

MANAGEMENT OF PRODUCED WATER IN OIL AND GAS OPERATIONS

A Thesis

by

CHIRAG PATEL

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE

December 2004

Major Subject: Petroleum Engineering

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Approved as to style and content by:

Maria A. Barrufet
(Chair of Committee)

Peter P. Valko
(Member)

Dragomir B. Bukur
(Member)

Stephen A. Holditch
(Head of Department)

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Major Subject: Petroleum Engineering

ABSTRACT

Management of Produced Water in Oil and Gas Operations. (December 2004)

Chirag Patel, B.E., Nirma Institute of Technology, India

Chair of Advisory Committee: Dr. Maria A. Barrufet

Produced water handling has been an issue of concern for oil and gas producers as it is one of the major factors that cause abandonment of the producing well. The development of effective produced water management strategies poses a big challenge to the oil and gas industry today. The conversion of produced water into irrigation or fresh water provides a cost effective tool to handle excessive amounts of the produced water. In this research we proposed on-site produced water treatment units configured to achieve maximum processing throughput. We studied various advanced separation techniques to remove oil and dissolved solids from the produced water. We selected adsorption as the oil removing technique and Reverse Osmosis (RO) as the dissolved solids removing technique as being the best for our purpose. We performed experiments to evaluate operating parameters for both adsorption and RO units to accomplish maximum removal of oil and dissolved solids from the produced water. We compared the best models fitting the experimental data for both the processes, then analyzed and simulated the performance of integrated produced water treatment which involves adsorption columns and RO units.

The experimental results show that the adsorption columns remove more than 90% of the oil and RO units remove more than 95% of total dissolved solids from the produced water. The simulation results show that the proper integration and configuration of adsorption and RO units can provide up to 80% efficiency for a processing throughput of 6-8 gallons per minute of produced water. From an oil and gas producer's viewpoint output from the produced water treatment system is a revenue generating source. The system is flexible and can be modified for the applications such as rangeland restoration, reservoir recharge and agricultural use.

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CHAPTER I

INTRODUCTION – EFFECTIVE MANAGEMENT OF PRODUCED WATER

1.1 Introduction

The composition of produced water is strongly field-dependent and includes a variety of inorganic and organic compounds. Produced water contains small amounts of emulsified oil, organic compounds including dissolved hydrocarbons, organic acids, phenols and traces of chemicals added during production, inorganic compounds, suspended solids, dissolved solids and natural low-radioactive elements.

The most popular option to handle produced water is to re-inject it back into the formation. Produced water re-injection (PWRI) requires minimal or modified treatment before injection to obtain better results, but the injectivity decreases with time. As the reservoir matures injected produced water swipes through to the producing zone and water production increases with time which causes abandonment of the well. Transportation of produced water from production to injection sites increases re-injection costs. Furthermore, the produced water rate can be as high as 10 bbl per bbl of hydrocarbons and it may not always be feasible to re-inject all produced water volumes. Several options are being employed to handle this remaining excessive amount of produced water. Disposal of produced water is costly (as high as \$4/bbl) depending upon its makeup and transportation volumes, which must be handled and also have to face stringent environmental regulations. There is a need for an effective produced water management strategy that handles large amounts of produced water and meets environmental regulations¹.

Approximately four million barrels of produced water is produced along with oil and gas per year in the state of Texas. In West Texas Coal Bed Methane (CBM) producing regions the fresh water is a scarcity and produced water is in excessive amount. If properly treated, produced water can be a source of fresh water and can prove beneficial to the society particularly in arid areas. Many efforts are being made to convert CBM produced water into usable water by EPA, DOE and other institutions.

This thesis follows the style of *SPE Reservoir Evaluation & Engineering*.

1.2 Conversion of produced water – A new approach

1.2.1 A background of produced water treatment

Evans et al.² have discussed several produced water handling options and associated dangers. Disposal, re-injection and treatment of produced water are the available options. Produced water disposal requires meeting stringent environmental regulations and requires proper treatment before the disposal. Mackay et al.³ described risk involved in re-injection. Produced water re-injection requires skillful planning and treatment to meet the quality of re-injection water to avoid formation damage. Jun Wan et al.⁴ showed treatment of produced water before re-injection gives better performance. Alonzo et al.⁵ assessed the produced water treatments as well as disposal practice and addressed the research needs in this area. Hughes et al.⁶, Tao et al.⁷ and Tsang et al.⁸ discussed conversion of produced water into irrigation or drinking quality water. The review of various produced water treatment technologies and its applications for Coal Bed Methane (CBM) operators are discussed in literature⁹.

The general approach for produced water treatment is de-oiling and de-mineralizing before disposal or utilization. The use of centrifuge¹⁰, air-floaters, emulsifiers, hydroclones¹¹, membrane separators¹² and adsorbers¹³ to remove oil and grease from the produced water is discussed in literature. Several methods such as micro-filtration (MF), ultra-filtration (UF), ion exchange, and reverse osmosis (RO)^{14, 15} are available for de-mineralization purpose. Roberts¹⁵ showed considerable reduction in de-mineralization cost with RO operation. Siddiqui¹⁶ suggested use of RO units to achieve maximum salt rejection and efficiency based on experimental results. The literature discussed above, do not provide sufficient information on modeling of separation technique for produced water treatment application. In this thesis, we model the best available technology and provide a static and a dynamic model of this technology. The static model refers to equipment sizing, while the dynamic model takes into account the process conditions. Our model can be used for a pilot scale operation and can be scaled up to a larger throughput.

1.2.2 Distributed water processing and recycling

There is a need to design and develop a general and effective produced water treatment system. We discussed the issue and approached to initiate development of

produced water treatment unit that would be feasible for field application. A Distributed Water Processing and Recycling (DWPR) system is being developed at Texas A&M University to treat produced water with a rate of 6 GPM or with a flux of 0.086 GPM/ft² at a pilot scale. It involves combinations of primary and polishing de-oiling and de-mineralizing units. Figure 1.1 shows a schematic of a possible DWPR system. Flux is defined as the ratio of the flow rate to the surface area of RO membrane.

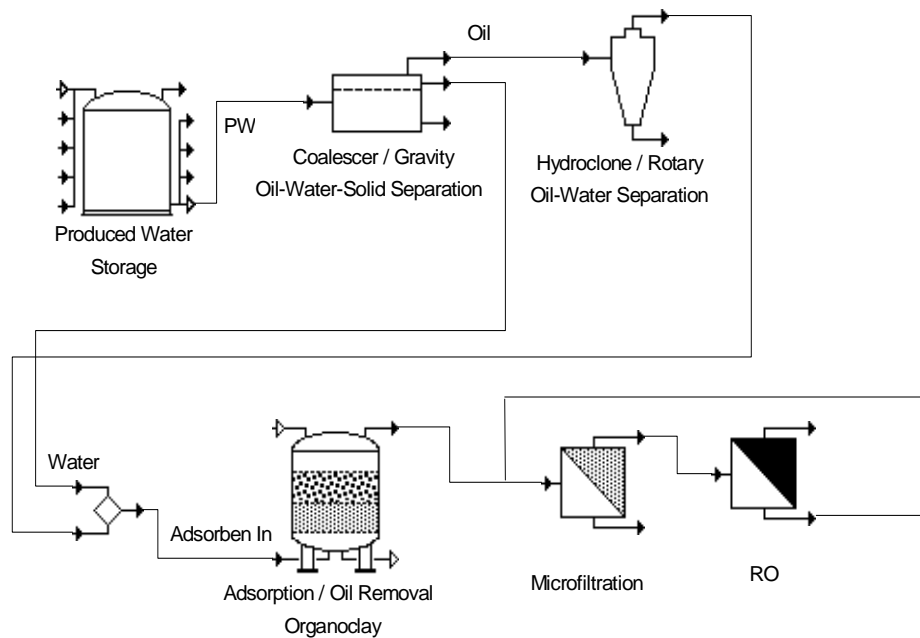


Fig. 1.1 – A schematic of produced water treatment cycle, a possible DWPR configuration.

The objectives accomplished in this research are;

1. Testing of new adsorbent organoclay-PS12385 for oil removal from produced water. The organoclay-PS12385 is structurally modified clay that does not swell upon adsorption of oil.
2. Testing of RO membrane-SWC 1 4040 for dissolved solids removal.
3. Development of models to fit experimental data for oil adsorption column and for salt removal.

4. Estimation of operating parameters for oil adsorption columns and RO units.
5. Simulation of transient performance of integrated adsorption-RO system.

CHAPTER II

OIL REMOVAL FROM THE PRODUCED WATER

2.1 Measurement of total oil content (TOC) in water

TOC analysis of oil containing samples and samples processed by oil removal units determines the performance of the oil removal unit in terms of oil removal capacity and efficiency. The definition of TOC is field specific. Environmental Protection Agency (EPA) defines crude oil content in water as the amount of hydrocarbons that can be extracted by solvents such as n-Hexane, Xylene or Freon in acidic media. Alternately, TOC can be defined as the amount of hydrocarbons in sample that releases carbon dioxide upon oxidation in acidic media. The values of the TOC obtained from both solvent extraction and oxidation may not be the same since the solvent extraction process only extracts aromatic hydrocarbons while oxidation process converts total organic carbon (aromatic, aliphatic etc) into carbon dioxide.

Calibration of the TOC analyzer is crucial in any oil analysis technique. A calibration factor is obtained by calibrating the analyzer response signal for samples with known oil concentrations. The calibration factors can be different for different types of oil present in the sample. For example, the calibration factor obtained for samples containing kerosene is different from the calibration factor obtained for samples containing diesel. However according to EPA, if the analyzer is calibrated with samples containing crude oil, it is sufficient for analyzing TOC of the sample.

TOC-700 (manufactured by O.I. Analytical) analyzer works on the principle of oxidation of total organic carbon. TD-500 (manufactured by Turned Design Inc.) works on the principle of solvent extraction of hydrocarbons. For non-uniformly mixed or emulsified samples TOC-700 may not provide accurate results as the amount of the sample injected into the analyzer may not be representative of the original sample. TD-500 eliminated this problem by extracting oil phase of the sample and analyzing only extracted oil phase. The main advantage of TD-500 is that it enables the user to use large amounts of sample (more than 50 ml compared to 1 μ l-2 ml in case of TOC-700) for analysis which reduces the chances of inaccuracy because the larger the amount of sample the higher the chances of good representation of the original sample.

In this work TOC-700 was used to analyze kerosene-water emulsions. To match TOC analysis with the EPA standard a TD-500 was used to analyze crude oil-water emulsion and produced water.

2.1.1 Oil in water analysis by TOC-700 analyzer

The analyzer is capable of measuring Total Inorganic Carbon (TIC), TOC, Dissolved Organic Carbon (DOC), Suspended Organic Carbon (SOC), Purgeable Organic Carbon (POC), Purgeable Organic Halide (POX) and Non-Purgeable Organic Carbon (NPOC). Only TOC analysis will be discussed in detail since the analyzer was only utilized to measure TOC of the sample.

TOC is determined by the measurement of carbon dioxide released by chemical oxidation of the organic carbon in the sample. First an appropriate amount of sample is injected into the reaction chamber by manual injection or auto-sampling loop. The sample is acidified to purge the TIC. Sodium persulfate, a strong oxidizer is added next. The oxidant quickly reacts with organic carbon in the sample at 100°C to form carbon dioxide. When the oxidation reaction is completed, the carbon dioxide is purged from the solution, concentrated by trapping and then desorbed and detected by a non dispersive infrared (NDIR) detector. NDIR converts the amount of carbon dioxide into equivalent milli-volt (mV) signal. The calibration factor converts the mV signal into ppm of oil.

It is essential to calibrate the analyzer before using it. The calibration factor relates the detected amount of carbon dioxide and hence mV response of the NDIR to the mass of organic carbon originally present in the sample.

Calibration of TOC-700

The calibration process is described in the following sections,

1. Preparation of reagent blanks.
2. Preparation of samples of various kerosene concentrations.
3. Sample injection into the analyzer.
4. Sample oxidation in reaction chamber.
5. Purging and trapping of released carbon dioxide.

6. Detection of carbon dioxide by NDIR and display result in ppm of TOC.

1. Preparation of reagent blanks.

Reagent water: Water used for preparing the reagent blanks should contain less than 200 ppb of TOC. We used distilled or deionized water.

Sodium persulfate (100 g/L): It is prepared by dissolving 100 g sodium persulfate into reagent water (1 liter total volume). The solution is stirred and then heated in a bottle with loose lid until the solution just comes to boil. As soon as the solution appears to start boiling the lid is tighten and the bottle is immersed in cold water. This procedure purifies the persulfate solution by reducing TOC content of reagent water that was added during preparation of the solution.

Phosphoric Acid (5% vol/vol): Acid for TIC removal is prepared by dissolving phosphoric acid (85% purity) into reagent water. A volume of 5 ml phosphoric acid (85% purity) is mixed with 95% reagent water to make 5% vol/vol solution.

2. Preparation of samples of various kerosene concentrations.

The NDIR linearity range of detection is 0-1000 mili-volt (mV). The concentration of kerosene in samples should not cause the mV response of NDIR to go beyond 1000 mV. Different concentrations of kerosene were tried and by observation the data were selected for the concentrations that provided less than 1000 mV response. The calibration curve is obtained by plotting these data. We tried samples with kerosene concentration ranging from 20 – 800 ppm for calibration purpose. For measuring a sample having concentration more than 800 ppm, we diluted the samples.

3. Sample injection into the analyzer.

One method for charging the sample to the analyzer is via a syringe (sampling volume of 5 - 100 μ L). Another is loop sampling, in which the sample loop introduction system allows repeatable analysis over a wide range of concentrations while avoiding the inherent dead volumes of syringe-based systems. On-line total organic carbon analyzer systems have an analyzer that is mounted in a process line and the sample is introduced via a automatic valve. Via auto samplers are another way to introduce the sample. The liquid-sample transfer auto-sampler removes specific sample volumes from a standard

vial and transfers the sample to the common analysis vessel. A sample carousel is loaded with up to fifty vials and placed in the auto-sampler for unattended analysis. In addition to measuring total organic carbon, total organic carbon analyzers may sometimes be used to detect total carbon, total inorganic carbon, and purgeable and nonpurgeable organic carbon.

Kerosene-water forms a very unstable emulsion therefore continuous stirring is necessary to avoid the two components to get separated. Because of stirring air is added to the sample and that causes the error in estimation of TOC. For smaller sample injection volume (0.025 ml to 0.5 ml) the air present in it causes error. By using larger sample (1 ml) injection volume the possibility of error due to air is minimized greatly. Auto sampling loop was used for analysis of each sample that allows injection of 1 ml of sample automatically.

4. Chemical oxidation of sample in reaction chamber.

The oxidation of the sample by sodium persulfate is carried out in an oxidization chamber at user defined temperature (we set the reaction temperature at 180 °C to ensure complete oxidation). The default reaction time is 5 mins. In some cases the default time was not long enough to oxidize the sample completely and that caused error in TOC quantification. This caused non-repeatability of the results. The reaction time can be extended further by user. We tried upto 8 min of reaction time.

The volumes of acid and persulfate solution are also determined by the user. The determination of volume of acid and oxidizer requires observation and experience with the equipment. We used excess amount of acid and oxidizer to ensure the completion of the reaction. The volume of reagents and the time of reaction should be large enough to oxidize the sample completely. If the chemical formula of the sample is known the volumes can be determined by stoichiometric calculations. If the chemical formula is unknown trial and error method is employed. Different volumes of reagents and reaction times are tried until the complete oxidation of the sample is obtained in quantification.

5. Purging and trapping of released carbon dioxide.

A molecular sieve column is installed in the analyzer to trap the carbon dioxide from the oxidization chamber. The time required for purging should be sufficiently long enough to trap all the carbon dioxide. In our analysis, we used purging time ranging from 1 min for less concentrated samples to 2 min for highly concentrated samples.

6. Detection of carbon dioxide by NDIR and display result in ppm C.

The infrared gas analyzer measures gas concentration based on the principle that each type of gas component shows a unique absorption spectrum in the infrared region. The IR analyzer contains an infrared light containing the gas component to be measured (CO₂). The light source emits infrared light in all directions. The IR light emitted backward is reflected and added to the IR light emitted forward. The IR light beam thus formed passes through the measuring cell and is partially absorbed or attenuated by any CO₂ present as a sample passing through. Both the front and the rear chambers of the detector are filled with gas. The IR light beam is partially absorbed in the front chamber and residual light is absorbed in rear chamber, thereby increasing pressures in both the chambers.

Between the IR light source and the measuring cell is a chopper blade which rotates to interrupt the IR light beat at regular frequency (10 Hz) so that it reaches the detector chamber intermittently. Therefore, pressure rises periodically in both chambers and produces a slight flow pulsation. The flow pulsation is converted into AC electric signals by a micro-flow sensor. The AC signals are amplified and rectified into DC voltage signal to be supplied to the microprocessor. The voltage output is linear with respect to the mass of carbon momentarily flowing through the cell.

Before the calibration process is started, the NDIR response for reagent blanks are observed and should be entered into the system calculations for determining the calibration factor.

Figure 2.1 shows the calibration curve obtained for kerosene-water emulsions. It is assumed that commercially available kerosene has 85% of C and 15% of H on a mass basis. The density of kerosene is measured to convert volume into equivalent weight of

kerosene. For example, 1 ml of kerosene is equivalent to 0.81 gm. The C content in the sample is 0.85 times the 0.81 gm. Finally, C content is calculated as mg of C per liter volume of sample.

