Produced Water Treatment for Beneficial Use: Emulsified Oil Removal

Basma Waisi

PRODUCED WATER TREATMENT FOR BENEFICIAL USE: EMULSIFIED OIL REMOVAL

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Graduation committee:

Prof. dr. ir. J.W.M. Hilgenkamp (<i>Chairman</i>)	University of Twente
Prof. dr. ir. A. Nijmeijer (<i>Promotor</i>)	University of Twente
Prof. dr. S.J.M.H. Hulscher (<i>Promotor</i>)	University of Twente
Prof. dr. J.R. McCutcheon (<i>Co-promotor</i>)	University of Connecticut

Members:

Prof. dr. ir. N.E. Benes	University of Twente
Dr. ir. D.C.M. Augustijn	University of Twente
Prof. dr. ir. K. Schroen	Wageningen University
Prof. dr. ir. M. Wessling	RWTH Aachen University
Prof. dr. ir. M. Van Sint Annaland	Eindhoven University of Technology

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Basma Waisi

born on the 29th October 1979

in Baghdad, Iraq.

This thesis has been approved by:

Prof. dr. ir. A. Nijmeijer (Promotor)

Prof. dr. S.J.M.H. Hulscher (Promotor)

Prof. dr. J.R. McCutcheon (Co-Promotor)

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Chapter 1

Introduction

1.1. General Introduction

The recovery of crude oil and natural gas from both onshore and offshore fields is usually associated with the co-production of oily wastewater which is termed produced water (PW) [1]. PW is by far the largest volume waste stream associated with oil and gas production. It includes any water brought to the surface along with the produced oil or gas streams during the various stages of the production process.

The oil recovery process from an oil reservoir is commonly divided into three subsequent production phases, namely: the primary, secondary and tertiary recovery phases [2]. The primary recovery phase first uses the natural reservoir pressure to push underground fluids to the surface. These fluids can be a pure oil or an oil-gas mixture both with a limited amount of co-produced oil-contaminated water. This water includes the water naturally present in the underground formation, so-called "formation water" and the wastewater from drilling and fracking stages "Flow-back water" [3,4].

Over time, the reservoir pressure declines and the rate of oil production falls, requiring an external energy supply to boost the declining hydraulic pressure and to enhance the oil recovery. This extra energy can be introduced by injecting water or gas into the reservoir or by supplying heat to the reservoir [3]. This phase of production is referred as "secondary oil recovery" phase. It allows for an additional 25-30% of the oil in the reservoir to be extracted. For injection purposes, water is commonly used because of the high costs of gas injection [3]. For water injection, a large amount of good quality water is needed to avoid clogging the formation by the suspended solids ($TSS < 10 \text{ mg/L}$) [5] and dissolved solids ($TDS < 4000 \text{ mg/L}$) [6]. This water is used to move the presented oil in the reservoir to the production wells by enhancing the reservoir pressure [3]. The required volume of injection water is ranging from one to three barrels of water per barrel of oil produced, depending on the oil type and production time of the field [7].

After some time of using the water injection technique, the water will have by-passed some oil containing areas of the reservoir especially by flowing through high permeability layers of the reservoir. As a result, the production wells will then produce an increasingly large quantity of water (as a PW) with the oil, which itself will be decreasing so that the water-cut (fraction of water in the total produced flow) rises to more than 93%. At this stage, large quantities of oil still remain in the reservoir. However because of the high water cut, using the water injection method becomes uneconomic and the production from the field must be stopped [3,8]. At this mature age of the field, one of the tertiary recovery methods might be used to recover more oil from the reservoir. The major tertiary recovery techniques involve thermal processes (e.g. steam flooding), miscible gas processes (e.g. CO₂ and hydrocarbon flooding), chemical processes (e.g. polymer and/or surfactants flooding), and biological methods (such as microbial injection) [9].

During the different oil production stages, PW is generated with different quantities and qualities depending on various factors such as the used extraction technology, the reservoir characteristics, the lifetime of the reservoir, and the rate of oil extraction [10–12]. At some sites, the amount of PW may reach up to ten times of the quantity of the produced oil [13]. As a global estimate, more than 200 million barrels (bbl) of PW are generated from the oil production processes each day [12]. Over time, the percentage of PW increases and the percentage of oil production declines [14]. In addition, PW is usually heavily contaminated with a wide range of organic and inorganic pollutants such as dispersed and soluble oil, salts, suspended solids, heavy metals and radioactive materials [13]. This vast amount of PW, if properly treated, could be a giant source of water for different purposes such as re-injection and irrigation.

Managing such a huge amount of poor quality PW is one of the biggest challenges for preserving the economic viability of the oil production in mature reservoirs and protecting

human health and the environment. The available options for managing produced water are [15]:

1. Reusing in oil and gas operations - Treat the produced water to meet the quality required to use it for drilling, stimulation, and workover operations.
2. Re-injection - Using the produced water as a resource for water injection involves transportation of produced water from the producing to the injection site. Also re-injecting produced water needs a treatment process for the produced water to reduce amongst others fouling and scaling agents, sulfates, and bacteria.
3. Discharging - Treat the produced water to meet onshore or offshore discharge regulations.
4. Treating for beneficial use - In some cases, significant treatment of produced water is required to meet the quality required for beneficial uses such as irrigation.

All these options of PW management include treating the PW to meet the required quality for the end use of the PW using a combination of unit operations. Actually, there is no possibility to recommend a single technology for treating PW to meet all the required quality standards of end-use purposes. A solution will therefore always consist of a treatment train of technologies to remove the several types of pollutants from the PW. Generally, the basic stages in the treatment train of the PW are oil and organics removal, suspended solids removal, sulfate removal, and desalination [16].

Oil and grease removal has the highest priority for all the end-use purposes of PW to avoid serious environmental, ecological and operational issues. The oil in water can cause various operational concerns in the treatment process equipment such as fouling which needs to be cleaned out and maintained regularly [17]. In addition, regarding the low biodegradability of

oil, many countries have implemented more strict regulatory standards for discharging oily wastewater such as PW. Based on the United States Environmental Protection Agency (USEPA) regulations, the monthly average limit of oil in water is 29 mg/L [15,18]. There are several conventional technologies for oil removal from PW including skimmers, gravity separators, clarifiers, air flotation, and hydrocyclones. These methods can effectively remove the large oil droplets (free and dispersed oil) but not the emulsified oil (oil droplets less than 20 μm). Therefore, these conventional methods are unsuccessful in achieving the required water quality standards for discharging, reinjection or beneficial usages [19,20].

1.2. Emulsified Oil Treatment Methods

Generally, oil and grease in oily wastewater can be classified into three categories according to the oil droplet size (d_p): free oil ($d_p > 150 \mu\text{m}$), dispersed oil ($150 \mu\text{m} > d_p > 20 \mu\text{m}$), and emulsified oil ($d_p < 20 \mu\text{m}$) [21,22]. Conventional methods are very effective for removing both free and dispersed oil types. However, these methods are not applicable to remove emulsified oil [23–26]. Emulsified oil can be efficiently removed by some advanced technologies such as membrane separation and adsorption technologies [27,28] as well as coalescence and electrocoagulation.

1.2.1. Membrane separation technology

Membrane filtration technologies have shown great development over the last 30 years and are becoming a promising and advanced technology for industrial wastewater treatment [28,29]. Membrane separations, particularly microfiltration (MF) and ultrafiltration (UF), have been reported as successful methods for oily wastewater treatment because of their advantages such as reducing sludge, working without chemicals addition, consistent high-quality permeate, small footprint, and ease of operation [19,21,28,30–34]. Typically, MF and UF membranes can be made of polymeric materials or ceramic materials [34]. Polymeric membranes are used for treating emulsified oil because of its low cost, and low energy

requirement [29,31,32,35]. However, the polymeric membrane suffers from membrane degradation and fouling problems when being applied for oily wastewater treatment [21]. Ceramic-based membranes, however, have good mechanical, chemical, and thermal stability and low fouling tendency. These ceramic membranes have relatively recently attracted a lot of interest for use in oily wastewater treatment [28,36,37].

The major drawback of membrane filtration technology is the significant decline in the flux rate due to the membrane fouling by the adsorbed oil droplets in the pores [38]. This fouling can be reduced by choosing the right pore size of the membrane (smaller pore sizes commonly deliver a higher stable permeability) as well as membrane material (ceramic materials commonly show less fouling tendency than polymeric materials). In general, for ceramic as well as polymeric membranes, the membrane performance in oil separation applications can be improved by enhancing the fouling resistance and permeability of the membrane by controlling the membrane surface wettability and structure [35,39,40]. The membrane antifouling properties can be enhanced using various approaches depending on the membrane material. For polymeric membrane, the fouling resistance can be enhanced by blending hydrophilic additives to the polymer to decrease the adhesion of oil droplets on the membrane surface. These additives could be a hydrophilic polymer (i.e. polyethylene glycol (PEG), Polyvinylpyrrolidone (PVP), Poly(methyl methacrylate) (PMMA), and Cellulose acetate) [29,31,33,35,40–42] or could be inorganic nanoparticles such as TiO_2 and SiO_2 which can be beneficial for the membrane performance by either changing the pore structure or increasing the hydrophilicity of the membrane [29]. For ceramic membranes, the antifouling property can be improved by surface modification methods such as coating with PU–polydimethylsiloxane [42] or coating with nano-sized ZrO_2 [33]

Increasing the permeability of the membrane seems also beneficial in reducing the fouling tendency of the membrane [43,44]. Recently, the electrospinning technique has been developed

for the manufacturing of fibrous membranes by extruding the material (polymer, ceramic, carbon, etc.) using an electrically forced fluid jet as shown in Fig. 1.1. The electrospun fiber membranes can be fabricated as nanofibers or as microfibers resulting unique features such as high surface-to-volume ratio, intrinsically high porosity, fully interconnected pore structures, low hydraulic resistance, tunable wettability, and ease of scalable synthesis. Thus, the electrospun nanofiber membranes are increasingly considered to be good candidates for water filtration applications with high permeability and low energy cost. In addition, it is an easy and controllable technique to incorporate various nanoparticles within the polymer matrix to enhance the membrane wettability [26,45]. Fig. 1.2 shows a PIM-1/POSS polymer composite electrospun fibrous membrane as an example of a fabricated fibrous membrane for oil separation applications with 99.95 % oil removal. It contains a polymer of intrinsic microporosity (PIM-1) as the base polymer and polyhedral oligomeric silsesquioxane (POSS) as nanoparticles [46].

Fig. 1.1 - A schematic diagram illustrating the formation process of porous fibers during electrospinning [26].

Fig. 1.2 - SEM image of the surface morphology of 40 wt. % PIM-1/POSS polymer composite electrospun fibrous membrane [46].

1.2.2. Adsorption method

Adsorption processes are considered one of the interesting methods for organic and inorganic contaminant removal from PW [14]. The adsorption columns are packed with a highly porous solid material (adsorbent) with a high surface area. The adsorption performance of the packed bed can be measured according to the height of mass transfer zone (MTZ) which is the region of the bed between the already-saturated adsorbent material and the point where the contaminant concentration in the effluent stream is at the maximum acceptable limit (Fig. 1.3). When the MTZ reaches to the end of the bed, the bed is said to have reached the breakthrough point.

Fig. 1.3 - Progression of the adsorption front through the adsorber bed. The gray color zone is the MTZ region [47].

Activated carbon is well suited for the removal of organic pollutants due to its highly porous structure and large internal surface area [48,49]. The two most important aspects to evaluate the sorbent performance are adsorption capacity and adsorption selectivity [50]. Generally, the adsorption capacity depends on the accessibility of the pollutant molecules to the inner surface of the adsorbent, which depends on their size [47]. The selectivity of the sorbent can be modified by chemical surface functionalities [49]. Commercially, for wastewater treatment, including oily wastewater, granular activated carbon (GAC) is packed in a fixed bed. However, emulsified oil droplets can blind the pores spaces of GAC and decrease the removal capacity significantly (Fig. 1.4) [51].

Fig. 1.4. - Granular activated carbon , pores clogged by emulsified oil [52].

Recently, activated carbon in the fibrous form has been investigated in various applications including organic pollutants adsorption due to its high porosity, hydrophobicity, thermal stability, and chemical stability [49,53,54]. The electrospinning fabrication method is considered to be the preferred method to produce continuously activated carbon in the nonwoven fibrous form with fiber diameters in the nanometer range [55]. The general procedure of activated carbon nanofiber nonwoven (ACNFN) fabrication involves the pyrolysis and steam activation of electrospun polymer nonwoven precursors. Commonly, polyacrylonitrile (PAN) is used as a precursor to produce ACNFN due its high carbon yield, high melting point, and low cost. ACNFN has high porosity, an interconnected porous structure, and high surface area. Unlike GAC, the available surface area of ACNFN is directly

accessible by the pollutant because of the short distances between the free surface and the interior of the fiber, ensuring superior performance (Fig. 1.5). The high accessible surface area allows much higher adsorption kinetics, adsorption capacity and lower pressure drop than observed in the granular form (GAC) because the pollutant molecules can reach the adsorption sites through the surface micropores without the additional diffusion resistance of passing through macropores, which is usually the rate-controlling step in the case of granular adsorbent media [47,56].

Fig. 1.5 - pore structure of (a) granular activated carbon(GAC) and (b) activated carbon fibers (ACF)
[57]

Although the unique characteristics of PAN-based ACNFN such as the high accessible surface area and high permeability, it suffers from brittleness and rigidity due to the significant weight loss and shrinkage during the various thermal treatment steps. The poor mechanical strength limits ACNFN to be used in water treatment applications [58]. In this research, the mechanical properties of ACNFN were improved by tuning the fabrication conditions to generate ACNFN with high accessible surface area and acceptable mechanical strength that can be used in wastewater treatment, more specifically, for emulsified oil removal from oily wastewater. Evaluation of the emulsified oil adsorption on ACNFN was done in a batch test scale, it demonstrated a high removal efficiency. A flow through study using ACNFN was

performed using a normal flow design packed bed. Also, a test of a novel flow through adsorption bed was done by passing the emulsion through the cross-sectional area of the ACNFN sorbent layer. The results showed good performance with no obvious increase in pressure drop across the bed.

1.3. Thesis Outline

This thesis focuses on two main goals:

1. Quantifying the required water (injection water) amounts and produced wastewater (produced water) amounts during oil recovery from five of the largest oilfields in the south of Iraq.
2. Fabrication and performance evaluation of electrospun activated carbon nanofiber nonwoven (ACNFN) using for emulsified oil removal from oily wastewater.

In **chapter 2**, the quantity of water consumption (injection water) and generation (produced water) during oil production from five of the super-giant oilfields in the south of Iraq is estimated up to the year 2035 depending on the oil production rate and the age of the oilfield. In addition, the potential usage of PW is studied according to the chemical composition of this type of wastewater in an area that already has severe water shortages.

Chapter 3 describes the fabrication and characterization of PAN-based ACNFN as a highly porous carbonaceous material. Carbon nanofiber nonwoven (CNFN) is fabricated by pyrolysis of electrospun PAN precursor nonwoven. Then, CNFN is activated using a steam flow producing ACNFN with a developed porous structure. This chapter deals with the impact of the various fabrication steps of ACNFN fabrication on the mechanical properties. The effect of polymer precursor concentration is examined as well as the carbonization temperature and time, activation time, and steam quantity on the fundamental characteristics of ACNFN such as surface morphology, specific surface area, and mechanical strength.

Then in **chapter 4**, the adsorption performance of emulsified oil on a PAN-based ACNFN is evaluated in a batch test scale. ACNFN shows to be a good adsorbent for emulsified oil droplets due to its high accessible surface area, highly porous structures, and hydrophobicity. The impacts of initial oil concentration, mixing rate, and solution salinity on the oil removal efficiency are investigated. Also, the performance of ACNFN is compared with that of CNFN and a commercial adsorbent (GAC).

In **chapter 5**, emulsified oil removal using ACNFN in a flow-through system is investigated. Two pieces of a holder are designed to fix a number of ACNFN mats and feed the emulsion solution through them in a vertical direction. ACNFN mats combine the high permeability of the electrospun membrane, the high adsorption capacity due to the high surface area, and the high affinity for oil due to the hydrophobicity of the material. To investigate the removal mechanisms, a comparison is made between the performance of eight layers of ACNFN, CNFN, and precursor mats with recording the corresponding pressure drop across the nonwovens. In addition, the impacts of inlet flow rate and the number of ACNFN layers are studied.

