CHAPTER: 3.0

LITERATURE REVIEW

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3.1 Review paper on Emulsion Liquid Membrane & others membrane

Industrial development is accompanied by a growing quantity of waste products harmful to the natural environment. Thus, there is a growing demand for new technologies allowing the re-use of raw materials recovered from waste products. The first scientists to describe liquid membranes (LM) in 1902 were Nernst and Riesenfeld [1]. They investigated the properties of systems consisting of an oil layer separating electrolyte solutions. Dr. Norman Li [2] invented emulsion liquid membrane (ELM) in 1968. The separation technique using liquid membranes has been used as a novel method for separation and concentration of a wide variety of solute materials as they are capable of giving a higher degree of concentration of solute in fewer stages while maintaining the high selectivity of the solvent extraction process [2,3].

A liquid membrane (multiple emulsion, water-in-oil-in-water (W/O/W)) method of separation of chromium (VI) from simulated waste water has been described by Chakravarti et al. in 1995 [4].

The effect of the membrane composition on the extraction rate is the most significant as the capacity of the membrane to extract solute as well as the stability of the emulsion globules is influenced by the nature of the surfactant and its concentration, the carrier concentration and the nature of the solvent used. The membrane composition should be such that the membrane should be stable and at the same time should have reasonable solute extraction capability. Studies by a number of researchers reveal that the initial extraction rate increases with increase in surfactant concentration [5-8].

Chromium(VI) transport across supported liquid membranes (SLMs) and polymer inclusion membranes (PIMs) with tertiary amines and quaternary ammonium salt (Aliquat 336) from chloride acidic aqueous solution to 0.1M NaOH has been studied by Cezary A. Kozlowski et al. in 2004 [9]. The initial flux of Cr (VI) decreases linearly with logarithm increasing of partition coefficient of n-octanol/water for R3N amines. The chromate ions are transported across polymer inclusion membranes with lower rate using polyvinyl chloride (PVC) instead of cellulose triacetate (CTA) support.

Levent G. et al. [10] had studied to remove of lead ions from industrial storage battery wastewater by ELM in 2007. Toluene, kerosene, mineral oil, and xylene, as organic diluents,
sorbitan monooleate (Span 80) and polyoxyethylene (20) sorbitan trioleate (Tween 85), as surfactants, and di-2-ethylhexyl phosphoric acid (D$_2$EHPA), as extractant, were used. In the process of lead ion removal from storage battery wastewater, while lead ion concentration decreased to < 0.4 mg/l from its initial value of 2.8 mg/l, the organic matter load (COD) of the treated wastewater increased to about 160 mg/l. Additionally, Span 80 exhibited better results than Tween 85 in terms of CODs and lead removal. Kerosene had a more stable membrane than the other organic diluents used. The optimum membrane components and their rates were 70% kerosene, 18% mineral oil, 3% Span 80, and 9% D$_2$EHPA. When wastewater pH was adjusted to improve lead ion removal, COD of the treated wastewater increased to > 200 mg/l.

In the year 2003, Sohair A. E.R. et al. was carried out experiments to assess LEM (Liquid Emulsion Membrane) technique for removal and recovery of certain pollutants, such as uranium, thorium, cobalt, copper, lead, and cadmium, to clean up waste effluents produced from nuclear activities as well as other industrial processes. The carriers employed were: di-2-ethylhexyl phosphoric acid (D$_2$EHPA) and triaryl phosphine oxide (Cyanex-921) for removal of U(VI), bis,2,2,4 trimethyl dithiophosphinic acid (Cyanex-301) for removal of Co(II), thenoyltrifluoroacetone (HTTA) for removal and recovery of U(VI), Th(IV) and Co(II) and finally, the carrier 2-hydroxy-5-nonyl-acetophenone oxime (Lix-84) for removal of Cu. It was concluded by him that the variety of carriers in LEM systems offered a broad range to remove many hazardous elements from different waste effluents. One of the main advantages of LEM is the high preconcentration factor. The LEM system could be a continuous one based on breaking the LEM to separate the pollutant from the stripping phase followed by recycling the organic phase for preparing a new LEM for reuse.

