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Adsorptive removal of nitrate from aqueous solution by polyacrylonitrile–alumina nanoparticle mixed matrix hollow-fiber membrane

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ABSTRACT

Hollow fiber mixed matrix membrane (MMM) of polyacrylonitrile and alumina nanoparticle was prepared. Incorporation of alumina in membrane matrix was confirmed by elemental analysis. The membrane was characterized by scanning electron microscopy, contact angle, permeability, neutral polymer rejection, pore size, mechanical strength and zeta potential. Hydrophilicity, mechanical strength and zeta potential of MMM increased with alumina concentration. Langmuir isotherm fitted the best for adsorption of nitrate by the membrane and it was confirmed by FTIR. The breakthrough performance of MMM was studied conducting continuous cross-flow experiments. Effects of operating conditions, like feed concentration, cross flow rate and transmembrane pressure on filtration performance, were investigated. The membrane was regenerated by passing 0.1 M sodium hydroxide solution for 15 min. Increasing cross-flow rate had an adverse effect and transmembrane pressure had a marginal effect on the removal of nitrate. The presence of other co-ions like chloride, sulfate and carbonate has a negative effect on nitrate removal.

1. Introduction

Contamination of nitrate in drinking water is a major concern all over the world. Concentration of nitrate in rainwater up to 5 mg/l has been normally observed in industrial areas [1]. World Health Organization (WHO) has recommended the maximum limit of nitrate concentration in safe drinking water as 10 mg/l [1]. Level of nitrate concentration in surface water is normally within low range (0–18 mg/l). It often reaches contamination level with excessive usage of fertilizer and runoff with human or agricultural wastes [2]. Nitrate-contaminated drinking water can potentially cause health problems like blue-baby syndrome or methemoglobinaemia in infants [3,4] and stomach cancer in adults [5–7]. Severe contamination can even cause coma, leading to death within a few hours [4].

Current methods for removal of nitrate from drinking water include ion-exchange resin, biological denitrification, chemical denitrification, electrodialysis, reverse osmosis, catalytic denitrification, etc. [8]. However, each of the processes has its own limitations. Ion-exchange resin needs to be regenerated [9], making the process complex and expensive. Biological denitrification causes organic contamination and excessive use of chlorine [10]. Safety, side reaction and additional cost of the chemicals used make chemical denitrification non-economical [11]. Electrodialysis is also not a simple and cost-effective process [12]. Reverse osmosis being energy intensive and having low throughput is unsuitable [13]. Catalytic denitrification becomes economically infeasible due to pre- and post-treatment steps and additional cost of chemicals [14].

Filtration by mixed matrix membrane (MMM) of polyacrylonitrile (PAN) and alumina nanoparticles can address the above limitations. It does not require any pre- or post-processing. In ultrafiltration (UF), throughput is high and no additional chemical is used. Probability of additional organic contamination, which is a drawback of currently practiced biological denitrification, is eliminated. Moreover, it may offer an effective solution for removal of suspended solids and high molecular weight solutes.

Nanoparticle doped MMM has generated considerable interest among researchers recently [15–17]. The presence of charged nanoparticles in the membrane matrix has potential application in wastewater treatment by electrostatic interaction [18–20]. MMMs improve various properties, like mechanical [21], thermal [22], magnetic [23] and electrostatic. It can enhance solute diffusivity [19], antibacterial property [24] and reduce flux decline [25,26]. MMMs have widespread application for gas separation and pervaporation [27]. In case of treatment of liquid stream, some of its applications include separation of sulfur from gasoline [28], silver using functionalized silica [29], humic acid using TiO_2 [30],

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metal ions using polyelectrolyte [31], lead by hydrous manganese dioxide [32] and arsenic [33] from aqueous stream. Micellar enhanced ultrafiltration (MEUF) for removal of methylene blue using titanium dioxide–polyvinyldene fluoride MMM is also reported [34]. Zeolite, modified silica and graphene impregnated composite membranes are also used for separation of salts in desalination applications [35–37].

In this work, polyacrylonitrile (PAN) was chosen as the base polymer for membrane fabrication. It is one of the most popular polymers used for membrane casting because of its sufficient chemical stability [38,39], good solvent resistance [40–42], excellent mechanical properties [43,44], and superior thermal stability [45]. Moreover, high permeate flux through PAN co-polymer-based membranes makes it an excellent choice for commercial application.

Among the various configurations of membrane modules, hollow fiber modules have several distinct advantages. These include: (i) large membrane area per unit volume leading to saving of space, (ii) ease of back flushing after the operation, (iii) ease of handling and operation and (iv) ease of scaling up [46]. In this work, mixed matrix hollow fiber membrane has been spun with PAN co-polymer and alumina nanoparticle. Efficacy of this novel MMM for removal of nitrate has been reported here. The membranes are characterized in terms of surface morphology, contact angle, permeability, zeta potential, etc. Effects of operating conditions like transmembrane pressure (TMP), cross-flow rate and feed concentration have also been studied. Regeneration study of the membrane has been performed and the influence of other ions in aqueous solution has been investigated.

