

Trend and Novel Possibilities of Dairy Wastewater Treatment by Membrane Filtration

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Abstract

Membrane separation processes for wastewater treatment in dairy industry gives so many benefits such as less ecological footprint, reliable contaminant removal, low cost, possibility of renewable energy use, simple technology and can easily integrate with other processes. However, the fouling issue limits its widespread application. Self-cleaning membrane technology, through membrane modification by heterogeneous photo-catalytic nanomaterials and their composites, has been given more attention by many researchers. In this paper, characteristics of dairy wastewater and possible membrane separation processes applications in dairy wastewater treatment are summarised and discussed. Fouling mechanisms of protein, the interaction of molecules, factors affecting fouling are highlighted. Physical, chemical, and self-cleaning fouling control and mitigation strategies are reviewed. Membrane modifications by renewable or non-renewable energy-driven heterogeneous photo-catalysis and possible ways that enhance the photocatalytic efficiency are also addressed. Finally, challenges and prospective solutions are reviewed.

Keywords: Dairy wastewater, membrane separation processes, fouling, heterogeneous photo-catalysis, renewable energy, self-cleaning membrane

1. Introduction

Protection of water resource is unquestionably among the most critical problems in the world. According to Mancosu et al [1], food production uses over 3/5 of the freshwater consumption of the world; among them dairy industry alone generates 9% of food industrial wastewaters [2]. Dairy industry of many countries generates huge volume and pollution load of wastewater [3]. The effluent is primarily made up of carbohydrates, proteins and fats and remaining cleaning agents. It contains high load of organic matter and nutrients (e.g., nitrogen and phosphorous) [4]. Discharging that kind of wastewater affects all types of ecosystems and result in severe environmental harms, for instance eutrophication due to high nutrient content of the wastewater [5]. Such problems brought an alarm that the dairy wastewater needs to be addressed before its release to the environment, for example, the high chemical oxygen demand (COD) value need to be decreased to acceptable level [6].

In most countries, the dairy wastewaters are treated with traditional techniques, aiming the minimal necessary reduction of COD or biological oxygen demand (BOD) to turn the wastewater handable together with municipal wastewaters. During the treatment, the valuable nutrients in the stream are converted into less harmful form: e.g., ammonia to nitrogen, phosphate is precipitated. In spite of their value, they are hardly used as nutrients or fertilizers; on the other hand, the modern industry uses huge amount of energy and non-renewable sources for fertilizer production:

energy, mineral P-sources or coal to generate hydrogen for ammonia synthesis [7]. Besides the evidence of necessity of the water reuse, the recovery of nutrients as N and P is rarely taken into consideration; however, the return of nutrients to agriculture may close the cycle [8].

By now, several methods were developed and applied for water reclamation and reuse [9], however, they had risks, e.g., wastewaters may contain potentially harmful pathogens, nanoparticles, disinfection by-products or cleaning agents and detergents. There are several newly developed methods to eliminate these problems, e.g., AOP's (advanced oxidation processes) became good alternatives to disinfection by chlorination [8]. Besides them, membrane technology also represents a good alternative to treat these waters.

In terms of nutrient recovery, several techniques are available, both physical, chemical, and biological processes. However, basic requirement for all these processes to separate the nutrients from other pollutants of wastewater. Nowadays, the most widely used N and P recovery method is the struvite formation by crystallization and precipitation [10]. As there are several difficulties linked to this process, applying membrane separation, which enable to concentrate or separate the nutrients may be advantageous.

Membrane technology is more energy-efficient, environmentally friendly, and low cost as compared with the conventional methods [11]. But these processes suffer from fouling. The fouling because of the hydrophobicity of the membrane decreases flux and increases energy use which hinder the wider application of the technology [12].

Previous dairy wastewater treatment studies mainly focused on physicochemical and biological methods [13] and membrane separation applications [14][15][16][17]. In recent years, the application of membrane separation for dairy

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wastewater treatment is growing, as several novel and emerging techniques have studied and developed to overcome the limitations of membrane separation processes. Recent publications have focused on fouling reduction by offering innovative cleaning processes, optimizing the existing techniques, or integrating devices to the membrane set-up.

In this paper, we provide a review of up-to-date literature and of the recent developments of membrane separation processes in dairy wastewater treatment. The review also provides current strategies used to control and to prevent fouling in the membrane separation processes. A summary of factors affecting fouling are also addressed. Finally, our paper summarizes the treatment possibilities which meet the requirements of circular economy and reveal the problems to be solved in the near future for making membrane technology good and environmentally friendly alternative in dairy wastewater treatment.