The effect of pH to remove of hexavalent chromium (Cr+6) was carried out by Muthukrishnan M. et al. with different nanofiltration (NF) membranes for varying concentration and pH of the membrane feed solution [12].

Batch extraction of nickel(II) with ELM from a dilute sulfate solution by using di-(2-ethylhexyl) phosphoric acid (D$_2$EHPA) as an extractant and hydrochloric acid as a stripping agent is reported by Chakraborty M. et al. Important variables affecting the stability of the emulsion, such as pH of the feed phase, speed of agitation, emulsion drops size per unit specific
interfacial area, surfactant concentration, pH in inner aqueous phase, and the presence of different tracers, are systematically investigated during the extraction of nickel(II) ions [13].

The use of Taylor–Couette flow for extraction by emulsion liquid membranes has been characterized by Parka Y et al [14] in 2004. The motivation for their study was the observation from earlier work of a cloudy residue in the form of droplet filamentary threads undoubtedly due to inertial stress on the droplet near the impeller region of a stirred tank. During mixing in tank, most of the energy dissipated per unit volume of the tank occurs in a small volume defined by the rotation of the impeller tip. In such flows the impeller surfaces are subjected to form drag and a large shear creating intense turbulence leading to the inertial dominated breakup of the emulsion globule. With equal power input per unit volume and roughly equal rotor and tank stirrer diameters, Taylor–Couette flow reduces the maximum shear stress by one to two orders of magnitude compared to a stirred tank, depending on the impeller design. The reduced shear stress is the result of an increase by one to two orders of magnitude in the area subjected to the constant maximum shear defined by friction drag on the large cylinder surfaces on the boundaries of Taylor–Couette flow [15-16].

About solid-stabilised foams, even less is known; these foams play a major role in many industries, including mineral recovery and wastewater treatment. Over the last decade, however, the number of studies involving solid-stabilised foams has been limited and few have focused on the benefits of complex systems such as those involving mixtures of more than one (hereafter referred to more simply as “mixed”) surfactant. The relationship between two surfactants and their stabilisation properties has been studied in thin films by Manev et al (1993). Little is known, however, about the effectiveness of using mixed surfactant systems as foam stabilisers at the bulk level [17].

The stability of foams formed using nonionic surfactants is also affected by electrolyte concentration. Müller and Rheinlander (1996) have found that the film thickness of foams stabilised with polyoxyethylene alkyl ethers depends on salt concentration and the number of ethylene oxide units in the hydrophilic chains [18].

The displacement mechanisms of alkaline flooding in enhanced heavy oil recovery (EOR) are investigated by Mingzhe D et al (2007). It has been observed that two mechanisms
govern the EOR process. One is a novel mechanism — *in situ* water-in-oil (W/O) emulsion and partial wettability alteration. Alkaline solution can penetrate into heavy oil in porous media, forming W/O emulsions. Due to the very high viscosity of the W/O emulsion, the resistance to water flow in high water saturation zone can be increased to improve sweep efficiency. The two displacement mechanisms can be applied individually or in combination for improving water flooding of heavy oils [19].

Removal of cadmium from wastewater using emulsion liquid membrane (ELM) is studied by Hamid R. M., et al (2009). A polyamine-type surfactant was used for stabilizing the emulsion phase. Tri-iso-octyl amine (TIOA) has been used as a carrier for transferring of cadmium through the membrane. The results show good performance in the separation process [20].

The removals of single aromatic alcohols, including *para* nitro phenol (PNP), *meta* nitro phenol (MNP), phenol (P), catechol (CC), beta napthol (BN) and *ortho* chloro phenol (OCP) from aqueous solution have been studied using micellar-enhanced ultrafiltration (MEUF) by Purkait M.K. et al (2005) [21].

