Faculty of Science and Engineering

Department of Chemical Engineering

Treatment of Oily Produced Water with Low-Cost Adsorbents and Ceramic Membrane Microfiltration

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DECLARATION

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgement has been made.

This thesis contains no material where has been accepted for the award of any other degree or diploma in any university.

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Date: 02/06/2015

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Al. Haddabi, M., Ahmed, M., Al. Jebri, Z., Vuthaluru, H., Znad, H., & Al. Kindi, M. 2015. Boron removal from seawater using date palm (Phoenix dactylifera) seed ash. *Desalination and Water Treatment*, 1-8 (DOI: 10.1080/19443994.2014.1000385)

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Al. Haddabi, M., Vuthaluru, H., Ahmed, M., & Znad, H. 2015. Investigations into adsorption of dissolved organic carbon from oily produced water using date seeds. International Desalination Association World Congress, San Diego, California, USA, August 30-September 4, 2015.

ABSTRACT

Huge quantities of water produced along with oil and gas makes it one of the main challenges in oil and gas industry across the globe. Produced water emanates from such processing facilities, contains oil which needs to be reduced in order to meet environmental regulations. There is a need for the application of new technologies to come up with better treatment methods for oily produced water to achieve better quality for beneficial uses such as injection to underground aquifers to enhance oil production, irrigation, aquifer recharge, and various industrial purposes. Most of the available technologies for the purification of produced water focus on the removal of dispersed hydrocarbons. This can be attributed to the fact that the environmental legislation aims to reduce the dispersed oil, recently the attention shifted toward the effect of other components of produced water. This led to better understanding of the impact of these constituents on the environment and eventually led to the application of new technologies to eliminate them. Therefore, new innovative technologies need to be implemented to comply with new level of required cleanliness.

Adsorption is one of the technologies used as a pretreatment to reduce the amount of suspended solids and oil. It is very efficient, cost effective and it can reduce the oil content to comply with the discharge standards. Membrane separation is another methodology which gained momentum over the last 30 years and is becoming a promising technology. Ceramic membrane is a promising technology which can be used to treat the produced water due to their superior mechanical, thermal, and chemical stability. However, fewer studies are related to the application of inorganic cross-flow ceramic membrane for produced water treatment.

In this study the application of date seeds and attapulgite were used as an effective alternative low-cost adsorbents for the removal of dissolved organic carbon (DOC) from oily produced water. Several techniques were employed to characterize the adsorbents such as Scanning Electron Microscope (SEM) and Fourier Transform Infrared (FTIR).Thermogravimetric analysis (TGA), specific area using BET method and particle density using pycnometer method were also obtained. The aim of this study was to understand the mechanism associated with the removal of DOC and to find the best equilibrium isotherms and kinetic models for DOC removal in batch adsorption experiments. The effect of various experimental parameters such as contact time, initial DOC concentration (18.5–93.5 mg/L), solution pH (4–9), temperature (25–45^{o}C), and adsorbent doses (0.5 –2.0 g) was evaluated. The removal rate of DOC was high at the beginning and then the rate starts to decrease with time until it reaches equilibrium. This can be attributed to the fact that at the beginning the adsorption sites were unoccupied and highly available and as time proceeds less sites become available. The equilibrium stage was attained within 120 min and thus, the rest of adsorption trials were conducted for a contact time of 120 min. The equilibrium data fits well with the Langmuir isotherm. The maximum monolayer adsorption capacity of date seeds was found to be 74.62 mg/g while for attapulgite A the maximum monolayer adsorption capacity was 40 mg/g for granular attapulgite and 49 mg/g for the powder attapulgite. For attapulgite B the maximum monolayer adsorption capacity was 31 mg/g for granular attapulgite and 65 mg/g for powder attapulgite. The parameters of Langmuir, Freundlich, and Dubinin-Radushevich models were calculated and tabulated. The separation factor, R_L, from the Langmuir isotherm and, n, constant from the Freundlich isotherm indicated a favourable adsorption. Pseudo-first order, pseudo-second order, intra-particle diffusion, liquid film diffusion, and double exponential models were applied to study the mechanism of adsorption. The adsorption follows the pseudo-second order process and it was found to be controlled by both surface and pores diffusion. The different kinetic parameters including diffusion coefficient, rate constant, half-adsorption time, and correlation coefficient were obtained at different physico-chemical conditions. The kinetic experiments showed that the adsorption of DOC can be summarized into two steps: external mass transfer of the DOC molecules to the external surface of the adsorbent through film diffusion at a fast rate, and intra-particle diffusion of DOC molecules into adsorbent particles through pores. Thermodynamic parameters including Gibbs free energy (ΔG^o), enthalpy (ΔH^o), and entropy (ΔS^o) were calculated. The thermodynamic analysis showed that the process is nonspontaneous and exothermic in nature.

The application of a cross-flow microfiltration using ceramic membrane (α-Al_2O_3) membrane with 0.05 μm pore size for the purification of oily water from oilfield was studied and investigated. The effect of applied pressure with different temperature on the removal of pollutants and impurities was tested through the measurement of permeate flux, total organic carbon (TOC), chemical oxygen demand (COD), oil in water (OIW) content, turbidity and total dissolved solids. The results show a very promising and excellent results where the reduction in oil in water (OIW) content ranged from 78 to 99.99 %. The oil in water content in permeates after filtration ranged from 0.15 mg/L to 35 mg/L. For turbidity, the reduction was above 96% for all the treatments. Temperature has a slight effect on turbidity reduction. TOC removal ranged from 30-60% while COD reduction was in the range of 0.36-62%. The presence of humic, carboxylic, and fulvic acids tend to increase the values of COD and TOC in permeate as they are very difficult to be removed by the

membrane. By increasing temperature, the flux increased due to the reduction in viscosity as well as solution diffusivity enhancement. Regeneration of the membrane is achieved through backwashing which proved to be an efficient way to clean the membrane and to recover the initial flux.

TABLE OF CONTENT

CHAPTER 1 INTRODUCTION

CHAPTER 2 LITERATURE REVIEW

CHAPTER 3 RESEARCH METHODOLOGY

CHAPTER 4 PHYSICO-CHEMICAL CHARACTERIZATION OF ADSORBENTS

CHAPTER 5 REMOVAL OF DOC BY DATE SEEDS

CHAPTER 6 REMOVAL OF DOC BY ATTAPULGITE

CHAPTER 7 APPLICATION OF CERAMIC MEMBRANE FOR THE PURIFICATION OF PRODUCED WATER

CHAPTER 8 CONCLUSIONS AND RECOMMENDATIONS

APPENDICES

LIST OF TABLES

LIST OF FIGURES

NOMENCLATURE

API	American Petroleum Institute
BTEX	Benzene, Toluene, Ethylbenzene and Xylene
C_e	residue DOC concentration at equilibrium , mg/L
C_f	Concentration of certain component in feed mg/L
C_l	final concentration of DOC, mg/L
C_o	initial concentration of DOC, mg/L
COD	Chemical Oxygen Demand
C_p	Concentration of certain component in permeate mg/L
DAF	Dissolved Air Flotation
DOC	Dissolved Organic Carbon
ε	Polanyi potential (KJ^2/mol^2)
FTIR	Fourier Transform Infrared
k_1	pseudo-first-order rate constant, L/minute
k_2	pseudo-second-order rate constant, g/mg min
K_d	distribution coefficient
K_f	Freundlich constant related to adsorption capacity, mg/g
k_{fd}	the film diffusion rate constant
k_{id}	intra-particle diffusion rate constant, mg/g min $^{0.5}$
K_L	the Langmuir constant, L/mg
m_o	mass of oven-dried date seed (g)
m_{sw}	mass air-dried seed + pycnometer + water (g)
m_w	mass of water + pycnometer (g)
n	empirical parameter related to the intensity of adsorption
OIW	Oil in Water
OSPAR	Oslo-Paris convention
PF	Permeate Flux
mg/L	Parts per million
q_e	amount of DOC adsorbed at equilibrium, mg/g
Q_f	Feed flow rate L/hr
q_m	maximum adsorption capacity, mg/g
Q_p	Permeate flow rate L/hr

q_t	adsorption capacity at time t, mg/g
R^2	linear regression coefficient
R_L	separation factor
rpm	Revolutions per minute
SEM	Scanning Electron Micrographs
t	time (min)
$t^{0.5}$	Square root of time, $\text{min}^{0.5}$
TGA	Thermogravimetric analysis
TOC	Total Organic Carbon
TPH	Total Petroleum Hydrocarbon
USEPA	United States Environmental Protection Agency
β	constant related to adsorption energy
ΔG^o	Gibbs free energy (KJ/mol)
ΔH^o	Change in Enthalpy (KJ/mol)
ΔS^o	Change in Entropy(J/mol K)
ΔS^o	Change in Entropy(J/mol K)
ρ_s	particle density of date seed (g/cm^3)
ρ_w	density of water (g/cm^3)

CHAPTER 1

INTRODUCTION

1.1. Background

The world daily consumption of petroleum products is estimated to increase from 85 million barrels in 2006 to 106.6 million barrels by 2030 (Outlook, 2010). During oil and gas production processes, huge quantities of water are also produced. This water is known as produced water or oilfield brine, accounting for the largest volume generated during oil and gas production processes (Reynolds Rodney, 2003, Chan et al., 2002). Presently, more than 90% of produced water is re-injected into the formation to enhance oil recovery or for disposal (Li, 2009). In the past the oil production water was considered as a troublesome by-product and it represented a significant liability and cost to the oil and gas production. Recently this attitude has changed and the oily produced water is now seen more as a resource than as a by-product. By 2025, 2.8 billion people (from 48 countries) will be living in water-scare and water-stressed countries. Sultanate of Oman is considered as a semi-arid country where the average annual rainfall is about 100 mm. Petroleum Development Oman (PDO) produces around 700,000 m^3/day of water associated with hydrocarbon production. Currently less than half of this amount is injected back into the producing reservoirs as water flood for reservoir management. The production of excessive quantities of water is the reason behind to abandon oil and gas wells, leaving huge quantities of hydrocarbons behind. Upgrading of low quality water (i.e.

oil production water) for greening the desert or growing biofuels is becoming a strategic alternative for the sustainable development of remote fields.

Produced water contains a mixture of organic and inorganic constituents such as dispersed oil compounds, heavy metals, dissolved formation minerals, production-chemical compounds, production solids, and dissolved gases (Hansen, 1994). The salt content present in produced water varies from a few parts per thousand to that of saturated brine (300,000 mg/l) (Neff, 2002b), total organic carbon (TOC) might reach up to 1500 mg/l and oil and grease concentration reaches up to 565 mg/l (Fakhru'l-Razi, 2009). Dissolved oil is more difficult to remove than dispersed oil. The dissolved oil components are polar organic compounds and ranged between low and medium carbon ranges (Hayes and Arthur, 2004). BTEX (benzene, toluene, ethylbenzene and xylene), organic acids and low molecular weight aromatic compounds are classified as dissolved oil (Igunnu and Chen, 2012a). Organic acids like formic acid, propionic acid, carboxylic acid, humic and fulvic acids are typically present. Dissolved organic carbon (DOC) represents the amount of dissolved organic compounds in water and operationally can be defined as organic matter that can pass through a 0.45 µm filter (Kitis et al., 2001). The presence of DOC in aquatic systems poses a threat to the human and aquatic environment (Gao et al., 1998, Liu et al., 2002, Santé, 2011). DOC (especially humic acids) can form disinfection by-products (DBPs) when it reacts with chlorine (Adin et al., 1991, Owen et al., 1995). Many of the existing and recently used technologies in the treatment and separation of oil and water are not capable to meet the new stringent environmental regulations. Environmental Protection Agency (EPA) developed guidelines for effluent discharge. Best Available Technology Economically Achievable (BAT) specifies a maximum of 29 mg/l oil in water as effluent limitations, averaged over 30 days. Best

Conventional Pollutant Control Technology (BCT) regulations for offshore disposal specify 48 mg/l, averaged over 30 days (Islam, 2006). Therefore, there is a great need for the application of new and innovative technologies to achieve the required oil and grease content in the effluent water disposed to the environment. Various physical, chemical and biological methods were used in oil-water separation and treatment. Some of the physical methods used are adsorption of dissolved organics using activated carbon, organoclay, zeolite and resins (Means, 1992), application of cyclones (Deng, 2002), and dissolved air precipitation (Thoma, 1999). Chemical methods include the use of coagulation and flocculation (Dallbauman, 2005, Garbutt, 1999b) and treatment with ozone (Morrow, 1999). Different methods produce different qualities of effluents. Combined methods were also proposed and tested where physical, chemical, and biological methods are used as a pretreatment before the application of membranes.

Although adsorption process has been practiced for so many years, it is only recently that it is recognized as a major purification technique for the oil and gas industry (Richardson et al., 2002). Adsorption is found to be efficient and cost effective and becoming the most popular technique for the purification of wastewater (Ali et al., 2012, Lin and Juang, 2009, Mohan and Pittman Jr, 2006). Adsorption does not produce harmful substances, flexible and simple in design, has low initial cost, easy to be operated and insensitive to toxic pollutants (Crini, 2006, Yang et al., 2002, Banerjee et al., 1997). There is a great need to search for non-conventional, low cost adsorbents that are abundantly available, efficient and economically feasible for removing dissolved organic compounds from oily water.

Membrane separation is another methodology which gained momentum over the last 30 years and is becoming a promising technology. Ceramic membrane is a promising technology which can be used to treat the produced water due to their superior mechanical, thermal, and chemical stability. However, fewer studies (Abadi, 2011, Zhong et al., 2003, Higgins et al., 1994) are related to the application of inorganic cross-flow ceramic membrane for produced water treatment with almost no study reported in the literature combining adsorption with ceramic membrane. The main drawbacks when using membranes for treating oily water are polarization/fouling, low selectivity and low membrane lifetime.

The main objectives of this study is to investigate the performance of adsorption to remove dissolved organic carbon using date seeds and attapulgite, to evaluate the performance of cross-flow ceramic membrane to purify produced water and to evaluate the quality of treated water in order to meet the reuse requirements and limits.

1.1.1. Produced Water Constituents

Produced water consists of different organic and inorganic compounds, Table 1.1. The composition of produced water is qualitatively similar to the oil and /or gas produced and can vary by order of magnitude (Fillo et al., 1992). The main constituents of produced water include: dispersed oil, dissolved oil, dissolved minerals, production chemicals, production solids, and dissolved gases.

Table 1.1 Composition of oily produced water (Igunnu and Chen, 2012b, Fakhru'l-Razi et al., 2009)

Parameter	Minimum value	Maximum value	Heavy metal	Minimum value (mg/l)	Maximum value (mg/l)
Density (kg/m^3)	1014	1140	Calcium	13	25800
Conductivity (µS/cm)	4200	58600	Sodium	132	97000
Surface tension (dyn/cm)	43	78	Potassium	24	4300
pH	4.3	10	Magnesium	8	6000
TOC (mg/l)	0	1500	Iron	<0.1	100
TSS (mg/l)	1.2	1000	Aluminium	310	410
Total oil (IR; mg/l)	2	565	Boron	5	95
Volatile (BTEX; mg/l)	0.39	35	Barium	1.3	650
Base/neutrals (mg/l)	-	<140	Cadmium	<0.005	0.2
Chloride (mg/l)	80	200000	Copper	<0.02	1.5
Bicarbonate (mg/l)	77	3990	Chromium	0.02	1.1
Sulphate (mg/l)	<2	1650	Lithium	3	50
Ammonium nitrogen (mg/l)	10	300	Manganese	<0.004	175
Sulphite (mg/l)	-	10	Lead	0.002	8.8
Total polar (mg/l)	9.7	600	Strontium	0.02	1000
Higher acids (mg/l)	<1	63	Titanium	<0.01	0.7
Phenol (mg/l)	0.009	23	Zinc	0.01	35
Volatile fatty acids (mg/l)	2	4900	Arsenic	<0.005	0.3
			Mercury	<0.005	0.3
			Silver	<0.001	0.15
			Beryllium	<0.001	0.004

Dispersed Oil

Dispersed oil is classified with oil droplets diameter in the range from 0.5 µm to more than 200 µm. The size of oil droplets is one of the key parameters affecting the performance of produced water treatment method. The efficiency of any gravity separation device decreases as the oil droplet decreases (Stewart and Arnold, 2008). Figure 1.1 represents a histogram of an oil droplet distribution.

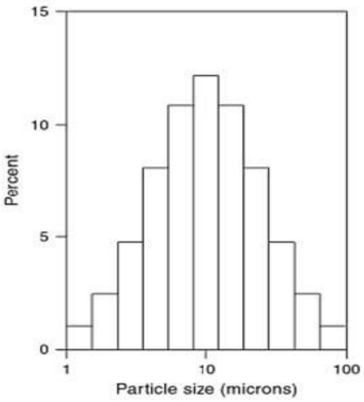
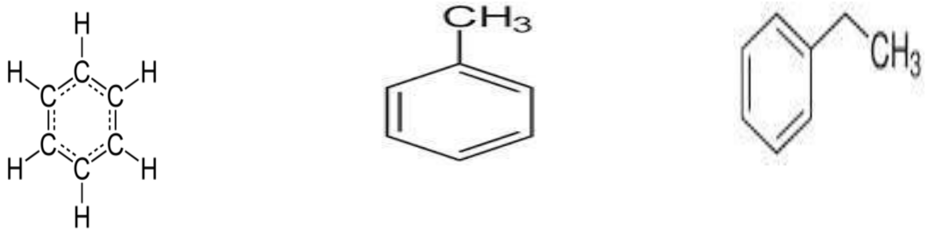


Figure 1.1 Histogram of oil droplet distribution

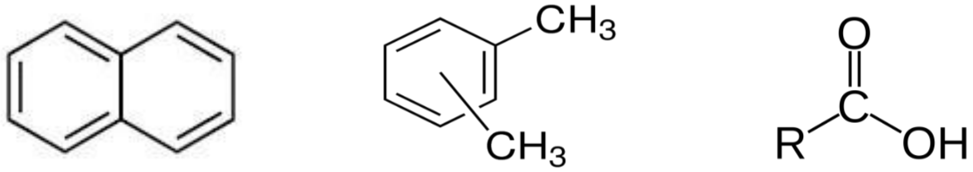
Many factors affect the size distribution of oil droplets like “interfacial tension, temperature, turbulence, system shearing (pumping, pressure drop across pipe fittings, etc.) and other factors” (Stewart and Arnold, 2008, Stephenson, 1992). Some compounds such as the aliphatic hydrocarbons, Polycyclic Aromatic Hydrocarbons (PAHs) and heavy alkyl phenols are classified as dispersed oil because of their solubility (Veil et al., 2004).

Dissolved Oil

The polar organic compounds in produced water are known as dissolved oil or soluble oil (Figure 1.2).



Benzene Toluene Ethylbenzene



Naphthalene Xylene Carboxylic acid

Figure 1.2 Common dissolved oils and their structures

Many complex and interrelated factors govern the amount of oil present in produced water (Hudgins, 1994, Hayes and Arthur, 2004, Veil et al., 2004). The composition of oil, pH, Salinity, total dissolved solids (TDS), temperature, Oil/Water ratio and type and concentration of chemicals used in oil production affect the level of dissolved and dispersed oil present in the produced water, prior to treatment (Fakhru'l-Razi et al., 2009).

Temperature changes the relative ratio of carbon ranges and affects the solubility of organics present in the produced water. Pressure enhances the solubility of organic compounds slightly. Salinity has no significant effect on the dissolved organics.

Dissolved Minerals

The dissolved inorganic minerals in produced water are usually present in very high levels. They consist of cations, anions, naturally occurring radioactive materials (NORM) and heavy metals. Salinity which is mainly caused by the presence of Na^+ and Cl^-, can vary from a few milligrams per liter to ~ 300,000 mg/l (Roach et al., 1993). Heavy metals present in trace levels depending on the geology and age of the oil aquifer (Fakhru'l-Razi et al., 2009, Hansen and Davies, 1994, Hudgins, 1994, Leifer, 2010, Reynolds Rodney, 2003, Sirivedhin et al., 2004).

NORM (mainly ^{226}Radium and ^{228}Radium) might be present in the produced water. The presence of barium ions in produced water might indicate the presence of radium isotopes (Fakhru'l-Razi et al., 2009, Jacobs et al., 1992, Jerez Vegueria et al., 2002, Lee, 2011).

Production Chemicals

Through the oil and gas production process, different types of chemicals are used to mitigate or prevent operational problem such as scale and corrosion inhibitors, emulsion breakers, antifoam and water treatment chemicals (Stephenson, 1992). The level of production chemicals in produced water is found to be as low as 0.1 mg/l.

The production chemicals can be used as pure compounds or compounds containing active ingredients dissolved as a solvent or a co-solvent (Hansen and Davies, 1994). It is difficult to determine the fate of these chemicals as they might deteriorate or consumed within the process (Hudgins, 1994).

Production Solids

Produced solids consist of variety of compounds such as clays, waxes, bacteria, carbonates and corrosion and scale products (Fakhru'l-Razi et al., 2009, Igunnu and Chen, 2012b, Neff, 2002a). Few microorganisms can survive in the produced water due to the presence of different toxic chemicals. Bacteria might clog and cause corrosion of equipment and pipelines (Veil et al., 2004)

Dissolved gases

The most abundant gases present in the produced water are carbon dioxide (CO_2), oxygen (O_2) and hydrogen sulphide (H_2S).

1.2. Problem Statement

Huge quantities of water are produced along with oil and gas operations. This water is heavily contaminated with hydrocarbon and other constituents which make it undesirable for any purposes unless it is treated. The disposal of this water is very costly and restricted by the stringent environmental regulations. The treatment of this water will allow many countries suffering from water scarcity or water stress to utilize it for different applications such as injection to underground aquifers to enhance oil production, irrigation, aquifer recharge, and various industrial purposes.

Several technologies have been proposed and applied to remediate this water but many of them failed to meet the environmental regulation while the others are not economically feasible and therefore still many works needs to be accomplished. Adsorption is one of the technologies used as a pretreatment to reduce the amount of suspended solids and oil. It is very efficient, cost effective and it can reduce the oil content to comply with the discharge standards. Ceramic membrane is a promising technology which can be used to treat the produced water due to their superior mechanical, thermal, and chemical stability. This research focuses on the application of low-cost adsorbents and ceramic membrane filtration for the purification of produced water.

1.3. Research Objectives

The overall purpose of the this study is to assess the feasibility of using date seeds and attapulgite as potential adsorbents for the removal of dissolved organic carbon (DOC) from produced water and to evaluate the application of ceramic membrane for the purification of produced water under different experimental conditions. The specific objectives include:

- Predict the adsorption isotherm to evaluate the adsorption capacity of the adsorbents.
- Explore the mechanism of adsorption and adsorption kinetics of DOC by date seeds and attapulgite.
- Evaluate the quality of the effluent from the adsorption process as well as from ceramic membrane combined module to explore the feasibility of reclamation and re-use of the treated produced water.
- Investigate the influence of parameters like Transmembrane Pressure (TMP), temperature, and oil concentration in feed on the separation process.
- Evaluate the performance of the ceramic membrane system to treat the produced water in terms of membrane fouling, removal efficiency and process stability.
- Optimize the operating conditions between the adsorption process and the ceramic membrane in order to produce better effluent's quality.

1.4. Significance of the research

Purification of produced water for beneficial uses is the best strategy to mitigate environmental and economic impacts associated with produced water treatment. Despite the fact that many technologies are available for produced water treatment but many of them are not typically capable of reaching the new levels of cleanliness set by the stringent environmental guidelines without producing high volumes of hazardous wastes and having high operating expenses. Several studies have been conducted to treat and purify the oily produced water. However, there appears to be a shortage or lack of information about the use of adsorption and inorganic ceramic membranes for the removal of DOC from produced water. Therefore the significances of the study are:

- The production of high quality water by eliminating the suspended and dissolved hydrocarbons
- Reduce the environmental risk caused by the disposal of untreated produced water in groundwater aquifers
- The treatment of produced water will provide huge quantities of water for other purposes
- Utilization of abundantly available low-cost adsorbents for the removal of DOC and other pollutants from oily produced water
- Optimization of the operational parameters of ceramic membrane filtration for better and more economical operation
- Reduction in the operational cost by using highly abundant low-cost adsorbents

1.5. Thesis organization

The thesis is divided into eight chapters and these chapters are organized as:

Chapter 1, provides a general overview of the background, problem statement, the objectives and significance of the research are also stated. The organization of the research work is also presented in this section.

Chapter 2, a detailed review for the most published research and the current state of developments in the area of the study. A detailed overview on the adsorption process, factors controlling the adsorption process, ceramic membrane, controlling factors and working conditions is also stated in this part.

Chapter 3, the methodology of the research is discussed in this part. The experimental part of the batch adsorption and ceramic membrane trials is presented. All analytical and instrumental procedures are discussed.

Chapter 4, this chapter provides detailed results of the characterization of the feed water and the different adsorbents used in this study.

Chapter 5, this chapter discuss the application of date seeds as adsorbent for DOC which include the findings from the batch experiments. The isotherms, kinetics and thermodynamics are discussed in this chapter.

Chapter 6 presents the detailed results for the application of attapulgite for the removal of DOC from produced water. The models used to fit the experimental part are discussed.

Chapter 7 covers the application of ceramic membrane for the purification of produced water. The evaluation of the effect of different working conditions on the process is documented in this part.

Chapter 8 summarizes the conclusions drawn from this study and recommendations for future research and further investigations. The schematic diagram of the thesis can be found in Figure 1.3.

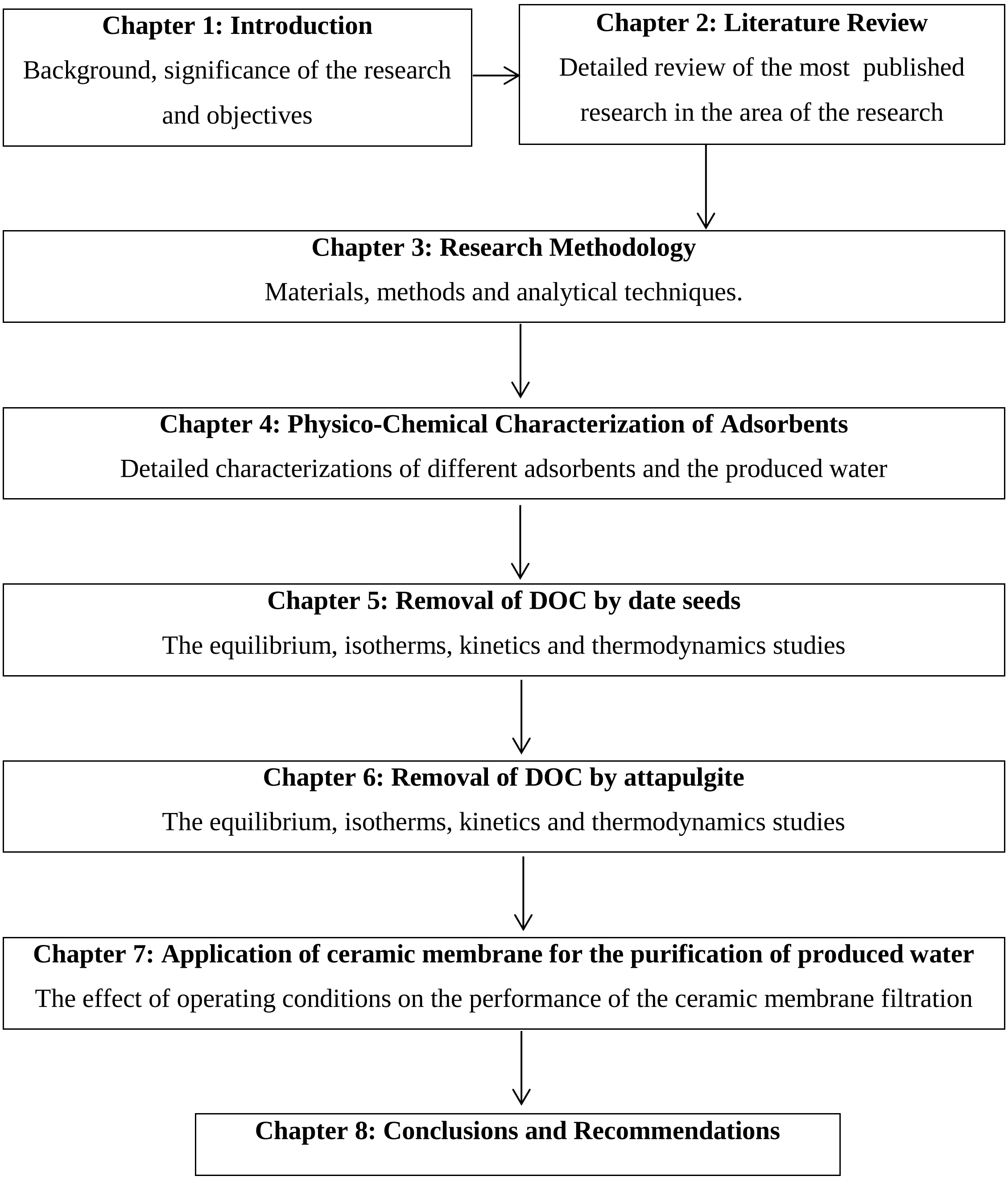


Figure 1.3 Schematic diagram of the thesis

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Produced water is found to be the utmost waste volume generated from oil and gas abstraction process. In some sites, the amount of water might be as much as ten times the amount of oil produced (Campos, 2002a). The amount of produced water is accounted for more than 80% of liquid waste (Azetsu-Scott, 2007) and as high as 90% in old oilfields(Kaur, 2009). The quantities of water produced are increasing as the oil wells mature. Wells operated for more than 10 years is considered as mature well and it produces an average of-about 10 bbl. of water for every bbl. of oil (Campos, 2002b). Around 250 million barrels of water is produced from oil and gas fields every day (40% of this amount is discharged into the environment) compared to 80 million barrels of oil per day (Dal Ferro and Smith, 2007, Fakhru'l-Razi et al., 2009). The water to oil ratio is around 3:1 or water cut around 75%. The water cut continuing to rise as the oil wells getting older (Dal Ferro and Smith, 2007). Many oil and gas producing countries, which are also classified as water stressed countries, are increasingly focusing on finding efficient and cost effect treatment processes for the huge quantities of produced water as an alternative source for fresh water supply (Fakhru'l-Razi et al., 2009). The effluent from onshore petroleum activities in the European standard is set to be less than 5 mg/l Total Hydrocarbons (THC) and less than 10 mg/l suspended solids (Ashaghi et al., 2007).

2.2 Produced Water from Petroleum Activities

The produced water generated from oil and gas production activities has very wide variations in composition from one field to another, within a field, and during the lifetime of production. The composition and constituents of produced water depend on the nature of geological location of the field, the operational conditions, type of hydrocarbon product being produced and chemicals used in process facilities (Chan et al., 2002, Hansen and Davies, 1994, Veil et al., 2004, Røe Utvik, 1999). Productivity of gas well is highly affected when significant quantities of water are also produced. Therefore, the quantities of water associated with gas production are relatively low. On the other hand, oilfields start with low oil to water ratio and with time the ratio between water and oil might reach up to 10:1 in some places. Produced water coming from gas production normally characterized by lower molecular-weight aromatic hydrocarbons compared to oilfields produced water. Therefore, it is considered relatively more toxic than produced water from oil production. Some studies reported that toxicity of produced water from gas/condensate platforms is almost 10 times higher than discharged from oil platforms (Jacobs et al., 1992). Produced water discharged from gas platforms tend to be more acidic (pH: 3.5 – 5.5) compared to produced water from oil platforms which has a pH in the range of 6 -7.7 (Jacobs et al., 1992).

2.3 Effect of Produced Water on the Environment and Legislations

Most of the treatment technologies (gravity-based separation) in treating produced water focus on the removal of dispersed oil while little attention is given to dissolved organics in produced water. Produced water contains constituents which might cause threat to aquatic life or to crops when it is used for irrigation (Olsgard and Gray, 1995, Davies et al., 1984). The aromatic hydrocarbons like Polycyclic aromatic hydrocarbons (PAHs) and alkylated phenols are mutagenic and harmful to reproduction, can increase the biological oxygen demand (BOD), toxic to aquatic organisms and can be carcinogenic to humans and animals (Veil et al., 2004, Grant and Briggs, 2002). Unless the level of an ingested constituent by an organism exceeds the set threshold, effects are not likely to happen. The discharge location and the concentration at the discharge point influence the impacts of the produced water and produced water components in the short term. Several countries start to implement more stringent regulatory standards for discharging produced water into the sea. The Oslo Paris Convention (OSPAR) set the maximum level of oil in discharged produced water (OIW) to 30 mg/l (Igunnu and Chen, 2012a). Australia permitted offshore discharge of oil and grease in produced water to be 30 mg/l while the Republic of China sets the monthly average limits of oil and grease at 10 mg/l (Fakhru’l-Razi et al., 2009).

2.4 Produced Water Treatment Technologies

Treatment and purification of produced water is required to meet the stringent environmental regulations for disposal purposes or to meet beneficial use specifications (irrigation, injection to underground aquifers to enhance oil production, aquifer recharge, and various industrial purposes). Oil needs to be removed / separated from produced water during production and before disposal. Produced water has the potential to be a valuable product rather than a waste.

Table 2.1 demonstrates the different produced water treatment methods employed and the type of equipment that fit to each method. Effective techniques to handle the huge quantities of produced water “depend on asset maturity, the type of reservoir, production rates, location and legislations” (Zara, 2002). In order to meet the treatment objectives, operators have applied many separate and combined physical, chemical and biological treatment processes. A wide range of technologies exist for the oil-water separation and treatment. The most well-known traditional processes are the gravity settling separation and mechanical coalescence methods. Chemical emulsion breaking is an effective way under certain conditions (Song et al., 1998, Meyssami and Kasaeian, 2005). Other processes include coagulation and air floatation (Deng et al., 2005, Zouboulis and Avranas, 2000, Garbutt, 1999a), electrostatic and electrocoagulation separation methods (Mostefa and Tir, 2004, Ma and Wang, 2006, Chen, 2004, Israilides et al., 1997, Murthy et al., 2007), microwave treatment (Chan and Chen, 2002, Fang and Lai, 1995), ultrasonic wave treatment (Pangu and Feke, 2004, Stack et al., 2005), thaw and heat treatment (Jean et al., 1999, Chen and He, 2003), photocatalytic treatment (Fujishima, 1972, Bessa et al., 2001, Li et al., 2006), cyclones (van den Broek et al., 1998, Knudsen et al., 2004, Seureau et al., 1994), Dissolved Air Precipitation (DAP) (Thoma et al., 1999), and evaporation (Bertness and Lipoma, 1989, Heins and Peterson, 2005).

Table 2.1 Produced water treating methods and equipment's (Arnold and Stewart, 1999)

Method	Equipment Type	Approximate Minimum Drop Size Removal Capacities (Microns)
Gravity separation	Skimmer tanks and vessels	100–150
	API separators	
	Disposal piles	
	Skim piles	
Plate coalescence	Parallel plate interceptors	30–50
	Corrugated plate interceptors	
	Cross-flow separators	
	Mixed-flow separators	
Enhanced coalescence	Precipitators	10–15
	Filters/coalesces	
	Free-flow turbulent coalesces	
Gas flotation	Dissolved gas	10–20
	Hydraulic dispersed gas	
	Mechanical dispersed gas	
Enhanced gravity Separation	Hydrocyclones	15–30
	Centrifuges	
Filtration	Multimedia membrane	+1

2.4.1. Membrane Separation Technology

Membranes act as selective barriers to retain certain components while allowing other components to pass through (Nehdi et al., 2010). There are four recognized membrane separation processes, including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) (Madaeni, 1999, Xu and Drewes, 2006, Bilstad and Espedal, 1996, Han et al., 2010). The classification of membrane separation processes is based on the size of the rejected particles. Table 2.2 represents the separation specification and the application of different membranes.

MF and UF is mainly used for treating industrial wastewater, while NF and RO are usually used in water desalination. There are two types of filtration processes in membrane technology, cross-flow filtration and dead-end filtration (Figure 2.1).

Table 2.2 Application of membrane filtration technologies (Arthur et al., 2005)

Membrane Filtration	**Separation specifications**	**Applications/Removal**
Microfiltration (MF)	>100,00 Daltons (10-0.1 µm)	Bacteria, viruses and suspended solids
Ultrafiltration (UF)	10,000 to 100,000 Daltons (0.05 5 e^{-3} µm)	Proteins, starch, viruses, colloid silica, organics, dyes, fats and paint solids
Nanofiltration (NF)	1,000 to 100,000 Daltons (5 e-3 to 5 e^{-4} µm)	Starch, sugar, pesticides, herbicides, divalent ions, organics, BOD, COD and detergents
Reverse Osmosis (RO)	Salts and lower MWCO (1 e^{-4} to 1 e^{-5} µm)	Metal ions, acids, sugars, aqueous salts, dyes, natural resins, monovalent salts, BOD and COD
Gas Liquid Membrane	CO_2 and H_2S	Decarbonation and hydrogen sulphide removal

Dead-end filtration leads to accumulation of product on the surface of the membrane which might damage product, lower recovery and cause fouling to the membrane. Fouling reduces the filtration rate until it ultimately stops. Cross-flow filtration involves recirculation of the retentate across the surface of the membrane. This will maintain a high filtration rate, reduces membrane fouling and maintains a higher recovery.

Membrane system is found to compete with different existing treatment technologies for treating oily produced water. UF is the most effective method for hydrocarbon removal in comparison with traditional separation processes (He and Jiang, 2008), and it is more effective than MF for the removal of oil, suspended solids and dissolved components from produced water (Bilstad and Espedal, 1996). MF and UF works at low transmembrane pressure (1-30 psi) but they cannot remove salts from water. Bilstad and Espedal (Bilstad and Espedal, 1996) in their study compared between MF and UF membranes to treat the North Sea oilfield-produced water. The results showed that UF, but no MF, could meet the effluent standards for total hydrocarbons (TH), suspended solids and dissolved compounds. With the use of 100,000 and 200,000 Da MWCO, ultrafiltration membrane, a 96% removal of the TH concentrations was achieved, 54% and 95% reduction were achieved for BTX and some heavy metals like Cu and Zn respectively.

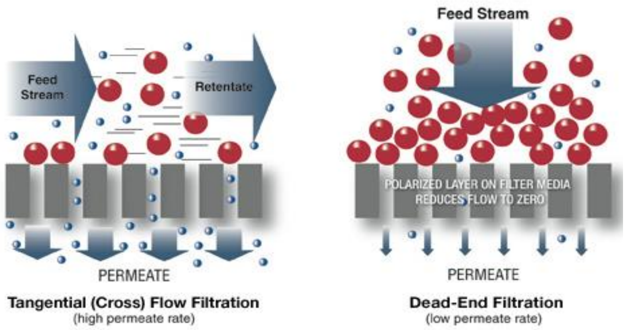


Figure 2.1 Cross-flow filtration and dead-end filtration

2.4.1.1. Ceramic membrane

Ceramic membranes are a new class of materials which can be made from different materials and fabricated in different ways to produce membranes with wide range of physical-chemical advantages and applications (Ashaghi et al., 2007). They have shown great potential for oily water purification due to their extraordinary properties, such as thermal stability, high mechanical strength and ease of regeneration after fouling (Abadi et al., 2011). Tubular ceramic membranes are produced by a porous support (generally α-alumina), one or more layers of decreasing pore diameter and an active or separating layer (α-alumina, zirconia, etc.) covering the internal surface of the tube (Ashaghi et al., 2007). The application of ceramic membranes for microfiltration and ultrafiltration solutions is becoming of great interest because of the potential to treat fouling problems which might strongly reduce volume flow and make the use of hard chemical and high temperature in cleaning procedures necessary (Xu et al., 2008).

Several researchers (Higgins et al., 1994, Yang et al., 1998, Jacobs et al., 1992, Descousse et al., Ebrahimi et al., 2010, Hua et al., 2007b, Ciora and Liu, 2003) identified the benefits of using ceramic membranes for separation of oil from produced water including:

- The ability to accomplish the current regulatory treatment objectives without chemical pretreatment.
- Thermal stability
- Ease of scale up, low running investment and small area requirements.
- Resistance to solvents, chemicals and thermal stress allows good recovery of membrane performance
- Mechanical strength and long life-time
- Application of harsh chemicals (if necessary) for membrane cleaning does not affect the performance stability of the membrane

- It has higher fluxes and higher oil rejection due to their high porosity and more hydrophilic surface, compared to polymer membranes.
- They are operational in pH-range from 1-14. Therefore, cleaning is not an issue.
- High oil removal efficiency
- Low energy requirements

Many researchers tested the application of ceramic membrane for the purification of oily produced water (Ciora Jr and Liu, 2003, Higgins et al., 1994, Yang et al., 1998, Zhong et al., 2003, Madaeni et al., 2012, Abadi, 2011). They investigated the effect of different operating conditions on the efficiency of ceramic membrane in terms of oil removal efficiency, flux and resistance to fouling. In some studies the oil removal reached more than 90% (Mueller et al., 1997, Hua et al., 2007a, Ebrahimi et al., 2010, Abbasi et al., 2010a). Zirconia ceramic membrane is found to perform better compared with alumina ceramic membrane. Fouling and concentration polarization is found to be the main challenge in the application of ceramic membrane. Several operating factors affect the efficiency of the ceramic membrane such as transmembrane pressure (TMP), cross-flow velocity (CFV), Temperature, oil content in feed water, pH and salt concentration.

Effect of Transmembrane Pressure (TMP)

The increase of TMP is found to have positive and negative effects on permeate. Higher TMP leads to high permeate flux but at the same time it force the oil droplets to pass through the membrane leading to the accumulation of oil in the surface and pores of the membrane and ultimately accelerate the process of fouling (the stage were the flux will start to decline) plus deteriorating the quality of permeate as more constituents will pass through the membrane (Hua et al., 2007a, Madaeni et al., 2013, Abadi, 2011). At low TMP the rejection rate organic constituents is high compared to higher TMP values.

Effect of Cross-flow Velocity (CFV)

High CFV will lead to a higher steady permeate flux. Increasing CFV will promote Reynolds number resulting in turbulent flow and high mass transfer coefficient. This effect will weakened the effect of concentration polarization as turbulent flow will remove the deposited particles from the surface of the membrane; therefore the fouling layer on the membrane surface become thinner which will result in more organic matter to pass through the membrane and the TOC removal efficiency decreases (Hua et al., 2007a, Abadi, 2011, Ahmad et al., 2005a, Mikulášek et al., 2004, Baker et al., 1985, Abbasi et al., 2010a, Mohammadi and Esmaeelifar, 2004).

Effect of Oil content

Increasing the oil content in the feed water will cause a decline in the permeate flux. The increase in oil content will enhance the formation of oil-layer on the membrane surface and as operational time proceeds this layer will become thicker and thicker. The formation of this thicker layer will restrict the passage of organic pollutants to the permeate leading to enhance the TOC removal efficiency (Abbasi et al., 2010a, Hua et al., 2007a).

Effect of pH

The pH of the feed water affects the stability of oil-in-water emulsion which found to be more stable at higher pH. The increase in pH will enhance the permeate flux as the oil layer in the surface of the membrane become more open due to the droplet repulsion which will reduce the TOC removal efficiency (Hua et al., 2007a).

