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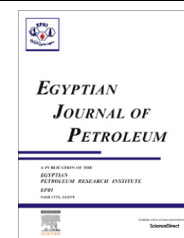
FULL LENGTH ARTICLE

# Treatment of the oily produced water (OPW) using coagulant mixtures

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**Abstract** Treatment of the oily produced water (OPW) before injection into oil reservoirs is necessary to reduce formation damage. This can be done using chemo-physical process to minimize the oil droplets in water. In this respect, this work aims to extract natural polymer (chitosan) from shrimp shells and mix it with coagulants (chitosan/carboxy methyl cellulose and chitosan/aluminum sulfate) to adsorb oil from OPW. Adsorption experiments were carried out in batch mode firstly to choose the best coagulants in water treatment, also to investigate the effects of pH on the adsorption uptake, adsorbent dosage, coagulant mixture doses and contact time. It was found that the oil removal by chitosan reached 96.35% and 59% at pH = 4 and pH = 9, respectively. The ability of chitosan to remove oil was increased after adding different coagulants CMC/or aluminum sulfate at average mixing time between 30 and 60 min. It was also found that the highest removal efficiency of chitosan/CMC is 99% at (90% chitosan: 10% CMC) and chitosan/$Al_2(SO_4)_3$ is 85% at (80% chitosan: 20% $Al_2(SO_4)_3$). The SEM photographs of chitosan, chitosan/CMC and chitosan/$Al_2(SO_4)_3$ mixture as oil removal showed that chitosan/$Al_2(SO_4)_3$ lies between chitosan alone and chitosan/CMC mixture. Generally chitosan/CMC characterized significantly by its high ability to adsorb petroleum oil and suspended solids from OPW, additionally, reduces the economic cost of water treatment.

## 1. Introduction

Produced water is one of the major technical, environmental, and economical problems associated with oil and gas produc-

tion. Produced water can limit the productive life of the oil and gas wells and can cause severe problems including corrosion of tubular, fines migratatic loading. Produced water represents the largest waste stream associated with oil and gas production [1]. Among several chemical and physical methods, adsorption process is one of the effective methods widely used in wastewater systems. Adsorption of waste oil using natural adsorbents such as peat, bentonite organo-clay, attapulgite and activated

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have been done [2]. In the present work, a series of adsorption experiments were conducted to evaluate the possibility of the use of chitosan powder with CMC or and $Al_2(SO_4)_3$ as adsorbent for residue oil removal from Oily produced water. Although many studies on adsorption using chitosan were done, the roles of chitosan in adsorbing residue oil were rare.

## 2. Materials

Produced water contaminated with oil droplets (oily produced water, OPW) sample was kindly obtained from the local Egyptian oilfield. The OPW used in these experiments are being brought from oilfield exposed to the atmosphere and then kept in an environment similar to their native habitat that contains oxygen until the treatment process is beneficial. The characterization of OPW is given in Table 1.

Shrimp shells that were used in these experiments were supplied in fresh condition from local market (Egypt, Cairo). The shells were separated from the head and legs. The shrimp shells were washed several times with tap water, and then dried out in a hot room at 70 °C. The dried shells were ground to fine powder. The flocculants used in this study are carboxy methyl cellulose, and $Al_2(SO_4)_3$ obtained from Sigma Aldrich.

## 3. Experimental

### 3.1. Extraction of chitin and chitosan

The chitin and chitosan sequence involves washing of crushed exoskeletons. Crushed shrimp exoskeletons were placed in 1000 mL beakers and soaked in boiling sodium hydroxide (2% and 4% w/v) for one hour in order to dissolve the proteins and sugars thus isolating the crude chitin. For chitin preparation 4% NaOH concentration was used as described by Sonat Corporation [3]. After the shrimp shell samples are boiled in the sodium hydroxide for 10 h the samples are removed and allowed to cool for 30 min at room temperature [4]. The exoskeletons are then further crushed to pieces of 0.5–5.0 mm.

