Available online at http://www.journalcra.com

International Journal of Current Research
Vol. 6, Issue, 03, pp.5413-5418, March, 2014

INTERNATIONAL JOURNAL
OF CURRENT RESEARCH

ISSN: 0975-833X

RESEARCH ARTICLE

PREPARATION AND CHARACTERIZATION OF NATURAL POLYMER FOR TREATMENT OILY PRODUCED WATER

***[1]Rasha Hosny, [2]Th. Abdel-Moghny, [1]Ramzi, M., [1]Desouky, S. E. M. and [3]Shama, S. A.**

[1]Production Department, Egyptian Petroleum Research Institute, 1Ahmed El-Zomer, Nasr City, Cairo, Egypt
[2]Applications Department, Egyptian Petroleum Research Institute, 1Ahmed El-Zomer, Nasr City, Cairo, Egypt
[3]Department of Chemistry Faculty of Science, Benha University, Fred Nada Street - Benha – Cairo, Egypt

ARTICLE INFO

Article History:
Received 05th December, 2013
Received in revised form
10th January, 2014
Accepted 14th February, 2014
Published online 25th March, 2014

Key words:
Oily produced water,
Emulsified oil droplets,
Water flooding,
Adsorption and Chitosan.

ABSTRACT

Treatment and disposal of large amount of oily produced water is a considerable economic and environment burden for oil and gas industry. The treatment of produced water requires the separation of suspended and dissolved component such as emulsified oil droplets. The goal of this research is to prepare chitosan as a natural polymer from chitin to yield clean oily produced water has enough beneficial uses like drilling, stimulating, or water flooding. The prepared chitosan characterized by the FT-IR spectrometry, and X-ray diffraction. Then, the percentage of oil droplets removal was evaluated by HPLC and SEM (scanning electron microscopy). It was found that the chitosan could successfully remove 81.45% of residual oil at 0.01ppm dosage, under mixing time at 20 min, mixing rate 200 rpm, sedimentation time for 30 min and a pH value ranging from 5.0 to 6.0.

INTRODUCTION

Produced water is defined as the water brought up from the hydrocarbon bearing strata during the extraction of oil and/or gas and can include formation water, injection water, and condensed water and trace amounts of treatment chemicals. The production stream containing the oil/gas/water mixture is passed through separation equipment to separate oil, gas, and water followed by treatment of the produced water for discharge or re-use. Produced water handling is a key challenge at most production facilities. It can be a crucial factor limiting the production of oil and gas. If the discharge requirements are not met, there may be a significant environmental and economic impact. Furthermore, produced water can take up valuable space in the oil transport lines, reducing the amount of oil that can be produced and transported. Produced water is the highest volume waste generated in association with oil and gas production operations. This waste stream is characterized as a high volume - low toxicity waste. Oil and grease in produced water includes free oil, dispersed oil (small oil droplets), and emulsified oil. Oil and grease removal methods depend on the end usage of treated water and composition of oil in the produced water (Daniel Arthur *et al.*, 2005). Treatment and disposal of oily wastewater, is presently one of the serious environmental problems contributors (Ahmad *et al.*, 2005). 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 (Zouboulis, and Avranas 2000). Numerous methods have been used to remove residual oil from wastewater, such as adsorption, flocculation, electrocoagulation and flotation (Andrew *et al.*, 2000).

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, biocompability, film-forming ability, bioadhesivity, polyfunctionality, hydrophilicity flocculating ability, polyelectrolisity and adsorption properties, in addition to its possibilities of regeneration in number of applications (Rinaudo 2006). Chitosan is a partially deactivated derivate obtained by alkaline treatment of chitin (Majeti 2000). Chitin is a long-chain of *N*-acetylglucosamine polymer as shown in Figure (1), and is found in the exoskeleton of crustaceans, the cuticles of insects, and the cells walls of fungi, is the most abundant aminopolysaccharide in nature (Synowiecki and Al-Khateeb 2003; Struszczyk 2002; Rinaudo 2006). Chitosan is a linear polysaccharide composed of randomly distributed β-(1-4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit) Figure (2). It is structurally