The ultrafiltration of two types of surfactants, sodium dodecyl sulfate (SDS, anionic) and Tergitol NP-9 (nonylphenol polyethylene glycol ether, nonionic), using a 20 nm ZrO2 tubular membrane was investigated by Fernández E., et al (2005) [22].

The osmotic swelling behavior of water-in-oil-in-water (W/O/W) type emulsion liquid membranes (ELMs) was investigated by Jun Yan et al (2001) [23]. Using an optical microscope equipped with a camera, the changes in the size of the W/O/W globules were monitored over a long period of time (up to about 4 h). The osmotic pressure gradient between the internal and external aqueous phases was induced by creating a concentration difference of d-glucose between the two aqueous phases. The results indicate that the swelling ratio, defined as the ratio of globule diameter at time $t$ to globule diameter at $t = 0$, (initial volume fraction of internal aqueous phase droplets). The swelling ratio generally increases with the increase in the concentration of surfactant present in the membrane (oil) phase. The permeation coefficient of water also increases with the increase in the surfactant concentration. The mechanism of water transfer in ELMs of the present work is reasoned to be the diffusion of hydrated surfactants.
Double emulsions have potential for the production of low calorie food products, encapsulation of medicines and other high value products. S. van der Graaf et al.(2005) had described the state of the art; the advantages and disadvantages of membrane emulsification in relation to the production of stable double emulsions are summarized and compared. Finally an outlook on further research in this field is given [24].

The influence of different additives on the effective HLB values of non-ionic emulsifiers was studied by S. Gasic et al.(2002). He used the method of the determination of the phenol index values and by the determination of the emulsion inversion point in the system with xylene as the oil phase. Ethanol, glycerol and ethylene glycol were investigated as additives [25].

Nurlan Sh. Stamkulov et al. examined the stabilisation of emulsions by using a combination of an oil soluble ionic surfactant and water soluble polyelectrolytes. He had demonstrated a novel way to stabilise oil in water emulsions by using a combination of an oil soluble surfactant (hexadecyl amine) and a high molecular weight polyelectrolyte, polyacrylic acid. It was found that neither component on its own produced a stable emulsion but in combination stable emulsions were formed [26].

Yinhua Wan et al carried out detailed theoretical and experimental analyses of the relationship between emulsion swelling and membrane breakage and to propose a new method so as to determine the osmotic as well as entrainment swelling of emulsion and the membrane breakage simultaneously. Factors affecting the membrane breakage and emulsion swelling, including the membrane formulation and operating parameters will also be focused [27].

A process for purifying waste waters containing heavy and toxic metal such as chromium has been studied by Aliane A. et al (2001). A batch complexation-ultrafiltration process was used to concentrate and recover chromium from sulphate solution. As the chromium ions are too small to be retained by the filter, they are first complexes with a water-soluble macro ligand (polyethylene-imine). Factors affecting the rejection rate and permeate flux such as pH, concentration ligand, chloride and sulphate concentration, membrane pore size, applied pressure and extraction factor were investigated. Best operating conditions can be obtained in order to achieve high levels of removal (>95%) .Then, decomplexation is obtained so that metal can be separated from macro ligand by a second ultrafiltration plant to reuse the macro ligand [28].
Uddin M. S. et al (2000) used polyethylene glycol as bi-functional surfactant in an ELM process for the extraction of metal ions from a ternary (copper, nickel and cobalt) aqueous solution. Dichloroethane, ammonium thiocyanate and potassium hydroxide were used as solvent, ligand and stripping agent, respectively. The paper presented the results on the characterization of the reactions (stoichiometry and reaction order) obtained through equilibrium and kinetic studies along with some batch emulsion extraction results [29].