2. Membrane filtration in dairy industry

Dairy industries produce several kinds of milk products (fluid milk, butter, cheese, yoghurt and so on) and by-products (dairy wastewater) [18].

Membrane filtration widely have been used in dairy industry for decades, mainly for protein recovery via ultrafiltration [19]. Caseins and whey proteins are the two kinds of milk proteins mainly found in skim milk and whey, respectively. Caseins are the primary group of milk proteins with small size micelles joined together by calcium phosphate bridges to form large size micelles in milk [20]. Caseins are classified as β -casein, κ -casein, α s1-casein, and α s2-casein and are the highest, moderate and lowest hydrophobic respectively [21]. The remaining milk proteins in the whey after cheese making is whey proteins. Bovine serum albumin (BSA), α -lactalbumin (α -LA), and β -lactoglobulin (β -LG) are whey proteins [22].

Beside the protein recovery, membrane technology is used for clarification of milk, separation of milk components by size or concentration of valuable components, moreover, it may provide environmentally friendly and economical alternatives to several unit operations of milk processing, such as centrifugation, whey demineralization or evaporation [23].

3. Characterization of Industrial Dairy Wastewater

The dairy wastewaters characteristics differ by technologies and factories. Processes in dairy industries involve multiple sections processing, cooling, heating processes cleaning (soda, nitric- and phosphoric acid or sodium hypochlorite) and washing [24][25]. Each of the various units in the process generates wastewater [4][25], and its characteristics strongly depends on the products, the operational circumstances, and the applied wastewater treatment process too. The chemical compositions may vary in a wide range, and generally it is characterized by COD (chemical oxygen demand), BOD (biological oxygen demand), pH, TSS (total suspended solids), TS (total solid), NH_3 (Ammonia), and PO_4^{3-} (Phosphate) as reported by authors are given in Table 1

4.1 Membrane fouling and mechanisms

Membrane separation process applications continue to increase, but these processes challenged by fouling that affect permeate flux with parallel increasing energy consumption [12]. Membrane fouling is the unwanted deposition of solutes

inside or outside parts of the membrane [36]. Various characteristics could be considered in to account to classify fouling. First, depending on foulant composition (biofouling, organic fouling, and inorganic fouling). Second, based on fouling reversibility (reversible and irreversible), and third, based on fouling location (concentration polarization, internal fouling, and external fouling). It is important to study the fouling mechanisms of each foulants. The fouling mechanisms can be through concentration polarization, adsorption, cake, gel, scaling, pore blocking, and biofilm [37].

Membrane fouling reduces separation efficiency of membranes, increase of maintenance and operation costs. As a result of its effect, fouling is nowadays becoming the main obstacles for development of membrane technologies [38].

Protein fouling

The protein content of the dairy wastewater was found to be severe foulant for polymeric membrane materials [6]. The study by Ng et.al., [22] have provided significant insight into fouling components and mechanisms of fouling are illustrated in Figure. 1.

As illustrated in Fig. 1., whey proteins (WPs) are smaller in size than casein micelles (CMs). The size variations between them bring about composition differences in the concentration polarization (CP) layer [22].

Generally, proteins, emulsified oils, microorganisms, and humic materials have a higher fouling propensity to hydrophobic membranes than hydrophilic membranes [12]. Therefore, many surface modifications deal to change hydrophobic membrane surface into hydrophilic. Because hydrophilic surfaces tend to bind a layer of water, which discourage the accumulation of foulants from the solution [39].

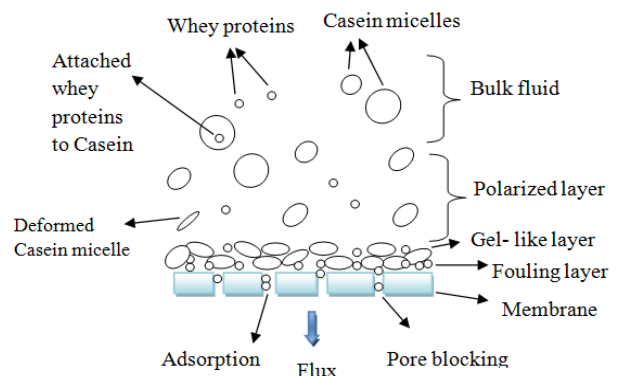


Fig. 1. Graphical representation of fouling process during skim milk UF (modified from [22]).

4.2. Factors affecting membrane fouling

There are three factors influencing fouling, these are membrane properties, feed water composition and hydrodynamic (also known as operating) parameters [40], as shown in Fig. 2.

