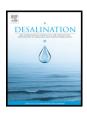
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Water desalination using visible light by disperse red 1 modified PTFE membrane



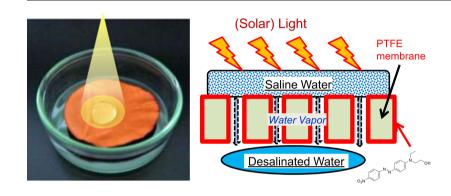
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HIGHLIGHTS

- Water permeated through DR1 modified PTFE membrane by visible light irradiation.
- Water penetration through the membrane took place with photo isomerization of DR1.
- Desalination of NaCl solution was achieved by the light induced membrane permeation.
- Simulated solar light from solar simulator was effective for the water desalination.

GRAPHICAL ABSTRACT



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ABSTRACT

Water purification and seawater desalination are current desired technologies because global water shortage becomes more serious. As this problem is related to global warming, the energy for the processes should be covered by renewable energies like solar light. It was found recently that water droplets on azobenzene modified anodized alumina membranes permeate the membrane under light irradiation to be purified and desalinated. This paper reports an advanced system of the light induced water treatment, where disperse red 1 (DR1) modified PTFE (polytetrafluoroethylene) membranes are employed. Hydrophobic PTFE membrane inhibits the natural infiltration of raw water into the membrane to prevent the contamination of treated water. Disperse red 1 photoisomerizes only with visible light to adopt to the utilization of solar light. Waters on the DR1 modified PTFE membrane penetrated the membrane under visible light irradiation. 3.5% NaCl solution was desalinated to purified water (<0.01% NaCl) by the membrane permeation process. A simulated solar light of a solar simulator was very effective for this desalination to produce clarified water from an artificial seawater. These results indicate that solar desalination is realizable with the DR1 modified PTFE membrane by the direct irradiation of solar light to the membrane.

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1. Introduction

Water purification and seawater desalination are now globally important technologies. As the shortage of fresh water is involved with global warming (climate change) by the consumption of fossil fuels and the resulting carbon dioxide emission, renewable energies,

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especially solar light, free from fossil fuels should be employed for these water treatments [1–4]. Recently, the energy of light is actively applied to water purification processes using light-to-heat conversion materials, which promote the steam generation by water evaporation under light irradiation [5–11]. For example, Au plasmonic nanoparticle enables localized heating and efficient water evaporation [6]. Titanium nitride nanoparticles as a lossy plasmonic nano-resonator are reported to be more active than gold nanoparticles for light induced steam generation [7]. Carbon materials based fluids are also claimed to be effective for the direct vapor generation with solar light [8]. As the steams thus formed by water evaporation must be recovered from the plate located above water pools containing these heating materials, the corresponding water purification apparatuses are essentially regarded as variations of solar still system, which generally requires complicated equipments to collect vaporized and condensed water [12,13]. The purified water condensed on the undersurface of transparent plate above raw water must be recovered carefully without its dripping into the raw water. This complicated operation is thought to prohibit the progress of the solar still. Membrane materials are also studied for the heat generation under light irradiation. For example, photo thermal membranes based on poly-pyrrole coated stainless steel mesh [9] and three layered membranes consisting TiO₂ nanoparticles, Au nanoparticles and anodized aluminum oxides [10] are studied for vapor generation. Double-layer structure consisting of a carbon foam layer supporting an exfoliated graphite layer is active for vapor generation as well [11]. However, even in these cases, no water vapors produced by the heating processes penetrate the membranes, and the recovery manners of the treated waters are essentially similar to the solar still [1-4,12,13]. Therefore, simpler systems of purified water production, especially in the recovery of the treated water, are desired for the practical water treatments with