Experimental results for the extraction of chromium (VI) from multicomponent acidic solutions by emulsion liquid membrane (ELM) using trioctylphosphine oxide (TOPO) as extractant were presented by Kumbasar R.A.et al. The membrane phase was consisted of kerosene as diluent, TOPO as extractant, ECA 4360J (a nonionic polyamine) as surfactant and (NH₄)₂CO₃ solution as stripping phase. Effects of various parameters such as mixing speed, type and concentration of stripping solution, surfactant and extractant concentrations, and volume ratio of the membrane phase to internal stripping phase on Cr (VI) extraction were studied and optimum conditions were determined. Results show that with proper adjustment of experimental conditions for the extraction of Cr (VI) can be enhanced to a great extent. This study also examined the effects of concentrations of acid and metal ions in the feed phase for the extraction of Cr (VI) ions [30].

Nosrati S. et al was studied where Cr (VI) was transported selectively with Cyanex 923 carrier from bulk feed phase to internal stripping phase using emulsion liquid membrane technique. The liquid membrane was prepared by loading with Cyanex 923 as the carrier, Span 80 as the surfactant, kerosene as the solvent and sodium hydroxide as the stripping agent. Their effect on the process parameters such as concentration of the surfactant, the ratio of organic phase to internal phase in the membrane and membrane to external phase ratio were also studied using Box–Behnken design and response surface method. A quadratic polynomial regression equation was used to analyze the experimental data. The experimental and predicted values were in good agreement [31].

The effect of a cationic surfactant on the adsorption of Cr(VI) on activated carbon was investigated using cetylpyridinium chloride (CPC) was carried out by Choi H.D. et al. To analyze adsorption phenomena of Cr(VI), adsorption kinetic and isotherm were used and fitted well with the pseudo-second order kinetic model and Langmuir adsorption model, respectively.
CPC introduced a cationic functional group on the surface of activated carbon and provided an adsorption site for Cr(VI) [32].

Kinetics of Cr(III) ions transport through a bulk liquid membrane containing dinonylnaphthalenesulfonic acid (DNNSA) as a carrier, flowing over aqueous phases, has been examined by Religa P. et al.. For the description of relationships of chromium(III) concentration in particular phases with the time, a model based on the assumption of consecutive first-order reactions was proposed by him. Satisfactory compatibility of experiments and model results have been obtained both for the membrane flow velocities below 0.0034 m/s when the interfaces begin to fluctuate slightly and for low initial Cr(III) concentration in the feed phase [33].

Chromium(VI) transport across supported liquid membranes (SLMs) and polymer inclusion membranes (PIMs) with tertiary amines and quaternary ammonium salt (Aliquat 336) from chloride acidic aqueous solution to 0.1M NaOH has been studied by Kozlowsk C.A. et al.. The comparative Cr(VI) transport studies of bulk, supported and polymer inclusion membranes were done by him. The highest permeability coefficient values for Cr(VI)was found for SLM, while the lowers values were observed for BLM. The repeated transport experiments of SLM and PIM were shown and the stability of PIM was described using the Danesi’s thermodynamic model. The long-term integrity of PIM was found. Non-contact atomic force microscope was applied to obtain images of pores in polymer inclusion membranes [34].

A comprehensive study in recovery of Cr (VI) from dilute HCl solution using liquid emulsion membrane (LEM) was done by Hassan M.A. et al.[35] The liquid membrane is made up of Tri-octylphosphine oxide (TOPO) as a carrier, cyclohexane as an organic diluent, sodiumhydroxide as a stripping solution and Span-80 (sorbitain monooleate) as an emulsifying agent. The selection of the extractant (TOPO) and the stripper (NaOH)was chosen on the basis of conventional liquid–liquid extraction studies. The important parameters affecting the permeation of Cr (VI) through the prepared membrane are hydrogen ion concentration in the external aqueous phase, stirring speed of mixing the two phases, type of diluents, carrier concentration, stripper concentration, membrane to feed ratio and volume fraction were systematically investigated. The effect of surfactant types and concentration on the stability of LEM were studied because of its important role in the permeation process.
3.2 Review paper on Mathematical Modeling of Liquid Membrane

The design of separation equipment using ELM requires a sound knowledge and understanding of the mass transfer mechanism involved. Therefore a number of studies have been reported in the literature for the development and testing of mathematical descriptions for solute transport through liquid membrane. The proposed models also identify the operating conditions and physical properties involved. But they vary in geometry and complexity ranging from planar geometry with the liquid membrane phase presenting a flat layer separating the continuous and reagent phase to spherical geometry and from lumped parameter approach to distributed resistance descriptions.

