LA-UR- 08-4343

Approved for public release; distribution is unlimited.

Title: Pilot Scale Test of a Produced Water-Treatment System for Initial Removal of Organic Compounds

Author(s): Soondong Kwon, UT-Austin Civil Engineering
E.J. Sullivan, Los Alamos National Laboratory
Lynn Katz, Kerry Kinney, Chia-Chen Chen; UT-Austin Civil Engineering
Rob Bowman, Josh Simpson; New Mexico Tech

Intended for: 2008 SPE Annual Technical Conference and Exhibition (ATCE) Denver, Colorado, USA, 21–24 September 2008.

Los Alamos
NATIONAL LABORATORY
EST.1943

SPE-116209-PP

Pilot Scale Test of a Produced Water-Treatment System for Initial Removal of Organic Compounds

Soondong Kwon, UT-Austin Civil Engineering
E.J. Sullivan, Los Alamos National Laboratory
Lynn Katz, Kerry Kinney, Chia-Chen Chen, UT-Austin Civil Engineering
Rob Bowman, Josh Simpson, New Mexico Tech

This paper was prepared for presentation at the 2008 SPE Annual Technical Conference and Exhibition held in Denver, Colorado, USA, 21–24 September 2008

Abstract

A pilot-scale test to remove polar and non-polar organics from produced water was done at a disposal facility in Farmington NM. We used surfactant-modified zeolite (SMZ) adsorbent beds and a membrane bioreactor (MBR) to reduce the organic carbon content of produced water prior to reverse osmosis (RO). Reduction of total influent organic carbon (TOC) to 5 mg/L or less is desirable for more efficient RO system operation.

Most water disposed at the facility is from coal-bed gas production, with oil production waters intermixed. Up to 20 gal/d of produced water was cycled through two SMZ adsorbent units to remove volatile organic compounds (BTEX, acetone) and semivolatile organic compounds (e.g., napthalene). Output water from the SMZ units was sent to the MBR for removal of the organic acid component of TOC. Removal of inorganic (Mn and Fe oxide) particulates by the SMZ system was observed. The SMZ columns removed up to 40% of the influent TOC (600 mg/L). BTEX concentrations were reduced from the initial input of 70 mg/L to 5 mg/L by the SMZ and to an average of 2 mg/L after the MBR.

Acetic acid (as acetate) input varied from 120-170 mg/L and was removed by the system up to 100%, while TOC was removed up to 92% of input (to 45 mg/L). Scaling of the MBR internal membrane occurred upon removal of the organic acid component, likely as a result of the subsequent rise in pH above 8 pH units; this effect may be reduced by metered addition of acid to reduce the pH as shown by additional laboratory studies. Significantly, organic removal was accomplished with a very low biomass concentration of 1 g/L throughout the field trial.

An engineering cost evaluation shows that the SMZ system with an RO system would cost from \$0.13 to \$0.20 per bbl at up to 40 gpm. Current estimated disposal costs for produced water are from \$1.75 to \$4.91 per bbl, with some regions at higher rates including transportation, indicating that treatment may be a feasible alternative.

Introduction

Co-produced water disposal represents a significant percentage of costs associated with oil and gas production operations. As disposal costs increase rapidly, treatment and reuse of a significant part of this waste stream becomes more feasible. Produced water is characterized by high levels of total dissolved solids (TDS), dissolved organics, and oil and grease. Among the wide variety of organics present in the water, the concentration of hazardous substances such as benzene, toluene, ethylbenzene, and xylenes (BTEX) can reach 600 mg/L and the concentration of non-hazardous carboxylates can be as high as 10,000 mg/L (API, 2002). In order to make salt removal processes such as reverse osmosis (RO) more effective, a reduction of the total organic concentration to a level at or below 5 mg/L is desirable.

Current methods used to remove organics after gross oil-water separation include hydrophobic filters such as paper filters or activated carbon to remove nonpolar organics. These methods do not remove polar organic compounds such as alcohols or carboxylates or dissolved nonpolar organics. While higher concentrations of these constituents can be biocidal, lower concentrations such as are found in produced water tend to be dissolved at levels that can be used as a food source by bacteria. Because bacteria are a prime source of fouling in membrane systems, removal of their food source in pretreatment stages may add increased lifetime to membranes and reduce cleaning and maintenance costs.

The main goal of this research was to investigate the feasibility of using a combined physicochemical/biological treatment system to remove the organic constituents present in saline produced water. In order to meet this objective, two separate treatment techniques were investigated: sorption of polar organics (both volatile and semivolatile) using surfactant-modified zeolite (SMZ); and a membrane bioreactor (MBR) to treat the carboxylate and BTEX constituents that can penetrate an upstream SMZ system. The primary objective of the field test was to evaluate a coupled SMZ/MBR system treating actual produced water with respect to its ability to reduce carboxylate concentrations and thereby minimize fouling of a downstream desalination system. A secondary objective of the field trial was to assess the efficiency of the SMZ/MBR system for the removal of BTEX in actual produced water.

SMZ has been evaluated for the removal of a number of dissolved contaminants from aqueous solutions, particularly for BTEX compounds (Janks and Cadena, 1992; Neel and Bowman, 1992; Bowman et al., 1995; Ranck et al., 2005). Zeolites are hydrated aluminum tectosilicates characterized by cage-like structures having high internal and external surface areas, and high cation exchange capacities (CECs). Low organic carbon contents (<0.5%) in natural zeolite limit the sorption of organic compounds, and this problem can be solved by adding a surfactant such as hexadecyltrimethylammonium (HDTMA) to the natural zeolite. HDTMA is commonly used in products such as hair conditioner, mouthwash, and fabric softener and was also found to be very stable on zeolite surfaces (Li and Bowman, 1998). Once SMZ is saturated with VOCs, it can be regenerated using air sparging (Li and Bowman, 2001). Ranck et al. (2005) reported successful removal of BTEX from produced water by adsorption on virgin and regenerated SMZ. They also verified that there was no significant reduction of sorption capacity of the SMZ for BTEX over 100 sorption/regeneration cycles (Altare et al., 2007).

This ability to regenerate SMZ and its low cost ($460/MT) make it a very promising sorbent for the treatment of produced water. However, the regeneration process produces a gas stream contaminated with VOCs. Thus a secondary treatment technique is necessary for gaseous VOCs. For example, a Vapor Phase Bioreactor (VPB) can be used to treat the volatile compounds in the gas streams used to regenerate a saturated adsorbent such as SMZ (Kwon, 2007).

MBRs also offer promise for produced water treatment. In particular, beneficial uses of the treated produced water often require the removal of the dissolved salts. Reverse osmosis is a proven technology for desalination but the presence of organics can foul the membrane (Agenson and Urase, 2007). Although no other researchers have used MBRs for produced water, they have been used to treat briny wastewaters. Bakx et al. (2000) observed more than 83% removal of COD in oil-contaminated water (sea water) from naval warships using an MBR. In other research, an MBR removed 88% of the COD and 99% of the BOD (biochemical oxygen demand) from a briny tannery effluent (Scholz et al., 2005). These results imply that biological options can be applied to the treatment of produced water.

The results of earlier tests (Kwon, 2007) indicated that several carboxylates such as acetate and malonate were present in the produced water at the field site at a total concentration on the order of 400 mg/L. Because they are polar in nature, carboxylates are not effectively removed in the SMZ columns. Thus, a technology to efficiently remove the carboxylates from the produced water is desirable. One option for removing organics such as acetate and malonate from produced water is to use a MBR system. Although direct biological treatment of briny produced water can be challenging, many of the organic contaminants in produced water are amenable to biological treatment. Indeed, several researchers have recently developed biological treatment systems that can treat high salinity waters containing dissolved organics (Bakx et al., 2000; Scholz et al., 2005). In particular, Tellez et al. (2005) operated a field-scale activated sludge system to remove petroleum hydrocarbons from produced water. Researchers achieved 92% removal of COD with a 12-hr HRT (Hydraulic Retention Time) and 20-day SRT in produced water containing 34,110 mg/L TDS. Dalmacija et al. (1996) increased the performance of an activated 12 sludge system by adding powdered activated carbon (PAC) and diluting the oil-field brine wastewater with river water. The objective of this work was to investigate the feasibility of utilizing an MBR system in the field to pretreat produced water to a level sufficient for subsequent treatment in a reverse osmosis system.