2. Materials and methods

2.1. Materials

Polyacrylonitrile (PAN) co-polymer (copolymer of acrylonitrile, methyl acrylate, methacrylic acid in the ratio 96:3:1) of average molecular weight 150,000 g/gmol was purchased from M/s, Technorbital, Kanpur, India. *N*,*N*-dimethyl formamide (DMF), polyethylene glycol (PEG) (Molecular weight 4,20,100 and 200 kDa) and potassium nitrate were procured from M/s, Merck (India) Ltd., Mumbai, India. The alumina nanoparticle was obtained from M/s, US Research Nanomaterials Inc. Houston, USA.

2.2. Hollow fiber module preparation

2.2.1. Preparation of casting solution

MMM using PAN and alumina nanoparticle was prepared by the phase inversion method. Initially, DMF was heated to 60 °C and alumina nanoparticles were mixed in various weight percentage. The mixture was sonicated for two hours to prevent agglomeration [47,48]. PAN being a nanoparticle-stabilizer itself was added slowly to the suspension under continuous stirring by mechanical stirrer. The mixture was again sonicated for six hours with occasional stirring to prevent agglomeration [49]. Casting solution for membrane without alumina was prepared by mixing PAN in DMF. Two MMMs were prepared with composition 15 wt% PAN–4 wt% alumina and 15 wt% PAN–5 wt% alumina. These membranes were named as PAN15Al4 and PAN15Al5. For comparison, hollow fiber of 15 wt% pure PAN membrane was also prepared and was named as PAN15.

2.2.2. Fiber spinning and module preparation

The casting solution was immediately transferred to the polymer tank of hollow fiber spinning machine. Procedure of preparation of hollow fiber spinning and module preparation is available in details [50]. Details of hollow fiber membrane preparation are given in Table 1. Hollow fiber was spun using distilled water as the bore fluid at room temperature, 25 °C. To flow the polymer, 690 kPa pressure was applied using a nitrogen cylinder in the polymer tank. The water flow rate was fixed at 20 ml/min and the flow rate of polymer solution was 3 g/min. Extruded hollow fibers were allowed to fall on a water bath, maintained at room temperature and was kept inside the gelation bath (water bath) for 5 min. After that, it was wound by a spool. The spool was kept in distilled water for 24 h to allow the phase separation to be complete. After the completion of the phase separation, the fibers were cut in 20 cm length. A bundle of total 70 numbers of fibers was packed in a 1/2″ inner diameter PVC pipe of length 20 cm. Two ends of the cartridge were potted using epoxy resin (brand name: araldite). The membrane area was 0.026 m^2.

Table 1
Operating parameters of spinning and specification of cartridge.

Parameter	Details
Spinning specification	
Outer diameter of the needle	0.0012 m
Inner diameter of the needle	0.0005 m
Fiber thickness	0.00035 m
Flow rate of polymer solution	5×10^{-5} kg/s
Flow rate of antisolvent (water)	3.3×10^{-7} m^3/s
Air gap	0.15 m
Coagulation bath composition	Tap water
Coagulation bath temperature	30 °C
Drawing speed	0.0167 m/s
Pressure applied by nitrogen cylinder	28 kPa
Residence time at coagulation bath	180 s
Time allowed for completion of phase separation	18 hours
Potting specification	
Diameter of the cartridge	0.0118 m
Length of cartridge	0.20 m
Length of each piece of fiber	0.20 m
Number of fibers	80
Area of filtration	0.024 m^2
Potting material for sealing two sides	Epoxy resin

2.2.3. Experimental set-up

The schematic of hollow fiber membrane set up is available [50]. The heart of the set-up was the hollow fiber module. The feed was pumped into the module by a booster pump. A needle valve in the retentate line was used for fine-tuning of pressure and flow rate through the module. A rotameter was attached to the retentate line and the retentate stream was recycled back to the feed tank. A bypass line was connected from the pump to the feed tank. By controlling the bypass and retentate valves, the flow rate and TMP across the module were controlled independently. The TMP was the arithmetic average of the readings in the pressure gauges at the two ends of the membrane module.

2.3. Membrane characterization

2.3.1. SEM analysis

The morphology of the top surface morphology and the cross section of the membranes were studied by scanning electron micrograph (model: ESM-5800, JEOL, Japan). For cross-sectional images, membranes were fractured after dipping in liquid nitrogen for 1 min.

2.3.2. EDX analysis

Presence of each element and their percentage in the hollow fiber membrane were detected by energy-dispersive X-ray spectroscopy, EDX (model EVO 600, Zeiss, Germany).