Effectiveness of N,O-carboxymethyl chitosan on destabilization of Marine Diesel, Diesel and Marine-2T oil for oil spill treatment

Bhairavi Doshi a,*, Eveliina Repo a, Juha P. Heiskanen b, Juho Antti Sirviö c, Mika Sillanpää a

a Laboratory of Green Chemistry, Lappeenranta University of Technology, Sammonkatu 12, Mikkelin 50130, Finland
b Research Unit of Sustainable Chemistry, University of Oulu, P.O. Box 3000, FI-90014, Finland
c Fibre and Particle Engineering Research Unit, University of Oulu, P.O. Box 4300, FI-90014, Finland

A R T I C L E   I N F O

Article history:
Received 24 October 2016
Received in revised form 16 March 2017
Accepted 19 March 2017
Available online 21 March 2017

Chemical compound studied in this article:
Chitosan (PubChem CID: 71853)

Keywords:
N,O-carboxymethyl chitosan
Oil droplets
Micro emulsions
Oil spill treatment
Marine diesel
Adsorption

A B S T R A C T

Oil spills are the significant sources of hydrocarbons entering in the receiving aquatic environment. An efficient method to remove hydrocarbons from water resources is adsorption. In this study, water soluble N,O-carboxymethyl chitosan (NO-CS) was synthesized by carboxymethylation of chitosan in a hydro-alcoholic medium at 50 °C by chloroacetic acid. The polymer was characterized through degree of deacetylation, degree of substitution, FTIR and 1H NMR. Effectiveness of NO-CS as an adsorbent was studied as a function of dosage, salinity and pH to destabilize the Marine diesel (Oil-1), Diesel (Oil-2) and Marine-2T oil (Oil-3) into small oil droplets of less than 100 μm. Optical microscope was used for studying the size of oil droplets and adsorption effect of the oils on this polymer. The destabilization of marine diesel was the most effective among the studied three oils, which showed excellent adsorption at sea water alkalinity and salinity.

© 2017 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

Oil entering the natural water resources originates from the accidental spills or leaks from ships or tankers, storm water drainage from cities and farms, untreated waste disposal from factories and industrial facilities, unregulated recreational boating, offshore drilling and production operations (Farrington and McDowill, 2004). Climatic change (Wassmann, Duarte, Agust, & Sejr, 2011) enables increase in transportation (Arrigo, 2013) and industrial activities in arctic regions by enhancing the oil spill rate (Nevalainen, Helle, & Vahnatulo, 2017). Oil spilled from the ships and tankers including the transportation fuel used by the vessels themselves or their cargos, such as crude oil, fuel oil, or heating oil are the significant sources of hydrocarbon inputs into the oceans, lakes, rivers, etc. These spills, not only destroy the marine life (DeLeo, Ruiz-Ramos, Raums, & Cordes, 2016; Sagerup, Nahrgang, Frantzen, Larsen, & Geraudie, 2016) and wetland, but also affects the estuarine habitat (Klemas, 2010).

Behavior of oil varies in different environments and, therefore it is important to know the type of oil spill (Dahlmann, 2003). The constituents of crude oil are saturates, aromatics, resins, and asphaltenes. Light crude oil contains a higher percentage of saturated hydrocarbons and aromatics, while heavy oil contains more resins and asphaltenes (Fan & Buckley, 2002). Diesel fuel is most often a light, refined petroleum product consists of hydrocarbon from C8-C26 which are either branched and/or linear. A small amount of diesel spills will usually evaporate and disperse naturally within a day or less. But marine diesel is often a heavier fuel oil that persist longer when spilled and in-situ burning may not be possible under Arctic conditions even though it is designed for combustion. Marine diesel and diesel contains about 1.2% and 2% of polyaromatics, respectively. Marine 2T-oil is the petroleum distillates consist of hydrocarbons, C11-C14, n-alkanes, isoalkanes, cyclics, butene, solvent-dewaxed heavy paraffinic and polyaromatics, and it is used in ships and, boats as a lubricant can easily react with water forming a creamy layer. A small amount of oil spill affects the marine ecosystem due to its toxicity (Peterson et al., 2003). In extreme cold conditions, natural weathering process such as evaporation and biodegradation (Wang & Fingas, 2003) rates reduce with increase in viscosity of oil. There is evaporative loss of about 30% for open water, 25% for the lighter ice coverage, and 19% for the heavier ice
coverage, due to differences in oil film thicknesses (Brandvik and Faksness, 2009). To clean up oil in the coastal environment, various spill containment methods such as use of booms, hard booms, sorbent booms, fire booms, skimmers, vacuum trucks, in situ burning, dispersants (Brlakstad et al., 2014), and chemical cleaners are used. A mixture of oil and water is generally unstable and addition of surfactants reduces the interfacial tension between the oil and water by breaking the oil into oil droplets and preventing coalescence of dispersed oil droplets. A surfactant used in oil spill treatment can either be adsorbed at the oil-water interfaces or form thicker slicks with oil. However, prolonged use of synthetic surfactants reflects toxic effects on the marine ecosystems (Claireauxa et al., 2013; Lewis & Pryor, 2013; Smit et al., 2009). Nowadays, replacement of these hazardous chemicals has been studied, either by using bio-surfactants (Silva et al., 2014) or biopolymers (Venkataraman et al., 2013) due to their biocompatibility, non-toxicity and sustainability in the oil-spill treatment.

