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Characteristics and kinetic study of chitosan prepared from seafood industry waste for oil spills cleanup

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ABSTRACT

Chitosan being a biodegradable material would be an eco-friendly and effective alternative in the cleaning up of oil spills. In the present study, adsorbent (Chitosan) was prepared from the seafood industry waste, prawn shells for removal of oil from aqueous solution. Batch experiments were carried out to study 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^{-1} 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 equilibrium data was tested with the Langmuir isotherm and excellent correlation was obtained.

Keywords: Prawn shells; Chitosan; Oil spills; Adsorption; Batch studies, Adsorption isotherms; Adsorption kinetics

1. Introduction

The marine environment is subject to contamination by organic pollutants from a variety of sources. Oil spills have been a matter of great concern for environmental scientists and ecologists since crude oil is one of the most important organic pollutants in marine environments and it has been estimated that worldwide approximately 1,300,000 metric tons of petroleum hydrocarbons impact water bodies annually [1]. The collision of two Panamanian cargo ships, namely MSC Chitra and MV Khalijia-111, in August of 2010 off the Mumbai coast spilt about 900 t of oil which polluted the waters and beaches in the area [2]. On 20 April of the same year, the accident on the Deepwater Horizonrig allowed hydrocarbons to escape from the Macondo well onto Transocean's Deepwater Horizon resulting in explosions and fire on the rig. Hydrocarbons continued to flow from the reservoir causing a spill of national significance [3].

Presently, oil spills are cleaned up using methods such as controlled burning, bioremediation, dredging and skimming. Controlled burning can effectively reduce the amount of oil in water, if done properly but can cause air pollution [4]. Bioremediation relies on improved detoxification and degradation of toxic pollutants either through intracellular accumulation or via enzymatic transformation to less or non-toxic compounds [5]. An important limitation of the technology is the difficulty in formulating treatment strategies that will produce a specified outcome in terms of degradation rate and

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residual contaminant concentration [6]. Although general statements can be made regarding the enhancement of biodegradation by nutrient amendment, there is no consensus on how to best optimize nutrient additions. Despite a relatively long history of research on oil-spill bioremediation, it remains an essentially empirical technology and many of the factors that control bioremediation have yet to be adequately understood [7]. Dredging operations are often needed for the improvement of a channel and/or harbour area. Unavoidably the water resources close to the dredging site will be contaminated to some degree [8].

As seen, an eco-friendly and effective alternative is required for the cleaning up of oil spills. Chitosan can be used for the adsorption of oil from water. Chitosan is an N-deacetylated chitin derivative though this N-deacetylation is almost never complete. Structurally, chitin is a linear polysaccharide whose unbranched chains consist of elementary units of 2-acetamide-2-deoxy-D-glucose linked through 1, 4-β-glycosidic bonds. Chitin and chitosan are heteropolymers. Neither random nor block orientation is meant to be implied for chitin and chitosan. Chitin is highly hydrophobic and is insoluble in water and most organic solvents [9,10]. At neutral and alkaline pH values, chitosan is insoluble, but salt formation is observed with inorganic and organic acids [11].

Chitosan is found naturally in fungi and arthropods in which it is the main component of the exoskeleton [12]. Chitosan can be prepared from chitin present in fishery waste such as skeletal material of crustacean shells, cuttle fish, squid as well as crab and shrimp [13].

Chitin and chitosan are of commercial interest due to their high percent nitrogen (6–89%) compared to synthetically substituted cellulose (1.25%). The nitrogen content in chitin varies from 5% to 8% depending on the extent of DA, whereas, the nitrogen in chitosan is mostly in the form of primary aliphatic amino groups [9]. Chitosan is a valuable nontoxic, biodegradable, and biocompatible natural polymer and can be used in a wide range of applications including the areas of water treatment, biomedicine, drug delivery systems, hydrogels, food packaging and so on [14].

Chitosan has an excellent chelating effect attributed to the abundant free amino and hydroxyl groups which enables efficient removal of metal ions, acids and synthetic surfactants for formation of complex precipitates [15]. Cervera et al. [12] have investigated the removal of heavy metals, Cd(II) and Cr(III) from wastewater using chitosan while the sorption of Re(VII) on fibrous chitosan–carbon materials has been presented by Plevaka et al. [16]. Other researchers [17,18] have studied the adsorption of Cu(II), Ni(II), and Zn(II) on chitosan.