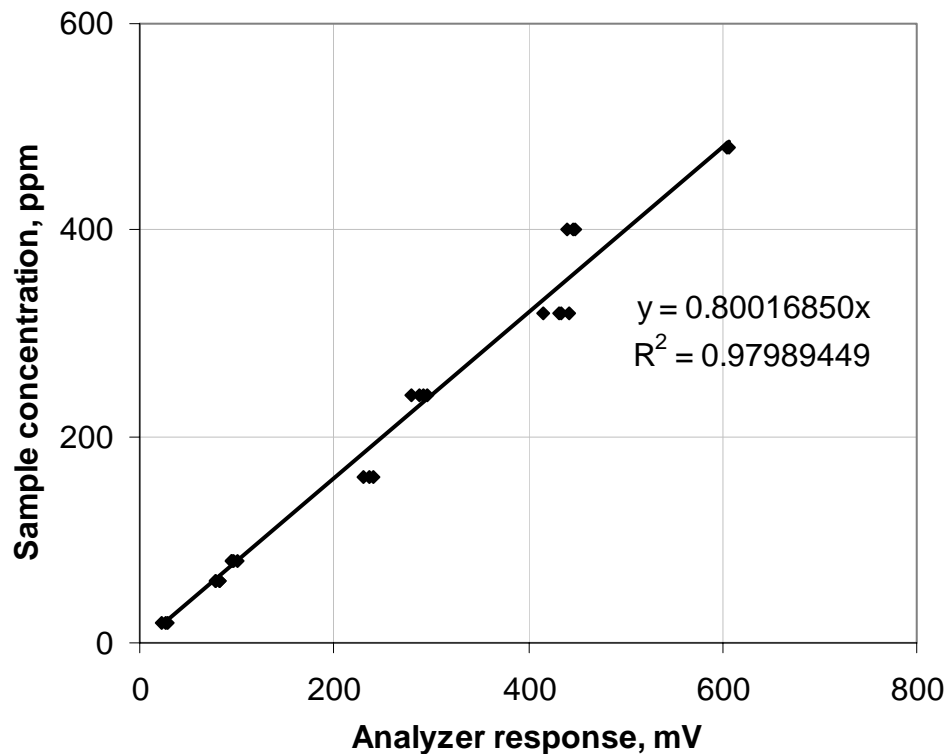


Fig. 2.1 – Calibration curve for TOC-700 analyzer that analyzes oil present in water.

The ppm concentration is plotted against the net mV response from NDIR. Net mV response is the value obtained by subtracting mV response of reagent blanks and distilled water from the mV response of the sample, e.g. kerosene-water emulsions. The curve is reasonably linear and covers wide range of concentration. Kerosene-water emulsions having concentration higher than the maximum limit of the calibration curve should be further diluted as without dilution the mV response would not be linear.

2.1.2 Oil in water analysis by TD-500 analyzer

TD-500 oil in water analyzer measures the oil content in the oily water containing crude oil or gas condensates using UV fluorescence. It works on produced water, desalter tail water, and crude storage tank water and in any application where crude oil may be in contact with the water.

TD-500 oil in water meter uses an easy to use solvent extraction procedure with high accuracy and repeatability. The standard procedure of solvent extraction is specified by EPA-1664A method better known as FastHex method of analysis. The analysis method is compatible with all popular solvents including n-Hexane, Vertrel, AK-225, Freon, Xylene and others. The sample analysis time is less than 4 minutes.

Calibration and sample analysis

1. Sample Preparation

A 90 ml volume of the sample to be analyzed is collected in a graduated cylinder. The pH of the sample is adjusted below value of 2 by adding hydrochloric acid or sulfuric acid. Solvent is added as 1 part in 9 parts of the sample on volume basis. The cylinder is rigorously shaken for couple of minutes. Solvent extracts soluble oil present in the sample and the two layers are formed. The extract layer contains solvent and oil extracted from the sample. The extract is carefully separated and collected into a separate cylinder or flask. The extract is analyzed by TD-500.

2. Sample Analysis

Before analyzing a sample the TD-500 meter is calibrated using standard samples. The standard samples of known oil content are prepared. We measured the density of oil to obtain equivalent weight per unit volume of oil. As a starting point, we prepared a mixture of 1 ml of oil in 9 ml of n-Hexane. This mother solution is diluted with various volumes of n-Hexane to create samples with different oil concentrations. TD-500 meter is set on calibration mode. The TOC value of standard is entered into the analyzer. In this case we obtained amount of aromatic oil content in sample unlike the case of TOC-700 where we obtained amount of total organic carbon content in sample.

The appropriate volume (0.075 ml to 1 ml) of extract is collected in clean minicell cuvettes or 8 mm round cuvettes. The cuvette filled with the extract is placed in a cuvette adapter. The adapter fits into the sample compartment of the analyzer. The analyzer responds within 5 seconds. The value of calibration factor is calculated by the analyzer according to the TOC content of standard and response of the analyzer.

Figure 2.2 shows the calibration curve for TD-500 prepared using crude oil (38⁰ API)-water emulsions.

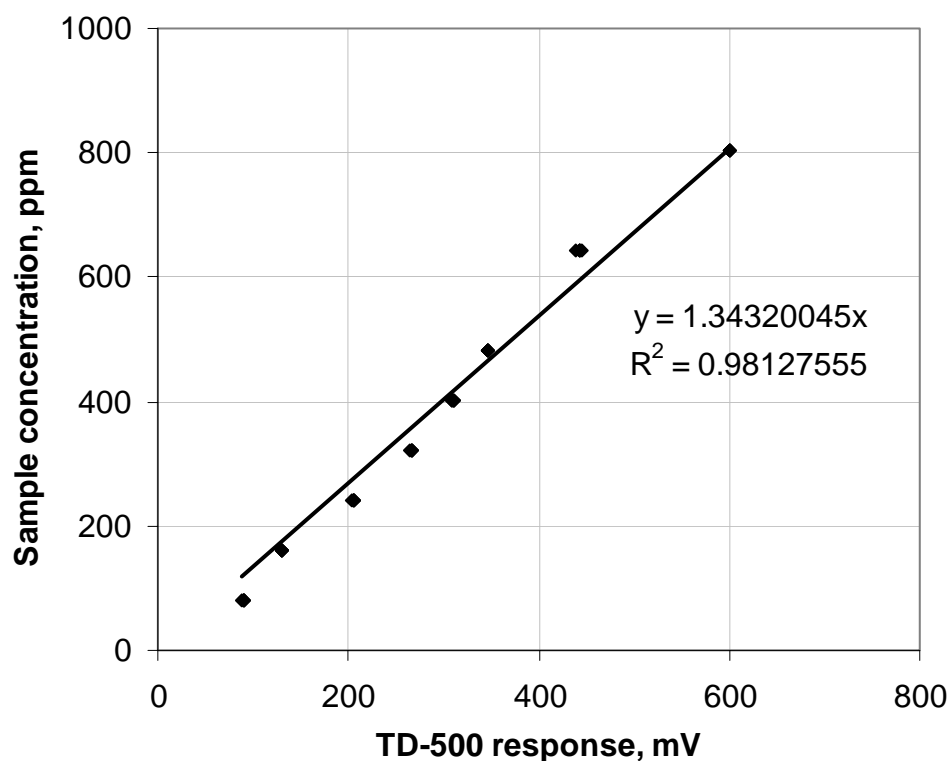


Fig. 2.2 – Calibration curve for TD-500 analyzer that analyzes oil present in water.

After calibration each sample is prepared by following the standard procedure and analyzed. Calibration should be performed frequently if needed.

The extraction method works for samples containing aromatic hydrocarbons. In case of aliphatic hydrocarbons the analyzer is not capable of detecting the UV signal emitted from the extract. This analyzer measured Total Oil Content on the basis of only aromatic hydrocarbons present in the sample.

2.2 Selection of adsorption for oil removal from produced water

A list of several oil removal techniques was discussed in the introduction section. Adsorption is a cheaper and feasible technique. Membrane technologies are not efficient because of power requirement and higher possibilities of membrane fouling while handling the oily water. Most of the other techniques such as gravity separation loose oil removal efficiency at lower concentrations, which is discussed in this work. Produced water typically contains oil ranging 30-200 ppm. Doyale et al.¹² performed several experiments to observe adsorption of oil and proved the efficiency of adsorption at lower concentrations. However, their work does not discuss about estimation of operating parameters, modeling or application of adsorption for produced water treatment at field scale.

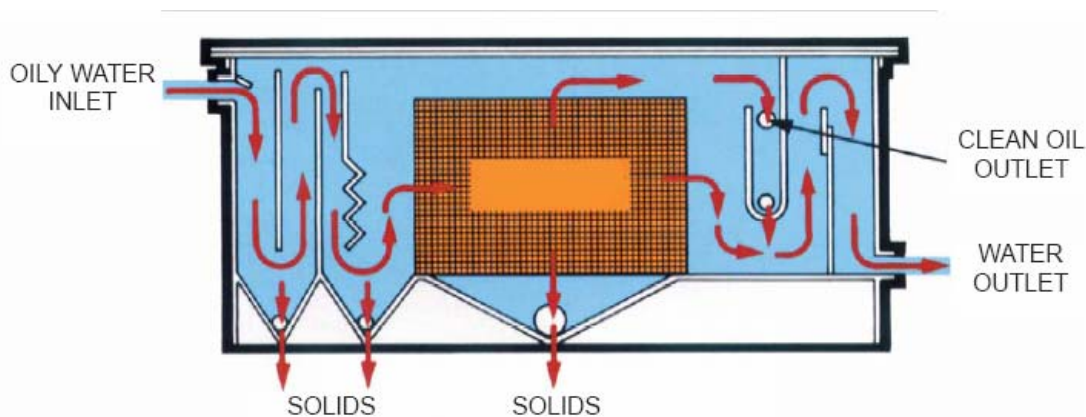


Fig. 2.3 – A schematic of FTS PHASE³ coalescer.

Several experiments were performed in this work to evaluate gravity separation with FTS PHASE³ (Figure 2.3) oil-water separator.

The methods and the equipments to perform this operation have been improvised often. For oil-water separation the use of the gravity separation method provide primary step and require the back up treatment like filtration or adsorption.

Coalescer works on the principle of forming larger oil droplets which travel at higher velocity and so the separation becomes rapid. A coalescing pack attracts oil droplets which form larger droplets that rise quickly and thus produce faster phase separation.

Oil-water separator should provide optimum efficiency in gravity separation between two immiscible liquid fractions depending on initial oil content. The horizontal orientation of the PHASE³ modules provides a uniform and non-clogging flow through the coalescing tubes. The coalescing pack features a structured polypropylene coalescing medium made of screen tubes unitized in removable baskets. The rectangular openings in its tubular construction allow for settling solids to pass through the coalescing medium. The design versatility of the PHASE³ also eliminates the staging that is necessary with other incline and horizontal coalescing plates.

The FTS PHASE³ oil-water separator is of a gravity accelerator design with coalescing slotted tube arrangements for processing both high oil and high solids content. The inlet baffles reduce the oil-water mixture feed to laminar flow. The liquid then enters the coalescing tubes under laminar conditions. According to Stoke's law, rise and fall velocity of dispersed phase droplet is exponentially increased with the droplet size. The oleophilic surfaces of the coalescing tubes attract small oil droplets which in turn, combine to form larger droplets for easier flotation. The oil rises to a collection point while the water continues through the medium to the water outlets. Some of the attracting features of this equipment are,

1. No pretreatment required.
2. High efficiency separation due to high surface area coalescing medium.
3. No moving parts

4. Easy cleaning; minimal maintenance.
5. All steel vessel construction.
6. Large solids settling area helps removing solids effectively if present in feed.

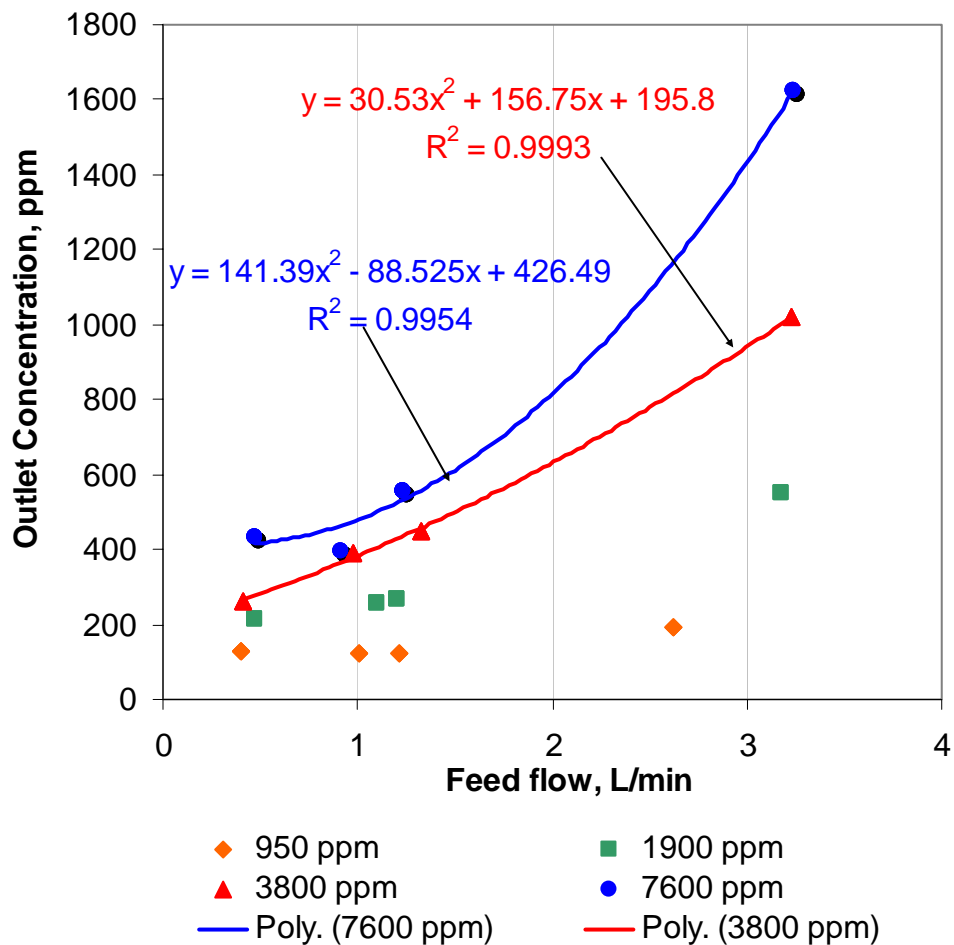


Fig. 2.4 – Effects of feed concentration and residence time on oil content of outlet from coalescer.

Coalescence efficiency is defined as the ratio of the outlet concentration to that of the feed. Figure 2.4 shows that as the feed flow rate increases the coalescence time decreases and so the outlet concentration increases. Figure 2.5 shows the coalescence

efficiency decreases as the inlet concentration and residence or coalescence time decreases (increasing flow rate).

The use of a coalescer in produced water treatment is restricted because the concentration of the produced water ranges from 30-200 ppm. The efficiency would be much lower at this range and the outlet concentration might not be decreased down to 20-30 ppm limit as required by EPA.

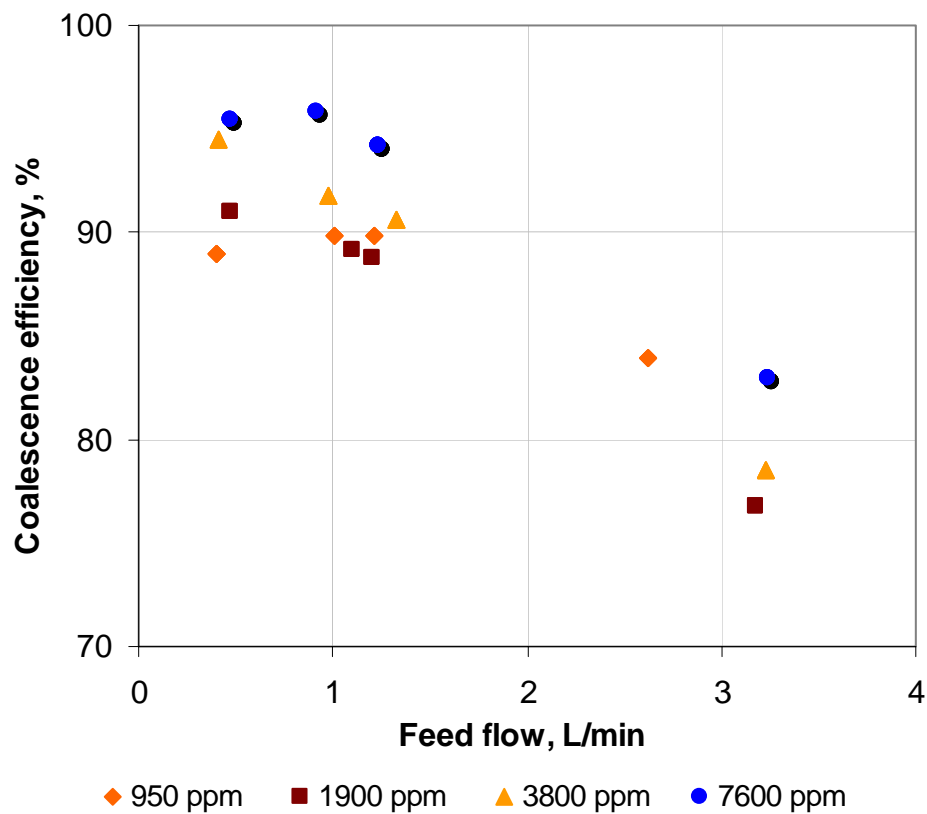


Fig. 2.5 – Effects of feed concentrations and residence time on oil removal efficiency of coalescer.

However, it might be effective and economical for suspended solids separation from the produced water which is necessary to perform before oil removal by adsorption.

To evaluate removal of oil by adsorption several experiments were performed. The analysis of results was accomplished by measuring TOC with TOC-700 and TD-500 analyzer. The next section discusses basic adsorption terminologies.

2.3 Adsorption terminologies

Loading Capacity or Adsorption Capacity (n):

It is the maximum amount of solute present in the liquid phase that can be adsorbed by adsorbent. It can be defined as gm of oil or solute adsorbed per gm of adsorbent.

Residence Time or Empty Bed Contact Time (EBCT):

Since the liquid flows through the pore space within adsorbent media residence time is the time for which liquid phase containing adsorbate (solute to be adsorbed) remains within the pore space in the packed bed.

The EBCT is defined as the time for which the liquid phase remains in the bed which is not packed.

$$EBCT = \theta = \frac{A_{cs}L}{Q} \dots\dots\dots(2.1)$$

$$(RT) = (EBCT)\varepsilon \dots\dots\dots(2.2)$$

where, ε = porosity of the packed bed

RT = residence time, [t]

θ = empty bed contact time, [t]

A_{cs} = cross sectional area of packed bed, [L]²

Q = volumetric flow rate through the packed bed, [L]³[t]⁻¹

Bulk Density (ρ_b):

The bed or bulk density is the mass of adsorbent in a specific volume. It is a measure of the amount of adsorbent that can be packed in a column of given volume.

