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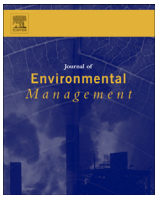

Research article

Application of saponin biosurfactant and its recovery in the MEUF process for removal of methyl violet from wastewater

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ABSTRACT

The potential of saponin, a biosurfactant, in the micellar enhanced ultrafiltration (MEUF) process was tested systematically for removal of methyl violet from wastewater. For this, the aqueous extract of reetha (*Sapindus mukorossi*) pericarp which contains saponin was used as the biosurfactant. First, the micellar solubilization of methyl violet in saponin micelles was investigated in terms of molar solubilization power (*SP*) of saponin. It was observed that the adsorption of methyl violet on the agglomerates of saponin micelles was mainly responsible for the enhanced solubilization. The Gibbs free energy of solubilization (calculated as -29.63 kJ mol^{-1}) suggested that process was feasible and spontaneous. The MEUF experiments were performed in batch as well as continuous mode using saponin biosurfactant, and the effect of operating parameters on permeate flux and solute retention were evaluated. The removal of methyl violet in MEUF process was >99% achieved with 10 kDa polyethersulfone (PES) membrane for feed dye concentration of 250 mg L^{-1} at studied conditions. Finally, the saponin in permeate was recovered using n-heptane and n-butanol by solvent extraction process. The solvent *n*-butanol showed better extraction efficiency as compared to n-heptane for saponin extraction.

1. Introduction

Dyes are one of the major class of pollutants in the aqueous system coming directly from various industries such as textile, dyeing, cosmetics, printing, etc. The treatment of dye-contaminated wastewater has been one of the important environmental problems due to their hazardous nature (Verma et al., 2012; Salleh et al., 2011). The removal of dyes from the aqueous system has been studied using various wastewater treatment methods such as adsorption, biological treatment, ozone treatment, coagulation, photocatalytic degradation processes, chemical oxidation and membrane processes (Holkar et al., 2016; Brillas and Martínez-Huitle, 2015; Dasgupta et al., 2015). But, their application is limited due to their disadvantages such as secondary pollution by byproduct formation, expensive or inefficient process (Yagub et al., 2014). On the other hand, the membrane integrated process such as micellar enhanced ultrafiltration (MEUF) process has shown advantages of high removal efficiency, high permeate flux, and lower energy consumption as compared to individual membrane processes (Shah et al., 2016; Purkait et al., 2004).

The micellar enhanced ultrafiltration technique utilizes the binding ability of a surfactant after a certain concentration called critical micelle concentration (CMC), to increase the hydrodynamic size of smaller solute so that they can be rejected by an ultrafiltration membrane (Purkait et al., 2004). The micelles of surfactant containing hydrophobic tail and hydrophilic head have the ability to bind the solute depending on the nature of solute and surfactant. The MEUF processes have been used frequently for the removal of various pollutants, such as dyes, heavy metal ions, pesticides, organic and inorganic compounds from aqueous systems using different surfactants (Shah et al., 2016; Purkait et al., 2004). The selection of surfactant is an important aspect of the MEUF process which depends on the nature of the solute to be separated. In the past, a numerous anionic surfactants, cationic surfactants, nonionic surfactants ionic-nonionic mixed surfactants were used in different MEUF processes (Schwarze, 2017; Das et al., 2008). Most of them have been chemically synthesized which are less biodegradable or persistent and may cause chronic toxicity and estrogenic activity (Pradhan and Bhattacharyya, 2017). In MEUF, the used surfactant remains in permeate stream at a high concentration which creates secondary pollution. Therefore,

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before disposing them to a water body, recovery or removal of these surfactants from permeate stream is necessary. However, very few researchers have focused on the recovery of surfactant in the MEUF process. The surfactants in MEUF were recovered by integrating various technologies, such as precipitation by counter ion, lowering the temperature below Kriff pint, foam fractionation and electrochemical treatment (Purkait et al., 2004; Huang et al., 2017). But, the application of these processes was limited due to the complex nature of the process, the lower recovery rate of the surfactant, inevitable damage to micelle molecules, and reduced surfactant efficiency after recovery.

In contrast to chemically synthesized surfactants, natural surfactants such as saponin have gained the significant interest of researchers, since it is biodegradable, renewable, environmentally safe as well as ecologically adaptable (Pradhan and Bhattacharyya, 2017; Schmitt et al., 2014). Saponins are mainly secondary metabolite present in various plant fruit seed, pericarp, root, leaf, bark, and flower. More than 100 families of plants and few marine sources have been reported for the occurrence of saponins (Cheok et al., 2014). The *Sapindus mukurossi,* also known as ritha, reetha or soapnut is a major source of saponin, is a widely distributed plant in India and other sub continent of Asia. The previous reports on saponin were mainly focused on the identification, extraction, quantification, and characterization of saponin (Cheok et al., 2014; Bottcher and Drusch, 2017; Li et al., 2013; Heng et al., 2014; Güçlü-Ustündağ and Mazza, 2007). Very few literature were found reporting the application of saponin surfactant in the various process such as soil washing (Zhou et al., 2013; Mukhopadhyay et al., 2015), surfactant enhanced oil recovery (Chhetri et al., 2009), solubilization of dyes (Samal et al., 2017) and synthesis of nanoparticles (Rao and Paria, 2015), etc. All these studies have mentioned about the adequate micellar property, solubilization performance and eco-friendly nature of saponin which motivated us to utilize it in the MEUF process. Further, the review of the literature suggested that the utilization of biosurfactant saponin in MEUF process was unexplored.

