermore, the results revealed that the NCS Schiff base is better than the AmCS and the CS for the sorption of spilt oil where the maximum oil adsorption capacity by the Langmuir has been improved by 100%. In conclusion, this naturally prepared sorbents from shrimp shells literally of no economic value proved to have a potential in the environmental remediation processes and can be developed to be used efficiently in the adsorption of the crude oil spill from seawater.

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