Particle Density (ρ_p):

Particle density is the mass of adsorbent per volume occupied by the particle. This is accurately and easily measured for true cylindrical pellets and beads, but is more difficult for distorted shapes and granular materials, though proprietary methods exist for obtaining accurate values even for those.

Solid Density (ρ_s):

Solid density is the mass of the adsorbent per volume occupied by the particle, but with the pores deducted.

Isotherm:

Adsorption equilibrium data are commonly gathered at a fixed temperature and plotted or tabulated as loading capacity or adsorption capacity of adsorbent versus the fluid-phase concentration (or partial pressure for gases and vapors).

The simplest equilibrium isotherm expresses loading as proportional to the fluid-phase concentration, and this results in Henry's law.

$$q^* = Ac \dots\dots\dots(2.3)$$

where, q^* = equilibrium solute concentration in adsorbent, gm of oil/gm of adsorbent

c = solute concentration in liquid phase that is contacted to adsorbent, ppm

A = Henry's law coefficient

In contrast, the Langmuir isotherm accounts for surface-coverage. That is, when the fluid concentration is very high, a monolayer forms on the adsorbent surface. For some systems, the apparent level of saturation may represent multiple adsorbed layers. The parameter, A , is referred to as the Henry's law coefficient, since it is the slope of the isotherm at zero coverage.

$$q^* = \frac{Ac}{1 + Bc} \dots\dots\dots(2.4)$$

The Freundlich isotherm is the result of fitting isotherm data to a linear equation on log-log coordinates. It is probably the most commonly used isotherm equation, despite

being “thermodynamically inconsistent,” in that it does not have a finite Henry’s law coefficient.

$$q^* = Ac^B \dots\dots\dots(2.5)$$

Several other forms of isotherms have been discussed in detail in available literature.

Adsorption Rate:

The rate of adsorption onto an adsorbent surface can be expressed as,

$$R_{ads} = kc^{n_k} \dots\dots\dots(2.6)$$

where, R_{ads} = adsorption rate

k = adsorption rate constant, $[T]^{-1}$

n_k = kinetic order coefficient

2.4 Evaluation of new organoclay adsorbent for oil removal

Produced water can be used as a source of fresh water after the oil content in produced water is removed below 30 ppm according to EPA standards. Adsorption of oil contents with organoclay bed is an economical method and the objective of this project is to evaluate the performance of organoclay bed.

PS 12385 is a modified organoclay mineral manufactured by Polymer Venture Inc. PS 12385 does not swell or blind when adsorbing contaminants, so it need not be blended with anthracite filter. Table 2.1 indicates physical properties of PS12385.

The adsorption depends on various parameters such as organoclay weight, porosity of bed, residence time in the bed, feed concentration and bed preparation techniques.

TABLE 2.1 – Properties of proposed new adsorbent organoclay PS18385 for oil removal from produced water.

Appearance	Gray to Tan Granules
Specific Gravity	2.0 – 2.2
Bulk Density	42 – 46 lbm/ft ³
Granule Size	8/30 mesh (US sieve, Average opening 1.6 mm)
Residence Time	2 – 4 min
Void Volume	35 – 45%

One of the analysis methods is the breakthrough curve. Breakthrough curve is the plot of outlet concentrations from packed bed vs. time. Obtaining breakthrough curve for each experiment and comparing these curves to do parametric analysis is one of the objectives of the project.

2.4.1 Packed bed adsorption experiments

To analyze the performance of organoclay bed several experiments are performed. Since it is necessary to achieve breakthrough of packed bed to analyze adsorption capacity and kinetics, highly concentrated influent are required. Experiments were performed with highly concentrated kerosene-water emulsions and crude oil-water emulsions. Several combinations of feed concentration, residence time and particle size distribution were used to evaluate the effects of these parameters on adsorption.

Methodology and procedure

The bed is packed to ensure minimum channeling and soaked with the feed water to wet the organoclay particles. The flowchart of experiment is given below in Figure 2.6. To maintain lower flow rate feed is recycled to feed tank in some experiments.

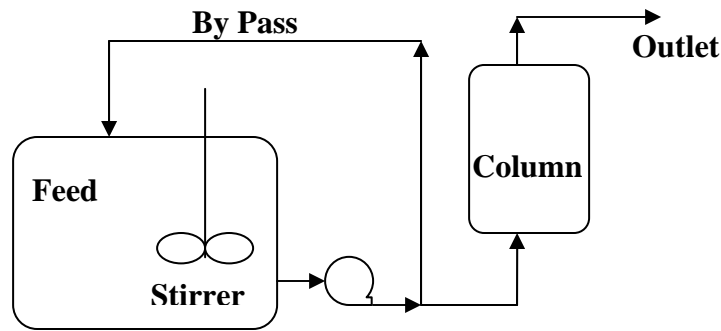


Fig. 2.6 - A schematic of experimental setup for adsorption operation.

To analyze kinetics of adsorption, effect of bed dynamics and loading capacity of adsorbent, it is necessary to achieve breakthrough curve for each experiment. The packed bed dimension, weight of organoclay, feed concentration, breakthrough time and residence time must be estimated before starting the experiment.

The EBCT suggested by the manufacturer is 3 to 6 min. The dimensions of the column are fixed on the basis of the amount of organoclay to be used. For same diameter column different amount of organoclay would give different Length of Column to Diameter of column ratio. The flow rate through the column is determined after measuring the porosity of the packed bed. The flow rate is adjusted to obtain EBCT value as low as 3 min. To maintain such low flow rate through the column for as long as experiment run with the available pump is accomplished by providing a by pass and controlling the flow by valves. The adsorbent is the material that is used in adsorption column as the filtering media. It must adsorb wide range of hydrocarbons and trace amount of heavy metals from produced water.

The pore network on the surface of the particles is clearly seen in Scanning Electron Microscopic (SEM) image (figure 2.7). Figure 2.8 clearly indicate the presence of diatoms in abundance. Diatoms are skeletons of dead micro organisms which are very porous in nature.

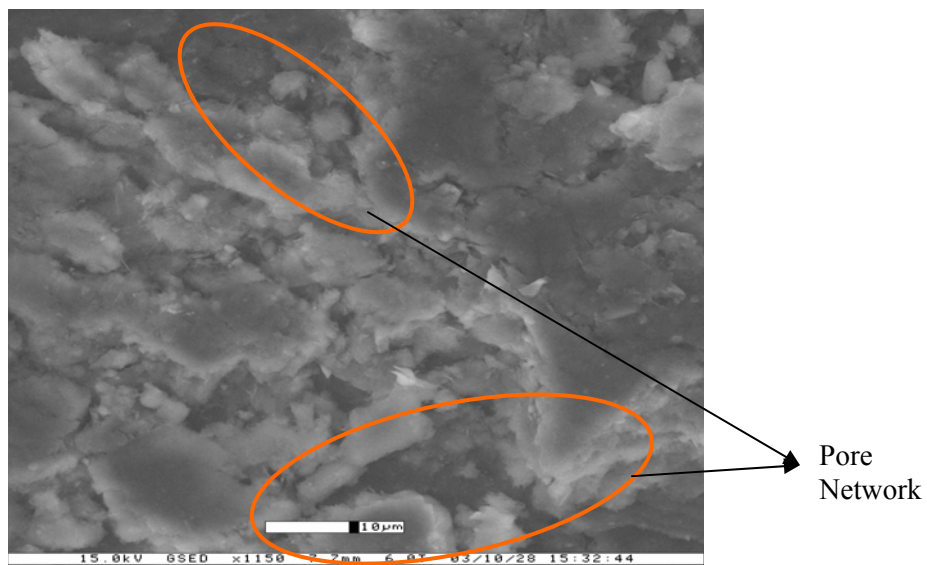


Fig. 2.7 – SEM image of un-crushed organoclay particle.

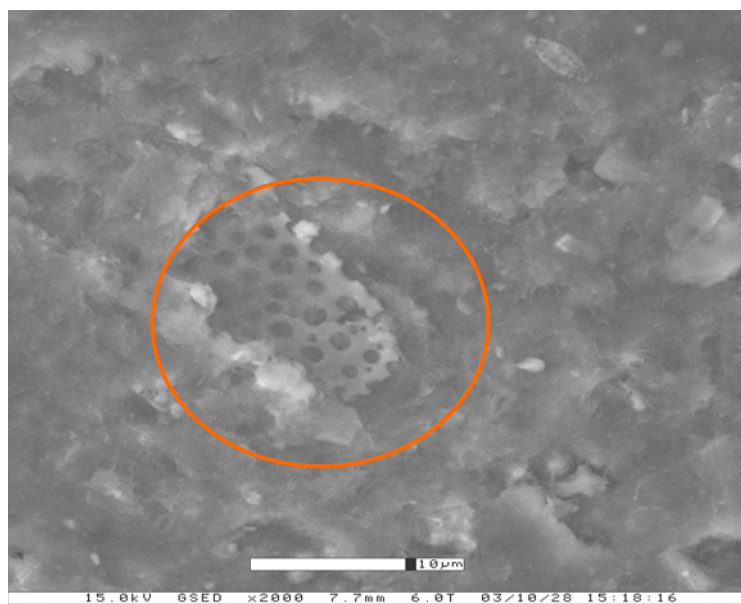


Fig. 2.8 – Diatoms provide porous structure to organoclay.

To minimize channeling and wall effects in a packed column the ratio of diameter of the column to the diameter of adsorbent should be within 30-60²⁰. To achieve the ratio

within this range in laboratory the organoclay particles were crushed and sieved (figure 2.9) before packing.

An advantage of size reduction of organoclay is the increase in fluid-to-particle mass transfer coefficient. Also size reduction increases the surface area of the particles and hence the fluid-solid contact area (adsorption area). It can be observed that for a given flow rate, reduction in particle size would increase mass transfer coefficient. Also increase in velocity would increase in mass transfer coefficient but it is obvious that as the velocity of fluid through the column increases the contact time or the residence time decreases which results into less time for adsorption and so lower loading capacity.

The conceptual difference in breakthrough curve under same operating conditions i.e. residence time, inlet concentration, porosity for different particle sizes is the difference in sharpness of the curve. In case of reduced or crushed particles the breakthrough curve is steeper because of faster adsorption kinetics, while for uncrushed particles the breakthrough curve is distended.



Fig. 2.9 – Reduction of size of organoclay particle in laboratory.

Another advantage of particle size reduction is decrease in length of unused bed (LUB). The LUB describes the percent of adsorbent packed bed that is not utilized due to the length of the adsorption zone or mass transfer zone (MTZ) within the bed. MTZ is defined as the region in which the concentration of the adsorbate of interest in the fluid decreases from influent concentration to the lowest detectable concentration. We observed MTZ as a region in which the color of organoclay in packed bed changes. Upon adsorption of oil, the organoclay color becomes dark brown and thus we distinguished used bed from unused bed. In case of length of the column less than MTZ the results obtained would under estimate the loading capacity of the organoclay. As the rate of the adsorption is higher in case with crushed particles the MTZ length is less and so adsorbent bed is fully utilized in this case. Figure 2.10 explains this concept.

The disadvantage of too small or powdered size particles is the increase in pressure drop across the packed bed. Also in case of powdered size particles the pore structure gets destructed.

The experimental observation of particle size reduction on breakthrough curve will be discussed in later sections.

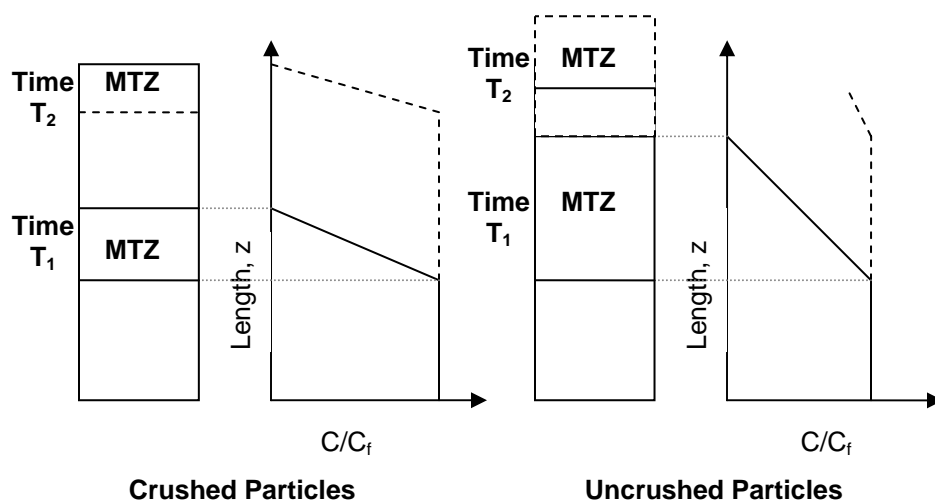


Fig. 2.10 – A conceptual diagram showing effect of particle size reduction on MTZ.

2.5 Data acquisition and presentation

The packed bed porosity was measured before starting an experiment. The packed bed is filled with water to hold maximum amount of water. The weight of water filled packed bed, organoclay and empty columns were measured accurately.

The weight of water that organoclay bed holds is,

$$W = W_{packed} - W_{oc} - W_c \dots\dots\dots(2.7)$$

where, W_{oc} = weight of organoclay packed within the column, gm

W_c = weight of unpacked column, gm

Volume of water is,

$$V_{water} = \rho_{water} W \dots\dots\dots(2.8)$$

We also have the volume of column (V_{oc}) that is packed with organoclay, which is obtained by multiplying the cross sectional area of unpacked column (diameter of column is known) with the height of the packed column.

The porosity of the bed is,

$$\varepsilon = \frac{V_{water}}{V_{oc}} \dots\dots\dots(2.9)$$

For each experiment breakthrough was achieved. The breakthrough curve is the plot of packed bed outlet concentration vs. time. For each experiment outlet samples were collected and analyzed to measure TOC by TOC-700 or TD-500 analyzer. Average residence time and pore volume processed before the breakthrough was calculated. Adsorption capacity was determined by performing material balance calculations. Table 2.2 shows the list of data acquired when performing adsorption experiments.

TABLE 2.2 – A list of parameters to be acquired in each adsorption experiment.

TOC content of inlet fluid or feed stream, C_{in}
Length and Diameter of packed bed, L and d
Amount of adsorbent (organoclay) packed in the column, W_{packed}
TOC content of outlet stream from packed bed at regular time intervals, $C(t)$
Flow rate of fluid stream through the column, Q
Breakthrough time, $t_{breakthrough}$

CHAPTER III

DISSOLVED SOLID REMOVAL FROM PRODUCED WATER

3.1 Selection of reverse osmosis (RO)

Reverse osmosis is capable of rejecting bacteria, salts, sugars, proteins, particles, dyes, and other constituents that have a molecular weight of greater than 150-250 Daltons. The separation of ions with reverse osmosis is aided by charged particles. This means that dissolved ions that carry a charge, such as salts, are more likely to be rejected by the membrane than those that are not charged, such as organics. The larger the charge and the larger the particle, the more likely it will be rejected. One of the factors for selecting RO over other membrane filtration processes such as Micro-filtration (MF), Ultra-filtration (UF) etc. is that mono-valent salt can not pass through RO membrane. RO can remove salt particles which can not be removed by MF or UF membranes.

The idea of RO is to use the membrane to act like an extremely fine filter to create drinkable water from salty (or otherwise contaminated) water. Osmosis is the movement of a solvent through a semi permeable membrane into a solution of higher solute concentration that tends to equalize the concentrations of solute on the two sides of the membrane. In RO, the salty water passes through on one side of the membrane and pressure is applied to stop, and then reverse, the osmotic process.

Reverse osmosis uses a membrane that is semi-permeable, allowing the fluid that is being purified to pass through it, while rejecting the contaminants that remain. Most reverse osmosis technology uses a process known as cross-flow to allow the membrane to continually clean itself. As some of the fluid passes through the membrane the rest continues downstream, sweeping the rejected species away from the membrane. The process of reverse osmosis requires a driving force to push the fluid through the membrane, and the most common force is pressure from a pump. The higher the pressure, the larger the driving forces. As the concentration of the fluid being rejected increases, the driving force required to continue concentrating the fluid increases. This pressure must exceed the osmotic pressure of the feed solution.

Siddiqui¹⁴ performed several RO experiments to evaluate its application for removing dissolved solids from the produced water and proved RO as the best and the most efficient technique for this particular application. Though Siddiqui¹⁴'s work discusses economical analysis of RO, it does not discuss modeling and up-scaling of RO for field scale application.

In this thesis, RO experiments were performed to duplicate Siddiqui¹⁴'s results and based on experimental data an empirical model is developed. The modeling and simulation of RO is discussed in later sections.

3.2 RO terminologies

Figure 3.1 shows a schematic of spiral wound RO membrane. The feed is passed through the membrane via feed spacer with cross-flow configuration. Only pure water present in the feed can pass through the semi permeable membrane leaving concentrated or salty water behind which eventually is collected as concentrate. Permeate is collected at the end of the perforated product line passes through the membrane. The transport of pure water from feed side to permeate side depends on the trans-membrane pressure across the RO unit, the feed flow rate and area of the membrane. To reduce the dimensionality of the RO designing problem we can define flux as the ratio of flow to the area.

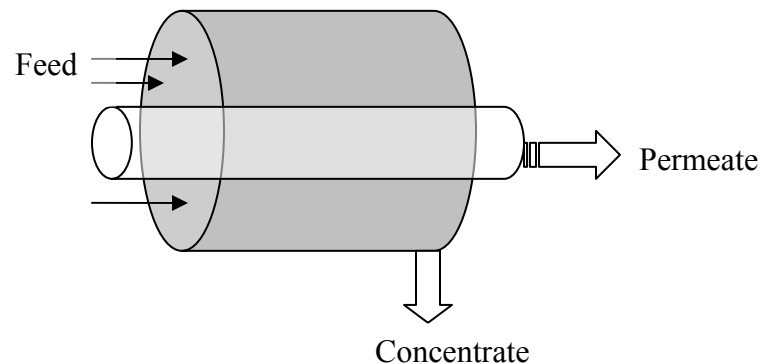


Fig. 3.1 – Schematic of spiral wound RO membrane in operations.