Chitosan shows a prominent flocculating effect attributed to abundant free amino groups along the chain backbone that were cationically charged in a wide range of pH values. The comparative performance of chitosan and a cationic polyacrylamide as flocculants has been presented by Pinotti et al. [19]. In addition to the flocculating effect, the chelating and adsorption effects of chitosan have prompted its use in wastewater treatment. The treatment of wastewater using fly-ash coated with chitosan and magnetic chitosan microspheres has been proposed by researchers [15,20].

In pharmaceuticals, chitosan is known to reduce friction during tableting and to produce controlled release tablets. Hydrogels, controlled release dosage forms, mucoadhesive dosage forms, microcapsules, microparticles, and nanoparticles have been developed using chitosan [21]. Borzacchiello et al. [22] have synthesized and characterized new hydrogels based on chitosan. Chitosan and its derivatives are suitable for tissue engineering applications due to their good physicochemical and biological properties.

Chitosan derivatives with high antimicrobial activity have been synthesized with potential for use packaging for a variety of foods. Chitosan glucose complex (CGC), a modified form of chitosan has been shown to exhibit excellent antioxidant activity. Additional applications of chitosan and its derivates have been discussed by Honarkar et al. [14].

In the present study, adsorbent (chitosan) was prepared from the seafood industry waste, prawn shells and studies were carried out for oil removal. Batch experiments were carried out to study the effect of influencing parameters such as contact time, pH, initial concentration of oil, and mass of adsorbent on oil adsorption using chitosan. The obtained experimental data were tested with Langmuir isotherm model and rate kinetic models.

2. Materials and methods

2.1. Adsorbent preparation

Seafood industry waste, dried/wet prawn shells without the heads are the raw material. The shells were cleaned and broken in the form of flakes. Deproteinization was done to remove protein adhered to the shells by boiling 100 g of the raw material with 250 ml of 3% sodium hydroxide for 30 min. Washing with distilled water removed all traces of sodium hydroxide. The demineralization involved treating the shells with 3% hydrochloric acid in excess of 2 h. Washing with distilled water removed all traces of hydrochloric acid. Chitin was obtained from this step in the form of flakes and DA of this chitin was necessary to produce chitosan. DA of chitin obtained was brought about by boiling it with 250 ml of 40% sodium hydroxide for 1 h, resulting in chitosan having a degree of DA up to 0.95. Drying of chitosan was carried out at a temperature lower than 60°C. A Ninhydrin test was conducted to confirm the formation of chitosan in which 100 mg of chitosan was dissolved in 5 ml Acetic acid (1% wt) and 5 ml of 2% Ninhydrin solution was added. The solution was stirred and then heated for about 20 min. The presence of a bluish-purple color confirmed the presence of chitosan. The yields of chitin and chitosan produced by the above procedure were 13.167% and 11.426% by weight of dry shells, respectively.

2.2. Batch experiments

The batch experiments with chitosan were carried out in 100 ml beakers. Adsorption isotherm study was carried out using 25 ml each of different concentrations of oil–water solution. Samples measuring 25 ml of a 10% (v/v) oil–water solution at 30°C were used to study the effect of contact time. Chitosan flakes weighing 0.05 g were added at the start of each experiment and removed after the specific time for that experiment. To study the effect of pH on adsorption of oil using chitosan, the pH of 10% oil–water solution was varied from 2.0 to 12.0. The effect of initial concentration was studied by varying the initial concentration of oil in the oil–water solution from 2% (v/v) to 25% (v/v). The quantity of chitosan flakes used was constant as 0.05 g for change in pH and initial concentration studies. Experiments were conducted by varying the mass of chitosan from 0.025 to 0.15 g in 25 ml oil–water solutions of 10% (v/v) concentration at 30°C. Experiments were also conducted to determine the adsorption capacity of commercially available chitosan (90–95% DA, Marine Chemicals, Kerala, India) for comparing the adsorption capacity of adsorbent prepared in the present study. The experiments are carried out twice and the average values are reported. The average values are obtained within the error limit of ±1.74%.

2.3. Analytical method

The Fourier transform infrared (FT-IR) Shimadzu Prestige 21 was used to obtain the FT-IR spectra of chitosan. The flakes were picked up and gravimetric analysis method was used to determine the weight of oil adsorbed. The weight of the flakes before and after adsorption was taken on a weighing machine (Presisa 125 ASCS). The volume of oil adsorbed was found using the known density of the oil. All the experiments were carried out twice and the average values of the results have been reported.