Mathematical modeling of a typical batch extraction system employing emulsion liquid membrane for dyes, namely, crystal violet and methylene blue is carried out by Agarwal A.K et al. An already available mass transfer model using spherical shell approach is used for one component dye extraction. The same model is extended for the binary system. The resultant ordinary differential equations of the model are solved using Laplace transform. The model parameters are obtained by comparing the experimental data with the calculated values of the dye concentration at various time points using an optimization algorithm. Effects of various process parameters, namely, concentration of surfactant, internal reagent, stirring speed, etc., have been analyzed for both single and binary mixtures using the model results [36].

Application of the liquid emulsion membrane (LEM) technology to the industrial scale is hindered by the challenges imposed by stability of the emulsion during the transfer of the solute (pertraction). One of the important factors which leads to the instability is swelling. Emulsion undergoes swelling due to the osmotic gradient across the membrane as well as due to the occlusion of the external phase into the membrane phase; the latter is caused by the hydrodynamic deformation of the membrane globules. Mukhopadhyay et al (2006) [37] have studied swelling of the emulsion phase in a water-in-oil-in-water type LEM system. Nitric acid is the internal aqueous phase and is encapsulated in organic membrane phase composed of D2EHPA–kerosene–SPAN80. Demineralised water is used as the external phase. The effect of the composition of the system and the hydrodynamic condition on the rate of swelling has been studied. A mathematical model has been developed to describe the effects of the relevant parameters on swelling of the emulsion. The predictions of the model are found to be in good
agreement with the experiments. The model would be useful for evaluating the rate of pertraction of a solute through the membrane–strip combination used in the present study. The study would also be useful for tuning the design and the operating parameters in LEM pertraction to achieve minimum swelling of the emulsion.

Mathematical Modeling for the extraction of Uranium and Molybdenum with ELM, including industrial application and cost evaluation of the uranium recovery was done by Basuki K T (2008) [38]. The models developed in this research can be used directly for the design of emulsion liquid membrane systems. The results of this study represent a very significant step toward the practical applications of the emulsion liquid membrane technology.

An emulsion liquid membrane system was applied to effectively separate nitrate ions from water. Batch experiments were performed to develop suitable emulsion liquid membrane systems, the standard of which stipulates that the efficiency of the extraction is more than 90%. A model was developed to simulate the batch extraction by Lin et al (1997)[39]. All parameters of the model were obtained from experiments. It was found that the model predictions fit the experimental data quite well.

A mathematical model is developed by Xingrong L. et al (1998) [40] to simulate the facilitated transport of phenylalanine (Phe) in emulsion liquid membrane (ELM) systems with di(2-ethylhexyl)phosphoric acid as a carrier. The model takes into account the mass transfer in both the external aqueous phase and the organic membrane phase interfacial reaction as well as membrane breakage during agitation. The model is tested by comparing theoretical predications with experimental results using Phe extraction by ELM processes. It is found that the model is valid for simulating the facilitated transport of Phe with ELM under various experimental conditions.

Paulo F. M. M. Correia et al (1999) had described advancing front model and three reversible reaction models where he applied to describe 2-chlorophenol permeation from aqueous solutions by emulsion liquid membranes. Similar results were obtained in most cases by using either of the reversible reaction models. Also differences between reversible reaction and the advancing front model were shown to be within experimental error in most cases (with the exception of low temperature permeation data) meaning that the role of reversibility of the
chemical reaction between internal phase reagent and 2-chlorophenol can be considered negligible. It is clearly indicate that both advancing front and reversible reaction models can be used with a reasonably accuracy as estimates of 2-chlorophenol permeation for design purposes [41].