Trans-membrane pressure:

It is defined as the average pressure applied across the membrane minus the pressure on the permeate side.

$$\Delta P = \frac{P_i + P_o}{2} - P_p \dots\dots\dots(3.1)$$

where,

P_i = pressure at the feed inlet side, psi

P_o = pressure at the concentrate outlet side, psi

P_p = pressure at the permeate outlet side, psi

Permeate recovery:

$$\text{Permeate recovery} = \text{permeate flow rate/feed flow rate} \dots\dots\dots(3.2)$$

Salt rejection:

Salt rejection represents the percentage of salt that can be removed from the feed.

$$\text{Salt rejection} = 1 - C_{perm}/C_{tds} \dots\dots\dots(3.3)$$

where,

C_{perm} = salt concentration in permeate, ppm

C_{tds} = average salt concentration in feed, ppm

Higher salt rejection and higher permeate recovery represents better purification of water using RO membrane. Optimum trans-membrane pressure should be determined to perform economic RO operations.

3.3 Experimental setup

A standard commercial 4X40 membrane (4 inch Diameter and 40 inch Length) was used for the experiments with produced water having TDS ranging from 10000-40000 ppm. The surface area provided by spiral membrane is 70 ft². Temperature has an effect on the trans-membrane pressure to be applied across the RO membrane. As the temperature increases the osmotic pressure increases, which requires higher trans-membrane pressure to get desired salt removal keeping all the other parameters

unchanged. Also as the temperature increases the viscosity decreases, which somewhat lowers the demand of trans-membrane pressure. So there is an offsetting effect of increase in temperature. In our experiments we kept the temperature constant at 35⁰C

The performance of the RO unit with a particular type of membrane, determined in terms of permeate recovery fraction, permeate flux, permeate concentration and salt rejection depend on the concentration (salinity) of the feed, feed flow rate through the RO unit and the applied trans-membrane pressure. Figure 3.2 shows a RO unit that was utilized to perform the experiments.

The feed was prepared using NaCl-water solution. The osmotic pressure of NaCl is higher than that is of various salts those may present in the produced water. The trans-membrane pressure required to remove NaCl salt from water would be higher that that is required in the case of other salts. For example if a trans-membrane pressure of 800 psi removes 90% NaCl salt from water then it would remove more than 90% of other salts such as barium, calcium salts etc. The result of the experiments performed with NaCl-water solution conservatively determines range of operating parameters.

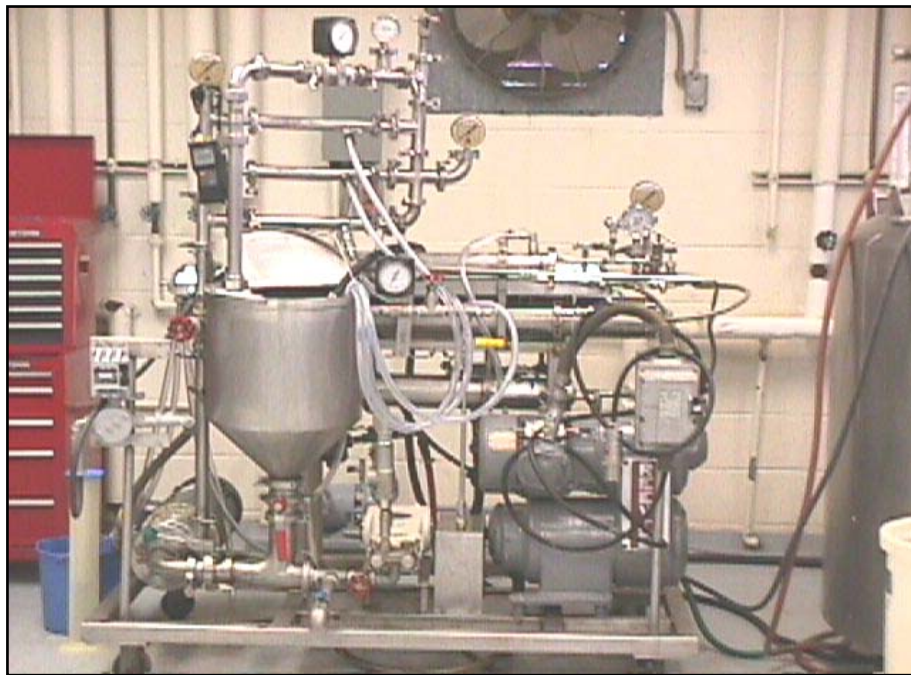


Fig. 3.2 – Laboratory unit to perform pilot scale RO operations.

3.4 Data acquisition and presentation

First the experiments were performed with pure water as feed to determine properties of membrane. If the clean water flux through the RO membrane is competitive, the membrane should be further investigated with salty water. Flux is defined as the ratio of flow rate to the membrane surface area. The content of TDS in each sample was measured by conductivity meter. The RO membrane was tested with feed having salt concentration upto 10000-40000 ppm.

The following parameters were measured at regular time interval,

- Trans-membrane pressure
- Feed flow rate
- Permeate flow rate
- Concentrate flow rate
- Feed concentration
- Permeate concentration
- Salt content in concentrate side

These measurements provided a definite tool for modeling transient RO filtration performance.

CHAPTER IV RESULTS AND DISCUSSION

4.1 Packed bed adsorption

The study of packed bed adsorption is accomplished by analyzing breakthrough behavior of packed bed. The breakthrough curve is a plot of outlet concentration vs. operation time. It can also be plotted as the ratio of outlet concentration to the inlet concentration vs. operation time. The adsorption is a two stage process.

Stage I: Diffusion of solute from bulk fluid phase to the surface of adsorbent particle. It is controlled by molecular diffusion. In most cases resistance to molecular diffusion is negligible.

Stage II: Adsorption or uptake of solute within the pore structure of adsorbent. It is controlled by surface diffusion or pore diffusion or combination of both.

The sharpness of the breakthrough curve near the breakthrough region represents adsorption kinetics. A sharper breakthrough curve indicates negligible resistance to the uptake or adsorption of solute in the adsorbent.

The adsorption rate is affected by size of adsorbent particle and feed concentration in isothermal operation. The adsorption capacity is affected by surface area of adsorbent, porosity of adsorbent particle and packed bed, solubility and type of solute in feed and EBCT.

To accomplish comprehensive analysis of oil adsorption by organoclay, the effect of the above parameters on adsorption capacity and breakthrough curve was observed. Loading capacity or adsorption capacity of packed bed can be calculated by performing material balance over the experiment run time until the breakthrough is achieved.

4.1.1 Effect of contact time

As the contact time between oil in feed and the organoclay particles increases, more amount of oil gets adsorbed within the pore structure of organoclay. Table 4.1 indicates that for experiments with approximately same concentration of kerosene in water, adsorption capacity for the experiment with longer EBCT was approximately 15%

more. The EBCT used in experiment A was approximately 3.5 times higher than EBCT used in experiment B.

It is interesting to observe the breakthrough curve for both experiments as it gives a hint about adsorption kinetics. Figure 4.1 shows that at early times the outlet concentrations for experiment B are higher than that of experiment A. For lower EBCT the organoclay particles require more time to get wetted. This type of concentration behavior indicates lower adsorption rate at early times when particles are in process of getting wetted with the oil present in feed. Once, the particles are wetted they respond more quickly and adsorption rate gets higher at large times. We soaked the column for more than 24 hrs before operation. As it can be seen from the figure that the breakthrough sharpness pattern is very much similar, this indicates minor effect of velocity of fluid (inverse of EBCT) on the adsorption kinetics at higher concentrations. This phenomena is important particularly in modeling point of view as the conclusion can be drawn based upon this behavior that at early times pore diffusion controls the adsorption and at large times film diffusion or combination of diffusions controls the adsorption.

TABLE 4.1 – Experiments with same feed concentration, particle size but different EBCT.

Experiment	A	B
Weight of organoclay packed, gm	25.00	20.00
Length of organoclay bed, cm	9.20	7.60
Volume of organoclay bed, cm ³	39.04	32.25
Porosity of packed bed	0.38	0.38
Feed Concentration, ppm	≈ 7000	≈ 7000
Average particle diameter, mm	0.95	0.95
Breakthrough time, min	275	212
EBCT, min	7.58	2.92
Average flow rate, ml/min	5.16	11.04
Adsorption capacity, gm oil / gm of organoclay	0.85	0.73

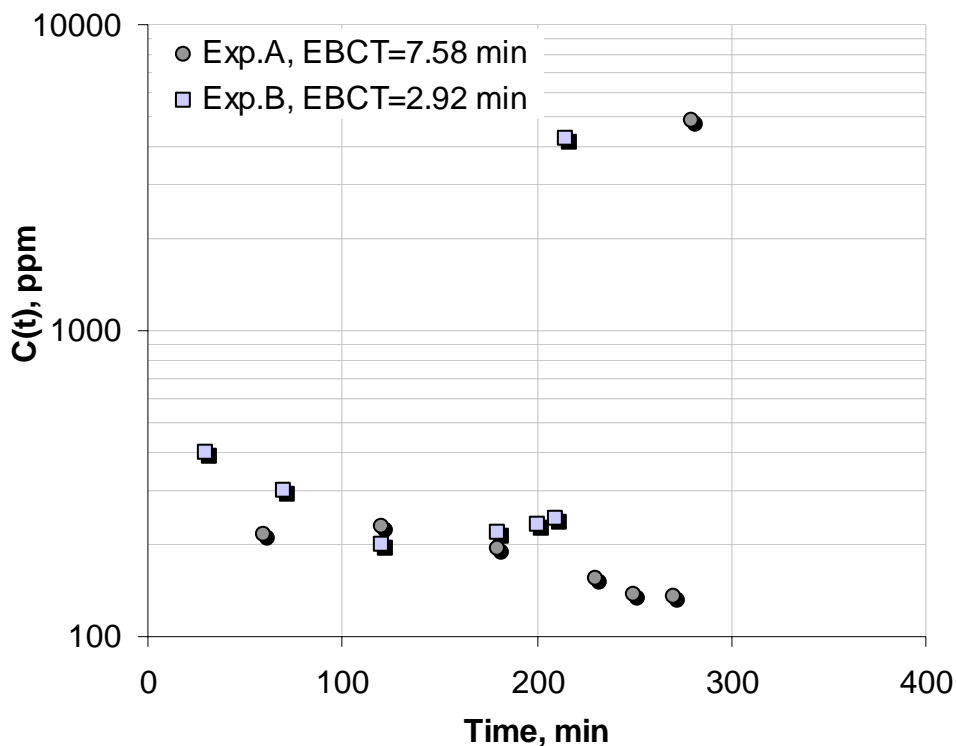


Fig. 4.1 – Comparison of breakthrough curve for experiments with different EBCT.

In either case, more than 90% of removal of oil is observed even with lesser EBCT and higher feed concentration.

4.1.2 Effect of size of organoclay particle

Smaller particle sizes provide larger contact area available for adsorption and consequently higher adsorption rate. Also it would be interesting to observe effect of particle size reduction on adsorption capacity. The particle size should be small but if the particles are in powdered form the porous structure of the particle would no longer be suitable for adsorption, also the pressure drop would increase and clogging may occur.

Table 4.2 shows parameters and results from two experiments with different particle size. The results have a combined effect of different particle size and different concentrations. The EBCT is approximately the same in both cases. The adsorption kinetics is much higher with smaller particle size. In this case a sharper concentration front was observed by noticing color change in a transparent column packed with organoclay. Figure 4.2 shows the concentration front pattern for both experiments and

Figure 4.3 shows the breakthrough curves. The decrement in adsorption capacity can be reasoned as a combined effect of increment in feed concentration and up to some extent higher particle size.

TABLE 4.2 – Experiments with different feed concentration and particle sizes.

Experiment	C	A
Weight of organoclay packed, gm	25.00	25.00
Length of organoclay bed, cm	9.20	9.20
Volume of organoclay bed, cm ³	39.04	39.04
Porosity of packed bed	0.38	0.38
Feed concentration, ppm	≈13600	≈ 7000
Average particle diameter, mm	1.60	0.95
Breakthrough time, min	210	275
EBCT, min	8.16	7.48
Average flow rate, ml/min	4.74	5.16
Adsorption capacity, gm oil / gm of organoclay	0.50	0.83

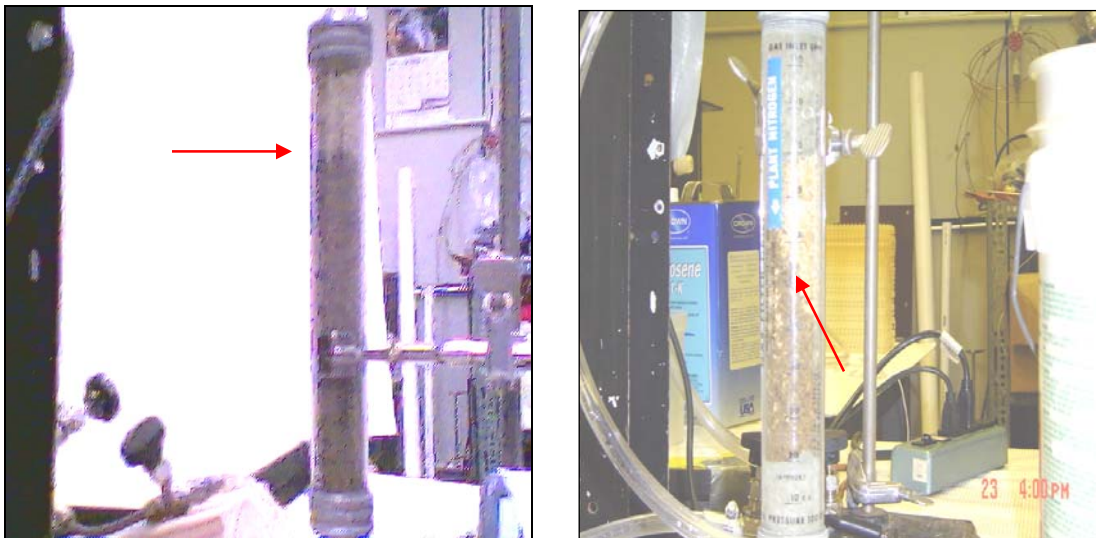


Fig. 4.2 – Concentration front is sharper with reduced particle size.

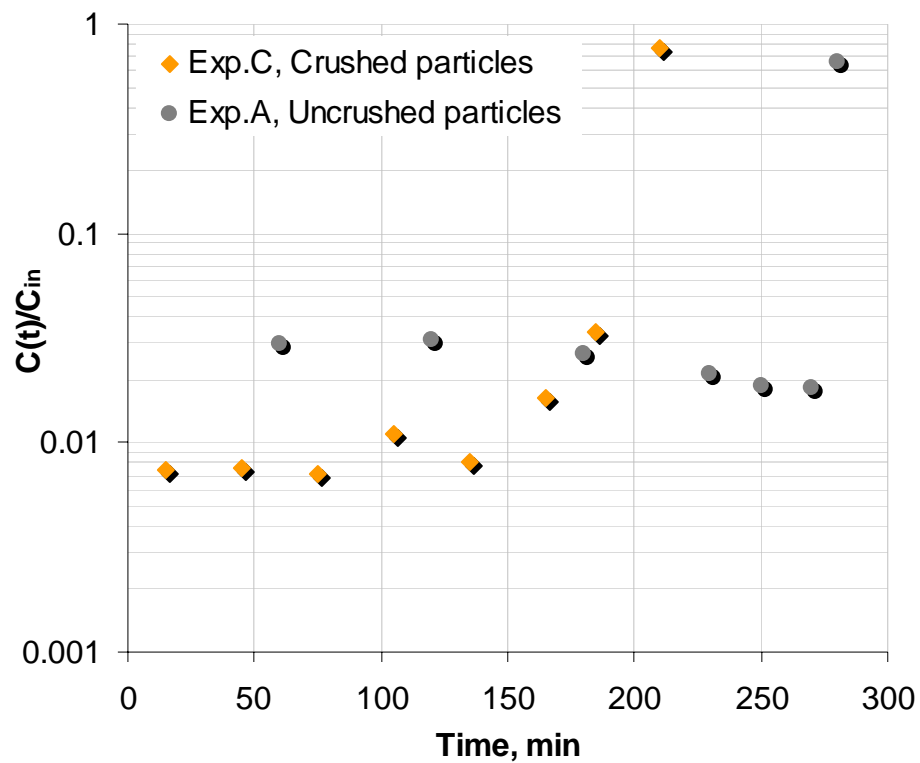


Fig. 4.3 – Comparison of breakthrough behavior for experiments with different size of organoclay particles.

4.1.3 Effect of feed concentration

Table 4.3 shows that for two experiments, experiment D and experiment E all the parameters but feed concentration are approximately same. The lower adsorption capacity observed for experiment D indicates the reduction in oil removal performance as the feed concentration decreases. However, for both experiments the oil removal efficiency is more than 90%. Figure 4.4 show that the breakthrough curve for both experiments follows a similar pattern. Feed concentration may have slight effect on adsorption rate. However, type of oil in feed has more significant effect on adsorption performance as discussed in a later section.

Table 4.3 – Experiments with different feed concentrations and approximately same EBCT.