---

****Corresponding author:* Rasha Hosny,** *Production Department, Egyptian Petroleum Research Institute, 1Ahmed El-Zomer, Nasr City, Cairo, Egypt.*

similar to cellulose, but it is an aminopolymer and has acetamide groups at the C-2 positions in place of the hydroxyl groups. The presence of these groups is highly advantageous, providing distinctive adsorption functions and conducting modification reactions. Chitin is extracted from crustaceans (shrimps, crabs, squids) by acid treatment to dissolve calcium carbonate followed by alkaline extraction to dissolve the proteins and by a decolorization step to obtain a colorless product (Struszczyk 2002; Rinaudo 2006) Figure (3). Chitin is an extremely insoluble material (Rinaudo 2006). Partial deacetylation of chitin results in the production of chitosan Figure (3) (Crini and Badot 2008), which is a polysaccharide composed by polymers of glucosamine and N-acetyl glucosamine. The ‘‘chitosan label’’ generally corresponds to polymers with less than 25% acetyl content. The fully deacetylated product is rarely obtained due to the risks of side reactions and chain depolymerization. Copolymers with various extents of deacetylation and grades are now commercially available. 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 (Peter 1995), which is unique among abundant polysaccharides and natural polymers. These numerous properties lead to the recognition of this polyamine as a promising raw material for adsorption purposes.

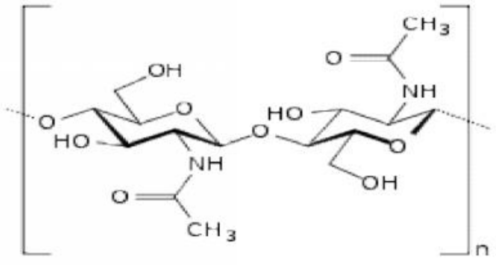

Fig. 1. Chemical structure of the chitin molecule

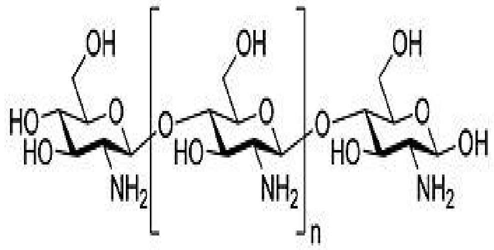

Fig. 2. Chemical structure of chitosan

MATERIALS 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

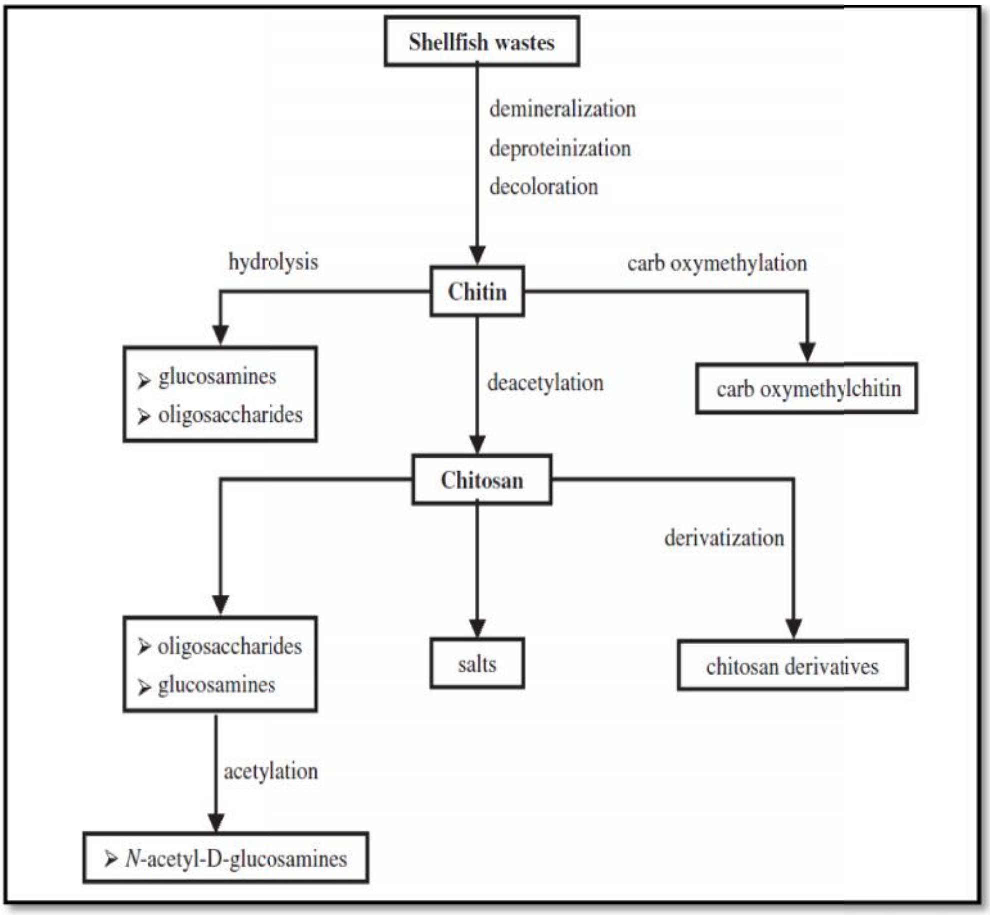

Fig. 3. Simplified representation of preparation of chitin, chitosan and their derivatives [Crini and Badot 2008]

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.