A steady-state model is presented by Harrington P J et al (2001) for a hollow fiber liquid membrane extractor which describes the mass transfer performance as a function of phase flows, geometry and system physical properties. The model is compared with the experimental results for Cr(VI) extraction with a tertiary amine carrier. Shell side mass transfer correlations, developed primarily for gas–liquid membrane contactors, are also incorporated into the model and compared. This model is subsequently used to optimise both operating and design parameters for maximum mass flux in hollow fiber liquid membranes[42].

A mathematical model for analysing the extraction of Cr(VI) from aqueous acidic solution by emulsion liquid membrane using Aliquat 336 as extractant and NaOH as stripping agent has been presented by Bhowal et al (2001). The existing models developed so far do not account for the existence of different forms of Cr(VI) ions in the aqueous phase depending on pH conditions. Accordingly, in the present model, reaction equilibrium has been considered instead of distribution coefficient to represent realistically the transport mechanism for this type of system through liquid surfactant membrane. Simulated extraction profiles developed through the model has been fitted to the experimental data obtained using commercial Aliquat 336 as extractant and NaOH as stripping agent [43].

Water transport through an organic membrane is predicted using a growing emulsion globule described as a three-dimensional network. Osmosis occurs due to solubilization of water by inverse micelles that diffuse through the membrane phase. Bart et al. (1995) had experimentally verify and determine solubilities and diffusivities of inverted micelles. The results should allow to predict the transport of water across the membrane and thus the osmotic swelling phenomenon quantitatively [44].

Kargari A. et al (2006) has studied Selective separation of gold(III) ions from acidic aqueous solutions, using MIBK as carrier and LK-80 as emulsifier, has been investigated. The extraction results from model solution containing Au$^{3+}$, Pd$^{2+}$, Pt$^{4+}$, Cu$^{2+}$ and Fe$^{3+}$, showed that
only the Au3+ ions transported across the liquid membrane and nearly all of other ions remained in the external solution without change in their concentration. Mathematical modeling of the system shows a good compatibility with experimental results for gold(III) ions transport. For other ions, the partition coefficient of the ions and membrane phase is nearly equal to zero. Then these ions form complexes with the carrier without stripping and remain unchanged in the system [45].

Membrane separation methods can be divided into classes according to their separation characteristics (i) separation by sieving action, (ii) separation due to a difference in affinity and diffusivity, (iii) separation due to a difference in charge of molecules, (iv) carrier-facilitated transport, and (v) the process of (time-) controlled release by diffusion. Berg et al had explained that in all these cases diffusion processes play an important role in the transport mechanism of the solutes. Various mechanisms have been distinguished to describe the transport in membranes transport through bulk material (dense membranes), Knudsen diffusion in narrow pores, viscous flow in wide pores or surface diffusion along pore walls. He stated that the transport can be a result of more than only one of these mechanisms For all of these mechanisms models have been derived by Berge (1992). He also explained that the characteristics of a membrane, e.g. its crystallinity or its charge, can also have major consequences for the rate of diffusion in the membrane, and hence for the flux obtained [46].

A mathematical model has been developed by Pal P et al (2000)[47], for analysis of the transient behaviour of a W/O/W-type enzyme emulsion liquid membrane reactor system using α-glucosidase and glucose oxidase as the first and the second enzymes for the sequential conversion of maltose to glucose to gluconic acid. The model developed by Pal, is free from adjustable parameters is based on a modified Michaelis–Menten equation where substrate–product inhibition aspects have been duly considered. Since the model developed for sequential bienzymatic reaction system involves quite a number of ordinary and nonlinear partial differential equations with different types of boundary conditions, their solution becomes difficult even using standard packages. Experiments have been carried out by Pal to test the validity of the proposed dynamic model. The simulated results (computed within 1% relative accuracy) are well in agreement with the experimental findings.
3.3 Paper / Report review based on waste water