3. Results and discussion

3.1. Characteristics of adsorbent

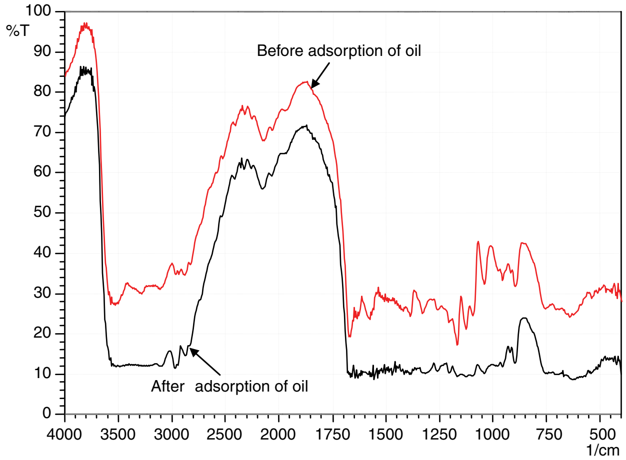

Fig. 1. FT-IR spectra of chitosan before and after adsorption of oil.

The FT-IR spectra of chitosan in KBr are shown in Fig. 1. The spectra of chitosan before the adsorption of oil and after the adsorption of oil had been recorded. The results are in agreement with the results reported in literature. The peak at 3000–4000 cm^{-1} originates from the OH and NH_2, whereas the peaks at 1716 cm^{-1} is due to C=O of $NHCOCH_3$, and those at 2900 and 1350 cm^{-1} are the C–H stretching and C–H bending modes [23]. A decrease in the percent transmittance is noted in the FT-IR spectra seen in Fig. 1 which indicates that both physical and chemical adsorption are taking place on chitosan in oil–water solutions. The peak at 1180 cm^{-1} is may be due to the presence of C–O (Ether/carboxylic acid, R–O–R linkage) bond which is disappeared after adsorption and reduced in some other form.

When the degree of DA of chitin reaches about 50% (depending on the origin of the polymer), it becomes soluble in aqueous acidic media. The solubilization occurs by protonation of the NH_2 functional group on the C-2 position of the D-glucosamine repeating unit, whereby the polysaccharide is converted to a polyelectrolyte in acidic media [14]. The protonation of amino groups on the biopolymer may have a positive effect on the uptake of anionic solutes or a negative impact for example in the case of cationic molecules [19,24].

Chitosan has amine (NH_2) functional group which is also supported by FT-IR spectra. This functional group attracts anionic ions such as OH^- to bind and bridge. Due to this reason, oil has more affinity to adsorb on the surface of chitosan flakes. Electrostatic forces of attraction are present between this positive charge on chitosan surface and the negative charge of fatty acids in oils. Also, chitosan a positively charged biopolymer could adsorb residue oil and destabilize the negatively charged colloids of residue oil by charge neutralization mechanism [25]. The adsorption properties of chitosan are mainly because of its positive charge however, the adsorption process could also be the result of other forces that might exist between molecules, such as hydrogen bonding or van der Waals forces [26]. Chitosan has high charge density due to which it can adsorb more oil by the use of less amount of chitosan adsorbent. Chitosan in form of flake has more adsorption capacity as compared to powder form [27], so in the present study flake form of chitosan is used for oil adsorption.oil was more compared to the powder.

3.2. Effect of contact time

The effect of contact time for the adsorption of oil on chitosan for a 10% (v/v) oil–water solution has been depicted in Fig. 2 where it is evident that there is a significant influence of time on the adsorption of oil on chitosan. The percent removal of oil from aqueous solution increases rapidly till 3 min and reaches a value of 33.616 and the percentage removal of oil further increases till 5 min and reaches a value of 41.28. The contact time for the adsorption of oil on chitosan for the remaining batch studies have been taken as 6 min since there is a negligible effect on the percentage removal on further increasing the contact time. Initially, the concentration gradient between the solution and the solid surface is large, and hence the transfer of solute onto the solid surface is faster. Initially, more active sites are also available. Thus, the percent removal of oil from aqueous solution increases rapidly till 3 min. As time increases, the percentage removal does not increase as rapidly due to the less driving force and availability of fewer active sites.