Effect of salt concentration

High salt concentration results in lower permeate flux. This can be attributed to the fact that high salt content will increase the viscosity emulsion and the salt concentration polarization in the surface will cause membrane fouling. The increase of salt content has two opposite effect on permeate flux. High salt content leads to bigger oil droplets which enhance the permeate flux but in the other hand high salt crystals will decrease the flux (Kuca and Szaniawska, 2009, Zhao et al., 2005, Elzo et al., 1998). Different and opposite findings are reported in the literature (Zhao et al., 2005, Tambe and Sharma, 1993, Elzo et al., 1998).

Effect of Temperature

Increasing temperature decreases the feed viscosity (i.e. increase the solvent and solutes permeability) which will eventually increase the permeate flux (Spricigo et al., 2001, Wang et al., 2000). At higher temperatures oil and grease will permeate easily through the membrane resulting in lower rejection rates (Abadi, 2011, Abbasi et al., 2010a).

2.4.2. Adsorption

Although many techniques are available for the purification of oily water, there is no single technique which is sufficient to eliminate the constituents in oil-water emulsions to comply with the stringent environmental regulations. Each technique works well for the removal of specific constituents. There is a need to apply different combinations of various technologies to achieve the target water quality for the treated water. Over the last four decades, adsorption has developed to a stage where it is now a major industrial separation technique for the oil and gas industry (Richardson et al., 2002). Adsorption refers to the process of adhesion of extremely thin layer of gaseous molecules, dissolved substances, or liquid (known as adsorbate) to the surface of solids (known as adsorbents) which they are in contact (Weber, 1972, Dąbrowski, 2001). Adsorption can be classified into two types namely physical and chemical sorption. In physical sorption or physisorption the attraction forces are van der Waals forces, and as they are weak, the resulting adsorption is reversible in nature (Allen and Koumanova, 2005, Cooney, 1998).Chemical sorption or chemisorption is characterized by a chemical bonding between the adsorbed molecules and the solid surface, which is generally due to the exchange of electrons and thus chemisorption is irreversible (Cooney, 1998, Allen and Koumanova, 2005). Adsorption is found to be efficient and cost effective and it is becoming the most popular technique for the purification of wastewater (Dąbrowski, 2001, Ali et al., 2012, Lin and Juang, 2009, Mohan and Pittman Jr, 2006). Adsorption does not produce harmful substances, flexible and simple in design, has low initial cost, easy to be operated and insensitive to toxic pollutants (Crini, 2006, Carvalho et al., 2002, Doyle and Brown, 2000, Yang et al., 2002, Banerjee et al., 1997). The adsorption process is greatly affected by the characteristics of the adsorbate (molecular size and form), adsorbent (the degree of ionisation, type of functional groups, size of adsorbent, surface area and distribution of pores) and the solution (pH, temperature and the presence of other competing adsorbate compounds (Slejko, 1985, Crini, 2006).

2.4.2.1. Type of Adsorbents

Several adsorbents have been investigated and applied for the uptake of impurities from wastewater by several researchers (Shichi and Takagi, 2000, Banat et al., 2000, Calace et al., 2002, Polati et al., 2006, Phan et al., 2000, Phan et al., 2002, Couillard, 1994, Denizli et al., 2005, Colella et al., 1998, Hindarso et al., 2001, Jain et al., 2004, Vázquez et al., 2006, Tor and Cengeloglu, 2006, Cengeloglu et al., 2007, Tor et al., 2006, Murray, 2000, Ahmad et al., 2007, Hameed et al., 2007). Each adsorbent has its own unique properties which might make superior for the removal of a certain constituent. Researchers are still looking for new adsorbents especially from the environment perspective. Efforts are put into utilizing the natural wastes as an adsorbent. The physical and chemical properties of the adsorbent will determine the ability and affinity of an adsorbent for a specific adsorbate.

Activated Carbon

Activated Carbon (AC) is considered as the most popular adsorbents for the removal of pollutants from wastewater (Babel and Kurniawan, 2003, Derbyshire et al., 2001). It is usually prepared from coal, coconut shells, lignite, wood, etc., using one of the basic activation methods (Bansal et al., 1988, Carrott et al., 2003, Lillo-Ródenas et al., 2007, Phan et al., 2006). The applications of AC for the removal of organic constituents have studied by several researchers (Carrott et al., 2005, Mourao et al., 2006, Urano et al., 1991). However, AC present several disadvantages (Babel and Kurniawan, 2003). Among them is the high cost of regeneration of the saturated carbon. The application of carbons based on relatively expensive starting materials is also unjustified for most pollution control applications (Streat et al., 1995). This has led many researchers to look for more economic adsorbents.

Low-cost alternative adsorbents

The interest to produce alternative adsorbents to replace the costly activated carbon has been investigated intensively in recent years. Attention has been directed towards various natural solids materials which are able to remove pollutants at low cost. An adsorbent can be classified as low-cost if it requires little processing and abundant in nature (Bailey et al., 1999). Waste material or by-products from industries and agricultural operations, natural materials represent potentially economical alternative adsorbents. Many of them have been tested for the removal of organic and inorganic compounds removal.

Clay

Natural clay minerals are well known and familiar to mankind from the earliest days of civilization. Because of their low-cost, abundance, high sorption properties and potential for ion-exchange, clay minerals are strong candidates as adsorbents (Crini, 2006). In recent years, the interest in utilizing clay minerals such as bentonite, kaolinite, diatomite and Fuller's earth like attapulgite has been increased due to their capacity to adsorb not only inorganic but also organic molecules. The adsorption efficiency of clays generally result from a net negative charge (McKay et al., 1985) on the structure of minerals. This negative charge gives clay the capability to adsorb positively charged species. Attapulgite or so called "special clay" is a hydrated magnesium aluminium mineral characterized by an elongated microfibrous morphology, moderate surface charge, moderate cation exchange capacity, high specific surface area, and high adsorption capacity (Murray, 2000, Al-Futaisi et al., 2007a). The basic mineral characteristics of attapulgite, as well as its wide range of applications has been reviewed by (Galan, 1996). Table 2.3 represents a comparison of various clay adsorbents for the adsorption of different organic compounds reported in the literature.

Agricultural solid wastes

The raw agricultural solid wastes such as leaves, fibers, fruit peels, seeds etc. and waste materials from forest industries such as sawdust, bark etc. have been used as adsorbents (Rafatullah et al., 2010). These materials are available in huge quantities and can be utilized as potential adsorbents due to their physico-chemical properties and low cost. Several researchers studied the application of different agricultural solid wastes like papaya seeds, guava leaves, cotton waste, coconut husk, coffee husks, rice straw, garlic peel, orange peel, wheat shells, wheat straw, etc. for the removal of organic wastes (McKay et al., 1986, Hameed, 2009, Ponnusami et al., 2008, Dutta et al., 2003, Vázquez et al., 2007, Khalid et al., 2000, Nakbanpote et al., 2000, Gong et al., 2007, Low and Lee, 1990, Hameed et al., 2008). Millions of tons of date palm wastes are generated annually in different date palm-growing countries. The utilization of these wastes as low-cost adsorbents and as a precursor for the production of activated carbon will provide a twofold advantages with respect to environmental management. First, huge quantities of agricultural wastes could be partly reduced, converted to useful, value-added materials, and second, the low cost adsorbent, if it proves its effectiveness, will overcome the wastewater pollution at a reasonable cost. Table 2.4 represents the maximum adsorption capacity of various date palm adsorbents for the adsorption of different organic compounds reported in the literature.

Table 2.3 Comparison of various clay adsorbents for the adsorption of different organic compounds

Adsorbent	Adsorbate	Maximum adsorption capacity (mg/g)	Solution	Reference
Montmorillonite	Methylene blue	289.12	Aqueous solution	(Almeida et al., 2009)
Diatonite	Methylene blue	198	Textile wastewater	(Al-Ghouti et al., 2003)
Bentonite	Methylene blue	151-175	Aqueous solution	(Hong et al., 2009)
Palygorskite	Methylene blue	50.8	Aqueous solution	(Al-Futaisi et al., 2007a)
Amorphous silica	Methylene blue	22.66	Aqueous solution	(Rafatullah et al., 2010)
NaOH-treated pure kaoline	Methylene blue	22.66	Aqueous solution	(Ghosh and Bhattacharyya, 2002)
Calcinated raw kaoline	Methylene blue	7.59	Aqueous solution	(Ghosh and Bhattacharyya, 2002)
Neutralized red mud	Phenol	4.127	Aqueous solution	(Tor et al., 2006)
Organo-clay (HDTMA$^+$-smectite)	Phenol	99.0	Aqueous solution	(Mortland et al., 1986)
Bentonite	Para-chlorophenol	10.6	Aqueous solution	(Koumanova and Peeva-Antova, 2002)
Modified bentonite	*p*-Nitrophenol	139.4	Aqueous solution	(Akcay and Akçay, 2004)
zeolite	*p*-Nitrophenol	1.02	Aqueous solution	(Sismanoglu and Pura, 2001)
Polyaniline/attapulgite	Humic acid	61.35	Aqueous solution	(Wang et al., 2011)

Table 2.4 Comparison of various date palm adsorbents for the adsorption of different organic compounds

Adsorbent	Adsorbate	Maximum adsorption capacity (mg/g)	Solution	Reference
Raw date pits	Methylene blue	80.3	Aqueous solution	(Banat et al., 2003)
Raw date pits	Phenol	2.852	Aqueous solution	(Banat et al., 2004)
Activated date pits	Phenol	46.076	Aqueous solution	(Banat et al., 2004)
Date pits activated carbon	Phenol	56.9	Refinery wastewater	(El-Naas et al., 2010b)
Date pits activated carbon	Chemical Oxygen Demand	191.58	Refinery wastewater	(El-Naas et al., 2010a)
Palm pith carbon	2,4-Dichlorophenol	19.16	Aqueous solution	(Sathishkumar et al., 2007)
Date stone activated carbon	Methylene blue	148	Aqueous solution	(Alhamed, 2006)
Date stone AC	Sulfur	42.56	Model diesel fuel	(Alhamed and Bamufleh, 2009)
Acid treated date stone	Aldrin	6.369	Pesticide solution	(El Bakouri et al., 2009)
Steam activated carbons date pits	Methylene blue	103-244	Aqueous solution	(Ashour, 2010)
Steam activated carbons date pits	Remazol	43-173	Aqueous solution	(Ashour, 2010)
Date stone	Acid green 25	36.496	Aqueous solution	(Mahmoodi et al., 2010)
Date stone	Acid black 26	39.526	Aqueous solution	(Mahmoodi et al., 2010)
Date stone	Acid blue 7	33.784	Aqueous solution	(Mahmoodi et al., 2010)
Date stone	Phenol	0.131	Aqueous solution	(Okasha and Ibrahim, 2010)
Date pits activated carbon	p-cresol	322.58	Aqueous solution	(Merzougui and Addoun, 2008)

2.4.2.2. Factors affecting Adsorption

Several factors affect the adsorption process such as adsorbent doses, initial solution pH, initial concentration of adsorbate and temperature. Brief discussion of these factors is detailed below.

Effect of adsorbent dose

The dose of adsorbents is another factor that affects the capacity of adsorbate. In general, as the amount of adsorbent increases the removal percentage of adsorbate increases and the uptake capacity, mg/g decreases (Hameed and Daud, 2008, Apiratikul and Pavasant, 2008, Senturk et al., 2009, Yagub et al., 2012). The increase in the percentage of adsorbate removal with the elevation of the adsorbent dose can be attributed to the increase in the active adsorptive sites. While the decrease in the equilibrium adsorption capacity can be due to the fact that adsorbent would tend to aggregate as the adsorbent increase resulting in lower surface area availability for adsorption and causing an increase in the diffusion path length of the adsorbate.

Effect of initial concentration of adsorbate

Investigating the effect of initial concentration of adsorbate is very important as it affects the adsorption kinetics. The increase in initial adsorbate concentration enhances the interaction between adsorbent and adsorbate as reported by (Sen and Sarzali, 2008, Ahmad et al., 2005b, Özacar et al., 2008, Dawood and Sen, 2012).

Effect of pH

The variation in pH leads to the variation in the degree of ionization of the adsorptive molecule and the surface properties of the adsorbent. The ability of an adsorbent and the active surface properties is determined by the point of zero charge (pH_{pzc}). It is the point at which the surface charge is zero and it is used to quantify or define the electrokinetic properties of surface. On studies related to the application of date seeds as an adsorbent, (El Nemr et al., 2008) studied the effect of pH in the range of 1-7.2 on the removal of chromium from wastewater and they noticed that the removal percentage of chromium decreases with increasing pH. On the other hand (Al-Haidary et al., 2011) studied the effect of pH on lead removal and they concluded that the adsorption of lead increases with the increase in pH in the range of 1–4.5. Another study done by (El-Naas et al., 2010a) on the reduction of COD from refinery wastewater concluded that uptake of COD increase with increasing pH from 2-10.

Studies related to the application of natural clay like attapulgite on the adsorption process, (Al-Futaisi et al., 2007a) found the adsorption of dye onto palygorskite increases with increasing pH in the range of 3-12, while (Narine and Guy, 1981) concluded that at pH > 4, adsorption of organic cations decreased fairly rapidly when using bentonite as an adsorbent.

Effect of Temperature

Temperature is found to have a significant effect on the adsorption capacity of the adsorbent. In general, increasing solution temperature will result in decreasing adsorption somewhat because adsorbed molecules have great vibrational energies and are therefore more likely to desorb from the surface (Cooney, 1998). The adsorption process can be endothermic or exothermic. The adsorption process is classified as endothermic if the uptake increases with the increase in temperature. This can be attributed to the increase in the mobility of solutes and the increase in the number of active sites for the adsorption when temperature increases. On the other hand, the adsorption process is classified as exothermic if the adsorption uptake decreases when temperature increases. This can be due to the fact that an increase in temperature leads to a decrease in the adsorptive forces between the adsorbate and the active sites on the adsorbent. (El-Naas et al., 2010a) in their study found the uptake of COD increases with increase in temperature and this is due to the increase in the kinetic energy of the adsorbate with temperature, which enhances the adsorbate availability at the active sites of the adsorbent. Another study done by (Wang et al., 2012) concluded the removal of humic acids by palygorskite decreases when temperature increases suggesting an exothermic adsorption.

2.4.2.3. Theory of Adsorption

2.4.2.3.1. Adsorption Isotherms

Adsorption isotherms are key factor for describing adsorption capacity to facilitate evaluation of the feasibility of the process for a given application, for selection of the most appropriate adsorbent, and preliminary determination of adsorbent dose requirements (Slejko, 1985). The correlation of equilibrium data by empirical or theoretical equations is essential for the operation adsorption systems and practical design. The following adsorption isotherms were carried out by using Langmuir (1918), Freundlich (1906) and Dubinin- Radushkevich (1946) to explain adsorbate-adsorbent interaction. Table 2.5 represents isotherm models obtained by different researchers for various organic compounds removal by low-cost adsorbents.

Table 2.5 Isotherm models for various organic compounds adsorption

Adsorbents	Organic compound	Isotherm model	Reference
Coconut-shell AC	4-Chlorophenol	Langmuir	(Radhika and Palanivelu, 2006)
Coconut-shell AC	2,4,6-trichlorophenol	Langmuir	(Radhika and Palanivelu, 2006)
Apricot stone shell AC	2,4-Dichlorophenol	Langmuir	(Daifullah and Girgis, 1998)
Kraft black liquor AC	phenol	Langmuir	(Gonzalez-Serrano et al., 2004)
Treated Loofa sponge	Phenol	Langmuir	(Cherifi et al., 2009)
Rice straw	Phenol	Langmuir	(Amin et al., 2012)
Date pits activated carbon	Phenol	Langmuir	(El-Naas et al., 2010b)
Date pits activated carbon	Chemical Oxygen Demand	Langmuir	(El-Naas et al., 2010a)
Rubber seed coat AC	Basic blue 3	Freundlich	(Hameed and Daud, 2008)
Acid activated red mud	Congo red	Langmuir	(Tor and Cengeloglu, 2006)
Coir pith activated carbon	Congo red	Langmuir and Freundlich	(Namasivayam and Kavitha, 2002)
Activated palm ash	Acid dye	Freundlich	(Hameed et al., 2007)
Modified barley straw	Emulsified oil	Langmuir	(Ibrahim et al., 2010)
Neutralized red mud	Phenol	Freundlich	(Tor et al., 2006)

2.4.2.3.2. Adsorption Kinetics

In order to examine the controlling mechanisms of adsorption process covering mass transfer, chemical reaction and diffusion control, several models are available. They are Pseudo first- and second-order equations, intra-particle diffusion equation, liquid film diffusion model and double-exponential model. The kinetics of DOC adsorption is a useful tool for choosing the best operating conditions for the full-scale batch process. The study of the adsorption kinetics illustrates the solute uptake rate and obviously this rate controls the residence time of the adsorbate at the solution interface. This rate is important when designing the adsorption system and this rate can be calculated. Brief description of each of these models is detailed below. Table 2.6 represents kinetic models obtained by different researchers for various organic compounds removal by low-cost adsorbents.

Table 2.6 Kinetic models of various adsorbents for different organic compounds adsorption

Adsorbents	Organic compound	Kinetic model	Reference
Coconut-shell AC	4-Chlorophenol	Pseudo-second order	(Radhika and Palanivelu, 2006)
Coconut-shell AC	2,4,6-trichlorophenol	Pseudo-second order	(Radhika and Palanivelu, 2006)
Date pits activated carbon	Phenol	Pseudo-second order	(El-Naas et al., 2010b)
Date pits activated carbon	Chemical Oxygen Demand	Pseudo-second order	(El-Naas et al., 2010a)
Rubber seed coat AC	Basic blue 3	Pseudo-second order	(Hameed and Daud, 2008)
Perlite	Methylene blue	Pseudo-second order	(Doğan et al., 2004)
Coir pith activated carbon	Congo red	Pseudo-second order	(Namasivayam and Kavitha, 2002)
Bentonite	Acid red 57	Pseudo-second order	(Özcan and Özcan, 2004)
Coconut coir pith	2,4-Dichlorophenol	Pseudo-second order	(Namasivayam and Kavitha, 2005)
Date pits	Methylene blue	Pseudo-second order	(Banat et al., 2003)
Date pits	Phenol	Pseudo-second order	(Banat et al., 2004)
Diatomaceous clay	Methylene blue	Pseudo-second order	(Shawabkeh and Tutunji, 2003)
Na-Bentonite	Oil	Pseudo-second order	(Viraraghavan and Moazed, 2003)
Oil shale	4-Nitrophenol	Pseudo-second order	(Al-Asheh et al., 2004)

2.5 Summary

This chapter demonstrates the issues related to produced water treatment and its impact on the environment. Despite the fact that many technologies are available for produced water purification, many of them are not typically capable of reaching the new levels of purification demanded by the stringent environmental regulations without producing high volumes of hazardous wastes and having high operating expenses. Several studies have been conducted to treat and purify the oily produced water. However, there appears to be a shortage or lack of information about the use of adsorption for the removal of dissolved organic constituents from produced water.

Adsorption technology employing solid adsorbents are widely used to remove certain classes of chemical pollutants from wastewater. Commercial activated carbon (CAC) is found to be the most popular for the removal of pollutants from wastewater. However, activated carbon presents several disadvantages such as the high cost of activation and regeneration. The high initial cost of the materials used in the treatment process makes it unjustified. This has directed the researchers to look for economic adsorbents. Attention has focused on various natural solid materials, which are capable to remove the pollutants from the contaminated waste water at low cost. Certain waste products from industries and agricultural operations, natural materials and bioadsorbents represent potentially economical alternative adsorbents.

Several studies from literature reported promising findings in term of the removal of inorganic and organic pollutants from wastewater. Nevertheless, most of these studies focus on the treatment of aqueous solution for few studies deal with real wastewater with almost no study deal with the removal of dissolved organic carbon from produced water. The application of membrane filtration is found to be an excellent alternative for the purification of waste water. Ceramic membrane is considered as a robust type of membrane for the removal of oil from wastewater. Therefore, this chapter present up to-date development on the application of adsorption and membrane filtration especially ceramic membrane for the purification of produced water.

CHAPTER 3

RESEARCH METHODOLOGY

3.1. Introduction

This chapter addresses all the experimental and analytical work performed to obtain a suitable treatment process and conditions for the purification of oily produced water by using low-cost adsorbents and ceramic membrane. The performance and suitability of local adsorbents for the removal of dissolved organic carbon from the oily water were investigated. Different analytical techniques were applied to determine the physicochemical properties of adsorbents and produced water. The effect of initial DOC concentration, initial solution pH, adsorbent dose and temperature on the adsorption of DOC by date seeds and attapulgite was investigated. Batch experimental adsorption models applied to explain adsorption process including kinetic and isotherms models are also discussed in this chapter. The application of ceramic membrane for the purification of oily produced water under different operating conditions was also investigated.

3.2. Source of oily produced water (adsorbate)

The oily produced water in this study was collected from an oilfield in the south of Oman (Figure 3.1). The water was collected from the outlet of the Corrugated Plate Interceptor (CPI) unit where the oil content range from 250 to 350 mg/L.

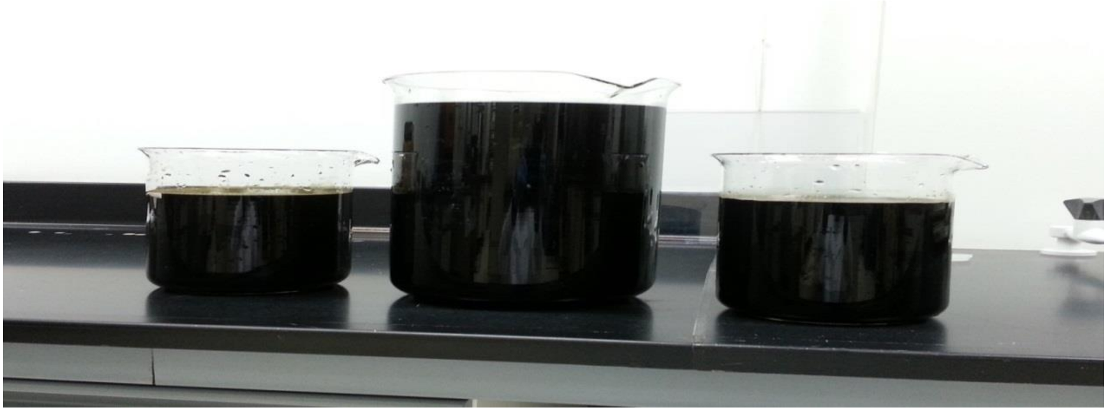


Figure 3.1 Oily produced water used in this study

3.3. Source of adsorbents

The date seeds were collected from local farm in Oman. The seeds were washed several times with distilled water to remove impurities and the residuals of the date fruit then dried in an oven at 65 ^oC for 24 hours. The dried biomass was crushed and then ground into small pieces by using grinder. The resultant powders were passed through British standard sieves with a size of 53-200 μm. Then the powder was placed in crucibles and left in the oven at 370 ^oC for 1 hour (Figure 3.2). The powder was stored in an airtight plastic container and used for analysis and adsorption trials.

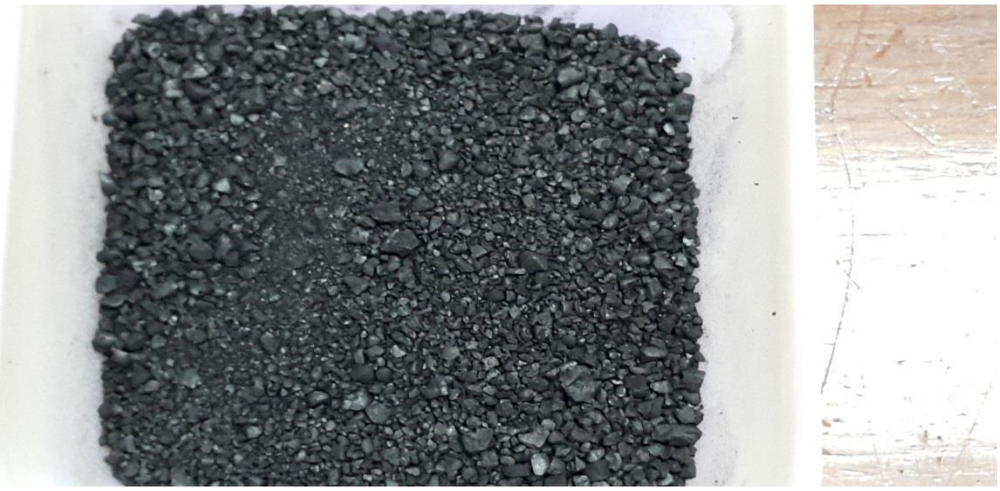


Figure 3.2 Date seeds used in this study

Another adsorbent material, namely attapulgite used in this study (Figure 3.3) was collected from Dhofar, southern part of Oman. The attapulgite was crushed by soil grinder into two different sizes granular (1 mm) and powder (0.25 mm).

(a) (b) (c) (d)

Figure 3.3 Attapulgite used in this study, (a and b) attapulgite B granular and powder respectively, (c and d) attapulgite A respectively.

3.4. Characterization of adsorbents

The adsorbents were characterized by using different types of analytical techniques such as Fourier Transform Infrared (FTIR), Scanning Electron Microscope (SEM), surface area (BET), Thermogravimetric analysis (TGA), particle density, and elemental oxides determinations.

3.4.1. Fourier Transform Infrared (FTIR)

In order to obtain the functional groups the adsorbents were analysed by using the Perkin-Elmer spectrum one FTIR spectrometer. A small portion of the adsorbent was mixed with Potassium Bromide KBr. The concentration of the sample in the KBr should be in the range of 0.2% to 1%. The mixture was ground in a mortar to a fine powder. A film was prepared by using hydraulic press. The film should be homogenous and transparent in appearance.

3.4.2. Scanning Electron Microscope (SEM)

A Scanning Electron Microscope (SEM) was used to study the morphological structure of adsorbent before and after adsorption. A small amount of adsorbent was placed on a 10 mm diameter Aluminum stub. Each sample was supported with a double side carbon adhesive on the stub. A secondary electron detector was used when dealing with secondary electron imaging and in case the image is not clear a conductive material like gold coating can be used. Samples were coated with a thin layer of gold using a sputter coating machine then screened using JEOL JSM-5600LV scanning electron microscope and micrographs were revealed

3.4.3. Surface area (BET)

The specific surface area of adsorbent was determined using the multi-point Brunauer–Emmett–Teller (BET) method. Nitrogen gas adsorption at 77.3 K was obtained using different values for relative vapour pressure (P/P_o).

3.4.4. X-ray diffraction

X-ray powder diffraction (XRD) patterns were performed on PANalytical X'Pert PRO diffractometer using Ni-filtered Cu-K_α radiation operating at a scan rate of 4 degree/min. The acceleration voltage and the applied current were 40 kV and 40 mA, respectively.

3.4.5. Thermogravimetric analysis (TGA)

Thermogravimetric analysis was performed to investigate the thermal degradation characteristics of adsorbent. TGA is widely used to study the thermal degradation properties of agricultural waste and other materials. TGA was performed using

Perkin Elmer (STA 6000) analyzer under inert atmosphere using N_2 gas. The experiments were conducted at heating rate of 5^oC/min and a gas flow of 20ml/min from 25^oC to 900^oC. At the start of the experiment, 30 min of N_2 purging was applied

3.4.6. Particle density

The particle density was measured using pycnometer method (a small glass container which can be filled repeatedly to a known volume) method. To calculate particle density the following equation was used

$$\rho_{s} = \frac{\rho_w m_o}{m_o - (m_{sw} - m_w)} \tag{3.1}$$

where ρ_s is the particle density of adsorbent (g/cm^3), ρ_w is the density of water (g/cm^3), m_o is the mass of oven-dry adsorbent (g), m_{sw} is the mass air-dry adsorbent plus pycnometer plus water (g), m_w is the mass of water plus pycnometer (g).

3.4.7. Elemental oxides

Major elemental oxides were determined by a Perkin Elmer AA 300 Atomic Absorption Spectrophotometer after the gravimetric determination of moisture at 103 -105 ^oC, Loss on Ignition at 1000 ^oC of the sample and then fused with Sodium carbonate at 1000 ^oC in a Muffle Furnace. The fused sample in the Platinum crucible was then treated with a 50:50 solution of Hydrochloric Acid: Hot water and the Silica separated on an ashless filter paper (No. 41). The silica in the ashless filter paper was then first ignited in a Bunsen burner and then place in the Muffle Furnace until constant weight. The Silica content was then determined by weight.

The filtrate after separation of silica was used to determine the other major elemental oxides except sodium and potassium.

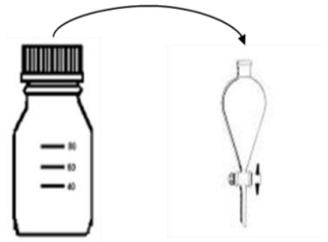
Sodium and potassium were determined by digesting a known quantity of the sample containing Hydrochloric Acid to Nitric Acid at a ratio of 3:1 and then filtered.

3.5. Characterization of oily water

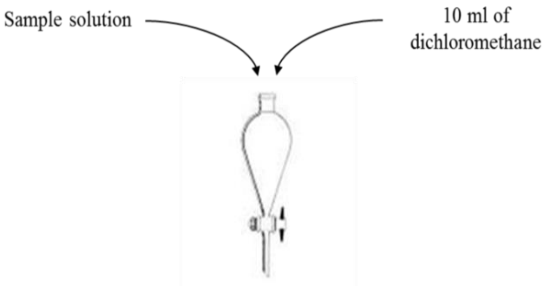
In order to evaluate the efficiency of the treatment process, the quality of water before and after the adsorption and membrane trials was evaluated. For the adsorption experiment dissolve organic carbon (DOC) was used as a key factor to check the efficiency of different adsorbents while total organic carbon, oil in water content, chemical oxygen demand, and pH were used for the feed and produced water from the ceramic membrane experiments.

3.5.1. Determination of oil in water content (OIW)

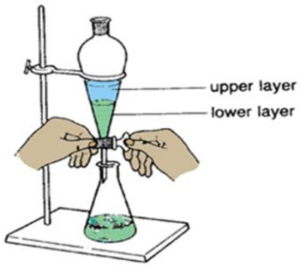
The oil in water content was obtained by using the step by step gravimetric method as shown in Figure 3.4. First of all, the sample is transferred to a separatory funnel. A sample amount of solvent (Dichloromethane) is added to the sample container to remove residues of hydrocarbons attached to the walls of the container. 10 ml of dichloromethane was added to the separatory funnel and the mixture was shaken for 5 minutes with regular pressure release. After 5 minutes the separatory funnel where left to stand so that the mixture is settled forming two layers where the bottom layer is the dichloromethane that is holding the dissolved oil. That layer was drained off and passed over anhydrous sodium sulphate to remove any water traces may present. The sodium sulphate is placed over a piece of non-absorbent cotton wool. This step is repeated twice to ensure that all the oil in sample is drained and removed from the mixture. The sample is collected in a boiling flask. Then the sample is placed in a rotary evaporator (Buchi R-215) to remove any solvent present. The rotary evaporator is set at (500 mbar) and (40 ^{o}C). Then, the flask was placed in a desiccator. Finally the weight of the dried sample with the flask is recorded and subtracted from the initial weight of the flask to determine the amount of oil present in the sample.



Step 1: Transfer sample to separatory funnel



Step 2: Extraction method



Step 3: Drain off the oily layer

Step 4: Rotary evaporator

Figure 3.4 Gravimetric method for OIW determination

3.5.2. Total Organic Carbon (TOC)

The determination of TOC was done by using TOC–V_{CPN} analyzer from Shimadzu, Japan (Figure 3.5). The samples were acidified with hydrochloric acid and sparged with zero air to remove inorganic carbon. The sample is then injected into a heated reaction chamber with catalyst at 680 ^{o}C. The water is vaporized and the organic carbon oxidized to carbon dioxide and water by catalytic combustion. The CO_2 formed is transported to the detector in a carrier gas stream. To measure the TOC concentration of the sample, the relationship between the TOC concentration and peak area (calibration curve) is predetermined using a TOC standard solution, to express the peak area as a ratio of the TOC concentration. The amount of CO_2 is directly proportional to the concentration of carbonaceous material in the sample.

Figure 3.5 TOC analyzer

3.5.3. Dissolved Organic Carbon (DOC)

Dissolved organic carbon (DOC) represents the amount of dissolved organic compounds in water and operationally can be defined as organic matter that can pass through a 0.45 µm filter. The samples were first filtered through 0.45 µm filter before they are analysed by TOC–V_{CPN}.

3.5.4. Chemical Oxygen Demand (COD)

Chemical Oxygen Demand (COD) is a measure of the oxidisable organic matter present in a wastewater sample. COD samples were prepared with a closed-reflux digestion using CHEMetrics COD reagent. Determinations were made colorimetrically with USEPA method for analysis of water and wastes, method 410.4. The sample was digested with an acidic solution of potassium dichromate in the presence of catalyst (silver) and digested for 2 hours at a temperature of 150° C. Oxidizable organic compounds reduce the dichromate ion ($Cr_2O_7^{2-}$) to the chromic ion (Cr^{3+}).

3.5.5. pH

The measurement of pH in the aqueous solution was measured with the use of a pH sensitive glass electrode, a reference electrode and a pH Meter. Glass electrodes are sensitive to the hydrogen ion activity in a solution. The measurements for pH were performed immediately to avoid any changes might happen due to the contact with air. The pH electrode was rinsed with distilled water before and after each measurement. The pH meter was calibrated periodically using buffer solutions (pH 4, 7 and 10) and the temperature was maintained constant during the measurement of pH.

3.5.6. Dissolved Organic Hydrocarbons

GC-MS analysis was performed on a Perkin Elmer Clarus 600 GC System, fitted with a Rtx®-5MS capillary column (30m × 0.25mm i.d. × 0.25µm film thickness; maximum temperature, 350℃), coupled to a Perkin Elmer Clarus 600C MS. Ultra-high purity helium (99.9999%) was used as carrier gas at a constant flow of 1.0 ml/min. The injection, transfer line and ion source temperatures were 290, 280 and 280 ℃, respectively. The ionizing energy was 70 eV. Electron multiplier (EM) voltage was obtained from auto tune. All data were obtained by collecting the full-scan mass spectra within the scan range 40-550 amu. The injected sample volume was 1 µl with a split ratio of 10:1. The oven temperature program was 80 ^{o}C (holds for 5 min) and accelerated at a rate of 10^{o} C / min until it reach 280 ^{o}C (holds for 30 minutes). The unknown compounds were identified by comparing the spectra obtained with mass spectrum libraries (NIST 2011 v.2.3 and Wiley, 9th edition). The standard mix solution (C7-C40) of concentrations 10, 20, 30, 40 and 50 mg/L were used for confirmation and quantification purposes

3.6. Adsorption experiments

The adsorption of DOC onto adsorbent was investigated through a batch process of known dose of adsorbent with 150 ml of oily produced water of known concentration in a series of 250 ml conical flasks. The mixture was agitated in a mechanical shaker at 150 rpm for 120 minutes (the time required to reach equilibrium between DOC adsorbed and DOC in solution). After reaching equilibrium, the suspension was filtered through 0.45 µm of cellulose nitrate filter and the filtrate was analyzed for DOC by using TOC analyzer.

The amount of DOC adsorbed by adsorbent at time t, q_t (mg/g) was calculated by the following equation:

$$q_t = \frac{(C_o - C_t)V}{m} \tag{3.2}$$

The DOC removal efficiency i.e. % of adsorption was calculated by the following equation

$$\% \, adsorption = (C_o - C_t) \times 100/C_o \tag{3.3}$$

Isotherm studies were conducted using fixed adsorbent dose and varying the initial concentration of the oily produced water in the range (18-93mg/l). The amount of adsorption at equilibrium q_e (mg/g) was calculated according to

$$q_e = \frac{(C_o - C_e)V}{m} \tag{3.4}$$

where C_o (mg/L) is the initial DOC concentration, C_t (mg/L) is the concentration of DOC at any time t, V (L) is the volume of solution and m (g) is the mass of adsorbent.

Adsorption experiments were conducted by varying the initial DOC concentration, initial solution pH, adsorbent dose and temperature to investigate the adsorption kinetics, adsorption isotherm and thermodynamics.

3.6.1. Effect of contact time

The adsorption of DOC onto the adsorbent as a function of contact time was investigated to determine the equilibrium stage. For this purpose, 0.5 g of adsorbent was placed in 150 ml of produced water with DOC concentration of 93.5 mg/L at a pH value of 8.9. The samples were taken at different intervals and the level of DOC in solution was measured with time to gauge the changes in concentration of DOC

3.6.2. Effect of adsorbent dose

The effect of adsorbent dose on the adsorption of DOC from oily produced water was investigated by using three different doses (0.5g, 1.0 g, 2.0 g), 150 ml of oily produced water with DOC concentration of 93.5 mg/L, pH of 8.9 and agitation speed set at 150 rpm.

3.6.3. Effect of adsorbate concentration

The effect of DOC concentration on the adsorption of DOC from oily produced water was investigated by using three different concentrations (18.5 mg/L, 57 mg/L, and 93.5 mg/L), 150 ml of oily produced water with 0.5 g of adsorbent, pH of 8.9 and agitation speed set at 150 rpm.

3.6.4. Effect of temperature

In order to investigate the effect of temperature on the removal efficiency of DOC, the experiments were carried out with DOC concentration of 97.3 mg/L, 1.0 g of adsorbent, pH of 8.9 and agitating speed of 150 rpm over the range 25–45 ^{o}C.

3.6.5. Effect of solution pH

In order to evaluate the effect of the initial pH on the uptake of DOC, the experiments were carried out with initial DOC concentration of 18 mg/L and 0.5 g of adsorbent and 150 rpm agitated speed over the pH range of 4–9. The pH of solution was adjusted by adding either 0.1 M of NaOH or 0.1 M of HCl.

3.6.6. Adsorption experimental models

3.6.6.1. Isotherms models

The distribution of adsorbate between liquid and solid phases is generally described by isotherm models. For this purpose the following isotherm models were used:

Langmuir Adsorption Isotherm

This model is based on the assumption that all adsorption sites are equivalent and the adsorbate form a monolayer on the outer surface of the adsorbent and after that no further adsorption will take place.

The linearized form of Langmuir equation is expressed as (Langmuir, 1918):

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m k_L C_e} \tag{3.5}$$

where q_e (mg/g) is the amount of DOC adsorbed per gram of adsorbent at equilibrium, q_m (mg/g) is the maximum adsorption capacity corresponding to complete monolayer coverage, C_e (mg/l) is equilibrium concentration of DOC in solution and K_L (L/mg) is the Langmuir constant. q_m and K_L can be found from the plot of 1/ q_m vs 1/ C_e.

Freundlich Adsorption Isotherm

This model is valid for multilayer adsorption on a heterogeneous adsorbent surface that has unequal available sites with different energies of adsorption. The linearized form of Freundlich model can be written as (Slejko, 1985):

$$\mathrm{lnq_e} = \mathrm{lnK_f} + \frac{1}{\mathrm{n}}(\mathrm{lnC_e}) \tag{3.6}$$

where q_e (mg/g) is the amount of DOC adsorbed per gram of adsorbent at equilibrium, and C_e (mg/l) is the equilibrium concentration of DOC in solution. K_f is the capacity of the adsorption constant and n is the empirical parameter related to the intensity of adsorption. K_f and n can be found by plotting ln q_e vs ln C_e.

Dubinin-Radushkevich Adsorption Isotherm

This model is applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface. The linearized form of D-R model can be expressed as (Dubinin and Radushkevich, 1966):

$$ln q_e = ln q_m - \beta \varepsilon^2 \tag{3.7}$$

where q_e (mg/g) is the amount of DOC adsorbed per gram of adsorbent at equilibrium, q_m (mg/g) is the maximum adsorption capacity, β a constant related to adsorption energy, and ε is the Polanyi potential which is related to the equilibrium concentration as shown in the following equation:

$$\varepsilon = RTln(1 + \frac{1}{C_e}) \tag{3.8}$$

where, R is the gas constant (8.314 J/molK) and T is the absolute temperature in K.

3.6.6.2. Kinetic models

The following kinetic models were used in this study:

Pseudo First-Order model

The differential equation is generally expressed as (Largergren, 1898)

$$\frac{dq_t}{dt} = K_1\,(q_e - q_t) \tag{3.9}$$

Where, q_t and q_e (mg/g) are adsorption capacity at time t and at equilibrium respectively, k_1 (L/min) is the rate constant of pseudo-first order adsorption, and t (min) is the contact time. The linearized integral form is:

$$Log(q_e - q_t) = Logq_e - \frac{K_1}{2.303}\,t \tag{3.10}$$

Plotting $Log\,(q_e - q_t)$ vs t give a linear relationship from which k_1 and predicted q_e can be determined from the slope and intercept of the plot respectively.

Pseudo Second-Order Model

The differential equation is generally expressed as (Ho and McKay, 1999)

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \tag{3.11}$$

Where, k_2 (g/mg min) is the second-order rate constant of adsorption. The linearized integral form is

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{3.12}$$

Plotting t/q_t vs t shows a linear relationship. k_2 and qe were obtained from the intercept and slope of the plot of t/q_t vs t. The constant k_2 is used to calculate initial sorption rate h, as follows

$$h = k_2 q_e^2 \tag{3.13}$$

3.6.6.3. Kinetic diffusion models

The diffusion study is significant as the pseudo first order and second order models failed to explain the diffusion mechanism during the adsorption process. Although the kinetic studies help to identify the sorption process, predicting the mechanisms is required for design purposes. For this purpose the following models were used:

Intra-particle Diffusion Model

This model is commonly used for identifying the adsorption mechanism for designing purposes. The so-called homogeneous solid diffusion model (HSDM), which can describe mass transfer in an amorphous and homogeneous sphere (Cooney, 1998). According to weber and Morris (1963), for most adsorption processes, the uptake varies almost proportionally with $t^{0.5}$ rather than with the contact time. The equation can be expressed as (Weber and Morris, 1963)

$$q_t = k_{id} t^{0.5} \tag{3.14}$$

Where q_t (mg/g) is the adsorption capacity at time t, k_{id} (mg/g min $^{0.5}$) is the rate constant of intra-particle diffusion, and $t^{0.5}$ (min) is the square root of time. Plotting q_t vs $t^{0.5}$ gives a linear relationship, k_{id} can be determined from the slope of the plot.

Liquid Film Diffusion Model

In liquid/solid adsorption systems the rate of solute accumulation in the solid phase is equal to that of solute transfer across the liquid film according to the mass balance law. This model can be written as (Boyd et al., 1947):

$$\ln\left(1 - {}^{q_t}/_{q_e}\right) = -K_{fd}t \tag{3.15}$$

Where $ln\ (1-\ q_t/q_e)$ is the fractional attainment of equilibrium, and k_{fd} is the film diffusion rate constant. Plotting $ln\ (1-\ q_t/q_e)$ vs t gives a linear relationship, k_{fd} can be determined from the slope of the plot.

