Journal of Water Process Engineering 19 (2017) 81–95

Contents lists available at ScienceDirect

Journal of Water Process Engineering

journal homepage: www.elsevier.com/locate/jwpe

Chemical cleaning of mullite ceramic microfiltration membranes which are fouled during oily wastewater treatment

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ARTICLE INFO

Keywords:
Chemical cleaning
Mullite ceramic membrane
Microfiltration
Fouling
Oily wastewater

ABSTRACT

In this study, chemical cleaning of home-made mullite ceramic membranes which are fouled during oily wastewater treatment was investigated. The high performance and low cost mullite membranes were prepared by local low cost kaolin clay using extrusion method and the characteristic of the fabricated membranes was studied by different methods such as SEM, XRD, mean pore size and porosity analysis. Four types of chemical cleaning agents were selected for chemical in place cleaning of the fouled mullite membrane: Acid (sulfuric acid (H_2SO_4)), surfactant (sodium dodecyl sulfate (SDS)), chelating agent (ethylene diamine tetra acetic acid (EDTA)) and alkaline (sodium hydroxide (NaOH)). The fouled membranes were cleaned with single, binary and ternary solution of these chemical agents with the concentrations of 5 mM and 10 mM under the best operating conditions. After first cleaning step, membranes cleaned with vinegar and sodium bicarbonate solution as a novel chemical cleaning agent and named as second cleaning step. Results showed that by using single component chemical agent, EDTA and SDS with concentration of 5 and 10 mM were the best cleaning agents which have flux recovery about 31.265% and 57.778% respectively after two steps of cleaning. Binary solution of SDS + EDTA with the concentration of 5 mM was the best cleaning agent among binary and ternary cleaning solution agents which led to 41.802% and 65.163% flux recovery in the first and second cleaning steps of chemical clanging process respectively.

1. Introduction

Oil, grease and organic emulsions in water are one of the great pollutants of environment in the world and have traditionally been great interest for wastewater treatment research due to their high volume and inherent complexity. This environmental pollution is due to the release of industrial oily wastewaters from sources such as refineries, petrochemical plants, transportation and metallurgy [1,2]. Discharging them without treatment can pollute underground water, soil and environment. The permitted oil and grease limits for discharging oily wastewater to environment is 10 mg/L and 20 mg/L for surface and coastal waters instantaneous [3]. Among all the ways for treating oily wastewaters, membrane techniques can meet these standards. Among membrane processes, microfiltration membranes especially ceramic microfiltration membranes are widely used for oily wastewater treatment in the world. Ceramic membranes have many advantages over polymeric membranes including thermal and chemical tolerance, resistance to abrasion, mechanical stability and higher permeation flux due to the higher porosity [4,5]. Most important issues in ceramic microfiltration membranes are fouling and concentration polarization. Fouling, which is common to all types of membrane separation methods, arises from a combination of chemical and physical interactions [6,7]. Fouling during oily wastewater treatment generally consist precipitation of oil, grease, solid suspension, colloidal and inorganic particles on the membrane surface and into its pores [8,9]. Oily wastewater contains some potential membrane fouling categories, lubricants, cutting liquids, heavy hydrocarbons (tars, crude oils, grease and diesel oil), and light hydrocarbons (kerosene, jet fuel and gasoline), microbial (bacteria, viruses, etc.), and inorganic (minerals) contents [10,11]. Fouling in membranes lead to permeation flux decline, decrease in the wastewater treatment efficiency, increase in energy and water consumption, treatment time and operation cost, therefore it is very important to find effective and efficient methods in order to control and minimization of membrane fouling. These methods such as physical cleaning, chemical cleaning and physical and chemical combined cleaning [11]. In the chemical cleaning process, choosing the best type of cleaning agent is critical. The optimal selection of the cleaning agent depends mainly on membrane material and type of foulant. These agents must be able to dissolve most of the deposited materials on the surface and remove them from the surface but not damaging membrane

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http://dx.doi.org/10.1016/j.jwpe.2017.07.012
Received 11 March 2017; Received in revised form 14 July 2017; Accepted 15 July 2017
2214-7144/

Nomenclature

EDTA	Ethylenediaminetetraacetic acid
SDS	Sodium dodecyl sulfate
TMP	Transmembrane pressure (bar)
CFV	Cross flow velocity ($m\ s^{-1}$)
T	Temperature (°C)
t	Time (min)
V	Volume of permeate (L)
A	Effectiveness area of membrane (m^2)
PF	Permeation flux ($L\ m^{-2}\ h^{-1}$)
FR	Flux recovery
PF_{wi}	Pure water permeation flux of virgin membrane (new membrane) ($L\ m^{-2}\ h^{-1}$)
PF_{ww}	Pure water permeation flux after fouling (after oily wastewater treatment) ($L\ m^{-2}\ h^{-1}$)
PF_{wc}	Pure water permeation flux after chemical cleaning ($L\ m^{-2}\ h^{-1}$)
W_1	Mass of dry membrane (g)
W_2	The soaked membrane's mass (g)
ρ_m	Water density at the experiments temperature ($Kg\ m^{-3}$)
V_M	Volume of the membrane (m^3)
r_m	Mean pore radius of membrane (μm)
ε	Porosity of the membrane
μ	Water viscosity at the operating temperature (Pa s)
L	Membrane thickness (m)
$d_{average}$	Average droplet size of oil in the emulsion (μm)
d_i	The each oil droplet diameter size in the emulsion (μm)
n	Volume fraction
ln	The natural logarithm
J	PF at any arbitrary time ($L\ m^{-2}\ h^{-1}$)
J_0	PF at initial time ($L\ m^{-2}\ h^{-1}$)
J_{ss}	Steady state PF ($L\ m^{-2}\ h^{-1}$)
K_{gl}	Constant parameter for cake/gel layer formation model ($s\ m^{-2}$)
Ki	Constant parameter for intermediate pore blocking model (m^{-1})
Kc	Constant parameter for complete pore blocking model (s^{-1})
Ks	Constant parameter for standard pore blocking model ($s^{-0.5}\ m^{-0.5}$)