## 4. Results and discussion

### 4.1. Batch adsorption studies

Conventional jar test procedures were used to adsorb oil from OPW using different coagulants. It was carried out as a batch test, accommodating a series of six beakers together with six-spindle steel paddles. The OPW samples were mixed homogeneously before being fractionated into the beakers containing 100 mL of suspension each. Prior to the test, the samples were measured for oil concentration, turbidity and TSS for representing an initial concentration. After the desired amount of chitosan was added to the suspension, the beakers were agitated at various mixing time and speed (250 rpm) for 15 min and slow mixing (30 rpm) for 30 min. After the agitation stopped, the suspension was allowed to settle undisturbed for 30 min. A sample was withdrawn using a pipette from the top inch of supernatant for oil concentration, turbidity and TSS measurements, representing the final concentration. The pH was controlled by adding either strong acid (5 M HCl) or strong base (5 M NaOH). All tests were performed at an ambient temperature in the range of 26–30 °C. The same steps repeated for chitosan, carboxy methyl cellulose and metal-based coagulant that aluminum sulfate. The best adsorbent and the best coagulants obtained were mixed together to form formulations.

Adsorption experiments of oil droplets in OPW are carried out in batch mode firstly to choose the best coagulants in water treatment, also to investigate the effects of pH on the adsorption uptake, adsorbent dosage, coagulant mixture doses and contact time.
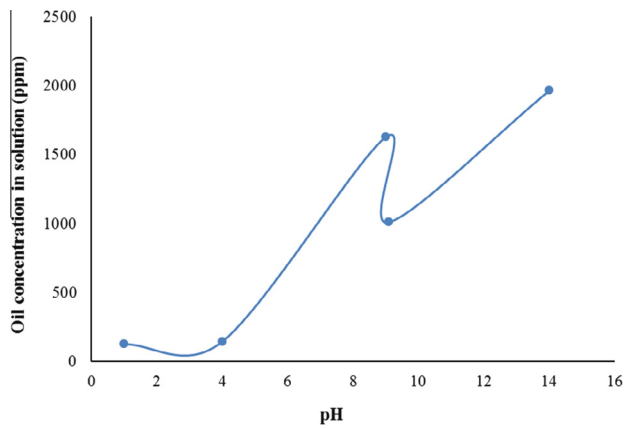
### 4.2. Effect of pH

Emulsion breaking and suspension precipitation are usually brought about by changing the pH value of sample. Therefore, pH adjusts to study the effect of adsorption of crude oil onto the natural polymer (chitosan) as shown in Fig. 1. The results illustrate that the adsorption of crude oil reaches 3854 mg/g at pH 4 that corresponds to 96.35% oil removal, whereas the adsorption recorded as 2371 mg/g corresponds to 59% oil removal at alkaline medium (pH = 9), this means 1.6 times lower than in case of acidic medium. It can be concluded that strong acidic conditions aggravate oil to form unstable folk, where chitosan provokes a physicochemical effect apparently serving to demulsify and increase the droplet size and enhance the adsorption of oil. This acidic condition acts as a catalyst for the reaction between the oil molecules and the adsorption site of chitosan (–$NH_2$ group) [5].

### 4.2.1. Distribution coefficient ($K_d$) values of oil on chitosan

The adsorption can also be quantified in terms of distribution coefficient ($K_d$), that is defined as the ratio of equilibrium concentration of the sorbed species (oil on chitosan) to

**Table 1** Extended water analysis for oily produced water sample.

| Total dissolved solids | | 141522.2 mg/L | pH | | 6.78 @ 25 °C |
|---|---|---|---|---|---|
| Salinity | | 141479.3 mg/L | Hardness | | 22170.8 mg/L |

| Constituents | mg/L | meq/L | Constituents | mg/L | meq/L |
|---|---|---|---|---|---|
| Lithium | 2.30 | 0.332 | Fluoride | 0.900 | 0.047 |
| Sodium | 45474.0 | 1978.119 | Chloride | 85745.0 | 2418.86 |
| Potassium | 847.09 | 21.669 | Bromide | 195.300 | 2.445 |
| Magnesium | 1058.8 | 87.134 | Bicarbonate | 122 | 2.00 |
| Calcium | 7132.7 | 355.922 | Sulfate | 836.5 | 17.416 |
| Strontium | 107.51 | 2.454 | Carbonate | Nil | Nil |

Figure 1 Effect of pH on the removal of oil residual from produced water using chitosan.



Figure 2 Effect of contact time on removal of oil by chitosan.