Double-Exponential Model

A double-exponential function proposed by Wilczak and Keinath (1993), is used to describe the adsorption process and can be divided into two steps, namely a rapid phase involving external and internal diffusions, followed by a slow phase controlled by the intra-particle diffusion. This model can be written as (Wilczak and Keinath, 1993):

$$q_t - q_e = \exp(-K_1 t) - \exp(-K_2 t) \tag{3.16}$$

If $k_1 >> k_2$, it means that the rapid process can be assumed to be negligible on the overall kinetics and the linearized form of the equation is

$$\ln(q_e - q_t) = -K_2 t \tag{3.17}$$

Where q_t and q_e (mg/g) are adsorption capacity at time t and at equilibrium respectively, k_1 (min^{-1}) is diffusion parameters of the rapid step and k_2 for the slow step. Plotting $ln\ (q_e-q_t)$ vs t gives a linear relationship, k_2 can be determined from the slope of the plot.

3.6.7. Thermodynamic Study

The feasibility of adsorption process can be evaluated by the thermodynamic parameters such as free energy (ΔG^o), enthalpy (ΔH^o), and entropy (ΔS^o). These parameters can be calculated from the following equations:

$$\Delta G^o = -RTlnK_d \tag{3.18}$$

Where

$$K_d = \frac{q_e}{C_e} \tag{3.19}$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{3.20}$$

Equation (3.20) can be written as

$$lnK_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{3.21}$$

Where q_e (mg/g) is the adsorption capacity at equilibrium, C_e (mg/l) is the equilibrium concentration of DOC in solution, T is the temperature in (K), K_d is the distribution coefficient and R is the universal gas constant (8.314 J/mol K). ΔH^o and ΔS^o were obtained from the slope and intercept of the plot between $ln\ K_d$ vs $1/T$.

3.7. Ceramic membrane Trials

In order to investigate the application of ceramic membrane for the purification of oily produced water a lab scale unit was designed for cross-flow ceramic membrane trials (

Figure 3.6 and Figure 3.7). The setup consists of a feed tank, two centrifugal pumps, and ceramic membrane (with 50 nm pore size). A mixer with temperature control device was placed in the feed tank in order to make the feed water homogenous and to control the temperature of the feed water. Three pressure gauges were installed, one for the feed water, the second one for the permeate water and the third one for the retentate or the brine. Two water meter were installed for the feed and the permeate water. During the experiment, three different temperatures were tested 25 ^{o}C, 35 ^{o}C and 45 ^{o}C. Four different pressure sets were investigated 1.3 bar, 3 bars, 5 bars and 7 bars. Samples were taken at different time intervals 5 min, 30 min, 60 min, 120 min and 180 min to monitor the quality of the permeate by checking the oil in water (OIW) content, COD, TOC, turbidity, Electrical conductivity (EC) and pH. The water volume in feed and permeate was recorded with time to check the performance of the membrane and to test for any membrane fouling.

Membrane cover module

Water flow meters

Ceramic membrane, pressure gauges and connectors

Figure 3.6 Parts of the ceramic membrane unit

Figure 3.7 Experimental set-up for ceramic membrane trials

The membrane was operated under different operating conditions. The removal of a certain compound from the feed is expressed as

$$Removal\ (\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \tag{3.22}$$

where C_p, mg/L is the concentration of a certain component in permeate and C_f, mg/L is its feed concentration.

The recovery rate of the membrane at different operating conditions was evaluated according to

$$Recovery\ Rate\ (\%) = \frac{Q_p}{Q_f} \times 100 \tag{3.23}$$

where Q_p, L/hr is the permeate flow rate and Q_f, L/hr is the feed water flow to the membrane unit.

The permeate flux (L/m^2 hr) was measured during the separation process by dividing the permeate volume (L) by the effective membrane area (m^2) and the sampling time (h)

$$permeate\ flux\ (J) = \frac{permeate\ volume\ collected}{membrane\ area\ \times time} \tag{3.24}$$

Backwashing was used to clean the membrane. The pump was run for 30 seconds at low pressure (less than 2 bars). This was enough to remove the oil droplets and other impurities from the membrane. Then the water was allowed to pass through membrane to clean-up the remaining impurities. This was done until the initial flux was recovered (5-10 min) at different pressures (2- 3 bars). Tap water at room temperature was used for backwashing and rinsing the membrane. The use of hot water at 50 ^{o}C would enhance the process of cleaning and to recover better flux.

CHAPTER 4

PHYSICO-CHEMICAL CHARACTERIZATION OF ADSORBENTS

4.1. Introduction

This chapter discusses the characterization of date seeds and attapulgite type A and B (granular and powder form). The characterization of the adsorbents, physico-chemical parameters, is of so important for the evaluation and development of the adsorption process. In this study, the adsorbents were characterized by using Scanning Electron Microscope (SEM), Fourier Transform Infrared (FTIR), and Thermogravimetric analysis (TGA). Specific surface area and particle density were also obtained by using BET method and pycnometer method respectively.

4.2. Characterization of Date Seeds

4.2.1. Morphology

The surface morphology of date seeds was investigated by using SEM analysis. Figure 4.1 represents the availability of pores, active sites for adsorption, in the surface of date seeds before treatment and the accumulation of organic compounds, i.e. different types of hydrocarbons presents in oily produced water, after the adsorption process. Most of the pores get filled with hydrocarbons after adsorption leaving no more sites for adsorption.

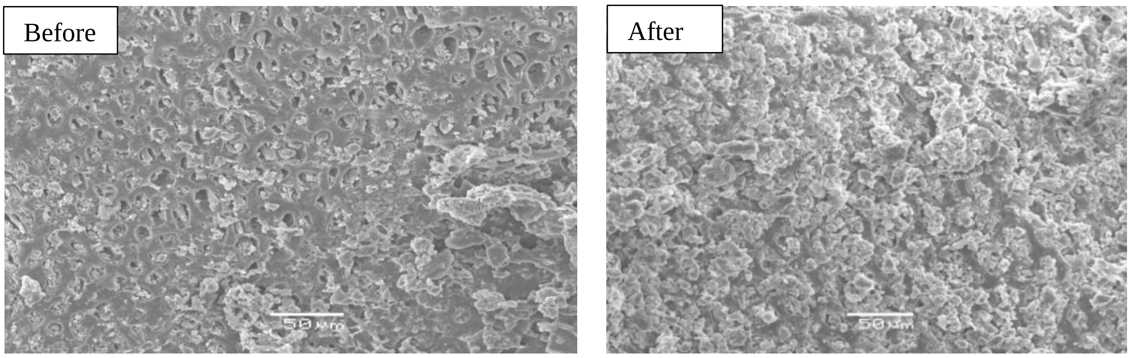


Figure 4.1 SEM images of date seed before and after DOC adsorption

4.2.2. Functional groups

Date palm seeds are composed mainly of protein, oil and carbohydrates. The most abundant fatty acids in date seeds are oleic, lauric, palmitic, capric, myristic and stearic (Nehdi et al., 2010, Besbes et al., 2004, Sait et al., 2012, Babiker et al., 2013). Date seeds contain different functional groups that form active sites for sorption on the surface of the material. The FTIR spectra patterns for date seed raw and ash are shown in Figure 4.2. The raw date seed is composed of a mixture of functional groups. The O-H stretch functional group can be seen by the band at 3342.7 cm^{-1} while the C-H stretch (alkane) is indicated by 2928.3 cm^{-1} and the C-H stretch appears at 2845 cm^{-1}. The rest of the functional groups ranges between C=O, C=C, C-N, P=O and =C-H bend. The main functional groups are O-H stretch, S-H, C-N stretch, N=O and P=O. Several functional groups were vanished during physical activation as volatile organic matter volatiles and consequently pores are formed.

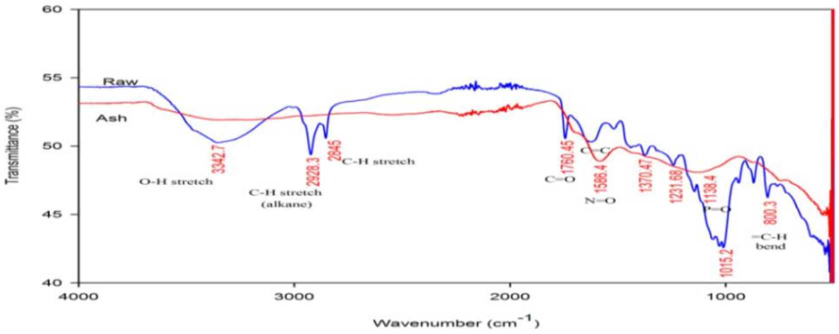


Figure 4.2 FTIR spectra of date seeds in raw and ashed form

4.2.3. Thermogravimetric analysis

The thermal decomposition of date seeds was obtained by the thermographimetric analysis. The initial mass loss region occurred between 30°C and 240°C which accounts for moisture loss and volatilization of light molecules. The major loss in mass, which is due to devolatilization, reaches its maximum around 430°C. From Figure 4.3 it was found that the glass transition point is at 370°C. After this temperature, there was gradual decrease in the weight loss. This can be attributed to the decomposition process of the remaining solid residues or char, which continued until 900°C. Delta T curve indicate that date seeds shows exothermic nature from 85-615 °C because of the physical transformation to the crystalline form probably while after 615 °C date seeds showed endothermic nature.

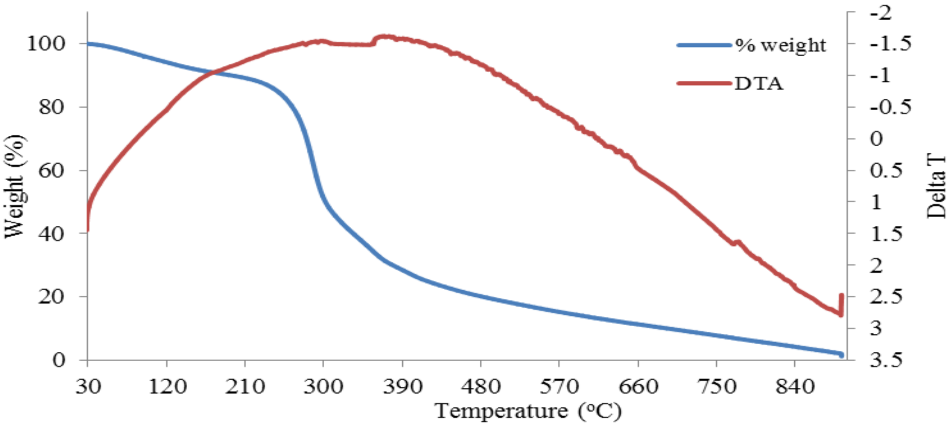


Figure 4.3 TGA and DTA of date seeds

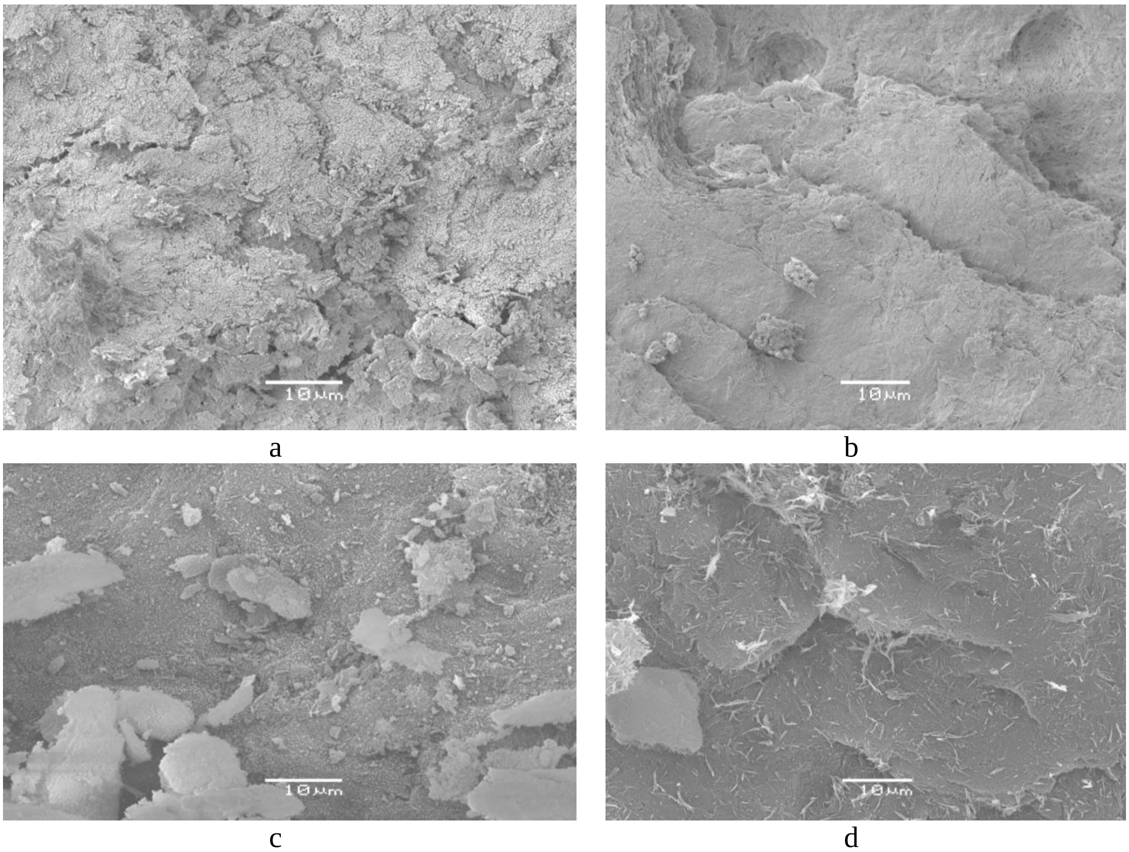
4.2.4. Surface area, Particle density and X-ray diffraction

The specific surface area of date seed was determined using the multi-point BET method and it is found to be 104 m^2/g. The particle density is analyzed by pycnometer method and it is found to be 2.83 g/cm^3. The X-ray diffraction analysis indicate that SiO_2 was the predominant crystalline phase. Specific surface area and particle density are of great importance for the adsorption process and the design of column or towers in a pilot scale or large commercial applications. The particle density is relatively well-defined quantity, as it is not dependent on the degree of compaction of the solid. The higher surface area indicates higher area for interaction and adsorption.

4.3. Characterization of Attapulgite

4.3.1. Morphology

Scanning Electron Microscope (SEM) of attapulgite type A (granular and powder) and attapulgite type B (granular and powder) before and after adsorption of organic compounds is shown in Figure 4.4 and Figure 4.5.

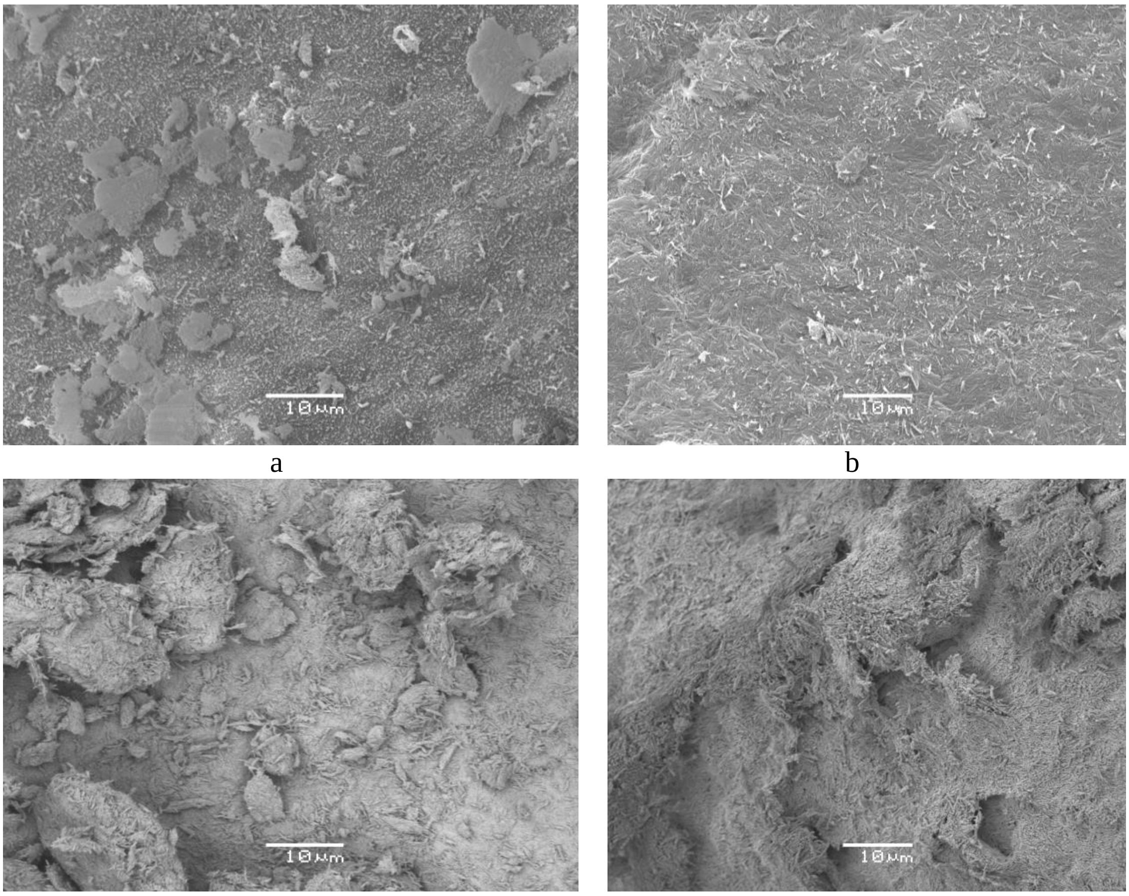


a b

c d

Figure 4.4 SEM of attapulgite type A, a) and b) granular attapulgite before and after adsorption respectively, c) and d) powdered attapulgite before and after adsorption respectively

SEM analysis reflects the richness of attapulgite fibers in the clay of Dhofar. The fibers may exist as well separated fibers or as aggregates of clay fibers (Al-Futaisi et al., 2007b). This variation in the form or existence of the fibers cause variation in the pore spaces ranging between tiny pores between the individual fibers and bigger pores between the aggregated fibers (Al-Futaisi et al., 2007a).



a b

c d

Figure 4.5 SEM of attapulgite type B, a) and b) granular attapulgite before and after adsorption respectively, c) and d) powdered attapulgite before and after adsorption respectively

4.3.2. Functional groups

The FTIR spectra patterns of attapulgite type A and type B are shown in Figure 4.6. The stretching of structural hydroxyl (OH) groups and Si-O stretching are the main functional groups in both types. Similar results were found by (García-Romero et al., 2004, Zhu et al., 2011, Chen and Zhao, 2009). The OH stretching vibration region can be seen at 3500 cm^{-1} while the Si-O can be seen at lower wavelength.

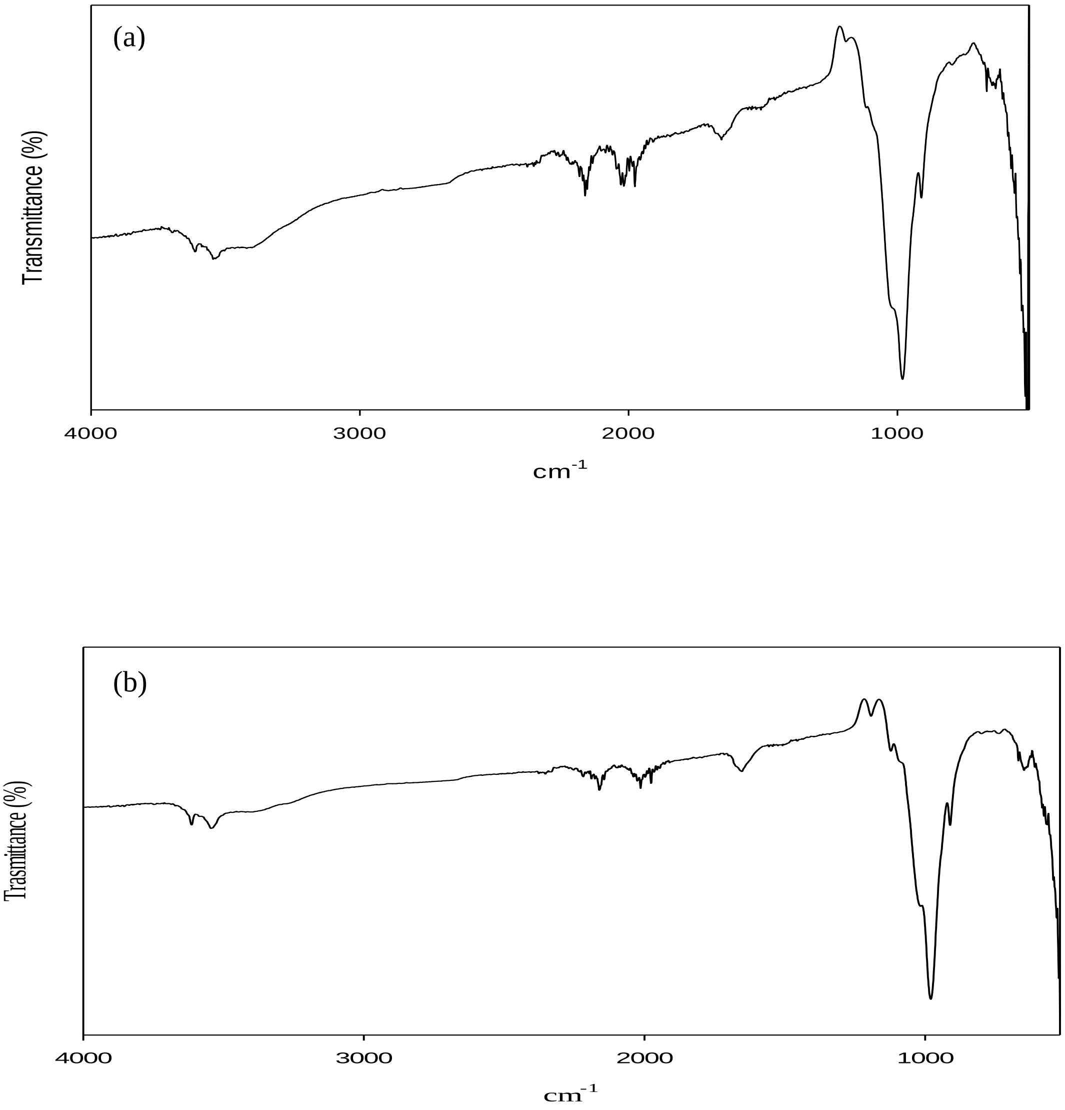
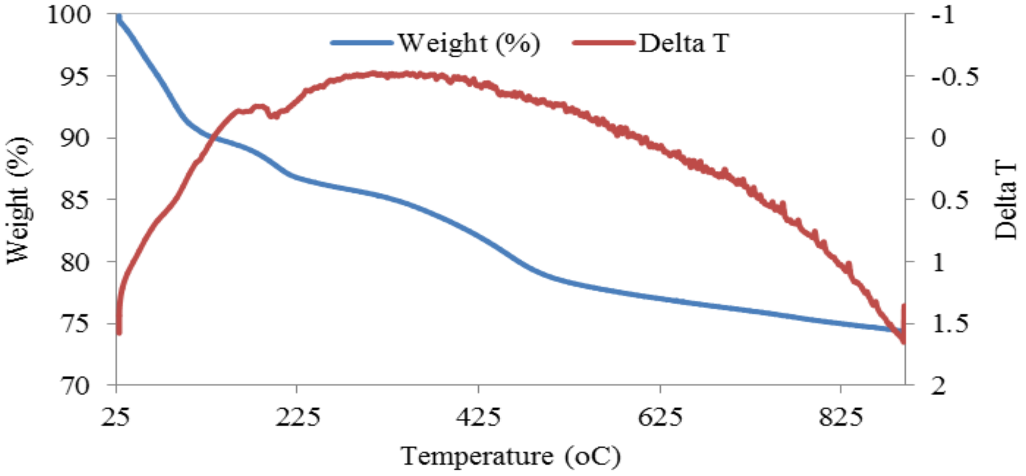


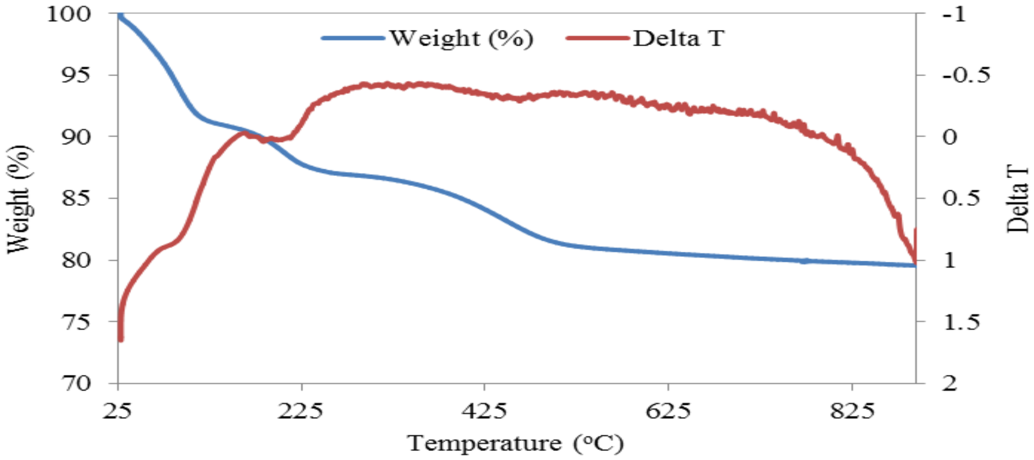
Figure 4.6 FTIR spectra's of attapulgite, (a) attapulgite A and (b) attapulgite B

4.3.3. Thermogravimetric analysis

Figure 4.7 shows the thermogravimetric analysis of attapulgite A and B. For attapulgite type A the mass loss is found to take place at 105 ^{o}C, 210 ^{o}C, 342 ^{o}C and 500 ^{o}C. Around 21% of the attapulgite A is lost between 25 ^{o}C and 500 ^{o}C and around 3% lost beyond 500 ^{o}C. While for attapulgite type B, the mass loss is found to take place at 120 ^{o}C, 235 ^{o}C, 375 ^{o}C and 520 ^{o}C. Around 19% of the attapulgite B is lost between 25 ^{o}C and 520 ^{o}C and there was no loses in weight beyond 500 ^{o}C. Delta T showed positive values which indicate an endothermic nature of the sample.



(a)



(b)

Figure 4.7 TGA and DTA of attapulgite, (a) attapulgite A and (b) attapulgite B

4.3.4. Surface area, particle density and X-ray diffraction

The specific surface area of attapulgite was determined using the multi-point BET method. For attapulgite A, the specific surface area was found to be 86.7 and 83.68 m^2/g for powdered and granular form respectively while the specific surface area of attapulgite type B was found to be 90.73 and 87.50 m^2/g for powdered and granular form respectively. The particle density was determined by pycnometer method. The particle density was found to be 2.42 and 2.28 g/cm^3 for granular and powder attapulgite A respectively and 2.47 and 2.42 g/cm^3 for granular and powder attapulgite B respectively. The X-ray diffraction analysis indicate the presence of Palygorskite ($(Mg, Al)_2Si_4O_{10}(OH).4(H_2O)$) in both types of attapulgite. Less palygorsite is present in Type A compared to Type B with the presence of other minerals like illite and chorite.

4.3.5. Elemental Analysis

The chemical composition of the attapulgite type A is presented in Table 4.1. The most abundant constituent of the attapulgite is SiO_2 (58.9%) followed by Al_2O_3 (13.3%). Fe, Ca and Mg oxides are found in lower percentages.

Table 4.1 Chemical composition (in wt. %) of attapulgite A

Composition	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	Loss On Ignition	Moisture
%	58.9	13.3	5.1	0.08	5.4	1.4	0.2	12.1	12.6

Similar results were found for attapulgite type B, Table 4.2. The most abundant constituent is SiO_2 (55.7%) followed by Al_2O_3 (11.5%). Fe, Ca and Mg oxides are found in lower percentages.

Table 4.2 Chemical composition (in wt. %) of attapulgite B

Composition	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	Loss On Ignition	Moisture
%	55.7	11.5	5.1	0.09	8.2	1.0	0.1	13.6	9.4

4.1. Summary

The characterizations of date seeds and attapulgite were presented in details in this chapter. The study of physico-chemical properties helps in understanding the adsorption process of DOC by date seeds and attapulgite. Table 4.3 represents the physicochemical properties of the adsorbents.

Table 4.3 various physico-chemical parameters of adsorbents

parameters	Date Seeds	Attapulgite A		Attapulgite B	
		Granular	Powder	Granular	Powder
Surface Area (m^2/g)	104	83.68	86.7	87.5	90.73
Particle Density (g/cm^3)	2.42	2.42	2.28	2.47	2.42
Functional Groups	SiO_2	Palygorskite Illite Chlorite	Palygorskite Illite Chlorite	Palygorskite Illite Chlorite	Palygorskite Illite Chlorite
X-ray diffraction	O-H stretch C=O C=C C-N P=O =C-H bend	O-H stretch Si-O stretch	O-H stretch Si-O stretch	O-H stretch Si-O stretch	O-H stretch Si-O stretch

CHAPTER 5

REMOVAL OF DOC BY DATE SEEDS

5.1. Introduction

This chapter discusses the investigation of effectiveness of date seeds as a low-cost adsorbent for the removal of dissolved organic carbon (DOC) from produced water.

The date (*Phoenix dactylifera*) is considered as a valuable crop in arid and semiarid regions. A date consists of a fleshy pericarp which forms around 85-95% of the fruit weight (Elleuch et al., 2008). Dates can be an excellent source of food energy because of the high content of carbohydrates (70-80%) while the date seeds are considered as a waste by-product constitutes around 10% of the fruit weight (Hamada et al., 2002). Date seeds are used as a feed for cattle, sheep, camel and poultry (Rahman et al., 2007). It plays an important part in the social and economic lives of the people living in these regions (Briones et al., 2011, Besbes et al., 2004) and it is used as an adsorbent to purify wastewater from different constituents (Al. Haddabi et al., 2015, Banat et al., 2003, Al-Ghouti et al., 2010, El Nemr et al., 2008, Haimour and Emeish, 2006, Alhamed, 2009, Hameed et al., 2009, Mane et al., 2005, El-Naas et al., 2010b, El-Naas et al., 2010a, Al-Muhtaseb et al., 2008, Ahmad et al., 2007, Hameed et al., 2007). Adsorption of organic compounds is practiced with different types of adsorbents (Yang et al., 2002, Banerjee et al., 1997, Doyle and Brown, 1997). There is a great need to look for non-conventional, low cost adsorbents that are efficient and economically feasible for removing dissolved organic compounds from oily water. Large quantities of date seeds are produced every year as agricultural by-product. Date seeds can be utilized as a low cost adsorbent for the removal of DOC form oily produced water. This study aims to explore the applicability of date seeds as an adsorbent for the removal of DOC from oily produced water. The study investigates the adsorption isotherms, adsorption kinetics and the mechanism of adsorption under different operating conditions including the effect of contact time, solution pH, initial DOC concentration, adsorbent dose and temperature on the uptake of DOC onto date seeds. Several kinetic models namely Pseudo-first order, pseudo-second order, intra-particle diffusion, liquid film diffusion, and double exponential models are applied to understand the mechanism of adsorption. The thermodynamic parameters such as free energy (ΔG^o), enthalpy (ΔH^o), and entropy (ΔS^o) were obtained to evaluate the feasibility of adsorption process.

5.2. Materials and methods

5.2.1. Produced water

The oily produced water in this study is collected from an oilfield located in the southern part of Oman. The oil content in produced water varies from 250 to 350 mg/L.

5.2.2. Adsorbent (date seeds)

Date seeds were collected from a local farm in Oman. The seeds were washed for several times with distilled water to remove impurities and the residuals of the date fruit and placed in an oven at 65^{o}C for one day. The dried biomass was crushed and then ground into small pieces by using grinder. The resultant powders were sieved to the desired size. The powder was placed in crucibles and left in the oven at 370^{o}C for 1 hour. The powder was kept in a plastic container. The glassware used in the experiment were soaked in a 10% (v/v) nitric acid for 24 hours before running the experiment and then washed with distilled water for several times.

5.2.3. Adsorption experiments

Adsorption measurements were performed through batch experiments of known amount of the adsorbent with 150 ml of produced water of known concentration in a series of 250 ml conical flasks. The mixture was placed in a mechanical shaker and agitated at 150 rpm for 120 minutes. After that, the mixture was filtered through 0.45 µm cellulose nitrate filter and the filtrate was analyzed for DOC by using a TOC analyzer. The effect of different physicochemical parameters like the initial DOC concentration, initial solution pH, contact time, date seeds dose and temperature on the removal of DOC was investigated

5.3. Results and Discussion

5.3.1. Effect of contact time

The removal rate of DOC was high at the beginning and then the rate starts to decrease with time until it reaches equilibrium (Figure 5.1). This can be attributed to the fact that at the beginning the adsorption sites were unoccupied and highly available and as time proceeds less sites become available. The equilibrium stage was attained within 120 minutes and thus, the rest of adsorption trials were conducted for a contact time of 120 minutes. The equilibrium time is independent of initial DOC concentration. The physico-chemical properties of the adsorbent play a major role to determine the equilibrium capacity and rate. System properties such as solution pH, temperature and mixing speed have an influence on the adsorption process (Crini, 2006, Slejko, 1985, Özacar and Şengil, 2003, Özacar, 2003).

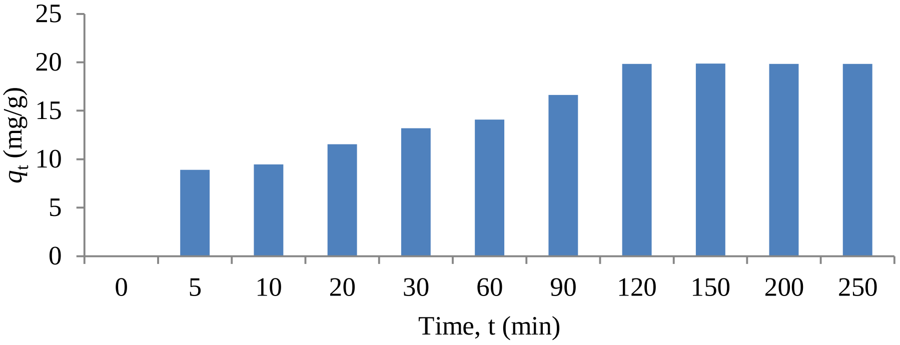


Figure 5.1 Effect of contact time on the adsorption of DOC onto date seeds (initial DOC concentration of 93.5 mg/l, pH: 8.9, date seeds dose: 0.5, agitation speed: 150 rpm, volume of solution: 150 ml)

5.3.2. Effect of adsorbent dose

Study of the effect of the amount of adsorbent, which is usually referred to as the adsorbent dose (grams of adsorbent per 150 ml of solution, the volume used in this study) give an idea of the effectiveness of an adsorbent and the ability of DOC to be adsorbed with a minimum dose. As the dose of date seeds increases from 0.5 g to 2.0 g, the removal efficiency was observed to increase from 70% to 82% whereas the equilibrium adsorption capacity decreased from 19.85 mg/g to 5.75 mg/g. The increase in the percentage of DOC removal with the elevation of the date seeds dose can be attributed to the increase in the active adsorptive sites (Figure 5.2a). While the decrease in the equilibrium adsorption capacity can be due to the fact that date seeds would tend to aggregate as the date seeds increase resulting in lower surface area availability for adsorption and causing an increase in the diffusion path length of DOC (Figure 5.2b). It was noticed that the final pH increases when increasing the adsorbent dose. This is due to the increase in the amount of negatively charged sites which can prompt more H^+ ions adsorbed on date seeds surfaces and ultimately resulting in an increase in the pH of final solution.

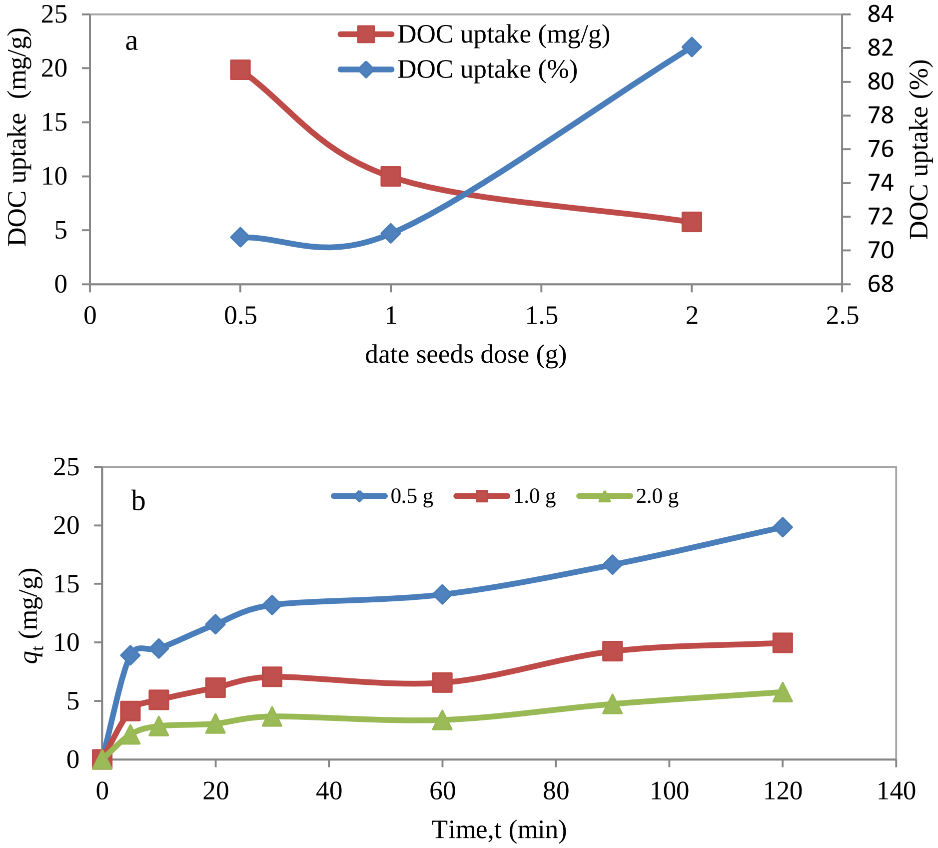


Figure 5.2 Effect of initial date seeds dose on DOC uptake (initial DOC concentration of 93.5 mg/l, pH: 8.9, agitation speed: 150 rpm, volume of solution: 150 ml)

5.3.3. Effect of the initial DOC concentration

The study pertinent to the effects of initial concentration of adsorbate is very important as it affects the adsorption kinetics. It was found that the amount of DOC adsorption on date seeds increases from 2.63 mg g^{-1} to 19.85 mg g^{-1} when initial concentration increased from 18.5 mg/l to 93.47 mg/l respectively. The increase in initial DOC concentration enhances the interaction between adsorbent and DOC. It can be noticed from Figure 5.3 that the uptake of DOC is very fast at the early stages of contact but it slows down as time proceeds. Kinetic experiments showed clearly that the adsorption of DOC on date seeds follow three-step process, a rapid initial adsorption followed by a period of slower adsorption and finally no substantial uptake (equilibrium stage). These observations pertinent to adsorption of DOC are in good agreement with those reported in the literature (Mohammad et al., 2010).

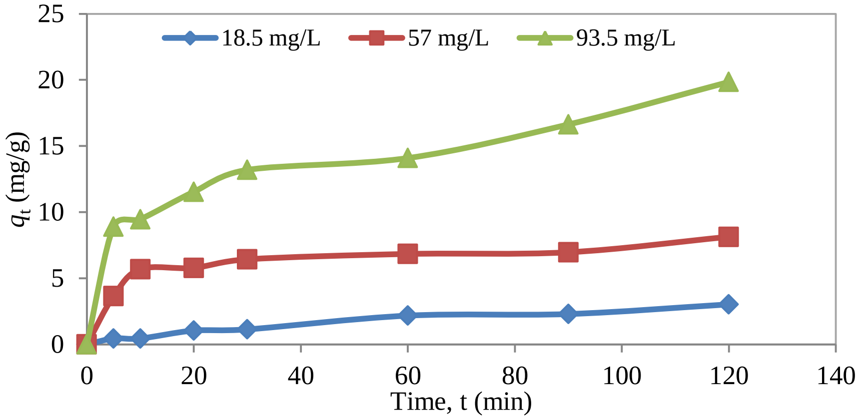


Figure 5.3 Effect of initial DOC concentration on adsorption of DOC onto date seeds (date seeds dose: 0.5, agitation speed: 150 rpm, pH: 8.9, volume of solution: 150 ml)

5.3.4. Effect of pH

The surface charge of the adsorbent and the ionization degree of the adsorbate are strongly affected by the initial pH of an aqueous solution; hence the uptake of DOC by date seeds would be affected by the solution pH. The uptake of DOC by date seeds is almost not affected in the pH range of 4-9. In other words, the pH of solution has very little effect on the uptake of DOC. However, it was noticed the uptake of DOC tends to decrease with increasing pH (Figure 5.4). As the initial solution pH increases from 4 to 9, the equilibrium adsorption capacity decreased from 2.06 mg/g to 1.82 mg/g. This might be due to high electrostatic repulsion between negatively charged surface sites of date seeds and DOC. Increased pH generally leads to increased ionization, solubility, and hydrophilicity, and thus decreasing adsorption of natural organic matter (Wang et al., 2007, Pan and Xing, 2008, Lu and Su, 2007). As a result, DOC uptake is more noticeable at lower pH compared to higher pH.

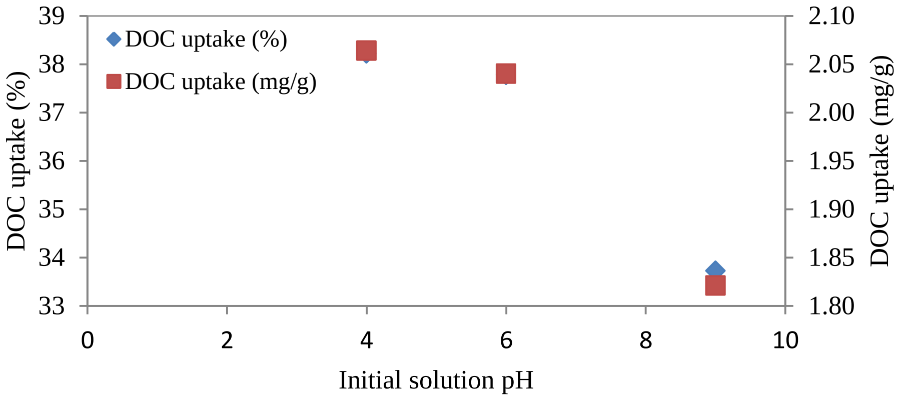


Figure 5.4 Effect of initial solution pH on DOC uptake by date seeds (initial DOC concentration of 93.5 mg/l, date seeds dose: 0.5, agitation speed: 150 rpm, volume of solution: 150 ml)

5.3.5. Effect of Temperature and Thermodynamic parameters

Temperature is found to have a significant effect on the adsorption capacity of the adsorbent. In general, increasing solution temperature will result in decreasing adsorption somewhat because adsorbed molecules have great vibrational energies and are therefore more likely to desorb from the surface (Cooney, 1998). The uptake of DOC by date seeds decreased from 4.92 mg g-1 (25.28% removal) to 3.7 mg g-1 (19.01% removal) when increasing temperature from 25 ^{o}C to 45 ^{o}C, indicating that the DOC removal was favoured at lower temperature. This fact indicates that the adsorption of DOC onto date seeds is exothermic process. This can be due to the weak adsorptive forces between the DOC and date seeds active adsorptive sites and also between the vicinal molecules of the adsorbed phase when temperature increases. Thermodynamic parameters were used to test the feasibility of the adsorption process. ΔG^{o}, ΔH^{o}, and ΔS^{o} are illustrated in Table 5.1 at different temperatures 298, 308, and 318 K. The negative value of ΔH^{o} indicates the exothermic nature of adsorption which also supported by the decrease in DOC uptake with the increase in temperature. The reaction is found to be nonspontaneous at these temperatures as the free energy change is > 1. The negative value of ΔS^{o}

indicates decreased randomness at solid/liquid interface during DOC adsorption onto date seeds.