Table 1. Extended water analysis

Total Dissolved Solids	325.8 mg/l	pH	6.4 @ 25 °C
Conductivity	0.0451x 10^{-2} mohs/cm @ 25.1°C	Density	1.00290 g/ml @ 60 F
Resistivity	22.17295 Ohm-m @25.1°C	Specific gravity	1.00389
Salinity	47.2 mg/l	Hardness	152.0 mg/l

Constituents	mg/L	meq/L	Constituents	mg/L	meq/L
Lithium	0.01	0.002	Fluoride	0.82	0.043
Sodium	35.58	1.548	Chloride	28.6	0.807
Potassium	5.11	0.131	Bromide	1.15	0.014
Magnesium	12.78	1.052	Nitrate	0.245	0.004
Calcium	39.78	1.985	Hydroxide	Nil	Nil
Strontium	Nil	Nil	Carbonate	24	0.800
Barium	Nil	Nil	Bicarbonate	131	2.147
Iron	0.10	0.005	Sulfate	46.6	0.970

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 15 min, washed, and then dried (Herasa *et al.*, 2001).

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 (Yen *et al.*, 2009).

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 (Maghsoodi and Yaghmaei 2010). 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°/ min. The oil concentration was determined using HPLC (Perkin Elmer series 200) with photodiode-array detector at λ= 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 (4) 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 (Majtán *et al.*, 2007; Paulino *et al.*, 2006). 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 (Morin and Dufresne 2002; Duarte *et al.*, 2002) Figure (5) depict the FTIR spectra of prepared chitosan.

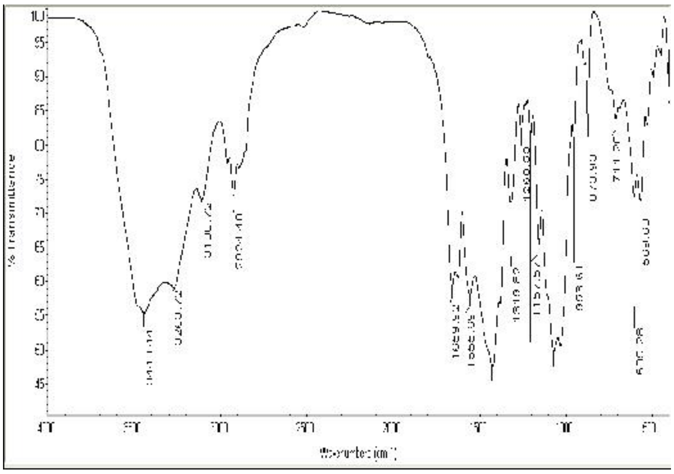

Fig. 4. FTIR spectra of chitin

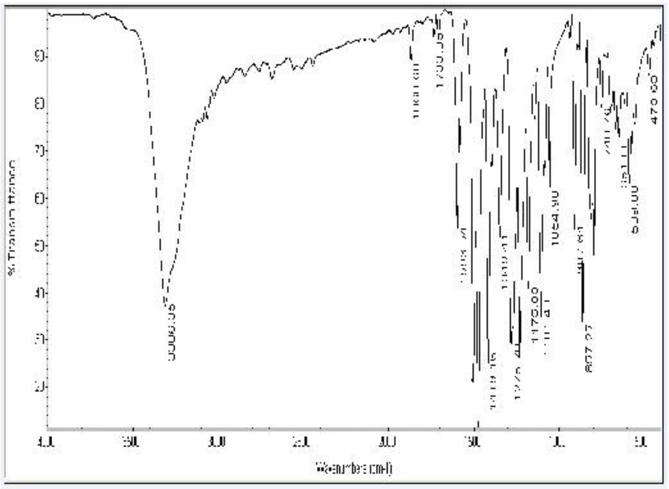

Fig. 5. FTIR spectra of chitosan

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 (6) and shows the same band appeared in prepared chitosan. Another major absorption band at 874- 580 cm^{-1} that represents the mono and di substituted aromatic ring of oil compound which indicates that chitosan absorb oil from water.

