Adsorption of Oil Droplets from Oily Produced Water Using Chitosan

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ABSTRACT
Treatment and disposal of oily wastewater, presently is one of the serious environmental problems contributors. Numerous methods have been used to remove residual oil from wastewater, such as adsorption, flocculation, electrocoagulation and flotation. The focus of this research was to prepare and investigate the using of chitosan as an oil adsorbent and coagulant of the excessive residue oil droplets from an oily wastewater. In this respect, shrimp waste (shell) was treated with 9% (w/w) NaOH at 65°C for 90 min to obtain a purified crab chitin, and then 1g of purified crab chitin was treated with (w/w) 50% sodium hydroxide solution at 136°C for 1h to obtain pure chitosan. The prepared chitin and chitosan were characterized by the FT-IR spectrometry, X-ray diffraction (XRD) and scanning electron microscopy (SEM). The FT-IR spectrum shows three characteristic absorption bands of chitosan one of them was very strong and appeared at about 3306 cm\(^{-1}\) this for stretching vibration bands of (N-H and O-H), the second strong one appeared at about 1593.54 cm\(^{-1}\) that assigned for (-CONH-) and the third band at 1054.90 cm\(^{-1}\) for (C-O-C). The XRD patterns of chitosan show two characteristics crystalline peaks at 20 of 9.24\(^{°}\) and 19.2\(^{°}\) indicates the formation of chitosan from chitin. The surface morphology of chitosan before and after oil adsorption was examined using SEM. Then, the percentage of oil droplets removal was evaluated by HPLC.

Fig. 1 Chemical structure of the chitin and chitosan
Chitosan and chitin are of commercial interest due to their high percentage of nitrogen compared to synthetically substituted cellulose. Chitosan is soluble in acid solutions and is chemically more versatile than chitin or cellulose. Most of the properties of chitosan can be related to its cationic nature [10], which is unique among abundant polysaccharides and natural shorter chain than the original chitin. It is insoluble in water, soluble in some aqueous monobasic acids, and insoluble in dilute or concentrated alkali solutions. Its solubility in aqueous mineral and organic acids is due to the formation of positively charged ammonium ions. Chitosan is insoluble in pure organic solvents, is insensitive to humidity, and contains 10–14% water. It decomposes when the temperature reaches 185°C [8].

Introduction
Treatment and disposal of oily wastewater, presently is one of the serious environmental problems contributors [1]. The major difficulty in disposing the oily residuals are the emulsified oil droplets, which are sheltered from spontaneous coalescence into larger flocculants, making oil separation by simple gravity a difficult and time consuming process [2]. Numerous methods have been used to remove residual oil from wastewater, such as adsorption, flocculation, electrocoagulation and flotation [3].

There are a number of natural adsorbents used to adsorb residual oil from oily wastewater such as chitosan. Chitosan is recommended as a suitable resource material, because it has excellent properties, such as biodegradability, biocompatibility, film-forming ability, bioadhesivity, polyfunctionality, hydrophilicity flocculating ability, polyelectrolysis and adsorption properties, in addition to its possibilities of regeneration in number of applications [4]. Chitosan is a partially deactivated derivate obtained by alkaline treatment of chitin [5]. Chitosan (1–4, 2-amino-2-deoxy-β-D-glucan) is a hydrophilic polyelectrolyte obtained by deacetylation of chitin. As chitin is one of the most abundant natural polymers, chitosan's potential industrial and special applications could be significant [6].

Chitosan is a biodegradable copolymer, consisting of 13–17% units of monomeric N-acetyl-glucosamine and 83–87% glucosamine units. It is environmentally and technologically acceptable in the repulping and recycling of paper, since structurally it is essentially cellulose with the 2-hydroxyl group replaced by a primary amino function [7] Figure (1). Because of its extreme alkaline deacetylation conditions, chitosan has a

Keywords
Oily produced water,
Oily wastewater treatment,
Shrimp waste,
Chitin, chitosan,
Oil droplets removal,
Adsorption.
polymers. These numerous properties lead to the recognition of this polyamine as a promising raw material for adsorption purposes.