Table 5.1 Thermodynamic parameters for adsorption of DOC onto date seed at different temperature

Temp (K)	ΔG^o (KJ/mol)	ΔH^o (KJ/mol)	ΔS^o (J/mol K)	R^2
298	6.723	-14.477	-71.14	0.95
308	7.435			
318	8.146			

5.4. Adsorption isotherms

Adsorption isotherms are very important for understanding the mechanism of the adsorption. Several isotherms equations are available. In this study, three isotherms models were used namely Langmuir, Freundlich, and Dubinin-Radushkevich isotherms models. The parameters of the three models are listed in Table 5.2. The correlation coefficient, R^2 is used as a tool to test the applicability of the isotherm equation.

Table 5.2 Langmuir, Freundlich and Dubinin-Radushkevich isotherm constants

Langmuir	
K_L *(L/mg)*	0.00466
q_m *(mg/g)*	74.62
R^2	0.92
Equation	$q_e = \frac{0.347778c_e}{1 + 0.00466c_e}$
Freundlich	
K_f	0.284
n	0.886
R^2	0.72
Equation	$q_e = 0.28436c_e^{1.1282}$
Dubinin-Radushkevich	
q_m *(mg/g)*	14.67
β	0.0135
R^2	0.76
Equation	$q_e = 14.67e^{-0.01347\varepsilon^2}$

The Langmuir isotherm model is found to have the best fitting for the adsorption of DOC onto date seeds with R^2 of 0.92. On the other hand, Freundlich and Dubinin-Radushkevich models showed poor linear regression coefficient, R^2, indicating the inapplicability of these models. The Langmuir isotherm confirms the monolayer coverage of DOC onto date seeds particles. The maximum mono-layer adsorption from Langmuir model, q_m, was found to be 74.6 mg g^{-1}. The separation factor, R_L, is considered as more reliable indicator of the adsorption process and it can be determined from the Langmuir plot as follows

$$R_L = \frac{1}{1 + K_L C_o}$$

where K_L is the Langmuir constant and C_o is the initial concentration of DOC. The separation factor, R_L values indicate the type of isotherm to be favorable $0 < R_L < 1$, unfavorable $R_L > 1$, linear $R_L = 1$ and irreversible $R_L = 0$.

To check the shape of the isotherm for the adsorption of DOC on date seeds, R_L was calculated for the initial DOC concentrations of 10-100 mg/L and it was found to range from 0.955 to 0.682. This indicates favorable adsorption as R_L falls in the category $0 < R_L < 1$.

5.5. Adsorption kinetic models

The adsorption kinetics is one of the important data in order understand the mechanism of the adsorption process and to evaluate the performance of the adsorbents. The information obtained from the batch adsorption kinetics can be used for the design of industrial adsorption columns. Different kinetic models including pseudo-first order, pseudo-second order, intra-particle diffusion, liquid film diffusion, and double exponential models were applied for the adsorption experimental data of DOC onto date seeds. These models were tested for different physico-chemical conditions (Table 5.3 and Table 5.4). The correlation coefficient (R2) is used to test the applicability of the adsorption kinetic models (Figure 5.5-Figure 5.10). The pseudo-second order kinetic model showed better fit when comparing the calculated and experimental (q_e) values, Table 5.3. For example, when 0.5 g of adsorbent was used q_e obtained from pseudo-first order kinetic model showed a difference of 8.52 from the experimental q_e value while q_e obtained from pseudo-second order kinetic model showed a difference of 0.56. Therefore, the adsorption of DOC onto date seeds is in consistent with the second-order reaction.

Table 5.3 Pseudo-first and second order kinetic parameters for adsorption of DOC on date seed

Parameters	Pseudo-first order kinetic parameters				Pseudo-second order kinetic parameters			
	q_e (mg/g) experimental	q_e (mg/g) calculated	K_1 (min^{-1})	R^2	q_e (mg/g) calculated	K_2 (mg/gmin)	h (mg/gmin)	R^2
Initial adsorbent dose (g)								
0.5	19.85	11.33	0.0136	0.96	20.41	0.0034	1.4205	0.91
1.0	9.96	6.26	0.020	0.81	10.46	0.0067	0.7276	0.95
2.0	5.75	3.52	0.012	0.82	5.87	0.0096	0.3316	0.97
Initial DOC concentration (mg/L)								
18.5	3.03	2.846	0.0164	0.95	4.57	0.00299	0.06246	0.86
57	8.14	3.228	0.0131	0.77	8.15	0.01599	1.06225	0.99
93.47	19.85	11.33	0.0136	0.96	20.41	0.00341	1.4205	0.97
Initial pH								
4	2.06	1.63	0.03	0.98	2.44	0.01906	0.11313	0.99
6	2.04	1.95	0.02	0.94	2.78	0.00569	0.04396	0.77
9	1.82	1.17	0.01	0.85	1.86	0.02655	0.09199	0.92

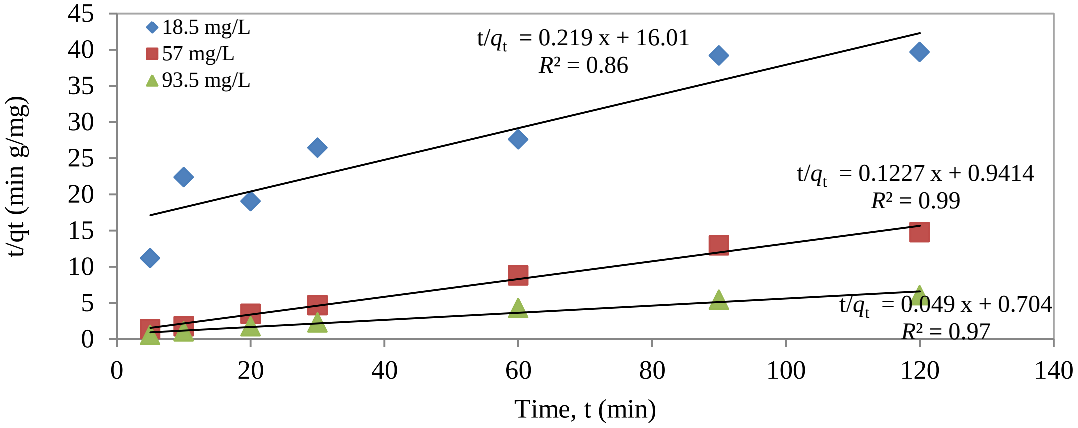


Figure 5.5 Pseudo-second order plot for DOC adsorption by date seeds at different initial DOC concentrations

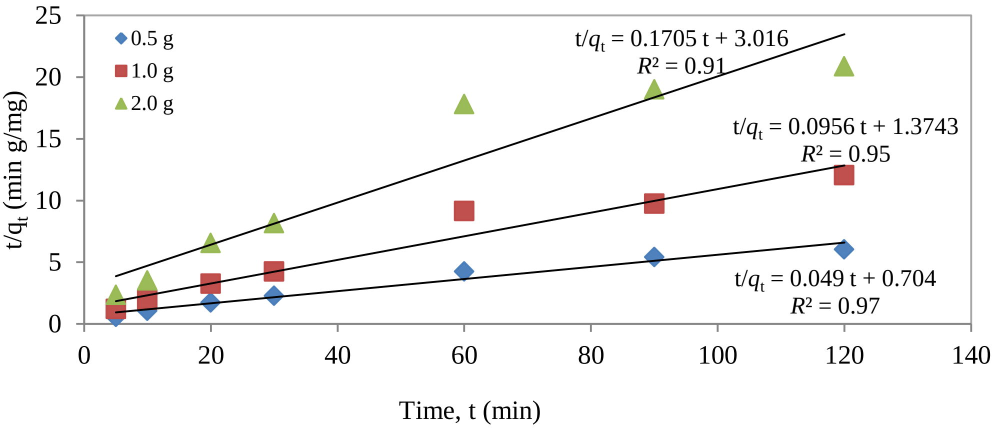


Figure 5.6 Pseudo-second order plot for DOC adsorption at different date seed doses

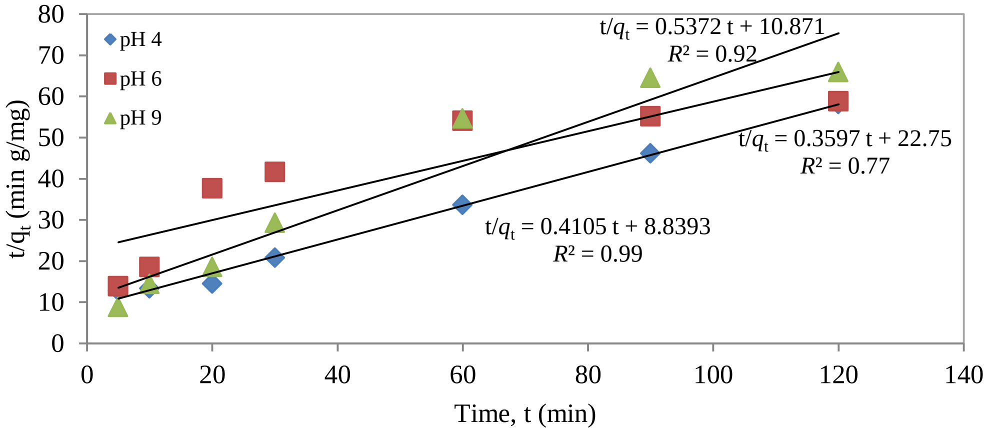


Figure 5.7 Pseudo-second order plot for DOC adsorption by date seeds at different pH

Table 5.4 Intraparticle diffusion, liquid film diffusion and double exponential model for adsorption of DOC on date seed

Parameters	Intrapartical diffusion		Liquid film diffusion		Double exponential model	
	K_{id} (min^{-1})	R^2	K_{fd} (min^{-1})	R^2	K_2 (min^{-1})	R^2
Initial adsorbent dose (g)						
0.5	1.5117	0.90	0.0135	0.96	0.9831	0.87
1.0	0.7828	0.89	0.0242	0.99	0.9739	0.96
2.0	0.4332	0.90	0.0141	0.97	0.98373	0.88
Initial adsorbate concentration (mg/L)						
18.5	0.2311	0.92	0.0164	0.95	0.9837	0.95
57	0.6858	0.77	0.0097	0.90	0.9903	0.90
93.47	1.5293	0.85	0.0135	0.96	0.9866	0.96
Initial pH						
4	0.195	0.92	0.0304	0.98	0.969	0.98
6	0.1787	0.96	0.0157	0.94	0.983	0.98
9	0.1407	0.92	0.0107	0.85	0.986	0.90

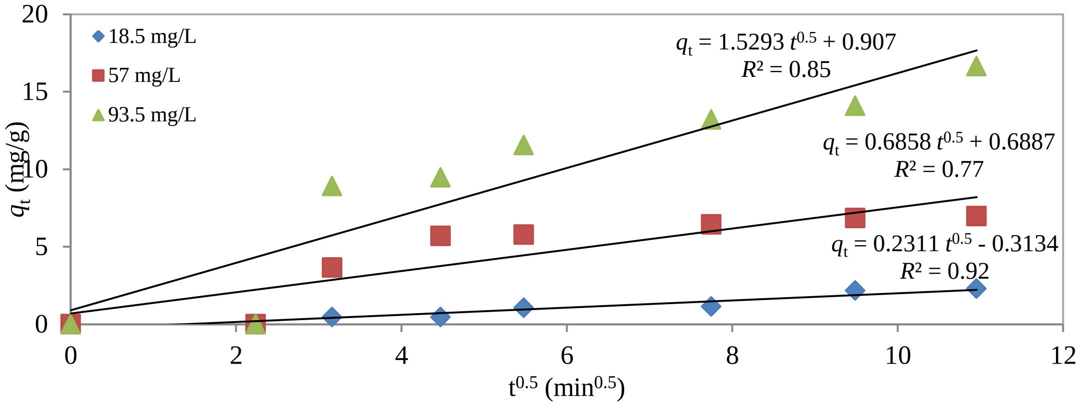


Figure 5.8 Intraparticle diffusion plot for DOC adsorption by date seeds at different initial DOC concentrations

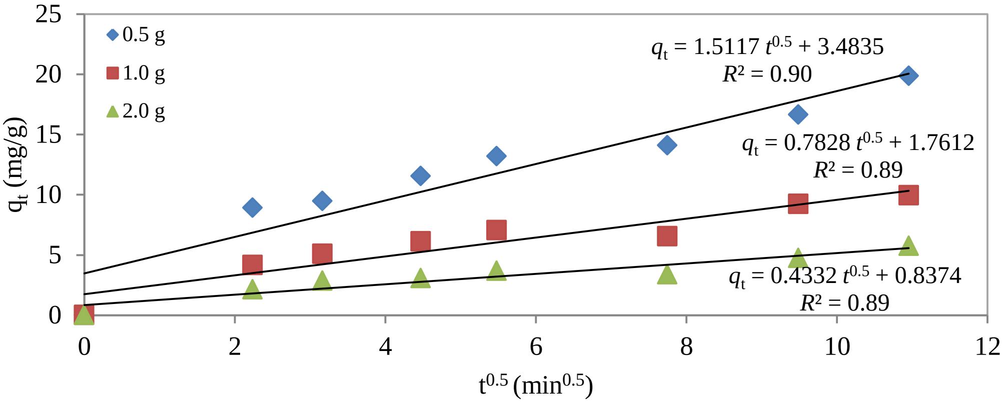


Figure 5.9 Intraparticle diffusion plot for DOC adsorption at different date seed doses

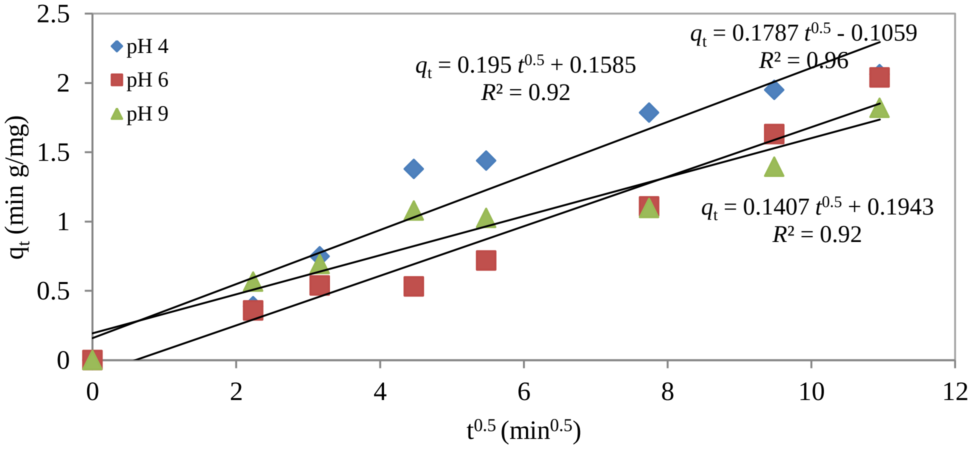


Figure 5.10 Intraparticle diffusion plot for DOC adsorption by date seeds at different pH

The values of the rate constant K_2 increase with the initial date seeds dose. This can be attributed to the higher availability of active adsorptive sites and consequently higher sorption rates obtained. The sorption rate K_2 increased when increasing initial DOC concentration from 18.5 to 57 mg/L due to the enhancement in the interaction between the adsorbent and DOC (see Table 5.3). However, it decreases when DOC concentration increases from 57 to 93.47 mg/L. This can be due to the high competition for the surface active sites and consequently lower sorption rates. The mechanism of DOC uptake from aqueous phase by adsorption can be summarized into four steps: the first step involves the migration of the DOC molecules from the bulk solution to the surface of date seeds, the second step represents the diffusion of DOC molecules through the boundary layer to the surface of the sorbent, the third-step is adsorption at sites, and finally the intra-particle diffusion into the interior of the sorbent (Nandi et al., 2009, Oladoja et al., 2008).

The adsorption of DOC onto date seeds during earlier stages might be controlled by film diffusion and as the time proceeds, i.e. date seeds get loaded with DOC, the sorption process may be controlled due to intra-particle diffusion. The plot of intra-particle diffusion model, i.e. q_t vs $t^{0.5}$, is commonly used to identify the mechanism involved in the sorption process (Figure 5.11 and Figure 5.12). The plot confirms the multi-stages of adsorption as the fitted experimental data are not linear suggesting that the reaction starts with external mass transfer of the DOC molecules to the external surface of the date seeds through film diffusion and its rate is fast followed by the entrance of DOC molecules into date seeds by intra-particle diffusion through pores.

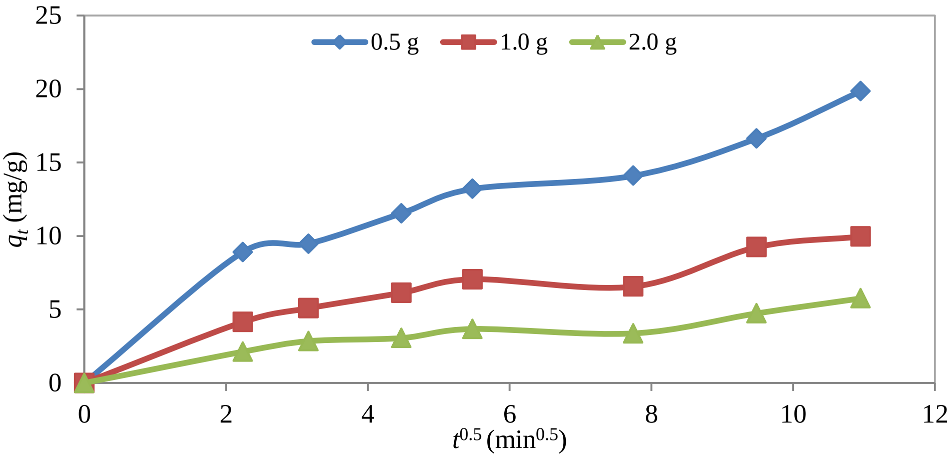


Figure 5.11 Intra-particle diffusion model for DOC adsorption by date seeds at different date seeds doses

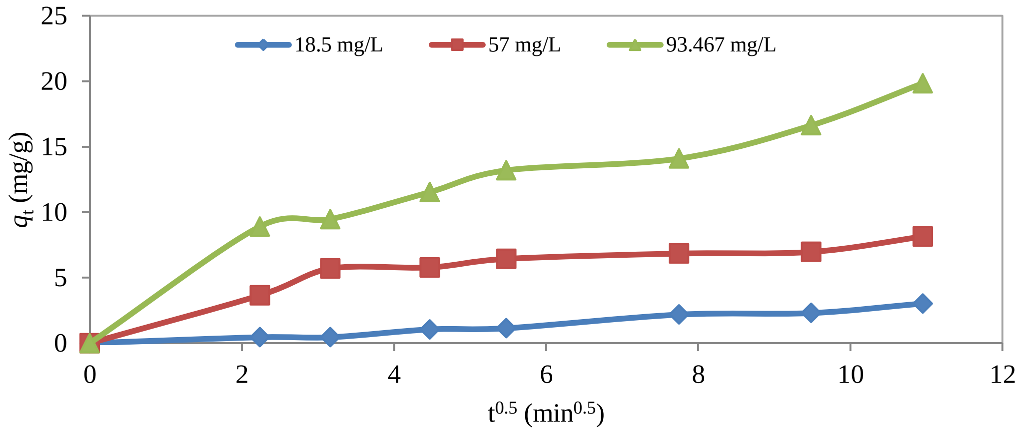


Figure 5.12 Intra-particle diffusion model for DOC adsorption by date seeds at different initial DOC concentrations

5.6. Design of single-stage batch absorber from isotherm data

Adsorption isotherms can be utilized to predict the design of single batch adsorption system (McKay et al., 1985). The main design objective is to find the amount of adsorbent, m (g) required to reduce the initial DOC concentration of C_o to C_l (mg/L) for which total solution is V (L). When attapulgite is added to the system the DOC concentration on the surface of the solid changes from q_o=0 to q_l. The mass balance for the sorption system under equilibrium is given by

$$\mathrm{V}(\mathrm{C_o} - \mathrm{C_e}) = \mathrm{m}(\mathrm{q_e} - \mathrm{q_o}) = \mathrm{mq_e} \tag{5.1}$$

Since Langmuir isotherm model shows the best fit for the equilibrium data, equation 5.1 can be rewritten after substituting q_e from Langmuir model

$$\frac{m}{V} = \frac{(C_o - C_e)}{q_e} = \frac{(C_o - C_e)}{\left[\frac{q_m K_L C_e}{1 + K_L C_e}\right]} \tag{5.2}$$

Figure 5.13 shows a sequence of plots derived from equation 5.2. Different solution volumes (1-8 L) were used to predict the amount of date seeds (m) required to achieve target DOC removal efficiency (85, 75, 65, and 55%), given that the initial concentration of DOC is 50 mg/ L.

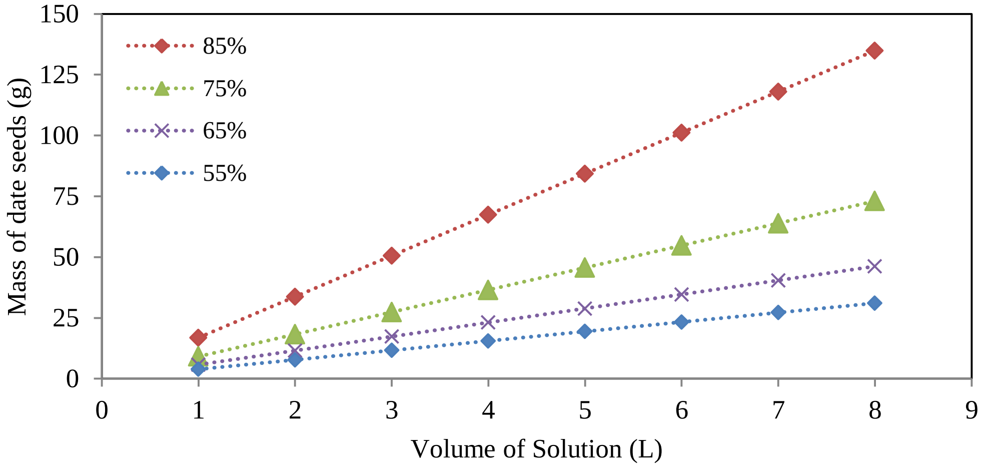


Figure 5.13 Date seeds mass (m) versus volume of solution (L)

5.7. Summary

Experimental results revealed that the adsorption of DOC onto date seeds increases with the increase in initial DOC concentration, contact time, and amount of adsorbent dose, however, the adsorption of DOC decreases with increase in temperature, and solution pH. A Langmuir equation is applicable for the adsorption of DOC onto date seeds. The parameters of Langmuir, Freundlich, and D-R models were calculated and tabulated. The adsorption process follows the pseudo-second order process. Pseudo-first order, pseudo-second order, intra-particle diffusion, liquid film diffusion, and double exponential models were applied to study the mechanism of adsorption. Based on the kinetic experiments adsorption mechanism of DOC onto date seeds can be summarized into two steps: external mass transfer of the DOC molecules to the external surface of the date seeds through film diffusion at a fast rate followed by intra-particle diffusion of DOC molecules into date seeds particles through pores. The thermodynamic analysis showed that the process is nonspontaneous, exothermic and chemisorption in nature. Overall, the results from the adsorption tests indicate that the date seeds, an agricultural waste can be utilized as a potential alternative low-cost adsorbent for the removal of DOC from oily produced water.

CHAPTER 6

REMOVAL OF DOC BY ATTAPULGITE

6.1. Introduction

This chapter investigates the applicability and feasibility of using attapulgite for the adsorption of DOC from oily produced water.

Attapulgite belongs to the Fuller’s Earth group and it gains it’s high sorbent properties from its compound structure known as hydrated magnesium aluminium silicate with a fibrillar structure (Wang et al., 2011). Attapulgite is found to exist in Oman in huge quantities and high purities. The estimated amount of attapulgite from two places in Dhofar, Southern part of Oman is around 300 million to 400 million tons in Shuwaymiyah deposit and 200,000 to 1 million tons in Tawi Attair deposit (Al-Futaisi et al., 2007a). Presently these huge quantities of attapulgite are not mined or utilized. Attapulgite has been considered and utilized as an adsorbent for the removal of many pollutants due to the fact that it is a natural, cheap and available in huge quantities with large specific area and porous structure. Many researchers applied attapulgite for the removal of heavy metals (Veli and Alyüz, 2007, Álvarez-Ayuso and García-Sánchez, 2007, Potgieter et al., 2006, Chen et al., 2007, Kong et al., 2011, Cui et al., 2012) while others investigated the adsorption of organic compounds (Wang et al., 2011, Zhang et al., 2012, Chang et al., 2009, Safari Sinegani et al., 2005, Al-Futaisi et al., 2007a, Wang et al., 2012). Most of the studies done on the removal of organic compounds focused on the removal of cationic dyes and humic acids from aqueous solutions. There is no study in literature which report or investigate the removal of DOC from oily produced water. In this study, the applicability of attapulgite as an adsorbent for the removal of DOC from oily produced water is explored. The study investigates the adsorption isotherms, adsorption kinetics and the mechanism of adsorption under different operating conditions including the effect of contact time, solution pH, initial DOC concentration, adsorbent dose and temperature on the uptake of DOC onto attapulgite. Several kinetic models namely pseudo-first order, pseudo-second order, intra-particle diffusion, liquid film diffusion, and double exponential models are applied to understand the mechanism of adsorption. The thermodynamic parameters such as free energy (ΔG^o), enthalpy (ΔH^o), and entropy (ΔS^o) were obtained to evaluate the feasibility of the adsorption process.

6.2. Materials and methods

Attapulgite used in this study was collected from Dhofar, southern part of Oman. The attapulgite was crushed by soil grinder into two different sizes, i.e. granular (1 mm) and powder (0.25 mm). The oily produced water used in this study was collected from an oilfield.

The adsorption of DOC onto attapulgite was investigated through a batch process using a known dose of attapulgite with 150 ml of oily produced water of known concentration. The mixture was placed in a mechanical shaker and agitated at 150 rpm for 120 minutes. After that, the mixture was filtered through 0.45 µm cellulose nitrate filter and the filtrate was analyzed for DOC by using a TOC analyzer.

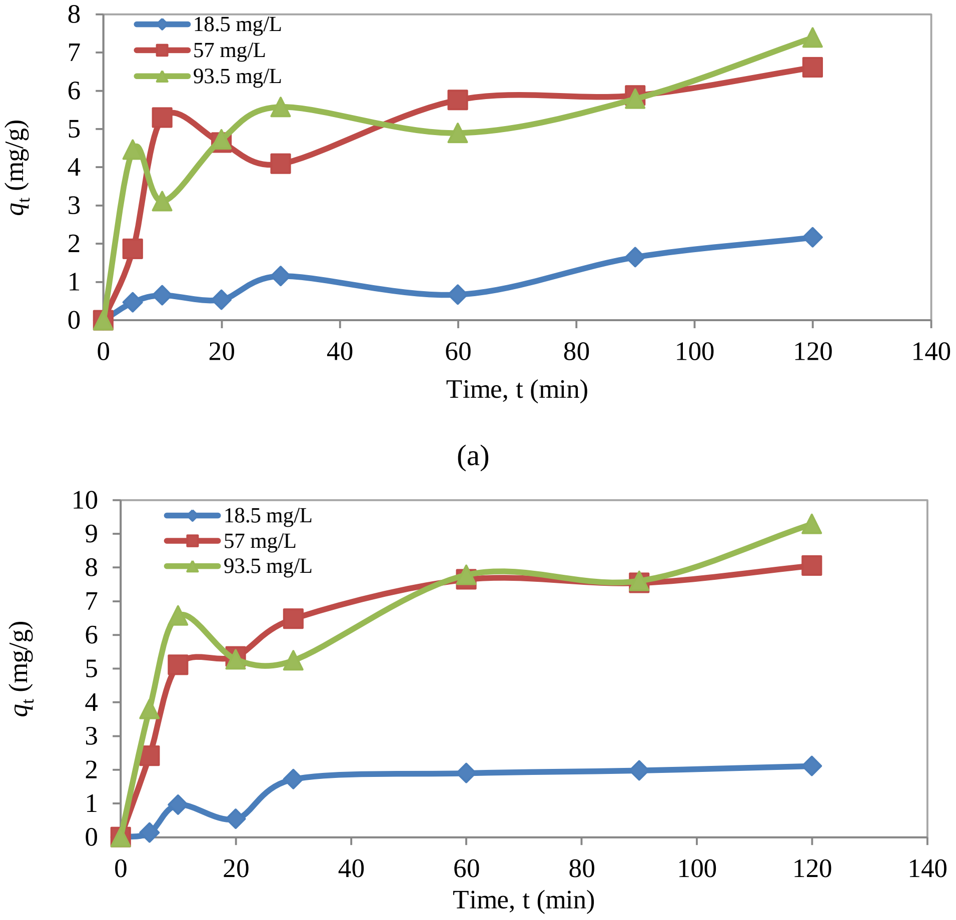
6.3. Results and Discussion

6.3.1. Effect of contact time and initial DOC concentration

The adsorption of DOC onto the attapulgite as a function of contact time was investigated to determine the equilibrium stage. The samples were taken at different intervals and the level of DOC in solution was measured with time. The removal rate of DOC was high at the beginning and then the rate starts to decrease with time until it reaches equilibrium. This can be attributed to the fact that at the beginning the adsorption sites were unoccupied and highly available and as time proceeds less sites become available. The equilibrium stage was attained within 120 minutes and thus, the rest of adsorption trials were conducted for a contact time of 120 minutes. The equilibrium time is independent of initial DOC concentration.

The study of the effect of initial concentration of adsorbate is very important as it affects the adsorption kinetics. It was found from this study that the amount of DOC uptake by attapulgite (granular and powder) increased when initial DOC concentration increases from 18.5 mg/L to 93.47 mg/L. The DOC uptake by the granular attapulgite A increased from 2.16 mg/g to 7.16 mg/g as the initial concentration increased from 18.5 mg/L to 93.47 mg/L while the increase in DOC uptake by the powder form was from 2.11 mg/g to 9.29 mg/g. The DOC uptake increased from 2.62 mg/g to 8.67 mg/g with the granular attapulgite B while the increase with the powder form was more noticeable where DOC uptake increased from 4.67 mg/g to 18.02 mg/g when initial concentration increased from 18.5 mg/L to 93.47 mg/L respectively. It is expected that the powder attapulgite would show better uptake since it has more surface area and as result more available adsorptive sites compared to granular attapulgite. The increase in initial DOC concentration improves the interaction between adsorbent and DOC. It can be noticed from

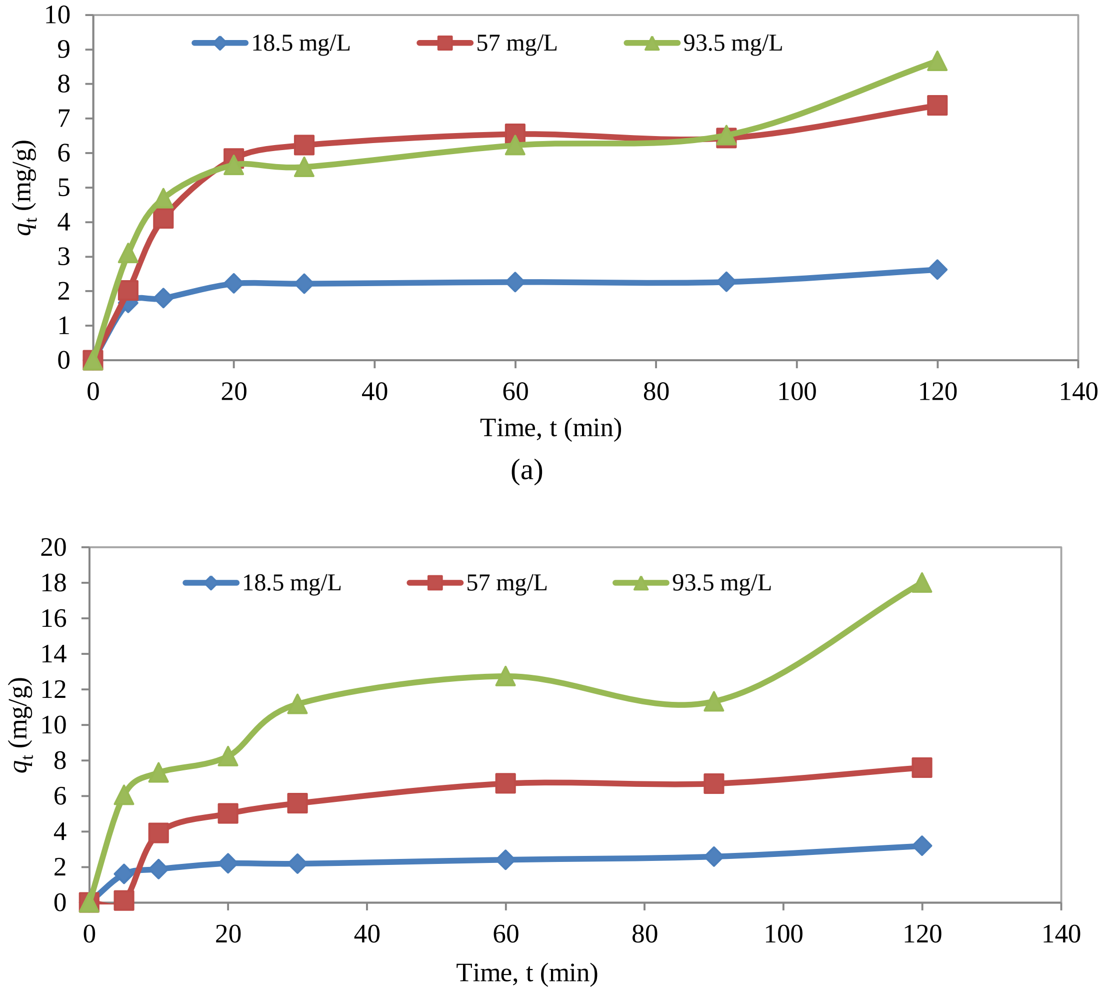
Figure 6.1 and Figure 6.2 that the uptake of DOC is very fast at the early stages of contact but it slows down as time proceeds. Based on the kinetic trials, the adsorption process of DOC onto attapulgite can be summarized in three-steps, a quick initial adsorption after that the uptake will slow down and finally the adsorption will reach the equilibrium stage where no substantial uptake is taking place. These observations pertinent to adsorption of DOC are in good agreement with those reported in the literature (Mohammad et al., 2010).



(a)

(b)

Figure 6.1 Effect of initial DOC concentration on adsorption of DOC onto attapulgite A, a) granular attapulgite and b) powder attapulgite (attapulgite dose: 0.5 g, agitation speed: 150 rpm, pH: 8.9, volume of solution: 150 ml)



(a)

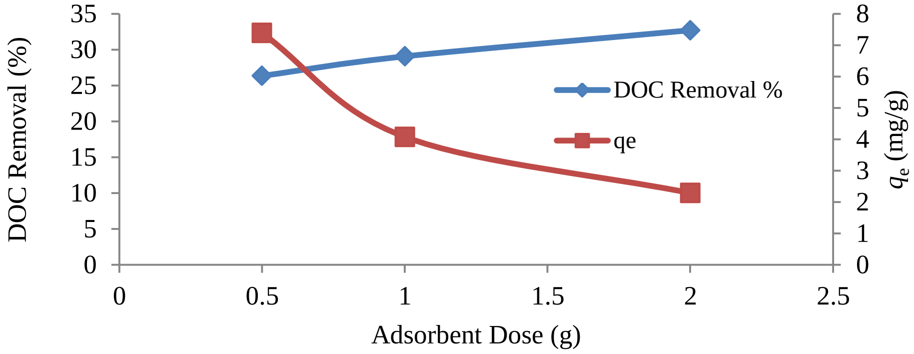
(b)

Figure 6.2 Effect of initial DOC concentration on adsorption of DOC onto attapulgite B, a) granular attapulgite and b) powder attapulgite (attapulgite dose: 0.5 g, agitation speed: 150 rpm, pH: 8.9, volume of solution: 150 ml)

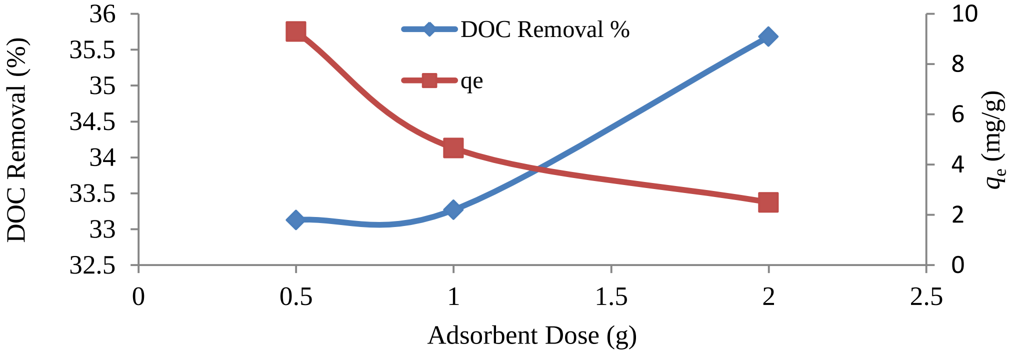
6.3.2. Effect of adsorbent (attapulgite) dose

The effect of attapulgite dose on the adsorption of DOC from oily produced water was investigated by using three different doses (0.5 g, 1.0 g and 2.0 g). As the dose of granular attapulgite A increases from 0.5 g to 2.0 g, the removal efficiency was observed to increase from 26.35% to 32.71% and the equilibrium adsorption capacity decreased from 7.39 mg/g to 2.29 mg/g (Figure 6.3 a). The same trend was observed with powdered attapulgite A where the DOC removal efficiency increased from 33.13% to 35.68% and the equilibrium adsorption capacity decreased from 9.29

mg/g to 2.5 mg/g when the dose of attapulgite increases from 0.5 g to 2.0 g (Figure 6.3b).



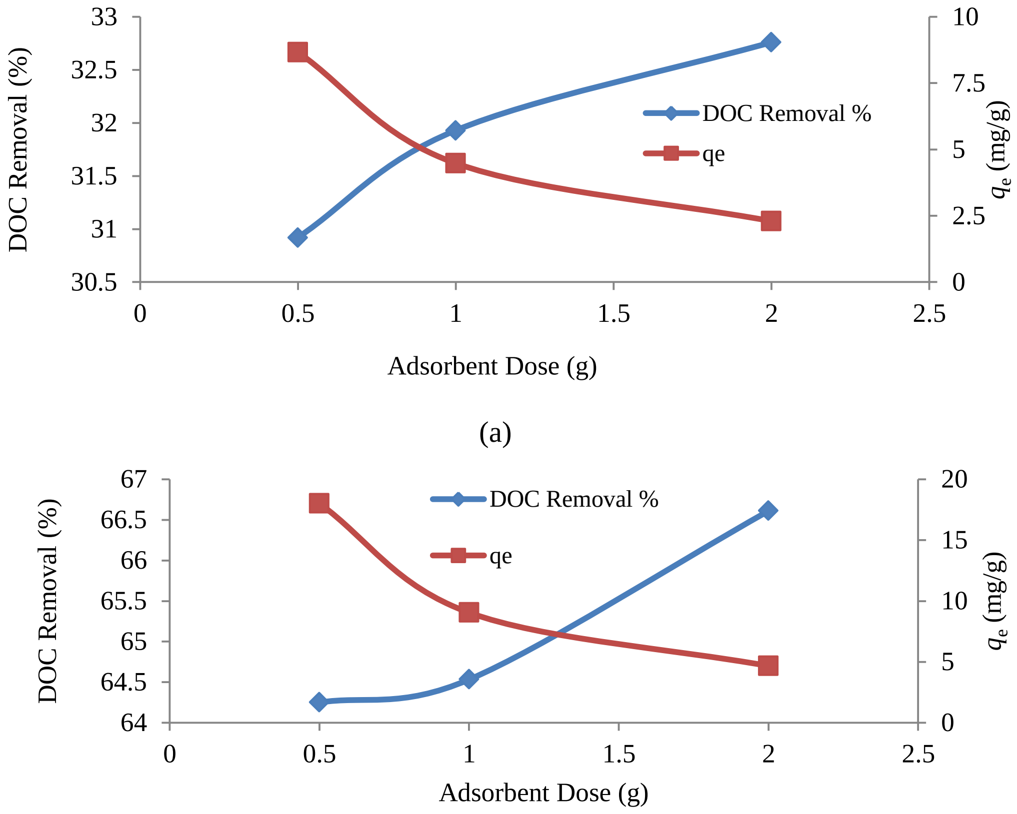
(a)



(b)

Figure 6.3 Effect of initial attapulgite A dose on DOC uptake, (a) granular and (b) powder (initial DOC concentration of 93.5 mg/L, pH: 8.9, agitation speed: 150 rpm, volume of solution: 150 ml)

In the other hand as the dose of granular attapulgite B increases from 0.5 g to 2.0 g, the removal efficiency was observed to increase from 31% to 32.7% while the equilibrium adsorption capacity decreased from 8.67 mg/g to 2.3 mg/g (Figure 6.4 a). The decrease in the equilibrium adsorption capacity can be due to the fact that attapulgite would tend to aggregate as the attapulgite increase resulting in lower surface area availability for adsorption and causing an increase in the diffusion path length of DOC (Srivastava et al., 2006). The same results were obtained for the powdered attapulgite B, as the dose increases from 0.5 g to 2.0 g, the removal efficiency was observed to increase from 64% to 66.6% and the equilibrium adsorption capacity decreased from 18.02 mg/g to 4.67 mg/g (Figure 6.4 b). A higher attapulgite to DOC ratio will tend to give better removal of DOC compared with lower attapulgite to DOC ratio. This is due to the fact that a fixed amount of attapulgite can only adsorb a fixed amount of DOC. Thus, the increase in the attapulgite doses will result in increase in the volume of effluent that a certain mass of attapulgite can treat. It was clear from the results that attapulgite B was more effective in removing DOC from oily produced water compared to attapulgite A.