3.3. Effect of pH

The effect of varying pH on the adsorption of oil using chitosan from oil water solutions was studied. The pH was varied from 2.0 to 12.0 in 10% (v/v) oil–water solutions and a vast difference was observed in the performance of chitosan in acidic and basic mediums as shown in Fig. 3. The quantity of oil adsorbed by chitosan was larger in the acidic medium as compared to the basic medium. The removal efficiency increased from 34.72% to 56.87% by decreasing the initial pH of the solution from 12.0 to 2.0 respectively. As discussed in Sect. 3.1, chitosan is converted to a polyelectrolyte in acidic media. The high numbers of-NH^{3+} groups present on chitosan in acidic media have a positive effect on the uptake of negatively charged ions as seen in Fig. 3 [19,24].

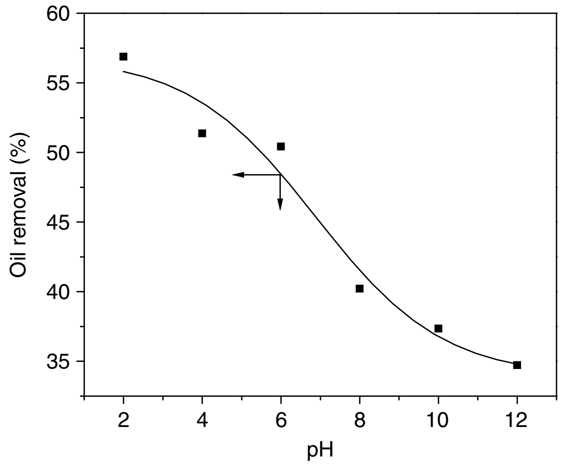

Fig. 3. Effect of pH on oil adsorption.

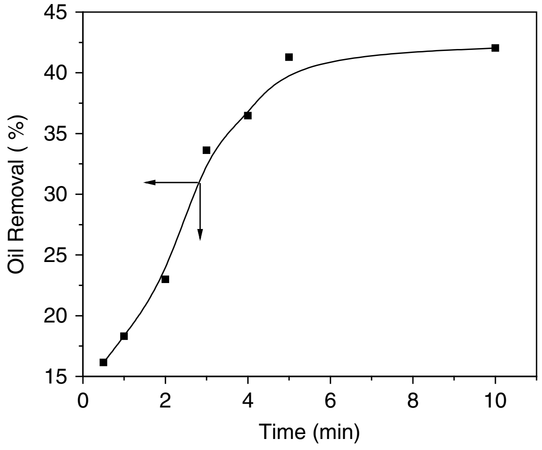

Fig. 2. Effect of contact time on oil adsorption.

3.4. Effect of initial concentration

Fig. 4 shows the effect of initial concentration on percentage removal of oil and adsorption capacity of chitosan. The results were obtained by varying the initial concentration of oil in the solution from 2% (v/v) to 25% (v/v) for 0.05 g of chitosan utilized keeping the contact

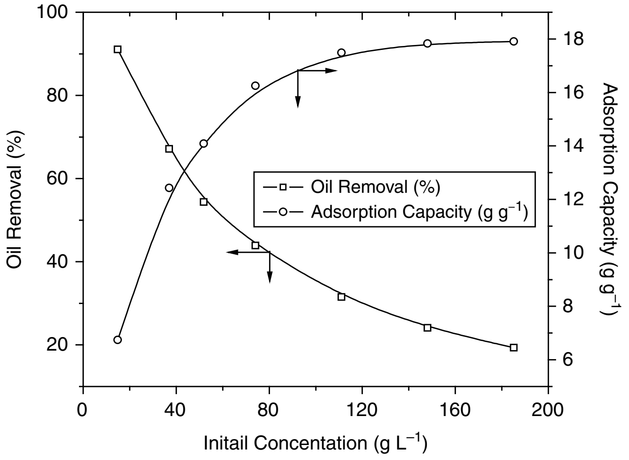

Fig. 4. Effect of initial concentration on oil adsorption.

time of 6 min and temperature of 30°C constant. It is apparent that oil adsorption is significantly influenced by initial concentration of oil in aqueous solution as the percent removal decreases from 91.08% to 19.35% and adsorption capacity increases from 6.74 to 17.91 g g^{-1} for initial concentration varying from 14.81 g l^{-1} [2% (v/v)] to 185.12 g l^{-1} [25% (v/v)]. The increase in adsorption capacity may be due to the higher rate of adsorption and proper utilization of active sites available for the adsorption at higher concentration. The decreasing trend of percentage removal can be explained with the fact that all the adsorbents had a limited number of active sites, which would have become saturated above a certain oil concentration.