The major goal of the current study was aimed to prepare and investigate of chitosan as an oil adsorbent. The prepared chitin and chitosan were characterized by the FT-IR spectrometry and X-ray diffraction. The surface morphology of chitosan before and after oil adsorption was examined using SEM. Then, the percentage of oil droplets removal was evaluated by HPLC.

Material and methods

Experimental materials

Water sample was collected from Egyptian petroleum fields and analyzed to determine the residual oil content, suspended solid and pH properties, the analysis results are given in Table (1).

Chitin was extract from shrimps and then converted into off-white fine powder chitosan with mesh size less than 120.

Distilled water was used to dilute hydrochloric acid solution and dissolve sodium hydroxide pellets to obtain solutions of 5M. These solutions were then used to adjust the pH during the treatment process. N-hexane was used as the oil extraction in the oil analysis.

Preparation of chitin

Chitin was isolated from shrimp shells waste. The material was homogenized and the product was rinsed in order to remove the organic material, and then treated with 9% (w/w) NaOH at 65°C for 90 min to remove proteins. After that it was demineralized by treatment with 10% (v/v) HCl at 20°C for 1h. After filtration, washing with deionized water till neutralization then drying [11].

Preparation of crab chitosan

Chitosan was prepared directly by treated 1 g of purified crab chitin with (w/w) 50% sodium hydroxide solution at 136°C for 1h. After filtration, washing with deionized water till neutralization then drying [12].

Measurements

Fourier transform infrared measurements model Nicolet 8700, Thermo Scientific, USA was used to confirm the structure of chitin, chitosan and chitosan after adsorbed oil. The X-ray diffraction analysis was measured with a Rigaku D/MAX RINT 2500 X-ray diffractometer operated at 36 kV and 20 mA. X-ray diffraction (X-RD) was used to examine the crystallinity/crystal structure and phase constituents of samples [13]. The surface morphology of the polymer was investigated by using scanning electron microscopy (SEM) (Superscan SSX-550, Shimadzu Co., Kyoto, Japan). The scan speed was 1/9 min. The oil concentration was determined using HPLC (Perkin Elmer series 200) with photodiode-array detector at $\lambda= 254$ nm and a Brownlee Analytical PAHs 4μm (250×4.6 mm) column. The mobile phase was acetonitrile / water with a gradient elution in which a change in the ratio of acetonitrile to water from 60:40 to 100 was used for 20 min at a flow rate of 1.2 ml min$^{-1}$.

Results and discussion

FTIR characterization

Figure (2) depict the FTIR spectra of prepared chitin. The spectrum show a sharp band at 1319 cm$^{-1}$ which is due to the symmetrical deformation or rocking of the CH$_3$ group, a band at 1659 cm$^{-1}$ is attributable to the stretching vibration of CN superimposed to C=O group linked to–OH group by hydrogen bonding [14, 15]. The absence of a peak at 1540 cm$^{-1}$, demonstrates that the successive treatment of chitin is strong enough to eliminate all the proteins, thereby; we obtain pure chitin [16, 17].

Figure (3) depict the FTIR spectra of prepared chitosan. This spectrum shows three characteristic absorption bands of chitosan one of them was very strong and appeared at about 3306 cm$^{-1}$ this for stretching vibration bands of (N-H and O-H), the second strong one appeared at about 1593.54 cm$^{-1}$ that may assigned for (-CONH-) and the third band at 1054.90 cm$^{-1}$ for (C-O-C). In addition the two peaks at 1319 cm$^{-1}$ and 1659 cm$^{-1}$ are weakly apparent, this may be due to high deacetylation. Further the peak at ~1645 cm$^{-1}$ indicated that the hydrogen interactions are less accentuated and the hydroxyl groups exist freely due to removal of acetyl group.