Interactions between the membrane and dairy wastewater components

Surface hydrophilicity, surface charge, and surface smoothness are important membrane surface properties that affect membrane fouling [41]. Hydrophilic, smooth, and low surface charge membranes have shown a better fouling resistance at the beginning phase of fouling. But severe fouling obtained at later phase of fouling due to foulant-to-

foulant interactions. Repulsive charges between membrane and foulant may reduce fouling by repelling [42]. The resultant attraction or repulsion forces are mainly influenced by hydrophobicity and the charge of the membrane which finally affect the degree of fouling [43]. More benefits can be obtained in terms of protein-membrane interaction by manipulating hydrophobicity and their charge, which is minimal at their isoelectric point. Their hydrophobic interactions and aggregation lead to their deposition and fouling [44]. The membrane-solute interactions are summarized in Fig.3.

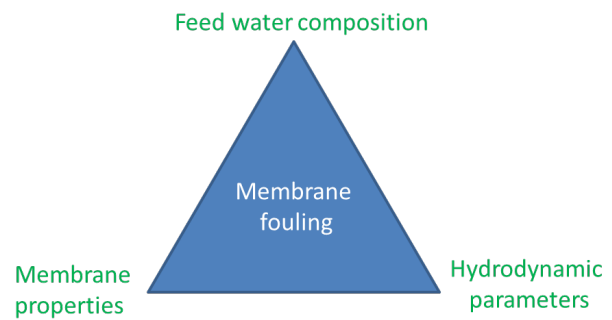


Fig. 2: Factors affecting membrane fouling

Table 1. Characteristics of dairy wastewaters

Waste type	Constituent in mg/L except pH							References
	COD	BOD	pH	TSS	TS	NH ₃	PO ₄ ³⁻	
Dairy effluent	190 - 2700	120 - 1800	7.2-8.8	500 - 740	900-1350	-	-	[3]
Dairy wastewater	890 ± 14	216.17 ± 4.17	6.035 ± 0.065	-	938 ± 6	69.96 ± 1.16	69.96 ± 1.16	[26]
whey	71526	20000	4.1	22050	56782	-	-	[27]
Dairy wastewater	2,500-3,000	1,300-1,600	7.2- 7.5	72,000-80,000	8,00-10,000	-	-	[28]

Feed water composition is among one of the factors influencing fouling. Proteins show amphoteric or hydrophobic behaviour and can easily adsorb on hydrophobic membranes, but the extent and rate of adsorption depends on the nature of dairy proteins, protein type, the ionic concentration and pH [61]. The presence of many ions in the solution shields the charged ions of protein molecules exposure from one another and result in high transmission [62].

High ionic strength and low pH favours fouling due to compression and deprotonation effect. Fouling is very high in a low pH or high ionic strength condition during UF of proteins. The electrical double layer (EDL) of protein molecules is compressed by high ionic strength. Because of this effect, protein molecules become small and tend to aggregate to form fouling. Functional groups in proteins undergo deprotonation at low pH. This decreases the repulsive force of protein molecules and lead to fouling [46][48][50].

During BSA filtration protein fouling is strongly associated with zeta potential of BSA which is affected by pH. Around isoelectric points (IEP) of BSA (pH 4.7), BSA molecules tend to come together due to low repulsion force. Therefore, the fouling mechanism is expected to be complete blocking and standard blocking. However, at higher pH both BSA and membrane are negatively charged and repel each other, reducing sever fouling of BSA, but cake layer could be formed slowly.

The impact of ionic strength on fouling depends on pH. At pH 3.0 and 5.8 an increasing and decreasing fouling trend were observed as ionic concentration went up from 1 to 10 and then to 100 mM NaCl while it did not show substantial effect at pH 4.7 and 7. The lowest flux throughout the ionic strength were observed at pH 4.7 [51]. Another fouling mitigation mechanism may be a charge shielding effect. This is obtained by increasing ionic strength and reduced protein deposition [52].