The application of azobenzene modified materials to control mass transport and diffusion under light irradiation are previously reported [14,15]. For example, the release of cholesterol from an azobenzenetethered mesoporous silica powder is promoted by the simultaneous irradiation of UV and visible lights [14]. The flow rate of organic solvents through an azobenzene modified silica gel column can be accelerated by the same simultaneous light irradiation [15]. The UV and visible lights isomerize the azobenzene molecules from trans to cis isomer and from cis to trans isomer, respectively. The simultaneous irradiation of these two lights induces the repetitive photo isomerization of the azobenzene between the trans and cis isomer in the small spaces of silica pores, activating the movement of nearby molecules to enhance their transfer. Although the molecular motions of azobenzene derivatives are well utilized for some intelligent and functional materials [16–18], the applications of these repetitive photo isomerizations are not so often reported [19–21]. Recently, azobenzene modified anodized alumina membranes were employed for a light promoted mass transfer [22]. When a water droplet on the azobenzene modified membrane was exposed to UV and visible lights, a certain volume of the water was recovered under the membrane by membrane penetration, while no water permeation occurred without the UV and visible lights irradiation. It is thought that the repetitive photo isomerization of azobenzene elicited by the simultaneous irradiation provokes the evaporation of the water to result in the membrane permeation of water. When the solutions of rhodamine B and NaCl were used in the light induced membrane permeation, the penetrated waters were purified or desalinated. No rhodamine B was contained in the treated water and the salt water was converted into fresh water. From these results, an installation of seawater desalination using the azobenzene modified membrane under solar light irradiation was proposed in the paper [22]. Fig. 1 illustrates the concept of this system that seawater in a pool on an azobenzene modified membrane is exposed to solar light to produce purified desalinated water under the membrane, which is readily collected in the container under the membrane. In this system, the energy for seawater desalination is provided from solar light.

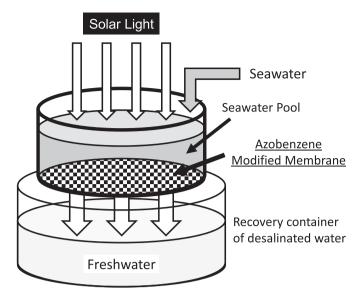


Fig. 1. A proposed membrane seawater desalination equipment using solar light energy.

In the system of Fig. 1, the natural dropping-down of seawater through the membrane must be avoided for preventing the contamination of the desalinated water under the membrane. In this point, the anodized alumina membrane is not suitable because of its hydrophilic and fragile property. The hydrophilicity facilitates the natural droppingdown of raw water and the fragility is unfavorable in large scale systems. On the other hand, 4-phenylazophenol mainly employed as the azobenzene compound in the previous paper [22] is inappropriate in the system of Fig. 1 using solar light, because its photo isomerization from trans to cis isomer requires UV light with wavelength of 350 nm that is scarcely contained in solar light. Then, this paper reports an improved light induced water treatment process, where PTFE (polytetrafluoroethylene) membrane that is highly hydrophobic and more robust than the anodized alumina membrane and disperse red 1 (DR1) that photo-isomerizes only with visible light of wavelength from 420 to 550 nm (Fig. 2) [23–27] were employed as alternative membrane and azobenzene compound, respectively. DR1 is known as a water-insoluble azobenzene dye, which is profitable for preventing the contamination of treated water with DR1. This paper also presents the desalination of 3.5% NaCl solution and an artificial seawater using the DR1 modified PTFE membrane under a simulated solar light, which is an important step toward the direct solar desalination using the system shown in Fig. 1.

2. Experimental section

2.1. Materials

Polytetrafluoroethylene (PTFE) membranes used in this study were Advantec PTFE membrane filters from Toyo Roshi Kaisha, 47 mm in diameter and 0.8 µm or 3.0 µm of pore size. Polyethersulfone (PES) membrane was PES membrane filter of As One Corporation (47 mm in diameter). Disperse red 1 [N-ethyl-N-(2-hydroxyethyl)-4-(4-nitrophenylazo)aniline] (Fig. 2) was purchased from Sigma-Aldrich Co. LLC. MARINE ART SF-1 for artificial seawater [28] was bought from Osaka Yakken Co., Ltd. Other organic reagents and NaCl (special grade) were obtained from Wako Pure Chemical Industries, Ltd.

2.2. Preparation of disperse red 1 modified membranes

After wetting a sheet of PTFE membrane filter with isopropanol, 2 mL of 0.1 g/mL solution of disperse red 1 (DR1) in DMF (N,N-dimethylformamide) was embrocated to the membrane filter in a

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