3.5. Effect of mass of adsorbent

The mass of chitosan was varied from 0.025 to 0.15 g by keeping the concentration at 10% (v/v), contact time of 6 min and temperature of 30°C. It was observed from Fig. 5 that with increase in mass of chitosan from 0.025 to 0.15 g, the adsorption capacity decreased from 19.77 to 8.16 g g^{-1} and the percentage removal of oil increased from 26.72% to 66.16% respectively. The increase in oil removal with an increase in the chitosan amount is due to the increase in surface area and adsorption sites available for adsorption. However, the decrease in adsorption capacity by increasing the adsorbent amount is basically due to the sites remaining unsaturated during the adsorption process. It means that if adsorbent amount is increased by keeping the oil concentration constant, the amount of oil adsorbed per unit mass of adsorbent showed a decrease due to availability of less amount of oil per unit mass of the adsorbent.

3.6. Adsorption isotherm

The equilibrium studies are useful to obtain the adsorption capacity of chitosan for oil. The obtained data from equilibrium study can be represented in the form of adsorption isotherm. If a quantity, q, of adsorbate is absorbed by an adsorbent at constant temperature and steady state equilibrium concentration, c, then the function $q(c)$ describes the adsorption isotherm.

3.6.1. Langmuir isotherm

The equilibrium data was tested with the Langmuir isotherm. This isotherm is applicable when the extent of adsorbate coverage is limited to one molecular layer. The isotherm assumes a dynamic equilibrium between the adsorbed phase and the liquid phase. Langmuir described chemisorption as the formation of an ionic or covalent bond between adsorbent and adsorbate. The isotherm equation is given below in Eq. (1):

$$\frac{C_e}{q_e} = \frac{1}{bQ_m} + \left(\frac{1}{Q_m}\right)C_e \tag{1}$$

where, the parameter b is the Langmuir constant and Q_m is the quantity of adsorbate required to form a single monolayer on unit mass of adsorbent. q_e and C_e are the amounts adsorbed on unit mass of the adsorbent, g g^{-1} and equilibrium concentration, g l^{-1} in fluid phase respectively. Fig. 6 shows the graph plotted between (C_e/q_e) and C_e which yields a straight line where the slope and intercept of this line give the values of Q_m and b [28]. The respective values of Q_m and b are calculated as 18.52 g g^{-1} and 0.195 l g^{-1}. The value of correlation coefficient

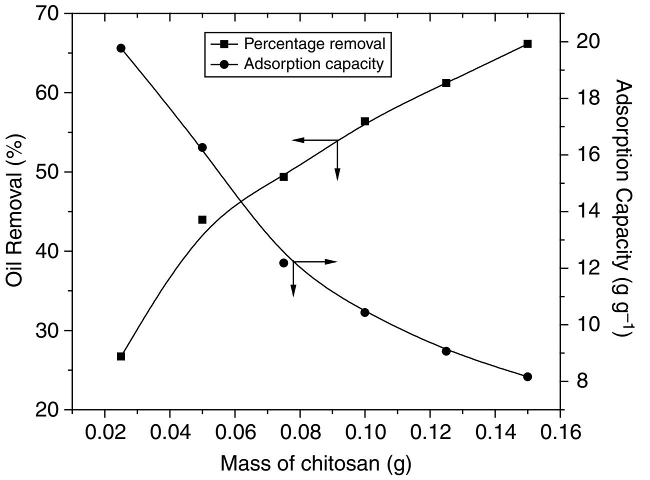

Fig. 5. Effect of mass of adsorbent on oil adsorption.