In **chapter 6**, the design of a novel adsorption cell is described. This cell is used for fixing an ACNFN layer between the two parts of the cell and allowing the emulsion solution to enter the cell in an axial direction across the surface of the ACNFN layer. The effect of inlet flow rate, the height of the ACNFN mat, and the number of ACNFN layers are investigated. In addition, the ACNFN is regenerated by rinsing with an organic solvent to remove the adsorbed oil.

Finally, **chapter 7** is presenting some thoughts and recommendations for more applications of ACNFN in water treatment.

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Chapter 2

A Study on the Quantities and Potential Use
of Produced Water in Southern Iraq

Abstract

This paper presents the results of an analysis of volumes and chemical composition of produced water (PW) accompanying oil production from five of the largest oilfields in the world situated in Basrah, Iraq. PW is potentially a valuable water resource particularly there where the ramp up of oil production puts further strains on water and the environment in an area already having severe water shortages. PW should, therefore, be seen as part of the country's strategic water reserves rather than as effluent. This study gives first estimates of anticipated PW volumes correlated to peak oil production and water consumption needs with time up to 2035. At least a fivefold increase of PW within the next two decades relative to the current 1 Mbbbl/d can be anticipated. The estimated PW quantity before 2030 represents nearly third of water injection or salt-tolerant plant irrigation needs. These quantities and the chemical composition of PW from these fields indicate that quality standards for these purposes can be technically attained and sustained for use in Basrah.

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2.1. Introduction

Produced water (PW) is the water that accompanies the petroleum during oil and gas production and represents the largest waste stream in the petroleum industry. It tends to be heavily contaminated with immiscible oil and organics, suspended solids, salts, heavy metals, and radioactive components. The worldwide estimate of its volume is around 200 Mbbl/d (1 barrel (bbl) = 159 L) which is about three times the oil production rate [1]. Particularly in arid, oil-producing regions, PW is a viable option for addressing the increasing mismatch between limited water resources and rising water demand. Discharging such effluent can pollute surface water, soils, and groundwater. If PW is treated, it could be a significant alternative water resource for various needs as injection for enhance oil recovery and irrigation purposes, providing a sustainable water balance for the future, especially in the major oil producing countries.

Iraq is one such country that can tap on PW production. At present Iraq is one of the top three countries in the world with largest oil exports and reserves. About 75% of the total oil reserves in Iraq are concentrated in the giant and super-giant oilfields in the southern provinces with over 55% in and around the province of Basrah [2]. The quantity and quality of the available water resources in this region have been sharply declining while the demand is increasing due to population growth and economic development making it necessary to look for alternative resources [3].

The objective of this paper is to quantify the available volumes and typical quality of PW for the five super-giant oilfields in Basrah province. Prospects are made here up to the year 2035 and cover what is expected to be the most active oil production period based on International Energy Agency (IEA) estimations. Available data from different oilfields are studied to evaluate the water needs and production in Iraqi southern region where the oilfields are situated. The approach and findings in this paper on possible alternatives for reuse of the

treated PW can also be relevant for other countries and situations. This study advocates using PW if quantities are sufficient as an additional water resource for specific purposes, as in the example of Basrah and other oil regions in the world.

2.2. Water Consumption and Production in Oil Industry

Upstream oil production and water consumption and production are closely linked. The petroleum industry is a large consumer of freshwater and generator of polluted water. The quantities of injected water (used) and wastewater (produced) vary considerably depending on geographic location of the field, geological formation, type of hydrocarbon being produced, production method, and oil field's age [4].

2.2.1. Water consumption

Water is extensively consumed throughout an oilfield's production life at the various stages of the production process. During the drilling stage, water is mixed with clay and used as drilling mud to carry rock cuttings to the surface and cool the drill bit. In the following hydraulic fracturing stage fracking fluid (water, sand, and chemicals) is pumped into deep formations at high pressure to stimulate reservoir rock to produce oil. During the "primary oil recovery" phase, the natural reservoir pressure is sufficient to force oil into a wellbore. Over time, the production from a well starts to decline. During the "secondary oil recovery" phase, water injection is commonly used to boost declining pressure and force the oil from the reservoir. An early start of the secondary oil recovery phase commonly leads to higher oil recovery rates [5]. Water injection requires a large amount of good quality water, ranging from one to three barrels of water per barrel of oil produced, depending on the oil type, production strategy and well age [6]. Finally, the extracted crude oil normally contains relatively high content of salts and salt precursors (Nitrogen and Sulfur compounds) which can cause corrosion and plugging in columns and associated equipment. Freshwater with added emulsifiers is needed to wash the extracted crude oil in a desalter process.

2.2.2. Water production

Crude oil extraction produces different quantities and qualities of wastewater during the various stages of production process referred to as produced water (PW). After the first month, most of the used fluid during drilling and fracturing stages returns as flow-back wastewater. During the production stage, the produced wastewater is the formation water which is presented naturally in the reservoir. When the oilfield matures, the waste of flood water (the water injected into the formation) will be added to this type of wastewater. As a result, PW volumes increase with the age of the well. In Oman, a water content (cut) has been observed as high as 93% [7 and 8]. PW properties vary widely depending on the geological formation, production process, the type of hydrocarbon produced, and the lifetime of the reservoir [4]

The average U.S. water-to-oil ratio is estimated to be about seven barrels of PW for each barrel of oil produced [9]. The current water/oil ratio is estimated at 2:1 to 3:1 worldwide, translating to a water-cut of 50% to 75% [10]. The PW is often heavily contaminated with dissolved, immiscible and suspended material, both natural and artificially added during drilling and hydraulic fracturing processes [11].

2.3. Water and Oil Resources in Iraq

2.3.1. Water resources

Surface water in Iraq flows primarily through Euphrates and Tigris rivers, both of which originate in Turkey as shown in Fig. 2.1. In the deltas of the two rivers in the south of Iraq, there are some of the largest wetlands in southwest Asia covering 15,000-20,000 km². After the confluence of these rivers into Shatt Al-Arab, water drains into the Arabian Gulf from Al Basrah city [12].

Fig. 2.1 - (a) Rivers basins and oilfields in Iraq [13], (b) Super-giant oilfields in Basrah [14].

Over recent decades, the surface water availability throughout Iraq has been substantially reduced due to the many dams built by Turkey, Iran, and Syria. Water flowing into Iraq has been reduced drastically by more than 75% of the flow in 1990 [15]. The upstream damming combined with massive drainage of the marshes carried out from 1985 until 2000 resulted in irreversible changes to the region [12]. All these factors combined with increasingly warmer weather conditions contributed to the shortages of freshwater in Iraq's southern provinces. An emergency situation is expected to arise around 2020 because the annual 4 km³ of water remaining as surplus in the two main rivers will be insufficient [16].

2.3.2. Oil resources

Iraq is one of the world's main oil producing countries with the third largest proven oil reserves and the second-largest oil exporter in the world [17]. It has nine fields that are considered "super-giants" (over 5 billion bbl of reserves) as well as 22 known "giant" fields

(over 1 billion bbl of reserves). The cluster of super-giant and giant fields in the south of Iraq forms the largest known concentration of such oilfields in the world and accounts for two-thirds of the country's proven oil reserves. There are five super-giant oilfields in the southern region: Rumaila, West Qurna, Zubair, Majnoon and Nahr Umr containing about 55% of the Iraq's total oil reserves.

The IEA's central case projects that Iraq's oil production will increase to 6.1 Mbbl/d by 2020 and reach 8.3 Mbbl/d by 2035. Oil production increase is mainly driven by the five southern super-giant oilfields. Based on data from Iraq's Ministry of Oil and the IEA estimates, we can predict the productivity of the five super-giant oilfields in Basrah up to 2035 as shown in Fig. 2.2 [2].

Fig. 2.2 - Estimated oil production for five super-giant oilfields in Basrah up to 2035.

2.4. Estimation of Water Consumption, PW Quantity, and Quality

2.4.1. Consumed water

The required water for injection in Basrah province can be estimated using the world average range of 1-3 barrels of water per barrel of oil [6]. We estimated the amount of injection water (Fig. 2.3) by multiplying the oil production (Fig. 2.2) with a factor increasing from 1 to 3 over the period from 2010 to 2035 depending on the oil field's age and production strategy.

Fig. 2.3 - Estimated water injection quantities for the five super-giant oilfields Basrah.

2.4.2. Produced water

The water cut is the fraction of water in the produced fluid. The water cut usually increases with increasing age of the oilfield depending on the amount of formation water and injected water for enhancing oil recovery. At some point, an oil well becomes uneconomical as revenue from a declining oil supply fails to cover the costs of processing the high water fraction [18]. Every oilfield has a unique production profile which could be long or short depending on the total volume of oil present and production rate. All the oilfields go through a build-up, plateau production and decline phases [19]. The southern Iraq's oilfields are in different phases; the Rumaila oilfield will enter its depletion phase in 2020, Zubair, Majnoon and Nahr Umr oil

fields will reach their plateau phases by about 2023 while West Qurna will remain in the buildup phase until 2035.

To predict the amount of PW, we need to estimate the present and future water-cut of these oilfields. Various oilfield profiles were studied: the North Ain Dar Saudi oilfield and the North East Atlantic oil fields [20 and 21]. Based on these profiles, at the peak oil production rate, the water cut is less than 50% (one barrel of water with each barrel of oil). As a result, the water-cut of these oil fields is estimated as follow: the water-cut of Rumaila was 25% in 2004 [22] and it will reach 45% when its depletion phase starts in 2020 followed by further increasing to 60% in 2030; the Zubair, Majnoon, and Nahr Umr are predicted to have a water cut of 35% by 2030, while the water-cut of West Qurna is estimated to reach 30% in 2030. Based on these estimations and Fig. 2.3, we can make an estimate of PW volume in time for the five super-giant oilfields in Basrah as plotted in Fig. 2.4. The total PW rate is estimated to reach 2 and 4.7 Mbbl/d in 2020 and 2035, respectively.

Fig. 2.4 - The estimated volumes of PW for the five super-giant oilfields in the south of Iraq.

Moreover, this PW is heavily polluted and is considered as brine water because of its extremely high salinity (TDS > 35,000 mg/L). Table 2.1 shows the PW characteristics of (North and South) Rumaila, Zubair and West Qurna oilfields.

Table 2.1 - Characteristics of the produced water of the four oilfields [23]

Water quality parameter	(North & South) Rumaila	Zubair	West Qurna
pH (-)	4.1-4.8	6.6	4.9
Total Dissolved Solids (TDS) (mg/L)	246,000-247,000	268,000	300,000
Total Suspended Solids (TSS) (mg/L)	141-260	110	75
Bicarbonate as (CaCO ₃) (mg/L)	40,000-54,000	50,000	43,000
Oil content (mg/L)	36-53	66	57
COD (mg/L)	800-1,400	1,800	1,500
TOC (mg/L)	300-500	610	520
Sulfate (mg/L)	108-116	104	94
Iron (mg/L)	10-18	0.6	0.61
Manganese (mg/L)	1-2.5	2.2	1.5
Calcium (mg/L)	17,000-13,000	14,000	12,000
Magnesium (mg/L)	1,900-2,600	3,600	3,100
Sodium (mg/L)	89,000-91,000	87,000	98,000
Chloride (mg/L)	138,000-141,000	134,000	151,000

Currently, part of this PW is disposed of through injection into Dammam formation [24] causing pollution of underground aquifers. The other part is discharged directly to the surrounding environment leading to environmental problems in the region as the oil and organics, heavy metal, and radioactive materials contents are very toxic for plants, animals, and humans. These pollutants can be absorbed by the ground and pollute the groundwater. In addition, the high salinity is considered as a major contributor of toxicity and it reduces water uptake by lowering the soil osmotic potential and permeability.

2.5. Recycling of PW

Water recycling refers to reusing treated wastewater for beneficial purposes such as re-injection, irrigation and even drinking water. Recycling water curbs the amount of consumed

freshwater and decreases the adverse effects of wastewater discharging. An example where PW is reused successfully already in a comparable environment to that in Iraq is in Oman. There the Nimr project plant handles on average about 45,000 m³/d of PW which is then used for irrigation [25].

A choice is made in this study to consider PW for injection and (or) irrigation purposes. The main water quality parameters of concern are oil and hydrocarbons, suspended solids, and salinity. Membrane technology has shown promise for converting a waste fluid to a usable resource. However, PW can cause severe fouling problems on most membranes [26]. Although there are some methods to reduce fouling problems [27], PW should be processed through different separators and filters as pre-treatment steps to reduce oil and hydrocarbons, gas, and (suspended and dissolved) solids.

There are different technologies that can be used to reduce hydrocarbon content effectively such as membrane bioreactors, wetlands, nanofiltration and adsorption technologies. The dissolved gas can be separated by gas separator technology while the suspended solids can be reduced by filtration system [8]. Application of softening as a pretreatment step is effective in reducing carbonate ions which form the main precipitations (scales) in the desalination process [28]. The most effective technologies for desalination of high-salinity PW are mechanical vapor compression, membrane distillation, and forward osmosis [11].

2.5.1. Reuse for re-injection

The demand for water injection to enhance oil production is high. As previously discussed, this rate will further increase as future oil production in Iraq ultimately rises to designated level. At present, Garmat Ali River (which receives its water from the Euphrates) is the main water source for the southern oilfields [29], but it will be insufficient for the anticipated increased water demand of the future.

To solve this problem, Iraq has chosen the Common Seawater Supply Facility (CSSF) Project to bring in and treat seawater from the Arabian Gulf (TDS = 50,000 mg/L) [30] to supply the southern oilfields with injection water. The project will start in 2017 with an initial phase of 2 Mbbl/d and will be developed in stages over the following years: 4 Mbbl/d in 2018, 6 Mbbl/d in 2021, and 8 Mbbl/d in 2027. Before using this water for injection, it should be treated to meet the water injection quality standards. Meeting these quality standards is essential for preserving the permeability of a reservoir formation otherwise serious problems can occur such as corrosion of pipes and clogging of the formation resulting in needing higher than anticipated injection pressures and the loss of affected injection wells [31]. The most critical parameters for injection are TSS (should be less than 10 mg/L) and TDS (should be in the range of 1,000-12,000 mg/L). About 50% more oil can be produced if low salinity water (TDS < 4,000 mg/L) is injected into the reservoir compared to using higher salinity water [32].

As the CSSF will be insufficient to provide enough injection water for the oilfields in the south of Iraq, treated PW can be used as a supplement. Treated PW can contribute in providing up to 35% of the required water for injection in the five southern super-giant oilfields (see Fig. 2.3 and 2.4).

2.5.2. Reuse for irrigation

In the southern region of Iraq, water shortage is the most important factor that affects agricultural production and water-reliant industries. According to irrigation water quality standards, TSS and TDS values should be less than 30 mg/L and 2,500 mg/L respectively while the oil content should be less than 0.5 mg/L [33]. The solids content is important because high TSS reduces soil porosity while high TDS reduces water uptake by plants by increasing the soil osmotic potential.

The date palm is a main commercial plant in Basrah, and it is considered as one of the most salt-tolerant plants found in the region. The water shortage for the date palms irrigation is estimated at 600 Mm³/year (13.8 Mbbl/d) [3]. At present, the treated PW could meet 8% of the water needed for date palms in Basrah and could overcome 15% of the shortage water in 2020 and more than 33% in 2035.

2.6. Conclusion

Upstream oil production and water consumption and production are closely linked. To extract oil huge amounts of fresh water are used in the various stages of the oil production process (drilling, fracturing, injection and washing). Part of this water in combination with water naturally present in the formation is extracted again with the oil, producing a large amount of wastewater referred to as PW.

In Basrah province in the south of Iraq, five super-giant oilfields are located which contain 55% of Iraq's oil reserves. The production rate of these oilfields is expected to increase to 4.4 Mbbl/d in 2020 and 5.7 Mbbl/d in 2035. It is estimated that this requires about 8.5 Mbbl/d of injection water in 2020 and 13.7 Mbbl/d in 2035. This will generate an increasing amount of PW estimated at 2 Mbbl/d in 2020 and 4.7 Mbbl/d in 2035.

