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A Short Review of Fouling & its Control Through Hydrophilic Modifications in Ultrafiltration Membranes

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Abstract—*Ultrafiltration is a promising membrane process in treating wastewater, protein concentration and other applications. Mostly ultrafiltration is used to produce good quality of drinking water. The most important problem with the ultrafiltration membrane separation process is fouling. Due to the adsorption of foulants (like macromolecules, microorganisms and proteins) on the surface of membrane,pores get blocked and results in the decrease in permeate fluxand lessens the lifeof membrane. Cost of operation, maintenance and cleaning is increased due to fouling. To overcome this problem we need to have a profound understanding of fouling of membranes and methods that are being used for the control and mitigation of fouling. This review paper outlines the factors causing fouling to ultrafiltration membranes and the hydrophilic mo-dificationsthat are used in ultrafiltration membranes to reduce fouling.*

Keywords*: Ultrafiltration, Membrane Fouling, Hydrophilic.*

Introduction

Ultrafiltration is a membrane process where pressure gradients lead to separation of suspended solids or macromolecules through a semipermeable membrane. Ultrafiltration is known as low pressure separation membrane process with pore dia between 10 A^o to 1000 A^o. Most of the membrane processes are consi-dered an attractive replacement for conventional waste treatment .Membrane process possess numerous advantages over conventional treatment like selective separation, continuous and automatic operation, less area requirement and purification done without chemicals. Most prominent problem with the actual application of ultrafiltration membrane is higher cost and low selectivity. One of the reasons for the higher cost is the membrane fouling. Natural and waste water steams contains impurities in the form of physical, chemical and biological nature. When waste water or natural water is passed through membrane, the foulants (like macromolecules, microorganisms and proteins) are adsorbed on the surface ofmembrane leading to pore blockage, decrease in permeate flux, and lessens the life of membrane. Fouling increases operational cost, labour for maintenance and cleaning costs. Efficient and effective methods are used for the control and minimization of fouling.Ultrafiltration has gained tremendous importance anddevelopments in recent two decades. However, the membrane fouling has remained one of the major challenge with ultrafiltration. This paper reviews the major issues on fouling and its control.

Membrane fouling

Fouling is caused by the impurities present in the feed solution. These impurities may interact with each other or with the surface of membrane. The interaction of impurities with the surface of membrane is called fouling. The fouling results in decline of permeate flux which ultimately limits the wider application of membranes. Numerous work has been carried out to understand the behaviour of fouling [1,2]. Fouling is divided into three types:

Organic and inorganic fouling: organic matter is naturally present in the feed water. Rivers and lakes typically contain more organic matter than ground-water. Feed water of high organic matter is accepted to be a noteworthy factor for flux decline. Most natural organic compounds contain a range of compounds such as humic substance, proteins and amino acids.Zulairasm etal. [3] reported the mechanism account-ting for organic fouling. The impurities present in the water streams may be hydrophobic, hydrophilic and transphilic in nature. They studied that the fouling takes place due concentration polarization, adsorption and cake layer deposition on the surface of membrane.Natural organic matter (like humic acids and fulvic acids) is a major foulantin ultrafiltrationprocesses. Humic acids impact more severely to the ultrafiltration membranes than some other common natural organic matter.Humic acidis a mixture of negatively charged macromolecules, branched with aromatic, phenolic and carboxylic functional groups[4].Kulovaar et al. [5] reflected that humic acids at low pH increase the rate and amount of fouling. Humic acids precipitate at low pH but are soluble at high pH.

Inorganic fouling: Inorganic fouling is caused by multivalent ions present in the feed.These ions precipitate on the membrane due to hydrolysis or oxidation during filtration. Precipitates are formedwhen the concentration on the membrane surfaceexceedsthan the saturation concentration. The term scaling is used for inorganic fouling.Scaling takes place in Nanofiltration (NF) and Reverse osmosis (RO) asthese processes reject inorganic substances.However, scalingis lessprevalent in microfiltration and ultrafiltration but may exist with interaction between ions and other substances.Potts et al. [6] found that the calcium, magnesium, carbonate, sulfate, silica and iron are the main inorganic substance causing inorganic fouling of the reverse osmosis membrane.EI-Manhaaway et al. [7**]** studied that major cations accounting for precipitates directly or indirectly in water include Ca^{2+}, Mg^{2+}, Fe^{3+}, and Al^{3+}.

Particulate fouling: Fouling caused by the adsorption of large particles on the membrane surface and smaller particles on the inside of pore. Particulates have inflexible shape. Contingent upon the proportion of molecule size to that of the membrane pore, particles may totally blind or partially blind the pore[8].As a result cake formation starts on the membrane surface.