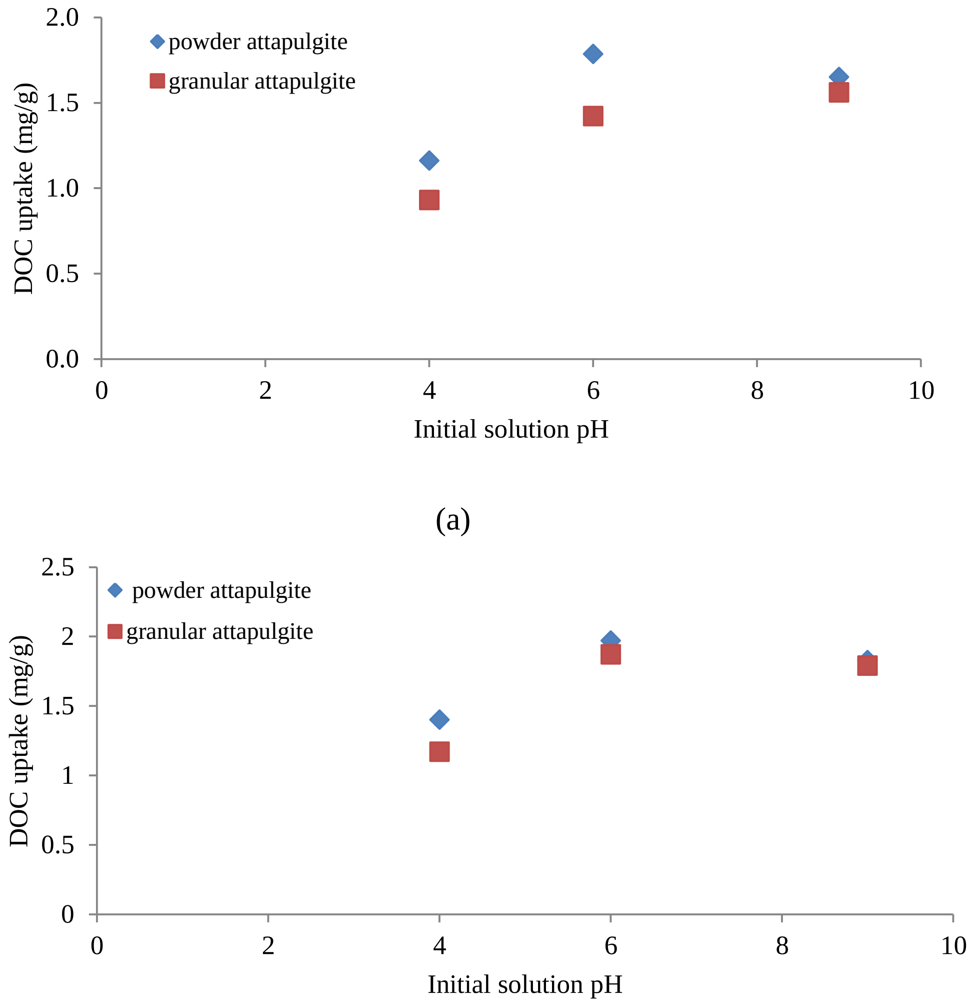
(a)

(b)

Figure 6.4 Effect of initial attapulgite B dose on DOC uptake, (a) granular and (b) powder (initial DOC concentration of 93.5 mg/L, pH: 8.9, agitation speed: 150 rpm, volume of solution: 150 ml)

6.3.3. Effect of initial pH

Figure 6.5 (a and b) represents the effect of pH on DOC adsorption by attapulgite A and B respectively. In this study, changes in pH of oily produced water have no significant influence on adsorption capacities. It was noticed that the uptake of DOC is lower at pH 4 compared with pH higher than 4. This can be explained based on the study made by Neaman, A., et al. (Neaman and Singer, 2000). They observed that at pH ≥ 9 the fibers of attapulgite (palygorskite) tend to repel each other because the magnitude of the negative charge is high resulting in high surface area. While at pH ≤ 9 the fibers of attapulgite tend to aggregate because the magnitude of negative surface charge is relatively low and van der Waals attraction predominates over electrostatic repulsion. There are several different views reported in the literature on the effect of pH on the adsorption of organic compounds. A study done by Narine, D. R., et al. (Narine and Guy, 1981) reported that the adsorption capacity of bentonite was independent of pH in the range 4.5 to 8.5 similar results were found by Bilgiç (Bilgiç, 2005) for the adsorption of organic cations on silicate minerals. In the other hand studies done by (Wang et al., 2011, Wang et al., 2012) reported that higher adsorption rates of humic acids were found at low pH.



(a)

(b)

Figure 6.5 Effect of initial solution pH on DOC uptake by attapulgite, (a) attapulgite A and (b) attapulgite B (initial DOC concentration of 18.5 mg/L, attapulgite dose: 0.5, agitation speed: 150 rpm, volume of solution: 150 ml)

6.3.4. Adsorption kinetic

In order to understand the mechanism of the adsorption process and evaluate the performance of the adsorbents, different kinetic models were applied. In this study, the applicability of pseudo-first order, pseudo-second order, intra-particle diffusion, liquid film diffusion, and double exponential models were investigated for the adsorption experimental data of DOC onto attapulgite.

These models were tested for different physico-chemical conditions (Table **6.1**and Table 6.2). The linear plot of t/q_t versus t for the pseudo-second-order kinetic model is shown in Figure 6.6 Figure 6.9. The correlation coefficient (R^2) is used to test the applicability of the adsorption kinetic models. In the view of these results, the pseudo-second order kinetic model showed better correlation coefficient (R^2) compared to pseudo-first order kinetic model. The $q_{e\ cal}$ determined from pseudo-second order kinetic model showed better fit when compared with $q_{e\ exp}$ in contrast to the other kinetic models. Therefore, the adsorption of DOC onto attapulgite follows the second-order reaction. The values of the rate constant K_2 increase with the initial attapulgite dose for both for both types of attapulgite. This can be attributed to the higher availability of active adsorptive sites and consequently higher sorption rates obtained. The sorption rate K_2 for granular and powder attapulgite A increased when increasing initial DOC concentration from 18.5 to 57 mg/L due to the enhancement in the interaction between the adsorbent and DOC. However, it decreases when DOC concentration increases from 57 to 93.47 mg/L. While the sorption rate K_2 for the granular and powder attapulgite B decreases when DOC concentration increases from 18.5 to 93.47 mg/L. This can be due to the high competition for the surface active sites and consequently lower sorption rates.

Table 6.1 Pseudo-first and second order kinetic parameters for adsorption of DOC on attapulgite A

		Pseudo-first order kinetic parameters				Pseudo-second order kinetic parameters			
Type	Parameters	q_e (mg/g) experimental	q_e (mg/g) calculated	K_1 (min^{-1})	R^2	q_e (mg/g) calculated	K_2 (mg/gmin)	h (mg/gmin)	R^2
Granular	Initial attapulgite dose (g)								
	0.5	7.39	3.29	0.0078	0.53	7.22	0.0116	0.605	0.94
	1.0	4.08	1.81	0.0052	0.59	3.81	0.0244	0.353	0.93
	2.0	2.29	1.09	0.0039	0.46	2.10	0.0352	0.155	0.89
	Initial DOC concentration (mg/L)								
	18.5	2.16	1.82	0.011	0.65	2.37	0.0084	0.047	0.45
	57	6.61	3.01	0.017	0.63	6.99	0.0174	0.574	0.98
	93.47	7.39	3.29	0.008	0.53	7.22	0.0116	0.605	0.94
	Initial pH								
	4	0.93	0.75	0.01	0.58	1.11	0.0208	0.0255	0.81
	6	1.42	2.24	0.06	0.89	1.73	0.0162	0.0488	0.88
	9	1.56	1.26	0.02	0.81	1.98	0.0137	0.0535	0.95
Powder	Initial attapulgite dose (g)								
	0.5	9.29	4.64	0.013	0.68	9.56	0.0078	0.716	0.96
	1.0	4.66	2.28	0.0025	0.54	4.17	0.0159	0.277	0.85
	2.0	2.50	1.31	0.0053	0.42	2.27	0.0308	0.158	0.86
	Initial DOC concentration (mg/L)								
	18.5	2.11	1.84	0.032	0.88	3.81	0.0032	0.0467	0.52
	57	8.05	4.43	0.029	0.85	8.68	0.0109	0.824	0.99
	93.47	9.29	4.64	0.013	0.68	9.56	0.0078	0.716	0.96
	Initial pH								
	4	1.16	0.74	0.05	0.90	1.42	0.0274	0.0552	0.95
	6	1.79	1.54	0.02	0.82	2.38	0.009	0.0509	0.79
	9	1.65	0.77	0.02	0.77	2.02	0.0149	0.0609	0.95

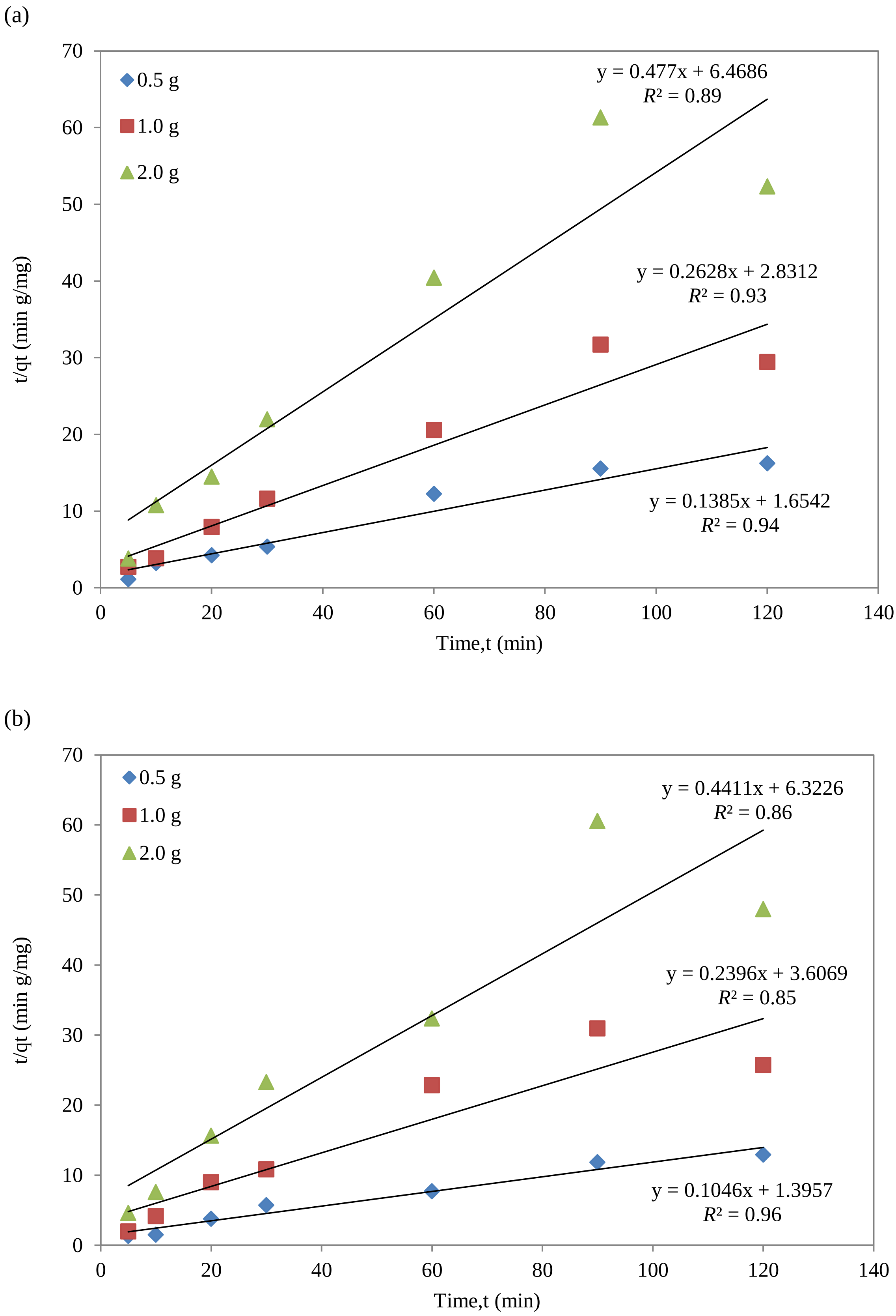


Figure 6.6 Pseudo-second order kinetic model for DOC adsorption at different attapulgite A doses, a) granular attapulgite A and b) powder attapulgite A

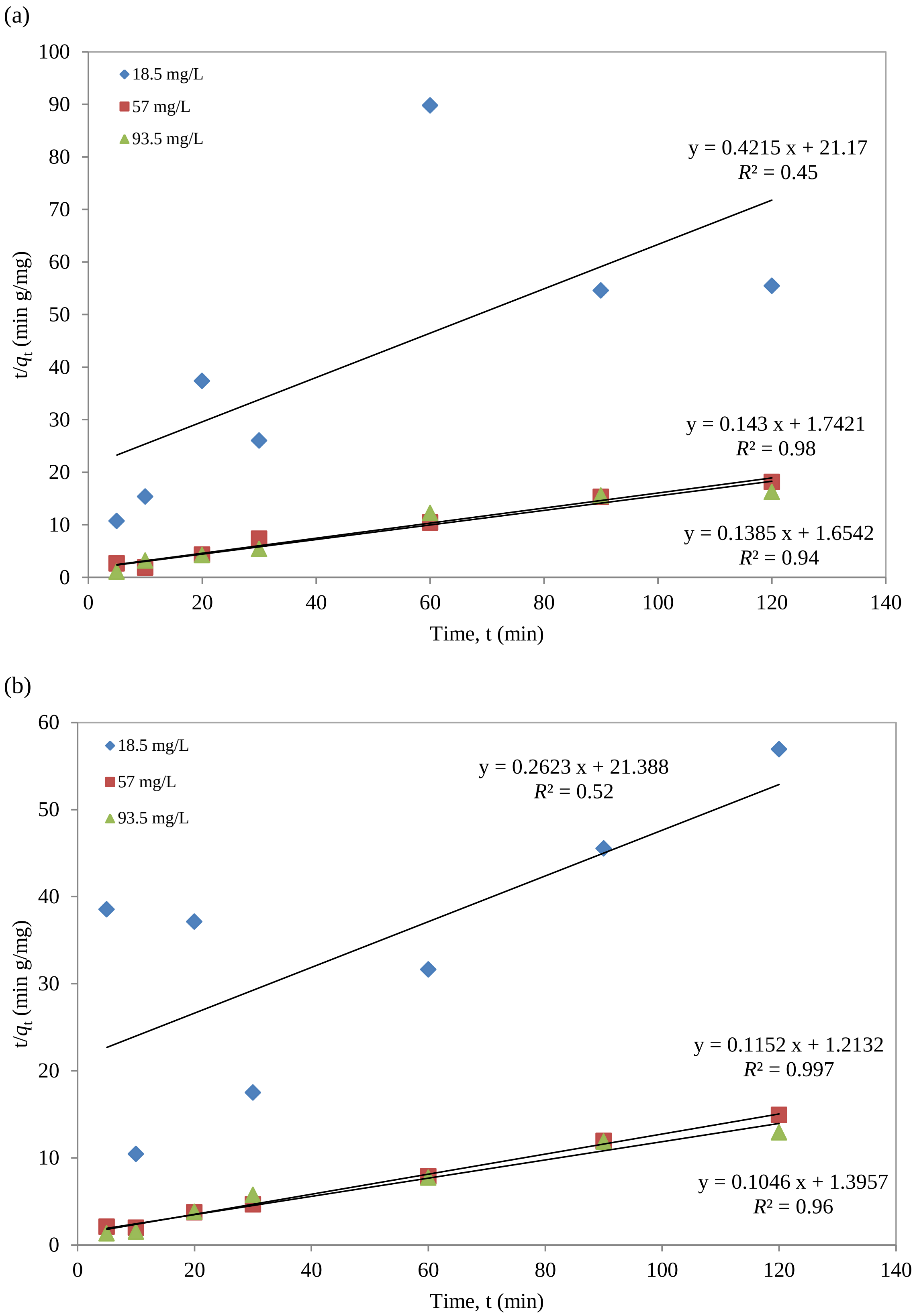


Figure 6.7 Pseudo-second order kinetic model for DOC adsorption by attapulgite A at different DOC concentration, a) granular attapulgite A and b) powder attapulgite A

Table 6.2 Pseudo-first and second order kinetic parameters for adsorption of DOC on attapulgite B

Type	Parameters	Pseudo-first order kinetic parameters				Pseudo-second order kinetic parameters			
		q_e (mg/g) experimental	q_e (mg/g) calculated	K_1 (min^{-1})	R^2	q_e (mg/g) calculated	K_2 (mg/gmin)	h (mg/gmin)	R^2
Granular	Initial attapulgite dose (g)								
	0.5	8.67	4.188	0.0074	0.51	8.35	0.0096	0.667	0.93
	1.0	3.83	2.177	0.0081	0.73	4.41	0.0167	0.325	0.94
	2.0	1.82	1.033	0.0088	0.66	2.28	0.0391	0.204	0.96
	Initial DOC concentration (mg/L)								
	18.5	2.62	0.7303	0.0101	0.56	2.58	0.0809	0.537	0.99
	57	7.38	4.307	0.0179	0.63	7.69	0.0132	0.777	0.99
	93.47	8.67	4.188	0.0074	0.51	8.35	0.0096	0.667	0.93
	Initial pH								
	4	1.17	1.32	0.03	0.98	2.11	0.00497	0.0222	0.97
	6	1.87	1.53	0.05	0.95	2.41	0.0101	0.0590	0.90
	9	1.79	0.64	0.02	0.65	1.92	0.0507	0.1878	0.98
Powder	Initial attapulgite dose (g)								
	0.5	18.02	10.8	0.0078	0.63	17.15	0.00336	0.987	0.89
	1.0	9.05	5.32	0.0094	0.87	8.95	0.00686	0.5499	0.94
	2.0	4.67	2.42	0.0067	0.60	4.38	0.01716	0.3295	0.91
	Initial DOC concentration (mg/L)								
	18.5	3.19	1.42	0.0101	0.90	3.15	0.032	0.317	0.97
	57	7.60	4.98	0.0228	0.82	8.11	0.0097	0.0097	0.99
	93.47	18.02	10.80	0.0078	0.63	17.15	0.00336	0.9875	0.89
	Initial pH								
	4	1.4	1.75	0.03	0.95	2.96	0.00263	0.0230	0.83
	6	1.97	1.97	0.02	0.95	2.91	0.00516	0.9163	0.94
	9	1.83	1.45	0.02	0.98	2.17	0.0206	0.9865	0.99

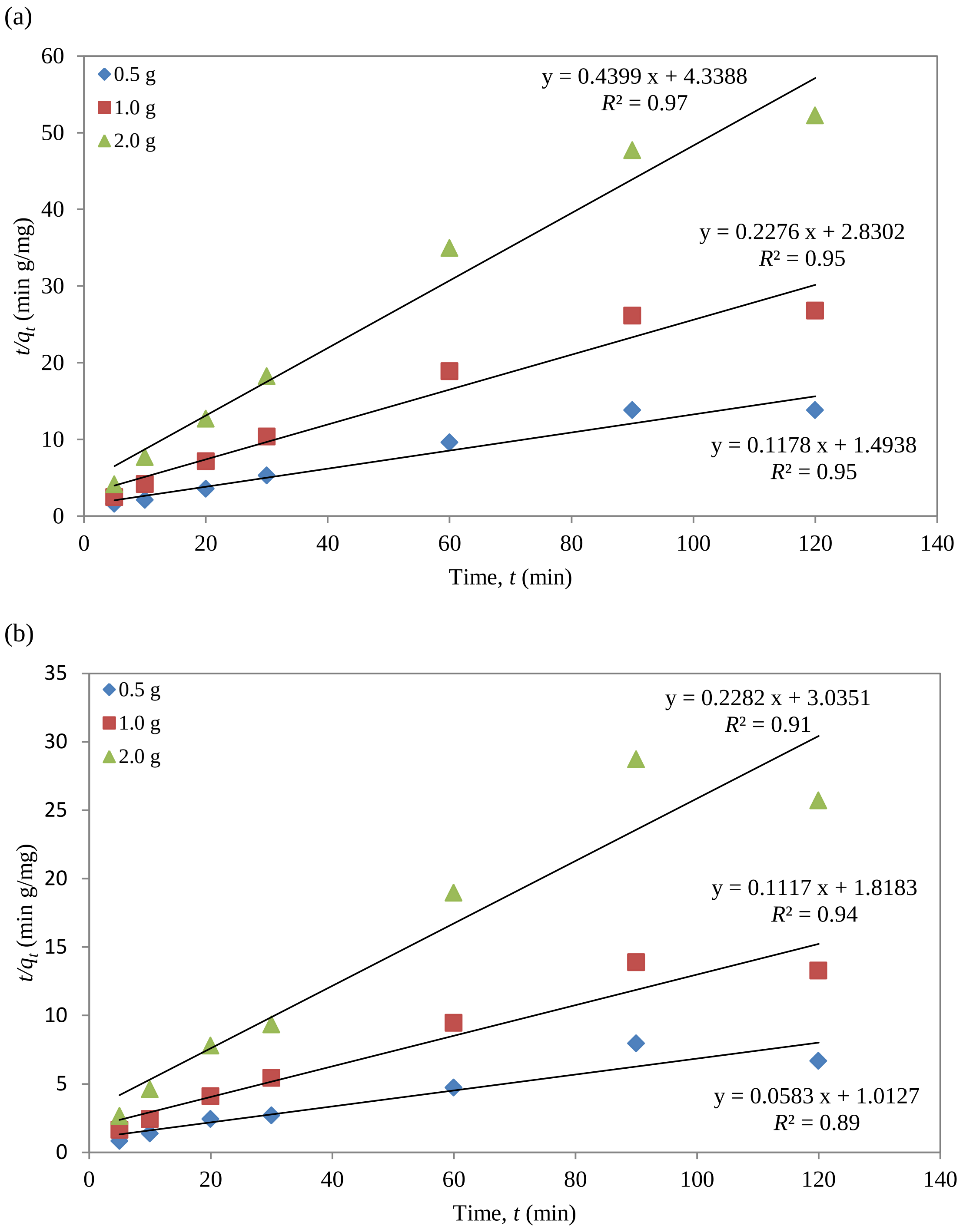
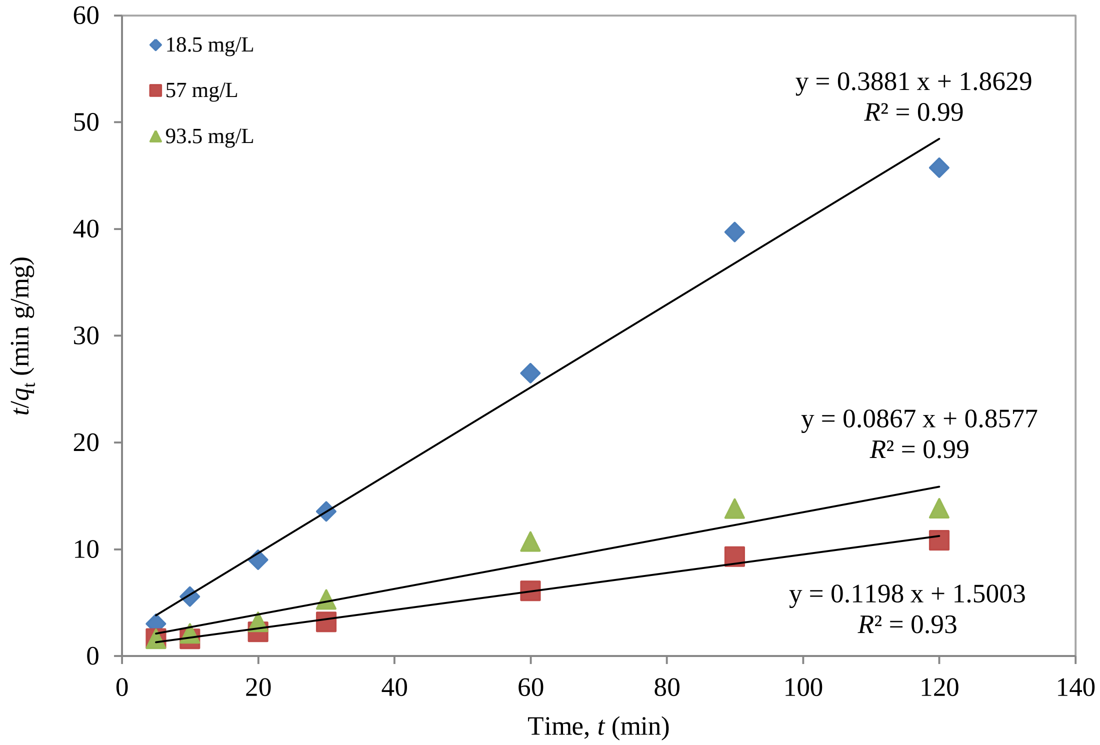


Figure 6.8 Pseudo-second order kinetic model for DOC adsorption at different attapulgite B doses, a) granular attapulgite B and b) powder attapulgite B

(a)



(b)

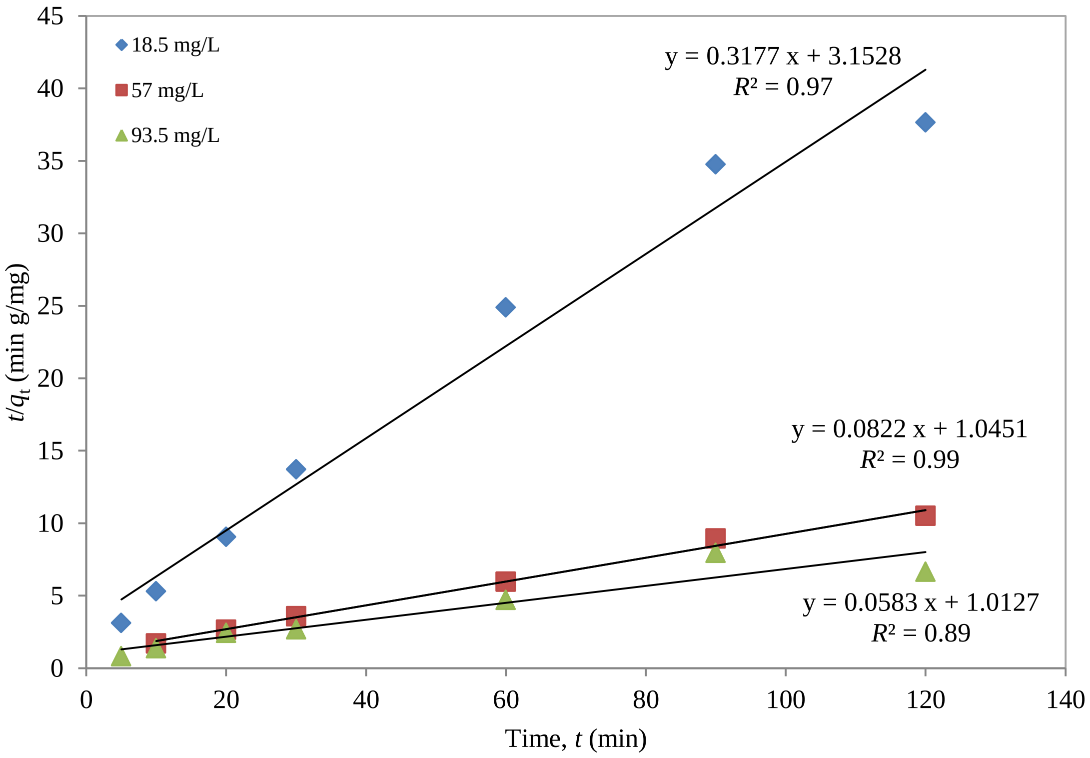


Figure 6.9 Pseudo-second order kinetic model for DOC adsorption by attapulgite B at different DOC concentration, a) granular attapulgite B and b) powder attapulgite B

The diffusion mechanism could be explained by using the intra-particle diffusion model (Fierro et al., 2008). The removal rate of DOC by adsorption on attapulgite was found to be fast in the early stages of contact and then tend to slow down until it become stagnate as time proceeds. For a solid/liquid sorption process, the solute transfer is usually characterized by either external mass transfer or intra-particle diffusion or both. The DOC is most probably transported from the bulk of the solution into the solid phase of attapulgite through intra-particle diffusion transport process. The applicability of intra-particle diffusion model indicates that it is the rate determining step. The following diffusion kinetics models were used to test the adsorption mechanism of DOC onto attapulgite: intra-particle diffusion model, liquid film diffusion model and double exponential model. Table 6.3 and Table 6.4 represent the linear regression coefficient R^2 obtained from the three diffusion models. The linear plot of $t^{0.5}$ versus q_t for the intra-particle diffusion kinetic model is shown in Figure 6.10 - Figure 6.13. The plots represent the linear plot of $t^{0.5}$ versus q_t at different initial DOC concentration and different attapulgite doses.

Table 6.3 Intra-particle diffusion and liquid film diffusion and double exponential model for adsorption of DOC on Attapulgite A

		Intra-particle diffusion		Liquid film diffusion		Double exponential model	
Type	Parameters	K_{id} (min^{-1})	R^2	K_{fd} (min^{-1})	R^2	K_2 (min^{-1})	R^2
Granular	Initial attapulgite dose (g)						
	0.5	0.506	0.75	0.008	0.53	0.992	0.53
	1.0	0.270	0.76	0.005	0.59	0.995	0.59
	2.0	0.147	0.73	0.004	0.46	0.996	0.46
	Initial DOC concentration (mg/L)						
	18.5	0.183	0.95	0.0136	0.94	0.986	0.94
	57	0.549	0.83	0.0153	0.90	0.980	0.82
	93.47	0.506	0.75	0.008	0.53	0.992	0.53
	Initial pH						
	4	0.081	0.91	0.0136	0.58	0.986	0.58
	6	0.133	0.87	0.0246	0.37	0.976	0.38
	9	0.147	0.93	0.0208	0.80	0.979	0.81
Powder	Initial attapulgite dose (g)						
	0.5	0.219	0.89	0.013	0.68	0.987	0.68
	1.0	0.2908	0.74	0.003	0.53	0.997	0.54
	2.0	0.1743	0.85	0.005	0.42	0.995	0.42
	Initial DOC concentration (mg/L)						
	18.5	0.219	0.90	0.0327	0.91	0.968	0.91
	57	0.6934	0.84	0.0301	0.91	0.970	0.91
	93.47	0.7258	0.89	0.013	0.68	0.987	0.68
	Initial pH						
	4	0.107	0.89	0.053	0.93	0.954	0.90
	6	0.163	0.89	0.021	0.82	0.979	0.82
	9	0.153	0.93	0.020	0.77	0.980	0.77

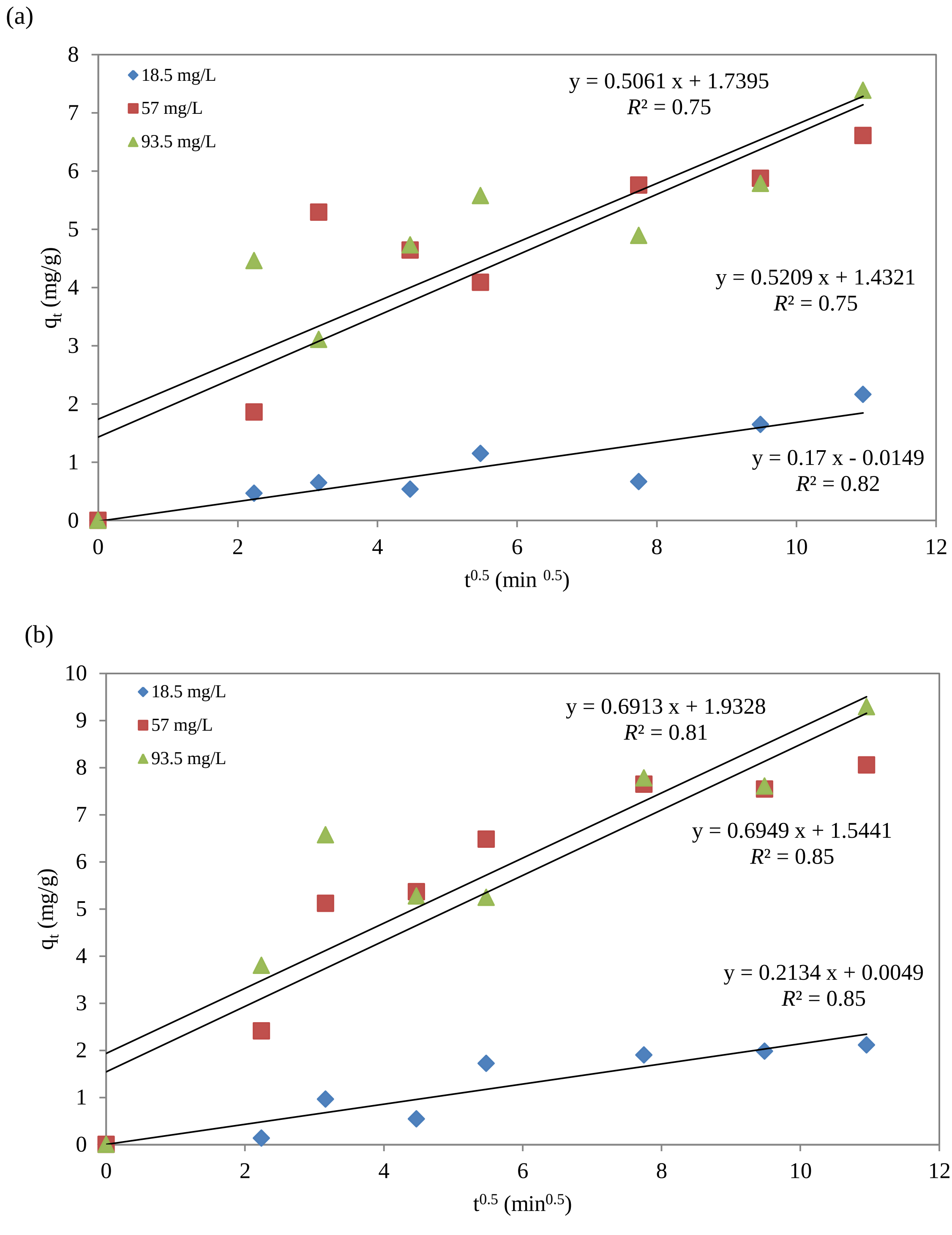


Figure 6.10 Intraparticle diffusion kinetic model for DOC adsorption by attapulgite A at different DOC concentration, a) granular attapulgite A and b) powder attapulgite A

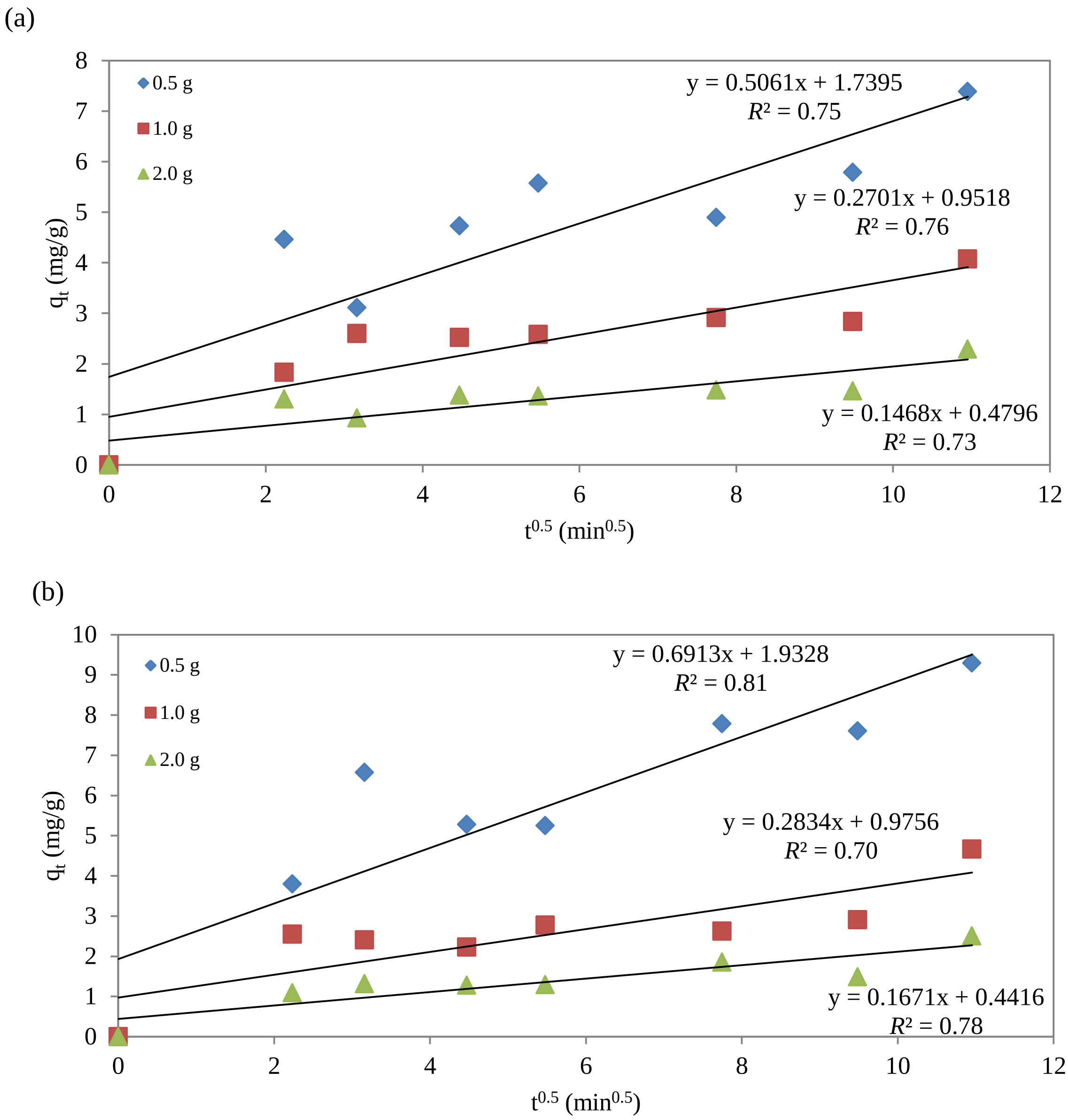


Figure 6.11 Intraparticle diffusion kinetic model for DOC adsorption by attapulgite A at different attapulgite doses, a) granular attapulgite A and b) powder attapulgite A

Table 6.4 Intra-particle diffusion and liquid film diffusion and double exponential model for adsorption of DOC on attapulgite B

		Intra-particle diffusion		Liquid film diffusion		Double exponential model	
Type	Parameters	K_{id} (min^{-1})	R^2	K_{fd} (min^{-1})	R^2	K_2 (min^{-1})	R^2
Granular	Initial attapulgite dose (g)						
	0.5	0.6176	0.80	0.0075	0.51	0.9925	0.51
	1.0	0.3087	0.79	0.0081	0.73	0.9919	0.73
	2.0	0.1545	0.73	0.0089	0.65	0.9911	0.66
	Initial DOC concentration (mg/L)						
	18.5	0.2174	0.68	0.010	0.56	0.990	0.56
	57	0.692	0.83	0.018	0.63	0.982	0.63
	93.47	0.6176	0.80	0.009	0.77	0.990	0.77
	Initial pH						
	4	0.195	0.92	0.0253	0.98	0.976	0.98
	6	0.179	0.96	0.03	0.87	0.984	0.93
	9	0.141	0.92	0.0136	0.88	0.987	0.88
Powder	Initial attapulgite dose (g)						
	0.5	1.334	0.88	0.0151	0.94	0.9850	0.94
	1.0	0.6827	0.91	0.0095	0.87	0.9852	0.94
	2.0	0.3295	0.84	0.0114	0.73	0.9930	0.86
	Initial DOC concentration (mg/L)						
	18.5	0.225	0.81	0.010	0.90	0.989	0.83
	57	0.719	0.84	0.0341	0.91	0.967	0.91
	93.47	1.334	0.88	0.0151	0.94	0.9850	0.94
	Initial pH						
	4	0.117	0.98	0.0284	0.94	0.9734	0.94
	6	0.1734	0.98	0.0196	0.95	0.9806	0.96
	9	0.1466	0.67	0.0249	0.98	0.9736	0.97

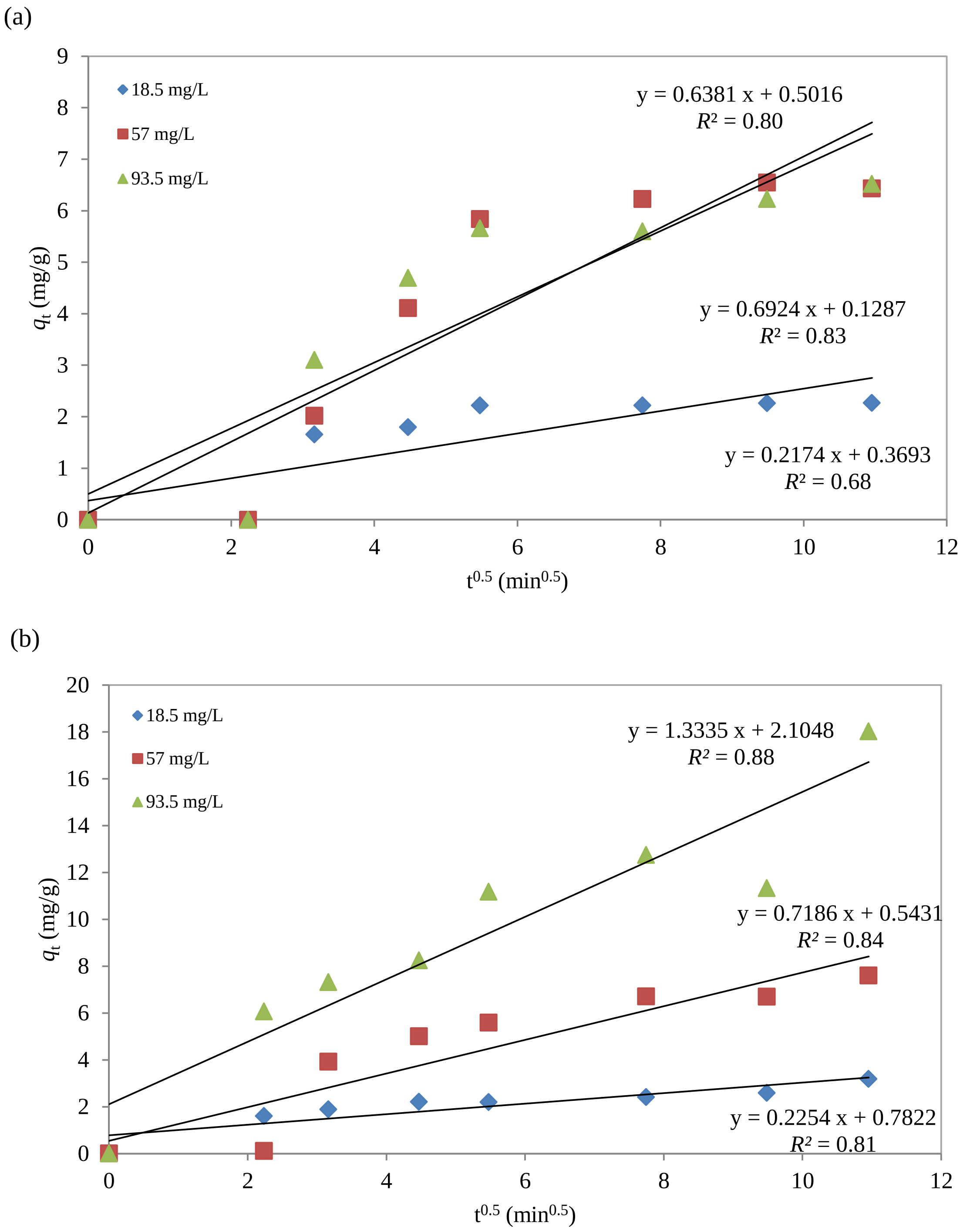


Figure 6.12 Intraparticle diffusion kinetic model for DOC adsorption by attapulgite B at different DOC concentration, a) granular attapulgite B and b) powder attapulgite B