In Iraq, PW is currently discharged directly into the environment with devastating impacts. When treated, this PW could be used for beneficial purposes. As the PW is heavily contaminated it needs to be treated with advanced technologies before reuse. A possible application of the treated PW is as injection water for enhanced oil recovery. The PW makes up 23% (in 2020) to 35% (in 2035) of the required injection water. This is a valuable addition to the planned seawater treatment plant that is anticipated to supply part of the injection water (8 Mbbl/d in 2027). Another potential application of the treated PW is as irrigation water. As PW in south Iraq has high salinity, it may be most suitable for salt-tolerant plants irrigation

such as date palms. By 2035, treated PW could make up 33% of the irrigation water required for date palms in Basrah province. This study shows that PW in the south of Iraq forms a substantial amount that after treatment could be used as a valuable resource saving the environment and fresh water resources in a region with increasing water shortages.

2.7. References

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Chapter 3

Activated Carbon Nanofiber Nonwovens:
Improving Strength and Surface Area by
Tuning Fabrication Procedure

Abstract

Electrospun based activated carbon nanofiber nonwovens (ACNFN) are interesting candidate materials for adsorption processes, due to their high surface area and low flow-through resistance. However, the mechanical properties of these materials must be sufficient to withstand the application conditions, for instance, the forces associated with viscous flow in aqueous applications. Improvements in the mechanical properties of the ACNFNs should not be accompanied by deterioration of other properties, in particular, the high specific surface area. Here, the optimization of ACNFN material properties for use as high-performance nonwoven mats or sorbent is presented via systematic variation of the fabrication process parameters. The following fabrication parameters have been identified to have a critical impact: polymer concentration, carbonization temperature and time, activation time and steam amount.

3.1. Introduction

Activated carbon nanofiber nonwovens have been attracting increased attention due to their unique physical properties, such as a high electrical conductivity, a high specific surface area, and biocompatibility [1]. Applications range from the removal of volatile organic compounds (VOCs) by adsorption [2], electrodes in microbial fuel cells [3], electrochemical capacitors [4], and lithium-ion batteries [5].

Fabrication of activated carbon materials requires a precursor material that is carbonized and activated through sequential thermal and chemical treatments. To make an activated carbon nanofiber nonwoven (ACNFN), the precursor must be provided in the desired architecture (in this case a nanofiber nonwoven). Commonly, nonwoven nanofibers are fabricated via the electrospinning process, which is a versatile method to produce ultrathin and continuous fibers from a polymer solution [6]. The properties of the precursor fibers and the carbonation and activation conditions determine the final properties of the ACNFN [7]. Polyacrylonitrile (PAN) is not only one of the easier polymers to electrospin, it also serves as a popular carbon precursor material due to its thermal stability and high carbon yield [8]. Carbonizing electrospun PAN nanofiber requires moderate heating in an air atmosphere, followed by high-temperature carbonization in an inert gas. The result is a carbon nanofiber nonwoven (CNFN). This material can be further treated with steam or other chemical exposure to produce an activated carbon nanofiber nonwoven (ACNFN) [9–11].

Fundamental changes in both chemical composition and physical properties occur during each of these fabrication steps. For instance, stabilization, which occurs in an oxidizing atmosphere at temperatures of 180 - 300 °C, causes a number of chemical reactions including cyclization, dehydrogenation, aromatization, oxidation, and crosslinking among linear polymer chains [12–14]. These various reactions can result in weakening of the mechanical strength of the fiber [13]. During the early stages of carbonization, intermolecular dehydrogenation, and

crosslinking reactions occur in the oxidized PAN, leading to cyclic structures. Then by dehydration and denitrogenation, these cyclized structures start to link to each other [12]. A variety of gases (e.g., H₂O, N₂, HCN, and others) are evolved, and the carbon content increases to higher than 85 wt.% leading to fiber diameter reduction [15,16]. The reduction in fiber size can weaken individual fibers and detach fibers from each other at their junction points.

The prepared CNFN is activated to produce meso- and microporosity, which yields high specific surface area and high basic oxygen groups content [17]. Carbon activation can be done by steam [18] or carbon dioxide [19]. Steam is commonly used because of its low cost and low environmental impact [20]. At a temperature higher than 700 °C, the steam reacts with the carbon atoms of the CNFN, thereby eliminating heteroatoms and releasing CO and H₂ gasses. The removal of carbon atoms from the structure creates small and large pores on the CNFN surface that result in an increase in the specific surface area [12,21].

The weight loss and shrinkage during carbonization and activation steps have a negative effect on the mechanical strength of an ACNFN [10,18]. Decreased mechanical properties can hamper the value of the ACNFN in applications such as microbial fuel cells [3,22] and water filtration [23]. Understanding how the fabrication approach impacts the mechanical properties is the first step in fabricating a material with the necessary strength for certain applications [24]. This work seeks to elucidate how various processing steps of the ACNFN fabrication impact the mechanical properties. The impact of the polymer precursor concentration, the carbonization temperature and time, the activation time, and the steam quantity on the characteristics of an ACNFN, such as the fiber size, surface morphology, mechanical strength, flexibility, and specific surface area is examined.

3.2. Materials and Methods

3.2.1. Electrospinning of polymer precursors

Polyacrylonitrile (PAN) from Scientific Polymer Products Inc. (Average molecular weight 150,000 g/mol) and Dimethylformamide (DMF) from Acros Organics were used to prepare 10, 14, and 16 wt. % PAN in a DMF solution by constant stirring at 60 °C for 2h. A high-pressure syringe pump (KD Scientific) was used to dispense the charged solution at a constant rate of 1 mL/h through a 20 gauge blunt end needle. The fiber was spun onto a collector (grounded) rotating at 70 rpm. The applied voltage was 27, 24 and 21 kV (for 10, 14 and 16 wt. % PAN respectively) and the tip to collector distance was held constant at 18 cm. Based on previous work the precursor mats were all spun at room temperature under a relative humidity of 10 – 20% [25].

3.2.2. Fabrication of CNFN and ACNFN

To make CNFN, the PAN nanofiber mats were stabilized in air at 280 °C for 1 h in a muffle furnace (Carbolite) using a ramp rate of 1 °C/min. The stabilized nanofibers were then carbonized in a tube furnace (Lindberg Blue M, Thermo Scientific) in an inert nitrogen atmosphere with a ramp rate of 3 °C/min. The 14 wt. % PAN fibers were carbonized for 1 h at three different temperatures (600, 750, and 850 °C). The 600 °C carbonization was conducted for three different dwell times (1, 2, and 3 h). To make an ACNFN from this CNFN, the CNFN was activated in the same furnace using steam in an inert nitrogen atmosphere at 750 °C. The activation process carried at different times (30 or 60 minutes) using different steam flow rates (30 or 60 g/h).

3.2.3. Nonwoven characterization

3.2.3.1. Fiber morphology and size

CNFN and ACNFN samples were sputter coated with gold and imaged using field emission scanning electron microscopy (FESEM, JEOL 6335F) to observe the surface

structure/morphology. To obtain fiber size distributions and the average fiber diameter, thirty individual fiber sizes were measured using Image J software (National Institutes of Health, USA).

3.2.3.2. Mechanical properties

The tensile strength and flexibility of the samples were used as parameters to quantify the mechanical strength of the carbonized and activated samples. A Dynamic Mechanical Analyzer (DMA) from TA Instruments was used to derive the tensile strength and Young's modulus. Sample sizes of 3 cm x 6 mm were used for the tests which were all performed at 25 °C and ambient humidity. All results presented were the average of three individual tests from different samples.

3.2.3.3. Surface area measurements

Specific surface areas were measured using an ASAP 2020 Physisorption Analyzer (Micromeritics Instrument Corporation). The samples were degassed at 300 °C for 2 h and then analyzed for nitrogen sorption at 77 K. Adsorption isotherms were used to calculate the specific surface area through application of the Brunauer–Emmett–Teller (BET) model. All results presented were the average of three individual tests from different samples.

3.2.3.4. Surface chemistry (FT-IR)

The surface chemistry of the nonwoven samples was analyzed using Fourier transform - infrared (FT-IR), Nicolet iS10 FT-IR (Thermo Scientific). Infrared spectra were recorded in the wave number range of 500 – 4000 cm^{-1} with a resolution of $\pm 4 \text{ cm}^{-1}$ and a total of 16 scans per sample. The attenuated total reflection mode with a diamond crystal was used to scan the samples.

3.3. Results and Discussion

3.3.1. Fiber morphology

Fig. 3.1 a-c show the SEM images and the corresponding fiber size distributions of PAN-based CNFN carbonized at 600 °C for 2 h as a function of PAN concentration (10, 14, and 16 wt. %). The average fiber diameter increased from 160 nm at 10 wt. % PAN to 760 nm at 16 wt. % PAN. The increases in fiber diameter are primarily due to the higher viscosity of the spinning solution, which reduces the drawdown of the fiber prior to solidification [26]. This result has been well documented in other studies on electrospinning [27–29].

Fig. 3.1 d shows SEM images and the corresponding fiber size distribution of 14 wt. % PAN-based CNFN after an activation step at 750 °C for 1 h using 60 g of steam. The activation decreases the average fiber size from 350 nm (CNFN) to 250 nm (ACNFN). This is consistent with previous work [18] and is attributed to the weight loss and compacting of the fibers [23].

Fig. 3.1 - SEM images and fiber size distributions of (a) 10 wt. % PAN-based CNFN , (b) 14 wt. % PAN-based CNFN, (c) 16 wt. % PAN-based CNFN, and (d) 14 wt. % PAN-based ACNFN, (The number of individual fibers (N)=30)

3.3.2. Surface chemistry

A comparison of FT-IR spectra of 14 wt. % PAN-based stabilized, carbonized (at 600 °C for 2 h), and activated (at 750 °C for 1 h using 60 g of steam) nanofiber nonwoven samples is shown in Fig. 3.2 a. The effect of carbonization temperature and time on the surface chemistry of 14 wt. % PAN-based CNFN is shown in Fig 2 b and c, respectively.

In Fig. 3.2 a, the main peaks groups in the FT-IR curve of the stabilized nanofiber are observed at 1270 cm^{-1} , 1350 cm^{-1} , and 1450 cm^{-1} for the aliphatic CH groups, at 1590 cm^{-1} for a mixture of C=N, C=C, and N-H groups, and at 1732 cm^{-1} for the C=O group [30]. During stabilization (at $280\text{ }^{\circ}\text{C}$), various reactions occur, such as cyclization, dehydrogenation, and oxidation. These reactions produce C=N, C=C, and C=O groups, respectively [18,30]. Also, a small peak can be noticed at 2242 cm^{-1} , which is attributed to a $\text{C}\equiv\text{N}$ group in the stabilized nanofibers. The intensity of all these groups in the curve of stabilized sample was decreased significantly by performing the carbonization step (at $600\text{ }^{\circ}\text{C}$) due to the cyclization and crosslinking reactions [31]. Exposing the CNFN to a higher temperature ($750\text{ }^{\circ}\text{C}$) during steam activation results in peak shifts from $1350 - 1450\text{ cm}^{-1}$ (aliphatic CH groups peaks) to 1160 cm^{-1} (O-H bond in the phenolic group) after steam activation. The peak at 1580 cm^{-1} becomes more pronounced due to an increase in a number of carbonyl groups during steam activation [18,30].

Fig. 3.2 b shows the effect of carbonization temperature on the CNFN surface chemistry. A reduction of the intensity of the C=N and C=O peaks can be observed with increasing carbonization temperature. At a carbonization temperature between $400\text{ }^{\circ}\text{C}$ and $600\text{ }^{\circ}\text{C}$, intermolecular dehydrogenation occurs linking the cyclic structures. The remaining linear segments either become cyclized or suffer chain scission with the evolution of gaseous products. At a temperature higher than $600\text{ }^{\circ}\text{C}$, denitrogenation reactions take place, resulting in the removal of structural defects and non-carbon elements (not only nitrogen but also oxygen, hydrogen, and sulfur) and forming the sheet-like structures [12].

Fig. 3.2 c shows the effect of carbonization time on the two main permanent peaks height differences. A very small peak of $\text{C}\equiv\text{N}$ can be noticed at 2242 cm^{-1} , which indicates that 1 h carbonization at $600\text{ }^{\circ}\text{C}$ is not enough to convert all $\text{C}\equiv\text{N}$ to C=N through cyclization and cross-linking. This peak no longer exists when the carbonization continues for a longer time (2 and 3 h).

Fig. 3.2 - FT-IR analysis of 14 wt. % PAN/DMF based nonwoven (a) Stabilized (280 °C for 1 h), CNFN (600 °C for 2 h), and ACNFN (750 °C for 1 h using 60 g of steam) (b) CNFN at various carbonization temperature for 1 h time, and (c) CNFN at 600 °C for various carbonization time.

3.3.3. Specific surface area

Fig. 3.3 a shows the surface areas of CNFN fabricated from different concentrations of PAN precursors and carbonized at 600 °C for 2 h. It is found that an increase in polymer concentration correlates to a decrease in surface area, as a result of an increase in fiber size [32]. The specific surface area of the CNFN decreases from 45 to 5 m²/g, upon increasing the polymer concentration from 10 to 16 wt. % PAN.

Fig. 3.3 b shows the surface areas of 14 wt. % PAN based ACNFN using a steam at 750 °C for various activation times and steam delivery rates. Steam exposure creates micro- and mesoporosity in the carbon nanofiber mat, due to the reactions of water molecules with the

carbon atoms. These reactions are strongly affected by the activation temperature and time [21]. The specific surface area of the carbon nonwoven mat indeed substantially increases during steam activation: 60 g/h of steam for 30 min results in an increase of the specific surface area from 19 m²/g (CNFN) to 380 m²/g (of ACNFN). The specific surface area is further increased to 520 m²/g by doubling the activation time. This is consistent with previous work [21,33].

Fig. 3.3 - Specific surface areas of (a) CNFN (at 600 °C for 2 h) from different PAN concentrations and (b) 14 wt.% PAN-based ACNFN fabricated using various steam mass and activation time (number of samples (N)=3).

3.3.4. Mechanical strength

Fig. 3.4 a shows the tensile strength and Young's modulus (both averaged from three individual samples) as a function of polymer concentration. These results show that the 16 wt. % PAN-based CNFN has the highest tensile strength and Young's modulus, while the 10 wt. % PAN-based CNFN has the lowest tensile strength and Young's modulus.

Increasing polymer concentration increases the polymeric nanofibers size and mechanical properties (Young's modulus and tensile strength) [34]. This is attributed to the fact that at higher concentration the number of polymer chains per unit volume of solvent is higher than that at a lower concentration. The higher number of polymer chains results in enhanced chain interaction and entanglement [35]. In general, larger fibers lead to stronger nonwovens. Larger

fibers also contain a residual solvent that slowly evaporates after spinning. The evaporation of the solvent facilitates bonding of fibers, which improves the strength of the mat.

The effects of the carbonization step on the mechanical properties are depicted in Fig. 3.4 b. The strength and the Young's modulus decrease with increasing carbonization temperature. For the strength, both the temperature and time appear to have a threshold value. Carbonization at 600 °C for 1 and 2 hours results in a similar mechanical strength, whereas treatment at the same temperature for 3 hours results in a pronounced decrease in mechanical strength. Keeping the treatment time fixed at 1 hour, and increasing the temperature from 600 °C to 750 °C has a pronounced effect on the mechanical strength, but a further increase in temperature to 850 °C does not substantially further reduce the strength.

The mechanical properties of the ACNFN obtained using different activation conditions are shown in Fig. 3.4 c. The mechanical strength decreases substantially upon activation from CNFN to ACNFN, for all activation conditions. This decrease in strength is attributed to an increase in porosity and loss of weight, during activation [36]. The variation in the strength of the fibers obtained after activation is not strongly dependent on the exact activation conditions, i.e., the amount of steam and the activation time. A distinct behavior is observed for the Young's modulus. The decrease of in the Young's modulus is approximately twice as large when the activation time is doubled, as compared to when the amount of steam is doubled. A combined increase in activation time and amount of steam results in a further decrease of the Young's modulus.

Fig. 3.4 - Mechanical properties (Tensile strength and Young's modulus) of 14 wt. % PAN/DMF based (a) CNFN based on different polymer concentration, (b) CNFNs at different carbonization temperatures and time, and (c) ACNFN activated at different activation time using different amounts of steam. (N=3).