A report based on Water Treatment for fossil fuel power generation by Dr Alan Paton had been studied. The report assess objectively the current state of development and application of water treatment technologies relating to fossil fuel power generation world-wide. Critically assess the strengths and shortcomings of existing technologies in relation to commercial or near-commercial needs and to provide information on manufacturers, suppliers, developers, consultants and major users. A review report based on current activities and capabilities of companies/organisations working in the water treatment technology sector [48].

The performance of a bench scale aerobic sequencing batch reactor (SBR) was investigated by Durai G et al (2011) [49] for the treatment of tannery wastewater. Mixed culture obtained from the activated sludge process treating tannery wastewater was used in the reactor. He had operated SBR at different operating conditions by changing the hydraulic retention time. In this study, first order and diffusional models are used to describe the kinetics of the degradation of tannery wastewater in SBR.

The wastewater of leather industry which is one of the most widespread industries having large amount of water consumption and very high pollution loads, may be characterized by several key parameters including toxic pollutants exhibiting toxicity. Therefore the effluent of leather tanning industry must be handled carefully during both treatment plant design and operation. Lofrano G et al (2006) was tried to improve the coagulation process for toxicity reduction of raw wastewater taken from a leather tanning district central treatment plant. The optimum coagulation conditions for the first sample were determined as 8.5 pH and 900 mg l-1 dose of PAFC (poly aluminium ferric chloride) with the addition of Ca(OH)2. The results that, recently developed coagulant, PAFC is the most promising one reagent for leather tanning wastewater, which improved coagulation followed by biological treatment can result in safe effluent to aquatic environment [50].

A comparative study based on tannery effluent collected by Oral R et al from different level of treatment methods in effluent plant. The samples collected were raw wastewater (R), the effluents of coagulation/flocculation process (CF), biological treatment (B) and dried sludge
(DS). Samples were analyzed for their metal contents. Confirming the data from a previous study, a concentration-related toxicity was exerted by effluent or sludge samples according to the following rank: DS > CF > R > B [51].

3.4 Literature survey based on Ultrafiltration

The removals of single aromatic alcohols, including para nitro phenol (PNP), meta nitro phenol (MNP), phenol (P), catechol (CC), beta naphthol (BN) and ortho chloro phenol (OCP) from aqueous solution have been studied using micellar-enhanced ultrafiltration (MEUF) by Purkait et al (2005)[52]. He had conducted experiments by using unstirred batch cell and a continuous cross flow cell. The effects of surfactant-to-solute concentration ratio in the feed, transmembrane pressure drop and cross flow rate on the permeate flux and observed retention of each solute have been studied in detail. Free surfactant molecules present in the permeate and retentate are then recovered by a two-step chemical treatment process. In the first step, the surfactant is precipitated by potassium iodide and in the second step, the surfactant is recovered from the precipitate by the addition of cupric chloride. Optimum consumptions of potassium iodide and cupric chloride are also obtained experimentally.

Simultaneous removal of chromate and nitrate, major anionic pollutants in subsurface water system, was investigated by Baek K et al (2004)[53]. He had used micellar-enhanced ultrafiltration (MEUF) with cetylpyridinium chloride as a cationic surfactant. Rejection of nitrate and chromate was expressed as a function of molar ratio of surfactant to pollutants. It was observed that, with the molar ratio of 1:1:10 (chromate: nitrate: surfactant), rejection of nitrate and chromate reached 80% and 98%, respectively. Rejection of surfactant was observed to be >95% under the same conditions. The rejection of nitrate was inhibited by co-existence of chromate. It was due to the differences in binding power between ionic micelles and counter ions, which is proportional to the valence of counter ions; the valence of chromate was higher than that of nitrate.