Experiment	D	E
Weight of organoclay packed, gm	65.00	65.00
Length of organoclay bed, cm	22.00	22.00
Volume of organoclay bed, cm ³	93.36	93.36
Porosity of packed bed	0.38	0.38
Feed concentration, ppm	≈785	≈5000
Average particle diameter, mm	0.95	0.95
Breakthrough time, min	795	220
EBCT, min	1.85	2.09
Average flow rate, ml/min	50.99	44.48
Adsorption capacity, gm oil / gm of organoclay	0.51	0.69

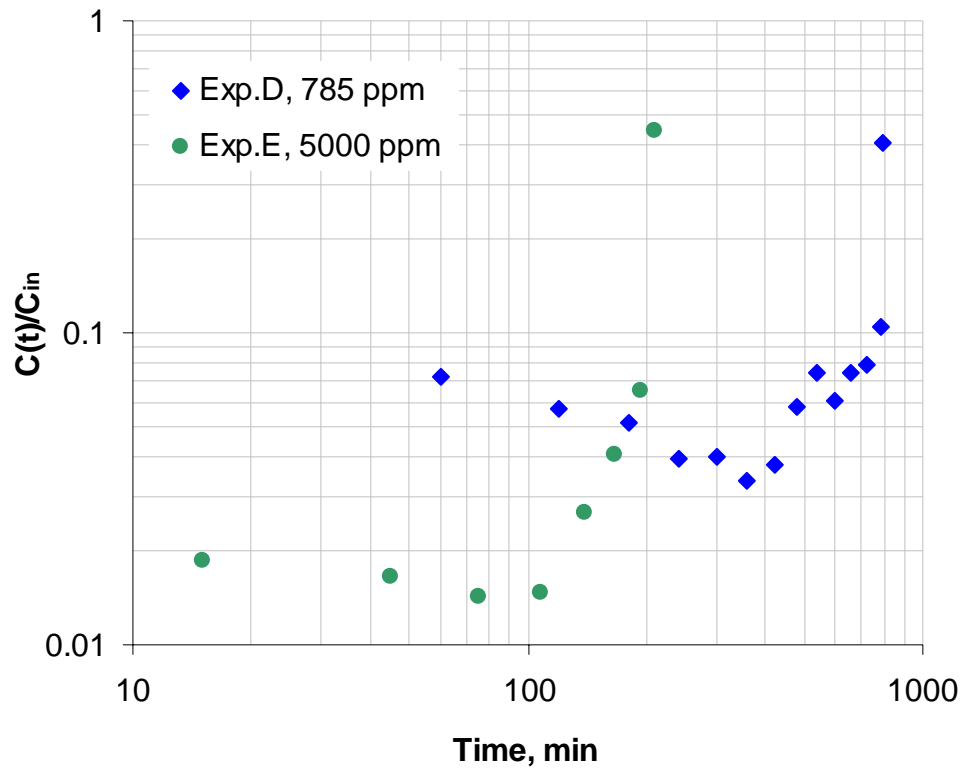


Fig. 4.4 – Comparison of breakthrough behavior for experiments with different feed concentrations.

Table 4.4 shows results obtained for an experiment with produced water as feed. The inlet is oil field produced water having TOC of approximately 59 ppm. The EBCT of 6 min is used to accomplish oil removal. The results indicate approximately 80% oil removal by packed bed adsorption operation.

Table 4.4 – Experimental results with produced water as feed. The column had not received the breakthrough (sharp increase in concentration is not observed).

Time Min	Outlet Concentration ppm
20	12.90
45	11.64
60	13.20
120	13.00
160	12.26
250	13.12

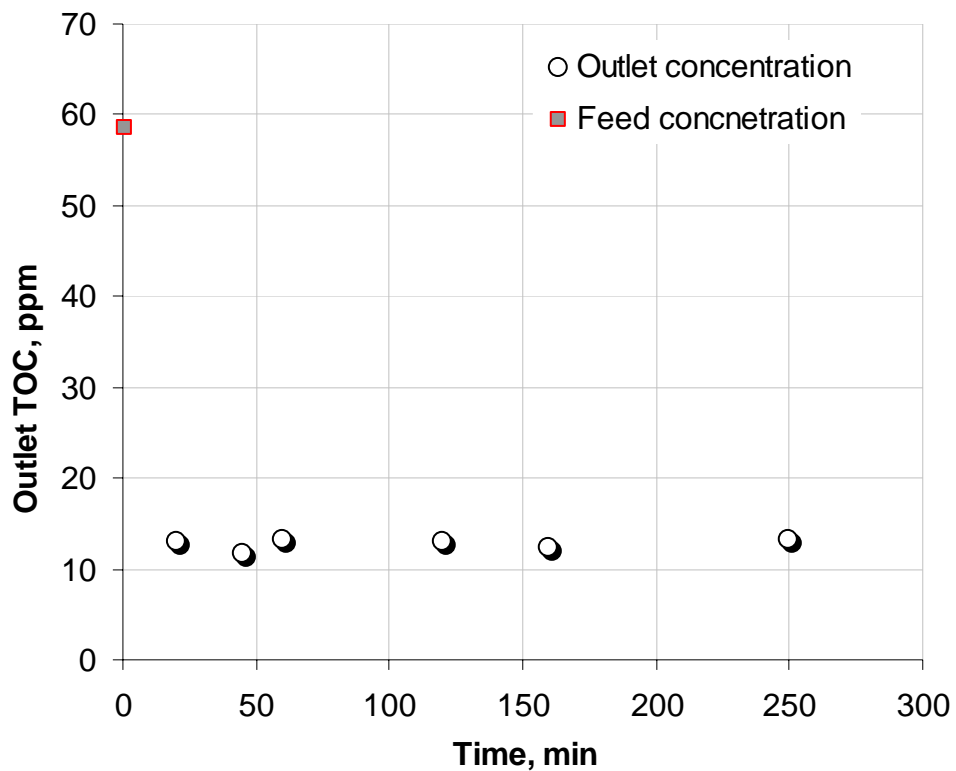


Fig. 4.5 – Results for an experiment with produced water as feed.

Figure 4.5 represents data for the experiment that has not yet achieved the breakthrough. Obviously, as EBCT increases the percentage of adsorption would also increase as discussed earlier. The underperformance of the packed bed can be justified by the fact that the produced water contains trace amount of suspended solids, salts, microorganisms and other impurities. Alternately, using packed bed adsorption columns in series facilitates lesser EBCT or higher throughput operation. The outlet from first packed bed adsorption column can be used as feed for the second column. The number of columns to be configured in series depends on feed concentration and desired outlet concentrations.

4.1.4 Effect of type of oils

Table 4.5 shows the comparison of experimental parameters and results for experiments with kerosene-water emulsions and crude oil-water emulsions. Experiment F is for a crude oil-water emulsion while experiment G is for a kerosene-water emulsion is used as feed.

TABLE 4.5 – Experimental parameters for experiments with different types of oil present in feed.

Experiment	F	G
Weight of organoclay packed, gm	30.00	20.00
Length of organoclay bed, cm	11.30	7.5
Volume of organoclay bed, cm ³	59.41	31.83
Porosity of packed bed	0.40	0.38
Feed concentration, ppm	1650	8495
Average particle diameter, mm	0.95	0.95
Breakthrough time, min	1330	155
EBCT, min	6.20	3
Average flow rate, ml/min	9.80	10.55
Adsorption capacity, gm oil / gm of organoclay	0.55	0.71
Type of oil content in feed	crude oil	kerosene

Total experimental run time is the time at which the column achieved breakthrough and was observed during experiment. As shown in Figure 4.6 the breakthrough curve is distended in the case of crude oil-water emulsion even at higher EBCT. The x-axis is a dimensionless time representing the ratio of sampling time to the total experimental run time.

It can be concluded that the presence of heavier and impure hydrocarbons tend to lower the adsorption rate, oil removal efficiency and loading capacity.

On the basis of these results it can be recommended to operate the column at higher EBCT with produced water as it contains impurities and heavier hydrocarbons.

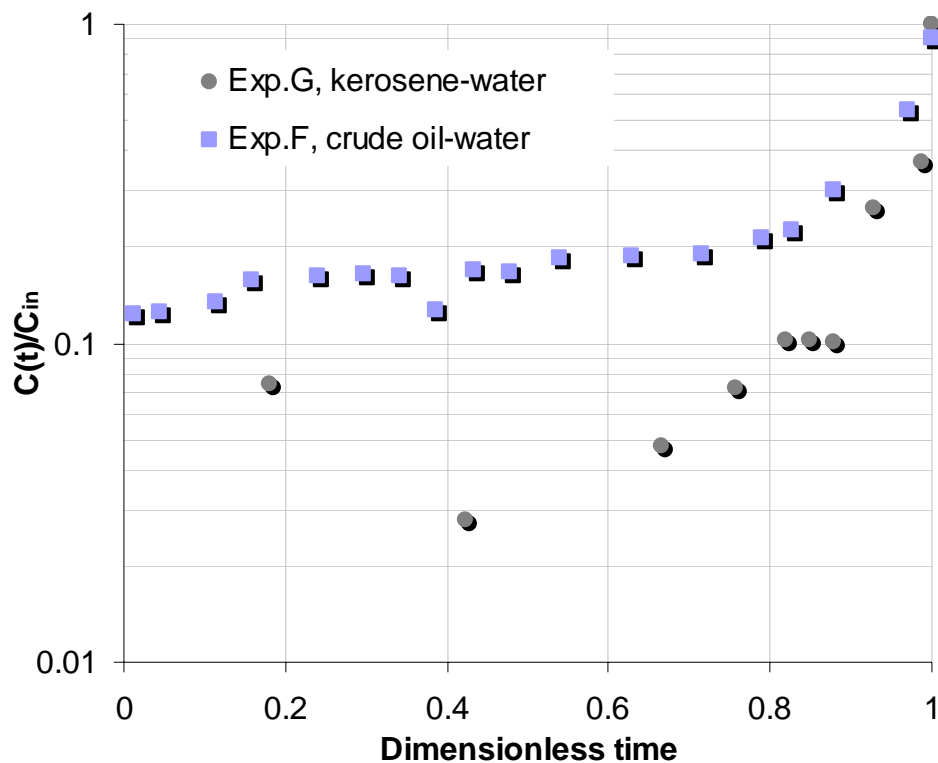


Fig. 4.6 – Breakthrough behavior for experiments with different types of oil in feed.

4.1.5 Change in organoclay structure

Figure 4.7 shows electron scan images of organoclay particles after and before adsorption operation. The images indicate that the organoclay particle gets destructed upon adsorption of oil and desorbs oil after getting saturated with oil.

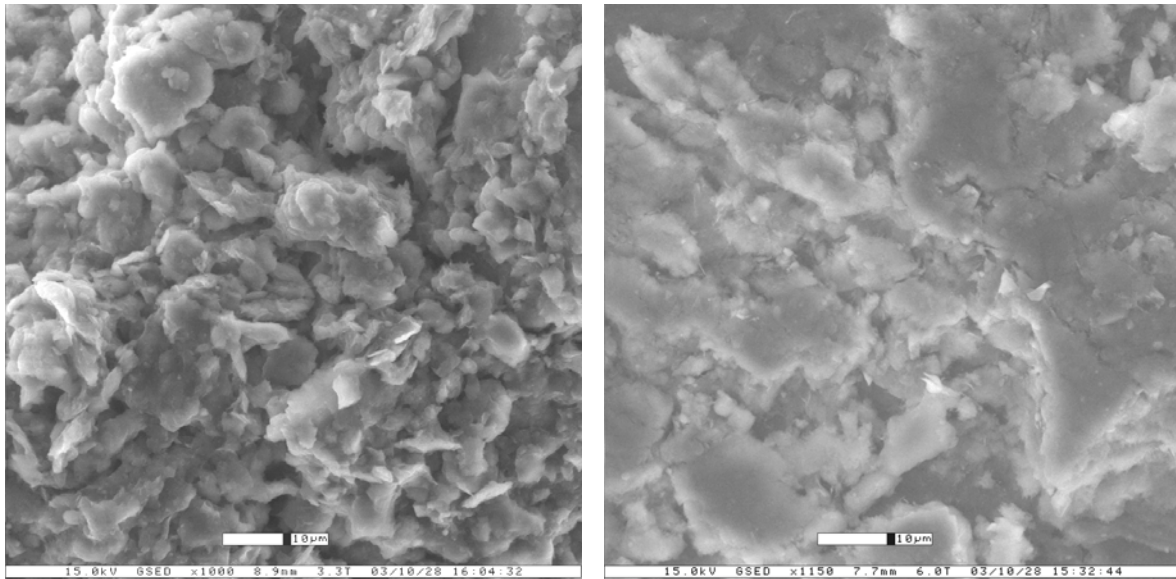


Fig. 4.7 – 1000X magnification of organoclay particle after adsorption (left hand side) and before adsorption (right hand side).

4.2 RO results and discussion

The performance of the RO unit with a particular type of membrane, determined in terms of permeate recovery fraction, permeate flux, permeate concentration and salt rejection depends on the concentration (salinity) of the feed, feed flow rate through the RO unit and the applied trans-membrane pressure.

4.2.1 Effects of various parameters on permeate recovery fraction

Figure 4.8 shows that the permeate flux decreases with increase in salinity of the feed. To obtain better performance at higher salinity a higher pressure should be applied across the membrane. In other words more energy is required. The optimization of the

RO parameters for a particular type of feed is the maximum permeate recovery at the minimum energy requirement.

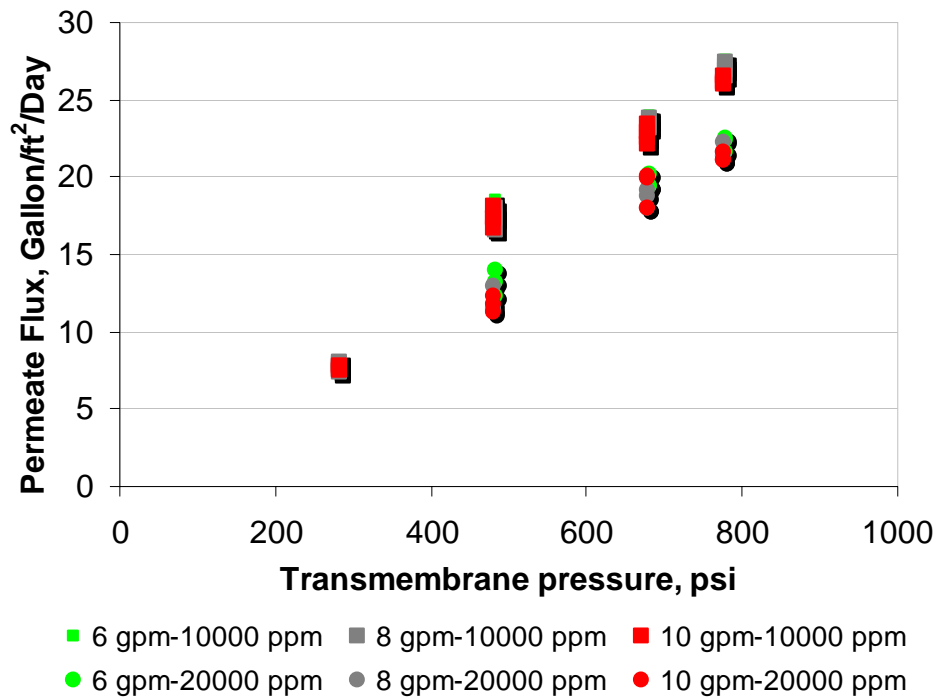


Fig. 4.8 – Effects of TDS content and flow rate of feed on permeate flux at various transmembrane pressure.

Figure 4.9 shows that the permeate recovery is higher for lower salinity feed for all the feed flow rates compared to higher salinity feed. Also for a particular salinity feed the permeate recovery increases as the feed flow rate decreases. At higher feed flow rate to get better performance more pressure should be applied across the membrane.

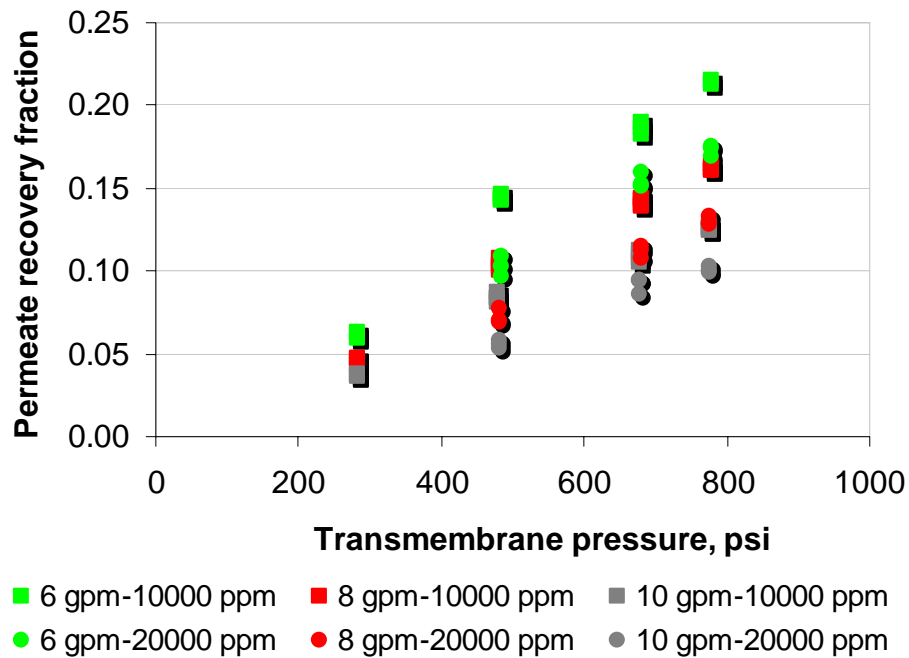


Fig. 4.9 – Effects of TDS content and flow rate of feed on permeate recovery fraction at various transmembrane pressure.

4.2.2 Effects of various parameters on salt removal

Figure 4.10 and Figure 4.11 shows the permeate concentration and the salt rejection respectively for different salinity feed at different flow rates and trans-membrane pressures.

For a particular salinity feed at a particular feed flow rate the salt rejection increases as the trans-membrane pressure increases up to a certain limit after which the salt rejection remains the same even if the trans membrane pressure increases. The experimental permeate concentration and salt rejection data can be expressed by a second order polynomial equation. Such models would be limited for only one set of feed salinity or trans-membrane pressure. The development of a general empirical model that incorporates all sets of feed salinity, trans-membrane pressure and flux is discussed in next chapter.