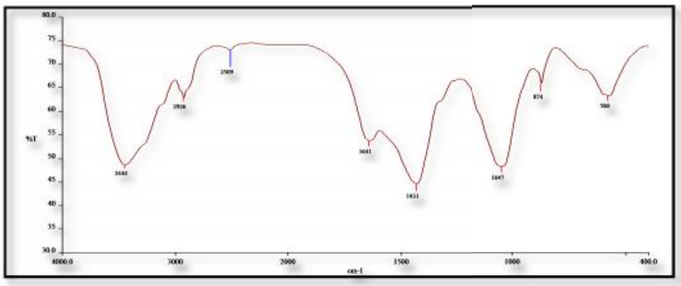

Fig. 6. FTIR spectra of chitosan after adsorbed oil

X-ray diffraction study

The conversion process was further confirmed by XRD analysis Figures (7 and 8). The characteristic sharp peak of chitin at 2θ 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*. (2005). Comparison of X-ray diffractograms of chitin and chitosan formed. Decrease of peaks at 2θ 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.

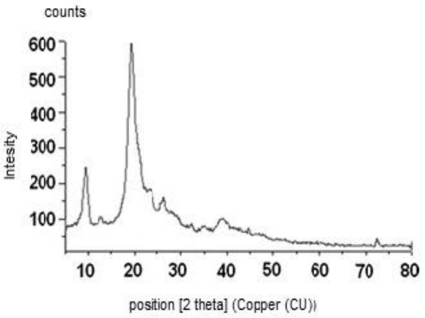

Fig. 7. X-ray diffraction of chitin

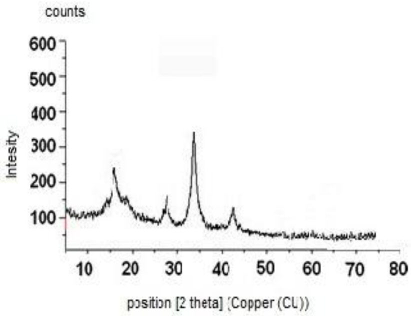

Fig. 8 X-ray diffraction of chitosan

Oil contents by using HPLC

Figures (9 and 10) show the HPLC analysis of the untreated oily produced water and water treated with chitosan, respectively. Figure (9) 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 (10). 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).