3.4. Conclusions

In this work, we have demonstrated that ACNFN with enhanced mechanical strength and specific surface area can be fabricated by optimizing the conditions of the electrospinning step, the carbonization step, and the steam activation step. In the electrospinning process, the concentration of the polymer solution is identified as a critical parameter that dictates the average fiber diameter, as well as the width of the fiber diameter distribution. For higher polymer concentrations larger fibers are found with a larger standard deviation. In the carbonization step, the temperature and treatment time have a pronounced effect on the CNFN strength and flexibility. For both the temperature and treatment time, threshold values exist. Below these threshold values (a temperature of 600 °C for 2 h) the effect of the carbonization on the mechanical properties is minor, above these threshold values the strength and Young's modulus are reduced substantially. During steam activation, the strength of the fibers decreases, yet the change is relatively insensitive to the amount of steam used and the activation time. A decrease in Young's modulus is observed during activation that is more pronounced for longer activation time than for larger amounts of steam. Tuning the fabrication conditions is essential to produce high specific surface area ACNFN with good mechanical strength. Such ACNFN can be an excellent material for many pressurized applications, for instance in water treatment.

3.5. References

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Chapter 4

The Use of Electrospun Polyacrylonitrile-based Activated Carbon Nanofiber Nonwoven for Emulsified Oil Adsorption from Oily Wastewater

Abstract

Activated carbon nanofibers nonwoven (ACNFN) have been attracting increased attention from a wide variety of applications, due to their high porosity and large surface area. In this work, the batch-wise removal of emulsified oil from oily wastewater, using ACNFNs, has been investigated. The ACNFNs were prepared by thermal treatment of electrospun polyacrylonitrile and exhibit high specific surface area, high hydrophobicity, and substantial mechanical strength. In batch dynamic adsorption tests the oil removal efficiency of the ACNFN appears to be affected by, in particular, the initial oil concentration, the mixing rate, and the salt concentration. The ACNFNs exhibit a very high removal efficiency of up to 95%, thereby outperforming (non-activated) carbon nonwoven and a commercial granular activated carbon.

4.1. Introduction

A massive amount of oily waste water is generated from various industrial sources such as petroleum refineries [1], manufacturing plants [2], mines and metal-processing industries [3]. The discharge of oily wastewater endangers terrestrial and aquatic ecosystems, due to the low rate of oil degradation [4,5]. Oil in water can be classified into three types, based on the size of the oil droplet (d_p): free-floating oil ($d_p > 150 \mu\text{m}$), dispersed oil ($150 \mu\text{m} > d_p > 20 \mu\text{m}$) and emulsions ($d_p < 20 \mu\text{m}$) [6,7]. Free-floating and dispersed oil can be removed using traditional methods, such as gravity separation, skimming, air flotation, centrifugation, coagulation and flocculation [8–10]. These methods, however, cannot effectively remove stable emulsions [11,12].

Adsorption is one of the interesting methods for the removal of emulsions from wastewater [7]. A variety of adsorbents have been used for emulsified oil removal, including biomaterials [13], coal [14], barley straw [15], silica aerogel [16] bentonite [17], meshed corncobs [18], and carbon [19]. Commercially available activated carbon, in powder or granular form, is widely used as an adsorbent to remove a range of pollutants, including oil [20]. However, for oil, such activated carbons have shown slow kinetics and limited oil removal capacity [7,21]. This can be explained by the large diameter of oil droplets compared to the diameter of pores of activated carbon, resulting in blocking of the pores and preventing further adsorption of oil droplets [22]. Favorable adsorption behavior can be achieved by optimizing the porous structure [23]. In addition, the surface hydrophobicity is essential for oil adsorbent material [16].

Activated carbon nanofiber nonwoven (ACNFN) is a form of activated carbon that is attracting increasing attention due to its unique characteristics, in particular, associated with porous ultrafine fibers [24]. ACNFNs can be fabricated via the electrospinning technique. This technique is considered to be versatile and effective for the fabrication of polymeric nanofibers with high surface-to-volume ratio and multi-porous structures [25]. Polyacrylonitrile (PAN) is

one of the most widely used precursor materials to produce carbon fibers. PAN allows a high carbon yield and has high thermal stability [26]. A series of thermal treatments can convert a PAN-based precursor of an ACNFN, fabricated by electrospinning, into the desired carbon-based form [26–28]. The general sequence of thermal treatment processes involves: stabilization (usually at air atmosphere) [29], carbonization (at inert atmosphere) [30], and activation (using oxidizing agent) [31]. The produced activated carbon nanofiber (ACNFN) has a high specific surface area and multi-porous structures [32]. As compared to granular activated carbon, the length of the diffusion paths in ACNFNs are small and most of the ~nm size pores are accessible to the pollutants.

The electrospun ACNFN is considered as a good candidate for adsorption materials due to its high thermal and chemical stability, meso-microporous structure, high specific surface area and hydrophobicity [26]. Therefore, ACNFN attracted considerable attention in gas treatment, such as the adsorption of toluene [33] gaseous formaldehyde [34], and other volatile organic compounds (VOCs) [27], and the treatment of toxic industrial gas [35]. However, electrospun ACNFNs are quite rigid and brittle due to the significant weight loss and shrinkage induced by the thermal treatment steps [36]. The poor mechanical strength can be a reason for avoiding the use of electrospun ACNFN in water treatment technologies.

Recently, we reported the optimized fabrication conditions to obtain ACNFN with good mechanical strength, a high specific surface area, and a high hydrophobicity. Here, we describe the emulsified oil adsorption capacity and rate of such ACNFNs using a batch test. The effects of the initial oil concentration, salinity, and the agitating speed on adsorption performance are studied in detail. A comparison is made between the performance of the ACNFNs, CNFNs and commercial adsorbents (GAC).

4.2. Materials and Methods

Petroleum oil (18% aromatics basis, B.pt (180-220) °C) was ordered from Sigma-Aldrich; it was used to prepare the oil in water emulsion in the batch experiments. To prepare the adsorbent materials, the polyacrylonitrile (PAN) powder was purchased from Scientific Polymer Products Inc. (Average molecular weight 150,000 g/mol) and dimethylformamide (DMF) as a solvent was purchased from Acros Organics. For comparison purposes, Granular Activated Carbon (GAC) was used in this study as a commercial adsorbent. GAC (Pfaltz and Bauer) was ordered from Fisher Scientific. For adjusting the water salinity, sodium chloride (NaCl) was purchased from Fisher Scientific.

4.2.1. Adsorbent fabrication via electrospinning

Polyacrylonitrile (PAN) and dimethylformamide (DMF) were mixed to prepare 14 wt. % PAN in DMF solutions, under constant stirring at 60 °C for 2 h. The solution was dispensed using a high-pressure syringe pump (KD Scientific), at a constant rate of 1 mL/h from a 20 gauge blunt-end needle. The collector was a grounded drum rotating at 70 rpm. The needle to collector distance was 18 cm and the applied voltage difference between needle and collector was 22- 24 kV.

The electrospun nonwoven precursor was then stabilized in air at 280 °C for 1 h in a muffle furnace (Carbolite), followed by a carbonization step in a tube furnace (Lindberg Blue M, Thermo Scientific) at 600 °C for 2 h in an inert nitrogen atmosphere to make a carbon nanofiber nonwoven (CNFN). The ramp rate was 1 °C/min for stabilization, and 3 °C/min for carbonization. Activated carbon nanofiber nonwovens (ACNFNs) were produced by an activation step in the same furnace, using 1 g/min of steam in an inert nitrogen atmosphere at 750 °C for 1 h. The ramp rate for activation was 5 °C/min.

4.2.2. Preparation of synthetic emulsified oil wastewater

Petroleum oil was used to prepare a synthetic oily wastewater. An adequate amount of petroleum oil was added to 500 mL of distilled water, this mixture was then emulsified in a high-speed blender (Waring Two-Speed Blenders) at 24000 rpm for 8 minutes, at room temperature. Emulsions were prepared with three different petroleum oil concentrations: 100, 500, and 1000 mg/L. The effects of solution salinity were studied by adding a certain weight of NaCl (1 M and 3 M) to the emulsified oil solution, followed by mixing for 30 min using a magnetic stirrer.

4.2.3. Characterization of the adsorbents

Scanning electron microscopy (SEM) images of ACNFN samples were obtained before and after the batch tests, using field emission scanning electron microscopy (FESEM, JEOL 6335F) to determine the surface morphology. The average fiber diameter of fifty individual fiber sizes was measured using Image J software (National Institutes of Health, USA).

Nitrogen adsorption/desorption isotherms of the adsorbent samples were obtained using Physisorption Analyzer (Micromeritics Instrument Corporation). The specific surface area of each sample was calculated through application of the BET model. For carbon materials, the surface hydrophobicity was determined by measuring their contact angle with water, using a CAM 101 series contact angle goniometer. The average of ten measurements was taken, with a water droplet volume of 5 ± 0.5 μ L.

4.2.4. Characterizations of emulsions

The droplets size distribution of the prepared emulsions was evaluated by laser light scattering using a submicron Particle Sizer (NICOMP, Santa Barbara, California, USA). The measurements were assessed over time (1, 2, and 6 hours), for different NaCl content (0, 1, and 3 M). The total measurement time for each sample was 10 minutes.

Oil concentrations were measured using a UV/Vis spectrophotometer (Thermo Scientific Genesys 10S) at a wavelength of 260 nm. The viscosity (μ) and refractive index (n) of the samples were measured at 25 °C using Brookfield viscometer (LVDV-I Prime Cone/Plate) and Refractometer (Bausch and Lomb Abbe) respectively.

4.2.5. Batch adsorption studies

Oil adsorption was conducted by agitating 0.1 g of adsorbent material and 250 mL synthetic emulsified oil in a glass beaker, using a magnetic stirrer at room temperature (Fig. 4.1 a). Blank experiments (without using adsorbent) were conducted to ensure that a decrease in oil concentration was not caused by instability of the emulsion during the experiments.

There are various variables that affect the adsorption process. In this research, the effects of the initial oil concentration (100, 500, and 1000 mg/l), the mixing rate (100, 200, and 300 rpm), and the NaCl concentration (0, 1, and 3 M) were studied. The adsorption performance of the ACNFNs was compared with those of CNFNs and GACs. In all adsorption experiments, the dimensions of the ACNFN and CNFN pieces were 4 by 2 cm. A stir-bar cover was designed to prevent nonwoven pieces from coming into direct contact with the stir-bar, which would break them up. As can be seen in Fig. 4.1 b, the stir-bar cover contained a plastic ring with some holes on its sides to allow the solution go through them during the mixing. On the top of the ring, there was a plastic mesh that prevents the nonwoven pieces from coming into direct contact with the underneath stir bar. The initial pH was 7.3 for all solutions.

Fig. 4.1 - (a) Schematic diagram of the batch test and (b) Image of the designed stir-bar cover.

4.3. Results and Discussion

4.3.1. Adsorbent characterizations

Fig. 4.2 shows SEM images and fiber diameter distributions of 14 wt. % PAN based nonwoven structures of carbon nanofibers (CNFNs) and activated carbon nanofiber (ACNFNs). During activation, the fiber size distribution shifts to lower values and the average fiber diameter decreases. This is consistent with previous work [31,36,38] and is related to the weight loss during activation. Steam reacts with the carbon atoms and causes several gases evolving from these reactions and the creation of small spaces and nanometer-sized pores in the carbon [32].

Fig. 4.2 - SEM images (magnification 5,000 X) and the derived fiber diameter distributions of PAN-based nanofibers ($N=50$) (a) CNFN and (b) ACNFN

Fig. 4.3 depicts typical N_2 adsorption/desorption isotherms for the carbon-based adsorbents. The CNFN sample shows a graduate increase in N_2 adsorption as the relative pressure (P/P_0) increases. This is referred to as type II adsorption according to the IUPAC classification [38]. Most of the nitrogen adsorption on GAC occurs at low relative pressure ($P/P_0 < 0.1$), and a long plateau appears at higher relative pressures. This is referred to as Type I sorption and is characteristic for microporous materials (pore size < 2 nm). The adsorption isotherm of ACNFN shows high N_2 adsorption at $P/P_0 < 0.1$ and a continuous increase of N_2 adsorption over the region of $0.1 < P/P_0 < 0.9$, suggesting the presence of both microporous and mesoporous in the ACNFN which is consistent with previous work [36].

The specific surface area and the contact angle of each used adsorbent are presented in Table 4.1. The high contact angle of the CNFN indicates a high surface hydrophobicity. After steam activation, the ACNFN surface exhibits a lower hydrophobicity. This is attributed to the

increased oxygen content of the material; oxidation of the carbon by the steam results in acidic surface groups [35,36]. As compared to the GAC the hydrophobicity of both the CNFN and ACNFN is high. This is due to the differences in the surface hierarchical structures [34].

Fig. 4.3 - Nitrogen adsorption isotherms of ACNFN, GAC, and CNFN from BET analysis.

Table 4.1 - Adsorbents properties (specific surface area and contact angle)

Material type	BET (m ² /g)	Contact angle (ϕ)
CNFN	15 ± 5	135 ± 5
ACNFN	520 ± 20	120 ± 5
GAC	260 ± 10	25 ± 3

4.3.2. Emulsion stability

Emulsion stability refers to the ability of an emulsion to resist changes in its properties over time. The oil droplet size is one of the most important parameters to evaluate emulsion stability [39]. For a more stable emulsion, the droplet size changes slower [40]. A wide droplet size distribution may potentially lead to decreased emulsion stability. The emulsion stability is

highly impacted by the salinity; adding salt to the emulsion decreases the energy barrier between oil droplets, facilitating droplet agglomeration [41].

Fig. 4.4 presents the histograms of the oil droplet size distribution of emulsions (with various NaCl content) over time. The droplet size measurement range depended on the emulsion salinity. The droplet size was measured in the range of (0.005-5, 0.2- 50, and 1-100) μm for the emulsions (0, 1, and 3 M NaCl), respectively. The histograms of the emulsion with no salt content (0 M NaCl, Fig. 4.4 top left) confirms the successful preparation of an emulsion without the use of an emulsifier. The average droplet size is less than 6 μm and remains below this value for more than 6 h (Fig. 4.4 , left top to bottom). This indicates that the oil in water emulsions produced in our experiments can really be classified as emulsions.

The oil droplet size is affected by the salt content of the emulsion. The presence of the salt ions lowers the electrostatic repulsive forces between droplets, facilitating their aggregation [41,42]. An increase concentration of NaCl to 1 M results in a larger average droplet size, and in a wider droplet size distribution (Fig. 4.4, top middle). The reduced stability of the emulsion is manifested by a shift of the droplet size distribution in time, to larger values (Fig. 4.4, top-bottom middle). These observations are in a good agreement with previous work [43]. A further increase in concentration, to 3 M NaCl, results in a further increase in the average droplet size, and a change in the shape of the distribution: relatively larger droplets are formed at the higher salt concentration (Fig. 4.4, top right). The higher salt concentration also substantially further reduces the stability of the emulsion: the changes in the droplet size distribution in time become more apparent (Fig. 4.4, top-bottom right). For all salt concentrations, the kinetics of emulsion destabilization are sufficiently slow to neglect their effects on the time-scale of the batch adsorption tests.

Fig. 4.4 - Evolution of the droplet size distributions and average droplet size of emulsions (500 mg/L oil) with 0, 1, and 3 M NaCl, at 25 °C.

4.3.3. Adsorption dynamic study

Fig. 4.5 shows the emulsion solution before and after the batch test. It is obvious from the clearance of the solution that almost all the emulsified oil was removed by the entire nonwoven pieces which were not broken down during the mixing.

Fig. 4.5 - Batch experiment images (a) adsorbent material and emulsion before the batch experiment (oil concentration was 500 mg/L), and (b) adsorbent material and solution after the batch experiment (oil concentration was 5 mg/L oil).

4.3.4. Effect of initial oil concentration

Fig. 4.6 a shows the removal of emulsified oil by ACNFN as a function of time, at 25 °C, for different initial oil concentrations. For the various initial oil concentrations, the plots show increasing oil adsorption over time. For short times, the change of the normalized concentration in time is similar for the three oil concentrations. This would imply that the kinetics of the process are roughly first order in the oil concentration ($\ln(C/C_0) \sim (-k.t)$, with k the overall rate constant). Indeed, for all three emulsions the $\ln(C/C_0)$ versus $\sim (-k.t)$ (Fig. 4.6 b) gives a straight line with slope $k = (1.5 \pm 1) \cdot 10^{-4} \text{ s}^{-1}$. For low concentration, this linear relation persists for up to 4 hours. For the highest initial concentration of 1000 mg/L, a deviation of the linear trend is observed, which is attributed to saturation of the adsorbent material, and a more pronounced shift to larger droplet sizes for the more concentrated oil in water emulsions (Fig. 4.7). First order kinetics of sorption processes have been observed frequently by others, see e.g., [19, 44]. In our study, the reason can be external mass transport resistance, from the liquid bulk towards the surface (of the individual fibers) in the ACNFN, even at the high stirring speed that was applied.