Methods and Materials

A test of the coupled SMZ adsorption and MBR system was done at a salt water disposal (SWD) facility in Farmington, New Mexico. Most water delivered to the site is from gas production wells, with 50% or less from oil production locations. Produced water delivered to the site is pretreated using oil-water separation, sand filtration, fiber-wound five-micron and one-micron filters prior to deep well re-injection. The water used for this test was selected randomly from the post 5-micron filtered stream and was stored at ambient temperature in a plastic 500 gallon tank prior to our treatment tests.

The zeolite used in the study was obtained from the St. Cloud mine near Winston, New Mexico. It was subsequently crushed and sieved to grain sizes of 1.4~0.4 mm (14-40 mesh). Ranck et al. (2005) characterized the mineral composition of the zeolite as: 74% clinoptilolite, 5% smectite, 10% quartz/cristobalite, 10% feldspar, and 1% illite. HDTMA-Cl was used as the surfactant in the production of HDTMA-zeolite, as described by Bowman et al. (2001) with 14-40 mesh zeolite particles similar to material used in previous laboratory and field testing.
A Culligan fiberglass tank (14" ID, 48" H) was packed with SMZ (bottom 65%) and raw zeolite (top 35%) to a total packed capacity of 3.7 ft^3. With this packing method, any surfactant potentially desorbed from the SMZ could be captured by the raw zeolite placed downstream of the SMZ. Free surfactant can be biocidal and therefore was scavenged from the treatment stream before contact with the biological system in the MBR.

An MBR was designed and constructed to assess the feasibility of using this technology to treat produced water containing carboxylates and BTEX compounds. Photographs of the system and of the membrane used are shown in Figures 1 and 2. One of the unique features of this bioreactor was that it could be sealed to enable collection of gas phase effluent samples.

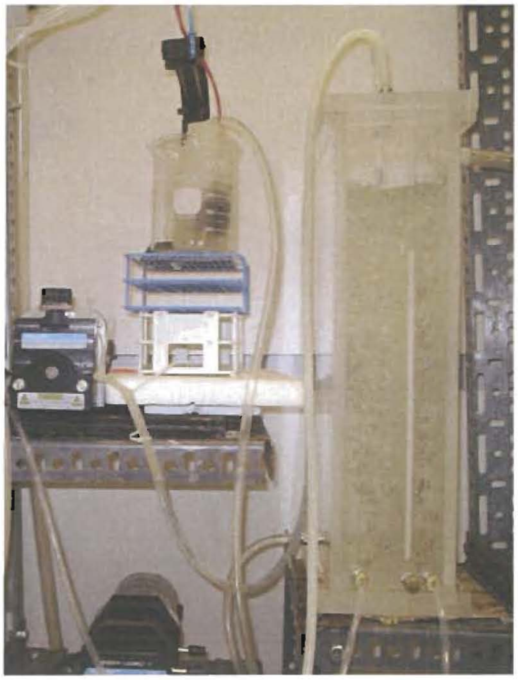


Figure 1. Experimental MBR System.

Figure 2. Ultrasonically welded polyethylene membrane sheet on an ABS plastic housing. Membrane was provided by Enviroquip, Inc. (Austin, TX).

A schematic of the experimental system is shown in Figure 3 and the operating parameters of the system are summarized in Table 7.1. The experimental bioreactor depicted was 8 L in volume, rectangular in shape (10 cm x 22 cm x 49 cm high) and constructed of 0.5″ Plexiglass. Preliminary testing showed that adsorption to the bioreactor was negligible. The system was aerated at 10 L/min via a line air diffuser located directly beneath the bioreactor membrane. The aeration system provided sufficient oxygen to sustain the microorganisms and provided membrane scouring to minimize fouling. A flat sheet of microfiltration membrane (Enviroquip, Inc., Austin, Tx) consisting of a 0.4 µm pore size, ultrasonically welded polyethylene sheet was suspended in the MBR as shown in the schematic. The dimensions of the membrane plate were 22.5 cm x 32 cm x 0.6 cm yielding a total membrane area of 1,170 cm2. Photographs of the experimental MBR system and polyethylene membrane sheet are provided in Figures 3 and 4. The same MBR (i.e., 8 L of total reactor volume) and polyethylene membrane (0.4 µm pore size), was operated in both laboratory tests and the field test. Biomass used in preliminary laboratory tests (Kwon, 2007) also was transported to the field site and used to reduce the acclimation period.

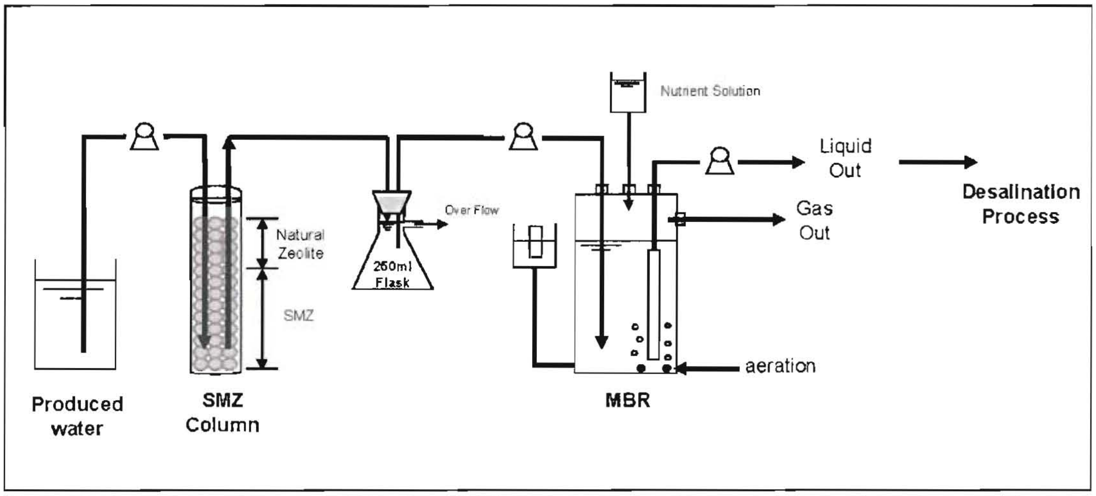


Figure 3. Schematic diagram of the SMZ/MBR treatment system used to treat produced water at the field site near Farmington, New Mexico.

Table 1 lists the operating conditions of the MBR during the field test. During the test, produced water passed through the SMZ adsorption column prior to entering the MBR. The SMZ system was operated upstream of the MBR to assess carboxylate removal efficiencies in the MBR in the absence of BTEX and other hydrophobic contaminants which are removed on SMZ. The produced water flow rate through the SMZ column was set at 25 ml/min. This produced water passed through a small Erlenmeyer flask containing a rubber cap before it was directed to the MBR. The design flow rate to the MBR was 14 ml/min, and the remaining SMZ treated produced water was discharged to a sump. For the operation of the MBR, external nutrients were supplied directly to the MBR as shown in Figure 3. A stock nutrient solution consisting of 4.0 g/L of KNO_3, NH_4Cl, and KH_2PO_4, was continuously pumped into the bioreactor. The resulting design HRT was 9.6 hours in the MBR. The SRT was 100 days by withdrawing 80 ml of biomass solution daily from MBR. Compressed air was supplied at a flow rate of 7.5 L/min to an air diffuser located directly beneath the bioreactor membrane.

Table 1. Operating conditions of the SMZ/MBR system

Operational Parameters	Values
SMZ column Volume (L)	105
MBR Volume (L)	8
Flow rate (ml/min)	
--Through SMZ column	25

--Through MBR	14
Aeration rate in MBR (L/min)	7.5
HRT 1) in MBR (hours)	9.6
SRT 2) in MBR (days)	100
PAC 3) amount (g/L)	2~5
pH of influent	8.5
Temperature (°C)	21

1) HRT : Hydraulic Retention Time
2) SRT : Solids Retention Time
3) PAC : Powdered Activated Carbon

Due to the accumulation of biomass on the membrane over time, the effluent flow rate slowly decreased with time resulting in an unbalanced flow rate between the influent and effluent streams. To address this problem, a water level controller (Vertical mounted liquid level switch, Omega Engineering Inc.) was installed to control the influent pump rate and to maintain a constant water level in the MBR.