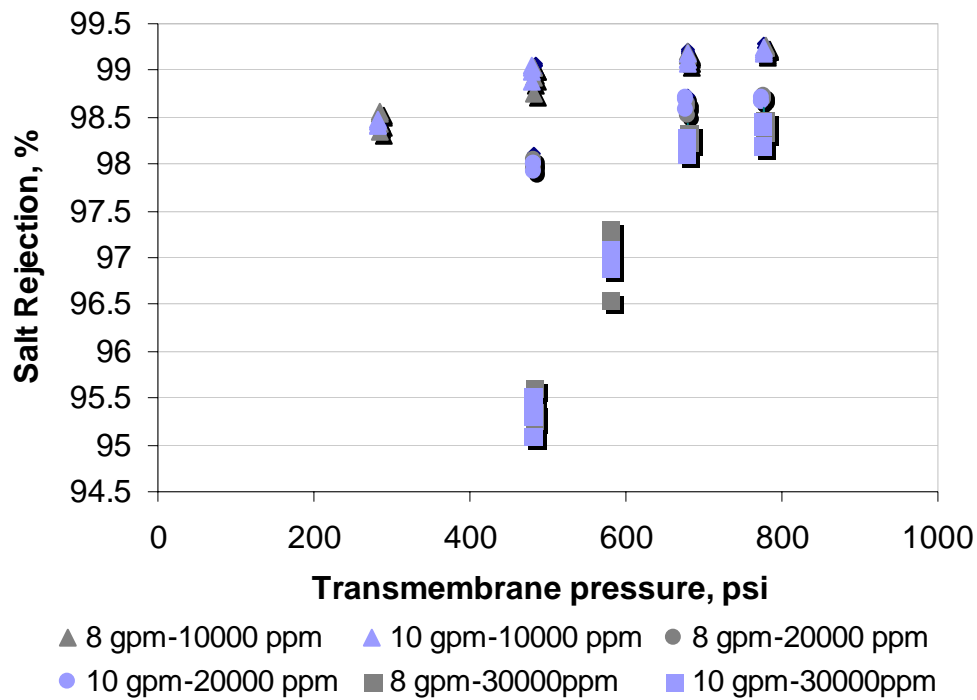


Fig. 4.10 – Effects of TDS content and flow rate of feed on salt rejection at various transmembrane pressure.

The permeate concentration can be obtained as low as 30 ppm with RO units for produced water up to 40000 ppm TDS. The configuration of two or more RO units in series can be helpful in further lowering permeate (outlet) concentration.

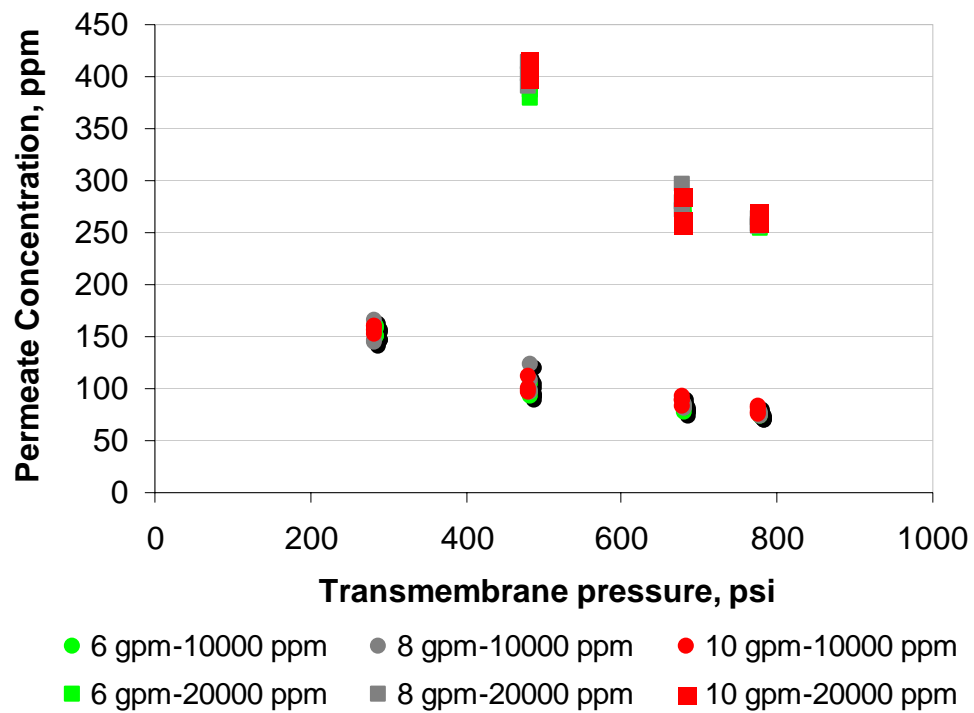


Fig. 4.11 – Effects of TDS content and flow rate of feed on permeate concentration at various transmembrane pressures.

CHAPTER V MODELING AND SIMULATION

5.1 Literature review

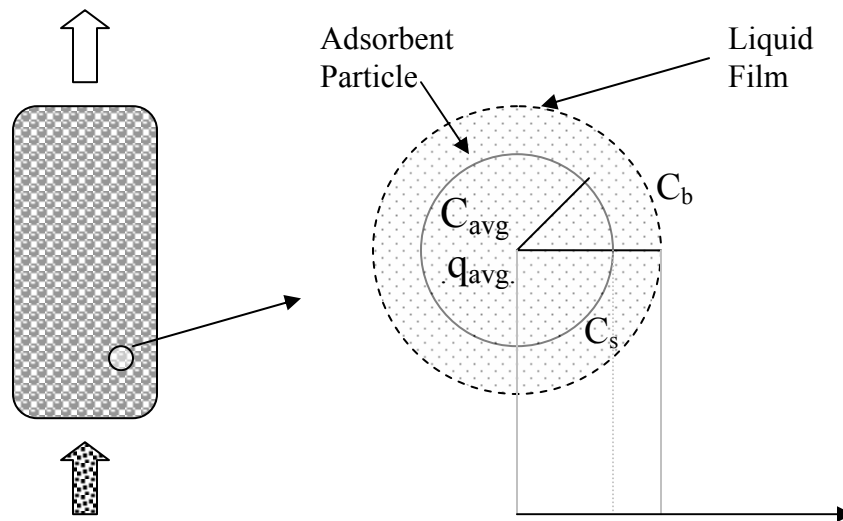


Fig. 5.1 – A schematic diagram of packed bed adsorption column.

The packed bed adsorption process can be described as a stage wise process (figure 5.1). The solute (oil particles in our case) present in the bulk liquid phase first migrates through to the surface of the adsorbent particle. Adsorbent particle can be visualized as having a stagnant liquid film surrounding it. Transfer of solute through this film can only occur by molecular diffusion. If it is a slow process then in most of the packed bed adsorption it is the process that controls adsorption rate. If it is faster then the concentration at the surface of the adsorbent particle, C_s , is same as the concentration in bulk phase, C_b . The resistance offered by liquid film is termed as external mass transfer resistance.

In next stage, the solute on the surface of the adsorbent particle migrate through the porous structure of the adsorbent particle and attach itself in a vacant site. The resistance offered by this step is termed as internal mass transfer resistance. The mass transfer of solute from the surface in to the adsorbent can be described by two mechanism, pore diffusion and surface diffusion. Surface diffusion is the diffusion of solute along the surface of the adsorbent particle and pore diffusion is the diffusion of solute within the pore structure of solid itself.

The rate at which the solute particle from bulk fluid phase is transported through and adsorbed on to the porous structure of adsorbent particle is referred as solute uptake rate or adsorption rate. Several uptake rate models and associated assumptions have been discussed in the literature¹⁷⁻²⁵.

The differential mass balance equations of solute in a packed bed can be written in the following form. To make the model simpler the axial dispersion is neglected, which is an excellent assumption in case of liquid flow through the packed bed.

$$\frac{\partial}{\partial z}(vc) + \frac{\partial c}{\partial t} + R_a = 0 \dots\dots\dots(5.1)$$

where, v = interstitial velocity of fluid within packed bed, cm/min or inch/min

z = length of packed bed, [L]¹

t = time of operation, [t]¹

c = concentration of solute in fluid phase changing with z and t , ppm

R_a = overall adsorption rate, [t]⁻¹

The adsorption rate equation comprises of one or more diffusion mechanism (molecular diffusion, surface diffusion and pore diffusion) with associated boundary conditions, incorporating equilibrium constraints to which the mass transfer rate or adsorption rate expression must reduce at sufficiently long times.

Analytical expressions for overall adsorption rate are available in literature. These expressions involve different types of diffusion control mechanism and isotherms.

For example, Crank's^{19, 20} solution considers adsorbent surface diffusion control mechanism and a linear isotherm. Thomas^{19, 20} developed a general model for Langmuir isotherm that can be applied to any order of driving force considering film diffusion or molecular diffusion mechanism. Glueckauf²⁰ developed LDF (Linear Driving Force) model for pore diffusion and surface diffusion that can be applied to any isotherm. Yao and Tien²² developed approximate uptake rate expression that can be solved using numerical techniques.

The mass balance differential equation and the linear isotherm and LDF rate law were solved by Beaton and Furnas²³. The expression is valid for the case of a uniform feed concentration to an initially solute-free adsorbent.

$$\frac{C}{C_{in}} = J(\xi, \tau) \dots\dots\dots(5.2)$$

where, ξ = a dimensionless distance

τ = a dimensionless time

$$\xi = Z(k / \epsilon v) \dots\dots\dots(5.3)$$

$$\tau = [k / K(1 - \epsilon)] [t - (Z / v)] \dots\dots\dots(5.4)$$

where, k = uptake rate kinetics, $[t]^{-1}$

K = linear isotherm constant, gm oil adsorbed/gm adsorbent/ppm

Z = length of packed bed, [L]

v = interstitial velocity of fluid in packed bed, $[L][t]^{-1}$

$$J(\xi, \tau) = 1 - \int_0^\xi \exp(-\xi - \tau) I_0(2\sqrt{\tau\xi}) \partial\xi \dots\dots\dots(5.5)$$

where, I_0 = hyperbolic zero-order Bessel function of first kind

Thomas^{19, 20} provided an expression for LDF rate law and Langmuir isotherm system using the J function.

Rice²⁰ proved that the J function provides exact solution for systems that can be characterized by a combination of molecular diffusion and solid-phase diffusion (surface diffusion or pore diffusion).

To solve a breakthrough behavior using analytical solution, through knowledge of driving force law, type of isotherm and controlling mechanism is required. In our case the experimental results do not provide sufficient information which is required to obtain analytical solution.

If the all of the mass transfer resistances are too small, breakthrough front approaches as a step change or a shock wave through the packed bed.

The experiments performed with kerosene-water emulsion as feed exhibited same breakthrough behavior. The resistances offered by adsorbent particles to the kerosene molecules were negligible. The step behavior of breakthrough curve can be modeled easily by solving for solute material balance.

An alternate approach is to develop an empirical model for uptake rate that can be applied to any isotherm form. The concept assumes that the transition of concentration from the initial to that of feed is due to mass transfer resistance only. The empirical model doesn't take into account the isotherm expression and constants, this facts makes its application limited to estimate rate constant and not the percentage of adsorption. The Wheeler – Robell^{19, 20} equation is an empirically corrected local equilibrium model. Like other simple models it neglects axial dispersion. Unlike most other equation-based models, however, it applies to any isotherm form. Finally, assuming first order adsorption the empirical equation can be written as,

$$C_d = \frac{c(z = L, t)}{c_{in}} = \exp \left[\frac{k_w}{Q} \left(\frac{C_{in} Q}{n \rho_b} t - A_{cs} L \right) \right] \dots \dots \dots (5.6)$$

In above equation if we choose outlet concentration equals to the inlet concentration and solve the equation for time the resultant time is referred as stoichiometric time.

$$t_s = \frac{A_{cs} L}{QC_{in} \rho_b n} \dots\dots\dots(5.7)$$

where, ρ_b = bulk density of packed bed, gm of adsorbent/volume of packed bed

Q = volumetric flow rate through the column, [L]³[t]⁻¹

A_{cs} = cross-sectional area of empty bed, [L]²

k_w = adsorption rate coefficient, [t]⁻¹

n = adsorption capacity or loading capacity, gm oil/gm of adsorbent

L = length of the packed column, [L]

The values of adjustable parameters k_w and n depend on operating parameters such as feed concentration, particle size, column length to diameter ratio and amount of adsorbent being used.

To determine these parameters, the breakthrough data for each experiment is fitted to above equation using non-linear regression code in Mathematica. It utilizes Levenberg-Marquardt algorithm. Figure 5.2 shows an example of fitting of empirical model to the experimental data obtained for the experiment with crude oil in water (experiment G). The adjusting parameters were obtained for each experiment. The empirical model fits well with the experimental results near breakthrough region. It matches the sharp breakthrough curve pattern at large times. However, the model fits poorly with experimental data at the beginning of the experiment and early times data because of the exponential nature of the model. The model is fair enough to estimate and analyze uptake or adsorption kinetics. The fitting model parameters were,

$$k_w = 0.66 \text{ min}^{-1}$$

$$n = 0.54 \text{ gm oil adsorbed/ gm of organoclay}$$

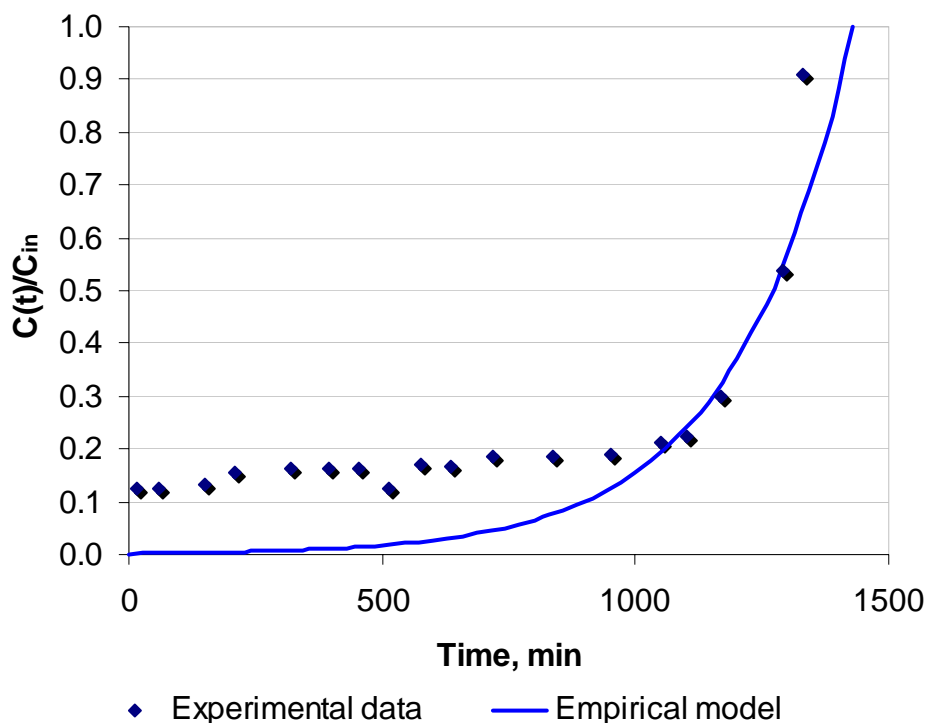


Fig. 5.2 – Fitting an empirical model to the breakthrough data for experiment G.

The use of analytical models and empirical models are limited because of lack of isotherm data and knowledge of uptake rate mechanism. In the next section, a hybrid approach to match breakthrough behavior is discussed.

5.2 A new approach for modeling of adsorption

The idea is to fit the data from the experiment in which the feed is crude oil and water mixture. Fitting the ratio of amount of oil adsorbed per unit of amount of oil charged at various times. The ratio of instantaneous amount of oil adsorbed to the instantaneous amount of oil inflow to the packed column exhibits a hyperbolic behavior with respect to time axis. The time axis is taken as the ratio of time to the stoichiometric time to make the time axis dimensionless. The expression for this approach would be,

$$\frac{W_{ads}}{W_{in}} = \frac{m_{ads}}{(1 + bD(t/t_{stoichiometric}))^{(1/b)}} \dots\dots\dots(5.8)$$

where, W_{ads} = instantaneous amount of oil adsorbed in packed bed, gm

W_{in} = instantaneous amount of oil flowing into the packed bed, gm

b, D = hyperbolic parameters depend on operating conditions

m_{ads} = coefficient of adsorption

Figure 5.3 shows a hyperbolic function fits to the data for experiments with crude oil in water.

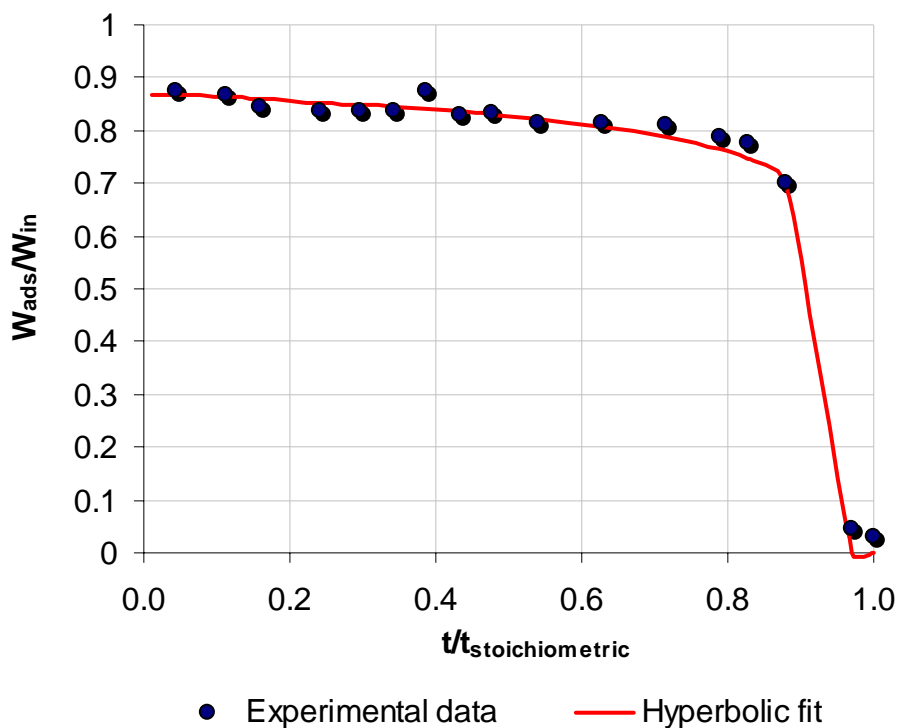


Fig. 5.3 – Fitting hyperbolic function to the experimental data of percentage of oil adsorbed with time.