Biopolymer chitosan is a deacetylated form of chitin used widely as a biomaterial in drug delivery and tissue engineering (Martinoa, Sittingerc, & Risbud, 2005), as a sorbent in waste water treatment for removal of metals (Bhatnagar & Sillanpää, 2009; Crini, 2005; Ngaha, Teonga, & Hanafahah, 2010; Repo, Warchol, Bhatnagar, & Sillanpää, 2011), and in food industry as it is abundant, versatile, non-toxic, biocompatible and biodegradable (Khora & Lim, 2003). Chitosan has excellent adsorption characteristics due to the presence of large number of hydroxyl groups, which gives hydrophilicity and large number of amino groups with high activity as adsorption sites (Mourya, Inamdar, & Tiwari, 2010). However, the formation of protonated amino group contributes to the solubility of chitosan in acidic solutions (Bee, Oben, Mbolantenaina, Welschbillig, & Talbot, 2016). This variable functionality of amino groups at different solution pH, can be used to stabilize oil-in-water emulsions (Colombo, Cavikeri, & Muthupandian, 2015). Emulsion stability also depends on the hydrophobicity and hydrophilicity of the particles, so to get oil-in-water emulsion, particles should be hydrophilic (Tsabet & Fradette, 2015).

Carboxymethylation is a reaction of an alkaline pre-treated chitosan with chloroacetic acid in the presence of isopropanol as a solvent. The presence of sodium hydroxide in the reaction mixture results in swelling of chitosan and consequently better diffusion of chloroacetic acid into the rigid structure of chitosan (Chen, Du, & Zeng, 2003) and, appropriate amounts of isopropanol together with water facilitates the reaction (Chen & Park, 2003). Reaction time and amount of chloroacetic acid and sodium hydroxide have a significant effect on the solubility of the carboxymethyl chitosan in water (Bidgoli, Zamani, & Taherzadeh, 2010). Depending on the reaction conditions, there is a selectivity substitution site for N- versus O-carboxymethyl chitosan derivative. Hence, the overall properties of carboxymethylation is structural dependent and mainly on degree of substitution (An, Thien, Dong, & Dung, 2009). Carboxymethyl chitosan is used in waste water treatment (Boricha & Murthy, 2010), in cosmetics (Juntaisong & Saeawan, 2014), in biomedical and pharmaceuticals (Chen, Wang, Chen, Ho, & Sheu, 2006) due to its biological properties, and as a sorbent for removal of metals (Sun & Wang, 2006) and dyes (Wang & Wang, 2008), etc. N-O-carboxymethyl chitosan (NO-CS) is a water soluble derivative of chitosan, enhancing biodegradability and biocompatibility, physicochemical and biological properties (Upadhyaya, Singh, Agarwal, & Tewari, 2013), in comparison to chitosan. However, the applicability of NO-CS with degree of substitution lower than 0.5, has not been studied much for in oil spill treatment.

This study was carried out to investigate the effectiveness of NO-CS on three different oils by considering dosage, salinity, and pH. As NO-CS was hydrophilic, the effect of dosage was limited only to destabilization of oil inhibiting coalescence due to electrostatic interaction between negatively charged carboxylate ion attached to amino group of NO-CS and hydrocarbons in oil with oil droplets size less than 100 μm. Here the amino groups which were not carboxymethylated remains unaffected. Sodium chloride was used as an electrolyte to study the salinity effect on NO-CS solution on oil. Ionic strength of the NO-CS solution increased due to increase in the salinity. This decreases the critical micelle concentration (CMC) of NO-CS for the formation of oil droplets for oil-1 and oil-2 compared to oil-3. Therefore, the amount of NO-CS dosage decreases with increases in salinity.