After the system reached stable operating conditions, 2~5 g/L of powdered activated carbon (PAC) (NUCHAR SA-T 1320-R-05, MeadWestvaco inc., Covington, VA) was added into the MBR (2g/L on Day 27, another 3 g/L on Day 29) to investigate the effect of PAC on the performance of the MBR, particularly for organic removal and potential flux increase. The average PAC particle size of 100 µm was produced by passing the material through a 120×200 mesh sieve.

Treatment system monitoring included both on-site and off-site analyses. The on-site analyses included measuring aqueous phase BTEX concentrations as well as gas phase BTEX concentrations in the MBR off-gas. Off-site analyses of the produced water included analyzing VOCs, SVOCs, cations and anions, carboxylates and TOC concentrations. The on-site aqueous and gaseous BTEX concentrations were measured using a Hewlett-Packard (HP) Model 5890A GC with a 10-m, 0.53-mm I.D. HP-5 capillary column and flame ionization detector. The carrier gas (He) had a flow rate of 35 mL/min and the split gas (He) flow rate was 28 mL/min. No makeup gas was utilized. The analyses were performed isothermally at 55°C, with an injector temperature of 210°C and detector temperature of 240°C. For the analysis of BTEX concentrations in aqueous samples, 2.5 mL aliquots of each water sample were placed in a 10mL vial fitted with a Teflon-faced butyl septum. The vial was placed in a heating block and equilibrated at 80°C for 15 minutes. A 0.5 mL gas-tight syringe was used to extract gaseous samples from the headspace for subsequent analysis on a GC. The BTEX concentrations in gaseous samples from the sampling ports of the MBR were analyzed by direct injection into the same GC. *p*-xylene and *m*-xylene were not resolved by this method and were treated as a single compound. On-site analyses also included DO (Dissolved Oxygen), temperature, conductivity, and TMP. The TMP was measured in-line with a manometer connected to the tubing on the suction side of the permeate pump.

Carboxylates concentrations were measured at the University of Texas in Austin using a Dionex AS 40 autosampler attached to DX-600 Ion Chromatograph (IC). The IC was equipped with a Dionex CS25A conductivity detector, as ASRS ULTRA 4mm suppressor, an EG50 eluent generator, and an IonPac AS11-HC analytical column. The oven temperature was maintained at 30oC for each run, the suppressor current was set at 300 mA, and the flow rate of the eluent (KOH) through the column was 1mL/min. The eluent concentrarion was set as follows: 1 mM for the first 4 minutes, 2 mM from 4.2 to 13.2 minutes, 10 mM from 13.5 to 28 minutes, 2 mM from 28.5 to 30 minutes, 30 mM from 30.5 to 40 minutes, and 0.5 mM from 40.5 to 44 minutes.

Total suspended solids (TSS) and volatile suspended solids (VSS) were measured at the University of Texas at Austin according to Standard Methods (APHA 1995) Section 2540D and 2540E respectively.

Description and Application of Equipment and Processes

Overview of Membrane Bioreactors

MBRs have been in development for over 30 years and have been used successfully to treat municipal wastewater, industrial wastewater, and drinking water. MBR combines biological treatment and physical separation by a porous membrane in a single process. Organic pollutants in the influent are degraded biologically in a well mixed, aerated bioreactor by microorganisms, and microorganisms are removed from the treated wastewater by a membrane. The membrane provides a physical barrier for the suspended solids, that retains all of the activated sludge in the bioreactor and produces permeate free of suspended solid matter, bacteria, and viruses (Marrot et al., 2004). This part of the system substitutes for the clarifier in traditional systems. Currently, more than 2,200 MBRs are in operation or under construction worldwide with 75% located in Great Britain, United States, Japan, France, China, South Korea, Germany, and Canada (Yang et al., 2006).

The membranes can be placed either outside (external) or inside (submerged) the bioreactor (Figure 4). We used a submerged MBR, where the filtration is performed in the aeration tank via suction through a membrane separator. In an external MBR, the permeate flux generally varies between 50 and 120 L/hr-m^2 and the TMP is in the range of 100 to 400 kPa. In the submerged MBR, the permeate flux varies between 15 and 50 L/hr-m^2 and a typical TMP is approximately 50 kPa (Marrot et al., 2004). Submerged configurations are gaining favor recently since they have lower energy consumption (Huang et al., 2001). Some advantages offered by an MBR include a more compact footprint, higher biomass concentrations, shorter HRTs, less disinfection, and reduced sludge production. Although some of these aspects reduce overall costs, generally MBRs operate at higher cost than traditional activated sludge systems. Disadvantages include high capital costs, elevated energy costs, and high maintenance requirements. Membrane fouling also introduces some limitations to this technology and increases maintenance requirements as discussed below (Marrot et al., 2004).

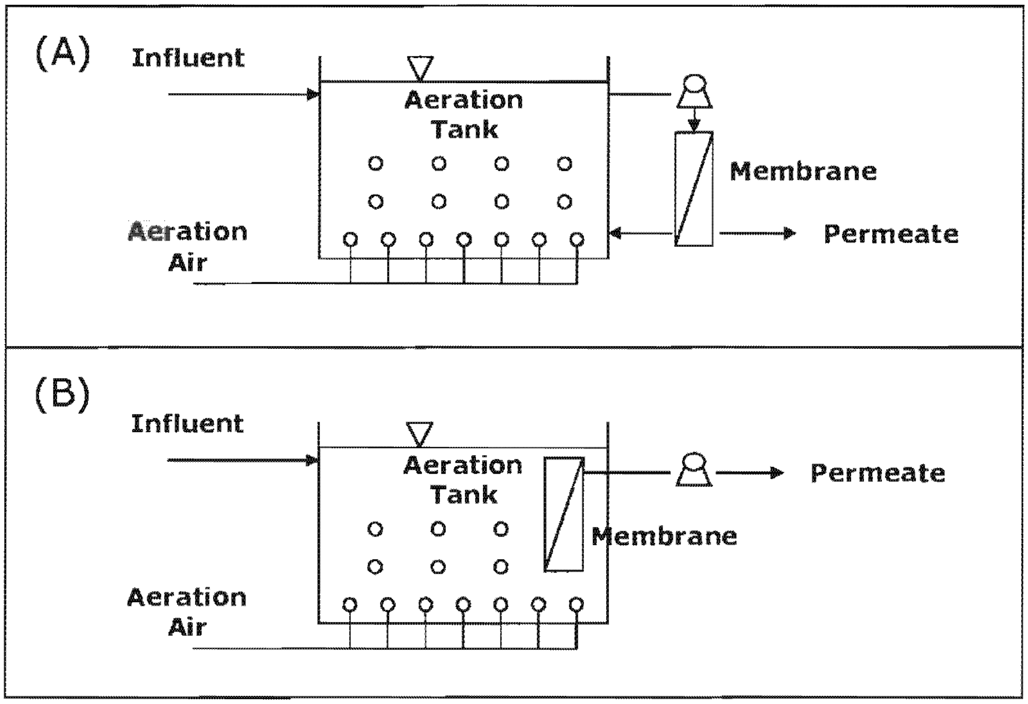


Figure 4. Configurations of the MBR: (A) external and (B) submerged.

Membrane Fouling

One of the major problems in the operation of membrane processes is membrane fouling. Membranes work by providing a selective barrier, rejecting the transport of some constituents when a driving force is applied. Mechanical sieving provides rejection of all particles larger than the pore size and partial rejection of particles smaller than the pore size. As particles accumulate on the membrane surface, they partially block the pores, reducing the effective pore size which reduces the flux through the membrane.

