Desalination 280 (2011) 305–312

Contents lists available at ScienceDirect

Desalination

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

Fabrication optimization of acrylonitrile butadiene styrene (ABS)/polyvinylpyrrolidone (PVP) nanofiltration membrane using response surface methodology

S.S. Madaeni [a,*], N. Arast [a], F. Rahimpour [a], Y. Arast [b]

[a] Membrane Research Center, Chemical Engineering Department, Razi University, Kermanshah, Iran
[b] Department of Occupational Health, Qom University of Medical Sciences, Qom, Iran

ARTICLE INFO

Article history:
Received 11 February 2011
Received in revised form 10 July 2011
Accepted 11 July 2011
Available online 4 August 2011

Keywords:
Nanofiltration
Phase inversion
Factorial design
Optimization

ABSTRACT

This paper introduces response surface methodology (RSM) as an efficient approach for modeling and optimization nanofiltration (NF) membrane preparation via phase inversion. RSM statistical design (full factorial) was applied to develop the predictive regression models for optimization. This design provides a model with small prediction error, and permits a judgment of the model adequacy. NF acrylonitrile butadiene styrene (ABS)/polyvinylpyrrolidone (PVP) blend membranes were fabricated using phase inversion induced by immersion precipitation method. Dimethylacetamide and water were used as solvent and coagulant respectively. Polymer concentration, evaporation (EVP) time and additive concentration were the preparation factors which their main and interaction effects on membrane morphology and performance were investigated. Membrane morphology was characterized by scanning electron microscopy (SEM). Cross flow permeation experiments were applied for performance tests. According to the analysis of variance (ANOVA) all three independent parameters were statistically significant and the final model was accurate. Response surfaces and contours were plotted for representation of the regression equations and interpretation. Finally, the RSM optimizer supplied three optimized conditions for each main ABS concentration level. These optimum conditions were proven to have high performance, where deviations between predicted and actual responses fall within 4%.

1. Introduction

Nanofiltration, which has been largely developed and commercialized over the past decade, is one of the promising technologies that have found various applications in many industries including water softening, water treatment, pharmaceutical and biotechnology [1,2].

Most NF membranes are negatively or positively charged by the dissociation of surface functional groups, such as sulfonic or carboxyl acids [3]. Accordingly the separation mechanisms involve both steric (sieving) and electrical (Donnan) effects. This combination allows NF membranes to be effective for a range of separations such as mixtures of small organic solutes (either neutral or charged) and salts. Negatively charged membranes are widely used because they can selectively partition ions in the salt mixture solutions through the electrostatic interaction between ions and membranes [4].

Major applications of NF include: removing hardness and dissolved organics from surface and groundwater [5], removal of heavy metal ions like arsenic [6], nickel [7], cadmium [8], chromium [9] and copper [10,11] from wastewater and demineralization in the dairy industry [12]. Moreover nanofiltration can be successfully applied in drinking water production [13,14], textile industry [15], food industry [16,17] and other manufacturing processes [18–20].

Cellulose acetate, polyamide, polyimide, and acrylonitrile are polymeric materials which are extensively used for preparation of NF membranes. Nowadays new polymeric and copolymeric materials are investigated to produce high performance membranes. Acrylonitrile butadiene styrene (ABS) is a new copolymer with good filtration characteristics. ABS is a commercial material with relatively low cost and good balance of mechanical properties and moderate glass transition temperature (110 °C). This copolymer is a mixture of styrene, butadiene and acrylonitrile. Styrene and butadiene are hydrophobe and acrylonitrile has a hydrophilic nature. ABS also provides strength, rigidity and toughness [21–23]. Hence, ABS was selected as the main polymer for preparation and characterization of the NF membrane in our study.

Fabrication of polymeric flat-sheet membranes by dry/wet phase inversion processes has been extensively studied [24,25]. Phase inversion effective parameters such as polymer concentration, evaporation time, and composition of the casting solution can extremely influence membrane structure and performance i.e.

* Corresponding author. Tel.: +98 831 4274530; fax: +98 831 4274542.
E-mail address: smadaeni@yahoo.com (S.S. Madaeni).

0011-9164/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.desal.2011.07.020

permeate flux and solute rejection. For example increasing polymer concentration usually decreases flux as a result of the viscosity increment of casting solution [25].

Polymeric additives such as polyvinylpyrrolidone (PVP) have been extensively used as pore former and to control the membrane structure in the preparation of micro, ultra and nanofiltration membranes. PVP is a non-toxic polymer which is miscible with many membrane materials. Its solubility in water and organic solvents makes PVP one of the best polymeric additives in membrane fabrication [26,27].

Evaporation of solution solvent(s), before immersion in coagulation bath is a simple treatment technique to ameliorate the membrane structure. According to the open publications, molecular weight cut-off (MWCO) and mean pore size of the membranes are decreased by increasing the solvent evaporation time. The evaporating step can prevent the shrinkage of membrane during the immersion step which makes membrane surface full of wrinkles. Moreover this pre-evaporation is known as an efficient method to suppress the formation of macro voids [28].