The pH effect of NO-CS leading to destabilization of oil droplets was also studied. At acidic pH, the amino groups (free as well as carboxymethylated both) were protonated and the negatively charged carboxylate ions attached to amino groups underwent electrostatic repulsion towards negatively charged hydrocarbons forming Winsor type-III (Winsor, 1947) micro emulsions. Whereas at alkaline pH, those protonated amino groups of NO-CS undergoing electrostatic attraction with the hydrocarbons of oils enhancing adsorption over formation of oil droplets. The pH of seawater before industrial era began was about 8.2 (slightly basic) and nowadays it is about 8.1. So it was important to study the effect of NO-CS on oil-1, oil-2 and oil-3 at alkaline pH in presence of salinity. The destabilization of oils using NO-CS was investigated by this study.

2. Materials and methods

2.1. Materials

Chitosan from crab shells (CAS No. 9012-76-4, Lot #BCBPS349V, highly viscous, viscosity >400 mPas in 1% acetic acid at 20 °C), chloroacetic acid (CAS No. 79-11-8, Lot #SHBD8969V, >99%), hydrochloric acid (CAS No. 7647-01-0, Lot #S2BF2070V, 37%) and sodium chloride (CAS No. 7647-14-5, Lot #SZBB0170V) were purchased from Sigma-Aldrich Finland Oy. Sodium hydroxide (CAS No. 1310-73-2, Lot #SZBEI130V) and methyl red (CAS No. 493-52-7, Lot 80950) were purchased from Fluka. Isopropanol (CAS No. 67-63-0, Lot #K40448334) was purchased from Merck. Ethanol (99.5%) was purchased from Altia Oyj. All chemicals were used without further purification. Oil-1 is a sulfur-free marine diesel oil (winter grade) with a density of 828 kg/m3 at 15 °C and viscosity of 1.846 mm2/s at 40 °C, which was received from Fibre and Particle Engineering Research Unit, University of Oulu, whereas Oil-2 is the diesel (summer grade) with a density of 803 kg/m3 at 15 °C and viscosity of 2.1 mm2/s at 40 °C and Oil-3 is the Neste Marine-2T oil with a density of 872 kg/m3 at 15 °C and viscosity of 8.5 mm2/s at 40 °C were purchased from Neste Oyj, Finland. Deuterium chloride solution (35 wt.% in D2O, 99 atom-% D, CAS No 7698-05-7, Lot #MB1157V) was obtained from Sigma Aldrich. D2O was obtained from Eurisotop (99.96% atom-% D, CAS No 7789-20-0, Lot #D215FL0701). During all the experiments deionized water (Siemens Ultra Clear RO with Conductivity 0.055 µS/cm) was used. All the experiments were carried out at room temperature (21 °C).

2.2. Synthesis and characterization

2.2.1. Degree of deacetylation

One of the important chemical characterization of chitosan is the degree of deacetylation (DDA), which determines the content of free amino groups in the polysaccharides. The degree of deacetylation of chitosan from crab shells was determined by acid-base titration as mentioned in (Barros, Vasconcellos, Carvalho, & Nascimento, 2014) with some modification. 0.1 g of chitosan from crab shells was dissolved in 25 mL 0.1 M HCl solution. This solution was titrated against 0.1 M NaOH solution using methyl red as an indicator. For blank reading, the same titration was performed.
without addition of chitosan. This titration was carried out in triplicate. The degree of deacetylation is given by

\[
DDA = \frac{(V_{\text{initial}} - V_{\text{used}}) \times 0.162 \times N}{W \times (1.00 - LOD)},
\]

where \( V_{\text{initial}} \) is the volume of NaOH used in blank titration, \( V_{\text{used}} \) is the volume of NaOH used in sample titration, \( N \) is the molarity of NaOH, \( W \) is the weight of sample, and LOD is the loss on drying in chitosan sample.