Biofouling: Biofouling result when micro-organisms like algae adhere to the surface of membrane, forming biofilm on reproducing and producing an extracellular substance which increases the resistance,resulting in decrease in permeate flux. Ivnitsky et al. [9]reported that bacteria accumulate on membrane by two mechanisms (i) attachment by bio adhesion and bio adsorption (ii) growth by reproduction. Biofouling isa prone and major concern forultrafiltration membranes used in dairy industries. Pan et al.[10] analyzed that some microorganisms develop resistance to the sanitizing agents used in cleaning cycles. Overthe time microorganisms adapt to sanitizing agents used during cleaning.

Hydrophilic modification of membrane surfaces in ultrafiltration membrane

Ultrafiltration membranes are generally presented in the asymmetric form of the thin microporous top skin layer and thick sublayer for mechanical strength. Ultrafiltration membranes can be made fromthe inorganic substance (ceramic, glass, metal and zeolite) and from polymers.The materials used in the preparation of ultrafiltration membranes have different properties such as cellulose acetate the first polymer used in the preparation of membranes has a good hydrophilicity, low cost, a wide range of pore size from reverse osmosis to microfiltration [11]. Poly-sulfone (PS) material with wide pH tolerance, good chlorine resistance, wide range of pore size, good thermal and chemical resistance [12]. Polyvinylidene with good chemical resistance and better resistance to chlorine than sulfone family [11].However, these materials are not ideal for membrane preparation because of their inborn hydrophobic properties which makes them prone to fouling. Chemical cleaning or frequent membrane replacement significantly enhances the operation cost and limiting their use [13,14]. Therefore to reduce the fouling, hydrophilic modifications are used on various ultrafiltration membranes to increase its ability in permeate flux and service life. Numerous methods are applied to increase the hydrophilicity and decrease the fouling in ultrafiltration membranes. Membrane modifications can be divided into two categories (i) matrix modifications of membranes including blending and copolymerization. (ii) Membrane surface modifications including plasma modifications,and Surface coating modifications.

Blending and copolymerization

Blending refers to the preparation of polymer from two or more kind of polymers. The resulted polymer has a property of both and some exceptional properties that overcome their respected shortcomings. In preparation of modified ultrafiltration membranes, a highly hydrophilic polymer is blended with base polymer like polysulfone, polyethersulfone, poly-vinylidene etc. The addition of highly hydrophilic polymer increases permeate flux and decreases the fouling of ultrafiltration membranes. Cherdon et al. [15] blended the polyaramide with polyvinylpyro-lidone and prepared a modified membrane with enhanced hydrophilicity and antifouling properties. Recent work showed that a blend of zwitterion with other polymers imparted greater hydrophilicity and anti-fouling properties. Wang et al. [16] prepared the blend of polyethersulfone (PES) and sulfobetaine (SB). He observed thatantifouling and permeate flux was significantly improved. Kumar et al. [17] prepared a modified ultrafiltration membrane by blending the polysulfone and naturally occurring biopolymer chitosan. Results showed substantial enhancement in antifouling and permeate flux with the increase in the concentration of chitosan. By the reasonable selection of polymer blends, blending and copolymerization technique canbecome very effective in improving antifouling and permeate flux.

Plasma modification

In this technique surface is modified by plasma, it is a useful and effective technique to make the surface of material hydrophilic. By the plasma modification of surface, free radicals are formed and allowed to bond with hydrophilic polymers. Dung et al.[18] used plasma modification technique on polyacrylonitrile with plasma gases plasma and grafted acrylic acid as a monomer. The membrane showed thesignificant increase in permeate flux and higher hydrophilicity than the pristine membrane. Ulbricht et al. [19] modified the polyacrylonitrile (PAN) and polysulfone (PS) ultrafiltration membrane by plasma technology and grafted acrylic acid and methacrylic acid as a monomer and noticed the significant increase in permeate flux in the modified membrane.

Surface coatingmodification

Surfacemodification ofmembrane is an important and effective technology to enhance antifouling perfo-rmance, a membrane may be directly coated with the material having high hydrophilicity to impart anti-fouling properties to the membrane surface. The coated material interacts with membrane surface through secondary interactions like van der walls or electrostatic interaction or by cross-linking. Hyun etal.[20] coated the polysulfone ultrafiltration mem-brane with double amphilic comb polymer and results showed better flux recovery than the pristine one. Revanur et al. [21] coated the polyvinylidene fluoride (PVDF) ultrafiltration membrane with amphiphilic polymer and found its improved anti-fouling and anti-peeling capacity. The Coating of ultrafiltration membrane surfaces can significantly enhance the anti-fouling capacity and permeate flux however the issue with coatingis that it gets removed with time.

Conclusion

Fouling is one of the major issues in ultrafiltration membrane for their wider applications.Membrane fouling decreases permeate flux, increases maitai-nence cost and cleaning cost. Numerousmembrane alterations can help to improve antifouling and permeate flux.For eachmodification, there are advantages and disadvantages. Therefore better comprehension of fouling is the prime concern to develop a new method and material to mitigate fouling in ultrafiltration membranes.

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