A pilot scale concurrent removal of fluoride, arsenic, sulfate and nitrate by using nanofiltration: Competing ion interaction and modelling approach

Sachin V. Jadhav, Kumudini. V. Marathe, Virendra K. Rathod *

Chemical Engineering Department, Institute of Chemical Technology, (University under Section 3 of UGC Act 1956; Formerly UDCT/UICT), Nathalal Parekh Road, Matunga (East), Mumbai – 400 019, INDIA

ABSTRACT

The application of nanofiltration membranes to remove multiple contaminants such as fluoride, arsenic, sulfate and nitrate, was investigated. The central composite design was applied to evaluate the influence of transmembrane pressure, cross-flow velocity and initial concentration of each solute on rejection and flux. The predictive quadratic models were developed for each response and the analysis of variance was applied to test the response surface models. The average rejection for the NF90 membrane was observed to be 95, 98, 87, and 76% for SO_4, As, F, and NO_3, respectively, whereas the NF270 membrane rejected the said ions around 90, 94, 57, and 60%, respectively. The NF270 membrane delivered 1.5 times better flux than the NF90 membrane. The experimental results were successfully predicted by the multiple solute models. Membrane resistance, permeability coefficient and mass transfer coefficient were also established for each membrane. The gel layer thickness was determined to better understand the hydrodynamics and it validated the assumption of negligible fouling.

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1. Introduction

Water scarcity, either fresh or used, has its adverse effects on each and every continent around the globe. The ever intensified growth in population is taking its toll on the available natural resources and out of those, water is the first priority. This situation confirms from the WHO and UNICEF reports where a millions of people do not have sufficient and safe water supplies for consumption and other routine tasks [1].

The occurrence of several naturally occurring and human induced elements such as arsenic, fluoride, nitrate, sulfate, chloride, iron, selenium, manganese, and heavy metals can seriously deteriorate the water quality resulting in environmental and health concerns. Out of which, arsenic and fluoride are the most toxic inorganic contaminants present in groundwater recognized by the WHO [2]. Although a small amount of fluoride is required for bone and dental development; often prolonged exposure to fluoride concentration greater than $1.5\,mg\,L^{-1}$ can cause dieses called as fluorosis [3]. The danger of arsenic being present in water has emerged as more alarming than fluoride hazards because it is extremely

carcinogenic even at minute concentrations [4]. Arsenic toxicity can cause certain forms of lung, kidney, skin, liver and bladder cancers in humans. Coexistence of fluoride and arsenic in groundwater has been commonly reported in many countries including Argentina, China, Mexico, and Pakistan, where concentrations up to $5300\,\mu g\,L^{-1}$ of arsenic and $29\,mg\,L^{-1}$ of fluoride were detected in the same groundwater sample [5]. Therefore, strict legislations have been applied over the discharge of these two components by the WHO, USEPA and EU. The concentration less than $1.5\,mg\,L^{-1}$ for fluoride and $10\,\mu g\,L^{-1}$ for arsenic has been established by the WHO as a safe in drinking water [6]. On the other hand, nitrate and sulfate have increasingly become the most common contaminants in groundwater. Excessive consumption of nitrate can cause methaemoglobinaemia in infants and hypertension, thyroid malfunctioning and even the possibility to trigger the threat of cancer in adults due to formation of nitrosamine and nitrosamide [7]. Hence, the WHO has guided the maximum permissible limit for nitrate in drinking water as $50\,mg\,L^{-1}$ [6]. While the WHO mentions no evident negative effect of sulfate consumption on human health, some researchers have reported problems such as long term gastrointestinal irritation if consumed more than 500 mg per day [8,9]. However, based on aesthetic effects (taste and odour etc.), USEPA has recommended not more than $250\,mg\,L^{-1}$ sulfate in drinking water. The co-existence of these contaminants offer

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* Corresponding author.
E-mail address: vk.rathod@ictmumbai.edu.in (V.K. Rathod).

Nomenclature

a_1, a_2, a_3	Constants in Eq. (8) defined by Eqs. (9)–(11)
A_m	Effective membrane area (m^2)
As	Arsenic concentration ($\mu g\,L^{-1}$, $kg\,m^{-3}$)
C_b	Concentration in the bulk ($kg\,m^{-3}$)
C_g	Concentration in the gel layer ($kg\,m^{-3}$)
C_p	Concentration in the permeate ($kg\,m^{-3}$)
F	Fluoride concentration ($mg\,L^{-1}$, $kg\,m^{-3}$)
J_v	Permeate flux ($L\,m^{-2}\,h^{-1}$, $m^3\,m^{-2}\,s^{-1}$)
k	Mass transfer coefficient ($m\,s^{-1}$)
M.W.	Molecular weight ($g\,mol^{-1}$)
MWCO	Molecular weight cut off
NF	Nanofiltration
NO_3	Nitrate concentration ($mg\,L^{-1}$, $kg\,m^{-3}$)
P_i	Inlet pressure (bar, $N\,m^{-2}$)
P_m	Permeability coefficient (m^2)
P_o	Outlet pressure (bar, $N\,m^{-2}$)
P_p	Permeate side pressure (bar, $N\,m^{-2}$)
R	Solute rejection
R_m	Membrane resistance (m^{-1})
RO	Reverse osmosis
SO_4	Sulfate concentration ($mg\,L^{-1}$, $kg\,m^{-3}$)
t	Filtration time (s)
USEPA	United States environmental protection agency
V_g	Total volume of gel layer up to time t (m^3)
V_p	Total volume of permeate up to time t (m^3)
WHO	World health organization
ΔP	Transmembrane pressure (bar, $N\,m^{-2}$)
$\mathbb{Z}$	Effective gel layer thickness (m)
ν	Superficial velocity ($m\,s^{-1}$)
$J_{v,ss}$	Steady state permeate flux ($m^3\,m^{-2}\,s^{-1}$)
μ	Viscosity of the solution (Pa s)