Nowadays, membranologists try to improve the membrane morphology and to optimize the process conditions through statistical approaches [29,30]. The techniques such as response surface methodology (RSM) and other methods are promising in calculating the complex interactions among the independent process factors. Sivakumar et al. [31] studied ultrafiltration separation of bovine serum albumin using cellulose acetate/polyurethane blend membrane and Box–Behnken design of experiments with three variables i.e. additive, time and transmembrane pressure. Three levels of complete factorial design were developed for the estimation of parameters in a second order model. Khayet et al. [32] applied the central composite design of orthogonal type in desalination by direct contact membrane distillation using different membrane types and various factors. Canonical analysis was employed for optimization and the response surface model was tested with ANOVA analysis. Cojocaru and Zakrzewska-Trznadel [29] presented application of RSM for optimization of ultrafiltration. The experiments were performed according to statistical designs. Idris et al. [33] used the Taguchi design of experiment to determine the significant factors affecting spinning parameters of cellulose acetate hollow fiber reverse osmosis membranes. For all mentioned researches, an acceptable agreement was observed between experimental and predicted data.

Generally, for optimization and analysis of factors affecting membrane preparation via phase inversion, a statistically designed experimental plan with minimum runs is greatly desired. The RSM experimental plan can supply appropriate modeling and optimization before any experimentation. The efficient response surface illustrates main and interaction effects of process parameters.

In this study the effects of preparation parameters including polymer concentration, evaporation time and additive concentration on morphology and performance of ABS nanofiltration membranes were investigated. Controlling aspects of these factors on permeation properties of final membranes were statistically analyzed using RSM as a technique for experimental design, modeling and optimization.

2. Experimental

2.1. Design of experiments

Preliminary experiments were carried out to screen the appropriate parameters and to determine the experimental domain. RSM was used for experimental design and membrane preparation modeling. Traditionally, RSM has been the acronym for response surface methodology, reflecting the predominant view that extensive use of response surface plots is advantageous for finding an optimal point. Good RSM designs estimate the parameters of the model with low uncertainty. RSM designs should give rise to a model with small prediction error, and permit a judgment of the model adequacy. This latter aspect means that the design must contain replicated experiments enabling the performance of a lack of fit test. In addition, RSM designs should encode as few experiments as possible [34].

In our research three-level full factorial design was selected among several classical RSM design families to fulfill the requirements. This design was carried out with three effective formation factors i.e. concentration of main polymer (ABS), additive polymer (PVP) and evaporation time. Modde 8.0 software from Umetric (Umea, Sweden) was used to develop the full factorial experimental design and RSM modeling and optimization. The ranges of different parameters were adjusted based on primary investigations on single factors.

The generated experimental plan using software is shown in Table 1. The setup of a 30-experiment design run in random order allows modeling of quadratic effects as well as main effects and their interactions on response variable. In Table 1, the processing factor range and the levels of considered variables are given in actual and coded values. Each factor is varied over three levels: the high level (+1), the center point (0) and the low level (−1).

2.2. Chemicals

Acrylonitrile butadiene styrene (ABS) purchased from TPC, Iran, under CHEIL license. Coagulation medium was distilled water. Polyvinylpyrrolidone (PVP, with Mw = 25,000 g/mol), dimethylacetamide (DMAc), sodium chloride (NaCl (and sodium sulfate (Na_2SO_4) were supplied by Merck. All materials were used as received.

2.3. Membrane preparation

A multi-component dope solution, consisted of ABS, PVP and DMAc was cast on a glass plate at ambient temperature by manual casting knife with desired thickness (180 μm). The membrane surface was exposed to air at 28 ± 1 °C for free-convective solvent

Table 1
Experimental design layout; actual and coded levels of variables; observed and predicted results of response.

Exp name	ABS (% w/w)	PVP (% w/w)	EVP time (min)	Coded levels of factors			Ln flux (observed)	Ln flux (predicted)
N1	16	0	0	−1	−1	−1	7.13505	6.90036
N2	20	0	0	0	−1	−1	6.09582	6.09355
N3	24	0	0	1	−1	−1	4.94164	5.28674
N4	16	4	0	−1	0	−1	6.57925	6.74231
N5	20	4	0	0	0	−1	6.2691	6.11432
N6	24	4	0	1	0	−1	5.71175	5.48633
N7	16	8	0	−1	1	−1	6.46272	6.58426
N8	20	8	0	0	1	−1	5.8659	6.13509
N9	24	8	0	1	1	−1	5.78074	5.68592
N10	16	0	2.5	−1	−1	0	7.0132	6.66731
N11	20	0	2.5	0	−1	0	5.78074	5.70184
N12	24	0	2.5	1	−1	0	4.56435	4.73637
N13	16	4	2.5	−1	0	0	6.24611	6.75153
N14	20	4	2.5	0	0	0	5.8522	5.96488
N15	24	4	2.5	1	0	0	5.3033	5.17823
N16	16	8	2.5	−1	1	0	7.09008	6.83575
N17	20	8	2.5	0	1	0	6.51026	6.22792
N18	24	8	2.5	1	1	0	5.71175	5.62009
N19	16	0	5	−1	−1	1	6.29157	6.43426
N20	20	0	5	0	−1	1	5.15906	5.31014
N21	24	0	5	1	−1	1	4.27667	4.18601
N22	16	4	5	−1	0	1	6.38486	6.76074
N23	20	4	5	0	0	1	6.26454	5.81544
N24	24	4	5	1	0	1	5.20401	4.87014
N25	16	8	5	−1	1	1	7.2385	7.08723
N26	20	8	5	0	1	1	6.54535	6.32074
N27	24	8	5	1	1	1	4.78749	5.55426
N28	20	4	2.5	0	0	0	5.95064	5.96488
N29	20	4	2.5	0	0	0	5.8861	5.70211
N30	20	4	2.5	0	0	0	5.8522	5.86543