Fig. 4.6 - The effects of the initial oil concentration on (a) oil removal percentage, and (b) the kinetics of the adsorption process. All experiments were done at 25 °C, the mixing rate was 300 rpm, the ACNFN dose was 100 mg, and the emulsion volume was 250 mL.

Fig. 4.7 - Oil drop size distribution and average droplets size for different oil concentration emulsions after 1 h of preparation, at 25 °C.

4.3.5. Effect of stirrer speed

Fig. 4.8 (a-c) depicts the effect of the stirring speed on the oil removal rate. Clearly, the rate of oil removal increases with increasing stirrer speed. The same behavior was noticed by [18] for oil adsorption using meshed corncobs. It confirms that the external mass transport resistance has a pronounced effect on the kinetics of the adsorption process. An increase in the stirrer speed corresponds to an increase in the Reynolds number, which is well-known to result in an increase in the Sherwood number and hence in the mass transfer coefficient. In the batch set-up used in this study, the stirrer speed could not be increased further, implying that the kinetics of oil removal are dictated by the process conditions rather than by the inherent kinetics of the sorption of oil into the nano-sized pores of the ACNFN.

Fig. 4.8 - The effect of the rotating speed on the adsorption process (a) oil removal percentage, (b) the kinetics of the adsorption process, and (c) effect of the rotating speed on mass transfer coefficient. All experiments were done at 25 °C, the initial oil concentration was 500 mg/L, the ACNFN dose was 100 mg, and the solution volume 250 mL.

4.3.6. Effect of solution salinity

The effects of salt content on the oil removal rate are presented in Fig. 4.9. Despite the fact that the oil removal rate is dominated by external mass transport limitations, a pronounced effect of the presence of salt on the removal rate is observed. In the presence of salt much higher removal rates are observed. This might be explained by the destabilizing effect that the salt has on the oil solutions (Fig. 4.3). Adding salt to the emulsion results in a shift of the oil droplet size distribution to larger values. The ultimate result is that in the presence of salt oil droplets aggregated and that these become adsorbed on the outer surface of the fibers in the ACNFN (Fig. 4.10), rather than only inside the nano-sized pores. This additional adsorption process drastically increases the oil removal rate.

Fig. 4.9 - The effects of NaCl concentration on the oil removal process. All experiments were done at 25 °C, initial oil concentration was 500 mg/L, the stirrer speed was 300 rpm, the ACNFN dose was 100 mg, and solution volume was 250 mL.

Fig. 4.10 - SEM images of ACNFN after an oil adsorption batch experiment at different NaCl concentration (a) 0 M, (b) 1 M, and (c) 3 M. All experiments were done at 25 °C. Initial oil concentration was 500 mg/L, the stirrer speed was 300 rpm, the ACNFN dose was 100 mg, and solution volume was 250 mL.

4.3.7. Effect of adsorbent type

Fig. 4.11 represents the oil removal efficiency of an ACNFN compared with a CNFN and GAC. The adsorbents show different oil removal rates and capacities. The GAC displays a low rate of oil removal, in spite of its relatively high surface area. This behavior has been associated with the hydrophilicity of the pore surface of the GAC, which would favor the formation of "water clusters" that block some of the pores [45]. The rate of oil uptake of the CNFN and GAC are similar for the first ~4 hours. After this, the rate of oil removal appears to increase for the CNFN. This is attributed to the more hydrophobic surface characteristics of the CNFN, which implies a higher affinity of oil for this surface and prevents the formation of water

clusters. For the ACNFN, the kinetics are limited by external mass transport resistances. Consequently, the oil removal rate is first order in the oil concentration (*vide supra*), and much faster than observed for the other adsorbents, with the ACNFN, ~50% of the emulsified oil was removed within 2 h.

Fig. 4.11 - Effect of adsorbent type on the adsorption effectivity. All experiments were done at 25 °C, mixing rate was 300 rpm, initial oil concentration was 500 mg/L ACNFN dose was 100 mg, and solution volume was 250 mL.

4.4. Conclusion

In this work, we have demonstrated that PAN-based electrospun ACNFN can be used for emulsified oil adsorption from oily wastewater. The ACNFN has unique surface properties and exhibits a high rate of, and capacity for, oil removal. It has a high specific surface area, mesoporous structure, and high hydrophobicity. In batch experiments, the initial oil removal rate is roughly first order, and strongly dependent on the stirrer speed. This implies that the inherent oil sorption kinetics of the ACNFN are fast compared to the external mass transport resistances. Adding salt to the oil solution further increased the oil removal rate, due to the destabilizing effect that the salt has on the oil emulsion stability. The result is an additional adsorption of (aggregated) oil droplets on the outside of the fibers in the ACNFN, in addition to the uptake of oil in the nano-sized pores of the fibers.

The results imply that the ACNFN allows for much faster removal of larger amounts of oil from oil-water emulsions, as compared to other (commercially available) forms of activated carbon.

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Chapter 5

Nonwoven Activated Carbon Nanofiber Sorbent in a Fixed Bed for Emulsified Oil Removal

Abstract

The operating conditions for the removal of emulsified oil from water were investigated using an activated carbon nanofiber nonwoven (ACNFN) sorbent mat in a flow-through system. ACNFN is fabricated from the carbonization and activation of a polyacrylonitrile electrospun nonwoven precursor. The material was tested in a dead-end normal flow system with different flow rates and thicknesses. Characteristic breakthrough behavior was observed with subsequent clogging. Removal efficiency increased with contact time and thickness. The activation itself, which creates high surface area through mesoporosity, was shown to play a role in smaller droplet removal.

5.1. Introduction

A large amount of emulsified oil can be present in wastewater generated from manufacturing industries. These include food processing [1], metal finishing [2], petroleum production [3], petrochemical, and metallurgical industries [4]. The direct discharge of oil in water emulsions into the environment can result in environmental problems, due to the limited biodegradability of oil [5,6]. Removal of oil is complicated by the propensity of oil to foul most membranes or filter media [7]. Other oil removal approaches, such as flotation, centrifuges, chemical coagulation, and magnetic separations are ineffective for separating emulsified oil, especially for emulsions with oil droplets below 1 μm in size [8–11].

Microfiltration and ultrafiltration membranes can efficiently remove emulsified oil from oil-water mixtures. Flux and rejection rates, however, can decrease rapidly in time due to pore clogging and fouling [11–15]. Many approaches have been used to improve the antifouling performance of membranes [16–18]. Membranes should also be highly porous, with suitable pore size distributions to ensure high water flux and good rejection of the emulsified oil droplets.

Adsorption is another option for the removal of emulsified oil. Several adsorbents in packed beds have been extensively studied, such as polymeric resin beads [10], organoclay [19], activated carbon [8] and hydrophobic silica aerogel [9]. Granulated activated carbon (GAC) is a widely used commercial adsorbent for removing oil and other organics from water, because of its porous structure that provides large internal surfaces for adsorbing molecules. The large particle size of the GAC has been linked to slow adsorption kinetics and limited capacity [9,20,21]. Large diffusion distances from the particle surface may render large portions of the internal surface area of the GAC unusable.

An ideal adsorbent material would have an easily accessible surface area. This can be achieved by lessening the distance a sorbate must diffuse before attachment. While this is made possible by making the GAC particle smaller (or using powdered activated carbon, PAC), smaller particles lead to high-pressure drops in packed beds. A material that has the high surface area of PAC with the low-pressure drop of GAC would perform better than either material alone.

Activated carbon nanofiber nonwoven (ACNFN) mats have the benefit of small feature sizes (submicron fiber diameters) combined with low hydraulic resistance. Fabricated through the thermal treatment [22,23] of an electrospun polyacrylonitrile precursor [24], ACNFN exhibits surface areas that match PAC, yet have the permeability of GAC. They are available in nonwoven structures that enable their use in applications that require integrated or flexible sorbents. They have been considered for gas adsorption for removal of toxins [9], volatile organic components [25], and gaseous formaldehyde [26]. For this work, the use of these materials for the removal of emulsified oil is examined.

5.2. Materials and Methods

5.2.1. Fabrication of ACNFN

Polyacrylonitrile (PAN) from Scientific Polymer Products Inc. (Average molecular weight. 150,000 g/mol) and dimethylformamide (DMF) from Acros Organics were used to prepare 14 wt. % PAN in DMF solution with mechanical stirring at 60 °C for 2 h [23]. A precursor nonwoven mat was fabricated by dispensing the charged polymer solution using a high-pressure syringe pump (KD Scientific) at a constant rate of 1 mL/h onto a grounded collector drum rotating at 70 rpm. The applied voltage was 22-24 kV, and the distance from the tip to the collector was 18 cm.

Electrospun precursor nanofibers were converted to carbon nanofibers by sequential thermal treatments. The nanofibers were stabilized at 280 °C for 1 h in a muffle furnace (Carbolite) in an air atmosphere. The stabilized nanofiber mat was carbonized by heating at 600 °C for 2 h in a tube furnace (Lindberg Blue M, Thermo Scientific) in an inert nitrogen atmosphere. The ramp rate for carbonization was 3 °C/min. The CNFN nanofibers were then activated in the same furnace by steam in an inert nitrogen atmosphere at 750 °C for 1 h at a steam flow rate of 60 g/h. The ramp rate for activation was 5 °C/min. The ACNFN adsorbent was the material produced after activation.

5.2.2. Preparation of the oil in water emulsion

Petroleum oil (18% aromatics, boiling point 180-220 °C) was purchased from Sigma-Aldrich for preparing the oil in water emulsions. The oil-water emulsion was synthesized by mixing 250 mg of petroleum oil with 500 mL of distilled water and emulsifying by shear forces using a high-speed blender (Waring Two-Speed Blender) at 24,000 rpm for 10 min at room temperature. After 1 h of preparation, the emulsion was continuously mixed using an agitating tank at a stirring speed of 500 rpm to avoid the destabilization of the oil droplets throughout the experiment.

5.2.3. Nonwoven characterization

The surface morphology of the fabricated nonwoven mat was examined by field emission scanning electron microscopy (SEM, JEOL 6335F). SEM images were obtained for the various fabricated nonwoven mats before and after their use in oil-removal experiments. Average fiber diameter and fiber size distribution of fifty individual fiber sizes were measured using Image J software (National Institutes of Health, USA). The specific surface area and pore size distribution of the nonwoven mats were measured by a physisorption analyzer (Micromeritics Instrument Corporation).

5.2.4. Oil in water emulsion characterization

Mean droplet diameters and droplet-size distributions of the prepared emulsion was evaluated by laser-light scattering using a submicron particle size analyzer (NICOMP, Santa Barbara, USA). The measurement was assessed during the experiments over time to ensure that the oil droplet sizes were consistent throughout the experiment. The droplet size was measured in the range of 0.005-5 μm . The total measurement time of each sample was 10 min.

Oil concentrations in the solution were measured using a UV/Vis spectrophotometer (Genesys 10S, Thermo Scientific) at a wavelength of 260 nm. The viscosity and refractive index of the samples were measured at 25 °C using an LVDV-I Prime Cone/Plate viscometer (Brookfield) and an Abbe refractometer (Bausch and Lomb), respectively.

5.2.5. Experimental setup

A schematic diagram of the experimental setup used to remove emulsified oil from water by the fabricated nonwoven mat is shown in Fig. 5.1. The setup consisted of a separation module, syringe pump, pressure gauge and a UV detector connected to a computer. The separation module included two conical pieces designed to hold the nonwoven mat layers in the system. The two pieces of the module were manufactured from the acrylic acid resin using a Form 1+ stereolithographic 3D printer (Formlabs, Somerville, USA).

The nonwoven mats were cut into 3.8 cm discs to fit the designed holder. The effective area of the nonwoven mat was 7 cm². The syringe pump (KD Scientific) was used to feed the oil in water emulsion into the system. The outlet from the adsorption set up was sent to a UV detector (Model Gynese 10S UV/Vis) to detect the variation of oil concentration over time.

Fig. 5.1 - Schematic diagram of the flow system.

5.3. Results and Discussion

5.3.1. Nonwovens characterization

The surface morphologies and corresponding fiber size distributions of the PAN-based nonwoven precursor, CNFN, and ACNFN mats are shown in Fig. 5.2 (a-c), respectively. The average fiber size is decreasing during carbonization and activation due to the weight loss and shrinkage.

The precursor nanofibers in the nonwoven structure are bead-free and straight with diameters in the range of 430-700 nm (Fig. 5.2 a). The carbonization to the CNFN is accompanied by a significant reduction in fiber size (Fig. 5.2 b). The fibers shrink as small molecules (e.g. H_2O , N_2 , and HCN) evolve from the polymer during carbon cyclization reactions [22,23]. In the additional steam activation step, a further reduction in fiber size occurs. In this step, steam reacts with the carbon releasing CO and H_2 and creating many defects on the surface [27]. The fiber size of the final ACNFN is distributed over a narrow range, with an average size of 250 nm (Fig. 5.2 c).

Table 5.1 presents the contact angle and the specific surface area of the nonwoven mats at various stages in their fabrication. The PAN-based precursor mat has a hydrophilic surface and small specific surface area. The surface of the CNFN mat becomes hydrophobic during carbonization due to the increase in carbon content, and the specific surface area increases

slightly due to the release of gasses and the loss of non-carbon elements. Steam activation induces small open pores in the fiber structure, which increases the specific surface area. Steam activation also causes hydroxyl groups to form on the surface which increases hydrophilicity [24].

Fig. 5.2 - The SEM images and fiber size distributions of 14 wt. % PAN-based nonwoven: (a) electrospun precursor, (b) CNFN, and (c) ACNFN. ($N=50$).

Table 5.1 - Specific surface areas and contact angles of the tested nonwoven

Nonwoven type	Specific surface area (m^2/g)	Contact angle ($^\circ$)
Precursor	7 ± 2	80 ± 5
CNFN	15 ± 5	135 ± 2
ACNFN	520 ± 20	120 ± 3

5.3.2. Emulsion characterization

Fig. 5.3 shows the droplet size distribution of the o/w emulsion, as analyzed by particle size analysis (NICOMP, Santa Barbara, California, USA). This figure shows a typical histogram of the oil droplet size distribution of the oil in water emulsion. The histogram divides the particle counts into discrete size ranges along the horizontal axis. The height of each vertical bar corresponds to the volume percentage of oil droplets in each range. The oil droplets size is distributed in the size range of 0.005-2 μm , with an average diameter of 380 nm.

Fig. 5.3 - Oil droplet size distribution of feed oil in water emulsion.

5.3.3. Oil removal performance

5.3.3.1. Effect of the nonwoven mat material

Fig. 5.4 a shows the removal of emulsified oil as a function of time using eight layers of the PAN-based precursor, CNFN, and ACNFN nonwoven mats in a flow-through system using an influent emulsion flow rate of 400 mL/h. The corresponding pressure drop in the system is shown in Fig. 5.4 b. Table 5.2 shows SEM images of both sides of the first layer of the mats used for oil removal.

The PAN-based precursor nonwoven mat decreases the concentration of the permeate oil to half of that in the feed stream, which continued to decrease during the experiment. The corresponding pressure drop in the system increases over time (Fig. 5.4 b), suggesting fouling, which is verified by the clogging the feed side of the nonwovens as shown in Table 5.2. This

phenomenon may have been exacerbated by the coalescence of oil droplets at the surface of the nonwoven mat.

The CNFN behaves differently. The concentration of the permeate oil is initially quite low, then increases over 15 min, and then decreases again. This characteristic breakthrough curve suggests an adsorption of oil and then breakthrough, but then coalescence of oil and clogging. The same behavior is seen for the ACNFN, which exhibits even better oil removal and retarded breakthrough.

