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Sulfur-containing air pollutants as draw solution for fertilizer drawn forward osmosis desalination process for irrigation use

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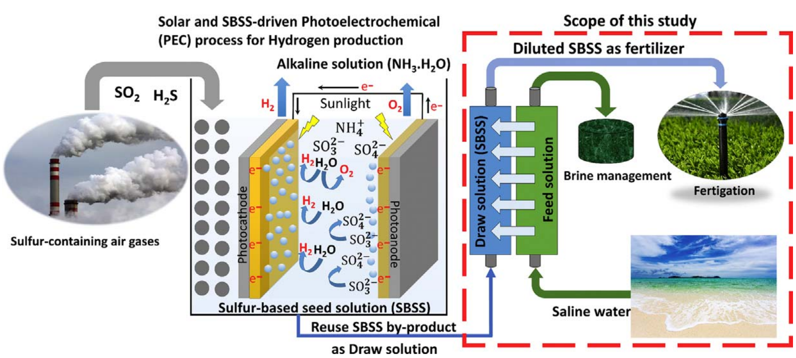
GRAPHICAL ABSTRACT



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ABSTRACT

This study investigated suitability and performance of the sulfur-based seed solution (SBSS) as a draw solution (DS), a byproduct taken from the photoelectrochemical (PEC) process where the SBSS is used as an electrolyte for H_2 production. This SBSS DS is composed of a mixture of ammonium sulfate ($(NH_4)_2SO_4$) and ammonium sulfite ($(NH_4)_2SO_3$), and it can be utilized as fertilizer for fertilizer drawn forward osmosis (FDFO) desalination of saline water. The FDFO process employed with thin-film composite (TFC) membrane and showed that the process performance (i.e. water flux and reverse salt flux) is better than that with cellulose triacetate (CTA) membrane. In addition, it produced high water flux of 19 LMH using SBSS as DS at equivalent concentration at 1 M and 5 g/L NaCl of feed solution (model saline water). Experimental results showed that the reverse salt flux of SBSS increased with the increase in pH of the DS and that lowering the concentration of ammonium sulfite in the SBSS led to the higher water flux of feed solution. The result also demonstrated that this SBSS is practically suitable for the FDFO process toward development of water-energy-food nexus technology using sulfur chemicals-containing air pollutant.

1. Introduction

The world's population is growing rapidly and so are the issues related to fresh water, food and energy significantly affecting the global economies [1,2]. Among three elements in the energy-water-food nexus, water is perhaps the most essential part for enhancing agriculture's productivity and hence global food security. Agriculture sector uses over 70% of the world's total fresh water consumption [3].

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Nevertheless, water stress has been a severe issue for decades in many regions in our planet. The impact of climate change is further worsening the water stress such as through unpredictable rainfall events, extreme weather conditions and frequent drought [4–6].

Many attempts have been made to develop technologies and water management policies to combat water issues by using alternatives such as impaired water and unlimited saline water resources [2]. Desalination is one of the most reliable technologies for augmentation of limited fresh water sources [2]. While desalination is used for potable water supplies including for some industrial applications, it is still not a viable option for irrigation where the water requirement is huge. Currently available desalination technologies including reverse osmosis (RO) and thermal based processes are high capital and energy intensive [7–10] albeit significant improvement in membrane and energy efficiency has been made in the last few decades. Since energy, water and environment issues are all interconnected [9,10], it is vitally important for any desalination technology to have significantly lower energy consumption especially for large-scale irrigation purpose. For arid countries such as Qatar, Australia where there is abundant of brackish groundwater in the inland areas and seawater along the coastal areas, the availability and wide-range application of low cost desalination technologies might have substantial impacts on agriculture sector.

Forward osmosis (FO) has recently emerged as a novel process for various applications including for desalination. FO process is driven by the natural osmotic process without the need of high hydraulic pressure as for the RO process and hence the power consumption of FO process itself is much lower than the RO process although they use similar salt rejecting membranes [9,11–15]. In FO process, the main driving force is generated from the intrinsic osmotic pressure differential between the draw solution (DS) and the feed solution (FS) when separated by a semi-permeable membrane. DS plays a pivotal role in FO process since it is the primary source of net driving force across the membrane. The FO process therefore converts saline water sources into the diluted DS instead of pure water and hence post-treatment processes are necessary to obtain pure water for potable purpose. One of major challenges of the FO process however is the lack of appropriate draw solute [16]. The separation and regeneration of draw solutes from the diluted DS to obtain pure water and reuse of concentrated draw solute is complex which not only requires additional process but also requires significant energy. The ease and efficiency of DS recovery and separation will be the primary factors for the success of FO desalination in the future for portable applications [17]. However, if desalinated water can be put into use directly without the need for separation and regeneration of DS, FO has considerable advantage over RO desalination technology. Several small-scale applications have been developed based on this concept such as hydration bags for nutritious drinks useful in emergencies or in the boats [18].

