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Technical Paper

Dynamic Adsorption of Residual Hydrocarbon Oil from Treated Produced Water on Chitosan

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In this work Chitosan was investigated as an adsorbent for residual oil using real produced water stream from Kuwait oilfields. A laboratory bench-top glass tube column integrated with a dynamic flow loop was used in this investigation. Chitosan grains was packed into the glass tube column and real oily produced water was flowed through the tube. Experiments were performed to analyse the effects of several factor, such as initial oil concentration in the produced water feed, adsorption tube/Chitosan bed height and hydraulic loading, on the overall adsorption of oil from the produced water feed. The experimental data was also modelled using Langmuir and Freundlich isotherms to obtain adsorption capacity and intensity respectively.

Experimental adsorption results show that the feed oil concentration was reduced following oil adsorption by Chitosan from 126.40 mg/L to zero until oil breakthrough; concentration of oil in the effluent also increased until full oil loading in the Chitosan adsorption bed; the turbidity of the effluent was reduced from 70.3 NTU to 0.11 NTU which is less than the recommended turbidity level of 0.5 NTU in drinking water. The modelling results show that Chitosan adsorption capacity is significantly dependent on the initial oil concentration and that the intensity of adsorption was generally constant and above unity.

1 INTRODUCTION

Hydrocarbon extraction processes and production operations yield large volumes of formation water containing residual oil droplets either suspended freely in solution or emulsified [1]. Produced water from oil bearing reservoirs is considered the largest waste from the oil industry constituting large volumes of liquid production. Reservoir studies conducted by KOC [2] forecast water cut to increase from current rates of 23% to nearly 60% in year 2030 while daily produced water will reach 3 MMBWPD for giant greater Burgan oil field [2]. There are many treatment technologies available in the oil and gas industry; however, scavenging the minute residual oil particulates remaining suspended in solution after treatment of produced water still a challenge.

With the environmental regulations becoming increasingly tight on surface discharge of produced water owing to the detrimental effects this has on soil and shallow water tables, operators are increasingly looking to improve and enhance existing technologies or develop new technologies and processes that will help them achieve the discharge water quality benchmark.

A variety of adsorbents have been used in the oil and gas industry including organic and inorganic materials; among which are: activated carbon, bentonite, peat, sand coal, fiberglass, polypropylene, amberlite, organoclay, and attapulgite [3]. In a comparative study [4] used Commercial activated carbon, chitosan and bentonite to investigate adsorption properties a batch experiment to adsorb palm oil from palm oil mill effluent water and found that chitosan adsorbed 99% with less amount need and shorter time of mixing. Kapok sorbent by sun-drying technique adsorbs 5-6 grams of crude oil per gram of fibre [5]. Nano-silica sorbent was used experimentally to adsorb gasoline and diesel form wastewater and they both were able to adsorb 15 and 14 grams per gram of nano-silica adsorbent respectively [6]. Rice husk, on the other hand, was found to adsorb 2.56 g/g fibre [5]. Chitosan, an organic material obtained from the deacetylation of chitin, is a highly promising material used in the pharmaceutical industry and many others as a highly effective adsorbent for many elements such as palm oil and lubricant oil [7].

This work explores the application of medium molecular weight chitosan bio-adsorbent in the removal of residual oil from treated produced water from oilfields of Kuwait.

2 DYNAMIC ADSORPTION EXPERIMENTS

The dynamic adsorption experiments are a continuous flow adsorption studies conducted at laboratory ambient temperature of 21oC in a specially fabricated 3.5 cm inner diameter Pyrex glass adsorption tubes (column) with two main heights 5 and 13.5 cm. Real produced water with known oil-in-water concentration was pumped from a reservoir via flexible tubes upward the bed of chitosan adsorbents with known quantity and measured mass (g) packed in the column. Samples were collected at regular time intervals from the outlet of the adsorption column for concentration of oil in water measurement.

A bench-top flow loop equipped with two transparent 3.5 cm ID Pyrex glass adsorption tubes standing vertically with heights of 5 cm and 13.5 cm (figure 1) and packed full of Chitosan bio-adsorbent was used to carry out the experimental work. The adsorption tubes were connected by pipework to a reservoir which was in turn connected to a pump. Dynamic adsorption method was used for all the tests carried out. Initial oil-in-water concentrations of the produced water samples used were measured using TD500D oil in water meter.