The behavior can be explained based on the oil removal mechanisms. The precursor simply removes the oil by coalescence and surface screening. This means that as oil droplets coalesce, they grow in size and the nonwoven screens them at the feed surface. As the PAN fibers clog, the effective pore size of the nonwoven decreases and the fiber becomes more size selective. This is a type of filter ripening effect and is indicated by the increased pressure drop across the fiber mat during the test (Fig. 5.4 b). The same effect would happen with the CNFN and ACNFN, but the relative hydrophobicity of those materials allow for wicking of the oil into the fiber matrix. This wicking produces the breakthrough effect noted in the first hour of the test for both materials. Eventually, the fiber is filled with oil and begins to clog, causing the oil removal mechanism to shift from adsorption to size exclusion as the effective pore size of the mat drops. This behavior is enhanced by the ACNFN nano-porosity, which allows for the adsorption of oil into the individual fibers. The increase in capacity for oil adsorption enables a longer breakthrough time prior to clogging and pore size shrinkage of the nonwoven mat. The lower propensity to clog for both CNFN and ACNFN is also demonstrated in the lower pressure drop across the mat for both materials (Fig. 5.4 b). Table 5.2 suggests that even for these materials, most of the clogging occurs in the upper layers of the nonwoven.

Fig. 5.4 - (a) Oil removal performance of the various nonwoven mat materials used in this study, (b) Corresponding pressure drop in the system for the various nonwoven. Feed flow oil concentration was 500 mg/L, Feed flow rate was 400 mL/h and eight nonwoven layers were used.

Table 5.2 - SEM images of the various nonwoven mat materials after their use in the flow-through system for oil removal at room temperature (25 °C). Feed flow oil concentration was 500 mg/L, feed flow rate was 400 mL/h and eight nonwoven layers were used.

	Feed side	Permeate side
Precursor	SEM image showing the feed side of the Precursor nonwoven mat. The surface is relatively smooth with some small, irregular features. A 1 μm scale bar is visible in the bottom left corner.	SEM image showing the permeate side of the Precursor nonwoven mat. The surface is composed of a dense network of intersecting fibers. A 1 μm scale bar is visible in the bottom left corner.
CNFN	SEM image showing the feed side of the CNFN nonwoven mat. The surface is highly porous and irregular, with many small voids and protrusions. A 1 μm scale bar is visible in the bottom left corner.	SEM image showing the permeate side of the CNFN nonwoven mat. The surface is highly porous and irregular, with many small voids and protrusions. A 1 μm scale bar is visible in the bottom left corner.
ACNFN	SEM image showing the feed side of the ACNFN nonwoven mat. The surface is highly porous and irregular, with many small voids and protrusions. A 1 μm scale bar is visible in the bottom left corner.	SEM image showing the permeate side of the ACNFN nonwoven mat. The surface is highly porous and irregular, with many small voids and protrusions. A 1 μm scale bar is visible in the bottom left corner.

5.3.3.2. Effect of number of nonwoven mat layers

The effect of the number of the nonwoven precursors, CNFN and ACNFN mat layers on the efficiency of oil removal is shown in Fig. 5.5 a-c, respectively. Using fewer layers of the precursor nonwoven mat had no obvious effect on the oil concentration in the effluent. This is due to the fact that oil drops were trapped by the nonwoven structure of the surface of the mat so they were removed by size exclusion on the top of the first layer at the inlet of the adsorption bed, so subsequent layers played a little role in the oil removal process. The number of nonwoven layers of the CNFN and ACNFN mats, however, has a clear effect on the amount of oil in the permeate stream. Since adsorption mechanisms were in part responsible for oil removal, thicker nonwoven mats provided more material for adsorption and longer residence times to adsorb. Activation of the carbon had a modest effect on the permeate quality as more surface area provided more adsorption area for oil removal.

Fig. 5.5 - Effect of layer number on oil removal using (a) precursor, (b) CNFN and (c) ACNFN nonwoven. Feed oil concentration was 500 mg/L, and feed flow rate was 400 mL/h.

5.3.3.3. Effect of feed flow rate

The effect of the feed flow rate on the removal of emulsified oil droplets using eight layers of ACNFN nonwoven at an inlet oil concentration of 500 mg/L and various feed flow rates (50, 100 and 400 mL/h) is shown in Fig. 5.6. The ACNFN mats removed emulsified oil droplets by the exclusion mechanism of oil droplets on the top surface of the nonwoven mat combined with the removal of the smaller oil droplets by adsorption on and in the fibers. Over the experiment time, the permeate oil concentration increased due to the saturation of the adsorption sites on and in the fibers. Also, the accumulated (captured) oil droplets created a distinct oil layer on the surface of the ACNFN mat (and hence the open spaces between the fibers are getting smaller) resulting into excluding more oil droplets and decreasing the permeate oil concentration over time of the remainder of the experiment. Decreasing the feed flow rate had a substantial effect on the concentration of permeate oil in water concentration and on the time required to reach the maximum oil in water concentration in the outlet water stream (Fig. 5.6 a). The contact time between the oil droplets and the adsorption sites increased by decreasing the feed flow rate, leading to an increase in oil removal by adsorption.

The slope of the breakthrough curve increased with feed flow rate. The curve when using a feed flow rate of 400 mL/h reached the maximum oil in water concentration in the outlet water stream faster than when using 100 or 50 mL/h feed flow rate. The residence time of the emulsified oil droplets in the nanofiber mat was too short for occupying all the adsorption sites leading to an earlier peak of outlet oil in water concentration and faster accumulation of the oil droplets on the top surface of the ACNFN for the high flow rate.

The variation in the concentration of the effluent as a function of the treated volume of oil in water emulsion is shown in Fig. 5.6 b. Treating the same volume of oil in water emulsion at a higher flow rate increased the oil concentration in the outlet due to a decrease in adsorption

on the nonwoven material. Decreasing the feed flow rate, however, increased the time for adsorption and enhanced oil removal.

Fig. 5.6 - Effect of feed flow rate on oil removal breakthrough at room temperature using eight layers of ACNFN, and feed oil concentration was 500 mg/L.

5.4. Conclusions

Activated carbon nanofibers nonwoven with a large surface area and hydrophobicity were fabricated by electrospinning followed by thermal treatments. The combination of a large surface area and high hydrophobicity make ACNFN nonwoven mat good candidates for removing emulsified oil from water. Using ACNFN mats in a flow system removed oil from water by two mechanisms, adsorption on and in the fibers itself and size exclusion by the open

spaces between the fibers. After the adsorption sites were saturated, oil droplets were excluded on the top surface of the ACNFN mats, which decreased the oil concentration in the permeate flow. The longer this mechanism (size exclusion mechanism) takes place the smaller the open spaces between the fibers become and the smaller droplets that will be excluded (trapped). The efficiency of removal increased by decreasing the feed flow rate due to an increase in residence time, allowing the oil drops to reach more adsorption sites. Increasing the number of layers of ACNFN mats also increased the efficiency of oil removal by increasing the amount of adsorbent material and therefore increasing the number of adsorption sites and the area of the hydrophobic surface.

5.5. References

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Chapter 6

Novel Testing Method for Fiber Based
Sorbents: Cross-Sectional Flow Cell for High
Residence Time Sorption

Abstract

The flow through performance of electrospun activated carbon nanofiber nonwoven (ACNFN) mats in oily water emulsion treatment was tested using a new testing method. The ACNFN sorbent was fabricated as a thin sheet and was placed in a measurement cell that allows the emulsion to enter through the cross-sectional area of the ACNFN mats. Crossflow column experiments were conducted at different flow rates and a number of ACNFN mat layers. The emulsified oil removal efficiency declined with decreasing contact time and number of ACNFN mat layers. The regeneration of the saturated ACNFN mats using an organic solvent has been investigated in a batch mode. The results demonstrate good regenerability with no significant change in the oil adsorption capability for three adsorption/regeneration cycles. The ACNFN mats showed an ability to efficiently remove emulsified oil from water in a continuous process using a cross-flow cell design.

6.1. Introduction

One of the most challenging environmental concerns is emulsified oily wastewater. This waste water is generated in large amounts from various process industries such as metallurgical, transportation, and petroleum industry [1–3]. Discharging such waste water can cause serious ecological and environmental concerns due to the low biodegradability of the emulsified oil [4,5]. In addition, the existence of oil droplets in the water can cause various operational issues in the water treatment equipment [6]. Moreover, the conventional treatment technologies such as skimming, centrifugation, coagulation, and flotation are not sufficient for the removal emulsified oil, especially when dealing with nanoemulsions [7–10].

Membranes have been successfully applied for the separation of emulsions [11]. Generally, the membranes are made of organic (polymeric) or inorganic (ceramic) materials. Membranes generally require limited chemical cleaning, have a small plot space and are energy efficient [12]. However, the most serious drawbacks of membrane technology are low flux and fouling issues due to pore plugging by oil droplets [12–15].

Adsorption is regarded as one of the interesting methods for water treatment [16]. Extensive research has been carried out on oil and organic pollutant adsorption from aqueous solutions in packed bed filters using various adsorbent materials including polymeric resin [2,9], sawdust [17], hydrophobic aerogel [8], and activated carbon [18]. In addition to the pore structure and surface chemistry, the adsorption capacity of carbon materials depends on the accessibility of the pollutant molecules to the inner surface of the adsorbent [19]. The widely used adsorbent in water treatment is activated carbon due to its porosity and large internal surface area per unit mass which can reach up to 1000 m²/g [20].

Commonly, activated carbon materials are fabricated in two main forms: powdered activated carbon (PAC) and granulated activated carbon (GAC) [20]. The adsorption

performance of PAC is better than GAC because of the easier accessibility of adsorptive surface in the powder form, However, PAC is not favorable to use in fixed bed adsorbers due to the difficulties in handling and regeneration of the powders [21]. At the meantime, GAC has slow adsorption kinetics, low adsorption capacities besides poor selective sorption and an insufficient regeneration ability [16,22]. As a result, high-performance oil-adsorption materials with improved properties are needed [21,23]. The ideal adsorbent material for organics and oil needs to be a hydrophobic material with large surface area, open pore structure and good stability.

Activated carbon is a material that has been considered for oil adsorption [18]. While typically used in the granular form (GAC), new architectures, such as fiber nonwovens, are emerging [24]. Small fiber diameters of these nonwovens are particularly attractive because they offer better accessibility to their surface area while not having the drawbacks of high-pressure drop (as would be encountered with powdered activated carbon). Activated carbon fiber can be prepared by an electrospinning method and subsequent carbonization and activation [25]. Electrospinning is a versatile technique to fabricate very fine nonwoven fibers in the submicron and nanometer range size from polymeric solutions [26,27,24,28]. The predominant polymer used for activated carbon fiber fabrication is polyacrylonitrile (PAN) due to its high carbon yield and thermal stability [27]. Electrospun PAN nanofibers can be converted into a carbon nanofiber through two subsequent thermal treatment steps, stabilization, and carbonization. To develop the high surface area and porous structure, the carbon nanofibers need to be chemically or physically activated using an activating agent [29]. Steam is commonly used to activate the carbon nanofibers, due to its low cost and environmentally friendly characteristics [28].

The resulting activated carbon nanofiber nonwoven (ACNFN) has unique properties such as chemical and thermal stability, interconnected porosity, large macroporosity, and accessible

surface area [19,21,30]. Therefore, it attracted considerable attention in various applications including the adsorption of gaseous pollutants [25,31–33]. The small size of the fibers in ACNFN offers the potential to overcome transport and diffusion limitations leading to a fast adsorption rate and excellent adsorption capacity [29]. However, the disadvantage of electrospun ACNFN is the poor mechanical strength due to the weight loss and shrinkage of the nanofibers during the subsequent heat treatment steps. Therefore, ACNFN has not been used widely in water purification [30]. For water treatment, ACNFN was used in a batch test to adsorb cationic dye [34] and emulsified oil [35]. ACNFN showed a much larger adsorption capacity compared with conventional activated carbon.

In our previous study [36], ACNFN was used in a flow through system for emulsified oil removal from water. Multiple layers of ACNFN were fixed between two plastic pieces and the feed stream moved through the nonwoven nanofibers in a vertical direction. Some of the emulsified oil droplets were adsorbed on the nanofiber surface. After a certain time, the collected oil droplets coalesced creating a distinct layer on the top surface of the first layer of ACNFN. The emulsified oil drops were removed effectively, but the pressure drop over the assembly increased due to clogging of the pores of the ACNFN.

In this work, emulsified oil was adsorbed on ACNFN using a new flow-through system, which allows the feed water to flow within nanofiber assembly and hence offering more accessible surface area. This design decreases the fouling problem and the pressure drop is not increased during the experiment. The effect of feed flow rate, the height of the ACNFN mat, and the number of ACNFN layers was investigated. After reaching saturation, the ACNFN was removed from the cell and rinsed with an organic solvent to remove the oil from the fibers. The regenerated ACNF was used for three times without a clear decline in oil removal efficiency.

6.2. Materials and Methods

6.2.1. Fabrication of ACNFN via electrospinning

Polyacrylonitrile (PAN) from Scientific Polymer Products Inc. (Average molecular weight 150,000 g/mol) and dimethylformamide (DMF) from Acros Organics were used to prepare 14 wt. % PAN in DMF solution by mechanical stirring for 2 h at 60 °C. The non-woven PAN precursor was fabricated via the electrospinning method by dispensing the charged polymer solution at a constant rate of 1 mL/h onto a grounded collector drum rotating at 70 rpm using a high-pressure syringe pump (KD Scientific). The applied voltage was 22- 24 kV and the tip to collector distance was 18 cm. The precursor nanofibers were prepared in relative humidity of 20% at room temperature.

The electrospun nanofiber can be converted to a carbon nanofiber through thermal treatment during stabilization and carbonization steps. In the stabilization step, the nanofiber mat was heated to 280 °C for 1 h in an air atmosphere at a rate of 1 °C/ min using a muffle furnace (Carbolite) in an air atmosphere [30]. For carbonization, the stabilized nanofiber mat was heated to 600 °C for 2 h in a tube furnace (Lindberg Blue M, Thermo Scientific) in an inert nitrogen atmosphere. The ramp rate for carbonization was 3 °C/min. After these steps, the carbonized nanofibers (CNFN) were activated in the same furnace in an inert nitrogen atmosphere at 750 °C for 1 h using a steam flow rate of 60 g/h. The ramp rate for the activation step was 5 °C/min. The produced material after the activation step was called activated carbon nanofiber nonwoven (ACNFN).

6.2.2. Oil emulsion preparation

Petroleum oil (18% aromatics basis, boiling point is 180-220 °C) was purchased from Sigma-Aldrich to prepare the oil in water emulsion. The oil-in-water emulsion was synthesized by mixing 250 mg petroleum oil with 500 mL distilled water. Emulsification occurred due to shear forces using a high-speed blender (Waring Two-Speed Blenders) at 24,000 rpm for 10

min at room temperature. After 1 h of emulsion preparation, the emulsion was mixed at 500 rpm to prevent oil droplets coagulation over time. No emulsifier was added.

6.2.3. Adsorbent characterization

The structure and morphology of the fiber sorbents were characterized by Scanning electron microscopy (SEM) images using field emission scanning electron microscopy (FESEM, JEOL 6335F). SEM images were obtained for the surface and the cross section of ACNFN before and after using them for oil removal experiments. The average fiber diameter and fiber size distribution of fifty individual fiber sizes were measured using Image J software (National Institutes of Health, USA). The specific surface area was determined with a Physisorption Analyzer (Micromeritics Instrument Corporation).

6.2.4. Oil in water emulsion characterization

The oil droplet size is one of the most important parameters to evaluate emulsion stability. The mean droplet diameters and droplets size distribution of the prepared emulsions were evaluated by laser light scattering using a submicron particle sizer (NICOMP, Santa Barbara, California, USA). The droplet size and droplet size distribution were assessed during the experiments over time to ensure that the oil droplet size was constant during the experiment. The droplet size was measured in the range of 0.005- 5 μm . The total droplet size measurement time of each sample was 10 minutes.

Oil concentrations in the feed and outlet streams were measured using UV/Vis spectrophotometry (Thermo Scientific Genesys 10S) at a wavelength of 260 nm. The viscosity and refractive index of the samples were measured at 25 °C using a Brookfield viscometer (LV DV-I Prime Cone/Plate) and a refractometer (Bausch and Lomb Abbe) respectively.

6.2.5. Column experiments

6.2.5.1. Cross-sectional flow cell design

Fig. 6.1 shows a schematic diagram of the novel cell that was designed for maintaining the structural integrity of the used ACNFN as an adsorbent mat for emulsified oil. The adsorption cell was made of two separate pieces of transparent acrylic material (Fig. 6.1). It has two rectangular shaped sections of equal dimensions (12 cm in height, 6 cm in width, and 1 cm thickness), one of the sections has a flow entrance with a width of 3 cm. The outlet point position is in the downstream part of the cell. The ACNFN mat (3 * 6 cm) was placed in the cell. Since the thickness of the ACNFN mat is difficult to keep constant for all the experiments, a thin gasket and Teflon tape were used around the ACNFN mat in the cell to prevent the bypassing and channeling around the nonwoven mat. The ACNFN sheet was fixed between the two parts of the cell and sealed using screws.