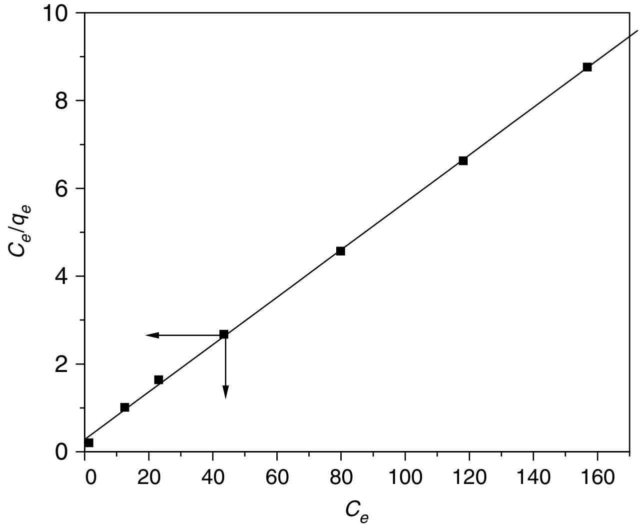

Fig. 6. Langmuir isotherm for adsorption of oil on chitosan.

R^2 is obtained as 0.999 which confirms the suitability of Langmuir isotherm to explain the equilibrium data for the adsorption of oil using chitosan.

3.7. Adsorption kinetics

The dynamics of adsorption process in terms of order of the rate constant can be evaluated using the kinetic adsorption data. Several kinetic models are in use to explain the mechanism of the adsorption process.

3.7.1. Pseudo-first-order kinetics

Lagergren showed that the rate of adsorption of solute on the adsorption is based on the adsorption capacity and follows a pseudo-first-order equation [29,30]. The non-linear form of pseudo-first-order equation is given by Eq. (2):

$$\frac{\mathrm{d}q_{\mathrm{t}}}{\mathrm{d}t} = k_1(q_e - q_t) \tag{2}$$

where, q_e and q_t are the amounts of oil adsorbed g g^{-1} at equilibrium time and at any instant of time, t respectively, and k_1 l min^{-1} is the rate constant of the pseudo-first-order adsorption operation. The integrated rate law after application of the initial condition of $q_t = 0$ at $t = 0$, becomes a linear equation as given by Eq. (3):

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1 t}{2.303}\right) \tag{3}$$

The plot of log $(q_e - q_t)$ versus t is a straight line for first order adsorption kinetics the adsorption rate constant, k_1 can be obtained. The linear plot between log $(q_e - q_t)$ and t was drawn. The k_1 and q_e values for the initial concentration of 10% (v/v) were found to be 0.3145 min^{-1} and 2.7944 g g^{-1}. The true value of q_e obtained from experiments is 16.25 g g^{-1}. Comparison between obtained and true values of q_e shows that the pseudo-first-order kinetics is inadequate to give a good representation of the kinetics of oil adsorption on chitosan (Table 1).

3.7.2. Pseudo-second-order kinetics

Pseudo-first-order kinetics differs from a true first order equation in two ways: (i) the parameter $k_1(q_e - q_t)$ does not represent the number of available sites, and (ii) the parameter log (q_e) is an adjustable parameter and often found not to be equal to the intercept of the plot of log $(q_e - q_t)$ versus t, whereas in a true first order log q_e should be equal to the intercept. In such cases, applicability of the second order kinetics should be tested with the rate equation given by Eq. (4) [31,32]:

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_2(q_e - q_t)^2 \tag{4}$$

where k_2 is the second order rate constant in g g^{-1} min^{-1}. From the boundary conditions, $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of the equation becomes:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \tag{5}$$

Which can be written in the linear form:

$$\frac{t}{q_t} = \frac{1}{h} + \left(\frac{1}{q_e}\right)t \tag{6}$$

where $h = k_2 q_e^{\,2}$ can be regarded as the initial adsorption rate as $t \to 0$. Under such circumstances, the plot of t/q_t versus t should give a linear relationship, which allows computation of q_e, k and h.

Application of second order kinetics by plotting t/q_t versus t yielded better results. There is also good agreement between experimental ($q_e = 16.25$ g g^{-1}) values and those obtained from the slope ($q_e = 18.1258$ g g^{-1}) of the second–order plots (Table 1). The second-order rate constant is found to be 0.0376 g g^{-1} min^{-1}.