The coefficient of adsorption can be found by plotting the cumulative amount of oil adsorbed vs. cumulative amount of oil charged. The coefficient of adsorption is different for different operation conditions and depends on EBCT, loading capacity and oil concentration in feed fluid stream. For each experiment the coefficient of adsorption can be evaluated by fitting a straight line to the experimental data.

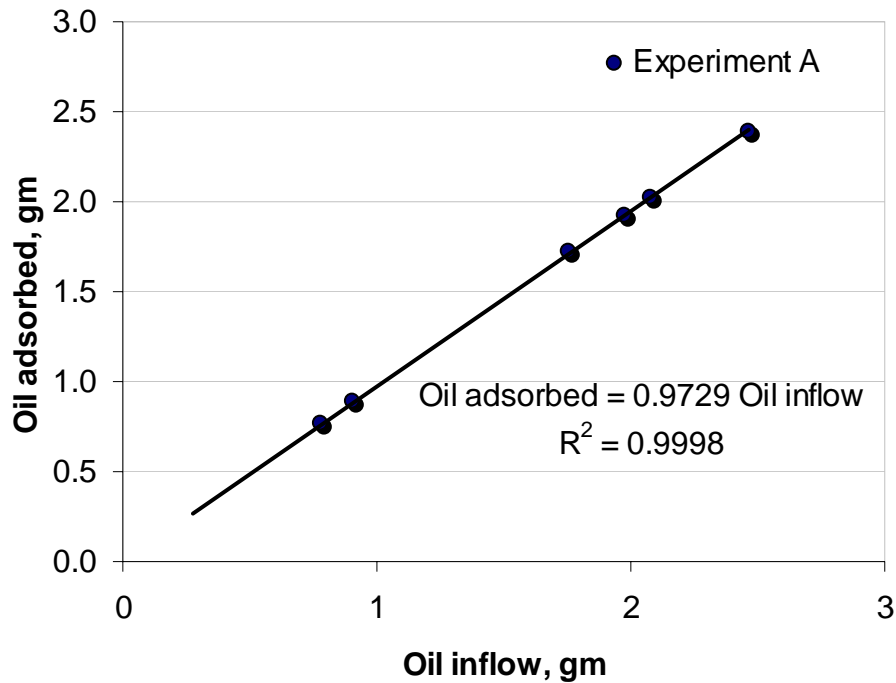


Fig. 5.4 – A straight line fit to the experimental data of oil adsorption vs. oil inflow.

For example, figure 5.4 shows a straight line fit for experiment A which was performed with kerosene in water. The slope also indicates the percentage of oil adsorbed by the adsorbent.

The adsorption coefficient is evaluated for each experiment. It is modeled by equation 5.9.

$$m_{ads} = K_{ads} \left(\frac{\log(EBCT(n))}{\log(C_{in})} \right) + c_1 \dots\dots\dots(5.9)$$

where, n = loading capacity, gm oil/gm adsorbent

m_{ads} = adsorption coefficient, gm oil adsorbed/gm oil inflow

C_{in} = oil concentration in inlet fluid stream, ppm

K_{ads} = slope of straight line

c_1 = intercept of straight line, gm oil/gm adsorbent

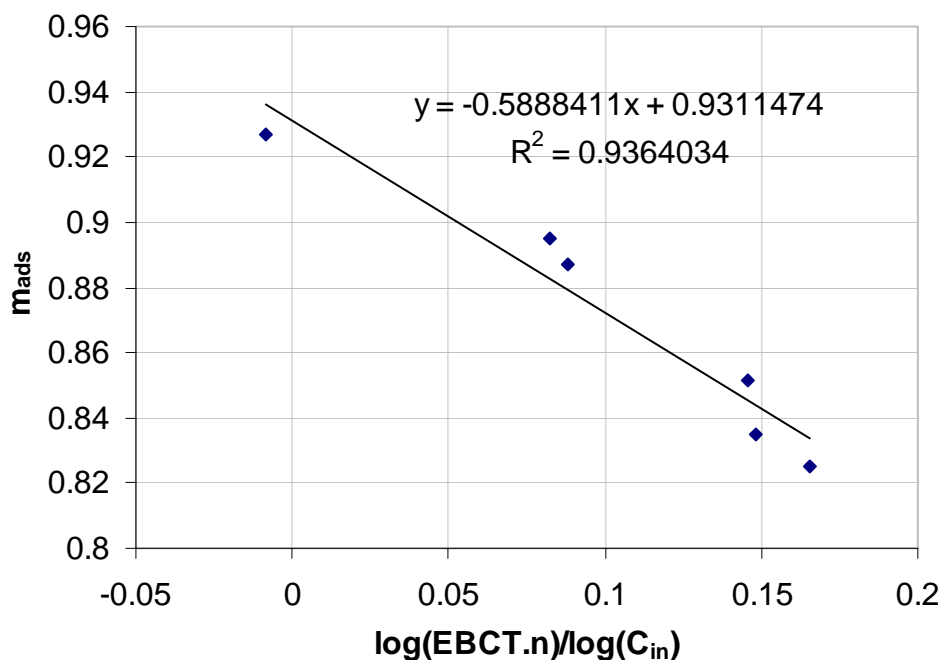


Fig. 5.5 – Linear fitting of an empirical model to estimate adsorption coefficient.

Figure 5.5 shows a straight line fit for above expression fitting six points.

The next step is to insert above expression in the oil material balance equation. The expression for calculating the amount of oil that is charged to the packed bed in gram is,

$$W_{in} = 10^{-6} Q C_{in} t \dots\dots\dots(5.10)$$

The amount of oil that can be adsorbed by the packed bed can be written by inserting hyperbolic function of time as discussed earlier.

$$W_{ads} = W_{in} \left(\frac{m_{ads}}{(1 + bD(t/t_{stoichiometric}))^{(1/b)}} \right) \dots\dots\dots(5.11)$$

Finally, the oil that can be not adsorbed by the packed bed and comes out from the packed bed can be written as,

$$W_{out} = W_{in} - W_{ads} \dots\dots\dots(5.12)$$

and

$$C_{out} = \frac{W_{out} 10^6}{Qt} \dots\dots\dots(5.13)$$

- where, W_{out} = oil out from the adsorption column, gm
- Q = flow through the packed bed, ml/min or GPM
- t = time of operation, min or hr

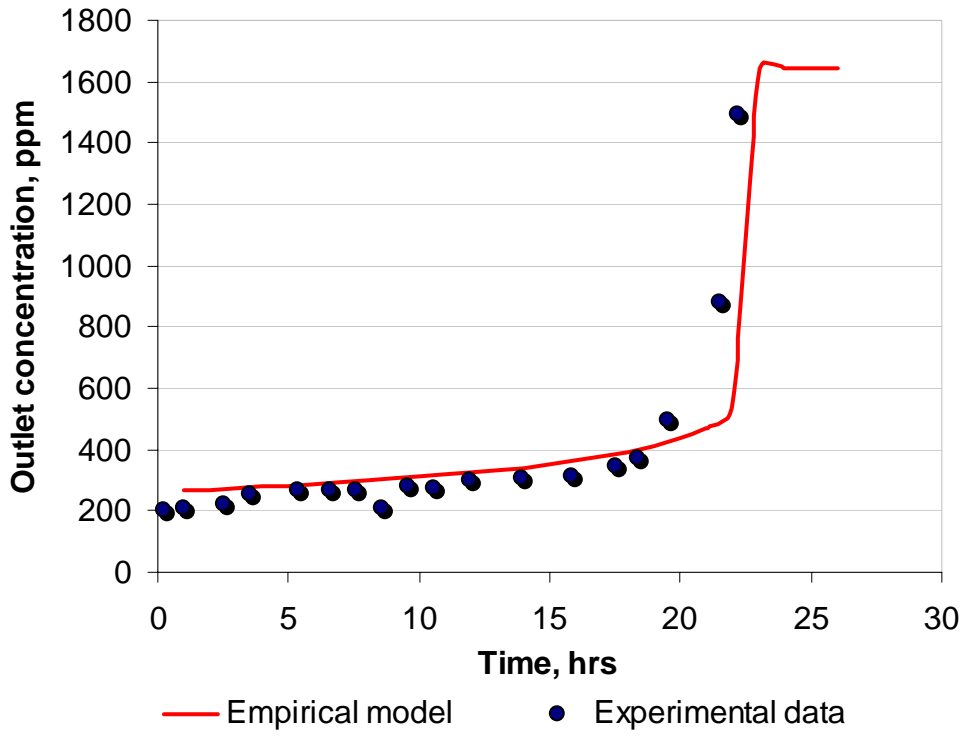


Fig. 5.6 – New empirical model fits the data for experiment G.

Figure 5.6 shows a match of empirical model with experimental data for experiment G that is experiment with crude oil-water emulsion. The limitation of this approach is that it can only be utilized for adsorption operation with organoclay PS12385.

The experiments with kerosene-water emulsion can be modeled with simple material balance. The other limitations of the proposed model are,

- Valid for EBCT range of 2-8 min
- Valid for up flow configuration
- Valid for feed stream containing crude oil
- Knowledge of loading or adsorption capacity is necessary which should be determined experimentally for specific oil removal application

The proposed model will be used for performing field case simulations in later section as crude oil-water emulsion would be a better representative of produced water from field.

5.3 Modeling of RO

The performance of a RO unit is analyzed by estimating permeate recovery and salt rejection. The permeate recovery and salt rejection depends on flow rate, cross sectional area of membrane, dissolved solid concentration in feed stream and trans membrane pressure applied across the membrane. The parameter estimation problem can be reduced by one dimension upon introduction of flux, which is defined as the ratio of flow to the cross sectional area of the membrane.

We developed empirical models by fitting over 500 data points. The model was selected by performing linear regression analysis for possible models. The best models to estimate permeate recovery and salt rejection were selected.

$$C_p = a_1 \left(\frac{P}{F_f} \right)^{a_2} + a_3 \left(\frac{C_{tds}}{P} \right)^{a_4} + a_5 \left(\frac{C_{tds}}{F_f} \right)^{a_6} \dots\dots\dots(5.14)$$

$$R_j = b_1 \left(\frac{P}{F_f} \right)^{b_2} + b_3 \left(\frac{C_{tds}}{P} \right)^{b_4} + b_5 \left(\frac{C_{tds}}{F_f} \right)^{b_6} \dots\dots\dots(5.15)$$

where, P = trans membrane pressure applied across the membrane, psi

F_f = feed flux across the membrane, GPM/ft²

C_{tds} = total dissolved salt concentration in feed stream, ppm

$a_1, a_2, a_3, a_4, a_5, a_6, b_1, b_2, b_3, b_4, b_5$ and b_6 = empirical constants

C_p = permeate recovery, %

R_j = salt rejection, %

$a_1 = 3.8444079558131$

$b_1 = 99.9901156315897$

$a_2 = 0.609914508930381$

$b_2 = -4.4974772258236E-03$

$a_3 = -0.02714266280317$

$b_3 = 9.3570231973E-06$

$a_4 = 1.04252671349594$

$b_4 = -1.2587309578386E-03$

$a_5 = -0.313312970859444$

$b_5 = 1.65746565923919$

$a_6 = 1.09629223446852$

$b_6 = 2.0710162623145$

Figure 5.7 verifies the accuracy of model for fitting the experimental permeate recovery data. Figure 5.8 shows predicted values of salt rejection using above model.

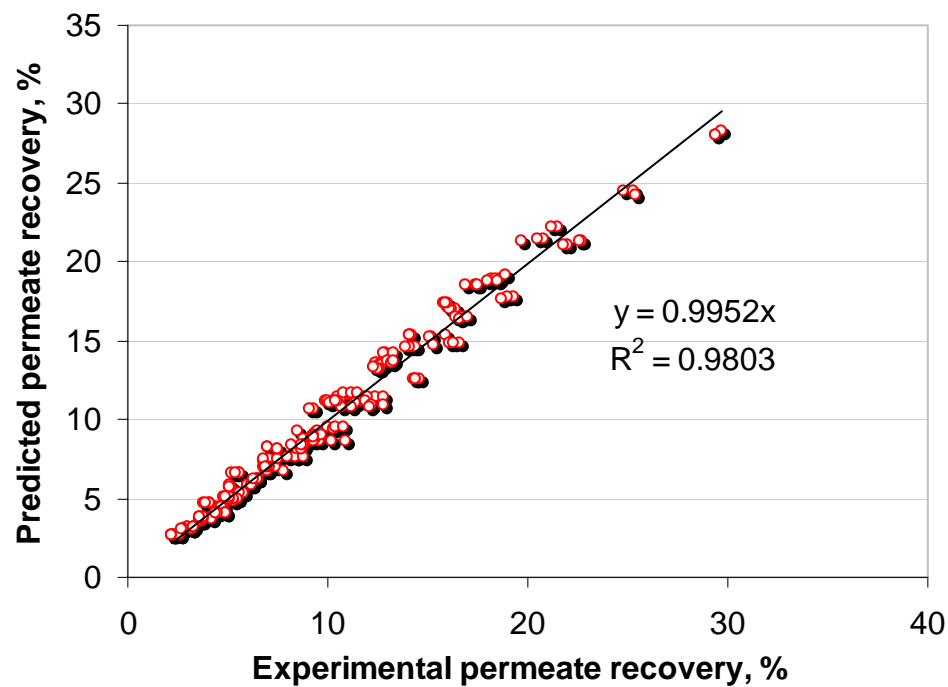


Fig. 5.7 – Model accurately fits the experimental permeate recovery data.

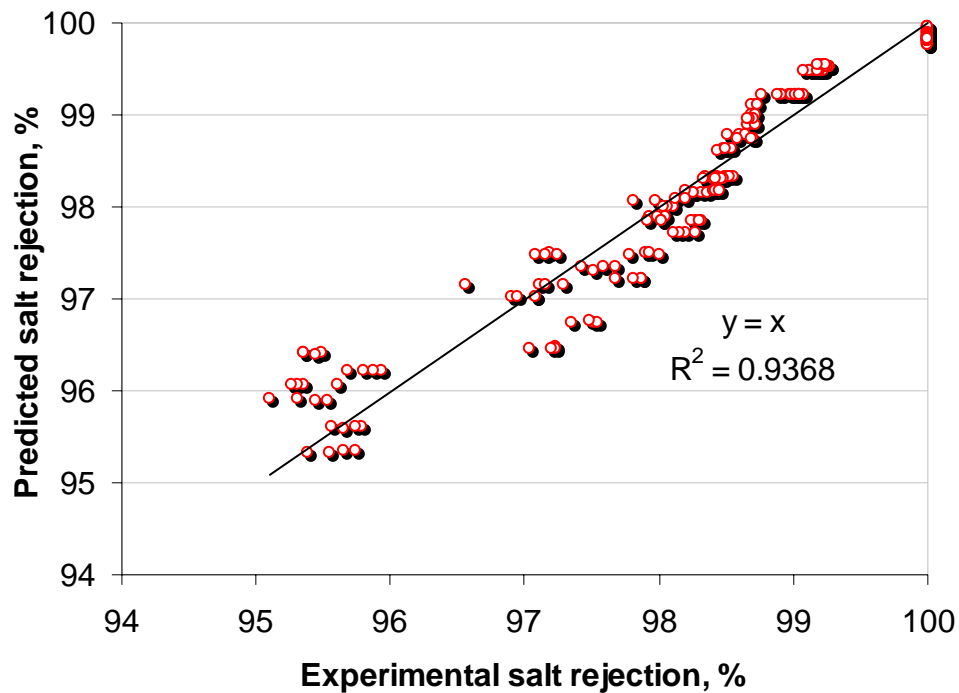


Fig. 5.8 – Model accurately predicts experimental salt rejection data.

The limitations of this model are,

- Valid for TDS concentration upto 40000 ppm
- Valid for trans membrane pressure of 200-1200 psi
- Valid for SWC-1-4040 membrane only
- Valid for flux ranges from 0.085 – 0.2 GPM/ft² which represents a flow range of 6 – 14 GPM for membrane surface area of 70 ft² and its multipliers

5.4 Case studies – Treatment of produced water

The empirical models discussed in the previous section can simulate the transient performance of packed bed adsorption and RO unit for removal of TOC and TDS from produced water. Patel et al.²⁶ suggested the use of integrated adsorption and RO system for produced water treatment and the range of operating parameters. The excessive amount of produced water can be used as a source of usable water by treating it to

remove hazardous oil (< 20 ppm) and salt contents (< 500 ppm). In this section the simulation results for the treatment of produced water from Powder River Basin area and West Texas Region are discussed. The processed water can be used as a source of fresh water for West Texas area after passing through the treatment system proposed in this work.

The produced water is first passed through a series of packed bed adsorption units to accomplish removal of oil from the produced water. The outlet of adsorption unit is then charged to RO units for TDS removal. The series configuration facilitates operation with lower EBCT and hence higher throughput. The schematic configuration of the treatment system is shown in Figure 5.9.

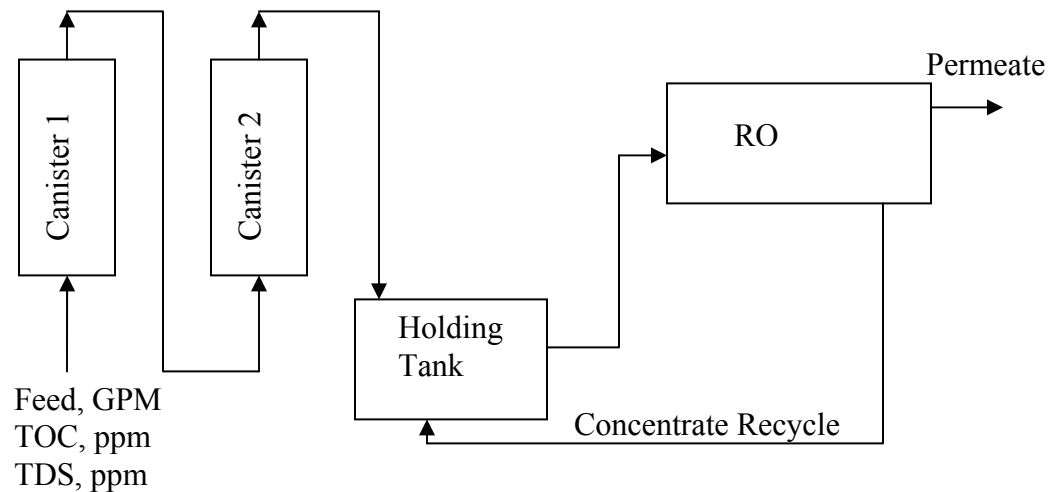


Fig. 5.9 – A schematic of sequence of operations for conversion of produced water into a fresh water source.