2.2.2. Synthesis of N,O-carboxymethyl chitosan

N,O-carboxymethyl chitosan (NO-CS) was synthesized based on previously reported method (Sun et al., 2008) with some modifications. Briefly, chitosan from crab shells (5 g), sodium hydroxide (5 g), isopropanol (40 ml), and water (100 ml) were added in a reaction flask and allowed to alkalize and swell for 1 h in water bath (IKA C-MAG HS 7 Digital) at 50 °C. Dissolved chloroacetic acid (7.5%) in isopropanol (10 ml) was added dropwise in the reaction mixture during the next 30 min. The reaction was allowed to continue at the same temperature for 4 h in order to complete the reaction between chitosan and chloroacetic acid. The reaction was then allowed to continue at the same temperature for 4 h in order to complete the reaction between chitosan and chloroacetic acid. At the end of the reaction, the mixture was stirred for 1 h. The solid was then filtered and dried at room temperature to give the solid product (NO-CS). SEM (Hitachi SU3500) was used to study the surface of the chitosan before and after carboxymethylation at accelerating voltage of 10 kV.

2.2.3. Degree of substitution

The degree of substitution (DS) also depends on the degree of deacetylation. The degree of substitution of NO-CS was determined by using potentiometric titration (Bidgoli et al., 2010; Ge & Luo, 2005) with some modifications. 0.2 g of NO-CS was dissolved in 40 ml water and the pH was adjusted below 2 by adding 0.1 M HCl detected by pH meter (WTW pH 3415). The solution was titrated against 0.1 M NaOH solution and simultaneously the pH was measured for each addition of NaOH solution. The amount of NaOH was used by determining the first order differential method. The degree of substitution was calculated by

\[
DS = \frac{(V_2 - V_1) \times DDA}{(V_3 - V_2)}
\]

where, \( V_1, V_2 \) and \( V_3 \) are the respective volumes of NaOH.

2.2.4. Characterization of NO-CS by FTIR and \( ^1\)H NMR

Chitosan from crab shells and NO-CS were characterized using Bucker FTIR (Vertex 70) from the range of 400–4000 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\) for 60 scans. For NMR measurement, samples of chitosan and NO-CS were dissolved in D\(_2\)O containing 0.7% of DCl and placed in 5 mm NMR tubes. The \( ^1\)H NMR spectra were recorded by using Bruker Ascend 400 MHz spectrometer and standard proton parameters with the delay time (d1) of 6 s at 70 °C.

2.3. Effect of dosage

For this study, different dosages of NO-CS (0–50 mg) were dissolved in water. Oil-1 was added in each and every NO-CS dosage solution, so that the concentration of NO-CS to oil was about 0–65 mg/g. The ratio of oil to water was 1:10, which remained constant throughout the study. The same procedure was repeated for oil-2 and oil-3. All the solutions were shaken at 2000 rpm with vortex mixture (VWR International) for 30 s and then 300 rpm for 30 min with shaker (using KS 4000 ic control from IKA) in order to study the formation of oil droplets with respect to NO-CS dosage. The mixture was allowed to saturate for 2 h and then centrifuged (Eppendorf 5810R) for 5 min at 1500 rpm. After centrifugation, separated oil was removed and weighed again. This procedure was repeated in triplicate. Oil droplet size was measured using optical microscope (Zeiss Axio using the camera unit Axio CamERc5s by ZEN software).

2.4. Effect of salinity

Different dosages of NO-CS (0–25 mg) were dissolved in saline water having concentration from 0 to 3.5%. Oil-1 was added to each concentration having different dosage of NO-CS (so that the concentration of NO-CS to oil was about 0–35 mg/g). The ratio of oil to water was 1:10, which remained constant throughout the study. The same procedure was repeated for oil-2 and oil-3. All the solutions were shaken at 2000 rpm with vortex mixture (VWR International) for 30 s and then 300 rpm for 30 min with shaker (using KS 4000 ic control from IKA) in order to study the behavior of NO-CS in the presence of salinity in destabilizing the oils. The oil-in-water solution was saturated for 2 h and then centrifuged (Eppendorf 5810R) for 5 min at 1500 rpm. The separated oil was removed and weighed again. The same was repeated in triplicate. Oil droplet sizes were measured using optical microscope (Zeiss Axio using the camera unit Axio CamERc5s by ZEN software) in order to show the effect of salinity.