The present study demonstrates the application of an eco-friendly biosurfactant (saponin) in micellar enhanced ultrafiltration process for removal of methyl violet dye from wastewater. The micellar solubilization of methyl violet by saponin micelle was examined in the aqueous solution of saponin at various saponin concentrations. The effect of solution pH and the addition of NaCl salt in surfactant solution on dye solubility was tested. The dye solubilization capacity of saponin micelle was calculated in terms of molar solubilization power (*SP*), partition coefficient (K_m). Thermodynamic property of solubilization process, the Gibbs free energy of solubilization (ΔG) was also calculated. The micelle shape was observed under an optical microscope, and the size of saponin micelle and dye solubilized micelle were measured. The feasibility of MEUF process using saponin as a surfactant was tested in a dead end batch cell using polyethersulfone (PES) membranes of different molecular weight cut-off (MWCO). The initial trials were done to investigate the effect of a change in saponin and dye concentration, transmembrane pressure drop, pH, NaCl salt concentration on permeate flux, dye and saponin retention. Then, for an extended operation and continuous separation, the MEUF experiments were performed in the continuous cross flow cell, in full recycle mode. The variation in permeate flux and solute retention with cross flow velocity, transmembrane pressure drop, and feed composition were evaluated. The recovery of surfactant is an important aspect of any MEUF process; therefore, recovery of saponin was also attempted by solvent extraction process using n-heptane and n-butanol as a solvent.

2. Materials and methods

2.1. Chemicals

Methyl violet ($C_{25}H_{30}ClN_3$; MW: 407.99; λ_{max}: 571 nm) was procured from HiMedia Laboratories Pvt. Ltd., India. Saponin purified was obtained from Loba Chemie, India, reetha fruits were collected from local market of Basna, India. The other chemicals, such as NaCl (Merck, India), NaOH (Rankem, India) and HCl (Rankem, India), n-heptane (Merck, India), n-butanol (Merck, India) were used as received. Deionized water was used as a solvent for all the experiments. The synthetic feed was prepared by dissolving an appropriate amount of dye in water.

2.2. Membranes

The flat sheet polyethersulfone (PES) membranes having MWCO of 10, 20, 30, and 50 kDa were purchased from M/s Permionics Membranes Pvt. Ltd., Gujarat, India and used without any further modification. Each fresh membrane was compacted using deionized water at a pressure of 500 kPa for 4 h before utilized in the experiments. The membrane permeability was calculated using the standard procedure to be 3.81×10^{-11} m s^{-1} Pa^{-1}, 4.97×10^{-11} m s^{-1} Pa^{-1}, 7.61×10^{-11} m s^{-1} Pa^{-1}, 1×10^{-10} m s^{-1} Pa^{-1} for membrane MWCO of 10, 20, 30, and 50 kDa respectively.

2.3. Biosurfactant

The biosurfactant saponin was extracted from the pericarp of dried reetha (*Sapindus mukorossi*) fruit using water as a solvent and used in the MEUF experiments. The extraction of saponin from reetha pericarp and its characterization is reported in our previous work Samal et al. (2017). The aqueous reetha was used as surfactant solution, and it is termed as aqueous reetha solution (ARS) in this report.

2.4. Experimental setup

2.4.1. Batch cell

The unstirred batch experiments were conducted in 350 mL ultrafiltration batch cell which can accommodate a membrane over a base support having a diameter of 80 mm. The effective membrane area was 4.3×10^{-3} m^2. The cell was equipped with a compressor for pressurizing the cell.

2.4.2. Cross-flow cell

A rectangular cross flow membrane module was fabricated with the help of mechanical engineering workshop, IIT Guwahati. The design of cross-flow membrane module and the experimental setup was similar as reported by Das et al. (2006). The effective membrane surface area of cross-flow cell was 1.64×10^{-2} m^2.

2.5. Experiments

2.5.1. Micellar solubilization

Batch micellar solubilization experiments were carried out by dissolving methyl violet in saponin solution of known concentration (200 mg L^{-1} to 10,000 mg L^{-1}) in 30 mL screw capped vials. The effect of pH and NaCl concentration on micellar solubilization of methyl violet was examined within the pH range of 3.0–12.5 and NaCl salt concentration range of 10–50 g L^{-1} respectively. The saponin micelles and its agglomerates were observed using an optical microscope. The solubilized methyl violet in agglomerates of saponin micelles was also noticed. The particle size of micellar saponin and methyl violet solubilized micelles were measured. The