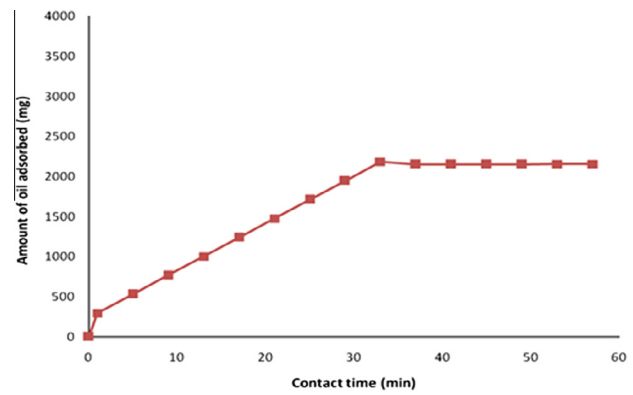Figure 3 Effect of contact time on removal of oil by chitosan/ CMC at different ratios.

equilibrium concentration of the dispersed species in solution (oil in water):

$$K_d = \frac{\text{wt. of oil on chitosan}}{\text{wt. of oil in water}} \times \frac{\text{vol. of produced water}}{\text{wt. of dry chitosan}}, \quad (1)$$
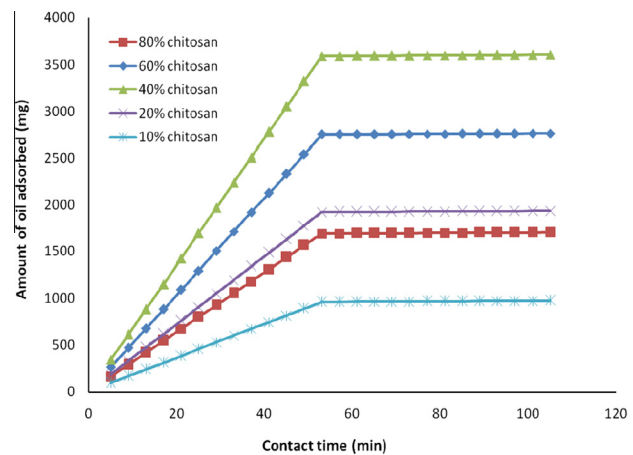
Although this distribution coefficient is measured on a batch basis, it can be used to predict elution behavior of oil eluted from sorbent column. The distribution coefficient values ($K_d$) for oil are determined by the batch equilibration method. The $K_d$ values of the oil are studied as a function of pH and the results are presented in Table 2. From the data it is found that the distribution coefficient ($K_d$) of oil on chitosan is 26384.62 at pH 4, so pH 4 is selected as a suitable pH value because as obvious from Table 2, the higher pH values weakness of chitosan sorption and decreases the $K_d$ values, i.e. the $K_d$ values decrease as pH values increase. Meanwhile, in all cases, the $K_d$ values increase with increasing oil concentrations on chitosan. Finally, to achieve higher oil removal, suitable $K_d$ values should be selected at the same experimental conditions.

### 4.3. Effect of contact time

The effect of contact time on the removal of oil by chitosan is illustrated in Fig. 2, which shows that the amount of adsorbed oil increased with the beginning of the contact times. It is suggested that not only an adsorption of oil on chitosan surface but also strong bonding of oil onto chitosan surface as a few diffusion of oil into chitosan particles. After reaching the plateaus, the equilibrium is achieved around 33 min at 2183 mg adsorbed oil. All the experiments are carried out with 2 h of contact time to obtain equilibrium at the solid/liquid interface. It is noticeable that there is no change in oil removal when the time is prolonged.

Figs. 3 and 4 show the effect of contact time of chitosan/ coagulant mixture at different mixing ratios of 80%, 60%, 40%, 20%, and 10% versus oil adsorbed (mg). A sharp increase is observed in the beginning of the adsorption curves followed by a bending in the curve at different contact times. The bending point of 40% chitosan: 60% CMC appears at 53 min and 3594 mg adsorbed oil. Generally, it is evident that there is no further oil adsorption after reaching equilibrium that is around 60 min. In addition for the mixture of 80% chitosan: 20% Al$_2$(SO$_4$)$_3$ the bending point appears at 49 min and 3104 mg adsorbed oil.