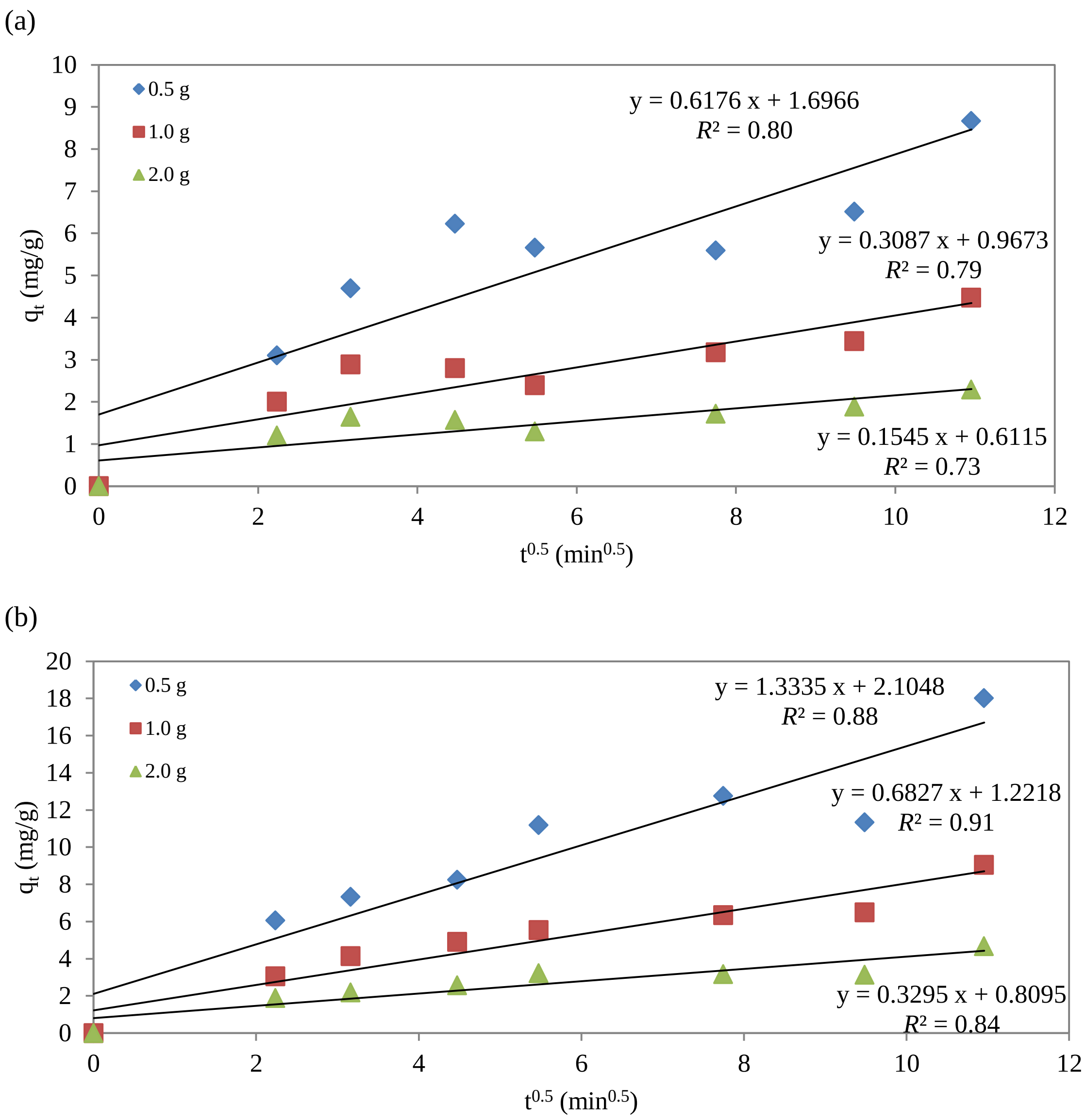
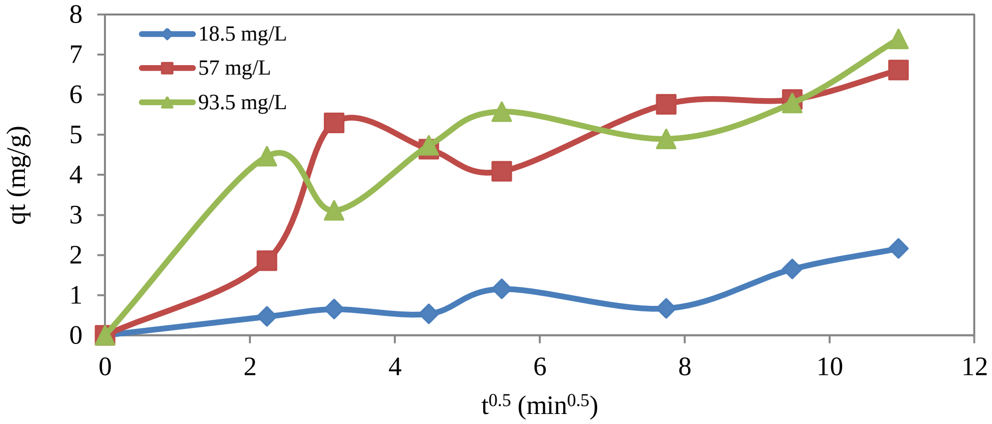
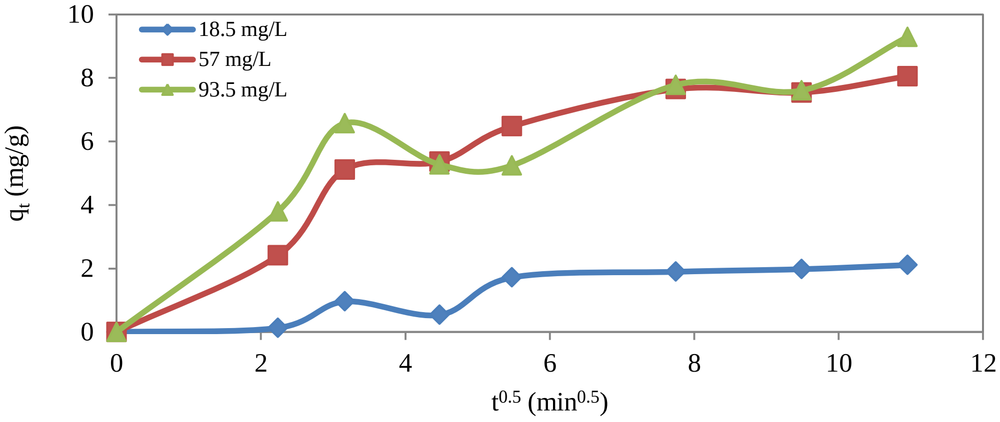


Figure 6.13 Intraparticle diffusion kinetic model for DOC adsorption at different attapulgite B doses, (a) granular attapulgite B and (b) powder attapulgite B

The adsorption of DOC onto attapulgite during earlier stages might be controlled by film diffusion and as the time proceeds, i.e. attapulgite get loaded with DOC, the sorption process may be controlled due to intra-particle diffusion. The plot of intra-particle diffusion model, i.e. q_t vs $t^{0.5}$, is commonly used to identify the mechanism involved in the sorption process (Figure 6.14 Figure 6.15). The plot confirms the multi-stages of adsorption as the fitted experimental data are not linear suggesting that the reaction starts with external mass transfer of the DOC molecules to the external surface of the attapulgite through film diffusion and its rate is fast followed by the entrance of DOC molecules into attapulgite by intra-particle diffusion through pores.



(a)



(b)

Figure 6.14 Intra-particle diffusion model for DOC adsorption by attapulgite A at different initial DOC concentrations, a) granular attapulgite A and b) powder attapulgite A

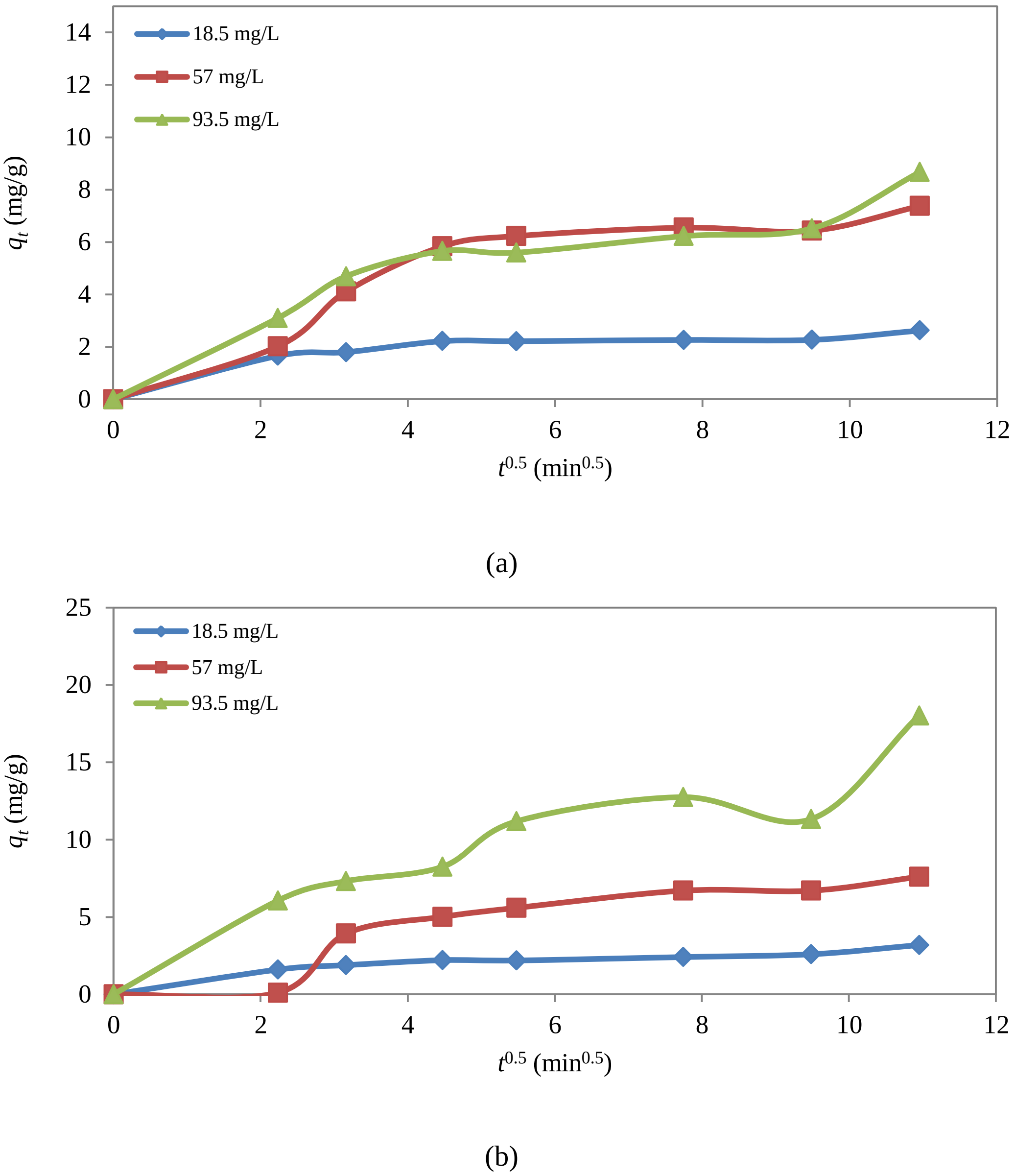


Figure 6.15 Intra-particle diffusion model for DOC adsorption by attapulgite B at different initial DOC concentrations, a) granular attapulgite B and b) powder attapulgite B

The mechanism of DOC uptake from oily produced water by adsorption can be summarized into four steps (Figure 6.16): the first step involves the migration of the DOC molecules from the bulk solution to the surface of attapulgite, the second step represents the diffusion of DOC molecules through the boundary layer to the surface of the sorbent, the third-step is adsorption at sites, and finally the intra-particle diffusion into the interior of the sorbent (Nandi et al., 2009, Oladoja et al., 2008).

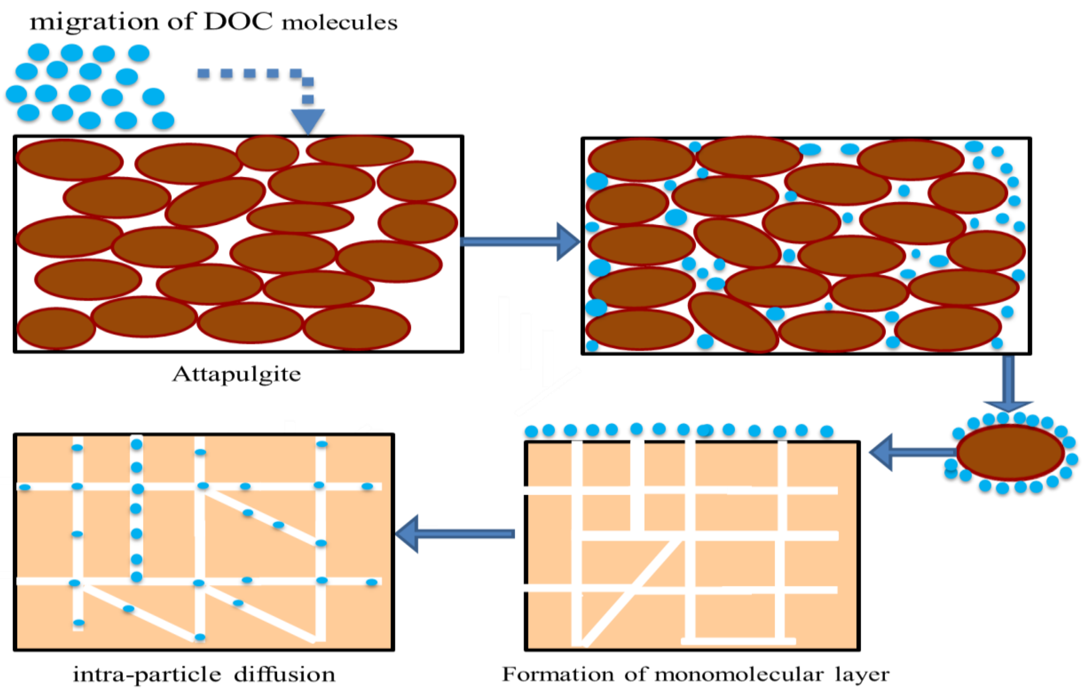


Figure 6.16 Schematic diagram represents the mechanism of DOC uptake

6.3.5. Adsorption isotherms

Adsorption isotherms are considered as an important tool to understand the mechanism of the adsorption. In this study, three isotherms models were used namely Langmuir, Freundlich, and Dubinin-Radushkevich isotherms models. The parameters of the three models are listed Table 6.5 Table 6.6.

The correlation coefficient, R^2 is used as a tool to test the applicability of the isotherm equation. Although Freundlich and Dubinin-Radushkevich models showed decent linear regression coefficient, R^2, but Langmuir isotherm model is found to have the best fitting for the adsorption of DOC onto attapulgite with R^2 of 0.996 for powdered attapulgite and 0.89 for granular attapulgite. The Langmuir isotherm confirms the monolayer coverage of DOC onto attapulgite particles. The maximum mono-layer adsorption from Langmuir model, q_m, was found to be 31.06 mg/g and 65.36 mg/g for granular and powdered attapulgite B respectively while it was found to be 40.98 mg/g and 6549.26mg/g for granular and powdered attapulgite A respectively.

The separation factor, R_L, can be obtained from the Langmuir plot as follows (Demiral et al., 2008)

$$R_L = \frac{1}{1 + K_L C_o} \tag{6.1}$$

where K_L is the Langmuir constant and C_o is the initial concentration of DOC. The separation factor, R_L values indicate the type of isotherm to be favorable $0 < R_L < 1$, unfavorable $R_L > 1$, linear $R_L = 1$ and irreversible $R_L = 0$.

To check the shape of the isotherm for the adsorption of DOC on granular and powdered attapulgite, R_L was calculated for the initial DOC concentration of 10-100 mg/L and it is found to be as follows:

R_L values of attapulgite A

C_o (mg/L)	10	20	30	40	50	60	70	80	90	100
Granular	0.922	0.854	0.797	0.747	0.702	0.663	0.627	0.596	0.570	0.541
Powder	0.934	0.876	0.825	0.780	0.739	0.702	0.669	0.639	0.611	0.586

R_L values of attapulgite B

C_o (mg/L)	10	20	30	40	50	60	70	80	90	100
Granular	0.899	0.817	0.748	0.690	0.641	0.598	0.560	0.527	0.498	0.471
Powder	0.949	0.903	0.862	0.824	0.789	0.758	0.728	0.701	0.676	0.652

This indicates favourable adsorption as R_L falls in the category $0 < R_L < 1$.

Table 6.5 Langmuir, Freundlich, and Dubinin-Radushkevich isotherm constants attapulgite A

	Attapulgite type	
	Granular	Powder
Langmuir		
K_L *(L/mg)*	0.008486	0.00706
q_m *(mg/g)*	40.98	49.26
R^2	0.90	0.667
Equation	$q_e = \frac{0.347768c_e}{1 + 0.008486c_e}$	$q_e = \frac{0.347776c_e}{1 + 0.00706c_e}$
Freundlich		
K_f	0.5745	0.653
n	1.555	1.482
R^2	0.74	0.54
Equation	$q_e = 0.5745c_e^{0.643}$	$q_e = 0.653c_e^{0.675}$
Dubinin-Raddushkevich		
q_m *(mg/g)*	8.23	11.93
β	0.0202	0.0269
R^2	0.99	0.85
Equation	$q_e = 8.23e^{-0.0202\varepsilon^2}$	$q_e = 11.93e^{-0.0269\varepsilon^2}$

Table 6.6 Langmuir, Freundlich and Dubinin-Radushkevich isotherm constants for attapulgite B

	Attapulgite type	
	Granular	Powder
Langmuir		
K_L *(L/mg)*	0.011198	0.00532
q_m *(mg/g)*	31.0559	65.3595
R^2	0.89	0.996
Equation	$q_e = \frac{0.347778c_e}{1 + 0.011198c_e}$	$q_e = \frac{0.347778c_e}{1 + 0.00532c_e}$
Freundlich		
K_f	0.87049	0.2660
n	1.7056	0.84724
R^2	0.74	0.98
Equation	$q_e = 0.87049c_e^{0.586}$	$q_e = 0.266c_e^{1.180}$
Dubinin-Radushkevich		
q_m *(mg/g)*	9.42	14.52
β	0.01348	0.01348
R^2	0.99	0.85
Equation	$q_e = 9.42e^{-0.01348\varepsilon^2}$	$q_e = 14.52e^{-0.01348\varepsilon^2}$

6.3.6. Effect of temperature and thermodynamics

Temperature is found to have a significant effect on the adsorption capacity of the adsorbent. In general, increasing solution temperature will result in decreasing adsorption capacity because adsorbed molecules have great vibrational energies and are therefore more likely to desorb from the surface (Cooney, 1998). The feasibility of adsorption process can be evaluated by the thermodynamic parameters such as free energy (ΔG^o), enthalpy (ΔH^o), and entropy (ΔS^o).

The uptake of DOC by granular attapulgite B decreased from 3.88 mg/g (19.94% removal) to 2.94 mg/g (15.1% removal) and the uptake of DOC by powdered attapulgite decreased from 4.28 mg/g (21.99% removal) to 3.26 mg/g (16.75% removal) when increasing temperature from 25 ^{o}C to 45 ^{o}C, indicating that the DOC removal was favoured at lower temperature. In the other side The uptake of DOC by granular attapulgite A decreased from 4.22 mg/g (21.69% removal) to 3.28 mg/g (16.86% removal) and the uptake of DOC by powdered attapulgite decreased from 4.08 mg/g (20.97% removal) to 3.84 mg/g (19.73% removal) when increasing temperature from 25 ^{o}C to 45 ^{o}C. This fact indicates that the adsorption of DOC onto attapulgite is exothermic process. This can be due to the weak adsorptive forces between the DOC and attapulgite active adsorptive sites and also between the vicinal molecules of the adsorbed phase when temperature increases. Thermodynamic parameters were used to test the feasibility of the adsorption process. ΔG^o, ΔH^o, and ΔS^o are illustrated in Table 6.8 and Table 6.7 at different temperatures 298, 308, and 318 K. The negative value of ΔH^o indicates the exothermic nature of adsorption which also supported by the decrease in DOC uptake with the increase in temperature. The reaction is found to be nonspontaneous as ΔG^o is > 1. The negative value of ΔS^o indicates decreased randomness at solid/liquid interface during DOC adsorption onto attapulgite.

Table 6.7 Thermodynamic parameters for adsorption of DOC onto attapulgite A at different temperatures

		ΔH^o	ΔS^o	ΔG^o (KJ/mol)			
		(KJ/mol)	(J/mol K)	298	308	318	R^2
Attapulgite Type	Granular	-12.37	-65.78	7.231	7.889	8.547	0.91
	Powder	-9.7	-56.81	7.229	7.797	8.365	0.95

Table 6.8 Thermodynamic parameters for adsorption of DOC onto attapulgite B at different temperatures

		ΔH^o	ΔS^o	ΔG^o (KJ/mol)			
		(KJ/mol)	(J/mol K)	298	308	318	R^2
Attapulgite Type	Granular	–13.270	–69.52	7.445	8.140	8.835	0.99
	Powder	–13.306	–68.56	7.124	7.810	8.496	0.99

6.4. Design of single-stage batch absorber from isotherm data

The Langmuir adsorption isotherm was used to predict the design of single batch system according to the method developed by (Senthil Kumar et al., 2010, McKay et al., 1985).A schematic diagram is shown in Figure 6.17.

The main design objective is to find the amount of adsorbent, m (g) required to reduce the initial DOC concentration of C_o to C_l (mg/L) for which total solution is V (L). When attapulgite is added to the system the DOC concentration on the surface of the solid changes from q_o=0 to q_l. The mass balance of DOC in the single-stage operation under equilibrium is given by

$$V(C_o - C_e) = m(q_e - q_o) = mq_e \tag{6.2}$$

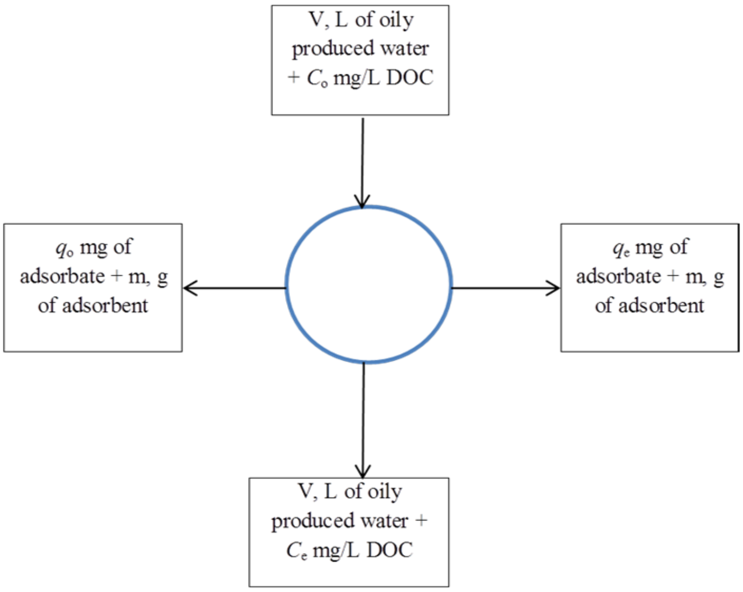
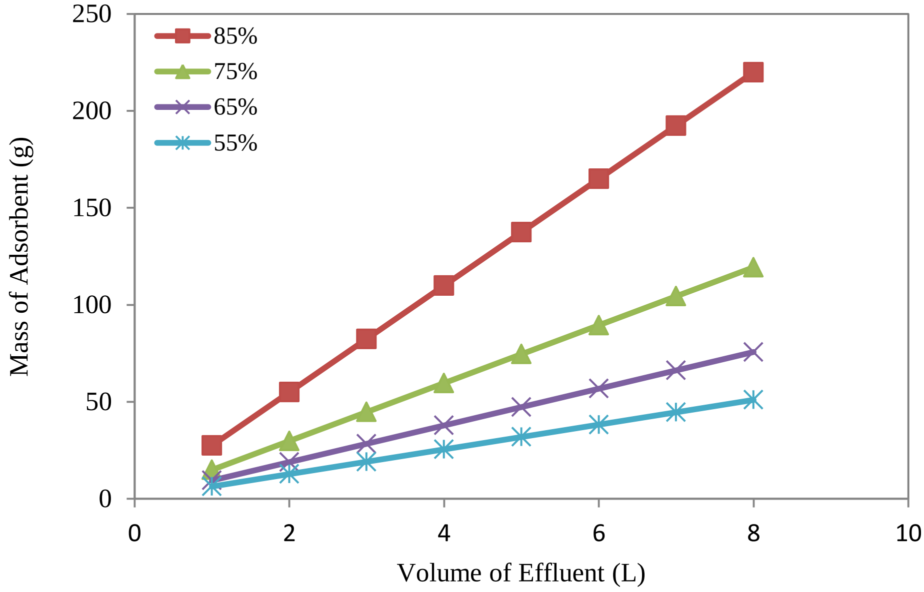


Figure 6.17 Schematic diagram of a single-stage batch absorber.

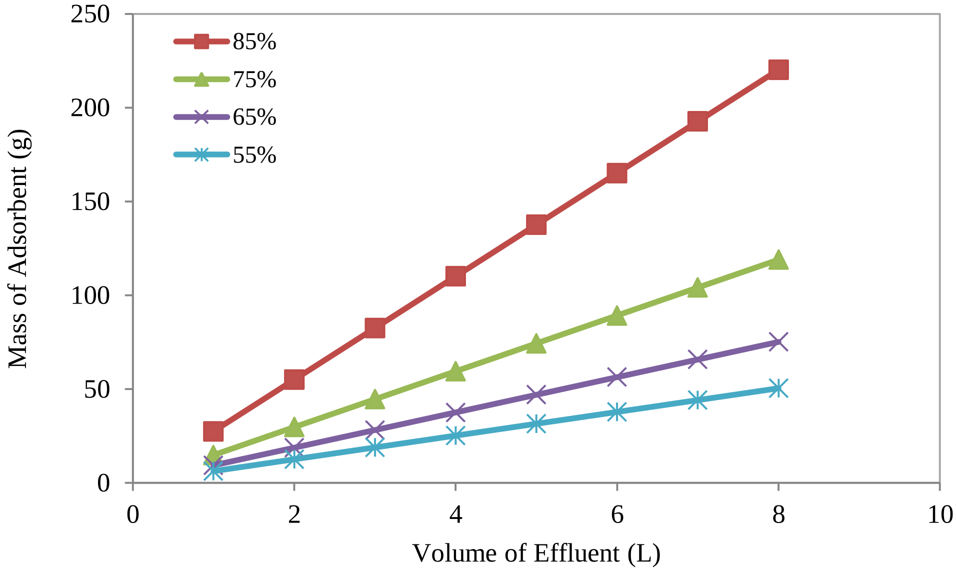
As previously mentioned, the Langmuir isotherm model shows the best fit for the equilibrium data and therefore, the above equation can be rewritten after substituting q_e from Langmuir model

$$\frac{m}{V} = \frac{(C_o - C_e)}{q_e} = \frac{(C_o - C_e)}{\left[\frac{q_m K_L C_e}{1 + K_L C_e}\right]} \tag{6.3}$$

Figure 6.18 (a and b) and Figure 6.19 (a and b) shows a sequence of plots derived from Equation (6.3) for attapulgite A and attapulgite B respectively. Different solution volumes (1-8 L) were used to predict the amount of granular and powdered attapulgite (m) required to achieve target DOC removal efficiency (85, 75, 65, and 55%), given that the initial concentration of DOC is 50 mg/L.

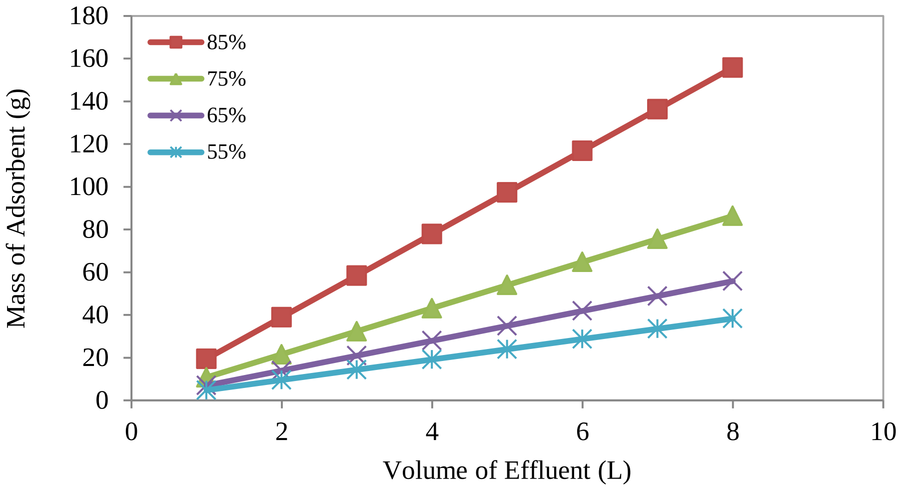


(a)

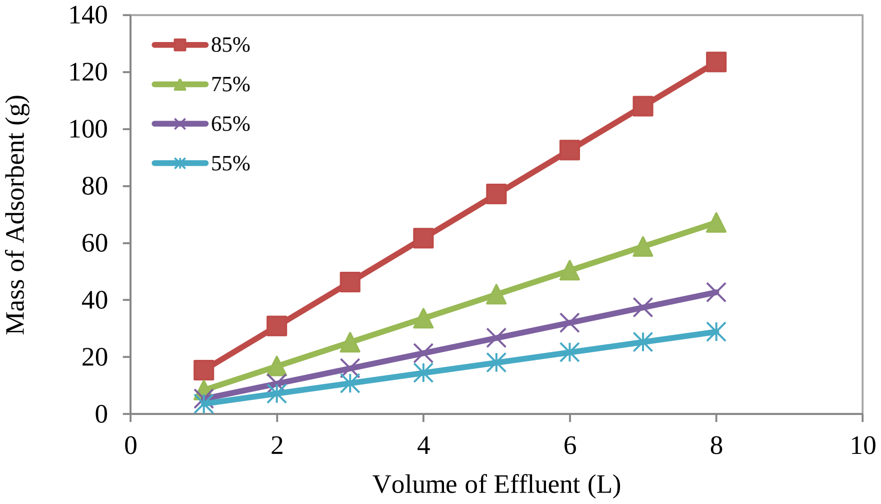


(b)

Figure 6.18 Attapulgite A mass (m) versus volume of solution (L), a) granular attapulgite A and b) powder attapulgite A



(a)



(b)

Figure 6.19 Attapulgite B mass (m) versus volume of solution (L), a) granular attapulgite B and b) powder attapulgite B

6.5. Summary

The results from the present study show that the attapulgite can be utilized as promising adsorbent for the removal of DOC from oily produced water. The experimental results revealed that the adsorption of DOC onto attapulgite increases with the increase in initial DOC concentration, contact time, and amount of adsorbent dose while, it decreases with increase in temperature, and solution pH. The

DOC uptake increased from 2.62 mg/g to 8.67 mg/g with the granular attapulgite B while the increase with the powder attapulgite B was more noticeable where DOC uptake increased from 4.67 mg/g to 18.02 mg/g when initial concentration increased from 18.5 mg/L to 93.47 mg/L respectively. With attapulgite A the DOC uptake increased from 2.16 mg/g to 7.39 mg/g with the granular attapulgite B while the increase with the powder attapulgite B was more noticeable where DOC uptake increased from 2.11 mg/g to 9.29 mg/g when initial concentration increased from 18.5 mg/L to 93.47 mg/L respectively. The changes in pH of oily produced water have no significant influence on adsorption capacities A Langmuir equation is applicable for the adsorption of DOC onto attapulgite. The parameters of Langmuir, Freundlich, and D-R models were calculated and tabulated. The adsorption process follows the pseudo-second order process. Pseudo-first order, pseudo-second order, intra-particle diffusion, liquid film diffusion, and double exponential models were applied to study the mechanism of adsorption. The kinetic experiments showed that the adsorption of DOC onto attapulgite can be summarized into two steps: external mass transfer of the DOC molecules to the external surface of the attapulgite through film diffusion at a fast rate, and intra-particle diffusion of DOC molecules into attapulgite particles through pores. The thermodynamic analysis showed that the process is nonspontaneous, exothermic and chemisorption in nature.

CHAPTER 7

APPLICATION OF CERAMIC MEMBRANE FOR THE PURIFICATION OF PRODUCED WATER

7.1. Introduction

This chapter covers the application of ceramic membrane for the purification of produced water and the evaluation of the effect of different working conditions on the treatment process.

Management of produced water is a key environmental, social, technical and economical challenge for oil and gas industry and for development of remote fields. Effective techniques to handle the huge quantities of produced water depend on asset maturity, the type of reservoir, production rates, location and legislations (Zara, 2002). In order to meet with the treatment objectives, operators have applied many standalone and combined physical, chemical and biological treatment processes. Most of the available technologies for the purification of produced water focus on the removal of dispersed hydrocarbons. This can be attributed to the fact that the environmental legislation aims to reduce the dispersed oil, recently the attention shifted toward the effect of other components of produced water such as dissolved oil and heavy metals. This led to better understanding of the impact of these constituents on the environment and eventually led to the application of new technologies to remove them.

Membrane separation has become the promising technology over the last 30 years (Sonune and Ghate, 2004). This technology has many advantages including stable effluent quality and small area requirements. Ceramic membranes are a new class of materials which can be made from different materials and processed in different ways to produce products with wide ranges of physical-chemical advantages and applications (Ashaghi et al., 2007). They have shown great potential for oily water purification due to their extraordinary properties, such as thermal stability, high mechanical strength and ease of regeneration after fouling (Abadi et al., 2011). To explore the excellent properties of ceramic membrane, the application of ceramic membrane for the treatment of oily produced water was investigated in this study.

The application of a cross-flow microfiltration using ceramic membrane (α-Al_2O_3) membrane with 0.05 µm pore size for the purification of oily water from oilfield was studied and investigated. The effect of applied pressure with different temperature on the removal of pollutants and impurities was tested through the measurement of permeate flux, total organic carbon (TOC), chemical oxygen demand (COD), oil in water (OIW) content and turbidity.

7.2. Materials and methods

7.2.1. Feed Water

The oily produced water in this study is collected from an oilfield located in the southern part of Oman. The characteristics of the oily produced water are presented in Table 7.1. The water was collected from the outlet of the Corrugated Plate Interceptor (CPI) unit wherein the oil content typically varies from 250 to 350 mg/L.

Before performing the experimental trials a thorough chemical analysis was done. The salinity was around 8.8 dS/m and pH around 9.1. Chloride was found to be the dominant anion present in the produced water. The dissolved organic compounds are found to be alkanes ranging from C_{10} to C_{30} based on the Gas Chromatography–Mass Spectrometry (GC-MS) analysis.

Table 7.1 Average characteristics of produced water

Parameter	Units	Value
Oil in Water (OIW)	mg/L	134.55
pH		9.1
Electrical Conductivity (EC)	dS/m	8.79
Chemical Oxygen Demand (COD)	mg/L	89.9
Total Organic Carbon (TOC)	mg/L	125
Fluoride	mg/L	1.820
Chloride	mg/L	2757.6
Bromide	mg/L	12.656
Nitrate	mg/L	0.931
Sulphate	mg/L	187.564
Aluminium	mg/L	16.7
Magnesium	mg/L	19.6
Calcium	mg/L	11.9
Iron	mg/L	< 0.4

7.2.2. Specifications of ceramic membrane

Ceramic membrane with 50 nm pore size, one meter long with 19 channels (6 mm diameter each and a diameter of 41 mm for the whole unit) was ordered from Germany, atech innovations GmbH, (Figure 7.1). The filter surface per element is approximately 0.36 m^2.

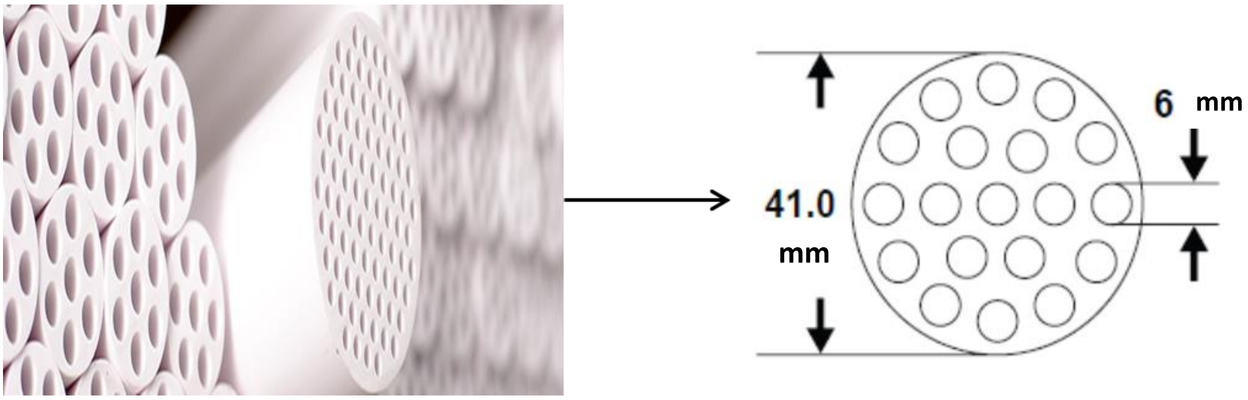


Figure 7.1 Ceramic membrane specification

7.2.3. Ceramic membrane set up

A laboratory scale unit was designed for cross-flow ceramic membrane trials (Figure 7.2). The setup consists of a feed tank, two centrifugal pumps, and ceramic membrane. A mixer with temperature control device was placed in the feed tank in order to make the feed water homogenous and to control the temperature of the feed water. Three pressure gauges were installed, one for the feed water, the second for the permeate water and the third one for the retentate or the brine. Two flow meter were installed for the feed and the permeate water. During the experiment, three different temperatures were tested 25°C, 35°C and 45°C. Four different pressure sets were investigated 1.3 bar, 3 bars, 5 bars and 7 bars. Samples were taken at different time intervals of 5 minutes, 30 minutes, 60 minutes, 120 minutes and 180 minutes to monitor the quality of the permeate by checking the OIW content, COD, TOC, turbidity, EC and pH. The water volume in the feed and permeate was recorded with time to check the performance of the membrane and to test for any membrane fouling.

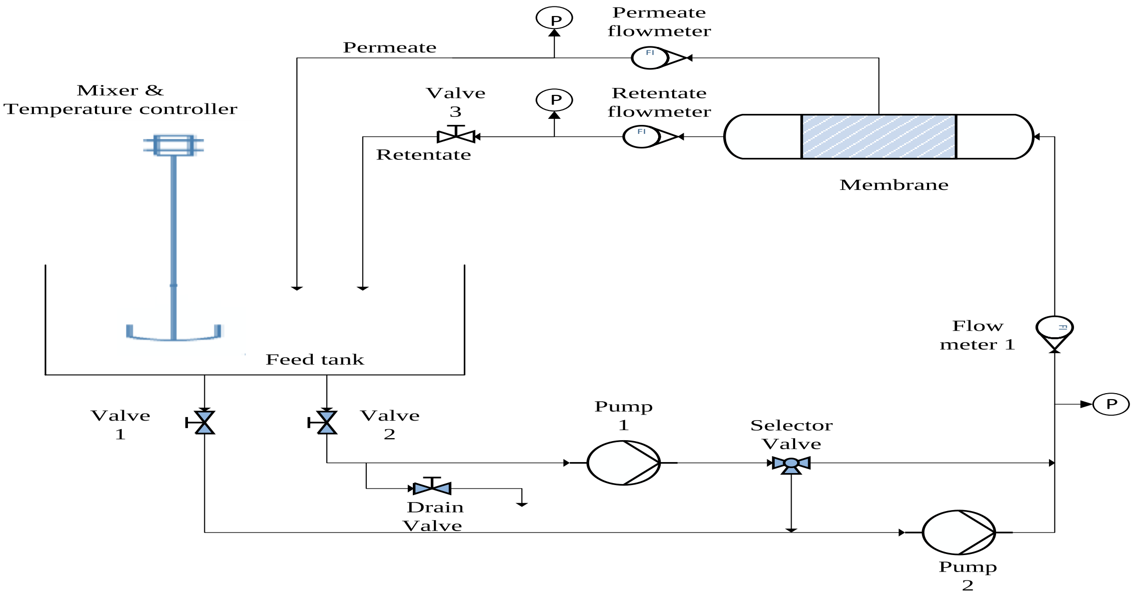


Figure 7.2 Schematic diagram for ceramic membrane set up

The membrane was operated under different operating conditions. The removal or rejection of a certain compound from the feed is expressed as

$$Removal\ (\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \tag{7.1}$$

where C_p, (mg/L) and C_f, (mg/L) are the concentration of a certain component (i.e. COD) in permeate and its feed concentration respectively.

The recovery rate of the membrane at different operating conditions was evaluated according to

$$Recovery\ Rate\ (\%) = \frac{Q_p}{Q_f} \times 100 \tag{7.2}$$

where Q_p, L/h is the permeate flow rate and Q_f, L/h is the feed flow to the membrane unit.

The permeate flux, J (L/m^2 h) was measured during the separation process by dividing the permeate volume (L) by the effective membrane area (m^2) and the sampling time (h).

$$Permeate\ Flux\ (J) = \frac{permeate\ volume\ collected}{membrane\ area\ \times time} \tag{7.3}$$

7.3. Results and Discussion

7.3.1. Effect of pressure on permeate flux

The results indicate clearly that increasing pressure increases PF and when pressure and temperature increase the oil droplets will find their way to block the membrane pores and eventually decrease PF (can be seen clearly with 7 bar at 35^{o}C and 45^{o}C) while with other sets of pressures it reaches a steady state after a certain period of time.