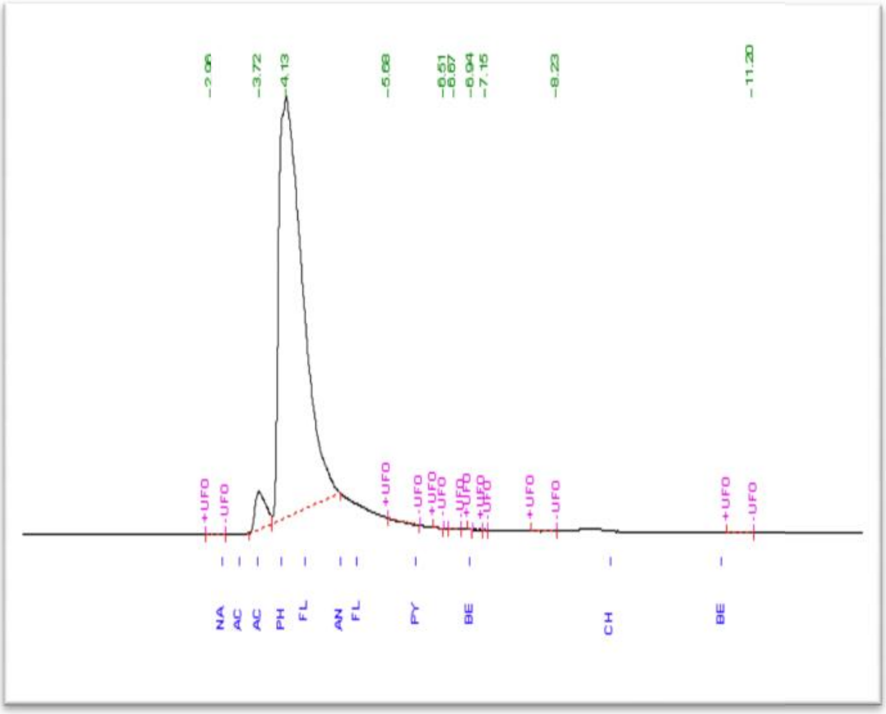

Fig. 9. HPLC analysis for untreated oily produced water

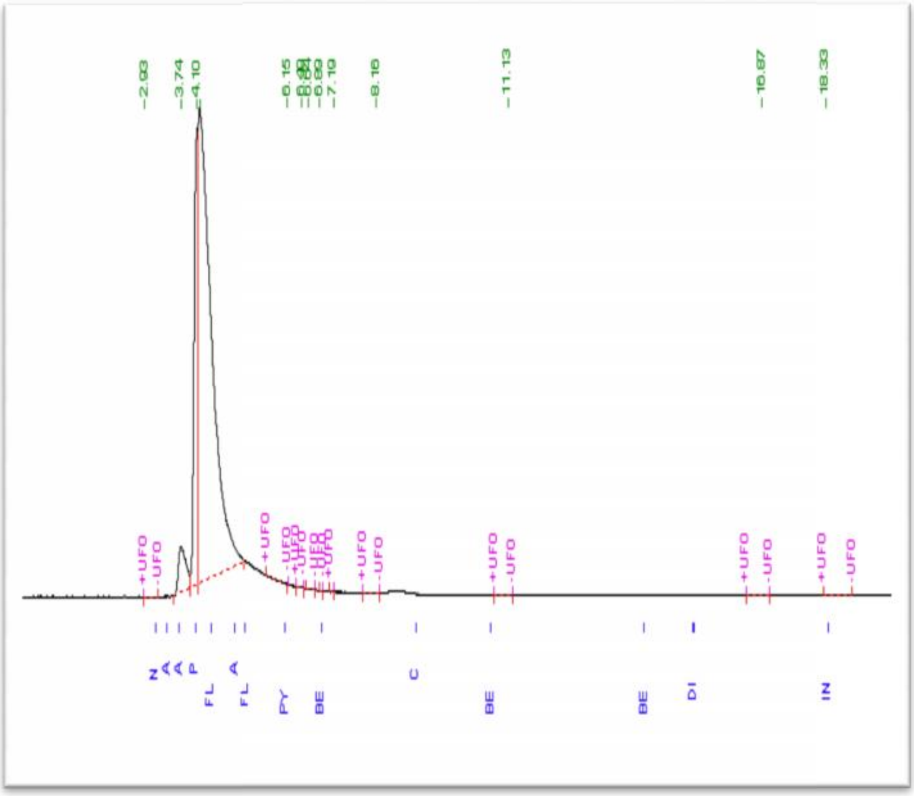

Fig. 10. **HPLC analysis for water treated with chitosan**

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

Sample name	Area (%)
untreated oily produced water	96.09
Treated oily produced water	17.82

SEM Study

The morphology of both chitin and chitosan were studied by SEM as illustrated in Figures (11 and 12). Chitin powder exhibit almost a smooth surface as shown in Figure (11), however, chitosan showed cracks and pores in its surface and the number of pores increased significantly as illustrated in Figure (12). 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 (13).