From these results, the good ability of individual chitosan to remove oil is demonstrated, thereby the ability of chitosan to remove oil increased after adding coagulant ratios especially with CMC with the average time to oil removal between 30

Table 2 Distribution coefficient of oil on chitosan.

| pH | Coagulant weight | Vol. mL in solution | Concentration (ppm) | Concentration in solution | $K_d$ |
| --- | --- | --- | --- | --- | --- |
| 1 | 0.1 | 100 | 3873.03 | 126.97 | 30504.42 |
| 4 | 0.1 | 100 | 3853.93 | 146.07 | 26384.62 |
| 7 | 0.1 | 100 | 2370.79 | 1629.21 | 1455.18 |
| 9 | 0.1 | 100 | 2988.76 | 1011.24 | 2955.56 |
| 14 | 0.1 | 100 | 2033.71 | 1966.29 | 1034.29 |
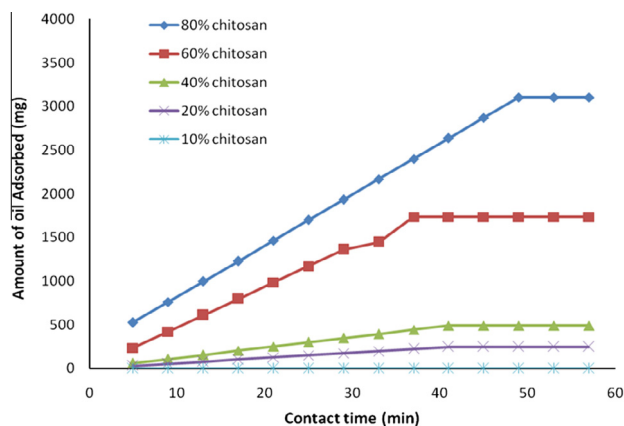
**Figure 4** Effect of contact time on removal of oil chitosan/ $Al_2(SO_4)_3$ at different ratios.
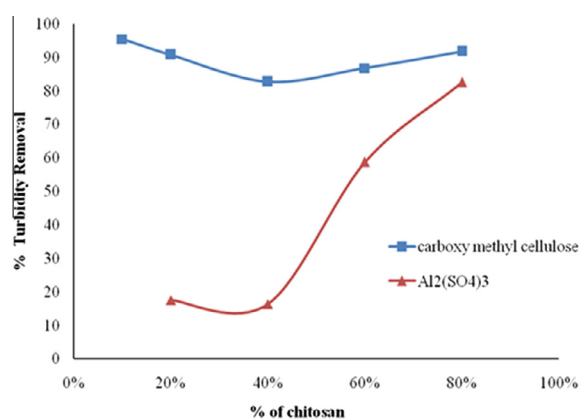
and 60 min. This leads to the reduction of economic cost of water treatment (oil removal from OPW).

In general, the mixtures of chitosan will be used in the column form to help recycling process, and not in the spray form as applied in the traditional treatment process.

## 4.4. Effect of coagulant mixture concentration

The effect of coagulant concentration on removing turbidity, TSS and oil has been widely used as pre-treatments. Chitosan formulations are prepared from mixing the best individual organic, inorganic or polymeric coagulants with chitosan to improve the efficiency of individual chitosan. On the other hand to reduce the amount and cost of coagulants used in the process of removing oil or suspended solids in water. In this respect, chitosan formulations are conducted at five chitosan to other coagulants at fixed unit weight with different ratios (10–90%) at pH = 4 and temperature of 30 °C to destabilize oil was recorded.

From the above previous data chitosan will mixed with different ratios of CMC and aluminum sulfate (90% to 10%) to determine the best mixture that give the highest removal efficiency as plotted in Fig. 5. It seems at the first view that the increase of chitosan dosage leads to better coagulation perfor-

mances (i.e. oil concentration, turbidity and TSS reductions). However it can also be seen that chitosan/CMC mixture gives the highest removal efficiency of 99% at (90% chitosan: 10% CMC), while the inorganic coagulant mixed with chitosan gives the highest removal efficiency of 85% at (80% chitosan: 20% $Al_2(SO_4)_3$). This is due to the special polymeric nature of CMC where there are many hydrophilic groups which make the surface area of CMC much higher than that of inorganic coagulant (aluminum sulfate), also, it is due to one unit of CMC equalling hundred units of aluminum sulfate. Generally CMC is characterized significantly by its high ability to adsorb petroleum oil and suspended solids from OPW.

## 4.5. Mechanisms of coagulation/flocculation using SEM analysis

The presence of reactive groups ($NH_2$, OH) on backbone of a versatile chitosan polymer led to a wide range of applications and properties. The mechanisms of chitosan coagulation/flocculation are involved in charge neutralization, adsorption (related to protonated amine groups), precipitative coagulation, bridge formation (related to the high molecular weight of biomacromolecules) and electrostatic patch [6,7]. The mechanism of chitosan in the current study is that coagulation by charge neutralization destabilizes colloidal impurities and transfers small particles into large aggregates (bridge formation) and adsorbs dissolved organic substances onto the aggregates by an adsorption mechanism which can then be removed easily by filtration and sedimentation.