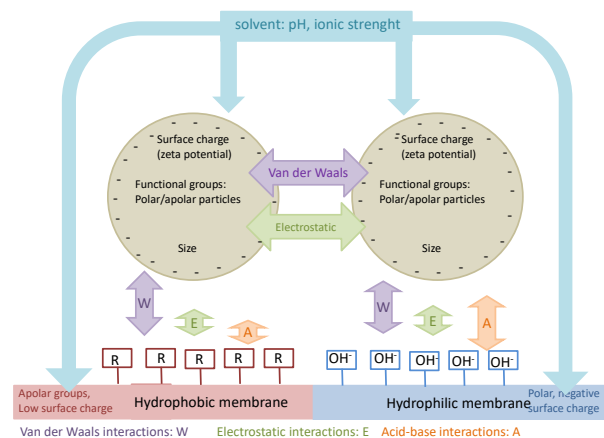


Fig. 3. Membrane-solute interactions

Hydrodynamic parameters

Velocity, trans-membrane pressure (TMP) and temperature are among hydrodynamic operating conditions that have effect on fouling. For example, low TMP results in not only lower fouling but also lower flux [53]. However, BSA fouling may be becoming severe as long as applied pressure increased; flux reductions were obtained 70.4%, 81.6%, and 92.2% at 100 kPa, 200 kPa, and 500 kPa, respectively, compared to only 28.5% reduction at 20 kPa [53], due to building up more compact protein layer on the membrane surface.

Flux performance was also investigated at various levels of velocities (13.9, 27.8, and 41.7 cm/s). Results indicated that flux reduction was decreased at increasing velocity. In this study best flux was obtained at the highest velocity (41.7 cm/s) which is about 137.4 L/m²h as compared with the flux 51.0 L/m²h at 13.9 cm/s and 74.7 L/m²h at 27.8 cm/s. Application of higher crossflow velocities is advantageous in terms of possibility of improved back transport and the reduction of concentration polarisation. Therefore, more extended fouling take place above the critical flux and lower crossflow [54]. The permeability of a membrane remains

almost constant with insignificant foulant deposition when the filtration is performed below the critical flux [55].

The effect of temperature is also one of the operational factors that can significantly affect fouling. BSA filtration at various temperatures was studied using ultrafiltration membrane. The outcome of the finding revealed that the membrane fluxes were declined from 0.68 at 20°C to 0.43, 0.30, and 0.28 at 27, 34, and 80 °C, respectively [46]. The influence of temperature can be explained by whey protein membrane fouling which was larger at temperatures less than 10 °C and more than 35 °C [30]. Both extreme temperatures affect protein structures and allow hydrophobic interactions that lead to protein deposition [56]. Denatured proteins aggregate and foul easily as compared with decreases protein solubility compared to normal protein [57].

Based on their materials they are produced membranes can be fabricated from polymeric or ceramic materials [58]. Filtration using polymeric membranes are more preferred than ceramic membranes because of low cost, no harmful by-products and can easily integrate with other methods [59]. However, polymeric membrane materials severely fouled by proteins [6]. Conventional polymers used for polymeric membrane manufacturing include polysulfone (PSF), polyethersulfone (PES), polyacrylonitrile (PAN), polyvinylidene fluoride (PVDF), cellulose acetate (CA) and polytetrafluoroethylene (PTFE) [59][60].

4.3. Fouling control and mitigation strategies

4.3.1. Physical methods

Physical cleaning changes hydrodynamics to a given solution to prevent foulant deposition on the membrane material. These methods may include cross-flow, hydraulic flushing, shearing, field (electric, ultrasonic, magnetic), concentration polarization absorber and adding activated carbon [63]. Backflush and backwash are commonly applied physical cleaning technologies. Unfortunately, these technologies require longer processing time [64].

By introducing vibration, it is possible to get an increased shear rate, which can reduce the membrane fouling and improve flux [65] [66]. The cleaning mechanism of vibration is achieved by generating an increased turbulence and shear forces on the membrane surface, to loosen and remove the deposits [67]. A study by Altaee et al., 2010 [67] revealed that fouling cleaning efficiency was enhanced with increased vibration frequency. The increased vibration frequency from 1.67 to 8.35 Hz leads to an increased critical flux from 27 to 56 L/(m²h) compared to 15 L/(m²h) without. Li et al. 2013 has also reported that membrane performance can be significantly improved when the vibration frequency or vibration amplitude increases above a threshold magnitude. Over 90 % membrane cleaning efficiency was attained at 8 mm amplitude and 8 Hz frequency vibration compared to no vibration [68].

Ultrasound is another physical method, and it has been applied for membrane cleaning in membrane filtration processes [72][76][77]. Ultrasound provides strong mixing both at a macroscopic (strong convective currents) and microscopic level (micromixing, pressure shockwaves, and microjetting). The strong convective currents known as acoustic streaming bring about increased fluid motion and turbulent mixing. At a microscopic level, there are physical effects from the collapse of cavitation bubbles that generate micromixing, pressure shockwaves, and micro jetting.