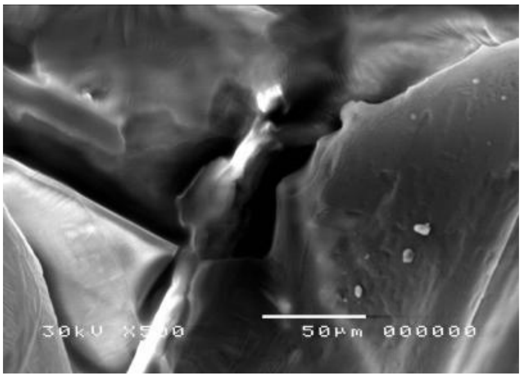

Fig. 11. SEM micrographs of chitin

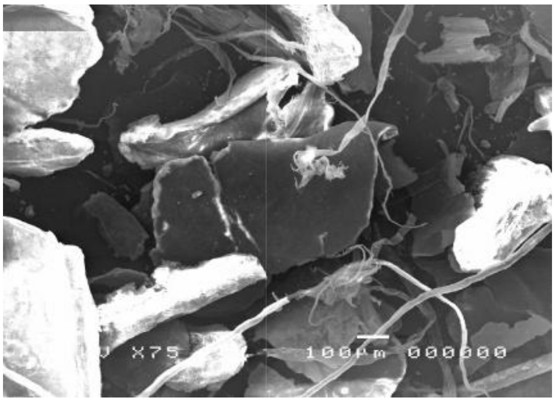

Fig.12. SEM micrographs of chitosan

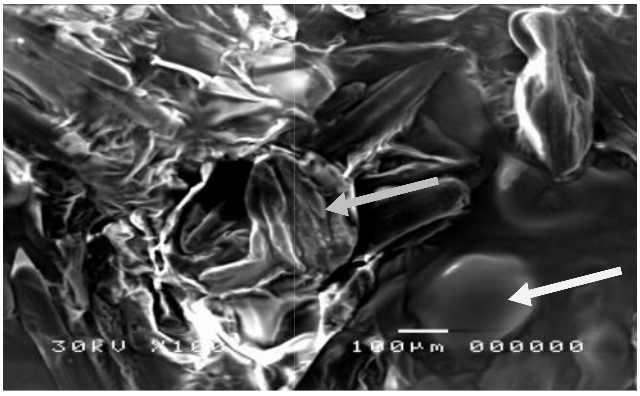

Fig. 13 SEM micrographs of oily chitosan

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 $2\theta=34^{O}$ and 41^{O}. 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

Ahmad A.L., S. Sumathi, B.H. Hameed, Residual oil and suspended solid removal using natural adsorbents chitosan, bentonite and activated carbon: A comparative study, *Chemical Engineering Journal* 108 (2005) 179–185.

Andrew K., G. Graeme, G. Jeff., R.S. Brian, Flocculation and coalescence of oil-in-water poly(dimethlysiloxane) and emulsion, *Colloid Interface Sci., Ideal Library* 227 (2000) 390–397.

Crini G., and P.-M. Badot. Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: review of recent literature, Prog. Polym. Sci. 33 (2008) 399–447.

Daniel Arthur J., P.E. Bruce G. Langhus, Ph.D., C.P.G. Chirag Patel, Technical summary of oil & gas produced water treatment technologies, all consulting, LLC 1718 South Cheyenne Ave., Tulsa, OK 74119, March (2005).

Duarte M.L., M.C. Ferreira, M.R. Marvão, J. Rocha, An optimised method to determine the degree of acetylation of chitin and chitosan by FTIR spectroscopy. *Int. J. Biol. Macromol.* 31, (2002)1–8.

Herasa A., N.M. Rodri´guezb, V.M. Ramosc, E. Agullo, Carbohydrate Polymers 44 (2001) 1–82.

Maghsoodi V., S. Yaghmaei, Comparison of solid substrate and submerged fermentation for chitosan production by Aspergillus niger. Trans. C: *Chem. Chem. Eng*. 17 (2010) 153-157.

Majeti N.V.R.K., A review of chitin and chitosan applications, React. Funct. Polym. 46 (2000) 1–27.

Majtán J., K. Bíliková, O. Markovič, J. Gróf, G. Kogan, J. Šimúth, Isolation and characterization of chitin from bumblebee (Bombus terrestris). *Int. J. Biol*. Macromol. 40, (2007) 237–241.

Morin A., A. Dufresne, Nanocomposites of Chitin Whiskers from Riftia Tubes and Poly (caprolactone), Macromolecules, 35, 2190 (2002).

Paulino A.T., J.I. Simionato, J.C. Garcia, J. Nozaki, Characterization of chitosan and chitin produced from silkworm chrysalides. *Carbohydr. Polymers* 64, (2006) 98–103.

Peter M.G., Application and environmental aspects of chitin and chitosan. J M S Pure Appl Chem 32 (1995) 629–40.

Rinaudo M., Chitin and chitosan: properties and applications. Prog Polym Sci 31 (2006) 603–32.

Rinaudo M., Chitin and chitosan: properties and applications. Prog Polym Sci 31 (2006) 603–32.

Struszczyk M.H., Chitin and chitosan—part I. Properties and production. Polimery 47 (2002) 316–25.

Synowiecki J. and N.A. Al-Khateeb, Production, properties and some new applications of chitin and its derivatives. Crit Rev Food Sci Nutrition 43 (2003) 145–71.

Yen M.-T., J.,-H. Yang, and J.,-L. Mau," Physicochemical characterization of chitin and chitosan from crab shells" Carbohydrate Polymers 75 (2009) 15–21.

Zhang Y., C. Xue, Y. Xue, R. Gao, X. Zhang, Determination of the degree of deacetylation of chitin and chitosan by X-ray powder diffraction. *Carbohydr. Res*. 340, (2005) 1914–1917.

Zouboulis A.I., and A. Avranas, Treatment of oil-in-water emulsions by coagulation and dissolved-air flotation, Colloids Surf. 172 (2000) 153–161.

****