The SEM of the adsorbed oil macromolecules Fig. 6 shows the tendency of oil to form loops and not extend some distance from the particle surface into the aqueous phase. The effective bridging occurs; where the length of the biopolymer chains sufficient to extend from one particle surface to another leads to high oil removal efficiency.

The general view of SEM photographs reveals that most of the chitosan areas are embedded and covered with adsorbed oil residue. The surface of the chitosan is spread and covered with a muddy-line or rough surface with crater-line pores due to the oil droplets cover chitosan. These images prove that, oil is adsorbed by chitosan into its pores and build up a layer of oil on the surface. The presence of oil droplets on chitosan surface confirms that the adsorption process tends to be physical rather than chemical as confirmed from isotherm and kinetic studied.



**Figure 5** Initial adsorbent concentration of chitosan/CMC and chitosan/$Al_2(SO_4)_3$.
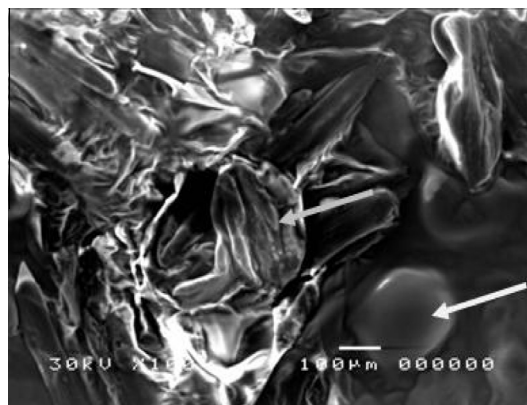


**Figure 6** SEM for chitosan oil adsorbent.

Patch flocculation occurs when macromolecules with a high charge density adsorb particles and locally form positively and negatively charged areas on the particle surface and that is clearly found in SEM photographs of chitosan/CMC mixtures. Chitosan/CMC mixture causes aggregation of particles and may act either by polymer bridging or charge neutralization (electrostatic patch effects) in addition to chitosan. The SEM photograph of chitosan/CMC mixture is evident the severity adhesion of oil to both CMC and chitosan. It is supposed that the susceptibility of oil molecules associated with CMC is much higher than chitosan, but in current case, the strong overlapping between both of CMC and chitosan working as one unit as shown in Fig. 7. It exhibits also that the chains of chitosan/CMC mixture are not clearly defined as in the case
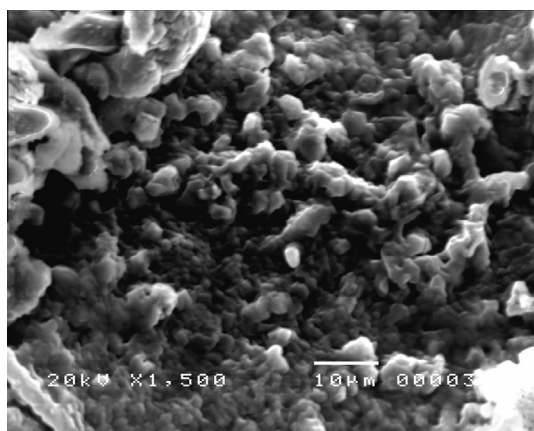


**Figure 7** SEM for chitosan/CMC mixture oil adsorbent.
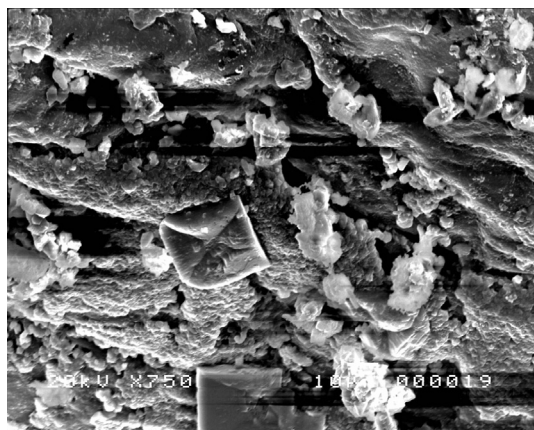


**Figure 8** SEM for chitosan/$Al_2(SO_4)_3$ mixture oil adsorbent.

of chitosan alone, taking into consideration that the mechanism of CMC flocculating agents was described in detail by O'Melia [8].