2.5. Effect of pH

Effect of hydrophilic NO-CS was studied with respect to pH. NO-CS (10–15 mg) was dissolved in water and pH of the solution was adjusted with either 0.1 M HCl solution or 0.1 M NaOH solution by using pH meter (WTW pH 3415). Oil-1 was added to each NO-CS solution having different pH (3–9). The ratio of oil to water was 1:10, which remained constant throughout the study. The same procedure was repeated for oil-2 and oil-3. All the solutions were shaken at 2000 rpm with vortex mixture for 30 s and allowed to saturate for 2 h. The effect of different pH solution of NO-CS on oils was studied using Optical microscopy (Zeiss Axio using the camera unit Axio CamERc5s by ZEN software).

2.6. Adsorption of oil

Adsorption was studied from the optimized conditions of dosage and pH with different salinity for NO-CS polymer. Sea water has a salinity of about 3.5% of dissolved salts, mainly in the form of sodium and chloride ions. Hence, this study was carried out to show the behavior of NO-CS in presence of salinity up to 3%. NO-CS solutions (0.10–0.15%) were prepared with different salinity (0–3.5%) with pH about 9. pH was adjusted using 0.1 M NaOH by pH meter (WTW pH 3415). Oils were separately added to NO-CS solutions and shaken at 2000 rpm with vortex mixture for 15 s. After that, the pH was adjusted to 7.5–8 by addition of 0.1 M HCl and mixed for 15 s with the same speed. The mixture was allowed to saturate for 2 h and adsorption was studied using Optical microscopy (Zeiss Axio using the camera unit Axio CamERc5s by ZEN software).

3. Results

3.1. Degree of deacetylation and degree of substitution

The measured degree of deacetylation of chitosan from crab shells was 74%, with reproducibility of less than 5% of standard deviation. The process of deacetylation involves the removal of acetyl
groups from the molecular chain of chitin, leaving behind amino group (−NH₂) (Khan, Peh, & Ch'ing, 2002) and chitosan versatility depends mainly on this highly reactive amino groups. Therefore, it was essential to determine degree of deacetylation prior to its utilization for oil spill treatment.

The degree of substitution was 0.40, which indicates that by increasing the ratio of water/isopropanol in the reaction solvent, the fraction of carboxymethylation decreases by increasing the insolubility of NO-CS at higher pH range (Chen & Park, 2003). This insoluble region was either due to aggregation of highly acetylated chain segments or to amide formation subsequent to thermal drying. Three inflection points in the titration curve of NO-CS as shown in Fig. 1, is due to the oppositely ionizable carboxyl and amino groups, which coexist on the same polysaccharide chains because of the carboxymethylation (Wang, Chen, Liu, Liu, & Zhou, 2008). First inflection point in Fig. 1, occurs due to neutralization of excess of HCl, followed by deprotonation of carboxylate ion and then deprotonation of ammonium ion of NO-CS.

The overall potentiometric titration of NO-CS can be expressed as follows:

\[
\text{CH}_2\text{COOH} \xrightarrow{\text{OH}} \text{CH}_2\text{COO}^- + \text{H}^+ \xrightarrow{\text{NH}_2\text{CH}_2\text{COO}^-} \text{NH}_2\text{CH}_2\text{COO}^- + \text{H}^+
\]

Where R is the glucopyranose unit of NO-CS.

In NO-CS, part of −NH₂ or −NHCH₂COOH groups exists in the form of −NH₃⁺ or −NH₃⁺CH₂COOH and so increase in carboxylic acid content in NO-CS, lowers the degree of substitution (Kong, 2012).

3.2. Structural characterization of NO-CS

3.2.1. SEM analysis

The surface morphology of chitosan before and after carboxymethylation was studied. SEM images of the chitosan surface before and after carboxymethylation are shown in Fig. 2.

3.2.2. FTIR analysis

The FTIR spectra for chitosan from crab shells (Fig. 3A) and NO-CS (Fig. 3B) were analyzed to determine the carboxymethylation process and possible substitution site of carboxymethylation in NO-CS as shown in Fig. 3. For NO-CS, the wide band at 3301 cm⁻¹ corresponds to the axial stretching of the O–H and N–H bonds (An et al., 2009) which shows more hydrophilic character of NO–CS compared to chitosan (Lusiana, Siswanta, & Mudasir, 2014). The peaks at 2887 cm⁻¹ corresponds to the axial stretching of the C–H bonds (Kong, 2012) and 1734 cm⁻¹ corresponds to the symmetric stretching vibration of C=O in the −COOH groups, which was not found in chitosan. Two bands at 1624 cm⁻¹ and 1519 cm⁻¹ assigned to NH₂⁺, indicates that the carboxymethylation occurred at OH position only (Mourya et al., 2010). In contrast, the peak at 3301 cm⁻¹ of NO-CS (Fig. 3A) is broader than chitosan (Fig. 3B), shows the presence of secondary amine indicating the carboxymethylation had also occurred at NH position in NO-CS. The peak at 1377 cm⁻¹ was related to the symmetric angular deformation of C–H bonds. The stretching vibration of C–O in CH₂COOH group gives rise to the peak at 1249 cm⁻¹, which was not observed in chitosan. The peaks, in the range of 1150–897 cm⁻¹ are the results of vibrations of C–O and C–O–C of polysaccharide chain also observed in chitosan. From FTIR, it is confirmed that the carboxymethylation takes place only at both amino groups and hydroxyl groups.