Medium molecular weight chitosan grains (9 grams for the 5 cm tube and 24 grams for the 13.5 cm tube) were used in this study. The injected produced water flowed upward to an outlet where samples of the effluent is collected for measurement of oil-in-water concentration at selected time intervals of 10 minutes for the first hours and 30 minutes afterwards until outlet effluent reached a plateau concentration equal to that in the inlet stream. This process was used further to investigate effects of initial oil concentration in the influent feed, hydraulic loading rate and bed height on the effectiveness of adsorption and removal of residual oil concentration in the produced water.

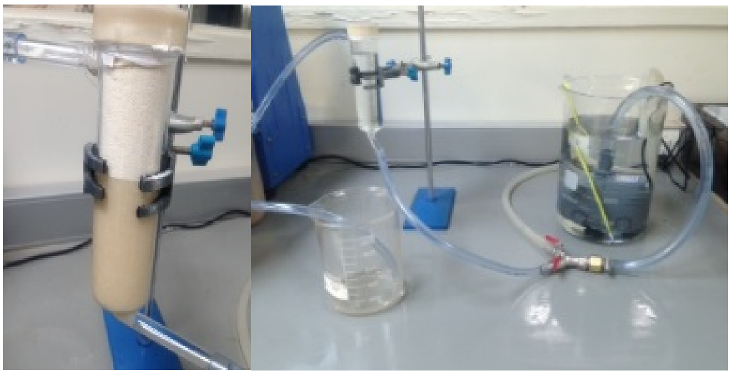

Fig. 1 – Bench Top Chitosan Adsorption

3 PRESENTATION OF DATA AND RESULTS

The results from the dynamic flow adsorption experiments were applied to obtain the breakthrough curves for the adsorption of residual hydrocarbon oil from aqueous solutions of produced water plotting the graph of C/C_0 versus time where C (mg/L) is oil effluent concentration while C_0 (mg/L) is the oil influent concentration. Each experiment was designed to examine the effects of key variable on adsorption behaviour of chitosan

Turbidity is a measurement of the degree of murkiness of water which might be due to the presence of suspended matter. These suspended particulates include silt, clay and sand sediments, the phytoplankton community and detritus [8]. Turbidity is classified into four grades: Low (<50 NTU), medium (50-100 NTU), high (100-200 NTU) and very high (>300 NTU) [9]. Turbidity improvement was visibly noticed in all the experiments and best in the case of 13.5 cm adsorption tube where turbidity was lowered from a value of 70.3 NTU to 0.11 NTU, representing a 99.84% reduction in turbidity (Figure 2).

Fig. 2 – Turbidity Improvement of ChitosanAdsorption Column

3.1 Effect of Inlet Oil Concentrations

The effect of inlet oil concentration on the breakthrough features was investigated at the adsorbent bed height of 5 cm and feed flow rate of 20 ml/min. As shown in Figure 3, adsorption was initially observed to increase rapidly due to the abundance of free adsorption sites on the surface of free Chitosan grains. As the oily solution continued to flow into the adsorption column bed, the uptake effectiveness was reduced due to the loading phenomenon indicated by increased outlet oil concentration until the saturation was reached in the adsorption tube.

The figure shows an inverse relationship is predominant between the initial oil concentration and the breakthrough time and volume of treated produced water, that is at higher initial oil concentration leads to shorter breakthrough time was achieved. Efficiency of the adsorption column was lowered by higher loading of oil molecules on the inlet face of the adsorption tube.

On the other hand, low initial concentration yielded longer breakthrough time and reduced the slope of the breakthrough curve. Earliest breakthrough of oil molecules was observed in the highest initial oil concentration of 126.4 mg/L as shown in the in figure 3.

At a low initial oil concentration extended breakthrough time is obtained reflecting a higher volume of oily water could be treated. It can also be determined that the higher the initial adsorbate (oil) concentration the steeper the breakthrough S-shape curves as seen in the case of the 126.4 mg/L case. The inlet oil concentration affected the shape and slope of the breakthrough curve and affect the overall adsorption process, the diffusion process is concentration dependent.

