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Aluminum electrocoagulation followed by forward osmosis for treating hydraulic fracturing produced waters

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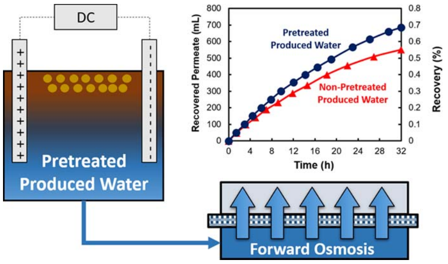
GRAPHICAL ABSTRACT



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ABSTRACT

Forward osmosis is an emerging membrane based separation technology that could find niche applications in the treatment of oil and gas produced water. Here, the feasibility of treating hydraulic fracturing produced waters using a combined electrocoagulation (EC) and forward osmosis (FO) process has been investigated. EC is shown to be effective in removing suspended solids and organic compounds which foul the membrane during FO. The amount of suspended solids and organic compounds that are removed depends on the EC reaction time. By accounting for internal and external concentration polarization as well as fouling due to deposition on the feed side barrier surface of the FO membrane, the expected flux may be determined. The effectiveness of removal of suspended solids and organic compounds may be modeled as changes in the permeability of the foulant layer that develops on the feed side of the membrane. The results obtained for real produced waters from Southwestern Energy operations in the Fayetteville Shale indicate that combined EC and FO could be an effective method for water recovery from hydraulic fracturing produced waters.

1. Introduction

Freshwater is a fundamental resource and integral to all ecological and societal activities. Improper wastewater discharge can adversely affect nearby communities and ecosystems [1]. Produced water is a by-product from oil and gas recovery operations. Often produced waters are highly impaired containing organic and inorganic contaminants. Development of cost-effective treatment processes for produced waters is of tremendous societal importance due to significant possibility of surface and underground water and soil pollution [2]. This is especially important for development of unconventional gas reservoirs, including coalbed methane, tight gas and shale gas [3]. Here we focus on hydraulic fracturing operations.

Economically viable gas production from shale reserves is achieved by horizontal drilling followed by hydraulic fracturing [4]. Hydraulic fracturing is a stimulation technique used to increase oil and gas

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production from shale and underground rock formations [5]. Hydraulic fracturing flowback water, a subset of produced water, is defined as the stream returning to the surface after the hydraulic fracturing process. This stream is often highly impaired containing hazardous organic and inorganic constituents. The concentration of total dissolved solids (TDS) in these streams can vary between about 13,000 to 400,000 mg L^{-1} [6,7]. Thus, treatment of these produced waters is critical for developing economically viable hydraulic fracturing operations.

Treatment of highly impaired produced waters is challenging given the very high TDS as well as the presence of dissolved organic contaminants. Membrane based separation technologies such as microfiltration, ultrafiltration and nanofiltration are routinely used for treatment of wastewater [8]. In addition, reverse osmosis (RO) is used for desalination of seawater to produce drinking water [9]. RO is a very effective and applicable desalination process for treatment of low TDS waters (TDS $<$ 47,000 mg L^{-1}) [10]. However, membrane fouling and scaling is a primary concern when operating RO systems [10,11]. The feed water requires rigorous pre-treatment to prevent fouling of the reverse osmosis membrane [11,12]. Many new processes involving osmotically and thermally driven membrane technologies are being investigated for desalination of highly impaired wastewaters [9–13]. Here we consider forward osmosis.

Osmosis is defined as the net movement of water across a selectively permeable membrane driven by a difference in osmotic pressure across the membrane [14]. In FO, a draw solution having a significantly higher osmotic pressure than the produced water flows on the permeate side of the membrane. Due to the osmotic pressure gradient water flows from the feed to the draw solution [15]. Using dense non-porous membranes with rejection properties similar to reverse osmosis membranes, the feed solution is concentrated and the draw solution diluted [14,15]. The advantages of FO include a high rate of water recovery, minimization of brine discharge, low fouling and low energy consumption [16]. However, the viability of FO depends on efficient regeneration of the draw solution. The availability of low-grade waste heat during oil and gas production provides the possibility of using a thermolytic salt such as NH_4HCO_3, as a draw solute, which can be easily regenerated by heating. Alternatively, nanofiltration or RO may be used to concentrate the draw solution. Ge et al. [16] highlighted the importance of optimizing the draw solute.

FO can be a very promising process for treating produced water streams especially as low-grade waste heat is often present to aid in regenerating the FO draw solution. Unlike RO, FO does not require the use of large hydraulic pressures [17]. FO can operate in harsh conditions (on-site) with minimal access to electric power and supplies [11]. Mazlan et al. [18] indicated that there is effectively no difference in specific energy consumption between FO combined with nanofiltration for draw solution recovery and RO treatment of produced waters.