It is effective in reducing the concentration polarization and eliminating cake layers on the membrane [74]. Ultrasonic

membrane cleaning applies high-frequency sound waves to agitate the aqueous medium which in turn acts on the foulants adhering to the membrane surface [75]; application of frequency between 20–28 kHz performed the best to control PVDF membrane fouling [69]. A study by Lee et al., [70] showed outstanding performance of ultrasound as compared to flushing alone. Yu [71] also indicated reduction of reversible and irreversible fouling by ultrasound. The performance of ultrasound can also improve by combining with other cleaning processes, like surfactant [64]. Unlike backwashing or chemical cleaning, ultrasonication can be integrated in the filtration process without stopping the filtration; since it does not use chemicals and backwashing water; it avoids the difficulties of chemical costs, waste disposal and environmental concerns [72].

In terms of fouling mechanism, ultrasonic enhancement of membrane filtration showed four main effects on whey protein fouling [76]. Firstly, sonication reduces pore blockage and cake compaction by promoting the agglomeration of fine particles. Secondly, sonication maintains particles suspended by providing mechanical vibrational energy to the system. Thirdly, sonication induces small vapour-filled cavities known as cavitation bubbles that scour the membrane surface and can reach areas not accessible to conventional cleaning methods. Finally, acoustic streaming causes turbulence and more intense mixing, which will result bulk fluid movement toward and away from the membrane cake layer.

4.3.2. Chemical cleaning

Chemical cleaning is a kind of using chemical agents that degrade the foulant or reduce the attractive force between the molecules of the solution and membrane [78]. It is mainly used to clean hydraulically irreversible foulants. It can be applied in various ways; firstly by cleaning the membrane by replacing the original feed with cleaning solution within the membrane reactor referred as cleaning-in-place (CIP), secondly by soaking the membrane in a separate tank outside the reactor, known to as cleaning out of place (COP), thirdly by adding chemicals in the feed stream, fourthly cleaning the membrane in physic chemical combination [79]. The chemicals could be acids, alkaline and oxidants. Commonly applied chemicals for membrane cleaning are sodium hydroxide, sodium hypochlorite, hydrochloric acid, sulfuric acid, nitric acid, ethylene domain tetra acetic acid and sodium dodecyl sulphate. Study results have shown that alkaline chemicals offer better cleaning performance in milk processing industry as compared to acids [78]. However chemical cleaning may damage the membrane, generate effluents and are expensive [80].

During chemical cleaning of membrane fouled by milk components cleaning agent diffuses into the fouled membrane surface and undertake chemical reaction between the cleaning agent and the deposited materials at the membrane surface. The reaction may be hydrolysis, dissolution or dispersion which results in removal of fouling materials from the membrane surface [81]. Alkaline offer better cleaning performance in milk processing industry as compared to acids, moreover combinations of chelating agent, surfactant and alkaline provide the best cleaning efficiency [81]. Ethylenediaminetetraacetic acid (EDTA) as a chelating agent has an outstanding ability to combine and form strong complexes with multivalent metal ions such as calcium and minerals in general. The effect of sodium dodecyle sulfate (SDS) as a surfactant can bring a change in interfacial tension of water. This results in superior separation of build-up materials from the membrane surface. Sodium hydroxide

(NaOH) alters pH of the solution and offers a favourable condition for the highest removal of foulants using EDTA and SDS [80][82].

An other study demonstrated, that alkaline, such as sodium hydroxide (NaOH), potassium hydroxide (KOH) can facilitate quick hydrolysis of proteins and polysaccharides into small amides and sugars; reduces the number of bonds between the foulant and the membrane surface and increase mass transfer of cleaning agents to the membrane surface. Acids such as hydrochloric acid (HCl), nitric acid (HNO₃) and sulphuric acid (H₂SO₄) can perform efficiently and effectively dissolve precipitates of inorganic salts and metal oxides or hydroxides [83].

4.3.3. Physicochemical cleaning

Physicochemical methods are the most used cleaning process. For instance, chemically enhanced backwashing (CEB) is widely used physicochemical method, in this case chemicals are used during backwashing [79].

One of the recent fouling cleaning trends is integrating physical and chemical cleaning in membrane cleaning processes. A research showed that effective chlorine addition (0.2–0.5 mg/L) and backwash at flux of 8.33 L/(m²h) reduced fouling rates by 63–77% compared to normal water backflushing in membrane bioreactors (MBRs) [84], while Zhou et al. 2014 reported that 0.01 mol/L NaOH at 0.3 h duration and backwash flux 8.33 L/(m²h) could reduce fouling rate by 50% compared to water backwashing method in MBRs [85].