The hydrophobicity of a membrane material affects membrane fouling. A hydrophobic membrane experiences higher fouling since it allows more organic compounds to accumulate on the membrane surface compared to a hydrophilic membrane (Choo et al., 2000; Sofia et al., 2004). Inorganic membranes can achieve higher fluxes than organic membranes, but the higher capital cost of inorganic membranes has prompted the use of membranes made of organic materials (Chen et al., 2005). Wastewater temperature is another factor affecting membrane fouling. Increasing the temperature of the wastewater decreases the viscosity of the fluid resulting in less fouling.

However, energy costs and biomass activity effects must be considered before increasing temperatures. The existence of extracellular polymeric substances (EPS) in wastewater is thought to be the primary cause of membrane fouling (Sperandio et al., 2005; Lee et al., 2001). EPS are high molecular weight metabolites consisting of polysaccharides, proteins, nucleic acids, lipids and other biological macromolecules. Due to the hydrophobicity of these metabolites, EPS adsorbs inorganic and organic compounds in the MBR system and adheres to the membrane. High concentrations of more soluble EPS in wastewater have been related to increased membrane fouling (Fan et al., 2006; Rosenberger et al., 2003).

Fouling can be reduced by increasing air sparging, backwashing the membrane, and/or by adding coagulants. When membrane operation is no longer feasible at high TMP, it must be cleaned, via physical and/or chemical means to restore the desired flux rate across the membrane.

Air sparging is universally used in aerobic MBRs as the primary method to reduce membrane fouling. Vigorous aeration is applied beneath the membrane which scours the membrane in submerged membrane systems (Ognier et al., 2002; Kishino et al., 1996; Gui et al., 2003). Typically, medium to fine bubblers are used by running a gas line containing a series of one to two millimeter holes under the membrane.

Backwashing, also called back-flushing, uses pressure to flow the permeate water or air back through the membrane for a set period of time. Periodic backwashing improves membrane permeability and reduces fouling, thus leading to more stable hydraulic operating conditions (Bouhabila et al., 1998). The frequency and duration of backwashing depend on the operational parameters of the membrane system. One study found optimal backwashing with air in an aerobic MBR to be 15 minutes of operation for every 15 minutes of aeration. This increased the flux from 6 to 30 L/hr-m2 (Visvanathan et al., 1997). Bouhabila et al. (2001) also observed that air backwashing (15 sec every 5 min) reduced the hydraulic resistance to less than a third of its value without backwashing.

Physical or chemical cleaning is a treatment to attempt to return the membrane back to its original flux capacity. Physical cleaning usually involves high pressure water and scrubber brushes to remove the deposits on the membrane surface. Chemicals commonly used for cleaning membranes in the water industry fall into five categories, as summarized in Table 2. Caustic solutions such as sodium hydroxide are used for organic and biological foulants while acidic solutions such as hydrochloric acid are used to remove inorganic foulants (Berube et al., 2006).

Table 2. Major categories of membrane cleaning chemicals.

Category	Major Functions	Typical Chemicals
Caustic	Hydrolysis Solubilization	NaOH
Oxidants Disinfectants	Oxidation Disinfection	NaOCl H2O2, Peroxyacetic acid
Acids	Solubilization	Citric acid Nitric acid Hydrochloric acid
Chelating Agents	Chelation	Citric acid EDTA
Surfactants	Emulsion Dispersion, Surface conditioning	Surfactants Detergents

Another approach is to modify the characteristics of the mixed liquor suspension using additives. The most common approach is the addition of PAC to the bioreactor. PAC addition affects fouling by reducing the concentration of EPS, increasing the average floc size, and providing shear force on the submerged membrane.

PAC adsorbs fine colloids and dissolved organics, resulting in a shift to larger particle sizes. One study found that the mean particle size went from 7.5 to 22 μm with the addition of 5 g/L of PAC (Park et al., 1999). Another study using 1.7 g/L PAC observed a similar trend which resulted in lower trans-membrane pressures (TMPs) (Hu et al., 2007). Also, it is thought that PAC has a shear effect on a membrane. It scours particles that are deposited on the surface. Increasing PAC concentrations has been found to increase the flux at various TMPs (Ng et al., 2006; Seo et al., 2004). In other studies, PAC has been found to reduce the cake layer, stabilize influent conditions to avoid toxic shocks in the bioreactor, and increase the effluent water quality (Yoon et al., 2005; Seo et al., 2004).

In addition to the fouling reduction, PAC addition to an MBR acts as a supporting medium for attached bacterial growth yielding biologically activated carbon (BAC). The biofilm on the PAC consists of immobilized (Dalmacija et al., 1996) and acclimatized bacteria (Lin et al., 2001) that can also partly bioregenerate the saturated BAC (Schloz and Martin, 1997). In addition, the bacteria in the PAC biofilm can enhance overall pollutant removal (Lin et al., 2001; Mochidzuki and Takeuchi, 1999).

Data and Results

Adsorption of BTEX on the SMZ Column

The breakthrough profiles of BTEX in produced water through the virgin SMZ columns from earlier field tests was used to determine operational parameters for the current test (Ranck et al, 2005, Kwon, 2007). Benzene breakthrough occurred first after 5 hours of operation at a 27 gph flow rate. Toluene breakthrough followed the benzene breakthrough, but the breakthrough of the other VOCs was much slower than that observed for benzene and toluene. Rapid breakthrough of benzene, compared to the other VOCs present is consistent with theoretical predictions based on solute hydrophobicity and lab test results, indicating the low affinity of benzene for SMZ (Ranck et al., 2005). This result implies that benzene removal will control the design of the SMZ adsorption system.

Preliminary laboratory studies (Kwon, 2007) evaluated the effectiveness of a submerged MBR for simultaneous removal of carboxylates and hazardous BTEX constituents from saline produced water. Results of batch biodegradation studies indicated that carboxylates can be biodegraded in produced water with a very high TDS concentration, but the removal of BTEX constituents is more difficult under high saline conditions. An aerobic, submerged MBR achieved 92% removal of carboxylates (100% acetate and 85% malonate removal) at a 9.6-hr HRT. Adding BTEX to the produced water feed increased the biomass concentration in the MBR but did not affect the carboxylate removal. Approximately 80% of BTEX was biodegraded in the MBR when it was provided in gaseous phase. However, biological removal of BTEX was increased up to 95% when same amount of BTEX was introduced through aqueous phase.

The chemical composition of the produced water used in the field test was analyzed by GEL laboratories LLC. (Charleston, SC) and summarized on Table 3. The total dissolved solid measurement of 10,717 mg/L was similar to the value determined in our previous tests. TOC concentration was 571 mg/L, and several VOCs and SVOCs were detected, with BTEX comprising the major percentage by mass. Several anions were identified including chloride, sulfate, acetate, and bromide. Metals and cations such as sodium, calcium, potassium, magnesium, and barium were also identified in the produced water samples.

Table 3. Composition of produced water used for field testing at the Farmington, NM field site, August 2007

Analysis	Concentration (mg/L)
Total suspended solids (TDS)	10717.00
Total organic carbon (TOC)	571.00
Oil & Grease	45.40
Volatile Organics	
2-Hexanone	0.47
Benzene	1.07
Carbon Disulfide	0.15
Ethylbenzene	0.46
Toluene	4.74
Xylene (total)	4.63
Acetone	2.17
Semi-Volatile Organics	
Phenol	0.26
Naphthalene	0.05
2-Methylnaphthalene	0.06
bis(2-Ethylbhxyl)phthalate	0.36
m,p-Cresols	0.11
o-Cresols	0.11
Anions	
Bromide	18.10
Sulfate	484.00
Chloride	5540.00
Acetate	150.00
Cations	
Barium	4.06
Calcium	108.00
Iron	1.37
Magnesium	28.80
Manganese	0.44
Potassium	104.00
Sodium	4160.00

Biomass concentrations (MLVSS) of approximately 1 g/L were maintained during the entire field trial which was comparable to laboratory MBR pretest conditions (Kwon, 2007). Considering the fact that a typical activated sludge system has biomass concentrations of 3 g/L while MBRs typically have even higher biomass concentrations of up to 30 g/L (Jefferson et al., 2000; Yamamoto et al., 1989), this biomass concentration is very low. Because high biomass concentrations tend to yield higher bio-fouling rates, it is of interest to note that treating briny produced water in an MBR resulted in lower biomass concentrations.