3.2.3. ¹H NMR analysis

The ¹H NMR spectra of chitosan and NO-CS are presented in Fig. 4. The spectrum of NO-CS shows the same characteristic proton signals as can be seen in chitosan spectrum. However, two new signals can be found in the spectrum of NO-CS compared to chitosan. The peaks at 3.78 and 4.61 ppm are assigned to N–CH₂– and –O–CH₂– protons at 2- and 6-positions, respectively (Chen & Park, 2003; Abreu & Campana-Filho, 2005). Thus, the NMR data also supports the interpretation of FTIR data that both the amino and hydroxyl groups at the 2- and 6-positions are partly carboxymethylated. Based on the integrals of peaks at 3.78 and 4.61 ppm, the ratio of carboxymethyl substituents at 2-N position to carboxymethyl substituents at 6-OH position is 5:7.

3.3. Effectiveness of NO-CS as a function of dosage

NO-CS is hydrophilic chitosan derivative and increase in the dosage leads to crowding effect of micelles, which increases the
viscosity of the solution. Fig. 5A shows the effect of dosage on the formation of oil droplets for all three oils. Fig. 5B and C show that, in the absence of NO-CS, oil-in-water emulsion was not stable as it undergoes coalescence forming two separate phase with oil-1 and oil-2 after saturation. Initial interfacial tension between NO-CS (0.1% solution) and oils was 19.77, 19.01 and 20.45 mN/m at 20°C respectively, which was measured by pendant drop method (Optical contact angle measuring instrument, DataPhysics OCA 15EC Series). In the presence of NO-CS, oils undergo the Winsor type-III micro emulsions by destabilization of oil into droplets with less than 100 μm measured by Optical microscope. NO-CS, with dosage of 20 mg/g destabilized 96% of oil-1 into small droplets, whereas 25 mg/g was needed to destabilize oil-2 with 37% of oil separation (Fig. 5A), which is critical micelle concentration (CMC) for oil-1 and oil-2 after which interfacial tension is independent of the concentration. This was because at lower concentration, the o/w emulsion was not very stable, as the amount of amphiphilic was not enough to cover the interface. For concentrated solutions, the stabilization of emulsion occurs because of the formation of a tighter monolayer with adsorbed species and stronger interparticle interactions inhibiting the coalescence of emulsion droplets in highly viscous medium. Oil-3, being highly viscous among the three, consists of alpha-olefins and paraffins which forms creamy layer with water even though NO-CS is absent, and small amount of NO-CS (5 mg) converts creamy layer to emulsify precipitates (Fig. 5D). Oil droplets formation for oil-3 with 10 mg/g of NO-CS is shown in Fig. 5E.
Fig. 4. $^1$H NMR Spectra (A) Chitosan and (B) NO-CS.
3.4. Effectiveness of NO-CS as a function of salinity