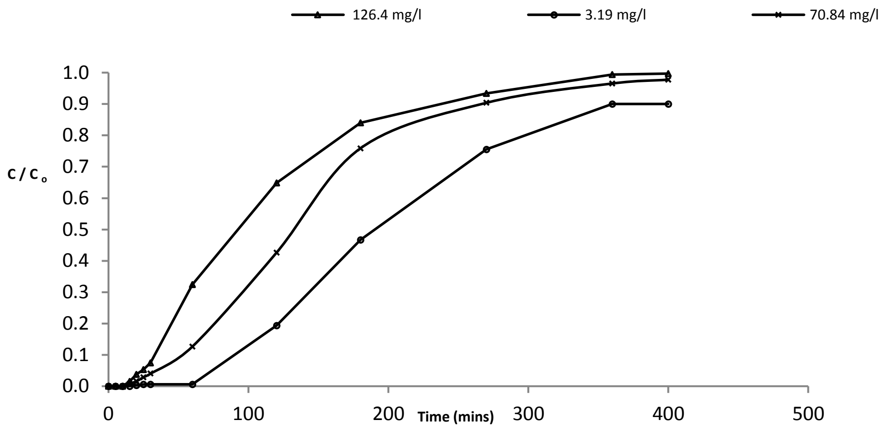

Fig. 3 – Breakthrough Curve for the Adsorption of Residual Hydrocarbon Oil from Produced Water onto Chitosan at Variable Inlet Concentrations

3.2 Effect of Hydraulic Loading Rate

The influence of feed flow rates was also investigated using a chitosan column height of 5 cm and inlet oil concentration of 126.4 mg/L. The breakthrough curve is presented in Figure 4. The effect of feed flow rate was investigated at the two constant hydraulic loading rates of 20 and 50 ml/min. It was clear from figure 4 that the breakthrough time was delayed at the reduced feed flow rate of 20 ml/min as anticipated. Flow rate gives an indication of the residence time allowed for oil molecules to be adsorbed on the surface of chitosan; therefore, the longer the residence time driven by low flow rate the longer it takes for oil to break through the outlet of the adsorption tube and the better the adsorption was achieved on the adsorbent surface. This may be explained by insufficient residence time for oil molecules to penetrate into the pores of chitosan at higher feed flow rate.

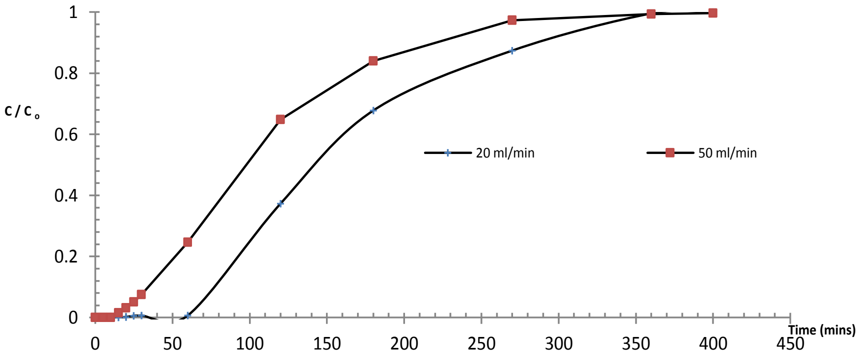

Fig. 4 – Breakthrough Curve for the Adsorption of Residual Hydrocarbon Oil from Produced Water onto Chitosan at Two Different Feed Flow Rates (Initial Oil Concentration = 126.4 mg/L; Bed Height = 5 cm

3.3 Effect of Bed Height

Bed height plays an important role in column adsorption system. The breakthrough behaviour was investigated for two adsorption column bed heights of 5 cm and 13.5 cm. Feed oil concentration was maintained constant at 126.4 mg/L and flow rate at 50 ml/min. The breakthrough curve is presented in Figure 5.
A reduction in the breakthrough time for the 5 cm bed height was seen; in addition to a dramatic increase in the overall adsorption uptake and less volume of oily produced water treated compared with the 13.5 cm tube. In the case of the 5 cm bed height oil molecules present in the solution had no sufficient residence time to spread into the surface pores of the chitosan adsorbent causing early breakthrough of the effluent at the outlet of the adsorption tube which is defined by a very steep C/C_o curve. Comparison between the performance of the two tubes also shows that the after oil breakthrough in the 5 cm tube there was a sharp increase of oil-in-water. The increase in adsorbent mass in higher bed signifies a larger surface area ad more abundant adsorption sites for the oil molecules to be adsorbed. The slope of the breakthrough curve decreased with increasing bed height which yielded a broadened mass transfer zone [10]. At the 5 cm tube, the effect of axial dispersion phenomenon prevailed and caused a reduction in the diffusion of oil molecules resulting in the oil molecules not having sufficient time to diffuse into chitosan grains and pores. Higher bed height gives rise to higher adsorption efficiency; this is due to the availability of abundant binding sites [11]. However, this is true for oil removal below the critical bed height. The phenomenon reverses and shows a decrease in removal efficiency at bed heights beyond the critical bed height which is explained in the decrease in coalescence efficiency where oil droplets are re-dispersed and re-coalesced multiple times while flowing through the adsorbent medium [12]