However, one of the most practical and novel applications of the FO process is in the desalination for irrigation purpose using concentrated fertilizers as DS. The diluted fertilizer DS can be used directly for fertigation without recovery and regeneration of DS. This fertilizer drawn forward osmosis (FDFO) desalination process [16,19] can use any commercially available soluble fertilizers as DS to produce high osmotic pressures that is able to extract pure water from the FS having low osmotic pressure. As the fertilizer nutrients are essential for plants, the need for draw solute separation and regeneration is avoided and hence saving energy for post-treatment [20]. Recently, the application of FDFO process has been examined for the desalination of brackish groundwater [20] and seawater [16,19] with promising results that FDFO can be extensively applied for fertigation.

With this vein, this study has explored to find appropriate DS to meet the global demand for sufficient food supply with less water usage and low energy consumption for fertigation under the category of development of water-energy-food nexus technology. Here, we used sulfur-containing chemical solutions that can be made by sulfur-containing air pollutants (e.g., SO_2).

One of the major air polluting gases released from the thermal power plants is the sulfur dioxide (SO_2). In the past decades, a huge amount of SO_2 is emitted into the atmosphere because of the increasing rate of burning the coal and other fossil fuel for energy [21]. The emission of SO_2 has resulted in serious environmental problems, such as acid rain and fine particles that can have a significant impact on the human health and the environment. There have been many in-situ pretreatment methods widely employed to lessen the emission of these polluting gases and to protect the global environment. Among these methods, SO_2 has been captured to produce wallboard (gypsum) [22,23], sulfuric acid and fertilizer [24]. Recently, Han and his colleagues [25] have proposed a new method to remove SO_2 and simultaneously produce renewable and clean hydrogen energy. A sulfur-based seed solution (SBSS) is made of byproduct of ammonia-based desulfurization process or purging SO_2 into alkaline-based (sodium hydroxide) solution. Consequently, removal of SO_2 in this SBSS solution occurs using a photoelectrochemical (PEC) process. In this PEC process, water molecules are split into oxygen and hydrogen gases under sunlight. This technology is considered one of the most advanced technologies to produce renewable and clean hydrogen. The experimental results from a study done by Han and his colleagues showed a very high removal ($>$ 97%) of SO_2 and successful production of hydrogen energy, simultaneously [25].

There are two main compounds formed at gas-dissolution reactor of ammonia-based desulfurization process when SO_2 is dissolved into ammonia-based solution are ammonium sulfate (SOA - $(NH_4)_2SO_4$), and ammonium sulfite (SIOA - $(NH_4)_2SO_3$). The solution can then be employed for the PEC system. SIOA can also be oxidized to SOA during PEC process:

$$(NH_4)_2SO_3(aq) + H_2O + \text{PEC process} + \text{sunlight} \rightarrow H_2\uparrow + (NH_4)_2SO_4$$

PEC water splitting process works as a concentrating process where SBSS is gradually concentrated, therefore, SBSS after going through PEC system, becomes highly concentrated ($>$ 2 mol/L) [26], meaning it can create high osmotic pressure and can be used in FDFO desalination process. It is highly likely that the composition of SOA and SIOA may vary during the H_2 production by the PEC system or the FO process. While SOA is a commonly used fertilizer and found that SOA is one of the most suitable fertilizers for FDFO desalination [16,27], the performance of the SIOA has not studied yet. It is therefore important to understand how this might affect the performance of the FDFO desalination process (Fig. 1).

As these two advanced technologies (PEC water splitting process and FDFO) have been proved to be compromising ones, the concept of this research is integrating the production of renewable and clean hydrogen energy and water for food production.

The main objective of this study is to evaluate the feasibility of using SBSS – a by-product from PEC process as a fertilizer DS for the desalination of saline water by FDFO process for irrigation. The study examines the effect of SBSS on FDFO desalination of saline water by using SBSS draw solutions containing different ratios of SOA and SIOA.

2. Materials and methods

2.1. Forward osmosis experimental set up

This current study used a bench-scale FO set up (Fig. 2), similar to the one used in the earlier studies [16]. The cross-flow membrane unit consists of an FO cell with channels sizes (77 mm length × 26 mm width × 3 mm depth) on both sides of the membrane to allow feed water to flow on active side of the membrane and draw solution on the support side of the membrane. Two types of commercial FO membranes were used in the experimental studies: cellulose triacetate (CTA) and thin-film composite (TFC) polyamide supplied by Hydro Technologies Inc. (HTI) and Toray Industries, Inc. (Toray) respectively. Two variable speed gear pumps (Cole Palmer model 75211-15, 50-5000 RPM and

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