The influent pH of the produced water was 8.5 and increased slightly (pH= 8.8) during the MBR operation period. The dissolved oxygen concentration in the MBR was maintained at approximately 2.5 mg/L.

Carboxylate Removal

One of the important objectives of this field test was to remove carboxylates from produced water. The predominant organic anion detected in this produced water was acetate, and its concentration was measured before and after the SMZ column, and after the MBR. The influent acetate concentration varied from 120 mg/L to 170 mg/L during the experiment. Consistent with the preliminary laboratory tests (Kwon, 2007), the SMZ column had little effect on the removal of carboxylates from produced water (Figure 5). However, acetate was removed to below detection limits in the MBR, indicating that the MBR system was very effective for treatment of carboxylates in produced water

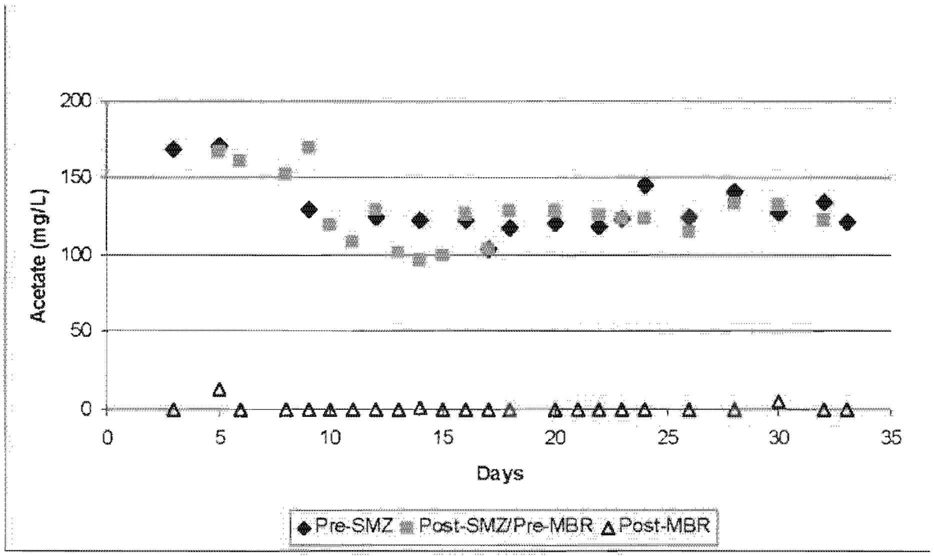


Figure 5. Acetate concentrations during SMZ/MBR operation.

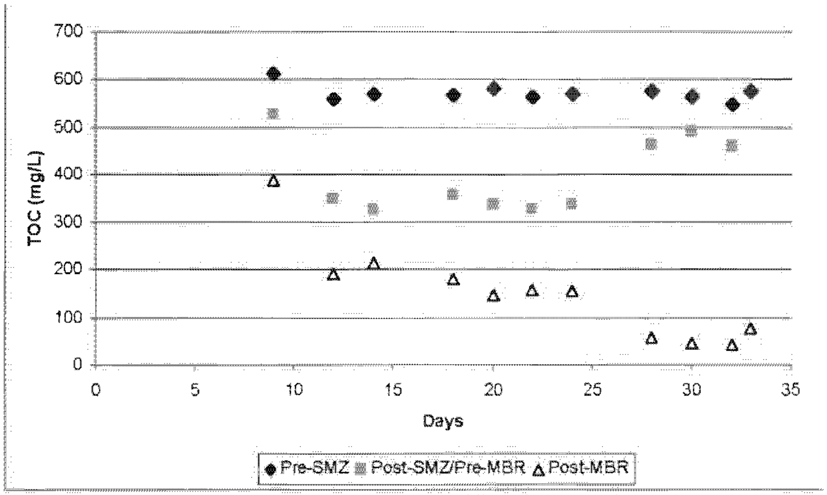


Figure 6. TOC concentrations during SMZ/MBR operation.

TOC Removal

Figure 6 shows the TOC concentrations in the SMZ/MBR system. The influent produced water contained an average TOC of 580 mg/L which was reduced to 350 mg/L in the SMZ column. However, as the SMZ column became saturated, the TOC level increased to 480 mg/L. This increase could be attributed to the increase in the effluent BTEX concentrations from the SMZ column. The TOC level in the effluent from the MBR decreased to approximately 150 mg/L, providing an overall TOC removal of 74% in the SMZ/MBR system.

PAC addition to the MBR on Day 27 resulted in an even more dramatic decrease in TOC. As shown in Figure 6, the MBR effluent TOC concentration after PAC addition decreased to 45 mg/L, providing an overall 92% removal of TOC. The necessity for PAC addition will depend on the particular treatment goals and final end use of the treated water.

BTEX Removal

BTEX are classified as hazardous materials even at low concentrations. For the discharge to surface or reuse applications, removal of these VOCs is strongly recommended. The previous SMZ/VPB field trial (Kwon, 2007) demonstrated that BTEX removal from produced water could be achieved using SMZ, and suggested that VPB treatment of the off-gas from any produced water would be effective regardless of the salt concentration since the BTEX are extracted and treated separately from the briny produced water. The lab-scale MBR experiment showed that the MBR could also remove these BTEX compounds in moderate salinity water, as described in previous chapter. Therefore, BTEX removal was also monitored in this field test. Figure 7 shows the BTEX concentration of produced water prior to and after SMZ and MBR treatment. As shown in the figure, the BTEX concentration in the influent produced water to the SMZ system decreased as the experiment progressed (from 70 mg/L to 10 mg/L). This decrease resulted from the increase in head space (and subsequent BTEX volatilization) in the produced water-storage tank used to supply water to the system. The BTEX concentrations in the SMZ treatment column effluent increased gradually as shown in the figure, due to slow breakthrough of BTEX from the SMZ. Individual analysis of BTEX compounds showed that only benzene exhibited complete breakthrough during the field test. BTEX was allowed to break through to provide a means of monitoring reduction of BTEX within the MBR, because BTEX removal efficiencies for SMZ are already well known (Altare, 2007; Ranck, 2005, Kwon, 2007).

A maximum BTEX concentration of almost 5 mg/L in the SMZ column effluent occurred at the end of the field test. The average BTEX concentration exiting the MBR ranged from 0.01 mg/L to 0.55 mg/L with an average value of 0.117 mg/L (Figure 7). With the exception of benzene, the maximum concentrations of the aromatic hydrocarbons detected in the liquid phase effluent from the MBR are far below the MCLs (Maximum Contaminant Levels) set by the U.S. EPA for drinking water (Table 4). These low BTEX concentrations in the MBR effluent resulted from a combination of volatilization and biodegradation.