The FTIR spectrum of chitosan after adsorbed oil is given in Figure (4) and shows the same band appeared in prepared chitin. The FTIR characterization of chitosan before and after oil adsorption was examined using spectroscopy and X-ray diffraction. The surface morphology of chitosan before and after oil adsorption was examined using FTIR and X-ray diffraction analysis was measured with a Rigaku D/MAX RINT for 1h. After filtration, washing with deionized water till neutralization then drying [12]. Figure (3) depict the FTIR spectra of prepared chitin. The characteristic sharp peak of chitin at 20 of 9.24° and 19.2° decreased considerably and became broad. It gave clear indication of the formation of chitosan as described by Zhang et al., [18]. Comparison of X-ray diffractograms of chitin and chitosan formed. Decrease of peaks at 20 of 9.24° and 19.2° indicates the formation of chitosan from chitin. From these figures it can be seen that the differences between them can be related to the change of the amorphous structure of prepared chitin into a crystalline phase of chitosan,
and the disappearance of former peaks with increasing in latter 3 peaks which other evidence for complete and succeed preparation.

Fig. 5 X-ray diffraction of chitin

Fig. 6 X-ray diffraction of chitosan

Oil contents by using HPLC

Figures (7&8) show the HPLC analysis of the untreated oily produced water and water treated with chitosan, respectively. Figure (7) show the area% peak of oil in untreated oily produced water recorded at 96.09, meanwhile area% peak of oil in treated oily produced water by 0.01 pm chitosan recorded at 17.82 as shown in Figure (8). The rate of decreasing oil % due to low concentration of chitosan, that indicated a complete coagulant phenomena and high removal efficiency reached to approximately 81.45% as illustrated in Table (2).

Fig. 7 HPLC analysis for untreated oily produced water treated with chitosan

Fig. 8 HPLC analysis for water

SEM Study

The morphology of both chitin and chitosan were studied by SEM as illustrated in Figures (9&10). Chitin powder exhibit almost a smooth surface as shown in Figure(9), however, chitosan showed cracks and pores in its surface and the number of pores increased significantly as illustrated in Figure (10). Generally we can conclude that chitosan have pores and cracks in its surface more than chitin, this give chitosan an ability to adsorb more oil than chitin as illustrated in the removal efficiency study as shown in Figure (11).

Fig. 9 SEM micrographs of chitin

Fig. 10 SEM micrographs of chitosan

Fig. 11 SEM micrographs of oily chitosan

Conclusion

In this work, chitosan was synthesized using chitin and characterized using SEM, FT-IR and XRD. Structural analysis by XRD proved that chitin initially is almost amorphous while chitosan have crystalline pattern. The crystalline phase of prepared chitosan shows peaks at 2θ=34° and 41°. The investigations by SEM analysis showed that the morphology of chitosan as initially prepared proceeds in irregular surface, also the SEM of chitosan showed an increase of pores and cracks in its surface. The chemical treatment of chitosan during its preparation process increases its crystalline volume fraction. Also, the HPLC analysis of the treated oily produced water with chitosan at low concentration shows decreasing in oil % reach to18.55 approximately with removal efficiency of 81.45 %. It can be conclude that chitosan has a cationic nature as indicated from all the above data.

References

Table 1. Extended water analysis

<table>
<thead>
<tr>
<th>Total Dissolved Solids</th>
<th>325.8 mg/l</th>
<th>pH</th>
<th>6.4 @ 25°C</th>
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<tbody>
<tr>
<td>Conductivity</td>
<td>0.0451x 10⁻⁷ mohs/cm @ 25.1°C</td>
<td>Density</td>
<td>1.00290 g/ml @ 60 °F</td>
</tr>
<tr>
<td>Resistivity</td>
<td>22.17295 Ohm-m @25.1°C</td>
<td>Specific gravity</td>
<td>1.00389</td>
</tr>
<tr>
<td>Salinity</td>
<td>47.2 mg/l</td>
<td>Hardness</td>
<td>152.0 mg/l</td>
</tr>
</tbody>
</table>

Table 2. Area % of untreated and treated oily produced water from HPLC analysis

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Area [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>untreated oily produced water</td>
<td>96.09</td>
</tr>
<tr>
<td>Treated oily produced water</td>
<td>17.82</td>
</tr>
</tbody>
</table>