surface, thus maintaining membrane properties. The most chemical cleaning agents are commercially available, they are often mixtures of compounds, and many of them are recommended by membrane manufacturers according to the type of foulant and membrane, although in the most cases the actual composition is not clearly specified [12,13]. Anyway, in general Table 1 shows the common cleaning agents which are used to cleaning membranes. In the recent years, the researchers investigated chemical cleaning of different membranes, while by looking up at the available literature; they are not any investigation about chemical cleaning of mullite ceramic membranes which are fouled by oil and organic pollutants. Ogunbiyi et al. [14] investigated chemical cleaning of tubular ceramic membranes with nominal pore size 0.5 μm which are fouled by yeast suspension. Chemical cleaning consisted of a sequential application of 1% caustic solution through the rig followed by 2% hypochlorite solution and 2% nitric solution, all at 50 °C. Results indicated that permeation flux values increased with an increase in system pressure and it reduced by enhancing of feed concentration. pH effects were also considered and the permeation flux values were higher at lower pH values. Avet et al. [15] investigated chemical and hydraulic cleaning of a tubular ceramic microfiltration membrane was fouled with a whey protein concentrate suspension. They employed a 0.1 μm tubular ceramic microfiltration membrane which was fouled by 3.5 wt% whey protein concentrate suspension. Results showed that cross flow velocity had no significant effect on flux recovery but flux recovery was greatly affected by *trans*-membrane pressure (TMP). Yin et al. [16] investigated chemical cleaning of ceramic ultrafiltration membranes with average pore size of 0.05 μm were fouled by desulfurization wastewater. Results indicates the best effective solution was adding 1% (w/w) NaOH solution mixed with 0.5% (wt%) NaClO, and then cleaning for 120 min at 50 °C. Eventually, the flux recovery ratio was always higher than 98%. Ahmad et al. [17] investigated the water flux recovery following the chemical cleaning of the commercial cellulose acetate membrane with pore size 1.2 μm which was fouled by micro algal biomass with the different chemical cleaning agents. Results showed that alkaline cleaning agents more effectively removed the foulant layer on the membrane surface than the acidic cleaning agents. In addition, among the tested alkaline agents, 0.75% NaOCl exhibited the best cleaning performance, obtaining approximately 98% flux recovery. Woo et al. [18] applied oxalic acid and sodium hypochlorite as chemical cleaning agents for cleaning of hollow fiber ultrafiltration membranes. The cleaning in series of oxalic acid–-sodium hypochlorite–oxalic acid showed the optimal cleaning efficiency and was applied for the consecutive chemical cleaning. The recovery efficiency of the cleaning in place after first, second, third and fourth cleanings was 96.8%, 95.8%, 98.3% and 99.9%, respectively. Chen et al. [19] used various composition of NaOH, NaOCl and sodium dodecyl benzene sulfonate (SDBS) for chemical cleaning of ceramic membranes which were fouled by designing wastewater. Results showed that solution of 1.0 wt% NaOH + 0.1 wt% SDBS was the best chemical solution which leads to 77% flux recovery. Silalahi and Leiknes [20] were used different commercial products that are biodegradable i.e. Ultrasil 115, Ultrasil 73, Surfactron CD 50 and Derquim+ for chemical cleaning of ceramic membranes with nominal pore size 0.1,0.2 and 0.5 μm which were fouled by oil and particulate matter. Results showed that at high temperature, the combination of alkaline (Derquim+, Ultrasil 115) and acid (Surfactron CD 50,Ultrasil 73) gave a good cleaning efficiency except for the 0.5 mm membrane pore size.

In this study, mullite ceramic membranes were fabricated by extrusion method using local low cost kaolin clay. These membranes were fouled by oil and organic matters during oily wastewater treatment. Chemical cleaning using EDTA, SDS, NaOH and acid sulfuric was performed and flux recovery using single, binary and ternary solution of these chemical agents at the optimum conditions was obtained. Therefore, vinegar and sodium bicarbonate were used as a novel

Table 1
Common chemical cleaning agents used for chemical cleaning of ceramic membranes [11].

Family	Examples	General functions
Acids	Strong: HCl, HNO_3 Weak: H_3PO_4, citric	pH regulation, dissolution of inorganic precipitates, acidic hydrolysis of certain macromolecules
Alkalis	Strong: NaOH, KOH Weak: Na_2CO_3	pH regulation, alteration of surface charges, alkaline hydrolysis of proteins, catalysing saponification of fats.
Oxidants	NaClO, H_2O_2	Oxidation of organics; disinfection
Surfactants	Anionic: SDS Cationic: CTAB Nonionic: Tween 20	Dispersion/suspension of deposits
Chelants	EDTA	Complexion with metals, removal of mineral deposits.
Enzyms	Proteases, lipases	Catalysing lysis of specific substrates (e.g., proteins, lipids)