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Journal of Industrial and Engineering Chemistry

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

Milk processing wastewater treatment in a bioreactor followed by an antifouling O-carboxymethyl chitosan modified Fe₃O₄/PVDF ultrafiltration membrane



Z. Rahimi, A.A. Zinatizadeh*, S. Zinadini

Water and Wastewater Research Center (WWRC), Department of Applied Chemistry, Faculty of Chemistry, Razi University, Kermanshah, Iran

ARTICLE INFO

Article history: Received 25 June 2015 Received in revised form 15 April 2016 Accepted 15 April 2016 Available online 23 April 2016

Keywords: Ultrafiltration membrane OCMCS-Fe₃O₄/PVDF Milk processing wastewater Fouling mitigation

ABSTRACT

In this study, a synthetic nanocomposite ultrafiltration membrane (prepared by blending polyvinylidene fluoride (PVDF) and hydrophilic O-carboxymethyl chitosan modified Fe_3O_4 (OCMCS- Fe_3O_4) nanoparticle) was applied in a bioreactor to treat milk processing wastewater (MPW). Experiments were carried out with two independent operating variables, mixed liquor suspended solids (MLSS) and hydraulic retention time (HRT). The region of exploration for the variables was taken as the area enclosed by MLSS (6000–14,000 mg/L) and HRT (8–44 h) boundaries. Throughout the experiments, high COD removal efficiency (92–99%) was obtained. The MLSS had an increasing impact on the removal efficiency of nitrogen and flux while had a reverse impact on the TP removal efficiency. The optimal membrane performance was compared to commercial microfiltration (MF) membrane and the results showed that the blended membrane with modified nanoparticles leads to a high flux ultrafiltration membrane.

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Introduction

The dairy industry is one of the major sources of food processing wastewater in many countries. Dairy wastewater contains high concentrations of biological oxygen demand (BOD), chemical oxygen demand (COD) (proteins, fats, and carbohydrates in the form of lactose) and inorganic ions which generate strong wastewaters [1,2]. Due to the high pollution load of dairy wastewater, discharging these untreated effluents may cause discomfort to the surrounding population [3]. Therefore, appropriate treatment is required prior to disposal into sewer network or receiving water bodies.

Common treatment techniques for the dairy wastewaters are: the use of primary treatment includes grease traps, oil water separators for separation of float-able solids, equalization of flow, primary sedimentation tank, coagulation, secondary biological treatment consists of the aerobic and anaerobic process, and membrane separation [4,5]. However, each of these treatment systems has drawbacks that caused by either high energy requirement or strong operational difficulty [6,7].

Membrane bioreactors (MBRs) are being successfully used as aneffective technology for high-strength industrial wastewater treatment [8] which is due to its superior merits over conventional activated sludge (CAS) systems, including highly-improvement effluent quality, small footprint, complete liquid-solid separation, high biomass concentration, high biodegradation efficiency, independent control of sludge retention time (SRT) and hydraulic retention time (HRT), and low sludge production [9]. However, it has also some disadvantages such as relative high energy consumption, more complicated operation compared to CAS systems. The major challenge in the MBR systems is membrane fouling, which results in a decrease in the MBR filtration performance with filtration time [10]. More severe fouling is expected when hydrophobic membranes are used in a biological system. Hydrophobic adsorption of sludge constituents such as sludge flocs, colloids and soluble microbial products (SMP) on membrane surfaces lead to biofouling of the membrane, which considered a dominant factor in the case of membrane fouling and makes the MBRs for wastewater treatment

http://dx.doi.org/10.1016/j.jiec.2016.04.011

1226-086X/© 2016 Published by Elsevier B.V. on behalf of The Korean Society of Industrial and Engineering Chemistry.

^{*} Corresponding author. Tel.: +98 9188581130; fax: +98 8334274559. *E-mail address:* zinatizadeh@razi.ac.ir (A.A. Zinatizadeh).

costly [11]. To prevent membrane fouling, hydrophilic membranes are normally favored [12,13]. However, most membrane materials are hydrophobic; therefore the surface property of membranes is one of the important key factors affecting membrane fouling in MBR systems [14]. To overcome severe membrane fouling, many efforts havebeen made including optimization of membrane characteristics, adjustment of operating conditions, and modification of biomass characteristics [15]. Among these methods, the hydrophilic modification of polymeric membranes is a potential fouling mitigation method. Different methods either by chemical or physical modifications such as UV irradiation [16], plasma treatment [17], blending with hydrophilic materials [18], graft polymerization [19], and so on, have been employed to modify the membrane surface. Of the above-mentioned methods, blending with inorganic materials, especially nanoparticles, has attracted much interest due to their simple operation and mild conditions [20].