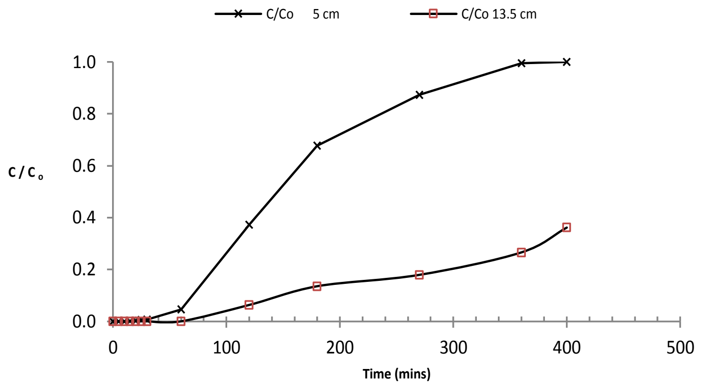

Fig. 5 – Breakthrough Curve for the Adsorption of Residual Hydrocarbon Oil from Produced Water onto Chitosan at Two Different Bed Heights (Initial Oil Concentration = 126.4 mg/L; Feed Flow Rate = 50 mL/min at Laboratory Ambient Temp. of 21°C

3.4 Freundlich Modelling

Freundlich isotherm [13] is the first known correlation describing the formation of multilayer adsorption onto solid surfaces [10]. This empirical model can be applied for non-uniform distribution of adsorption sites over heterogeneous surface (Adamson, 1997). Freundlich [13] adsorption isotherm model Equation (1)

$$Q_e = K_f \; C_e^{1/n} \qquad (1)$$

The linear form of Equation 1 is obtained by taking the logarithm of each side of the equation as shown in equation (2)

$$\log Q_e = \log K_f + \frac{1}{n}\log C_e \qquad (2)$$

K_f and n are obtained from the intercept and the slope respectively of the linear plot of experimental data of log q_e versus log C as shown in Figure 6. Table 1 lists the values of the constants obtained from the dynamic adsorption experimental data.

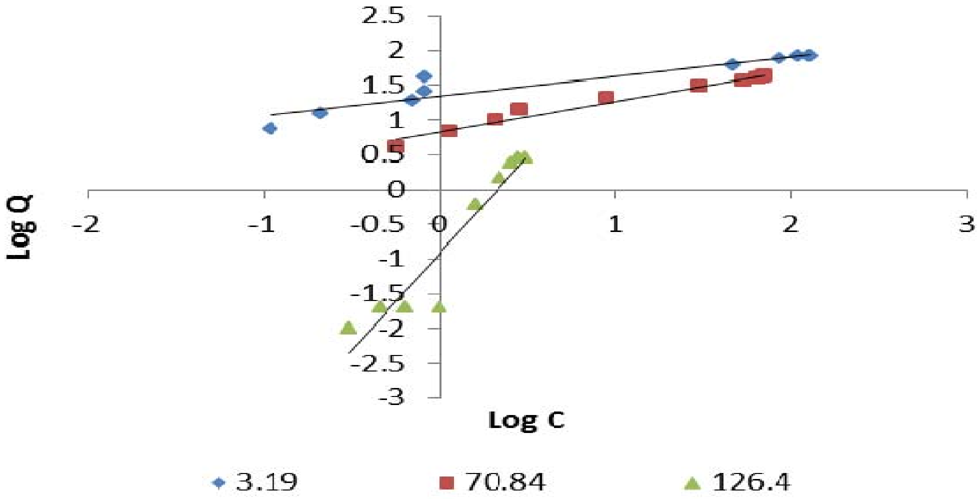

Fig. 6 – Freundlich Isotherm for the Sorption of HC Oil Produced Water onto Chitosan at Various Initial Oil Concentrations (mg/L)

From Equation (2), the slope n is an indication of the intensity of the adsorption or surface heterogeneity; as the slope approaches zero the heterogeneity increases. If the slope n is above unity cooperative adsorption takes place, whereas a value below unity reflects chemisorption dominance [14].