3.8. Comparison with other adsorbents

In the present study, the adsorption capacity of chitosan prepared for oil removal was compared with commercially available pharmaceutical grade chitosan (Table 2). The adsorption capacities of the chitosan

Table 1
Kinetic constants for first and second order kinetic models

C_0 (g l^{-1})	q_e (g g^{-1}) (xperimental)	First-order kinetic model			Second-order kinetic model		
		k_1 (min^{-1})	q_e (g g^{-1})	R^2	k_2 (g g^{-1} min^{-1})	q_e (g g^{-1})	R^2
74.046	16.25	0.3145	2.7944	0.926	0.0376	18.126	0.99

Table 2
Comparison of chitosan prepared in the present study and pharmaceutical grade chitosan

Initial concentration	Chitosan prepared in the present study		Pharmaceutical grade chitosan	
	Adsorption capacity (g g^{-1})	Percentage oil removal	Adsorption capacity (g g^{-1})	Percentage oil removal(%)
5% (v/v)	6.74	36.41	9.61	67.25
10% (v/v)	12.43	25.96	13.40	36.19

prepared in the present study for 5% (v/v) and 10% (v/v) oil–water solutions were found to be 6.74 and 12.43 g g^{-1} respectively as compared to 9.61 and 13.40 g g^{-1} for pharmaceutical grade chitosan. For a 5% (v/v) oil–water solution, the percentage removal of oil was 36.41% for chitosan prepared in the present study and 67.25% for pharmaceutical grade chitosan, respectively. The percentage removal of oil was found to be 25.96% in a 10% (v/v) oil–water solution for chitosan prepared in the present study while it was 36.19% when pharmaceutical grade chitosan was tested for a solution of the same concentration. These results indicate that the chitosan prepared from prawn shells (waste material) has less oil adsorption capacity with commercially available pharmaceutical grade chitosan. However, the commercially available pharmaceutical grade chitosan is very expensive.

Various materials have been investigated for the adsorption of oil. Li et al. [33] have studied the adsorption of oil on anthracite which follows the Freundlich isothermal adsorption law. In their study, given initial oil concentrations of 0.16 1 or 1.024 g l^{-1}, the absorption capacity was found to be 0.024 or 0.840 g g^{-1}, respectively. The oil absorption by the coal increased for a period of 1.5 h and then gradually tended toward an equilibrium value.

A study was conducted by Islam [34] using SAE 30 (Golden West Superior) motor oil as adsorbate and the organoclay as adsorbent. The Freundlich isotherm model was found to effectively provide the amount of organoclay for desired oil adsorption and the contact time was identified as 3 h. For the equilibrium concentration value of 0.654 g l^{-1}, the corresponding adsorption capacity was 0.5639 g g^{-1}. From this particular study, the percentages of oil removal were found to be 28.20% for 0.75 g l^{-1} emulsion, 35.75% 1.00 g l^{-1} emulsion and 40.036% for 1.50 g l^{-1} emulsion.

The studies conducted by Li et al. [33] using anthracite and Islam [34] using organoclay have been conducted for lower initial concentrations of oil–water solutions as compared to the present study using chitosan as an adsorbent. Further investigation of anthracite and organoclay as adsorbents for higher initial concentrations of oil–water solutions is necessary in order to compare their performance with that of chitosan. However, it can be noted that the contact time for adsorption of oil on anthracite and organoclay is significantly longer as compared to the contact time required for adsorption of oil on chitosan.

4. Conclusions

Chitosan prepared from seafood industry waste, prawn shells is found to be a suitable adsorbent for the removal of oil from oil–water solution. The kinetics study indicated that the rate of adsorption of oil on chitosan is very fast and equilibrium being reached in 6 min. The percentage removal increases with decrease in the value of pH. The percent removal decreases and adsorption capacity increases while oil concentration increases. Equilibrium data are well fitted with the Langmuir isotherm. The maximum adsorption capacity is obtained as 18.52 g g^{-1} with the application of Langmuir isotherm. The rate kinetics of oil adsorption on chitosan is better explained by second-order kinetics. The biodegradability and effectiveness of chitosan makes it an ideal alternative for cleaning up oil spills.

Symbols

b — adsorption equilibrium constant, l g^{-1}
C_e — concentration of oil at equilibrium, g l^{-1}
h — initial sorption rate, g g^{-1} min^{-1}
k_1 — pseudo-first-order rate constant, l min^{-1}
k_2 — pseudo-second-order rate constant, g g^{-1} min^{-1}
q_e — equilibrium solid phase concentration of oil, g g^{-1}
q_t — solid phase concentration of oil at time t, g g^{-1}
Q_m — maximum monolayer adsorption capacity, g g^{-1}
t — time, min

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