The study carried out by Maskooki et al. [86] demonstrated that using lower frequencies of ultrasound associated with EDTA is more effective than using each measure separately. The flux recovery rate by this physicochemical cleaning was about 4–10 times that of single ultrasound or EDTA cleaning.

4.3.4. Pre-treatment

In membrane separation processes pre-treatment is necessary to ensure reliable membrane operation, reduce membrane fouling risk and prolong membrane life. The extent of fouling risk reduction varies with type of pre-treatment method. Coagulation method is an attractive method for the removal of particles and dissolved contaminants but ineffective in removing the neutral hydrophilic and low molecular weight fractions [87].

Physicochemical pre-treatments such as coagulation/flocculation and oxidation practice have been used to reduce wastewater contaminants. However, they are expensive and poor in terms of contaminant removal [88]. They also generate chemical sludge that require additional treatment and require pH adjustment [89].

Oxidation pre-treatments such as use of ozone, ultraviolet (UV) radiation with hydrogen peroxide (H₂O₂) and ultraviolet (UV) radiation with persulfate (PS) were also applied as the pre-treatments for UF process. Among these pre-treatment methods ultraviolet (UV) and persulfate (PS) combination offered an outstanding result in mitigating membrane fouling and contaminant removal. This performance may be associated with PS, a powerful oxidant, ability to produce sulphate radicals (SO₄^{•-}) by catalyser activation in water. [90]. Combination of ferrous ion (Fe(II)) and sodium percarbonate (SPC) were performed better membrane fouling control than using each of them alone because Fe(II) serves as catalyst to activate SPC oxidation [91].

Pre-treatment of wastewater before ultrafiltration were investigated using advanced oxidation processes, that is, ultraviolet together with ferrous ion, ultraviolet together with persulfate, ferrous ion together with persulfate and combination of ultraviolet, ferrous ion and persulfate. The best performance was shown by combination of ultraviolet light, ferrous ion and persulfate followed by ferrous ion and persulfate. The lowest performance was observed in the combination of ultraviolet pre-oxidation together with ferrous ion pre-coagulation [92] as Fe(II) has high tendency to oxidize rapidly to Fe(III) in a reaction and the catalytic effect may decrease at neutral pH [93]. Degradation experiments of free-radical scavenger addition (sodium hyposulfite or tert-butanol) showed that the sulphate radical (SO₄^{•-}) was dominant in degrading organic compounds but the release of Fe(III) from water under UV radiation and its possible conversion to Fe(II) were observed on the surface of the fouled membranes and this caused decreased catalytic effect [92].

Combination of different methods such as disinfection, scale inhibitor (acid), activated carbon, coagulation/flocculation, and membrane filtration (UF)/MF) are widely used as effective pre-treatment methods for reverse osmosis (RO) [94]. In these processes, each pre-treatment methods control some contaminant for example part disinfection can destroy microorganisms which may cause diseases and membrane biofouling. Scale inhibitor (acid) remove inorganic molecules to control inorganic fouling. Activated carbon remove dissolved organic carbon (DOC) to control organic fouling. Coagulation/flocculation removes colloidal particles and dissolved organic carbon (DOC), while membrane filtration (UF)/MF) removes colloids, particles, and microorganism to control colloidal fouling, organic fouling and biofouling.

4.3.5. Membrane modification

Membrane surface is a part of the membrane that contacts the feed. Its properties basically determine the membrane performance. Membrane improvement has been performed by coating it with semiconductor heterogeneous photocatalysts or using hydrophilic polymers such as polyethylene glycol (PEG), polyvinylpyrrolidone (PVP) and poly(methyl methacrylate) (PMMA) and so on [95].

Membrane modification is intended to reduce fouling in dairy protein separation processes by changing the chemical nature and pore size of the membrane.[96][97].

Membrane modification by semiconductor heterogeneous photo-catalysts

Heterogeneous photocatalysis is a process, which transfer light energy into other form of chemical energy to use for several applications, particularly water and wastewater purification. It is able to degrade a many type of organic contaminants and mineralize the contaminant into water and carbon dioxide [98]. Heterogeneous photocatalysis do not transform the contaminant from one phase to another like coagulation and flocculation process, instead it eliminates the contaminants by mineralization. The basics of heterogeneous photocatalysis are summarized in Fig. 4.

Based on the energy source, the nano-catalysts used could be photocatalysts and electrocatalysts [99], and Fenton based catalysts [100]. They enhance the degradation of organic contaminants [101] and microbial foulants [102].