Table 1 compares antifouling performance of different UF membranes modified by various nanoparticles. As presented in the

table, the flux recovery ratio (FRR) for the modified membranes have been considerably improved in comparison with that obtained for the bare membranes. Although the initial flux was less for some modified membranes (when TiO₂ and elementalnanoparticles are used), but decrease in the flux during filtration time was less relative to the bare membranes in the all cases reviewed. As a result, use of hydrophilic agents as additive in the membrane structure showed to be an effective approach to provide antifouling properties. Maximous and his colleague [10] investigated the fouling mitigation effect of Al₂O₃ entrapped polyethersulfone (PES) ultrafiltration membranes during the activated sludge filtration. According to the results, Al₂O₃ entrapped membrane showed lower flux decline compared to neat polymeric membrane and fouling mitigated with increase nanoparticle content.

Lee and coworkers [11] demonstrated that nano plates of graphene oxide (GO) used in the membrane preparation suppressed the fouling to such an extent that a five fold lengthening is achieved of the time between chemical cleanings. Bae and

Table 1

Comparison between antifouling performances of different UF membranes modified by various nanoparticles.

Type of wastewater	Type of membrane	Wt.%	Pressure (bar)	Time of filtration (min)	Feed concentration (g/L)	MLSS (mg/L)	Initial flux (kg/m ² h) or (L/m ² h)	Final flux (kg/m ² h) or (L/m ² h)	FRR (%)	Type of filtration	References
Non-skim milk	TiO ₂ -coated	0.03	3	240	-	-	33 (kg)	23	63	Cross flow	[21]
	inclubranc	0	3	240	-	-	35	15	42	Cross flow	
BSA	The hydrophilic PVDF-g-PVP powder blended porous PVDF membranes	50	0.5	-	0.5		79 (L)	-	77.23	Dead-end	[22]
		0	0.5	-	0.5	-	20	-	37.50	Dead-end	
BSA	PVDF/SPES blended membrane and modified with TiO ₂ nanoparticles	4	5	120	0.5	-	500 (kg)	490	86.2	Dead-end	[23]
	F	0	5	120	0.5	-	600	200	64.6	Dead-end	
BSA	PANI/PMA nanoparticles modified PES UF membranes	5	3	180	0.9	-	276 (L)	187	77.2	Cross flow	[24]
		0	3	180	0.9	-	156	137	60.6	Cross flow	
BSA	The UF membrane containing PES-g-MPC	-	1	120	1	-	90 (L)	79	87.1	Dead-end	[25]
		0	1	120	1	-	95	69	60.6	Dead-end	
BSA	Surface modification of PEI UF membrane with PEG	2	1	120	1	-	105 (L)	100	85.6	Dead-end	[26]
		0	1	120	1	-	75	70	-	Dead-end	
Activated sludge	PES UF membrane modified by nSe and nCu particles	0.050 Se/PES	1	120	-	3600	25.3 (L)	18.98	-	Dead-end	[27]
		0	1	120	-	3600	74.4	52.82	-	Dead-end	
BSA	PES UF membrane prepared by mixing reduced GO/Ag nanosheets	0.2	3	90	0.5	-	429.8 (kg)	288.82	67.2	Dead-end	[28]
	. •	0	3	90	0.5	-	229	110.61	48.3	Dead-end	
Activated sludge	PES UF membrane prepared by embedding NH ₂ -MWCNTs nanofiller	0.1	2	60	_	1000	106.75 (kg)	95.75	89.7	Dead-end	[29]
		0	2	60	-	1000	79	55.30	70	Dead-end	

GO: graphene oxide, nCu: nano-sized copper, NH₂-MWCNTs: amino functionalized multi-walled carbon nanotubes, nSe: nano-sized selenium, MPEI: modified PEI membrane, PANI: polyaniline, PEG: poly(ethylene glycol), PES-g-MPC: poly(arylene ether sulfone) grafting poly(2-methacryloyloxyethylphosphorylcholine), PMA: phosphomolybdicacid, PVDF: poly(vinylidene fluoride), SPES: sulfonated polyethersulfone, and UF: ultrafiltration.

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