Based on Darcy's law, as the pressure increases the permeate flux (PF) increases, even though, fouling confines this fundamental law. Increasing pressure will compact the oil droplets and allow them to penetrate through the pores and eventually block the membrane pores, i.e. membrane fouling (ZHEN et al., 2006, Sun et al., 1998, Mohammadi and Esmaeelifar, 2004). Consequently, at an optimum pressure, PF is high, while tendency to cake/gel layer formation is low. The flux increases, in most suspensions, with increasing pressure until it reach to the limiting flux (Elmaleh et al., 1994, Elmaleh and Ghaffor, 1996). Beyond that optimum pressure, the PF will increase nonlinearly with pressure due to concentration polarization (Lee et al., 1984). Effects of pressure on PF during the treatment of oily produced water are presented in Figure 7.3 -Figure **7.5**.

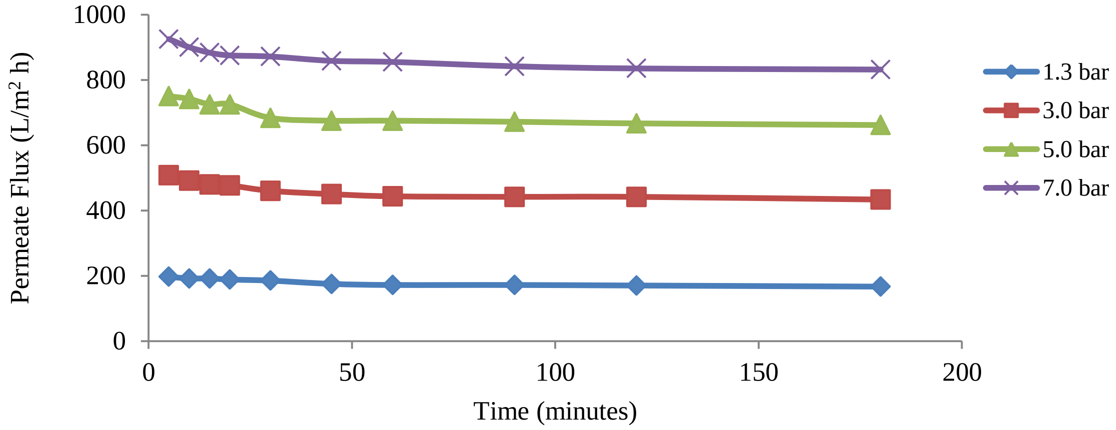


Figure 7.3 Effects of pressure on the permeate flux at 25^{o}C

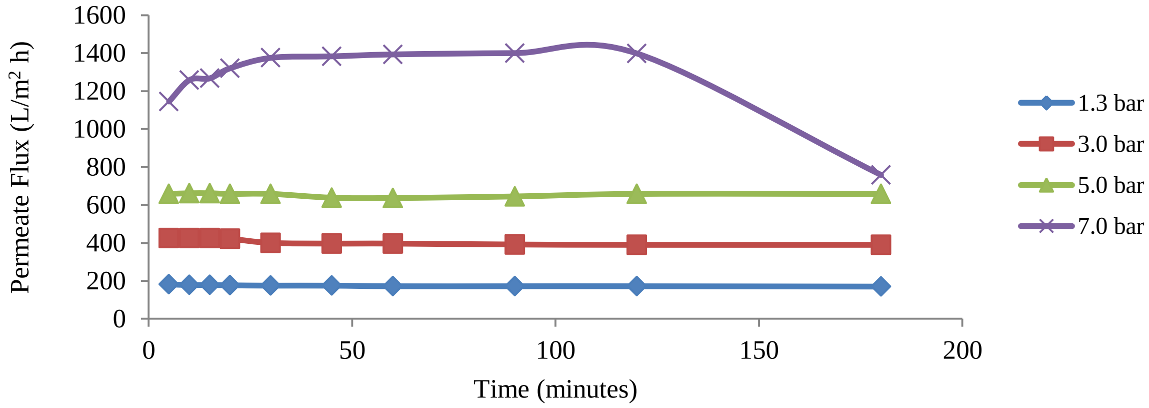


Figure 7.4 Effects of pressure on the permeate flux at 35^{o}C

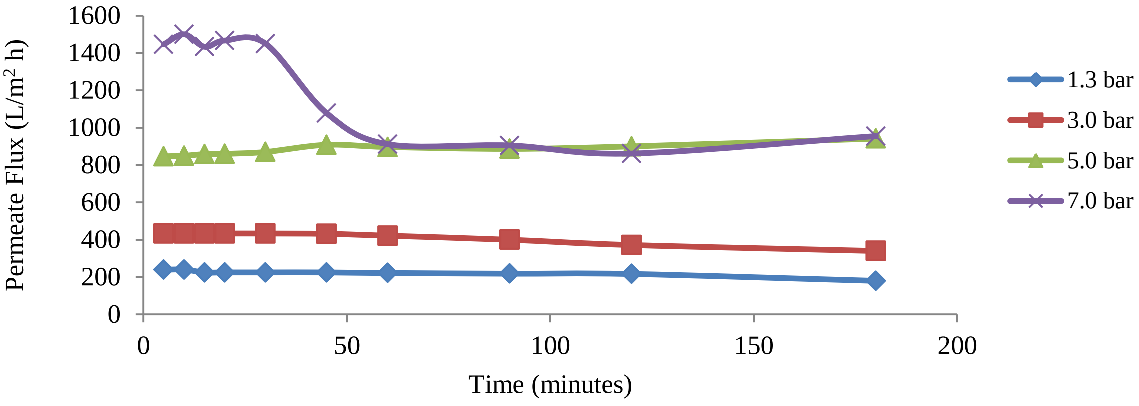


Figure 7.5 Effects of pressure on the permeate flux at 45^{o}C

It can be noticed from Figure 7.6, PF increases linearly with increasing pressure up to 5 bar, however, at higher pressure the change in PF become less until it nearly reaches steady state. This is due to the fact that the gel polarization layer becomes denser with high pressure causing the growth rate of PF to be low.

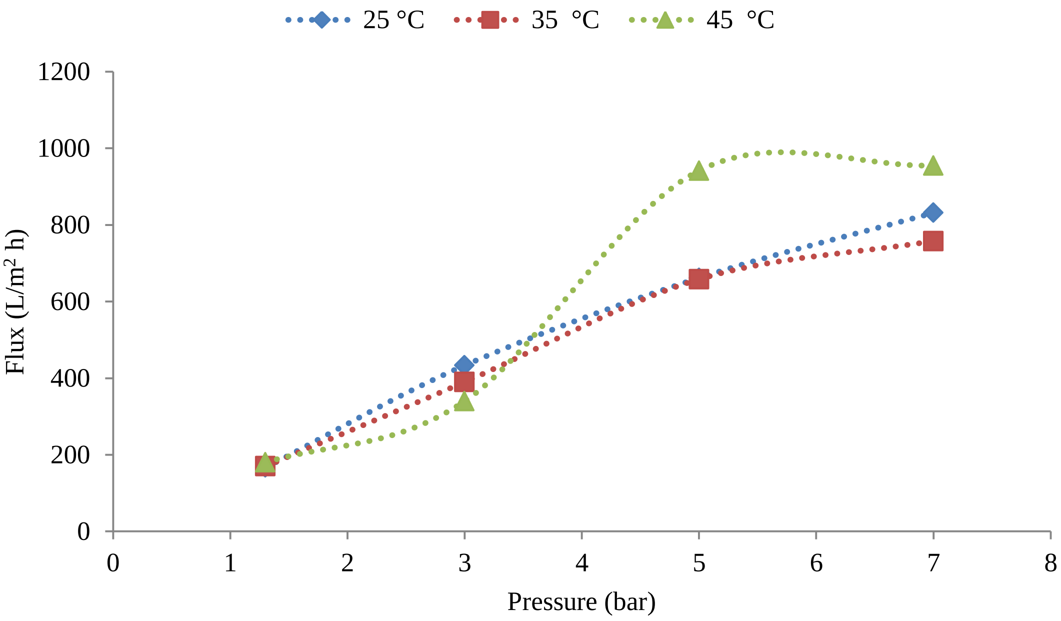


Figure 7.6 Variation of PF with pressure at different temperatures

7.3.2. Effect of pressure on OIW, TOC and COD rejection

The results revealed that increase in pressure has slight influence on OIW, TOC and COD rejection although the OIW rejection is more pronounced. From the results presented in Figure 7.7 -Figure **7.9**, it is evident that the OIW rejection ranged between 74 to 99.6% and the reduction in TOC ranged between 30.6 to 65.6% while the rejection of COD was in the range 9-47%. At elevated pressure, effect of pressure predominates over effect of pore size, and as a result, more organic constituents escape easily through the membrane (Sun et al., 1998).

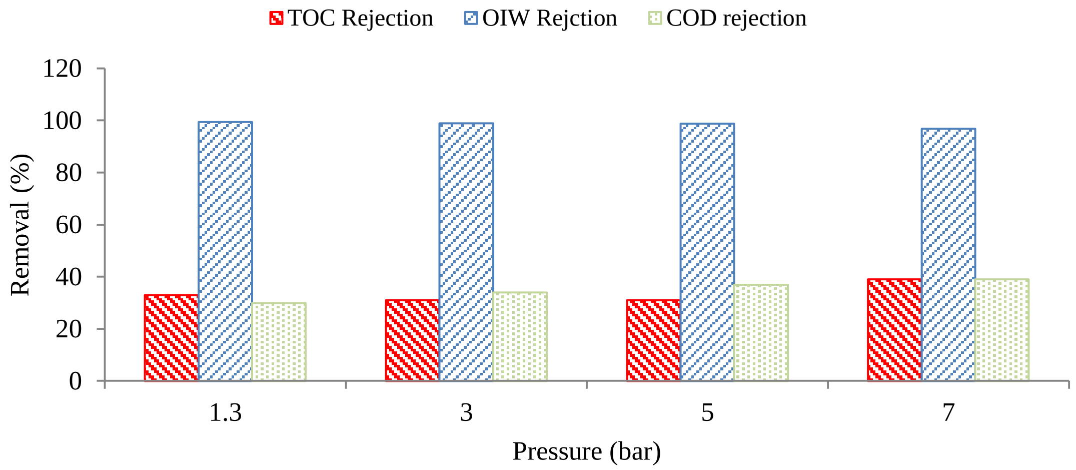


Figure 7.7 Influence of pressure on TOC, OIW and COD rejection at 25^{o}C

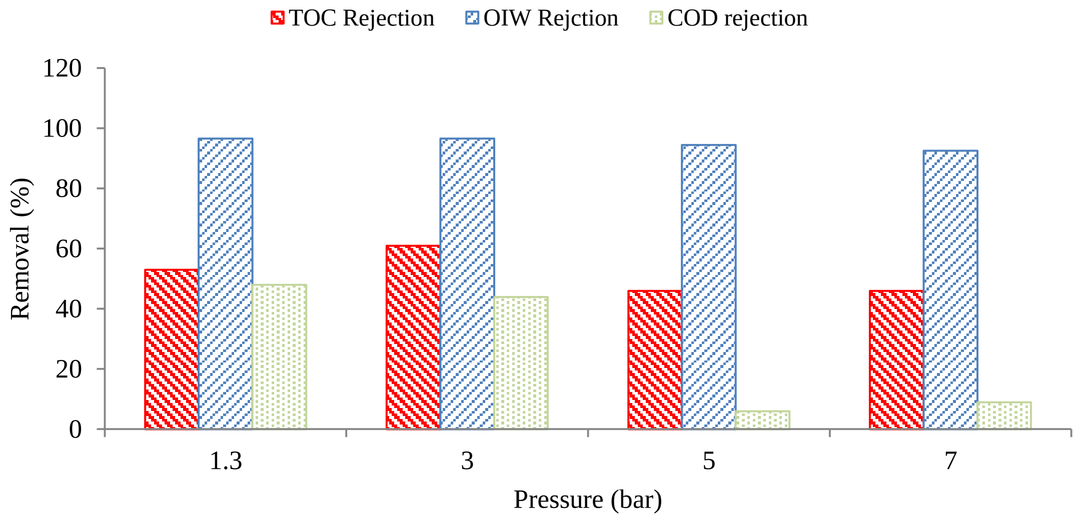


Figure 7.8 Influence of pressure on TOC, OIW and COD rejection at 35^{o}C

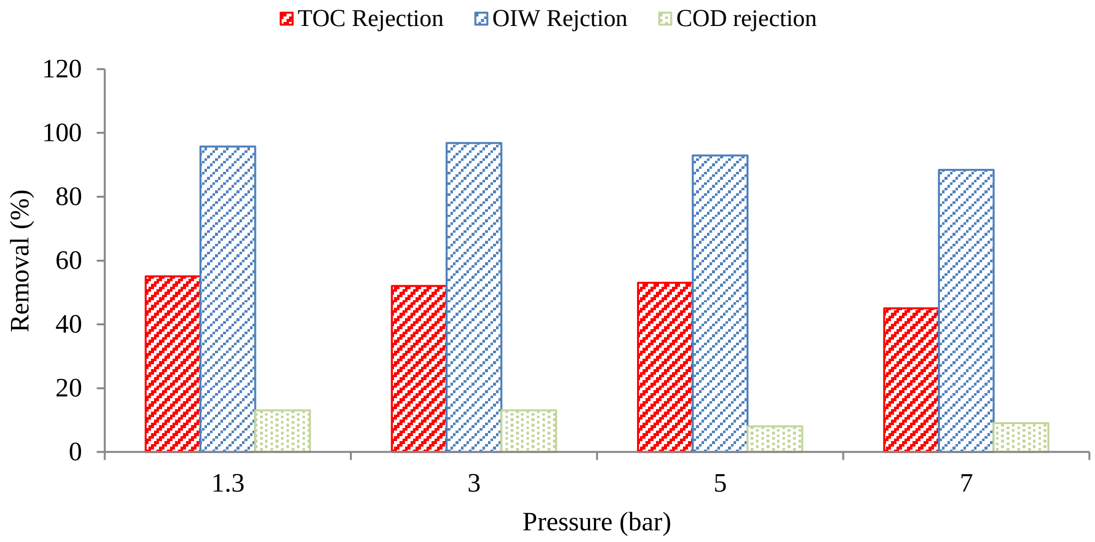
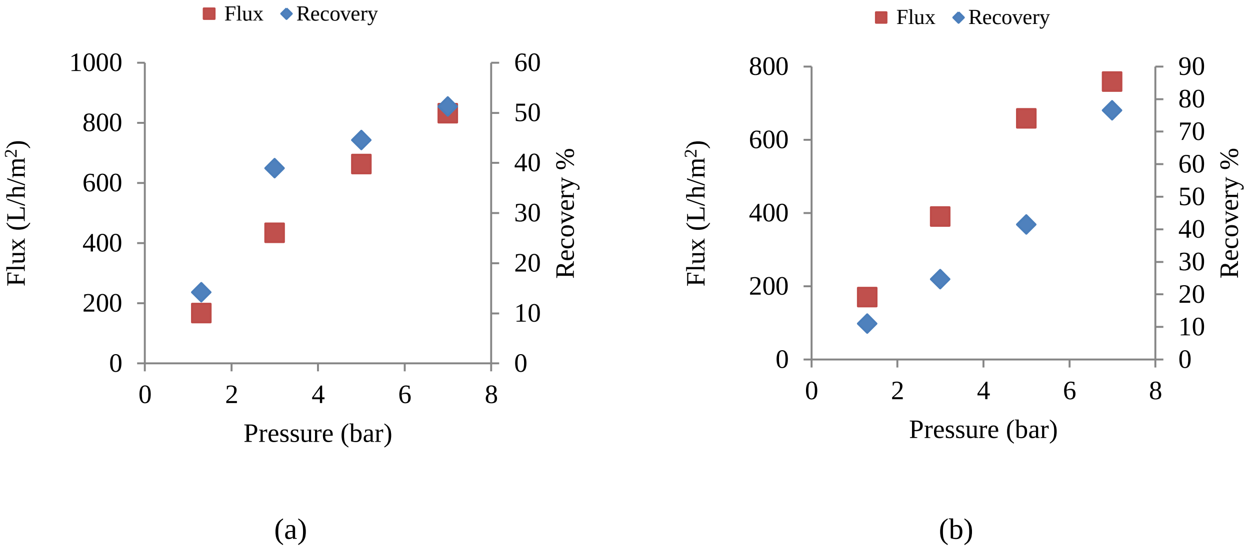


Figure 7.9 Influence of pressure on TOC, OIW and COD rejection at 45^{o}C

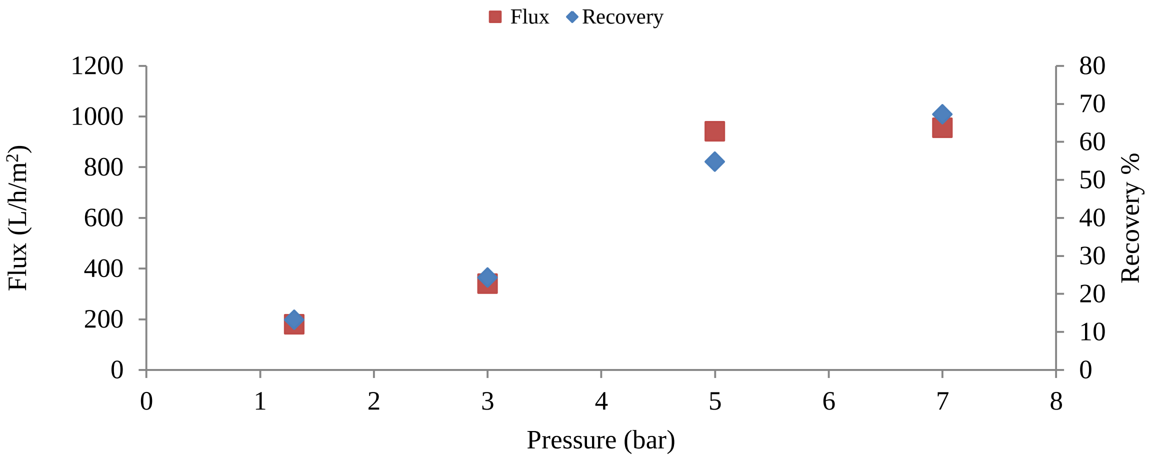
7.3.3. Effect of pressure on recovery rate

The effect of pressure on the recovery rate of the membrane was calculated at different temperatures (Figure 7.10). The recovery rate ranged between 10 to 58%, however, at early stages the recovery rate went up to 91% but as time precedes the tendency to cake gel layer formation increases. It can be observed that, as pressure increase the recovery rate increases due to increase in PF.



(a)

(b)



(c)

Figure 7.10 Effect of pressure on the recovery rate at different temperature. (a) 25°C, (b) 35°C °, and (c): 45°C

7.3.4. Effect of temperature on permeate flux

Temperature is found to have a bilateral effects on permeate flux. From one side increasing temperature will lead to a decrease in the feed viscosity, and as a result, increasing the solvent and solutes permeabilities (diffusivities) (Ohya et al., 1998, Abbasi et al., 2011, Wang et al., 2000, Scott et al., 2000) but from the other side increasing temperature increases osmotic pressure which will eventually decrease the permeation flux. Therefore an optimum temperature must be prescribed (Abbasi et al., 2010b) beside the increasing temperature will increase the operational cost. The results obtained from this study indicated clearly the bilateral effects of temperature on permeate flux (Figure 7.11).

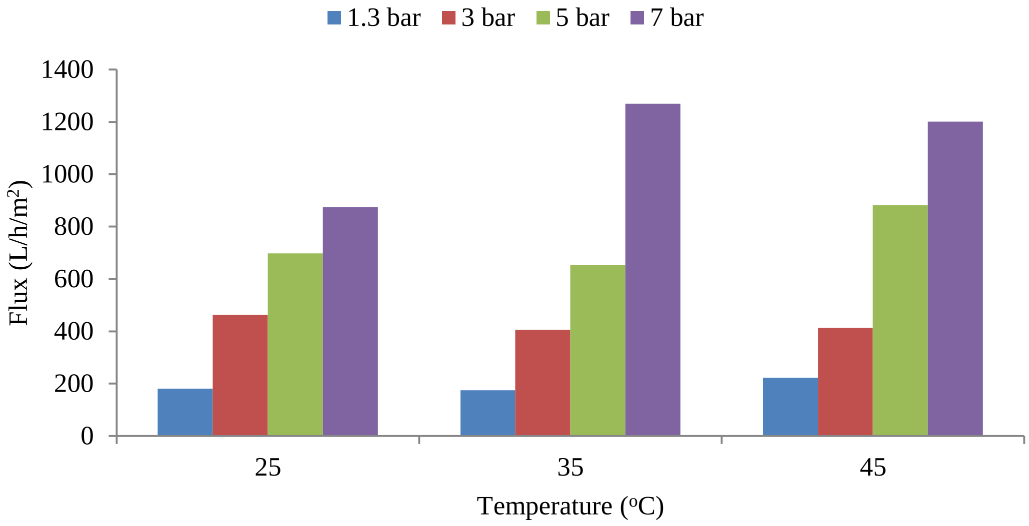


Figure 7.11 Effect of temperature on permeate flux (L/h/m^2) at different pressures

7.3.5. Permeate recovery rate

It was noticed from the results that the recovery rate increases as pressure increase (Figure 7.12 -Figure 7.14). The positive effect of applying high pressure is confronted by deterioration in the quality of the effluent as more pollutants will find there ways to permeate and also high pressure means high power consumption which will raise the cost of treatment and hence there is a need to find an optimum pressure. The accumulation of oil droplets (assorted sizes) and other constituents on the membrane surface and pores tend to decrease the permeate flux and eventually decrease the recovery rate. It can be seen from the results the fluctuation in the recovery rate during the operational time according to the movement of these droplets.

Recovery rate has a major impact on the economics of membrane filtration systems. The sizes of all process equipment which is determined according to feed or concentrate flow will decrease with increased recovery rate (Wilf and Klinko, 2001, Glueckstern et al., 2002). This applies to the size of the feed water supply system and power consumption of intake pumps. The size of all pretreatment equipment; storage tank, booster pumps, filtration equipment and chemical dosing systems is determined according to the feed flow. These considerations will affect the investment cost of the filtration system

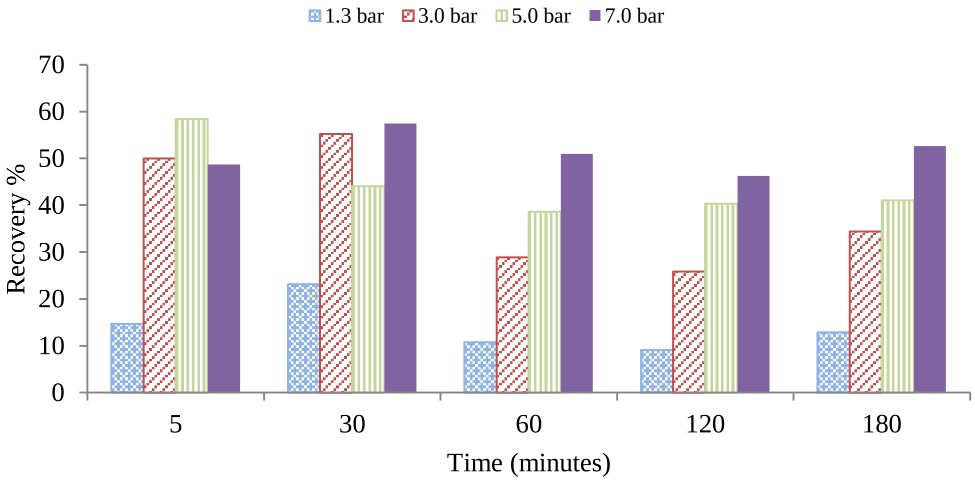


Figure 7.12 Permeate recovery rate at different pressures at 25^{o}C

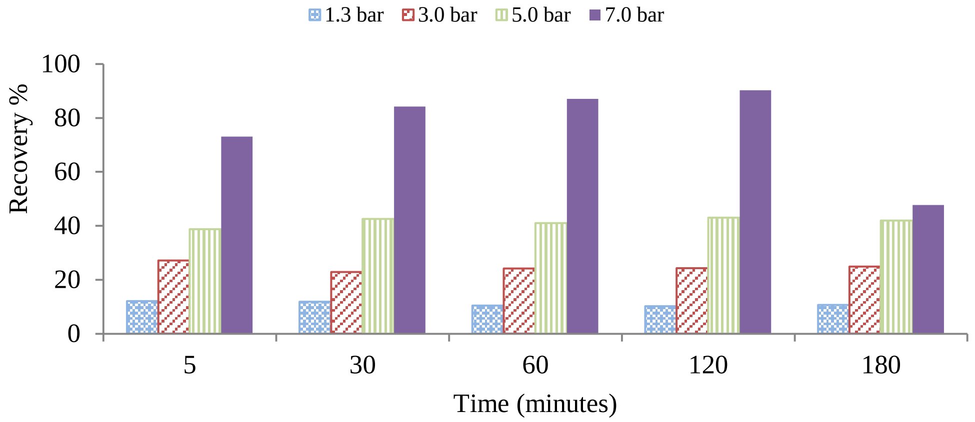


Figure 7.13 Permeate recovery rate at different pressures at 35^{o}C

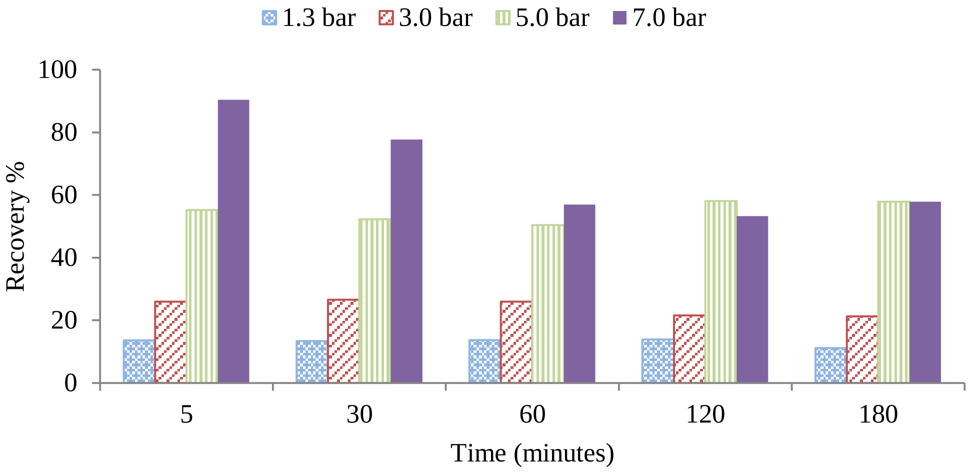


Figure 7.14 Permeate recovery rate at different pressures at 45°C

7.3.6. Permeate water quality

The results obtained from this study showed clearly ceramic membrane is so effective in purifying produced water for the removal of many constituents in significant proportions (Figure 7.15). However, the most prevalent reduction was noticed in the oil-in-water content and turbidity which reach more than 99% (0.02 NTU). The results showed also decent reduction with other constituents.

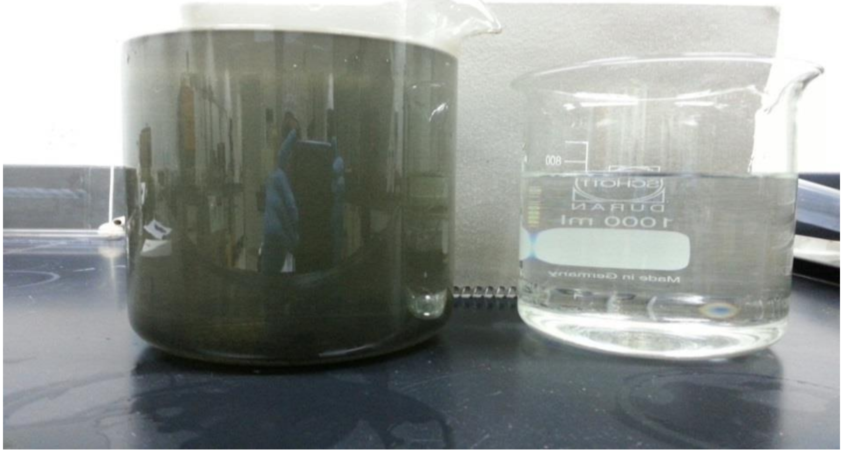


Figure 7.15 Comparison between feed produced water and permeate from ceramic membrane

7.3.6.1. Oil-in-Water content (OIW)

The oil present in produced water exists in different forms dispersed, dissolved, aromatics, aliphatics, organic acids, phenols and a variation of other substances (Yang and Nel, 2006). It is worth to mention that the value assigned to the concentration of oil in produced water is method dependent. Gravimetric method using dichloromethane as solvent is the method applied to measure oil content in this study. The results from this study revealed that the ceramic membrane performed excellently in removing the oil content. The maximum rejection rate was around 99.9% reducing the oil content from 134.55 mg/L in the feed water to 0.02 mg/L in the permeate. The effect of temperature and pressure on OIW rejection was investigated. The pressure is found to have adverse effect on the rejection rate of oil, as pressure increases the oil droplets gets compacted which allow them to pass through the membrane pores. Figure 7.16 represents the effect of pressure on OIW rejection rate at different temperatures. The average values of OIW rejection during the operational time indicated clearly as pressure increases from 1.3 bar to 7.0 bar the ability of the ceramic membrane to reject oil decreases.

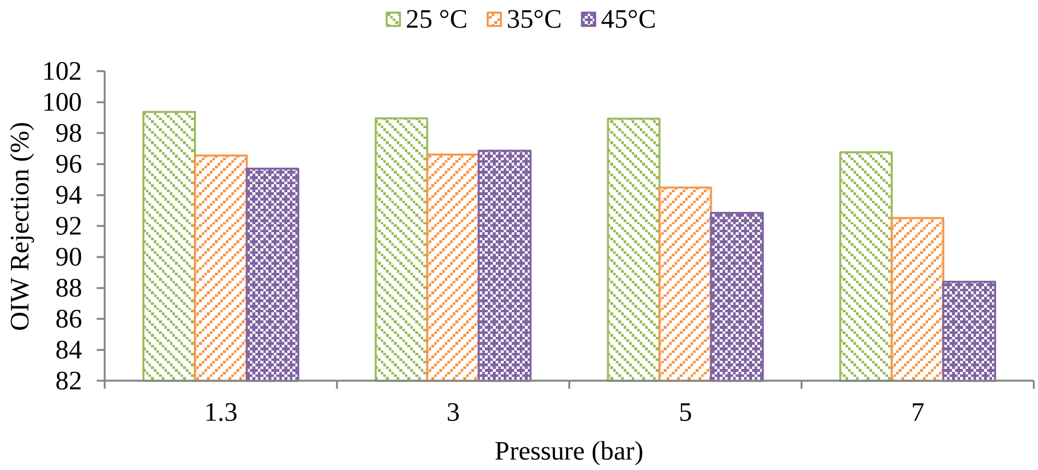


Figure 7.16 Effect of pressure on OIW rejection at different temperatures

The temperature is found to decrease the viscosity of the oil and consequently decreases the rejection rate of oil. Increasing temperature increases the permeabilities (diffusivities) of organic constituents. Figure 7.17 -Figure **7.20** represent the effect of temperature on OIW rejection rate during the operational time. It can be seen also, as the operational time increases cake/gel layer tend to form in the surface of the membrane. This layer will act as a barrier to prevent oil droplets to penetrate through the pores.

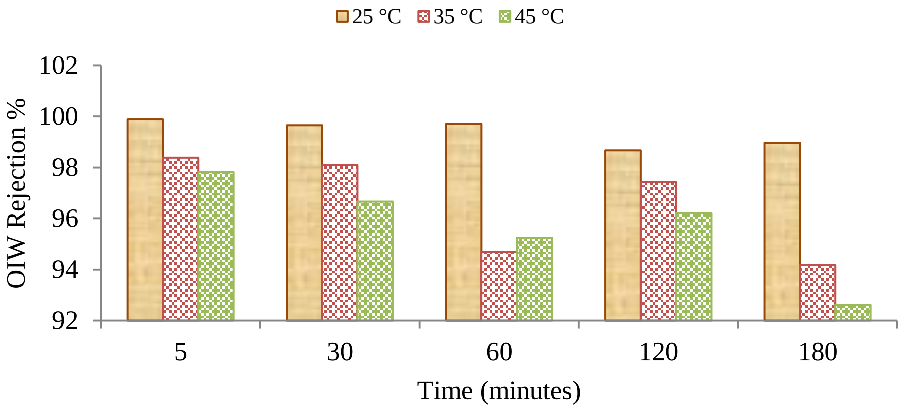


Figure 7.17 Effect of different temperature sets on OIW rejection rate at 1.3 bar

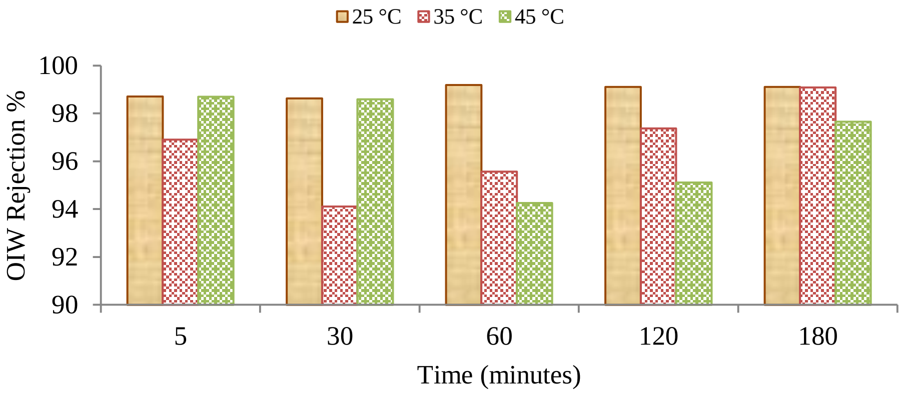


Figure 7.18 Effect of different temperature sets on OIW rejection rate at 3.0 bar

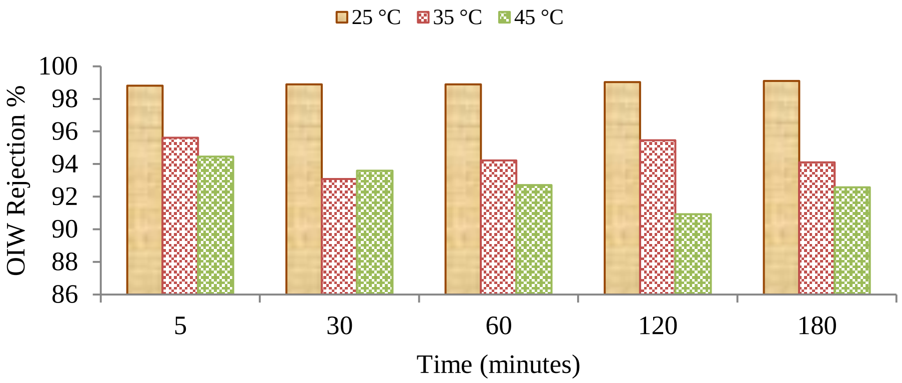


Figure 7.19 Effect of different temperature sets on OIW rejection rate at 5.0 bar

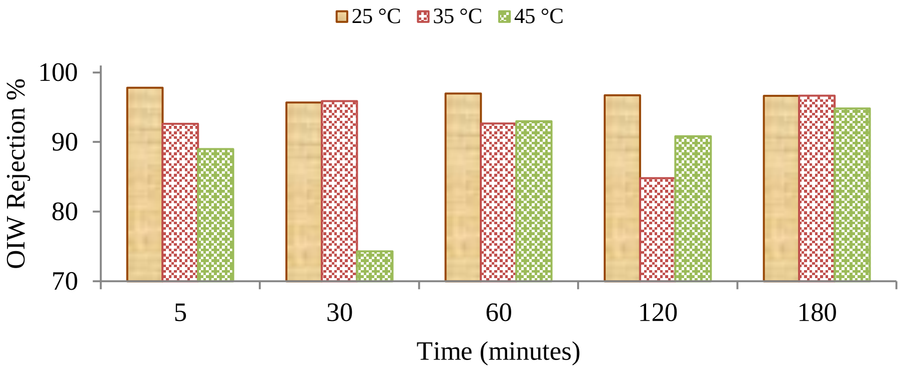


Figure 7.20 Effect of different temperature sets on OIW rejection rate at 7.0 bar

United States Environmental Protection Agency (USEPA) stipulate a daily maximum limit for oil and grease of 42 mg/L and the monthly average limit is 29 mg/L for treated produced water discharge offshore (USEPA), while Australia set a limit of 30 mg/L daily average and 50 mg/L instantaneous (Neff, 2002a) and Oslo-Paris convention (OSPAR) set the maximum discharge to be 30 mg/L (Igunnu and Chen, 2012a). People’s Republic of China set more stringent regulatory standards for produced water discharge were the monthly average limit of O&G discharge and chemical oxygen demand (COD) prescribed are 10 and 100 mg/L respectively (Tellez et al., 2002). The determined average values of OIW content in permeate from the ceramic membrane experiments range from 0.84 mg/L to 15.61 mg/L. These values match with the guidelines set by USEPA, Australia and OSPAR for treated produced water discharge offshore in terms of OIW content.

7.3.6.2. Total organic carbon (TOC)

Total organic carbon is a gross measure of all forms of organic carbon including total petroleum hydrocarbons (TPH) and natural organic matter (Schreier et al., 1999). TOC analysis can be performed easily and it encompasses all weight fractions of TPH. The results showed that TOC did not follow a certain trend but we can say figuratively that the TOC rejection rate decreases as pressure increases (Figure 7.21). This behaviour comparable with the trend of OIW rejection with pressure and this presumably because high pressure will make the oil droplets more compacted and allows them along with other organic constituents to pass through the membrane pores. While temperature is seen to have opposite effect indicating that TOC rejection is directly proportional with temperature. For example, at 1.3 bar the TOC rejection rate increases from 32% to 55% when temperature increases from 25 ^{o}C to 45 ^{o}C. This can be related to the formation of the gel layer which will act as a barrier preventing organic molecules to pass through.

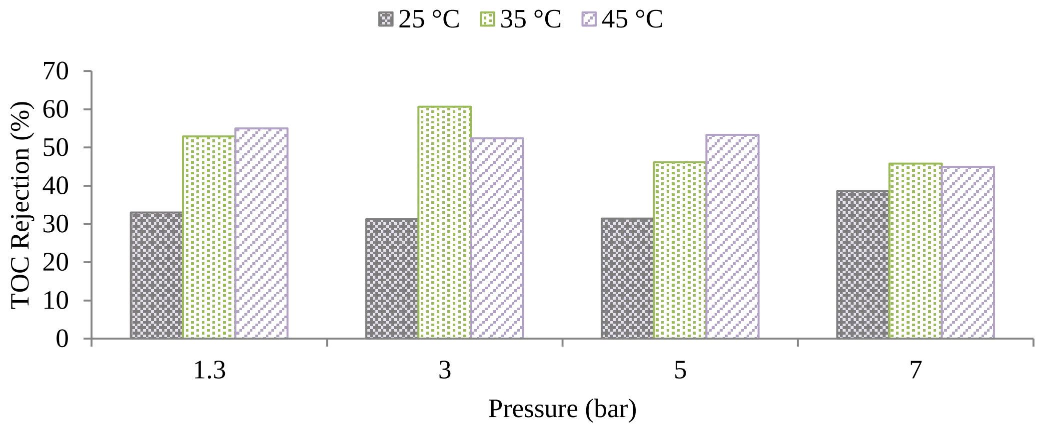


Figure 7.21 Effect of pressure on TOC rejection at different temperatures

7.3.6.3. Chemical oxygen demand (COD)

Chemical oxygen demand (COD) is a useful test that indirectly measures the amount of organic compounds in water. COD refers to the chemical decomposition of organic and inorganic contaminants, dissolved or suspended in water. The COD rejection ranges between 0.36-62%. Figure 7.22 represents the average COD rejection rate for different applied pressures at different temperatures. At low temperature (25°C), the pressure is found to have positive effect on COD rejection rate while, at elevated temperatures (35 and 45°C) a deterioration in the COD rejection is found to happen as pressure increases. This can be seen clearly from Figure **7.22**, as pressure increases from 1.3 bar to 7 bar the COD rejection decreases from 47.7 % to 9% and from 13.5% to 8.9% for 35 and 45°C respectively.

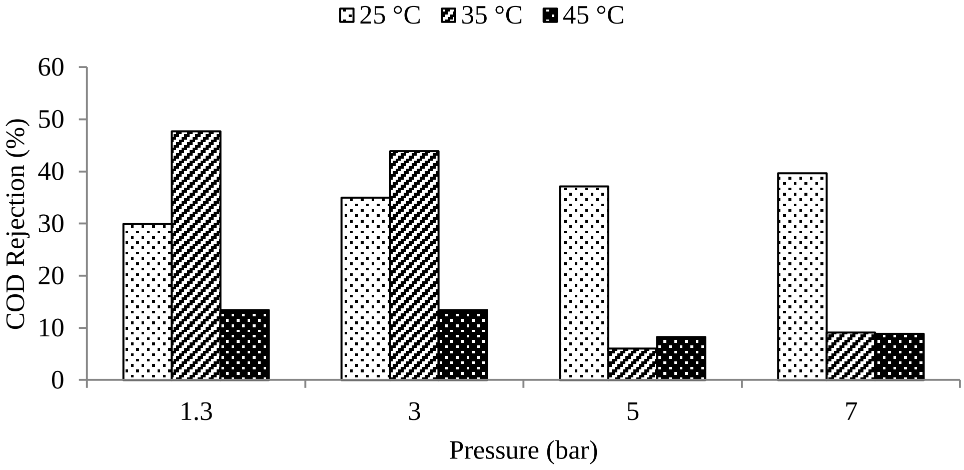


Figure 7.22 Effect of pressure on COD rejection at different temperatures

7.3.6.4. Turbidity

Turbidity which refers to the clarity of water caused by the suspended and dissolved particles was investigated in this study. The maximum attainable Turbidity rejection was around 99.99% (0.02 NTU) and the minimum value was around 97% (7.5 NTU) indicating that ceramic membrane performance was superb in reducing turbidity of produced water (Figure 7.23). It is apparent from the results that turbidity was primarily affected by the pore size and the level of contaminants in the feed water while pressure and temperature have no significant effect on the permeate turbidity.