Because of the many drawbacks associated with physical and chemical cleaning technique, nanostructured photocatalysts, such as tungsten-oxide (WO₃)[103], bismuth-

oxide (Bi_2O_3) [104], titania (TiO_2) [105][106], zinc-oxide (ZnO) [107], graphene oxide (GO) [108], zirconia (ZrO_2) [109][106], alumina (Al_2O_3) [109], and silica (SiO_2) [110] have been gaining considerable attention to enhance the hydrophilic and surface free energy character of the membrane surface.

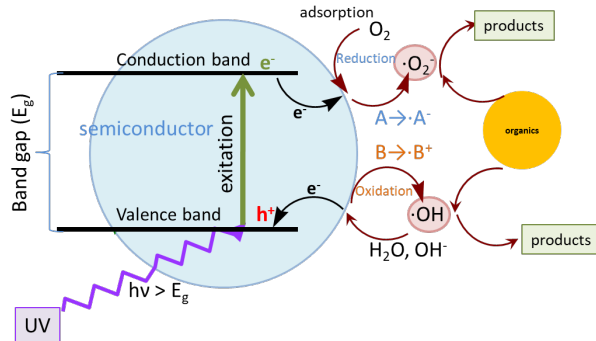


Fig. 4. Mechanism of heterogeneous photocatalysis

The photocatalyst titanium dioxide (TiO_2) is superior as compared with other photocatalysts, because it has excellent physical and chemical characteristics, low cost, high photocatalytic reactivity below 390 nm ultraviolet light required for most photocatalysis reactions, desirable hydrophilic and potential antifouling properties [111], [112]. It also has superior benefits to advanced oxidation processes. It is stable under photo and chemical exposure, cheap, reusable, and non-toxic [113]. Rutile, anatase, and brookite are the three structure polymorphs of titania; anatase shows the highest photocatalytic reactivity due to its lower recombination rate of electron-hole pairs [114]. For high photocatalytic performance, high anatase contents and relatively large specific surface areas for the coatings are required.

Since ZnO has a wide band gaps, similarly to TiO_2 , it has also been widely studied for photocatalysis [115]. Like polymer- TiO_2 , polymer- ZnO composite membranes attracted the attention of researchers in membrane technology. Zinc-oxide (ZnO) nanoparticles are a low-cost, environment-friendly, and hydrophilic inorganic material, that can provide composite polymeric membranes with excellent antifouling performance and photocatalytic self-cleaning benefits, furthermore it has comparable physical and chemical properties to TiO_2 [116][117].

Effects of membrane modification on fouling: enhancement by their properties and surface charge

Scaling and organic fouling are longstanding problems in RO membrane-based desalination, which requires frequent chemical cleaning, increases operation cost, and adversely impact the environment [118][119]. Membrane surface properties, including surface wettability, charge, and functionality, are the main factors governing the scaling and organic fouling on the membrane surface [120]. Tong et al., [120] revealed that surface functional groups with positive charge attract negatively charged dissolved silica species, thus accelerating silica scaling on the membrane surface. Hence, membrane fabrication or surface modification that can control scaling and fouling at the same time would be highly advantageous for more productive RO desalination.

More negatively surface charged membranes ($-\text{COOH}$), acrylic acid (AA) membranes were fabricated through redox free radical grafting method. Ethylamine (EA) and ethylenediamine (ED) membranes with neutral or less negative surface charge were fabricated through $-\text{CH}_3$ or $-\text{NH}_2$ functional groups grafting aimed in improving antifouling or anti-scaling properties. Compared to the pristine membrane, all the modified membranes possessed better salt rejection without sacrificing water permeability. The AA membrane also showed better antifouling property, less silica scaling and organic foulants [121].

Functionalized surface of thin-film composite (TFC) RO membranes by negative surface charge of sulfonic group (vinyl sulfonic acid) mitigates negatively charged silica scaling. It also effectively hinders bridging between organic foulant and the membranes [112]. Amine-functionalized osmotic membranes were fabricated by optimizing the grafting pathway of polyamidoamine (PAMAM) dendrimer to mitigate fouling and ammonium transmembrane diffusion. Compared to the control membrane, the PAMAM-grafted membranes with abundant primary amine group showed significantly increased hydrophilicity and positive charges (i.e., protonated primary amines) and thus exhibited superior anti-fouling capability and ammonium selectivity and eventually achieved an ultra-high ammonium rejection of 99.4% [123].