In some cases the throughput from the organoclay canisters unit get lower than 6 GPM. RO units should be operated on minimum of 6 GPM feed rate to avoid fouling of RO membrane and to achieve higher processing throughput. The solution to the problem of unequal throughput rate can be solved by placing a holding tank before RO unit. The outlet form the adsorption unit is charged into the holding tank till it accumulated enough

volume that can facilitate operation of RO unit at 6 GPM rate. The concentrate from the RO unit is recycled back to the holding tank and so in the feed stream to RO. The recycle ensures maximum removal of salt, the concentrate which is recycled into the holding tank increases the TDS amount in the holding tank and so in the feed stream to RO with time. Since permeate recovery and salt rejection depends on the TDS of feed stream, permeate throughput and TDS content would change with time.

We developed a simulator in Excel VBA to estimate transient results for this system. The adsorption is a continuous operation and RO is a batch operation.

Table 5.1 shows the list of parameters changing with time and the parameters doesn't change with time, which also are input parameters to the simulator.

TABLE 5.1 – List of dynamic parameters in produced water treatment simulator.

Input Parameters	Parameters changing with time
TOC and TDS in feed	Outlet TOC from both the canisters
Organocaly bed dimensions	Volume of the fluid inside the holding tank
EBCT	TDS content in holding tank, RO feed stream, permeate and concentrate
RO membrane cross sectional area	Volume of permeate, concentrate and recycle
Tran membrane pressure	Efficiency of the system

The simulator stops the run upon meeting one of the following constraints,

1. Permeate outlet concentration exceeds 500 ppm limit
2. Holding tank volume goes beyond its capacity or becomes less that it can no longer be able to feed RO unit
3. Average holding tank TDS content exceeds 40000 ppm
4. Recycling is no longer feasible

Figure 5.10 shows the configuration and specifications of treatment system and the summary of input parameters for the simulation of CBM produced water treatment. Figure 5.11 shows the performance of the adsorption canister unit. The inlet TOC content is 80 ppm. The selected dimensions of the canister unit provides an EBCT of 5 min for 1.3 GPM of throughput through the canister. Since, inlet to holding tank is the outlet from the last adsorption canister, it is continuously being filled. As soon as the holding tank is filled with 100 gallons of water, the RO batch would start. The RO batch runs until RO simulation stops. At the end of the simulation the concentrated volume to be discarded is 43.75 gallons in this case. A next RO batch starts again when the holding tank is filled with 100 gallons of water.

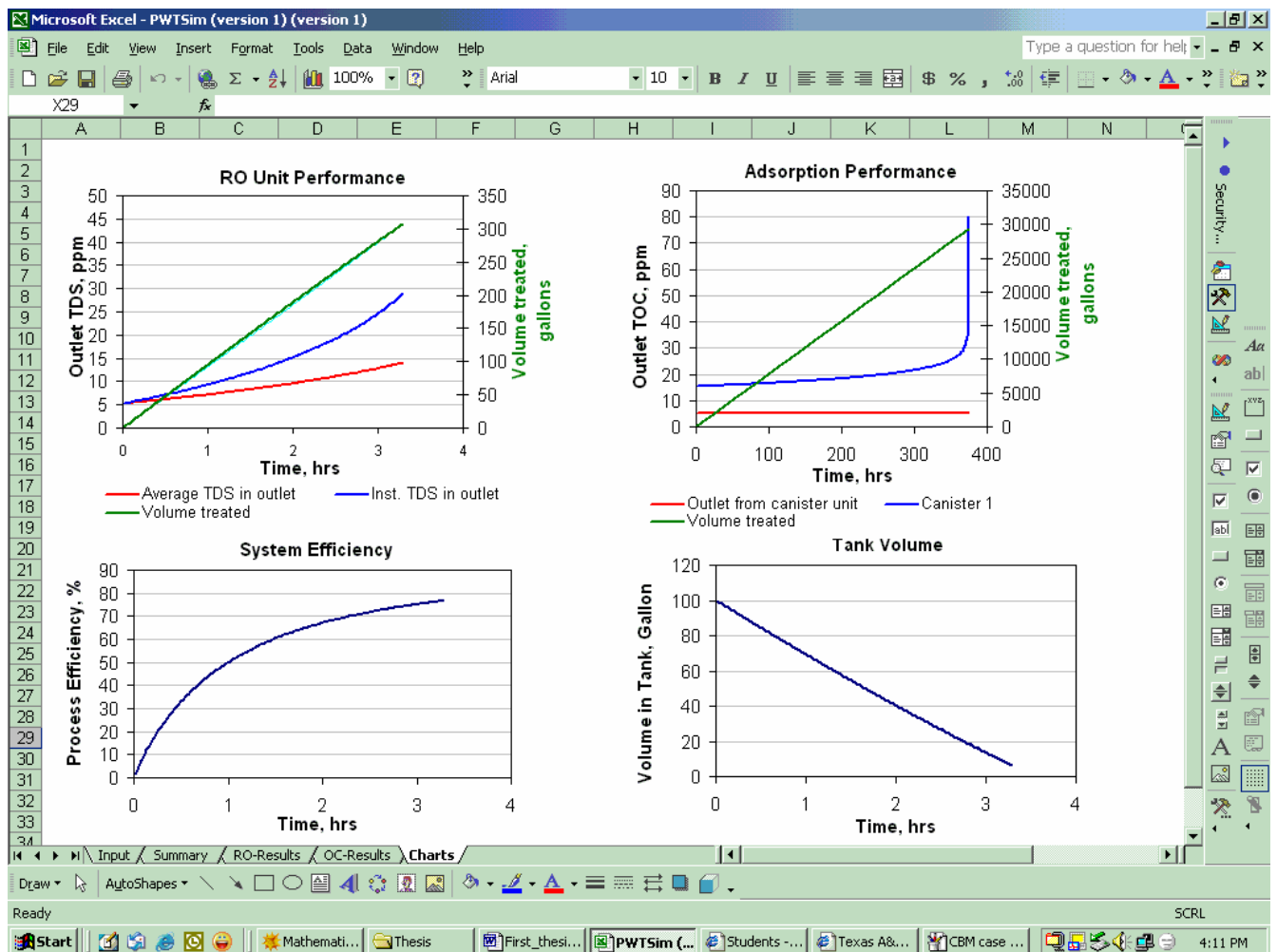


Fig. 5.11 – Simulation run showing TDS and TOC content in permeate stream or final outlet of produced water treatment system for CBM produced water treatment.

The system outlet has average TDS content of less than 20 ppm and TOC content of less than 5 ppm. The treated water meets the drinking water standards. However a minimum amount of minerals should be present in drinking water.

The tank became empty after 3 hrs and simulation stopped. Approximately 300 gallons of permeate was collected with an average TDS content of less than 20 ppm. The overall process efficiency was 80%. The process efficiency is defined as,

$$E = \frac{\int_0^{t_b} q_p dt}{(q_{oc} t_b) + HTV} \dots\dots\dots(5.16)$$

where, E = process efficiency or percentage of recovery, %

t_b = operation time for RO unit per batch, hrs

q_{oc} = continuous throughput of adsorption canister unit, GPM

HTV = initial volume of water in holding tank, gallons

In this case we obtained 80% process efficiency which means we could recover 80% of treated water and the remaining 20% volume is concentrated brine which can be discarded into the sea.

5.4.2 Case study 2 – West Texas produced water treatment

Consider a case of produced water from West Texas region. The produced water has average TDS content of 25000 ppm and TOC content of 100 ppm. Figure 5.12 shows the system configurations and specifications for the treatment of the produced water. Produced water flows through a series of three adsorption canister followed by a series of two RO units having different surface area.

UNIT INFORMATION						
	Total	Series	Parallel	Volume treated, gallons		
Canister	3	3	1	23568.983 till breakthrough		
RO	2	2	1	1317.3608 per batch		
OC CANISTER SPECIFICATIONS						
Bulk Density of Packed Bed, lbs/gal*			5.84			
Loading Capacity, gm Oil/gm Organoclay*			0.50			
Porosity of Packed Bed*			0.35			
Avg. Particle Size, mm			1.60			
Length of Canister, inch			32			
Length of Packed Bed, inch			30.00			
Diameter of Packed Bed, inch			8.00			
EBCT, min			5.00			
Volume of Canister, gal			6.52			
C.S. Area, ft ²			0.35			
Hydraulic Loading, gpm/ft ²			3.74			
Amount of Organoclay Packed, lbs			38.10			
Total Amount of Organoclay, lbs			0.00			
RO UNIT SPECIFICATIONS						
	Membrane area, sq.ft	Transmembrane pressure, psi	Min. flow rate, gpm	Operating rate, gpm	Recycle %	Volume discarded gallons
Primary	70	1200	5.9934	6	98	33.7728
Secondary	35	1200		6	98	
HOLDING TANK SPECIFICATIONS						
Holding tank volume, gal			1000			
Holding tank factor			2			
PRODUCED WATER QUALITY						
TOC, ppm			100			
TDS, ppm			20000			

Fig. 5.12 – Adsorption canister and RO unit specifications for West Texas produced water treatment case.

The total volume to be discarded is 33.77 gallons. The system has two RO units in parallel configuration. The first RO unit has surface area of 70 ft². The permeate from the first unit flows through the second RO unit. To maintain higher flux through second RO unit lower surface area is selected. Second RO unit has surface area of 35 ft². The process efficiency achieved with the system is 80%. Figure 5.13 shows the result of the produced water treatment.

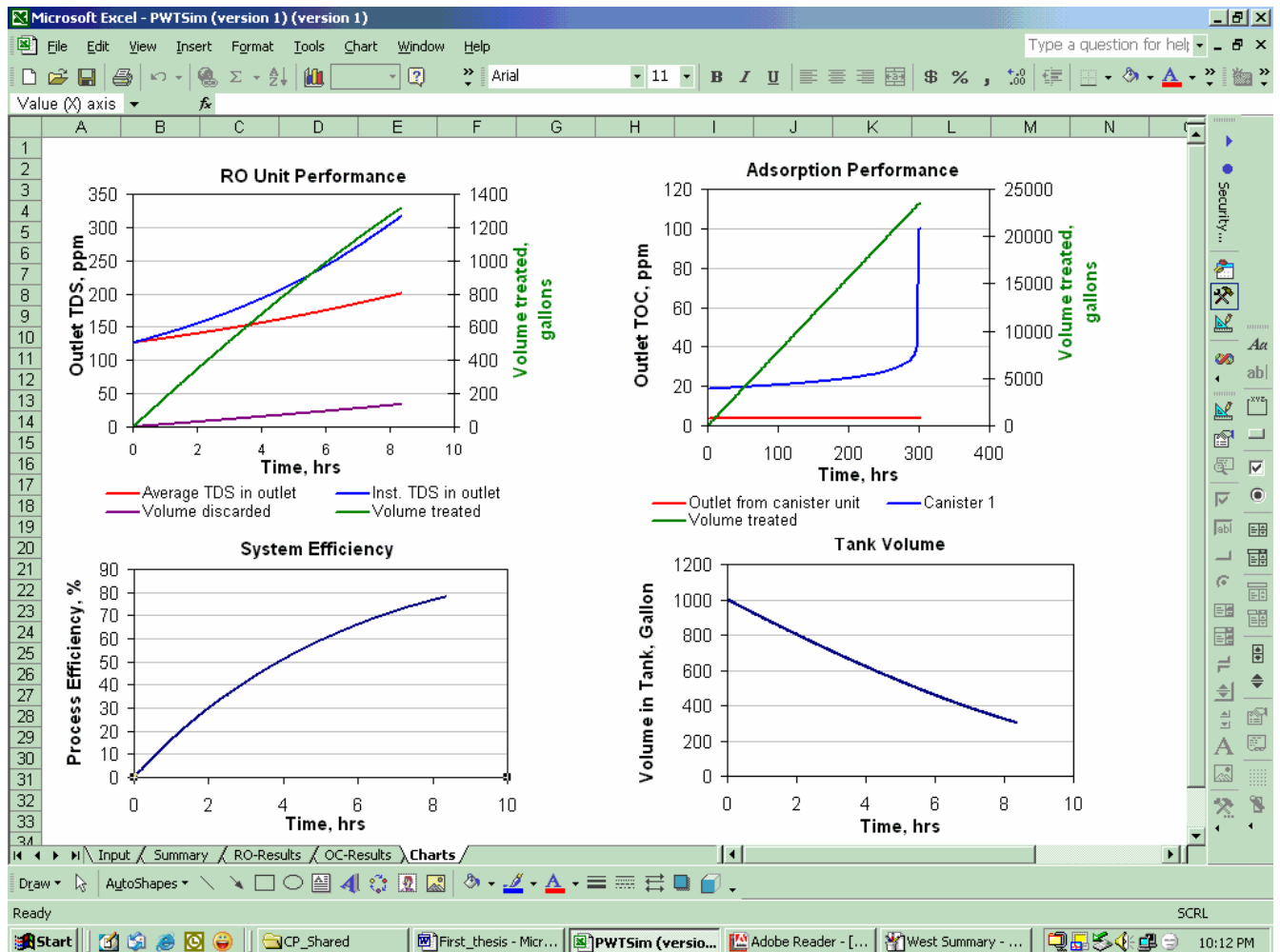


Fig. 5.13 – Simulation run showing TDS and TOC content in permeate stream or final outlet of produced water treatment system for West Texas produced water treatment.

The final outlet has TOC less than 5 ppm and TDS less than 250 ppm. The treated water meets the drinking water standards.

The produced water processed by water treatment unit having combinations of advanced separation techniques such as above can be termed as a source of fresh water, agricultural water or municipal water. Even an overall conversion of 10% of produced water can solve the problem of scarcity of water resources in arid areas such as West Texas.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

A new approach to manage excessive amounts of produced water is discussed which can convert produced water as a source of fresh water. We modeled and simulated the performances of advance separation techniques which can be used to remove oil, dissolved solids and other hazardous materials from produced water. Two case studies are discussed, one with lower feed TDS and other with higher feed TDS content to demonstrate the feasibility of the option of produced water treatment to manage resources effectively. Following conclusions can be drawn from this study,

1. The conversion of produced water into a source of fresh water is feasible for field scale application.
2. Organoclay PS12385 can remove more than 90% TOC content of produced water, provided the series/parallel operation.
3. RO is the best technology available to remove TDS from produced water. It can remove more than 95% TDS content of produced water.
4. A combination of continuous adsorption and batch RO units is an effective system for the treatment of produced water and it provides maximum treatment efficiency.
5. Produced water treatment simulator developed in this study based on empirical models can simulate produced water treatment process for produced water having TOC content ranging from 20 – 8000 ppm and TDS content ranging from 500 – 40000 ppm.

6.2 Recommendations

The following recommendations can be made on the basis of the results and conclusions.

1. Detailed experimentation of organoclay adsorption with produced water as feed is required to study adsorption kinetics and overall performance of fixed bed adsorption.
2. More RO membranes should be tested to evaluate application of RO operation for removal of TDS from produced water.
3. Separation techniques other than adsorption and RO should be evaluated to determine the cheapest and the most efficient of them for produced water treatment.
4. The research work is required to determine options for handling concentrated streams from the treatment unit discussed above that can have higher TDS content, e.g. concentrate to be discarded at the end of each RO batch.

NOMENCLATURE

Roman

- A = adsorption isotherm parameter
- A_{cs} = cross sectional area of packed bed, cm^2 or inch^2 or ft^2
- b = hyperbolic parameters depend on operating conditions
- B = adsorption isotherm parameter
- c = solute concentration in liquid phase that is contacted to adsorbent, ppm
- c_l = intercept of straight line, gm oil/gm adsorbent
- C_{in} = TOC content of inlet fluid stream to the adsorption column, ppm
- C_p = permeate recovery, %
- C_{perm} = salt concentration in permeate, ppm
- C_{ids} = average salt concentration in feed, ppm
- $C(t)$ = TOC content of adsorption column outlet at any time during operation, ppm
- D = hyperbolic parameters depend on operating conditions
- E = process efficiency or percentage of recovery, %
- HTV = initial volume of water in holding tank, gallons
- k = adsorption rate constant, min^{-1} or hr^{-1}
- K_{ads} = slope of straight line
- L = total length of adsorption column packed with organoclay, cm or inch or ft
- m_{ads} = co-efficient of adsorption, gm of oil adsorbed/gm of oil inflow
- m_b = loading capacity, gm oil/gm adsorbent
- n_k = kinetic order
- P_i = pressure at the feed inlet side, psi
- P_o = pressure at the concentrate outlet side, psi
- P_p = pressure at the permeate outlet side, psi

- Q = volumetric flow rate through the packed bed, GPM or ml/min
 q^* = equilibrium solute concentration in adsorbent, gm of oil/gm of adsorbent
 q_{oc} = throughput of adsorption canister unit, GPM
 R_{ads} = adsorption rate, [unit of k] [ppm] ^{n_k}
 R_j = salt rejection, % RT = residence time, min or hr
 t_b = operation time for RO unit per batch, hrs
 t_s = stoichiometric time, min or hr
 W_{packed} = weight of column packed with organoclay, gm or lbs
 W_{oc} = weight of packed organoclay, gm or lbs
 W_c = weight of unpacked column, gm or lbs
 W_{ads} = amount of oil cumulatively adsorbed in packed bed, gm or lbs
 W_{in} = amount of oil cumulatively get into the packed bed, gm or lbs
 W_{out} = oil out from the adsorption column, gm or lbs

Greek

- ε = porosity of the packed bed
 θ = empty bed contact time, min or hr
 ρ_b = bulk density of packed bed, gm of adsorbent/volume of packed bed

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VITA

Name:

Chirag Patel

Address:

285 Dorset Ct., Piscataway, NJ 08854, US

Education:

Bachelor of Engineering, Chemical Engineering, Nirma Institute of Technology,
Ahmedabad, India, July 01