



# Preparation, characterization and humic acid removal capacity of chitosan coated iron-oxide- polyacrylonitrile mixed matrix membrane



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## ABSTRACT

Flat sheet mixed-matrix membranes (MMM) were cast using amine stabilized iron oxide nanoparticles ( $\text{Fe}_3\text{O}_4$ ) and polyacrylonitrile (PAN) coated with chitosan. The effects of iron oxide impregnation ( $\text{Fe}_3\text{O}_4$ ) and chitosan coating on removal of humic acid were investigated. The cast membranes were characterized by scanning electron microscopy (SEM), permeability, molecular weight cut off (MWCO), pore size, hydrophilicity, mechanical strength, Fourier transform infrared spectroscopy (FTIR), zeta potential, surface area and surface roughness. Mechanical strength and zeta potential of MMM increased (more positively charged) with  $\text{Fe}_3\text{O}_4$  concentration. SEM images confirmed that MMM became denser with  $\text{Fe}_3\text{O}_4$  impregnation. Adsorption of humic acid on MMM was quantified and Langmuir isotherm was fitted. The adsorption of HA by MMM was also confirmed by FTIR. The long term stability of MMM was investigated in a cross flow filtration unit. Effects of various operating conditions like transmembrane pressure, cross flow rate and feed concentration on membrane performance were also investigated. Atomic force microscopy (AFM) showed that, surface roughness of membrane was reduced with nanoparticles impregnation. Flux recovery ratio (FRR) also confirmed the antifouling nature of MMM.

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## 1. Introduction

Human, animal, microbiological decay, surrounding vegetation are the potent sources of humic acid (HA) penetrating the surface water through heavy rainfall and run off in seasonal days [1]. HA is a major foulant containing carboxylic, phenolic, hydroxyl and quinine functional groups [2–4]. Exposure of HA may cause adverse health hazards to human being, viz., blackfoot disease, cancer and goiter [5]. According to Environmental Protection Agency (EPA), the concentration of HA in drinking water should not exceed 2 mg/L [6].

Conventional treatments like chlorination [2], coagulation [7], ion exchange [8] and photocatalytic oxidation [9] are reported in literature. However, chlorination may lead to further pollution by

releasing toxic and carcinogenic disinfection by-products (DBP) like trihalomethanes and haloacetic acid [2]. Coagulation may be ineffective in HA removal at low concentration [7]. Ion exchange may efficiently remove HA of lower molecular weight but, it fails to remove higher molecular weight species [8]. Photocatalytic oxidation mediated removal is also complicated and non-economical [9].

HA removal by membrane separation is well documented by a number of researchers [10–14]. However, flux decline and membrane fouling are two major issues to be addressed [11,12]. Mixed matrix membrane (MMM) is one of the latest developments in the field of membrane science, that integrates organic polymers with inorganic to form a mixed matrix offering improved rejection of humic acids, hazardous pollutants along with better antifouling property and higher throughput [13,14].

Recent studies by Shao et al. [15], investigated removal of HA and flux decline behavior of model HA solutions using negatively charged ultrafiltration (UF) membrane. However, lower throughput due to membrane fouling through high molecular weight cut off membrane was the key drawback of its application. Teow et al. [16], studied the antifouling property of PVDF/ $\text{TiO}_2$  MMM (with 1 mM  $\text{CaCl}_2$ ) using HA as natural organic foulant. The study indicates the long term stability of MMM with better antifouling property. How-

*Abbreviations:* MMM, mixed matrix membrane; MWCO, molecular weight cut off; HA, humic acid; NOM, natural organic matter; SEM, scanning electron microscopy; PAN, polyacrylonitrile; EPA, environmental protection agency; DBP, disinfection by-products; DMF, dimethylformamide; PEG, polyethylene glycol; FRR, flux recovery ratio; FTIR, Fourier transform infrared; AFM, atomic force microscopy; BET, Brunauer–Emmett–Teller; TMP, transmembrane pressure drop; CFR, cross flow rate.

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### Nomenclature

A	Membrane surface area, m <sup>2</sup>
C <sub>e</sub>	Equilibrium concentration of humic acid, mg/g
C <sub>f</sub>	Concentration of feed, kg/m <sup>3</sup>
C <sub>p</sub>	Concentration of permeate, kg/m <sup>3</sup>
HA <sub>f</sub>	Humic acid concentration in feed, mg/L
HA <sub>p</sub>	Humic acid concentration in permeate, mg/L
J <sub>w</sub>	Pure water flux, L/m <sup>2</sup> h
J <sub>p1</sub>	Initial water flux, L/m <sup>2</sup> h
J <sub>p2</sub>	Final water flux, L/m <sup>2</sup> h
k	Adsorption constant, L/mg
q <sub>e</sub>	Humic acid adsorbed, mg/g
mV	Millivolt
nm	Nanometer
R	Rejection, %
rpm	Rotation per minute
v <sub>m</sub>	Maximum adsorption capacity, mg/g
ΔP	Transmembrane pressure drop, kPa
Δt	Sampling time, s
μ	Viscosity of water, Pa s

ever, HA removal efficiency was not reported in the study. Hamid et al. [17], used the blending technique for PSF/TiO<sub>2</sub> to prepare hollow fiber membrane that enhanced HA removal efficiency up to 90% only. Patsios et al. [18], in a recent study introduced a novel photocatalytic method using ultrafiltration membranes for degradation of HA from waste water. This process limits its use due to heavy capital investment and is not affordable for drinking water. Hwang et al. [19], used polyphenylsulfone (PPSU)/polyetherimide (PEI) blend membranes to remove HA and evaluated their antifouling behaviour. However, lower HA removal upto 80% despite using some functional additives in the polymeric dope was the major critical issue with their invention.