As already mentioned, aluminum salt is widely used as coagulant in water and wastewater treatment for removing a broad range of impurities from effluent, including colloidal particles and dissolved organic substances. Their mode of action is generally explained in terms of two distinct mechanisms: charge neutralization in negatively charged colloids by cationic hydrolysis products and incorporation of impurities in an amorphous hydroxide precipitate (sweep flocculation). The relative importance of these mechanisms depends on pH and coagulant dose.

Aluminum salt gives cationic hydrolysis products that are strongly adsorbed on negative particles and can give effective destabilisation. The principles governing the action of hydrolyzing coagulant are well understood [9–12].

At higher coagulant dosages bulk precipitation of metal oxide hydroxide occurs. Prehydrolyzed coagulant is often more effective than simple metal salts [9,10,13]. The improved performance of these materials is probably due to the different nature of the precipitate formed, although more detailed studies are needed [14].

In addition $Al_2(SO_4)_3$ is characterized by different advantages including the immediate hydrolysis when contacted with water that gives rapid adsorption reactions. For this reason $Al_2(SO_4)_3$ mixes with chitosan to improve the oil adsorption on chitosan. It is note from SEM photograph Fig. 8, the diffusion susceptibility of $Al_2(SO_4)_3$ crystals in chitosan are very few and this because of the different nature of both coagulants, therefore it is observe scattering of some crystals of $Al_2(SO_4)_3$ on the chitosan surface.

On comparing the susceptibility of chitosan, chitosan/CMC and chitosan/aluminum sulfate mixture as oil removal from SEM photographs, it is shown that chitosan/$Al_2(SO_4)_3$ lies between chitosan alone and chitosan/CMC mixture, the reason could be due to the oil molecules scattered on the surface of chitosan/$Al_2(SO_4)_3$ are few with respect to its corresponding that on chitosan/CMC. The above SEM photographs are confirmed before from the kinetic study involving contact time, this shows that the mixture of chitosan/$Al_2(SO_4)_3$ has lower adsorption rate with respect to $Al_2(SO_4)_3$ alone.

### 4.6. Economic calculation

Through the study on the process of oil adsorption on adsorbents that have various compositions; medical, organic and inorganic, it is clear that the usage of the mixture of natural materials such as shrimp shell that is treated chemically with organic materials and inorganic leads to increased adsorption process and reduces the amount of organic materials and inor-

**Table 3** Economic study of chitosan and chitosan mixtures for oil removal from OPW.

| Sorbate | % mixture | % of oil removed | Oil concentration (ppm) | Price/gm of sorbent [EUR] |
|---|---|---|---|---|
| Chitosan | 100% | 20 | 3873.03 | 0.856 |
| CMC | 100% | 80 | 3873.03 | 0.496 |
| $Al_2(SO_4)_3$ | 100% | 60 | 3873.03 | 0.0694 |
| Chitosan/CMC | 90:10 | 99 | 3873.03 | 0.82 |
| Chitosan/$Al_2(SO_4)_3$ | 80:20 | 85 | 3873.03 | 0.69868 |

ganic used in petroleum industry, which in turn leads to the reduction of the cost of oil removal from produced water. A simple economic study has been set up on the laboratory level by this research which explained in Table 3 the cost of oil removal as the use of chitosan/$Al_2(SO_4)_3$ 0.69868 EUR with oil removal percentage 85% which is better than in case of chitosan/CMC mixture that the cost become 0.82 EUR with % oil removal 99%. So, from this table it is recommended that the use of chitosan/$Al_2(SO_4)_3$ mixture is economically the best in the removal of oil from oily produced water.

## 5. Conclusion

The results of chitosan/coagulant mixture clarify that ability of chitosan to remove oil increased after adding different coagulant ratios especially with both CMC and aluminum sulfate with the average time between 30 and 60 min, such high rate of chitosan mixtures, leads to reduction of the economic cost of water treatment. The highest removal efficiency of chitosan/CMC is 99% at (90% chitosan: 10% CMC) and chitosan/$Al_2(SO_4)_3$ is 85% at (80% chitosan: 20% $Al_2(SO_4)_3$). This was due to the special nature of CMC, where there were many hydrophilic groups which make the surface area of CMC much higher than that of inorganic coagulant (aluminum sulfate), also, it is due to one unit of CMC equalling hundred units of aluminum sulfate. Generally CMC is characterized significantly by its high ability to adsorb petroleum oil and suspended solids from OPW.

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