Fig. 1. Schematic of the cross flow pilot plant unit.

During past several years, the design of experiments methodology has been applied successfully in diverse number of fields e.g. chemical engineering, chemistry, physics, biochemistry, and environmental etc. Lately, it has also been practically used for a variety of membrane technologies [12,13].

Our current work emphasizes on simultaneous removal of multiple contaminants (fluoride, arsenic, sulfate and nitrate) by using a nanofiltration pilot plant. The behaviour of these competing ions on permeate flux and rejection was assessed by using response surface methodology carried out in Design Expert 9.0. Also, the experimental results were theoretically predicted by using multiple solute model solved by using Levenberg–Marquardt method in MATLAB. The ranges of feed value in Design Expert 9.0 were taken from the previously determined results in preliminary studies.

2. Materials and methods

2.1. Chemicals and reagents

All the reagents were pure and used as received in their commercial form without any further purification. Sodium sulfate (Na_2SO_4) (M.W. 142.04 $gmol^{-1}$), sodium arsenate (NaH_2AsO_4) (M.W. 163.92 $gmol^{-1}$), sodium fluoride (NaF) (M.W. 41.98 $gmol^{-1}$) and sodium nitrate ($NaNO_3$) (M.W. 84.99 $gmol^{-1}$) were procured from Sigma Aldrich. Pure deionized (DI) water (conductivity ~0.05 $\mu S\,m^{-1}$) was used to prepare the solutions with desired concentrations and for membrane cleaning. The water was simulated synthetically with chemicals used as received.

2.2. Equipment and membranes

The experiments were carried out on cross flow pilot plant obtained from Permeonics Membranes Pvt. Ltd. having active surface area of 0.016 m^2. The nanofiltration membranes used for this study were polyamide NF90 and NF270 obtained from Dow/FilmTec with Molecular Weight Cut-Off (MWCO) between 100 and 200 and 150–300 Da, respectively [14]. The membranes were used repeatedly by cleaning with pure DI before start of each experiment.

2.3. Pilot plant

A pilot scale cross flow nanofiltration assembly was used to perform experiments. The experimental rig consisted of a feed tank, a centrifugal pump and a membrane unit as shown in Fig. 1. It was provided with required accessories mounted at different positions.

their own set of complications on human health [10]. To overcome this problem, many treatment methods have been invented and employed for water purification namely precipitation/coagulation, adsorption, ion exchange, membrane separation, electrochemical methods, and some other low cost alternatives. Moreover, if present together they often compete with each other resulting in poor performance of the treatment method [10].

Nanofiltration (NF) is rather a recent development in membrane processes which poses its properties between reverse osmosis (RO) and ultrafiltration. Unlike RO membranes where complete demineralization can be achieved, NF operates in the safe region at far low pressures and rejects below 60% of the monovalent ions opening an opportunity to maintain the most favourable mineral content as required in treating waters. Therefore, they do not suffer from the disadvantages of RO systems such as high operating pressure and in turn high power consumption and significant water loss (low permeate flux) [11].

Generally, the classical methodology followed to perform the experiments engages optimizing one parameter at a time by varying its levels while keeping other influential parameters constant. This is cumbersome and time consuming method, as it requires more number of runs as well as it also discards the influence of interacting parameters which are held constant. This ultimately results in poor optimization of the dealt process. On the other hand, response surface methodology (RSM) takes statistical approach where all the variables are varied over a wide range of levels and in turn swiftly manages to eliminate the aforementioned drawbacks of the classical method. Design of experiments is a statistical tool to reduce the number of experiments and to ensure that the maximum data can b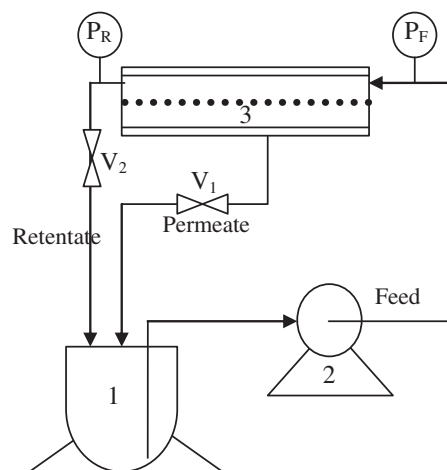e collected from the performed experiments.