Table 1 – Freundlich Model Constants and Correlation Coefficient for Adsorption of Hydrocarbon Oil from Produced Water onto Chitosan

	Parameters		R^2
	K_f (mg/g(L/mg)$^{1/n}$)	n	
H =5 cm	22.36	3.53	0.9026
H = 13.5 cm	9.3626	2.698	0.9520
C_o=3.19 mg/L	2.0408	2.910	0.9291
C_o=70.84 mg/L	6.669	2.250	0.9706
Rate = 20 ml/min	23.67	3.527	0.8936
Rate = 50 ml/min	18.97	2.270	0.9617

The magnitude of the exponent n provides an indication of the favourability of the adsorption. Whereby, values n>1 indicates favourable adsorption condition [15]. In these cases as shown in Table 1, all the calculated values of n were in the range of 2.25 to 3.53 indicating favourable adsorption of oil taking place on surface of chitosan grains. The correlation coefficient R^2 was relatively high for all data suggesting that Freundlich isotherm provided a good fit for the dynamic adsorption data. This is an indication that Freundlich isotherm is suitable for modelling the dynamic experimental data in order to develop an adsorption model for chitosan.

3.5 Langmuir Modelling

Langmuir isotherm model is a very common model which is based on reaction hypothesis; it assumes that all adsorption sites are identical, each site retains a single molecule of adsorbate and that all sites are energetically independent of the adsorbed quantity [16]. The Langmuir equation for solid-liquid system is presented in Equation (3)

$$Q = \frac{Q_{max} K_L C}{(1 + K_L C)} \qquad (3)$$

The linearized form of Langmuir isotherm is also expressed as in equation (4) below, where a linearized plot of (C_e/Q_e) vs. Ce gives K_L and Q_{max}.

$$\frac{C}{Q} = \frac{C}{Q_{max}} + \frac{1}{Q_{max} K_L} \qquad (4)$$

The dimensionless constant R_L expresses in equation (5) is an essential features of Langmuir isotherm which indicates the shape of the isotherm; it is also commonly known as the separation factor (Webber and Chakravorti, 1974), is expressed as [17]

$$R_L - \frac{1}{(1 + K_L C_0}) \qquad (5)$$

Table 2 shows the range of values of RL and their description

Table 2 – RL description

RL Value	Description
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

Langmuir isotherm fits well for majority of the data under the range of concentration investigated (correlation coefficient, R^2) as seen in Table 2. The computed values of R_L indicate favourable adsorption of oil onto chitosan has taken place as reflected by R_L values between zero and unity which means that chitosan is a good adsorbent for residual oil from produced water from the oil fields.

Table 3 – Favourability of Langmuir Isotherm According to the Value of RL

Experiment	1	2	3	4	5	6	7
RL	0.0205	0.03012	0.03303	0.07281	0.02066	0.01822	0.08275

The correlation coefficients (R^2) obtained for Langmuir isotherms were relatively and consistently higher than those obtained from Freundlich isotherm, providing good fits for the experimental data except for the a single case of the 13.5 column height of the column was 13.5.

Table 4 – Langmuir Model Constants and Correlation Coefficients for Adsorption of Hydrocarbon Oil from Produced Water onto Chitosan

Experimental Parameters	Parameters			R^2
	Q_o (mg/g)	K_L (L/mg)	R_L	
H =5 cm	83.3	0.377	0.0205	0.9898
H = 13.5 cm	250	0.2548	0.0301	0.7607
C_o=3.19 mg/L	2.845	9.1775	0.3303	0.9750
C_o=70.84 mg/L	43.29	0.17977	0.0728	0.9817
Rate = 20 ml/min	88.5	0.4264	0.0182	0.9901
Rate = 50 ml/min	161.3	0.0876	0.0827	0.9845

4 CONCLUSION

Dynamic laboratory experiments have been performed to investigate the residual oil adsorption behaviour of chitosan. The laboratory adsorption data were analysed by fitting them to Langmuir and Freundlich isotherms. The results showed favourable adsorption of residual oil molecules onto chitosan bed in a dynamic flow laboratory setting defined by high adsorption capacity and strength. Chitosan is therefore a suitable adsorbent material for the removal of residual oil in produced water. However, dealing with used chitosan fully covered with oil layer remains a challenge as desorption of oil requires additional processes to reactivate or regenerate the used adsorbent media. It was also observed that adsorption becomes less efficient at higher feed oil concentration where early breakthrough of oil takes place. In addition, adsorption was found to require a high retention time in order to achieve efficiency in adsorption. Research should not be limited to laboratory scale studies but also should take into consideration operational conditional such as field temperatures and pressures.

5 ACKNOWLEDMENT

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6 NOTATION

Q	Oil concentration per mass of Chitosan mg/g
C_{max}	Maximum quantity of Oil adsorped per mass of Chitosan mg/g
C_o	Adsorbate Oil Concentration mg/L
C	Oil Concentration per Volume of Solution mg/L
K_f	Freundlich constsnt (ml/mg)
K_L	Langmuir constsnt (L/mg)

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