Fig. 6.1 - Schematic diagram of adsorption cell for using an ACNFN mat as an adsorbent.

6.2.5.2. Experimental procedure

Column studies were conducted using the down flow system which is shown in the schematic diagram in Fig. 6.2. The ACNF nonwoven mat was cut in a rectangular shape with a width of 4 cm and various lengths (3, 6, and 9 cm) and placed in the cell channel. The emulsion with a concentration of 500 mg/L emulsified oil at pH 7.5 was fed through the cross section of ACNFN mat at constant flow using a syringe pump. Two different influent flow rates were investigated (100 and 400 mL/h). Prior to each experiment, the cell was first equilibrated with pure water until the effluent became clean. Once equilibration was achieved, the water feed was stopped for 10 min after which the emulsion feed was introduced into the cell. The adsorption cell was rinsed with pure water using the same conditions of the experiment (the desired flow rate and ACNFN height) to adjust the pressure drop over the cell and to eliminate any impurities. The pressure drop was fixed for all the experiments at 0.10 bar.

The adsorption unit used in this study consisted of a syringe pump, a pressure gauge, the adsorption cell, and a UV conductor. A syringe pump was used to feed the emulsion in the adsorption bed. Due to the hydrophobicity and the high specific surface area of the outer surface of the activated carbon nanofibers, the microdroplets of oil were captured forming a hydrocarbon film around the nanofibers. Some of the oil droplets agglomerated with each other creating some fouling inside the nonwoven structure.

The oil concentration was measured at the outlet of the cell using the in-line UV/Vis spectrophotometer which was logged to a computer to follow the oil concentration with time. A breakthrough curve was obtained by plotting the permeate oil concentration with time using different emulsion flow rates and bed heights. The effect of emulsion feed flow rate, ACNFN height (packed bed height), and the number of ACNFN layers (adsorbent thickness) was investigated.

Fig. 6.2 - Schematic representation of the flow-through system.

6.2.6. Regeneration

When exhausted, the ACNFN was taken out of the adsorption cell and rinsed with dichloromethane solvent in a batch process at room temperature. The regeneration was carried out by rinsing the saturated ACNFN piece in a pure dichloromethane solvent in a batch mode process. The batch system which was used for doing the regeneration is described in our previous study [35]. It contains a stir bar separator which was used to prevent the ACNFN mat from coming in contact with the stirrer bar which would break up the mat during regeneration. The regeneration process was performed using a stirring rate of 700 rpm for 30 min at room temperature. The ACNFN mat showed a good physical stability during the regeneration process.

6.3. Results and Discussion

6.3.1. Characterizations of ACNFN

The surface morphology, corresponding fiber size distribution, and cross-sectional SEM images of 14 wt. % PAN-based ACNFN are shown in Fig. 6.3. ACNFN was prepared with a good mechanical strength as can be seen in Fig 6.3 a. The cross-sectional morphology of the ACNFN mat (Fig. 6.3 b) showed that the sheet thickness was about 200 μm . The SEM image of the surface in Fig. 6.3 c confirmed that ACNFN mat was composed of continuous and long nanofibers with a nonwoven structure. In this work, the used conditions for ACNFN fabrication are chosen according to our previous study [37] to optimize the mechanical strength, surface

morphology, specific surface area, and the surface hydrophobicity properties of the produced ACNFN. The fiber diameter, specific surface area, and the contact angle are 250 nm, 520 m²/g, and 120°, respectively.

Fig. 6.3 – PAN-based ACNFN images (a) digital image (b) cross section SEM image (c) surface SEM image.

6.3.2. Emulsion characterization

The emulsion solution was prepared by the same preparation procedure that is used in previous work [35]. The droplet size distribution of the oil in water emulsion is shown in Fig. 5.3 as analyzed by particle size analysis (NICOMP, Santa Barbara, California, USA). The average oil droplet size was 380 nm.

6.3.3. ACNFN adsorption performance

6.3.3.1. Effect of flow rate

The results for different feed flow rates are plotted in Fig. 6.4 for an ACNFN bed height of 6 cm and an inlet oil content of 500 mg/L. The used flow rates are 400 and 100 mL/h. Fig 6.4 reveals that, as the flow rate increases from 100 to 400 mL/h, the breakthrough curve becomes steeper and the break-through time decreases rapidly. This is because of the residence time in the column, which is not long enough for the adsorption equilibrium to be reached at high flow rate. Hence, at high flow rate, the oil in water emulsion leaves the column before equilibrium occurs.

The ACNFN performs better at low flow rates. This might be explained by the residence time in the bed. Decreasing the feed flow rate increases the residence time of the oil in water emulsion resulting into more oil droplets adsorbing on the nanofiber surfaces. This entrainment ensures a better use of the filter bed layers.

The use of this design for the adsorption cell helped to decrease the fouling on the ACNFN surface and prevent the increase in pressure drop during the experiment. Fig. 6.5 a shows the SEM image of the flow area structure (ACNFN mat cross section). The emulsion flowed through the cross section of ACNFN mat along the nanofibers direction. As a result, the surface of the nanofibers was fully exposed to the oil in water emulsion. Most of the oil droplets were adsorbed on the adsorption sites along the nanofiber surface of the ACNFN. When the adsorption sites were occupied, the oil droplets started to coalesce, causing an oil layer on top of the nanofibers.

Flowing the oil in water emulsion through the cross section of the ACNFN decreased the role of the nonwoven structure in excluding the oil droplets on the surface of ACNFN layer. As a result, there was no clear fouling on the surface of the ACNFN as can be seen in Fig. 6.5 b

in which the morphologies of the surface area of ACNFN before and after oil removal experiments are compared.

Fig. 6.4 - Effect of feed flow rate on adsorption process. All experiments were performed at 25 °C, one layer of 6 cm height of ACNFN nonwoven, and feed flow oil concentration was 500 mg/L.

(a)

(b)

Fig. 6.5 - SEM images of 14 wt. % PAN based ACNFN before and after oil removal (a) cross section, and (b) surface area

6.3.3.2. ACNFN bed height

To study the influence of bed height on oil removal, the height of ACNFN mat was changed. As shown in Fig. 6.6, an increase in the bed height, which is directly related to bed mass, allows treating a larger volume of the emulsion. The constant pressure drop during the experiment suggests that clogging in the bed is minimal. As the bed height is increased, more adsorption sites are available for oil adsorption and the residence time in the bed is increased.

Fig. 6.6 - Effect of ACNFN height on the adsorption process. All experiments were performed at 25 °C, one layer of ACNFN, the flow rate was 100 mL/h, and feed flow oil concentration of 500 mg/L.

6.3.3.3. Effect of number of ACNFN layers

The number of ACNFN layers represents the ACNFN mat thickness. Fig. 6.7 shows the permeate oil concentration changing over time using 1 and 3 layers of ACNFN. An increasing number of ACNFN layers increased the oil removal efficiency. The significant increase in the oil removal efficiency can be explained by two points. Firstly, increasing the number of ACNFN layers means increasing the amount of the adsorbent and the adsorption sites. Secondly, increasing the number of ACNFN layers means increasing the thickness of the ACNFN mat which means increasing the cross-flow area.

Fig. 6.7 - Effect of ACNFN layers number on adsorption process. All experiments were done at 25 °C, 6 cm height of ACNFN, the flow rate was 100 mL/h, and Inlet oil concentration of 500 mg/L.

6.3.4. Regeneration

In the present study, the regeneration of the ACNFN mat was performed using a pure organic solvent (dichloromethane) in a batch mode experiment. The saturated ACNFN mat was removed from the adsorption cell (continuous mode) and was put in contact with the pure dichloromethane solvent in a glass beaker (batch mode). After 30 minutes of rinsing with dichloromethane, the ACNFN mat was washed with distilled water and again placed in the adsorption cell (in the continuous mode) to be used for emulsified oil adsorption. This process of ACNFN regeneration was repeated three times. Fig. 6.8 compares the oil removal efficiency of the several regeneration steps of the ACNFN referred to as 1, 2, and 3 cycle. Also, this figure includes the removal efficiency of the clean ACNFN nonwoven (referred to as ACNFN) and a reused (saturated by oil) ACNFN mat without doing the regeneration process (referred to as 0 cycle) to ensure that the ACNFN was saturated with oil before starting the regeneration process. It can be inferred from Fig. 6.8 that regeneration of the ACNFN with dichloromethane is sufficient for removing oil for 3 cycles. The efficiency of regeneration might be increased by performing the regeneration step for a longer time and using a faster mixing rate.

Fig. 6.8 - Effect of the number of regeneration cycles on adsorption process. All experiments were done at 25 °C, 6 cm height of ACNFN, the flow rate was 100 mL/h, and feed flow oil concentration of 500 mg/L.

6.4. Conclusion

The cross flow performance characteristics have been investigated for ACNFN sheets in a new design packed bed to remove emulsified oil from oily wastewater. The treatment of the oil in water emulsion with the ACNFN mat in a cross flow design packed bed showed the effect of bed height, the number of ACNFN mat layers, and flow rate on the oil removal efficiency. At a 500 mg/L oil concentration, 6 cm of bed height, 3 layers of ACNFN mat, and a flow rate of 400 mL/h, 90 % oil removal was obtained without an observable increase in pressure drop across the bed. This removal efficiency is quite high. It was found that the ACNFN mat packed bed is very efficient in emulsified oil droplet adsorption. The saturated ACNFN can be regenerated effectively by rinsing with an organic solvent with the aid of mechanical stirring, with no severe loss of sorption properties after re-using three times. The ACNFN mat is promising as a candidate for emulsified oil removal from oily wastewater

6.5. References

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Chapter 7

Reflections & Outlook

7.1. Reflections

7.1.1. Reflections on produced water management

Oil and gas extraction requires huge amounts of water and generates oily wastewater termed as produced water (PW). During drilling and hydraulic fracturing stages, a lot of water is introduced into the formation to increase the permeability; this water has the potential to return to the surface as a flow-back wastewater. During the secondary oil production stage, a massive amount of water needs to be injected into the well as injection water to support the pressure of the reservoir and push the oil towards the surface. This by-product water in combination with the formation water, water naturally present in the formation, is extracted again with the oil producing as produced water (PW).

Generally, PW is generated in huge amounts and the amount is increasing over the production life of the field. PW tends to be chemically very complex, it contains various pollutants in different concentrations. These contaminants include oil, dissolved organics, suspended solids, salts, heavy metals, and even radioactive materials. The quantity and quality of PW vary considerably from well to well depending on factors such as geographic location, geological formation, type of hydrocarbon being produced, production method and age of the oil field. Such a huge volume of poor quality water possesses several issues in the directly discharging into the environment. For both economic and management reasons, there has been increasing interest in turning PW to usable water for beneficial uses, especially in arid or semi-arid areas where water is scarce. If PW is treated properly, it could represent a valuable source of water to overcome the stringent need of fresh water for enhancing oil production (as injection water) or to be consumed for other beneficial uses such as irrigation.

In chapter 2 in this thesis, the production rate of the largest five oilfields in the southern region of Iraq was studied. The estimated volume of the generated PW from the five super-giant oilfields is 2 Mbbl/d in 2020 and is expected to increase to 4.7 Mbbl/d in 2035. This large

volume of PW is heavily contaminated with oil, suspended solids, heavy metals, and salts. It needs proper treatment to meet the water quality standards for the end use such as injection or irrigation. The treated PW could make up 23% (in 2020) to 35% (in 2035) of the required injection water for the largest five oilfields in the south region of Iraq. Another potential application of the treated PW is as irrigation water for salt-tolerant plants such as date palms. By 2035, treated PW could make up 33% of the irrigation water required for date palms in Basrah province.

7.1.2. Reflections on ACNFN fabrication

Among the diverse carbonaceous materials, electrospun activated carbon nanofiber nonwoven (ACNFN) is attracting more attention due to its unique properties such as high surface area, interconnected porosity, and permeability which contribute to increase their potential applications including adsorption. The first step of ACNFN fabrication is spinning a polymeric solution (polyacrylonitrile/dimethylformamide) on a collector to fabricate a thin layer of nonwoven nanofibers mat. The precursor nonwoven needs to be converted to carbon nanofiber media (CNFN) through subsequent thermal treatment steps (stabilization and carbonization). Then, an activation step using an oxidizing agent, such as steam, is required to produce activated carbon nanofiber nonwoven (ACNFN) with developed porosity and high surface area. Several reactions occur during the heat treatment steps resulting in a significant shrinkage and weight loss. Thus, the fabricated ACNFNs have a poor mechanical strength which hinders their use in some applications such as water treatment.

In chapter 3, the effect of polymer concentration, carbonization, and activation conditions on ACNFN properties was presented. The ACNFNs were characterized for surface morphology, specific surface area, and mechanical strength. The results showed the obvious effect of precursor polymer concentration on the fiber size and the mechanical strength of the resulting precursor and carbon nanofibers as well. Also, the pyrolysis temperature has a

substantial effect on the carbon nanofiber strength due to the increased weight loss with increasing the carbonization temperature and time. The activation step is essential to increase the specific surface area of the ACNFN, however, it has a detrimental effect on the mechanical strength. Increasing the steam amount and the activation time raises the specific surface area of the ACNFN considerably without a further clear decrease in the strength.

7.1.3. Reflections on the adsorption process

ACNFNs are attracting more attention in organic pollutants adsorption applications due to their large accessible surface area, porosity, high permeability, and hydrophobicity. In chapter 4, the adsorption efficiency of emulsified oil on a PAN-based ACNFN in a batch test is presented and compared with the efficiency of granular activated carbon (GAC). The results show 95 % removal efficiency of the ACNFN compared with the commercial adsorbent (GAC) which showed a removal efficiency of only 60%. The high efficiency of the ACNFN can be explained by the low diffusion limitations due to the short distance between the pore entrance and the adsorption sites in the pores. In addition, the ACNFN has a high affinity for emulsified oil because of the high hydrophobicity of the nanofibers' surface. The effect of initial oil concentration, agitating rate, and salt content on adsorption efficiency of emulsified oil on ACNFN is investigated. Increasing the initial concentration of oil increased the adsorption capacity due to an increased diffusion driving force. Using a higher mixing rate during the batch test showed an obvious increase in oil removal rate due to the reduction of the external mass transfer resistance. The effect of the emulsion salinity on the oil adsorption efficiency of the ACNFN surface is studied by using different concentrations of NaCl. Increasing the salt content resulted in a clear enhancement in adsorption rate due to the larger size of oil droplets in the high saline emulsion.

In addition to the high adsorption efficiency of emulsified oil on an ACNFN, the ACNFN has an open interconnected structure and accessible surface area making it a good candidate

for operating in a flow-through mode. For the first time, in chapter 5 the use of ACNFN in a fixed bed application was demonstrated. Multi-layers of ACNFN were fixed between two pieces of a holder and the emulsion solution was allowed to flow through the fixed layers in a vertical direction. The results showed efficient removal of emulsified oil by the activated carbon nanofiber. The nonwoven structure of the nanofibers showed to be very important in removing oil drops from the water.

To understand the oil removal mechanism, the oil removal efficiency of the ACNFN is compared with that of a carbon nanofiber (CNFN) and precursor nanofiber nonwoven mats by measuring the corresponding pressure drop across the holder. The precursor nanofiber nonwoven membrane removed the oil by size exclusion on the top of the first layer resulting a quick increase in the pressure drop across the precursor membrane. However, Carbon (CNFN) and activated carbon nanofiber nonwoven (ACNFN) showed better oil removal efficiency and a slower increase in the pressure drop due to their hydrophobicity. Using ACNFN sorbent, the oil is removed by a combination of two mechanisms (adsorption and size exclusion) due to the high porosity, the high specific surface area, and the nonwoven structure of ACNFN sorbent media. When the adsorption sites are fully saturated, the oil droplets are excluded on the top surface of ACNFN layer. The impact of the flow rate and the number of sorbent layers were investigated. Decreasing the flow rate allows for longer contact time between oil droplets and the adsorption sites on the surface of nanofibers resulting into enhanced oil removal by adsorption mechanism. Increasing the number of ACNFN layers increases the removal efficiency as a result of increasing the number of the adsorption sites.