Destabilization of the oil with increasing salinity was studied by measuring the size of the droplets after mixing. As the salinity increases, the solubility of NO-CS drops the CMC. Hence, lower ionic strength solutions favor emulsion stability (Wang & Alvarado, 2012). In contrast, increase in salinity forms electric double layer due to presence of ions in the aqueous phase and forming electrostatic repulsion with the carboxylic ions favoring hydrophobic interactions among the NO-CS polymer. With increase in salinity from 0.5% to 2%, there was a significant drop in formation of oil-droplets for oil-2 (Fig. 6B) compared to oil-1 (Fig. 6A). Whereas, the increase in salinity from 2% to 3%, shows slight more drop in the formation of oil-droplets for oil-1 compared to oil-2 may be because of the insolubility of NO-CS. For 3.5% salinity, the oil-droplets formation for oil-1 was about 48% and that of oil-2 was about 37%. Overall droplet size was less than 40 μm for oil-1 and Fig. 6D shows that in 1.5% saline solution 25 mg of NO-CS destabilized oil to form droplets of less than 30 μm whereas oil droplets of less than 50 μm were formed in 1% saline solution of 15 mg NO-CS. Overall droplet size was less than 75 μm for oil-2. Oil-3 consists of unsaturated hydrocarbons, and addition of electrolyte in small portion undergoes addition reaction, inhibiting the oil droplets formation more than 50% drop in comparison with 0% salinity. Droplet size with 1% salinity of 10 mg NO-CS was less than 35 μm as shown in Fig. 6F. Increase in salinity changes the formation of oil droplets but it does not affect the oil droplets size significantly.

3.5. Effectiveness of NO-CS as a function of pH

NO-CS was soluble in deionized water and pH of this solution was 3.5–4.5. It has been found that oil sorption on organic sorbent is highly affected by pH value (Rajakovic-Ognjanovic, Aleksic, & Rajakovic, 2008), as pH has a strong influence on the surface of
Fig. 6. Effect of salinity on formation of oil droplets (A) for Oil-1 (B) for Oil-2 (C) for Oil-3 and Microscopic images for o/w emulsion were (D) for 25 mg NO-CS with 1.5% Salinity for Oil-1 (E) for 15 mg NO-CS with 1% Salinity for Oil-2 (F) for 10 mg NO-CS with 1% Salinity for Oil-3.
3.6. Adsorption of oils by NO-CS

Adsorption is the one of the important step for the removal of oil from water. At alkaline pH the polymer re-precipitates because of lower carboxymethylation rate and decrease in ionic strength of the solution. Addition of salinity, increases the ionic strength of the solution and protonates the amino groups of NO-CS and hence enhances the adsorption rate. The presence of positively charged surface on NO-CS lowers the interfacial tension between two phases by stabilizing the droplets against coalescence by electrostatic repulsion. Fig. 8A shows the adsorption of oil-1 with 0.10% NO-CS solution with 2% salinity at pH 8 after drying the adsorbed oil. The adsorption of oil-2 was less than that of oil-1, due to presence of higher rate of polyaromatics and lower density. Fig. 8B shows the adsorption of oil-2 with 0.10% NO-CS solution with 0.5% salinity and Fig. 8C shows the adsorption of oil-3 with 0.15% NO-CS solution with 3% salinity. Addition of few drops of 0.1 M HCl gives lumps of oil as shown in Fig. 8D. This addition of HCl shows the ion exchange effect in o/w emulsion, which leads to NO-CS adsorption on to the surface of more than one droplet and linking them together to form bridging flocculation between the NO-CS and o/w emulsion droplets. This was studied to show the acidification effect on to oil-in-water emulsion and to extend its applicability to ocean acidification as this could affect most fundamental biological and chemical processes of the sea in coming decades.

4. Conclusions

This study explains how water soluble NO-CS with degree of substitution 0.40, breaks the dispersed phase into droplets by rising them to the surface resisting droplets to coalescence. For marine Diesel and Diesel, oil droplets of less than 100 μm were formed with 20–25 mg/g of NO-CS, whereas only 5 mg/g of NO-CS was needed for Marine 2T oil to form oil droplets of less than 100 μm. Addition of salinity reduces the dose of NO-CS to about 10–15 mg/g for marine Diesel and Diesel to form oil droplets and there was a reduction in formation of oil droplets with increasing salinity, but
it does not affect the oil droplets size significantly NO-CS behavior differs in acidic and alkaline medium. In acidic pH, NO-CS forms Winsor type-III micro emulsions in a separate phase between oil and water, which contains NO-CS, water and dissolved hydrocarbons from oils enhancing oil recovery process. Whereas in alkaline pH, it shows destabilization of oil followed by adsorption because of the removal of carboxylate ion by deprotonating the amino groups. This derivative was most effective with marine diesel and at the least with diesel, because density of marine Diesel > Marine 2T oil > Diesel. Therefore, the applicability of the synthesized NO-CS, can be extended to sea-water for the removal of marine diesel as a part of oil spill response.

Acknowledgement

This work was funded by the European Union Structural Funds as a part of VIKE project (A70963: Improvement of the oil spill prevention and response with the green chemicals).

References