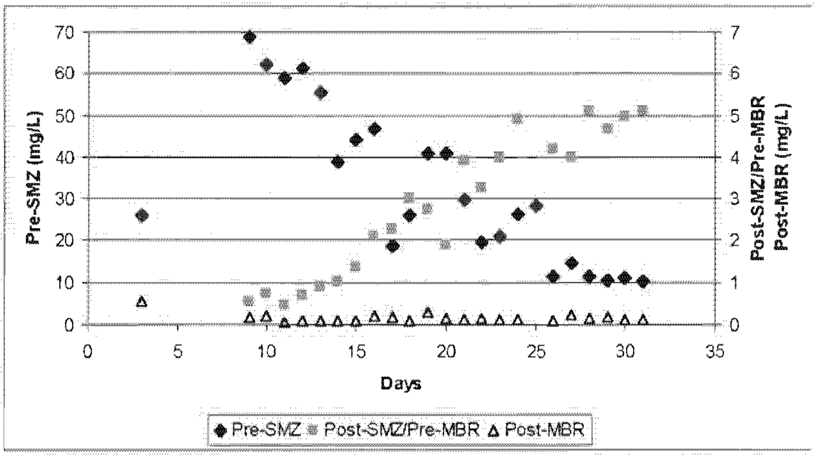


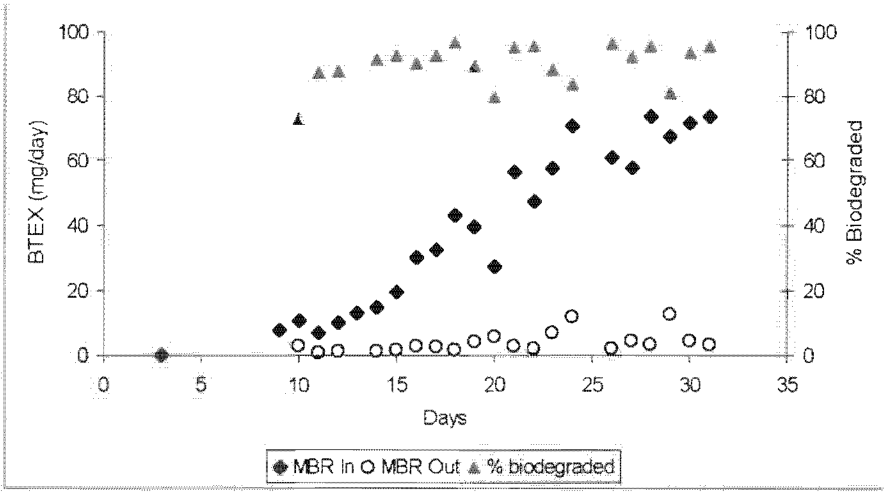
Figure 7.. Liquid phase BTEX concentrations during SMZ/MBR operation.

Table 4. Maximum BTEX concentrations in the MBR liquid phase effluent

Chemicals	Effluent (μg/L)	MCLs$^{(1)}$ (μg/L)
Benzene	88.0	5.0
Toluene	230.5	1,000.0
Ethylbenzene	48.8	700.0
Xylene (total)	182.7	10,000.0
Sum (BTEX)	550.0	11,705.0

1) Maximum Contaminant Levels in drinking water by US EPA

To provide a basis for determining the relative contribution of each of these mechanisms to BTEX removal, gas phase BTEX concentrations from the MBR were measured in addition to the aqueous phase concentrations. Figure 7.5 shows the total mass of BTEX introduced to the MBR (all liquid phase) per day and the total mass of BTEX (liquid and gas phase) exiting the reactor per day. Using mass balance calculations, the difference between these two values was attributed to BTEX removal by biodegradation. As shown in Figure 7.5, up to 95% of the BTEX introduced into the MBR was biodegraded, indicating that the MBR could be used effectively to remove VOCs from produced water without additional treatment. Removal of BTEX by volatilization was 2.9%, resulting in 97.8% overall removal efficiency (Table 7.4).



Symbolic representation:

Figure 7.5. BTEX amount degraded by biomass in MBR.

Table 7.4. BTEX removal in MBR.

	Percent removal (%)
Removal by Biodegradation	94.9
Removal by Volatilization	2.9
Total Removal	97.8

Kinetic coefficients measured in previous laboratory tests (Kwon, 2007) were modified and used to predict the benzene effluent concentrations from the field MBR system. Benzene was the only VOC evaluated because the SMZ column removed the other BTEX compounds to below detection throughout most of the MBR testing. Effluent benzene concentrations from the MBR were estimated using the mass balance equations shown below in conjunction with a modified volatilization coefficient and the laboratory determined biodegradation coefficient. The laboratory determined volatilization coefficient (*KV*) was modified to account for the different aeration rates used in the field test by linear correlation between volatilization coefficients and aeration rates observed in the toluene abiotic laboratory test for aeration rates ranging from 2 L/min to 10 L/min.

General word statement:

Rate of accumulation of VOC within the system boundary = *Rate of flow of VOC into the system boundary* - *Rate of flow of VOC out of the system boundary*

\+ *Amount of VOC removal through system boundary by stripping* + *Amount of VOC removal through system boundary by biomass*

$$\frac{dC}{dt}V = Q_l C_{in(l)} - Q_l C_{out(l)} - K_V C_{out(l)} V - k_d X C_{out(l)} V$$

(Eq. 7-1)

Where;

dC/dt = rate of change in VOC concentration in reactor

Q_l = Liquid flow rate

$C_{in(l)}$ = Influent VOC concentration (Liquid phase)

$C_{out(l)}$ =Effluent VOC concentration (Liquid phase)

V =Volume of reactor

K_V = overall VOC volatilization coefficient, 1/hr

X = Biomass Concentration (mass of cell/L)

k_d = specific first order biodegradation coefficient, L/hr-mass of cell

If steady-state conditions are assumed, then:

$$C_{out(l)} = \frac{Q_l C_{in(l)}}{Q_l + K_V V + k_d X V}$$

Eq. 1

Table 7.5. Benzene concentrations measured in field test and estimated using laboratory-determined kinetic coefficients.

K_v (1/hr)	k_d•X_1 (1/hr)	C_{in} (mg/L) Measured	C_{out} (mg/L) Measured	C_{out} (mg/L) Estimated
8.07	30.54	4.374	0.016	0.012

[1] Measured in Lab test at a biomass concentration of 1 g/L

As shown in Table 7.5, lab-determined kinetic coefficients estimated 25% lower concentrations than measured in the field test. These results seem quite reasonable given that the composition of the synthetic produced water used in the laboratory was a fairly simplified representation of the composition of the actual produced water. To identify whether the differences in the measured and predicted values were due to a decrease in the volatilization rate or due to a decrease in the biodegradation rate, values of the rate coefficients were determined from the field data and compared to the laboratory values.

First, the volatilization rate coefficient (*KV*) was calculated. It was assumed that the mass rate of VOCs removal by stripping (i.e., *KV Cout(l) V* in equation 7-1) was equal to the VOC mass detected in the exit gas per unit time (*Qg Cout(g)*).

Symbolic Representation:

Eq. 2

Eq. 3

$$K_V C_{out(l)} V = Q_g C_{out(g)}$$

Where;

$$K_V = \frac{Q_g C_{out(g)}}{K_V C_{out(l)}}$$

$K_V C_{out(l)} V$ = Amount of VOC removal through system boundary by Stripping

Q_g = Gas flow rate

$C_{out(l)}$ = Effluent VOC concentration (Liquid phase)

$C_{out(g)}$ = Effluent VOC concentration (Gas phase)

V =Volume of reactor

K_V = overall volatilization rate, 1/hr

Next, the overall VOC biodegradation coefficient was calculated by the following equations assuming steady-state conditions.

Eq. 4

Eq. 5

$$\frac{dC}{dt}V = Q_l C_{in(l)} - Q_l C_{out(l)} - K_V C_{out(l)} V - k_d X C_{out(l)} V$$

$$k_d X = \frac{Q_l C_{in(l)} - Q_l C_{out(l)} - K_V C_{out(l)} V}{V C_{out(l)}}$$

Where;

Q_l = Liquid flow rate

$C_{out\,(l)}$ = Effluent VOC concentration (Liquid phase)

$C_{in(l)}$ = Influent VOC concentration (Liquid phase)

$K_V \cdot C_{out(l)} \cdot V$ = Amount of VOC removal through system boundary by Stripping

V = Volume of reactor

K_V = overall volatilization rate coefficient, 1/hr

X = Biomass Concentration (mass of cell/L)

k_d = specific first order biodegradation coefficient, L/hr-mass of cell

Table 7.6. Kinetic coefficients for benzene removal determined in the field test and the lab tests.

K_V (1/hr)		$k_d \cdot X$ (1/hr)	
Field-measured	Lab-measured	Field-measured	Lab-measured
4.13	8.07	23.93	30.54

As shown in Table 7.6, the field-measured *KV* and *kd*•X values were 51% and 78% of the lab-measured values. Thus, both biodegradation and volatilization were reduced in the field system. There are several possible explanations for this discrepancy. As stated previously, the field produced water contained a broader range of compounds than the synthetic produced water used in the lab test. The pH of the produced water in the field test (8.8) was somewhat higher than in the lab test (8.0) and the dissolved oxygen level (2.5 mg/L) was lower than in the lab test (3.5 mg/L). All of these factors may have contributed to a reduction in biodegradation rates. The most probable reason for the decrease in the volatilization rate was the foam observed in the MBR during field operation. The raw produced water exhibited significant foaming when it was shaken in a 10 ml vial suggesting that an unidentified surfactant was present in the raw produced water. This surfactant appears to have penetrated through the SMZ column and into the MBR. The presence of foam in the MBR may have limited the mass transfer of BTEX compounds to the reactor headspace and decreased the volatilization rate as compared to the lab tests with synthetic produced water. Nonetheless, the predictions of effluent benzene concentrations were reasonable and suggest that the removal of benzene from produced water is primarily controlled by biodegradation.