Farahani & Vatanpour [124] compared pristine PVDF membrane with different loading of cloisite 30B clay, carboxyl- functionalized multi-walled carbon nanotubes, Silicon dioxide and titanium oxide). Pure water flux improvement for clay, MWCNTs-COOH, SiO_2 , and TiO_2 was 187%, 143%, 50%, and 111%, respectively. Because of hydrophilicity enhancement, the modified membranes showed better antifouling properties. Unlike clay and TiO_2 modified membranes MWCNTs-COOH and SiO_2 modified membranes showed better BSA rejection compared to pristine PVDF membrane. High loading of nanoparticles resulted in lower performance of the modified membrane by increasing dope viscosity, agglomeration and blocking the pores. In an other study, Susanto et.al.[125] compared three modified polyether sulfone (PES) ultrafiltration membranes. The highest flux and the lowest flux reduction were observed in case of PES/ TiO_2 3 wt% which was followed by ZnO 5 wt%.

4. Challenges and possible solutions

Nowadays fouling becomes a threat to a conventional polymeric membranes' application. Self-cleaning photocatalytic polymeric membranes have been shown better resistance to fouling [124]. However, electron/hole recombination and low photo-efficiency are the two disadvantages that limit its practical application. In photocatalysis, low photo-efficiency can be improved by utilising the solar/visible light spectrum.

The electron/hole recombination resulted in waste of energy. Several approaches have been applied for tackling the quantum inefficiency of a photocatalyst [126]. First, by using oxidants because the addition of oxidants adds acceptors of electrons in the process and increases the number of trapped electrons. Second by doping, pure and unmodified semiconductor surface like TiO_2 use only the UV spectrum and works at calm conditions with weak oxidants. So unmodified photocatalyst for practical treatment applications of industrial and environmental effluents of higher concentration of contaminants may require high costs

associated with artificial light. Hence, the drawbacks of unmodified photocatalyst must be solved by combining the photocatalyst with semiconductor with a narrower bandgap or doping the photocatalyst with a transitional metal ion, sulphur, nitrogen, and noble metals [126].

Applying photosensitizer on the surface of photocatalyst also may be an effective method. The photosensitizer does not act as a photocatalyst, instead, facilitate the semiconductor to carry out reaction using visible light by injecting its excited electrons to the conduction band of semiconductor. A photosensitizer is vital in industrial textile wastewaters as these wastewaters consist of a large number of dyes [104]. Graphene and carbon nanotubes are also reported to behave as photosensitizers under visible light by transforming wide band gap of the semiconductor to a visible light photocatalyst [127].

Another way of enhancing the photocatalytic efficiency is combining photocatalyst with other technologies, including ozone treatment, vacuum ultraviolet treatment or photocatalytic membrane reactor (PMR)[128]. Many researchers have reported several nanomaterials with photocatalytic activities using visible light. These are nanoparticles and quantum dots of cadmium sulphide (CdS) [129], bismuth vanadate (BiVO₄) [130], and nanocubes of silver-chloride (AgCl) [131], copper sulphide nanostructures (CuS NSs) [132], semiconductor β phase bismuth oxide (β -Bi₂O₃) [133], iron (Fe) (III) and active carbon [134].

5. Conclusions

Considerable volume and high pollution load of effluent is generated by food industries especially dairy industry. In dairy wastewater, proteins tack the lion share of fouling during polymeric membrane separation processes. Proteins are amphoteric molecules; the charge of their surface depends on the solution pH. Membrane separation processes may be advantageous to treat wastewater of dairy industries,

however, fouling issue limits their widespread application. Membrane fouling may be influenced by several factors, operating parameters, feed water composition, and membrane properties. Fouling in dairy wastewater treatment is primarily relying on the salt and the type of protein present.

Membrane separation processes offer possibilities to reuse dairy industrial wastewater effluent. Membrane fouling can be controlled and mitigated through physical, chemical, physicochemical, pre-treatment and self-cleaning membranes. Self-cleaning membrane is a promising method over the other methods because of low cost, less time, less ecological footprint, and efficient contaminant removal. Chemical oxidants, doping, photosensitizers, combining semiconductor photocatalysis with other AOPs are the most promising techniques applied to tackle electron/hole recombination and low photo-efficiency of heterogenous photo-catalytic materials.

Cadmium sulphide (CdS), bismuth vanadate (BiVO₄), nanocubes of silver chloride (AgCl), copper sulphide nanostructures (CuS NSs), semiconductor β phase Bismuth oxide (β -Bi₂O₃), Iron (Fe) (III) and active carbon are nanomaterials that can perform their photocatalytic activities using visible-light. Visible-light or solar energy driven photocatalysis applicable in a more extensive environmental conditions can be achieved through doping and modifications of membranes by heterogeneous photo-catalytic materials.

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