Although there is no pressure driven convection of rejected species towards the membrane in FO, internal concentration polarization (CP) leads to reduced rates of water recovery. Internal CP combined with the presence of small, highly fouling organic species can lead to significant flux decline due to fouling when treating produced waters [19]. Maltos et al. [20] reported major fouling of FO membranes while treating raw produced water. Thus, pretreatment of the produced water prior to FO is essential.

Numerous pretreatment processes have been considered prior to membrane filtration [21]. Biological pretreatment is impractical for treating hydraulic fracturing produced waters due to long retention times and the low biodegradability of most of the contaminants [22]. Coagulation, adsorption, preoxidation and prefiltration are among the most popular pretreatment methods prior to membrane filtration [23]. Chemical pretreatment such as coagulation is frequently used to remove colloidal and organic matter [23]. Here we focus on Electrocoagulation (EC) for removal of colloidal and dissolved organic compounds that could foul the FO membrane.

EC is an electrochemical method for treating polluted water whereby sacrificial anodes corrode to release active coagulant precursors into solution [24]. Compared to chemical coagulation (e.g., using alum), EC provides a number of advantages including simple equipment, easy operation, less maintenance, colorless and odorless effluent, low sludge production and efficient removal of colloidal particles. Flocs formed by EC are similar to chemical flocs, except that EC flocs tend to be much larger, contain less bound water, are acid-resistant and more stable, and therefore, can be separated faster [25,26]. Further, in EC there are no moving parts, thus requiring less maintenance compared to coagulation where efficient mixing is required. Use of electricity, which can be expensive in many places, and regular replacement of sacrificial electrodes are two major disadvantages of EC technology [25,27,28]. However, Kobya et al. [25] indicated that electrical energy consumption decreases dramatically when the wastewater has higher conductivity due to the presence of dissolved salts. In case of hydraulic fracturing produced waters, the conductivity is high due to high TDS.

In this study, and for the first time, we investigate the impact of produced water pretreatment via EC prior to FO for fouling mitigation and water recovery. We design and develop an EC system as a pretreatment operation prior to FO.

2. Theory

2.1. Mass transfer in FO system

The FO water flux may be represented by [29]:

$$J_w = A\,(\Pi_{Db} - \Pi_{Fb}) \tag{1}$$

where J_w is water flux across the membrane, A is the pure water permeability coefficient, Π_{Db} and Π_{Fb} are the osmotic pressures of the bulk draw and feed solution respectively. The pure water permeability coefficient will depend on the resistance to water flow through the membrane. In reality, CP compromises performance. Fig. 1 shows the effect of CP on the osmotic pressure across the membrane.

In FO, the high ionic strength draw solution is pumped parallel to the membrane support structure. External CP, leading to boundary layer formation adjacent to the support structure, will dilute the draw solute relative to the bulk solution. Consequently, the value of Π_{Db} will be higher than the osmotic pressure at the external surface of the support structure. Further, internal CP will occur within the support structure which will lead to a further dilution of the draw solute. This will lead to a further decrease in the osmotic pressure of the draw solute at the internal surface of the membrane barrier layer relative to Π_{Db}. On the feed side of the membrane, an external CP boundary layer will form leading to an increase in the solute concentration of the feed at the membrane surface relative to the bulk feed. This will lead to an increase in the osmotic pressure of the feed relative to Π_{Fb} [30].

Fig. 1(a) shows the variation of osmotic pressure across the membrane for a de-ionized (DI) water feed stream and a high concentration NaCl draw solution. A reverse salt flux from the draw to the feed side is included [30]. However, it is assumed that the reverse salt flux is low; therefore, there is no external CP boundary layer on the feed side. Fig. 1(b) shows the variation of osmotic pressure across the membrane when the feed consists of NaCl in DI water. This feed stream is referred to as synthetic produced water. Due to the presence of NaCl in the feed solution, an external CP boundary layer develops on the feed side of the membrane. As can be seen, the presence of internal and external CP will lead to a decrease in the osmotic pressure difference across the membrane which in turn will lead to a reduced flux.

In the case of real feed streams, fouling of the membrane by deposition of suspended solutes and dissolved organic compounds, will further compromise the permeate flux [31]. Fig. 1(c) shows the variation of osmotic pressure for a raw produced water feed stream and a draw solution consisting of NaCl in DI water. The fouling of the feed side of the membrane due to deposition of suspend solids and dissolved