Trans-Membrane Pressure

One of the main drawbacks of the MBR system is membrane fouling which reduces the flux through the membrane and increases the TMP. As described in Section 2.7.3, there are several possible methods to reduce the TMP in a MBR including physical removal techniques and chemical washes. During the initial 14 days of operation during the field MBR test, daily brushing of the membrane surface was used solely to prevent excessive membrane fouling and maintain the flux through the membrane (Figure 7.6). This method was sufficient to maintain the TMP levels below 30 kPa after brushing. However, after two weeks of operation, this simple brushing technique was not capable of reducing the TMP level to below 30 kPa and the TMP increase accelerated. Several membrane washing methods were then attempted to determine if they could clean the membrane and reduce the TMP during operation. The different methods attempted in the field included submerging the membrane for several hours in one of the following solutions: (1) 0.5% hypochlorite (NaOCl) solution , (2) 1% citric acid (C6H8O7) solution, and (3) 1% nitric acid (HNO3) solution. However, these washing techniques had little impact on membrane clogging. On Day 27, 2 g/L of PAC was added to the MBR, and another 3 g/L was added two days later. Adding PAC to the MBR is believed to enhance the removal of organic matter through contaminant adsorption. Also, in some systems, PAC addition has been shown to decrease the TMP by increasing the average floc size and providing a shear force on the membrane (Ng et al., 2006; Park et al., 1999; Seo et al., 2004). However, PAC addition to the MBR had little impact on membrane clogging in this field test.

During the laboratory-scale evaluation of the MBR, it was found that decreasing the pH of the influent below 7.0 decreased the TMP to below 25 kPa. In the field, the pH of the effluent from the MBR was 8.8 which enhanced the potential for forming inorganic precipitants that would foul the membrane and high TMP was not unexpected. Unfortunately, logistical constraints during the field trial precluded the implementation of a pH control system in the field to be able to confirm that reducing the pH of the solution in the MBR would reduce TMP and prevent fouling of the membrane. Future studies with actual produced water will be required to evaluate the impact of pH reduction or frequent membrane backwashing on TMP. However, fouling by inorganic precipitates is a problem that leads to high TMP and ultimately reduced flux across the membrane. Decreasing the pH of the solution crossing the membrane was effective at reducing the TMP, but the optimal pH that maximizes biological activity while minimizing the TMP still must be determined

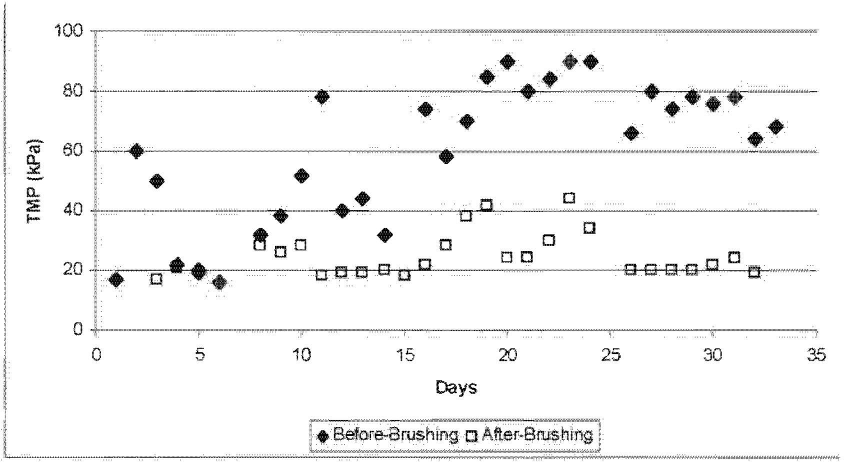


Figure 7.6. TMP in the MBR system during the field test.

Conclusions

The MBR system was operated as part of a field evaluation of an SMZ/MBR unit to pre-treat produced water for potential reuse applications. Consistent with the results of previous field trials, acetate (the predominant organic anion detected in the produced water) was not removed by the SMZ column. However, it was removed to below detection limits in the MBR, indicating that the MBR system was very effective for removing carboxy1ates from produced water. When the influent produced water containing 580 mg/L of TOC was supplied to the SMZ/MBR system, the SMZ column reduced up to approximately 40% of the influent TOC prior to breakthrough. After subsequent treatment in the MBR, greater than 74% of the influent TOC was removed and when the MBR was supplemented with PAC, the overall TOC removal efficiency of the SMZ/MBR system increased to 92%.

While most of the BTEX constituents of the produced water adsorbed onto SMZ during the field trial, approximately 95% of the BTEX that penetrated the SMZ and entered the MBR was biodegraded in the MBR. These results confirm that a MBR can be used to remove VOCs from produced water that has moderate TDS levels (e.g., 10 g/L). Kinetic coefficients measured in laboratory tests were modified and used to predict the benzene effluent concentrations from the field MBR system. The predicted effluent benzene concentrations were reasonable and suggest that the removal of benzene from produced water is primarily controlled by biodegradation.

As the field experiment progressed, severe membrane clogging was observed that resulted in high TMP and reduced flux through the membrane. Several cleaning methods, including physical and chemical membrane washing, had little effect on reduction of fouling. Further studies are required to optimize the system to reduce membrane fouling through either pH control and/or frequent membrane backwashing.

Specific conclusions reached by this study include:

1. A submerged MBR system can simultaneously biodegrade the carboxylate and BTEX constituents present in saline produced water. An aerobic, submerged MBR operated at a 9.6-hr HRT achieved 92% removal of acetate and malonate from synthetic produced water containing 10 g/L TDS. When BTEX was simultaneously supplied to the MBR in the gaseous phase, approximately 80% of the BTEX was biodegraded and when the BTEX was introduced in the aqueous phase, approximately 95% was biodegraded.

2. Fouling of an MBR membrane by inorganic precipitates is a significant problem that leads to high TMP and ultimately reduced flux across the membrane. For the synthetic produced water investigated in this research, decreasing the pH of the solution crossing the membrane was effective at reducing the TMP. However, the optimal pH that maximizes biological activity while minimizing the TMP must still be determined.

3. A coupled SMZ/MBR system can be used to simultaneously remove the carboxylate and BTEX constituents present in produced water under field conditions. Acetate (the predominant organic anion detected in the produced water at the field site in New Mexico) was not removed in the SMZ column; however it was removed to below detection limits in the MBR. The SMZ column removed most of the BTEX constituents in the produced water during the field trial; however, approximately 95% of the BTEX that penetrated the SMZ and entered the MBR was biodegraded in the MBR. Prediction of effluent benzene concentrations using lab-determined kinetic coefficients were reasonable, and suggest that the removal of benzene from produced water in the MBR is primarily controlled by biodegradation. Overall, the combined SMZ/MBR system achieved TOC removal efficiencies ranging from approximately 75 to 90%.

References

Agenson, K. O., Urase, T. (2007). "Change in membrane performance due to organic fouling in nanofiltration (NF)/reverse osmosis (RO) applications." Separation and Purification Technology 55(2): 147-156.

Altare, C. R., Bowman, Robert S., Katz, Lynn E., Kinney, Kerry A., Sullivan, Enid J. (2007). "Regeneration and long-term stability of surfactant-modified zeolite for removal of volatile organic compounds from produced water." Microporous and Mesoporous Materials 105(n3): 305-316.

API (2002). "Predictors of water-soluble organics in produced water - A literature review". Washington, D.C, American Petroleum Institute.