Using a novel method for fixing the thin layer of ACNFN adsorbent in a packed bed is explained in chapter 6. The emulsion solution passed through the cross section area along the nanofibers of the ACNFN sorbent. This design allowed to remove most of the oil droplets from water by an adsorption mechanism instead of size exclusion as in the previously used design

resulting into no clear fouling and without increasing the pressure drop across the adsorption cell. Using three layers of 6 cm of ACNFN height, and a flow rate of 100 mL/h of 500 mg/L emulsified oil solution, resulted in 90 % oil removal without increasing the pressure drop. The saturated ACNFN can be regenerated effectively by rinsing with an organic solvent using mechanical stirring, with no severe loss of sorption properties after re-using three times.

7.1.4. Reflections on produced water treatment

Oily wastewater including produced water contains a large amount of oil in different forms: free oil, dispersed oil, and emulsified oil. The conventional treatment methods such as skimming, flotation, coagulation, and gravity separation can effectively remove free and dispersed oil. The emulsified oil is the most difficult to be removed due to the small oil droplet size. The adsorption method is an effective method to treat emulsions. This study (in chapter 3) evaluated the effectiveness of ACNFN for the removal of emulsified oil from brine and oily wastewater. The ACNFN showed good removal efficiency up to 95% while the commercial granular activated carbon (GAC) removed 60% of the emulsified oil from water. The good adsorption performance of ACNFN was due to the high accessible surface area and the high hydrophobicity of the surface of the nanofibers. Increasing the salt content of the emulsion, by adding 3 M of NaCl, resulted in an even higher adsorption rate of emulsified oil on the ACNFN.

The performance of removing emulsified oil droplets from oily wastewater on ACNFN was also studied in a flow-through system in two different designs (normal flow through design and cross-sectional flow design). In the normal flow through design, oil droplets were adsorbed on the adsorption sites of the nanofibers of the ACNFN due to the high specific surface area. Due to the nonwoven structure of the nanofibers in the ACNFN, some of the oil droplets were excluded on the top of the ACNFN adsorbent layer making a distinct fouling layer. Although the ACNFN adsorbent showed to be efficient in the treatment of emulsions, the pressure drop across the ACNFN mat was increased significantly due to clogging and fouling issues. The

cross-sectional flow design allowed the emulsion solution to pass through the cross-section of the ACNFN in a novel method for adsorption. Emulsified oil was removed by 90% efficiency using three layers of ACNFN with 6 cm height without increasing the pressure drop across the bed. By comparing the adsorption capacity and efficiency in both flow design modes of the fixed bed, it appears that the use of a cross-sectional flow to remove oil from water may give better capacity and efficiency than using the normal flow through mode.

7.2. Outlook

In this thesis, the production rates from five supergiant oilfields in the southern part of Iraq were studied to estimate the production profile of these oilfields. Because of the little available information on the Iraqi's oil fields, the estimations were built on studying the production profile of other oilfields in the North Ain Dar Saudi oilfield and the North East Atlantic oilfields. Analyzing the actual quantities and qualities of the produced water from these oilfields can result in a more accurate prediction of the water consumption and produced water production in the oil production process in Iraq. The accurate estimation of the quantity and quality of the produced water is essential to determine the best option for managing and treating the produced water in a cost effective way.

In this work, we studied emulsified oil removal by adsorption on ACNFN material. The key properties for fabricating ACNFN as an effective adsorbent material for oil removal are the specific surface area, hydrophobicity, and mechanical strength of the material. It was observed that the properties of ACNFN strongly depend on the fabrication and heat treatment conditions such as the polymer concentration, carbonization temperature, and activation protocol. Possible avenues for increasing the strength of the ACNFN could be by blending nanoparticles or copolymers in the precursor polymer. Alternatively, using CO₂ as an oxidizing agent during the activation step might be more efficient than steam to increase the surface area without weakening the strength.

In addition to the high efficiency of emulsified oil adsorption, the surface of ACNFN can be functionalized by chemical methods to incorporate acidic and basic surface functional groups to enhance its selectivity to adsorb other types of pollutants from produced water such as dissolved organics (such as toluene, benzene, and phenol) and heavy metals (such as lead, chromium, and nickel). Characterization of both the equilibrium capacity and sorption kinetics of ACNFN sorbent in real produced water will also be essential to evaluate the potential application of ACNFN for industrial waste water treatment.

In this work, the presented idea of the adsorption testing through the cross section area of a thin layer of adsorbent media like ACNFN can be valuable to have a better removal efficiency using fibrous material without increasing the pressure drop across the adsorption cell. Using different feed solutions with different concentrations will be interesting to study the removal of different types of contaminant on one adsorbent material.

Summary

Summary

The development of novel carbon material, high accessible surface area, interconnected porosity, and stable nanofiber nonwoven media for emulsified oil droplets separation from oily wastewater, in particular for oilfields produced water treatment, is discussed in this thesis.

Chapter 1 provides a general overview of produced water quantity and quality, discussing the source of such a huge amount of polluted oily wastewater. Amongst the different types of pollutants in the produced water, emulsified oil removal is the aim of the work described in this thesis. A literature review is presented for using the advanced treatment technologies such as membrane separation and adsorption technologies to recover emulsified oil droplets from such oily wastewater.

Firstly, the quantity and quality of the generated produced water from five of the largest oilfields in the south of Iraq were studied in chapter 2. Based on the oil production profiles of these oilfields, the generated produced water is estimated to be 2 Mbbl/d in 2020 and 4.7 Mbbl/d in 2035. This type of wastewater is heavily contaminated with different types of pollutants such as oil, suspended solids, heavy metals, and salts. Proper treatment of the produced water can convert this wastewater to a significant alternative water resource for different purposes such as re-injection and irrigation. This study shows that the properly treated produced water in the south of Iraq could be a substantial valuable water resource in a region with increasing water shortages.

An adsorption process using activated carbon is a potential method for oil removal from oily wastewater. The fabrication process of activated carbon nanofiber nonwoven (ACNFN), which is a form of activated carbon, is illustrated in chapter 3. The carbon nanofiber nonwoven (CNFN) fabrication process includes subsequent thermal treatment steps of precursor electrospun nanofiber nonwoven membrane followed by a steam activation step for developing

the porosity of the produced ACNFN. The results show that optimizing the fabrication conditions during the electrospinning, the carbonization, and the steam activation steps are essential to produce ACNFN with enhanced mechanical strength and specific surface area. Furthermore, different characterization methods including SEM, FTIR, BET, and DMA are used to evaluate the surface characterizations and the mechanical properties of ACNFN. The results showed that ACNFN of high surface area (520 m²/g) with good mechanical strength is successfully fabricated via the electrospinning method using the following fabrication conditions: 14 wt. % PAN/DMF precursor, carbonizing at 600 °C for 2 h, and steam activation at 750 °C using 60 mL/h of steam for 1 h.

In chapter 4, the performance of ACNFN in emulsified oil removal is investigated using a batch dynamic adsorption test. It was found that the initial oil concentration, the mixing rate, and the salt concentration in the emulsions affected the oil removal efficiency of the ACNFN. The ACNFNs showed a very high removal efficiency of up to 95%, thereby outperforming (non-activated) carbon nonwoven (CNFN) and a commercial granular activated carbon (GAC), due to its high accessible surface area, porosity, and hydrophobicity.

Chapter 5 describes the use of the ACNFN nonwoven for emulsified oil removal in a flow-through system. A dead-end normal flow system was used to investigate the operating conditions for the removal of emulsified oil from water using nonwoven media. The impact of emulsions flow rate, the nonwoven's thickness, and the nonwoven's type was also studied. The results showed that the oil droplets were removed by size exclusion and adsorption mechanisms. Characteristic breakthrough behavior was observed with subsequent clogging. The high porosity of ACNFN was shown to play a role in the small oil droplets removal. Removal efficiency increased with contact time and thickness. However, the pressure drop over the system was increased due to the excluded oil droplets on the top side of the first layer of the nonwoven.

A novel testing method for fiber based sorbents was illustrated in chapter 6. This design of the flow-through cell allows the emulsion to pass through the cross-sectional area of the thin sheet of ACNFN nonwoven. The emulsified oil removal efficiency declined with decreasing contact time and the number of layers of ACNFN nonwoven. ACNFN nonwoven in a cross-sectional flow cell design showed an efficient ability to remove emulsified oil from water by adsorption in a continuous process without an obvious increase in pressure drop over the system. Furthermore, the regenerability of ACNFN for oil adsorption was studied by washing the saturated ACNFN sheet with an organic solvent. The results showed no significant change in the oil adsorption characteristics for three adsorption/cleaning cycles.

Finally, in Chapter 7, the reflections, results, and conclusions as reported in this thesis are summarized. It was shown that ACNFN sorbent can be used successfully to treat the oily wastewater in a continuous flow system. Some suggestions and ideas in the field of using ACNFN for treating the other type wastewater treatment are provided for future research.

Samenvatting

In dit proefschrift wordt ingegaan op de ontwikkeling van nieuwe koolstofmaterialen met een hoog toegankelijk oppervlak, intern verbonden poriën en een stabiele (nonwoven) structuur van nanovezels voor de scheiding van geëmulgeerde oliedruppels van olieachtig afvalwater met als specifieke toepassing de behandeling van afvalwater afkomstig van olievelden.

Hoofdstuk 1 geeft een algemeen overzicht van de kwantiteit, kwaliteit en de bron van het geproduceerde en met olie vervuilde afvalwater. Van de verschillende verontreinigingen die in het geproduceerde afvalwater voorkomen, richt dit proefschrift zich op het verwijderen van de geëmulgeerde olie. In dit hoofdstuk wordt een literatuuroverzicht gepresenteerd over het gebruik van geavanceerde technologieën, zoals membraanscheiding en adsorptietechnieken, die gebruikt kunnen worden om geëmulgeerde olie van het afvalwater te scheiden.

In hoofdstuk 2 wordt de kwantiteit en kwaliteit van het geproduceerde afvalwater van de vijf grootste olievelden in zuid-Irak onderzocht. Gebaseerd op de olieproductieprofielen van deze olievelden, wordt er naar schatting in 2020 2 Mbbl/d en in 2035 4.7 Mbbl/d afvalwater geproduceerd. Dit afvalwater is zwaar vervuild met verontreinigingen zoals olie, zwevende deeltjes, zware metalen en zouten. Een juiste behandeling van het geproduceerde water kan het afvalwater omzetten in water dat geschikt is als een alternatieve waterbron voor bijvoorbeeld herinjectie ten behoeve van de oliewinning en irrigatie. Deze studie laat zien dat, als het geproduceerd afvalwater goed wordt behandeld, het een belangrijke waterbron kan zijn in zuid-Irak, een regio waar het watertekort steeds meer toeneemt.

Adsorptie aan actieve kool is een potentiële methode om olie uit olieachtig afvalwater te verwijderen. In hoofdstuk 3, wordt het fabricageproces van een actieve kool gemaakt van nonwoven nanovezels (ACNFN) beschreven. Het fabricageproces van niet-geactiveerde koolstof nanovezels (CNFN) omvat opeenvolgende warmtebehandelingen van het elektro-gesponnen

nanovezel basismateriaal gevolgd door stoomactivatie voor ontwikkeling van de porositeit van het ACNFN. De resultaten laten zien dat het optimaliseren van de omstandigheden tijdens het elektrospinnen, de carbonisatie en de stoomactivatie, essentieel is voor het produceren van ACNFN met sterke mechanische eigenschappen en een groot specifiek oppervlak. Verscheidene karakteriseringsmethoden zoals SEM, FTIR, BET en DMA zijn gebruikt om de mechanische eigenschappen en de oppervlakte-eigenschappen van ACNFN te evalueren. De resultaten laten zien dat een ACNFN met een hoog specifiek oppervlak (520 m²/g) en goede mechanische sterkte succesvol gefabriceerd kan worden via het elektrospinningproces onder de volgende condities: 14 wt.% PAN/DMF precursor, 2 uur carboniseren op 600°C en een stoomactivatie op 750°C met 60 ml/uur stoom voor 1 uur.

In hoofdstuk 4, wordt de prestatie van de ACNFN voor het verwijderen van geëmulgeerde olie onderzocht tijdens een dynamische batch adsorptie test. De initiële olieconcentratie, de mengsnelheid en de zoutconcentratie in de emulsies beïnvloeden de efficiëntie waarmee de olie door de ACNFN wordt verwijderd. Een hoge scheidingsefficiëntie van 95% werd bereikt met de ACNFN, wat hoger was dan de scheidingsefficiëntie van de CNFN en de commercieel verkrijgbare actieve kool. Dit is te verklaren door het groot toegankelijk oppervlak, hoge porositeit en de waterafstotendheid van de ACNFN.

Hoofdstuk 5 omschrijft het gebruik van de ACNFN voor het scheiden van de geëmulgeerde olie in een doorstroomsysteem. Het effect van de stroomsnelheid van de emulsie, de dikte van het materiaal en het soort non-woven materiaal is onderzocht. De resultaten laten zien dat het verwijderen van de oliedruppels gaat via uitsluiting van grote deeltjes en adsorptie. Een typisch doorbraakcurve werd gevolgd door ophoping van de oliedeeltjes. De hoge porositeit van de ACNFN blijkt een belangrijke rol te spelen bij het verwijderen van de kleine oliedruppels. Verder kan de scheidingsefficiëntie worden verhoogd met langere contacttijden en een dikkere laag. De oliedruppels die aan de bovenkant van het non-woven materiaal werden

tegengehouden hoopten op en zorgden voor extra weerstand waardoor een verhoogde drukval werd waargenomen.

Hoofdstuk 6 beschrijft een nieuwe testmethode voor vezel-gebaseerde sorptiemiddelen. Het ontwerp van de doorstroomcel is zo gemaakt dat de emulsie door de dwarsdoorsnede van de dunne laag ACNFN gaat. De scheidingsefficiëntie van de geëmulgeerde olie neemt af bij een verlaagde contacttijd en een verminderd aantal ACNFN-lagen. In deze opzet heeft ACNFN voldoende capaciteit om in een continu proces de geëmulgeerde olie effectief te scheiden van het water, zonder dat er een significante drukval over het systeem ontstaat. Daarnaast is ook de regenereerbaarheid van de ACNFN onderzocht door de verzadigde ACNFN laag te wassen met een organisch oplosmiddel. De adsorptiekaracteristieken blijken onveranderd na drie adsorptie- en schoonmaakcycli.

In hoofdstuk 7 zijn alle discussies, resultaten en conclusies, zoals weergegeven in dit proefschrift, samengevat. Dit onderzoek laat zien dat ACNFN succesvol als sorptiemiddel kan worden toegepast voor het behandelen van olieachtig afvalwater in een continu stromingssysteem. Ook worden er in dit hoofdstuk suggesties en ideeën geopperd voor het gebruik van de ACNFN in het behandelen van andere typen afvalwater, waar in de toekomst aan gewerkt kan worden.

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About the author

Basma Waisi was born in Baghdad, Iraq, on 29th October 1979. She received her B.Sc. degree in chemical engineering from Baghdad University in June 2001. In the same year, she started working as a teaching assistant in the chemical engineering department at Baghdad University. In September 2005, she obtained her Master degree in chemical engineering from Baghdad University with a graduation project on the effect of the gas distributor on the heat transfer in a solid-gas fluidizing bed system. Then she worked in the department of chemical engineering as a faculty member from 2005 to 2011.

Starting from 2011, Basma continued her educational career as a Ph.D. candidate at the University of Twente, the Netherlands under the supervision of Prof. dr. Arian Nijmeijer and Prof. dr. Suzanne Hulscher. Her research was in the field of oilfield produced water treatment using activated carbon nanofiber nonwovens and was funded by the higher committee of education development (HCED) in Iraq. During her time as a Ph.D. candidate, she got the opportunity to do part of the research as a visiting scholar for two years at the University of Connecticut in Storrs, USA, under the supervision of Prof. dr. Jeffrey McCutcheon.

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 - 6- **B. Waisi** , N. Benes, A. Nijmeijer, and J. McCutcheon, Novel Testing Method for Fiber Based Sorbents: Cross-sectional flow cell for high residence time sorption. To be submitted.
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Conferences

- 1- North American Membrane Society (NAMS) 2015, Boston, the United States (oral presentation and poster presentation).
- 2- The Association of Environmental Engineering & Science Professors (AEESP) 2015 Conference, Yale University, Connecticut, the United States (poster presentation).
- 3- American Institute of Chemical Engineers (AIChE) 2015, Salt Lake City, the United States (oral presentation).

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