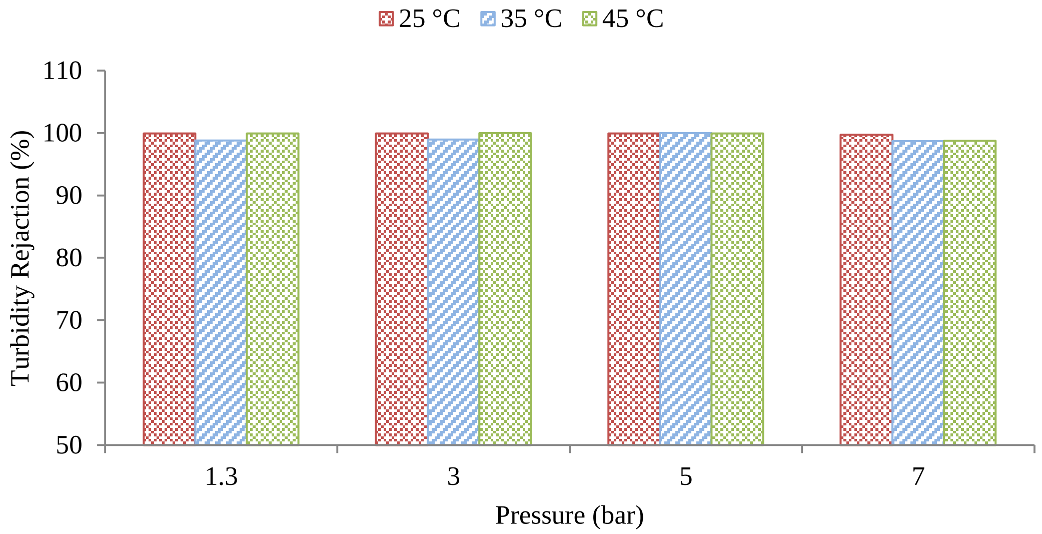


Figure 7.23 Effect of pressure on Turbidity rejection at different temperatures

7.3.6.5. Electrical conductivity and pH

The performance of ceramic membrane in removing salinity and the effect on permeate pH was investigated (Table 7.2). The salt rejection by the ceramic membrane is poor and is about 0-16%. The formation of the cake layer tends to enhance the salt removal as this layer traps salts along with other suspended and dissolved solids. It is apparent from the study that the treatment process has no influence on the pH. The results presented in Table 7.2, indicate that neither pressure nor temperature has effect on the pH while EC tend to decrease as temperature increases.

Table 7.2 Effect of the treatment process on EC and pH

			Pressure (bar)			
Parameter	Temperature (^oC)		1.3	3	5	7
Electrical Conductivity, EC (dS/m)	25	Feed	8.79	8.79	8.79	8.79
		Permeate	8.79	8.79	8.73	8.39
	35	Feed	8.79	8.79	10.58	7.35
		Permeate	7.76	7.79	9.95	7.14
	45	Feed	7.02	7.02	7.02	10.58
		Permeate	5.97	5.87	6.2	9.27
pH	25	Feed	8.5	8.8	8.9	8.8
		Permeate	8.9	8.8	8.9	8.8
	35	Feed	8.6	8.8	8.9	8.5
		Permeate	8.6	8.8	8.7	8.5
	45	Feed	8.9	8.9	8.7	8.5
		Permeate	8.9	8.9	8.7	8.5

7.3.7. Ceramic membrane cleaning

Backwashing is generally used to restore the declination in permeate flux (Lee et al., 1984, Mugnier et al., 2000). During this study, pure water backwashing was utilized to restore the flux declination and remove the deposited colloids and particles from the surface of the membrane and from the pores. Hot tap water (50^{o}C) was used for backwashing and rinsing the membrane. The pump was operated for 30 seconds at low pressure less than 2 bars during the back washing process. This was enough to remove the oil droplets and other impurities from the membrane. Then the water, at room temperature, was allowed to pass through membrane to clean-up the remaining impurities. This was done until the initial flux was recovered (5-10 minutes) at different pressures (2- 3 bars). During the experiment it was possible to recover the initial flux of the membrane but in case that backwashing and cleaning fail to maintain the initial flux, it is recommended to use alkaline cleaner such as sodium hydroxide solution (2%) to remove organic scales. To remove inorganic scales it is recommended to use citric acid solution (2%) and at the end of the cleaning process the membrane should be rinsed with water at room temperature (Abadi, 2011). Different strategies can be applied in order to mitigate effect of membrane fouling includes: pretreatment process can be applied to reduce the amount of oil and solids, application of high cross-flow velocity on the feed side, operating at high temperature, application of cleaning cycle and the utilization of backwashing.

7.4. Incorporation of adsorption with ceramic membrane filtration

Organic matter, oil and grease, and metal oxides can be removed by ceramic membrane but dissolved ions and dissolved organics cannot be separated and some pre-treatment processes like coagulation or adsorption can be utilized for this purpose. The objective of the pretreatment process is to minimize the concentration of fouling constituents in the feed water to the level that would provide stable, long term performance of membrane element. Various pretreatment processes, e.g. adsorption, flocculation and sedimentation, hydrocyclones and dissolved air flotation (DAF), can be applied individually or in combination with other processes to enhance the treatment process as well as considering the economic aspects of the treatment process. The application of low-cost adsorbents (i.e. date seeds and attapulgite) was investigated for the removal of dissolved organic carbon (DOC). The study showed that these adsorbents can be considered as a promising candidate for the purification of produced water. The results are shown in chapter 5 and 6. These results can be utilized to combine the adsorption process with ceramic membrane filtration or any other processes in order to achieve better quality of permeate. The application of date seeds as an adsorbent in the pretreatment process before ceramic membrane filtration will enhance the quality of the effluent. Date seeds prove their ability to remove organic and inorganic constituents from wastewater as reported by (Al-Haidary et al., 2011, Alhamed, 2009, Alhamed and

Bamufleh, 2009, Al-Muhtaseb et al., 2008, Banat et al., 2003, Banat et al., 2004). AS mentioned earlier, the results obtained from the ceramic membrane trials indicated clearly that OIW content in permeate match with the limits set by USEPA for treated produced water discharge offshore. The adsorption batch experiments using date seeds and attapulgite indicated the ability of these adsorbents for reducing DOC from produced water, so combining both processes will eventually enhances the removal of dispersed and dissolved organic constituents and it will be a cost effective solution for produced water treatment. Several studies reported the effectiveness, i.e. better removal of dissolved organics, of using adsorption as a pretreatment prior to the membrane filtration process (Guo et al., 2004, Vigneswaran et al., 2003, Oh et al., 2007, Abdessemed et al., 2000, Areerachakul et al., 2007).

Different scenarios can be proposed for the combined treatment system for the purification of produced water. The combination of both processes depends on the quality of the feed water and the degree of cleanliness to be achieved in the effluent. The first scenario is to have adsorbent unit before the membrane filtration element (Figure 7.24). This unit can be equipped with stirrer (with different speeds) to mix the adsorbent with the oily water or by having tank with air diffuser at the bottom to keep the adsorbent in the suspension and this will minimize the volatile compounds as well. The addition of the adsorption unit before the membrane filtration element prove to enhance the filtration flux dramatically and improve the removal of dissolved organics (Guo et al., 2004). A temperature controller can be added to the adsorption unit to control the temperature of the suspension. The loaded adsorbents can be separated from the produced water stream by separation process. These loaded adsorbents with organic constituents can be regenerated by using different techniques as reported successfully by several researchers. These techniques included the application of steam (San Miguel et al., 2001), pyrolysis (Sabio et al., 2004), surfactant (Purkait et al., 2007), wet peroxide oxidation (Okawa et al., 2007), microwave (Ania et al., 2004) and ultrasound (Lim and Okada, 2005). The data obtained from the adsorption experiments (chapter 5 and 6) can be utilized to design the adsorption unit.

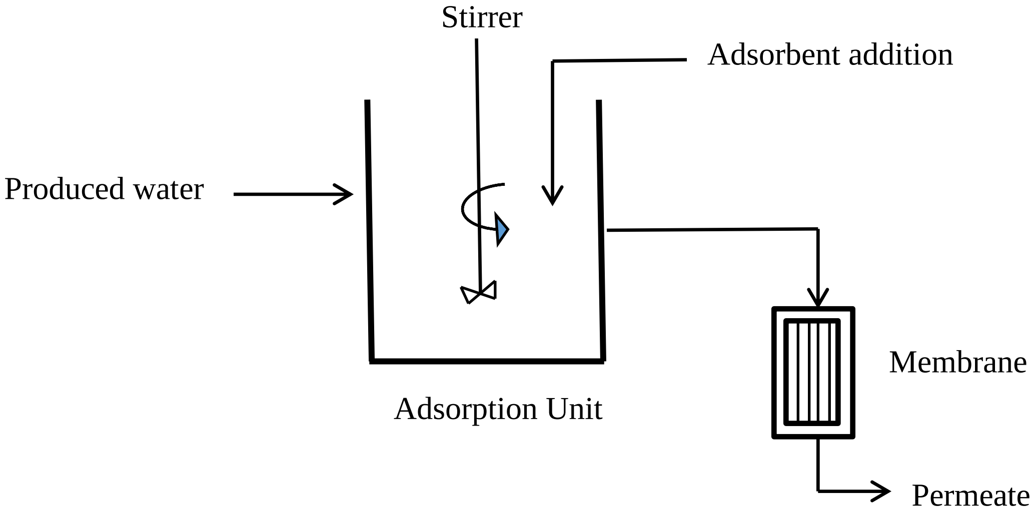


Figure 7.24 Adsorption with membrane system

The second scenario for the combined system is by introducing dissolved air floatation (DAF) tank before the adsorption column and membrane filtration system (Figure 7.25). The introduction of DAF before adsorption or membrane filtration will result in the enhancement of the treatment processes as reported by (Mavrov et al., 2003, Blöcher et al., 2003, Peleka et al., 2006). In floatation, different organic constituents (especially oil droplets) will be forced to colloid and the rising air bubbles will drive the highly concentrated (mass fraction) foam layer to the surface of the floatation tank where it can be skimmed and removed (Matis, 1994). This will minimize the load of organic constituents to the adsorption column/membrane system and it will allow recovering the dispersed oil present in the produced water. The amount of oil recovered will improve the economic part of the treatment process.

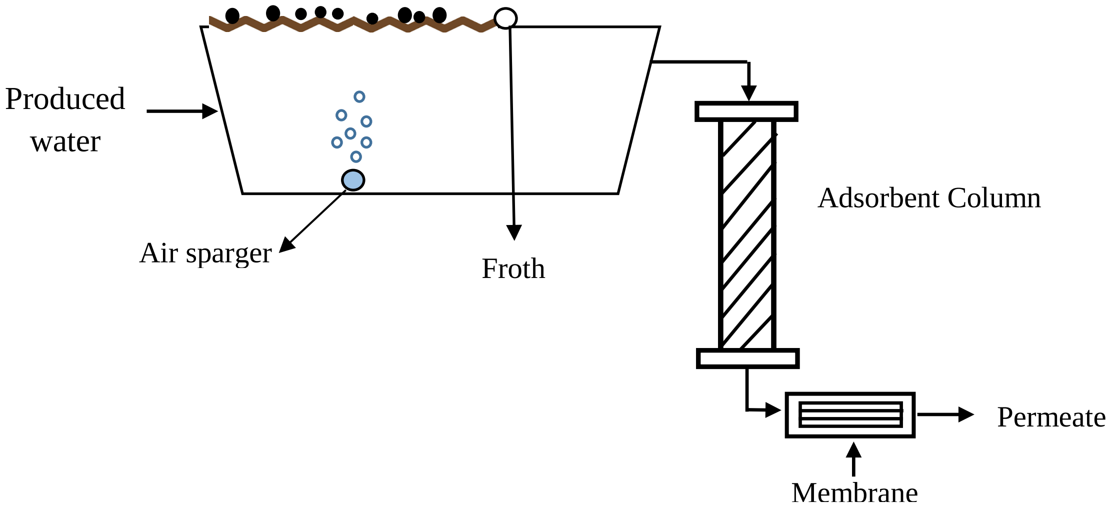


Figure 7.25 Flow diagram for DAF, adsorption column and filtration system

7.5. Summary

The application of ceramic membrane for the treatment and purification of produced water proved to be an excellent option. The reduction in the Oil content ranged from 78 to 99.99%. The reduction in turbidity was above 96% for all treatments. TOC removal ranged from 30-60% while COD reduction was in the range from 0.36-62%. The presence of low molecular weight aromatic, naphthenic acids, humic acids and fulvic acids tend to increase the values of COD and TOC in permeate as they are very difficult to be removed by the membrane. The highest membrane recovery was achieved with 7 bars and 45^{o}C. The application of low-cost adsorbents (i.e. date seeds and attapulgite) can be utilized as pre-treatment for the ceramic membrane filtration. The project needs to be implemented in larger scale to validate the results and to understand the real implications on the field.

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

8.1. Introduction

This chapter summarizes the major findings obtained from the experimental investigations on the application of adsorption process, using date seeds and attapulgite, and ceramic membrane filtration for the purification of oily produced water.

The batch experiments showed the effectiveness of date seeds and attapulgite in removing dissolved organic carbon (DOC). The influence of several physico-chemical parameters was investigated. Application of ceramic membrane for the purification of oily produced water was studied under different operating conditions. Future directions usually recommend the application of new materials or by trying different methodologies in order to complement the existing data.

8.2. Conclusions

The feasibility of using date seeds and attapulgite as an alternative low-cost adsorbent for the removal of DOC was thoroughly investigated under different physico-chemical conditions. The adsorbents were characterized using different techniques. The most important findings from the current studies on adsorbents include:

- FTIR indicated that date seeds are composed of a mixture of functional groups such as O-H stretch group, C-H stretch group, C=O, C=C, C-N, P=O and =C-H bend. On the other hand attapulgite is composed mainly of structural hydroxyl (OH) groups and Si-O stretching group.

- XRD analysis showed that SiO_2 is the dominant crystalline phase in date seeds and it also showed abundance of attapulgite with palygorskite mineral (magnesium aluminum silicon oxides).
- SEM analysis of attapulgite reflects the richness of fibers in attapulgite while it shows the availability of active pores in the surface of date seeds.
- Thermogravimetric analysis (TGA) of attapulgite indicates four distinct mass loses at temperatures from 25 ^{o}C to 900^{o}C. Around 20% of attapulgite was lost between 25^{o}C and 500^{o}C and there was no loss in mass beyond 500^{o}C. Delta T showed positive values indicating an endothermic nature of the sample. On the other hand, TGA of date seeds showed three mass losses during the thermal decomposition (30-900^{o}C). Around 80% of date seeds mass lost between 25-430^{o}C.
- Elemental analysis of attapulgite indicates the presence of SiO_2 followed by Al_2O_3 as the major elements accounting for almost 70% of the total elemental present. Fe, Ca, and Mg oxides are found in lower percentages.

The experimental data obtained from the batch adsorption process for the adsorption of DOC by date seeds and attapulgite were fitted to various isotherm and kinetic models in order to determine the best models that can represent the data obtained. The outcome of the adsorption process of DOC from produced water by date seeds and attapulgite can be summarized in the following sections.

Adsorption studies of DOC by date seeds:

- The adsorption process was fast and equilibrium was attained after a contact time of 120 minutes. The equilibrium time is independent of initial DOC concentration. The physico-chemical properties of the adsorbent play a major role to determine the equilibrium capacity and rate.
- The kinetic experiments, in batch study, revealed that the removal rate of DOC was high at the beginning and then the rate starts to decrease with time until it reaches equilibrium.
- As the dose of the date seeds increases from 0.5-2.0 g per 150 mL, the DOC removal efficiency was observed to increase from 70% to 82% whereas the equilibrium adsorption capacity decreased from 19.85 mg/g to 5.75 mg/g.
- The uptake of DOC by date seeds is almost not affected in the pH range of 4-9. However, it was noticed that the uptake of DOC tends to decrease with increasing pH.
- The equilibrium data fits well with Langmuir isotherm. The maximum monolayer adsorption capacity of date seeds was found to be 74.62 mg/g.
- The adsorption of DOC by date seeds follows the pseudo-second order model and it was found to be controlled by both surface and pores diffusion.
- The separation factor, R_L, from the Langmuir isotherm and n, constant from the Freundlich isotherm, indicated a favorable adsorption.
- DOC uptake by date seeds decreases when temperature increases.
- The adsorption process by date seeds found to be exothermic in nature.

Adsorption studies of DOC by attapulgite:

- For attapulgite type B the maximum monolayer coverage was found to be 31 mg/g and 65 mg/g for granular and powder attapulgite respectively while the maximum monolayer coverage for attapulgite A was found to be 40.95 mg/g and 49.26 mg/g for granular and powder attapulgite respectively.
- The experimental data of the two types of attapulgite fits well with the Langmuir isotherm.
- Changes in the pH have no significant influence on the adsorption capacity of DOC by both types of attapulgite.
- The governing transport mechanisms in the sorption process prone to be both external mass transfer and intra-particle diffusion.
- The adsorption process of DOC by attapulgite was found to be exothermic in nature.
- The kinetic experiments showed that the adsorption of DOC onto attapulgite can be summarized into two steps: external mass transfer of the DOC molecules to the external surface of the attapulgite through film diffusion at a fast rate, and intra-particle diffusion of DOC molecules into attapulgite particles through pores.

Design of single-stage batch absorber from isotherm data:

A single-stage batch absorber was designed using the Langmuir isotherm model equation for DOC adsorption onto date seeds and attapulgite. The design shows the amount of adsorbents required to treat different volumes of produce water to achieve target DOC removal efficiencies (55%-85%).

Ceramic membrane studies:

The application of cross-flow microfiltration using ceramic membrane (α-Al_2O_3) membrane with 0.05 µm pore size for the purification of oily water from oilfield was investigated. The outcome of the study can be concluded as follow:

- The applied pressure was found to have positive effect on permeate flux.
- The TOC rejection ranged between 30.6 to 65.6 % while the rejection of COD was found to be in the range of 9-47%.
- At elevated pressure, effect of pressure predominates over effect of pore size.
- The formation of cake gel on the surface of membrane tends to decrease the recovery rate.
- Temperature is found to have a bilateral effects on permeate flux. From one side increasing temperature will lead to a decrease in the feed viscosity, and as a result, increasing the solvent and solutes permeabilities (diffusivities) but from the other side increasing temperature increases osmotic pressure which will eventually decrease the permeation flux.
- The maximum rejection rate of OIW was around 99.9% reducing the oil content from 134.55 mg/L in the feed water to 0.15 mg/L in the permeate.
- Pressure is found to have adverse effect on the rejection rate of oil, as pressure increases the oil droplets gets compacted which allow them to pass through the membrane pores.
- The maximum attainable turbidity rejection was around 99.99% and the minimum was around 97%.
- The salt rejection is very low and it is about 0-16%.

- It is apparent from the study that the application of ceramic membrane has no influence on pH.
- Backwashing using hot water (50^{o}C) for 30 seconds at 2 bar is found to be effective in restoring the initial flux of the membrane.

8.3. Recommendations

The feasibility of using date seeds and attapulgite for DOC adsorption from produced water and the applicability of using ceramic membrane for the purification of oily produced water were thoroughly presented in this study. The results indicated the effectiveness of the adsorbents for DOC removal. The results revealed also the outstanding performance of the ceramic membrane in purifying oily produced water. However, several issues need to be addressed in order to improve the existing data before considering the real applications. The recommendations for future research include:

- The adsorbents can be modified physically or chemically to improve their competence. The application of surfactants or other chemicals can enhance the ability of the adsorbents to remove organic pollutants. The application of other biomass materials for the adsorption of oil and other organic constituents needs to be evaluated.
- The potential of using date seeds and attapulgite for the adsorption of oil or other organic wastes from refinery wastewater or industrial wastewater need to be explored.
- From literature review, most of the studies conducted on adsorption experiments focus on batch experiments and very few studies were conducted on column experiments although the main goal is to apply these adsorbents in

real oil-field sites. The column experiment is the most applicable method for scale-up design purposes.

- The stability and the regeneration of the adsorbents is considered to be of significant value in these adsorption processes and it requires further investigations.
- The results obtained from the filtration experiments need to be implemented in large scale to address the real field complications.
- Cost analysis for the filtration system needs to be performed. The initial capital cost along with other costs like the operational cost need to be included in the study.
- The incorporation of membrane filtration with other techniques like the application of a solar photo-catalytic as a pretreatment can be explored. At the same time the application of different membrane pore sizes can be examined as well.
- More investigations in the removal of dissolved hydrocarbons by membrane filtration are essential and necessary. One of the possible options could be to modify the membrane surface by using different chemicals to understand the chemical interactions between the membrane surface and the dissolved hydrocarbons.

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APPENDIX A

Raw data for adsorption of Dissolved Organic Carbon onto date seeds and attapulgite

Appendix A-1 Effect of initial DOC concentration on the adsorption of DOC by date seeds at initial concentration of 18.5 mg/L

Time (min)	C_t (mg/l)	DOC removal (%)	q_e (mg/g)
Initial	18.5		
5	17.01	8.05	0.45
10	17.01	8.05	0.45
20	15.003	18.90	1.05
30	14.715	20.46	1.14
60	11.2455	39.21	2.18
90	10.845	41.38	2.30
120	8.41	54.54	3.03

Experimental Conditions

Shaking speed	150 rpm
Experimental temperature	25 °C
Initial adsorbent dose	0.5 g
Volume of solution	150 ml

Appendix A-2 Effect of initial DOC concentration on the adsorption of DOC by date seeds at initial concentration of 57 mg/L

Time (min)	C_t (mg/l)	DOC removal (%)	q_e (mg/g)
Initial	57		
5	44.838	21.34	3.65
10	38.025	33.29	5.69
20	37.728	33.81	5.78
30	35.55	37.63	6.44
60	34.2	40.00	6.84
90	33.777	40.74	6.97
120	29.871	47.59	8.14

Experimental Conditions

Shaking speed	150 rpm
Experimental temperature	25 °C
Initial adsorbent dose	0.5 g
Volume of solution	150 ml

Appendix A-3 Effect of initial DOC concentration on the adsorption of DOC by date seeds at initial concentration of 93.467 mg/L

Time (min)	C_t (mg/l)	DOC removal (%)	q_e (mg/g)
Initial	93.467		
5	63.778	31.76	8.91
10	61.902	33.77	9.47
20	55.005	41.15	11.54
30	49.478	47.06	13.20
60	46.497	50.25	14.09
90	38.027	59.32	16.63
120	27.313	70.78	19.85

Experimental Conditions

Shaking speed	150 rpm
Experimental temperature	25 °C
Initial adsorbent dose	0.5 g
Volume of solution	150 ml

Appendix A-4 Effect of initial adsorbent doses on the adsorption of DOC by date seeds at 0.5 g

Time (min)	C_t (mg/l)	DOC removal (%)	q_e (mg/g)
Initial	93.467		
5	63.778	31.76	8.91
10	61.902	33.77	9.47
20	55.005	41.15	11.54
30	49.478	47.06	13.20
60	46.497	50.25	14.09
90	38.027	59.32	16.63
120	27.313	70.78	19.85

Experimental Conditions

Shaking speed	150 rpm
Experimental temperature	25 °C
Initial DOC concentration	93.467 mg/L
Volume of solution	150 ml

Appendix A-5 Effect of initial adsorbent doses on the adsorption of DOC by date seeds at 1.0 g

Time (min)	C_t (mg/l)	DOC removal (%)	q_e (mg/g)
Initial	93.467		
5	65.829	29.57	4.15
10	59.570	36.27	5.08
20	52.596	43.73	6.13
30	46.425	50.33	7.06
60	49.758	46.76	6.56
90	31.878	65.89	9.24
120	27.093	71.01	9.96

Experimental Conditions

Shaking speed	150 rpm
Experimental temperature	25 °C
Initial DOC concentration	93.467 mg/L
Volume of solution	150 ml

Appendix A-6 Effect of initial adsorbent doses on the adsorption of DOC by date seeds at 2.0 g

Time (min)	C_t (mg/l)	DOC removal (%)	q_e (mg/g)
Initial	93.467		
5	65.114	30.33	2.13
10	55.522	40.60	2.85
20	52.739	43.57	3.05
30	44.489	52.40	3.67
60	48.5155	48.09	3.37
90	30.332	67.55	4.74
120	16.769	82.06	5.75

Experimental Conditions

Shaking speed	150 rpm
Experimental temperature	25 °C
Initial DOC concentration	93.467 mg/L
Volume of solution	150 ml

Appendix A-7 Effect of initial DOC concentration on the adsorption of DOC by attapulgite type A at initial concentration of 18.5 mg/L

Time (min)	Attapulgite Type A Powder			Attapulgite Type A Granular		
	C_t (mg/l)	DOC removal (%)	q_e (mg/g)	C_t (mg/l)	DOC removal (%)	q_e (mg/g)
Initial	18.5			18.5		
5	18.0675	2.34	0.13	16.947	8.39	0.47
10	15.3	17.30	0.96	16.335	11.70	0.65
20	16.704	9.71	0.54	16.717	9.64	0.53
30	12.78	30.92	1.72	14.656	20.78	1.15
60	12.177	34.18	1.90	16.272	20.78	0.67
90	11.907	35.64	1.98	13.005	29.70	1.65
120	11.4705	38.00	2.11	11.290	38.97	2.16

Experimental Conditions

Shaking speed	150 rpm
Experimental temperature	25 °C
Initial adsorbent dose	0.5 g
Volume of solution	150 ml

Appendix A-8 Effect of initial DOC concentration on the adsorption of DOC by attapulgite type A at initial concentration of 57 mg/L

Time (min)	Attapulgite Type A Powder			Attapulgite Type A Granular		
	C_t (mg/l)	DOC removal (%)	q_e (mg/g)	C_t (mg/l)	DOC removal (%)	q_e (mg/g)
Initial	57			57		
5	44.946	21.15	2.41	47.7	16.32	1.86
10	31.428	44.86	5.11	30.519	46.46	5.30
20	30.195	47.03	5.36	33.795	40.71	4.64
30	24.615	56.82	6.48	36.558	35.86	4.09
60	18.774	67.06	7.65	28.197	50.53	5.76
90	19.296	66.15	7.54	27.612	51.56	5.88
120	16.731	70.65	8.05	23.949	57.98	6.61

Experimental Conditions

Shaking speed	150 rpm
Experimental temperature	25 °C
Initial adsorbent dose	0.5 g
Volume of solution	150 ml

Appendix A-9 Effect of initial DOC concentration on the adsorption of DOC by attapulgite type A at initial concentration of 93.467 mg/L

Time (min)	Attapulgite Type A Powder			Attapulgite Type A Granular		
	C_t (mg/l)	DOC removal (%)	q_e (mg/g)	C_t (mg/l)	DOC removal (%)	q_e (mg/g)
Initial	93.467			93.467		
5	80.81	13.54	3.80	78.600	15.91	4.46
10	71.56	23.44	6.57	83.099	11.09	3.11
20	75.89	18.81	5.27	77.698	16.87	4.73
30	75.99	18.70	5.24	74.877	19.89	5.58
60	67.54	27.74	7.78	77.148	17.46	4.90
90	68.12	27.12	7.60	74.173	20.64	5.79
120	62.5	33.13	9.29	68.838	26.35	7.39

Experimental Conditions

Shaking speed	150 rpm
Experimental temperature	25 °C
Initial adsorbent dose	0.5 g
Volume of solution	150 ml

Appendix A-10 Effect of initial DOC concentration on the adsorption of DOC by attapulgite Type B at initial concentration of 18.5 mg/L

Time (min)	Attapulgite Type B Powder			Attapulgite Type B Granular		
	C_t (mg/l)	DOC removal (%)	q_e (mg/g)	C_t (mg/l)	DOC removal (%)	q_e (mg/g)
Initial	18.5			18.5		
5	13.167	28.83	1.60	12.982	29.82	1.66
10	12.213	33.98	1.89	12.51	32.38	1.80
20	11.142	39.77	2.21	11.105	39.97	2.22
30	11.205	39.43	2.19	11.110	39.94	2.22
60	10.467	43.42	2.41	10.944	40.84	2.27
90	9.8685	46.66	2.59	10.953	40.79	2.26
120	7.875	57.43	3.19	9.7515	47.29	2.62

Experimental Conditions

Shaking speed	150 rpm
Experimental temperature	25 °C
Initial adsorbent dose	0.5 g
Volume of solution	150 ml

Appendix A-11 Effect of initial DOC concentration on the adsorption of DOC by attapulgite Type B at initial concentration of 57 mg/L

Time (min)	Attapulgite Type B Powder			Attapulgite Type B Granular		
	C_t (mg/l)	DOC removal (%)	q_e (mg/g)	C_t (mg/l)	DOC removal (%)	q_e (mg/g)
Initial	57			57		
5	56.466	0.94	0.11	46.908	17.71	2.02
10	37.377	34.43	3.92	36.459	36.04	4.11
20	31.959	43.93	5.01	25.857	54.64	6.23
30	29.061	49.02	5.59	27.81	51.21	5.84
60	23.49	58.79	6.70	24.255	57.45	6.55
90	23.508	58.76	6.70	24.84	56.42	6.43
120	18.999	66.67	7.60	20.115	64.71	7.38

Experimental Conditions

Shaking speed	150 rpm
Experimental temperature	25 °C
Initial adsorbent dose	0.5 g
Volume of solution	150 ml

Appendix A-12 Effect of initial DOC concentration on the adsorption of DOC by attapulgite Type B at initial concentration of 93.467 mg/L

Time (min)	Attapulgite Type B Powder			Attapulgite Type B Granular		
	C_t (mg/l)	DOC removal (%)	q_e (mg/g)	C_t (mg/l)	DOC removal (%)	q_e (mg/g)
Initial	93.467			93.467		
5	73.26	21.62	6.06	83.132	11.06	3.10
10	69.0745	26.10	7.32	77.825	16.74	4.69
20	65.9945	29.39	8.24	72.715	22.20	6.23
30	56.21	39.86	11.18	74.607	20.18	5.66
60	50.9795	45.46	12.75	74.811	19.96	5.60
90	55.7095	40.40	11.33	71.742	23.24	6.52
120	33.407	64.26	18.02	64.564	30.92	8.67

Experimental Conditions

Shaking speed	150 rpm
Experimental temperature	25 °C
Initial adsorbent dose	0.5 g
Volume of solution	150 ml

Appendix A-13 Effect of initial adsorbent doses on the adsorption of DOC by attapulgite type A at 0.5 g

Time (min)	Attapulgite Type A Powder			Attapulgite Type A Granular		
	C_t (mg/l)	DOC removal (%)	q_e (mg/g)	C_t (mg/l)	DOC removal (%)	q_e (mg/g)
Initial	93.467			93.467		
5	80.81	13.54	3.80	78.600	15.91	4.46
10	71.56	23.44	6.57	83.099	11.09	3.11
20	75.89	18.81	5.27	77.698	16.87	4.73
30	75.99	18.70	5.24	74.877	19.89	5.58
60	67.54	27.74	7.78	77.148	17.46	4.90
90	68.12	27.12	7.60	74.173	20.64	5.79
120	62.5	33.13	9.29	68.838	26.35	7.39

Experimental Conditions

Shaking speed	150 rpm
Experimental temperature	25 °C
Initial DOC concentration	93.467 mg/L
Volume of solution	150 ml

Appendix A-14 Effect of initial adsorbent doses on the adsorption of DOC by attapulgite type A at 1.0 g

Time (min)	Attapulgite Type A Powder			Attapulgite Type A Granular		
	C_t (mg/l)	DOC removal (%)	q_e (mg/g)	C_t (mg/l)	DOC removal (%)	q_e (mg/g)
Initial	93.467			93.467		
5	76.472	18.18	2.55	81.234	13.09	1.83
10	77.429	17.16	2.41	76.12	18.56	2.60
20	78.6335	15.87	2.23	76.638	18.01	2.52
30	75.0145	19.74	2.77	76.254	18.42	2.58
60	75.9715	18.72	2.62	74.036	20.79	2.91
90	74.0905	20.73	2.91	74.54	20.25	2.84
120	62.371	33.27	4.66	66.3	29.07	4.08

Experimental Conditions

Shaking speed	150 rpm
Experimental temperature	25 °C
Initial DOC concentration	93.467 mg/L
Volume of solution	150 ml

Appendix A-15 Effect of initial adsorbent doses on the adsorption of DOC by attapulgite type A at 2.0 g

Time (min)	Attapulgite Type A Powder			Attapulgite Type A Granular		
	C_t (mg/l)	DOC removal (%)	q_e (mg/g)	C_t (mg/l)	DOC removal (%)	q_e (mg/g)
Initial	93.467			93.467		
5	78.9965	15.48	1.09	76.045	18.64	1.31
10	75.9165	18.78	1.32	81.087	13.25	0.93
20	76.4225	18.24	1.28	75.038	19.72	1.38
30	76.285	18.38	1.29	75.249	19.49	1.37
60	68.7555	26.44	1.85	73.682	21.17	1.48
90	73.6505	21.20	1.49	73.89	20.95	1.47
120	60.12	35.68	2.50	62.89	32.71	2.29

Experimental Conditions

Shaking speed	150 rpm
Experimental temperature	25 °C
Initial DOC concentration	93.467 mg/L
Volume of solution	150 ml

Appendix A-16 Effect of initial adsorbent doses on the adsorption of DOC by attapulgite type B at 0.5 g

Time (min)	Attapulgite Type B Powder			Attapulgite Type B Granular		
	C_t (mg/l)	DOC removal (%)	q_e (mg/g)	C_t (mg/l)	DOC removal (%)	q_e (mg/g)
Initial	93.467			93.467		
5	73.26	21.62	6.06	83.132	11.06	3.10
10	69.074	26.10	7.32	77.825	16.74	4.69
20	65.994	29.39	8.24	72.715	22.20	6.23
30	56.21	39.86	11.18	74.607	20.18	5.66
60	50.979	45.46	12.75	74.811	19.96	5.60
90	55.709	40.40	11.33	71.742	23.24	6.52
120	33.407	64.26	18.02	64.564	30.92	8.67

Experimental Conditions

Shaking speed	150 rpm
Experimental temperature	25 °C
Initial DOC concentration	93.467 mg/L
Volume of solution	150 ml

Appendix A-17 Effect of initial adsorbent doses on the adsorption of DOC by attapulgite type B at 1.0 g

Time (min)	Attapulgite Type B Powder			Attapulgite Type B Granular		
	C_t (mg/l)	DOC removal (%)	q_e (mg/g)	C_t (mg/l)	DOC removal (%)	q_e (mg/g)
Initial	93.467			93.467		
5	73.1115	21.78	3.05	80.12	14.28	2.00
10	65.9065	29.49	4.13	74.21	20.60	2.89
20	60.8245	34.92	4.90	74.805	19.97	2.80
30	56.584	39.46	5.53	77.5	17.08	2.40
60	51.1555	45.27	6.35	72.3	22.65	3.18
90	50.2315	46.26	6.49	70.53	24.54	3.44
120	33.15	64.53	9.05	63.62	31.93	4.48

Experimental Conditions

Shaking speed	150 rpm
Experimental temperature	25 °C
Initial DOC concentration	93.467 mg/L
Volume of solution	150 ml

Appendix A-18 Effect of initial adsorbent doses on the adsorption of DOC by attapulgite type B at 2.0 g

Time (min)	Attapulgite Type B Powder			Attapulgite Type B Granular		
	C_t (mg/l)	DOC removal (%)	q_e (mg/g)	C_t (mg/l)	DOC removal (%)	q_e (mg/g)
Initial	93.467			93.467		
5	68.3045	26.92	1.89	77.407	17.18	1.20
10	64.427	31.07	2.18	71.56	23.44	1.64
20	59.169	36.70	2.57	72.5	22.43	1.57
30	50.6275	45.83	3.21	76.13	18.55	1.30
60	51.2435	45.17	3.17	70.58	24.49	1.72
90	51.6725	44.72	3.13	68.32	26.90	1.89
120	31.2015	66.62	4.67	62.85	32.76	2.30

Experimental Conditions

Shaking speed	150 rpm
Experimental temperature	25 °C
Initial DOC concentration	93.467 mg/L
Volume of solution	150 ml

Appendix A-19 Effect of Initial Solution pH on adsorption of DOC by date seeds

pH	C_e (mg/l)	DOC removal (%)	q_e (mg/g)
4	11.12	38.22	2.06
6	11.2	37.78	2.04
9	11.93	33.72	1.82

Experimental Conditions

Shaking speed	150 rpm
Experimental temperature	25 °C
Initial adsorbent dose	0.5 g
Initial DOC concentration	18 mg/L
Volume of solution	150 ml

Appendix A-20 Effect of Initial Solution pH on adsorption of DOC by attapulgite type A

Time (min)	Attapulgite Type A Powder			Attapulgite Type A Granular		
	C_e (mg/l)	DOC removal (%)	q_e (mg/g)	C_e (mg/l)	DOC removal (%)	q_e (mg/g)
4	14.13	21.50	1.16	14.9	17.22	0.93
6	12.05	33.06	1.79	13.26	26.33	1.42
9	12.5	30.56	1.65	12.8	28.89	1.56

Experimental Conditions

Shaking speed	150 rpm
Experimental temperature	25 °C
Initial adsorbent dose	0.5 g
Initial DOC concentration	18 mg/L
Volume of solution	150 ml

Appendix A-21 Effect of Initial Solution pH on adsorption of DOC by attapulgite type B

Time (min)	Attapulgite Type B Powder			Attapulgite Type B Granular		
	C_e (mg/l)	DOC removal (%)	q_e (mg/g)	C_e (mg/l)	DOC removal (%)	q_e (mg/g)
4	13.32	26.00	1.40	14.1	21.67	1.17
6	11.43	36.50	1.97	11.76	34.67	1.87
9	11.89	33.94	1.83	12.03	33.17	1.79

Experimental Conditions

Shaking speed	150 rpm
Experimental temperature	25 °C
Initial adsorbent dose	0.5 g
Initial DOC concentration	18 mg/L
Volume of solution	150 ml

APPENDIX B

Raw data for ceramic membrane experiments

Appendix B-1 Permeate flux for 1.3 bar at different temperatures

1.3 bar	25 °C	35 °C	45 °C
Time (min)	Permeate Flux L/hr/m^2	Permeate Flux L/hr/m^2	Permeate Flux L/hr/m^2
5	196.67	181.67	240.00
10	191.67	178.33	240.00
15	191.67	178.33	225.00
20	188.33	176.67	225.00
30	185.00	175.00	225.00
45	175.00	175.00	225.00
60	171.67	171.67	221.67
90	171.67	171.67	218.33
120	170.00	171.67	216.67
180	166.67	170.00	180.00

Appendix B-2 Permeate flux for 3.0 bars at different temperatures

3.0 bar	25 ^{o}C	35 ^{o}C	45 ^{o}C
Time (min)	Permeate Flux L/hr/m^2	Permeate Flux L/hr/m^2	Permeate Flux L/hr/m^2
5	508.33	425.00	433.33
10	491.67	425.00	433.33
15	480.00	425.00	433.33
20	476.67	421.67	433.33
30	460.00	400.00	433.33
45	450.00	396.67	431.67
60	443.33	396.67	421.67
90	441.67	391.67	400.00
120	441.67	390.00	371.67
180	433.33	390.00	340.00

Appendix B-3 Permeate flux for 5.0 bars at different temperatures

5.0 bar	25 °C	35 °C	45 °C
Time (min)	Permeate Flux L/hr/m^2	Permeate Flux L/hr/m^2	Permeate Flux L/hr/m^2
5	750.00	658.33	846.67
10	741.67	661.67	850.00
15	725.00	661.67	858.33
20	725.00	658.33	860.00
30	683.33	658.33	870.00
45	675.00	638.33	908.33
60	675.00	636.67	896.67
90	671.67	645.00	886.67
120	666.67	658.33	900.00
180	661.67	658.33	941.67

Appendix B-4 Permeate flux for 7.0 bars at different temperatures

7.0 bar	25 °C	35 °C	45 °C
Time (min)	Permeate Flux L/hr/m^2	Permeate Flux L/hr/m^2	Permeate Flux L/hr/m^2
5	1000.00	1145	1446.67
10	900.00	1258	1500.00
15	883.33	1267	1433.33
20	875.00	1320	1466.67
30	871.67	1375	1450.00
45	858.33	1383	1078.33
60	855.00	1393	911.67
90	841.67	1400	905.00
120	835.00	1398	861.67
180	831.67	758	955.00

Appendix B-5 Effect of pressure on water quality at 25 °C

Pressure (bar)	Time (min)	TOC (mg/L)	COD (mg/L)	Turbidity (NTU)	OIW (mg/L)
1.3	0	125	89.98	230	134.55
	5	82.61	58.14	0.23	0.15
	30	83.81	62.48	0.12	0.47
	60	84.07	63.9	0.1	0.41
	120	84.21	68.93	0.02	1.79
	180	84.14	61.63	0.09	1.38
3.0	0	125	89.98	230	134.55
	5	108.15	85.68	0.15	1.74
	30	109.5	84.84	0.18	1.85
	60	109.8	84.02	0.06	1.09
	120	110.2	74.73	0.1	1.2
	180	110.5	81.97	0.13	1.2
5.0	0	125	89.98	230	134.55
	5	85.77	55.95	0.31	4.54
	30	86.3	59.89	0.26	5.26
	60	85.17	55.13	0.18	1.5
	120	84.91	54.11	0.1	1.31
	180	86.68	57.79	0.1	1.21
7.0	0	125	89.98	230	230
	5	76.54	56.43	0.2	0.2
	30	76.6	49.73	0.19	0.19
	60	76.8	56.79	0.34	0.34
	120	77.18	54.14	1.05	1.05
	180	77.04	54.26	0.98	0.98

Appendix B-6 Effect of pressure on water quality at 35 ^{o}C

Pressure (bar)	Time (min)	TOC (mg/L)	COD (mg/L)	Turbidity (NTU)	OIW (mg/L)
1.3	0	125	89.98	230	134.55
	5	65.19	34.11	0.6	2.18
	30	65.29	38.06	1.3	2.56
	60	66.28	46.16	1.2	7.14
	120	50.36	69.7	2.9	3.46
	180	47.53	47.15	7.5	7.84
3.0	0	125	89.98	230	134.55
	5	45.92	50.21	2.6	4.16
	30	43.02	46.18	4.9	7.92
	60	45.58	51.37	1.12	5.96
	120	45.75	55.31	1.8	3.54
	180	65.68	49.25	1.4	1.22
5.0	0	125	89.98	230	134.55
	5	67.64	87.97	0.09	5.91
	30	67.42	87.23	0.02	9.30
	60	69.88	86.07	0.01	7.78
	120	66.53	80.88	0.01	6.12
	180	65.33	80.5	0.01	7.92
7.0	0	125	89.98	230	180
	5	63.25	81.85	7.11	13.30
	30	66.02	88.56	0.22	7.41
	60	69.54	79.47	0.18	13.21
	120	71.25	98.59	7.11	27.31
	180	68.71	79.73	0.14	6.04

Appendix B-7 Effect of pressure on water quality at 45 °C

Pressure (bar)	Time (min)	TOC (mg/L)	COD (mg/L)	Turbidity (NTU)	OIW (mg/L)
1.3	0	125	89.98	230	134.55
	5	55.61	75.8	0.08	2.72
	30	56.11	84.18	0.12	4.16
	60	56.47	74.04	0.02	5.96
	120	56.86	79.23	0.19	4.72
	180	56.4	76.14	0.11	9.24
3.0	0	125	89.98	230	134.55
	5	58.68	75.8	0.04	1.754
	30	59.2	84.18	0.02	1.9
	60	59.85	74.04	0.03	7.72
	120	59.65	79.23	0.03	6.56
	180	60.35	76.14	0.06	3.16
5.0	0	125	89.98	230	134.55
	5	59.9	60.93	0.1	7.45
	30	60.24	57.58	0.29	8.63
	60	58.72	47.16	0.18	9.8
	120	56.89	53.38	0.1	12.2
	180	56.43	50.24	0.05	10
7.0	0	125	89.98	230	160
	5	70.2	89.66	7.11	14.78
	30	73.28	87.6	7.11	34.58
	60	66.78	85.53	0.01	9.43
	120	67.29	75.59	0.01	12.31
	180	66.92	71.62	0.01	6.94