Bakx, T., Boom, S., Ramaekers, H. (2000). "Treatment of oil-contaminated water from naval warships." Water 21: 37-38.

Berube, P. R., Hall, E. R., Sutton, P. M. (2006). "Parameters governing permeate flux in an anaerobic membrane bioreactor treating low-strength municipal wastewaters: A literature review." Water Environment Research 78(8): 887-896.

Bouhabila, E. H., Ben Aim, R., Buisson, H. (1998). "Microfiltration of activated sludge using submerged membrane with air bubbling (application to wastewater treatment)." Desalination 118(1-3): 315-322.

Bowman, R. S., Haggerty, G. M., Huddleston, R. G., Neel, D., Flynn, M. M. (1995). "Sorption of Nonpolar Organic-Compounds, Inorganic Cations, and Inorganic Oxyanions by Surfactant-Modified Zeolites". Surfactant-Enhanced Subsurface Remediation. 594: 54-64.

Bowman, R. S., Li, Z., Roy, S.J., Burt, T., Johnson, T.L., Johnson, R.L. (2001). "Pilot test of a surfactant-modified zeolite permeable barrier for groundwater remediation". Physicochemical groundwater remediation. J. A. S. a. S.Burns. New York, Kluwer Academic/Plenum: 161-185.

Chen, X. B., Yang, W. S., Liu, J., Lin, L. W. (2005). "Synthesis of zeolite NaA membranes with high permeance under microwave radiation on mesoporous-layer-modified macroporous substrates for gas separation." Journal of Membrane Science 255(1-2): 201-211.

Choo, K. H., Kang, I. J., Yoon, S. H., Park, H., Kim, J. H., Adiya, S., Lee, C. H. (2000). "Approaches to membrane fouling control in anaerobic membrane bioreactors." Water Science and Technology 41(10-11): 363-371.

Dalmacija, B., Karlovic, E., Tamas, Z., Miskovic, D. (1996). "Purification of high-salinity wastewater by activated sludge process." Water Research 30(2): 295-298.

Fan, F. S., Zhou, H. D., Husain, H. (2006). "Identification of wastewater sludge characteristics to predict critical flux for membrane bioreactor processes." Water Research 40(2): 205-212.

Gui, P., Huang, X., Chen, Y., Qian, Y. (2003). "Effect of operational parameters on sludge accumulation on membrane surfaces in a submerged membrane bioreactor." Desalination 151(2): 185-194.

Hu, A. Y., Stuckey, D. C. (2007). "Activated carbon addition to a submerged anaerobic membrane bioreactor: Effect on performance, transmembrane pressure, and flux." Journal of Environmental Engineering-ASCE 133(1): 73-80.

Huang, X., Gui, P., Qian, Y. (2001). "Effect of sludge retention time on microbial behavior in a submerged membrane bioreactor." Process Biochemistry 36(10): 1001-1006.

Janks, J. S., Cadena, F. (1992). "Investigations into the Use of Modified Zeolites for Removing Benzene, Toluene, and Xylene From Saline Produced Water". Produced Water. F. R. E. J.P.Ray. New York, NY, Plenum Press: 473-487.

Jefferson, B., Laine, A. L., Judd, S. L., Stephenson, T. (2000). "Membrane bioreactors and their role in wastewater reuse." Water Science and Technology 41(1): 197-204.

Kishino, H., Ishida, H., Iwabu, H., Nakano, I. (1996). "Domestic wastewater reuse using a submerged membrane bioreactor." Desalination 106(1-3): 115-119.

Lee, J., Ahn, W. Y., Lee, C. H. (2001). "Comparison of the filtration characteristics between attached and suspended growth microorganisms in submerged membrane bioreactor." Water Research 35(10): 2435-2445.

Kwon, S., (2007). "Biological Pretreatment of Produced Water for Reuse Applications" Doctoral Dissertation, University of Texas at Austin, Department of Civil Engineering, December, 2007, 190 pp.

Li, Z. H., Bowman, R. S. (1998). "Sorption of perchloroethylene by surfactant-modified zeolite as controlled by surfactant loading." Environmental Science & Technology 32(15): 2278-2282.

Li, Z. H., Bowman, R. S. (2001). "Regeneration of surfactant-modified zeolite after saturation with chromate and perchloroethylene." Water Research 35(1): 322-326.

Lin, C. K., Tsai, T. Y., Liu, J. C., Chen, M. C. (2001). "Enhanced biodegradation of petrochemical wastewater using ozonation and BAC advanced treatment system." Water Research 35(3): 699-704.

Marrot, B., Barrios-Martinez, A., Moulin, P., Roche, N. (2004). "Industrial wastewater treatment in a membrane bioreactor: A review." Environmental Progress 23(1): 59-68.

Mochidzuki, K., Takeuchi, Y. (1999). "The effects of some inhibitory components on biological activated carbon processes." Water Research 33(11): 2609-2616.

Neel, D., Bowman, R.S. (1992). "Sorption of organics to surface-altered zeolites". 36th Annual New Mexico Water Conference, Las Cruces, N.M, New Mexico Water Resources Research Institute.

Ng, C. A. S., D., Fane, A. G. (2006). "Operation of membrane bioreactor with powdered activated carbon addition." Separation Science and Technology 41(7): 1447-1466.

Ognier, S., Wisniewski, C., Grasmick, A. (2002). "Characterisation and modelling of fouling in membrane bioreactors." Desalination 146(1-3): 141-147.

Park, H., Choo, K. H., Lee, C. H. (1999). "Flux enhancement with powdered activated carbon addition in the membrane anaerobic bioreactor." Separation Science and Technology 34(14): 2781-2792.

Ranck, J. M., Bowman, R. S., Weeber, J. L., Katz, L. E., Sullivan, E. J. (2005). "BTEX removal from produced water using surfactant-modified zeolite." Journal of Environmental Engineering-ASCE 131(3): 434-442.

Rosenberger, S., Kraume, M. (2003). "Filterability of activated sludge in membrane bioreactors." Desalination 151(2): 195-200.

Scholz, W. G., Rouge, P., Bodalo, A., Leitz, U. (2005). "Desalination of mixed tannery effluent with membrane bioreactor and reverse osmosis treatment." Environmental Science & Technology 39(21): 8505-8511.

Seo, G. T., Ahan, H. I., Kim, J. T., Lee, Y. J., Kim, I. S. (2004). "Domestic wastewater reclamation by submerged membrane bioreactor with high concentration powdered activated carbon for stream restoration." Water Science and Technology 50(2): 173-178.

Sofia, A., Ng, W. J., Ong, S. L. (2004). "Engineering design approaches for minimum fouling in submerged MBR." Desalination 160(1): 67-74.

Sperandio, M., Masse, A., Espinosa-Bouchot, M. C., Cabassud, C. (2005). "Characterization of sludge structure and activity in submerged membrane bioreactor." Water Science and Technology 52(10-11): 401-408.

Tellez, G. T., Nirmalakhandan, N., Gardea-Torresdey, J. L. (2005). "Kinetic evaluation of a field-scale activated sludge system for removing petroleum hydrocarbons from oilfield-produced water." Environmental Progress 24(1): 96-104.

Visvanathan, C., Yang, B. S., Muttamara, S., Maythanukhraw, R. (1997). "Application of air backflushing technique in membrane bioreactor." Water Science and Technology 36(12): 259-266.

Yamamoto, K., Hiasa, M., Mahmood, T., Matsuo, T. (1989). "Direct Solid-Liquid Separation Using Hollow Fiber Membrane in an Activated-Sludge Aeration Tank." Water Science and Technology 21(4-5): 43-54.

Yang, W. B., Cicek, N., Ilg, J. (2006). "State-of-the-art of membrane bioreactors: Worldwide research and commercial applications in North America." Journal of Membrane Science 270(1-2): 201-211.

Yoon, S. H., Collins, J. H., Musale, D., Sundararajan, S., Tsai, S. P., Hallsby, G. A., Kong, J. F., Koppes, J., Cachia, P. (2005). "Effects of flux enhancing polymer on the characteristics of sludge in membrane bioreactor process." Water Science and Technology 51(6-7): 151-157.

Acknowledgements