Exploitation of chitosan (CS) in MMM as a promising hydrophilic additive is a new research trend, due to its unique properties like biodegradability [20], low toxicity [21] and biocompatibility [22]. CS exhibits strong affinity toward HA [23]. There are methods, like, encapsulation, covalent bonding and cross linking of CS on various media to enhance adsorption of HA [22,24,25].

Iron oxide nanoparticles (Fe<sub>3</sub>O<sub>4</sub>), also received a great deal of attention as strong adsorbent of HA due to their large surface area to volume ratio [25–27]. Tombacz et al. [25], reported the interaction between HA and reactive surface of Fe<sub>3</sub>O<sub>4</sub> improving HA removal. Illes et al. [26], explored pH dependent adsorption of HA on magnetic Fe<sub>3</sub>O<sub>4</sub>. Giasuddin et al. [27], studied the efficiency of zero-valent Fe<sub>3</sub>O<sub>4</sub> to remove HA.

The present work describes, preparation of appropriate flat sheet MMMs using amine stabilized Fe<sub>3</sub>O<sub>4</sub> and polyacrylonitrile (PAN) coated with CS, for removal of HA from spiked solution. To the best of author's knowledge, this is a first ever attempt to explore the possibility of Fe<sub>3</sub>O<sub>4</sub>-CS-PAN MMM to remove HA. Four different membranes were cast and characterized in terms of permeability, contact angle, surface morphology, molecular weight cut off, pore size distribution, surface charge, surface area, roughness and tensile

strength. Adsorption of HA was also quantified. The positive charge of CS and amine stabilized Fe<sub>3</sub>O<sub>4</sub>, was likely to enhance the active cationic sites on MMM surface, facilitating adsorption of negatively charged HA. Effects of operating conditions like transmembrane pressure (TMP), cross flow rate (CFR) and feed concentration were also investigated.

## 2. Experimental

### 2.1. Materials

PAN copolymer with molecular weight 250 kDa was obtained from M/s, Technorbital Advanced Materials Pvt. Ltd. (Kanpur, India) and was used as base polymer. Solvent, dimethylformamide (DMF) was purchased from M/s, Merck (India Ltd.) Mumbai, India. Polyethylene glycol (PEG) (molecular weight 0.4, 4, 6, 10, 20 and 35 kDa) was supplied by M/s, S. R. Ltd. Mumbai, India. Dextran (average molecular weight 70 kDa) and polyethylene glycol of average molecular weight 100 kDa were procured from M/s, Sigma Chemicals and M/s, Aldrich Chemicals, USA, respectively. These neutral solutes were used to evaluate MWCO of the cast membranes. Chitosan (CS) of medium molecular weight was supplied by M/s, Aldrich Chemicals, USA. Acetic acid (glacial) of synthesis grade was procured from M/s, Central Drug House, New Delhi, India. Sodium hydroxide (NaOH) was procured from M/s, Merck, Mumbai, India. Humic acid was purchased from M/s, Loba Chemie, Mumbai, India. Glutaraldehyde was procured from M/s, Loba Chemie, Mumbai, India. Distilled water was used as the non-solvent in coagulation bath. All chemicals were of analytical grade without further purification. Non-woven polyester fabric of thickness 118 ± 22.8 μm (product number TNW006013) was supplied by M/s, Hollytex Inc., New York, USA.

### 2.2. Membrane preparation

Four sets of casting solution were prepared by dissolving 15 wt% PAN in DMF by stirring separately at 80 °C for 8 h. Two sets of polymer solution were then doped with Fe<sub>3</sub>O<sub>4</sub> (0.1 and 0.4 wt%), leaving two un-doped. The solution was again stirred for 2 to 3 h at room temperature (30 °C). The sealed casting solution was kept for an hour in a laboratory sonicator, Piezo-U-Sonic (P.U.S.) ultrasonic cleaner (power: 120 W) for complete degassing of bubbles. Non-woven polyester fabric was attached to a clean glass plate using adhesive tape. Four membranes were cast using a casting knife with an adjustable gate height fixed at 200 μm. At this condition, the membrane was allowed to phase separate at room temperature for 5 min till the CS coating process was initiated. The coating layer of CS was prepared by dissolving 3 wt% of chitosan in 2% (v/v) acetic acid solution with continuous stirring using 0.1% (v/v) glutaraldehyde as a cross linking agent [28,29]. Three membranes were then coated with CS solution, leaving one as control. The control membrane was immediately dipped into a coagulation bath containing distilled water. The CS coated membranes were immersed into 1N NaOH solution for 30 min at room temperature, to ensure the completion of neutralization process. The membranes were then washed thoroughly using distilled water to remove the excess

**Table 1**  
Casting solution composition of various PAN and PAN based MMM.

Polymer (PAN) (wt%)	Amine stabilized magnetic nanoparticles (ASMNPs) (wt%)	Solvent (DMF) (wt%)	Chitosan coating (Y/N)	Membrane code
15	0	85	N	PAN
15	0	85	Y	PAN-CS
15	0.1	84.9	Y	PAN-0.1 Fe <sub>3</sub> O <sub>4</sub> -CS
15	0.4	84.6	Y	PAN-0.4 Fe <sub>3</sub> O <sub>4</sub> -CS

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