The solubilization of three phenolic solutes in micellar solutions and surfactant–polymer mixtures was studied i.e. 2-monochlorophenol (MCP), 2,4-dichlorophenol (DCP), and 2,4,6-trichlorophenol (TCP). Komesvarakul N et al. had used equilibrium dialysis (ED) technique is used to determine the solubilization equilibrium constant as a function of added NaCl.
concentration. The added salt enhances the solubilization ability of surfactant micelles, but it only slightly affects the solubilization constant of surfactant–polymer aggregates. Understanding and quantifying this solubilization phenomenon by adding NaCl was crucial to optimization of the performance of colloid-enhanced ultrafiltration separation processes[54].

The effect of electrolyte on the critical micelles concentration (cmc) and bromide counterion binding in the micelles of cetylperidinium bromide (CPB) has been investigated by Chung J J et al (1991) [55]. Salt used by Chung in his study were salt of chloride, bromide and nitrate. The results showed the decreased order of cmc in the following order Cl⁻ < Br⁻ < NO₃⁻.

The feasibility of MEUF for washing effluent with removal efficiency, flux and COD reduction during the treatment of lab-scale soil washing effluent was determined by Jung J et al (2008)[56]. He reported that in the effluent from soil washing, total metal concentration and complexing agent was 10.14 and 9.03 mM respectively and the pH was 6.34. When the optimized conditions were employed to treat washing effluent, the removal efficiency and COD reduction reached over 92% and 80%, respectively. However the flux decline was severe, but this can be improved by introducing cross-flow filtration.

Micellar –Enhance ultrafiltration (MEFU) of the chromate anions from aqueous solutions has been studied by Kamble S B et al(2005), at room temperature, using cationic surfactants, cetyltrimethylammonium bromide (CTAB) and cetylperidinium chloride (CPC), micelles of which absorb the chromate ions by electrostatic interaction. The solution is processed by ultrafiltration using a membrane with pore size small enough to block the passage of the micelles and the absorbed ions. The process is highly efficient in removing the chromate ions. The presence of added NaCl reduces the chromate rejection but it was still considerable (up to 82%) even in the presence of 100mM NaCl [57].

A surfactant-based membrane process, micellar-enhanced ultrafiltration (MEUF), was studied in order to remove heavy metal ions from groundwater or wastewater by Hojeong K., et al (2006) [58]. The removal of phenol, p-cresol, xyleneol and Cr3+ ions in simultaneous micellar-enhanced ultrafiltration process was examined by Witek A et al (2006)[59]. Feasibility of cross-flow micellar-enhanced ultrafiltration was investigated by Baek K et al remove chromate and nitrate from water system using a cationic surfactant, cetylpyridinium chloride (CPC) (2004)
[60]. The removal of single metal ions including Cs\(^{+}\), Sr\(^{2+}\), Mn\(^{2+}\), Co\(^{2+}\), Cu\(^{2+}\), Zn\(^{2+}\), and Cr\(^{3+}\) from aqueous solutions (up to 200 mg/l) by ultrafiltration (UF) with the help of an anionic surfactant sodium dodecyl sulfate (SDS) was investigated by Juang R. et al (2003). Experiments were performed as a function of the membrane MWCO (1000–8000) and material (polyamide, polyethersulfone), solution pH (2–12), and molar concentration ratio of the surfactant to metals (the S/M ratio, 0.5–27). It was shown that complete removal of metal ions, except for monovalent Cs\(^{+}\), could be achieved as long as the SDS micelles were formed [61].

The extraction of Cephalosporin-C (CPC) from dilute fermentation broth of Cephalosporium acremonium was studied in a bulk liquid membrane as well as in an emulsion liquid membrane system. Aliquat-336 was used as the extracting agent to provide facilitated transport of CPC via liquid±liquid ion exchange mechanism. By maintaining an appropriate pH gradient in the feed and receiving phases, facilitated uphill transport could be achieved in the bulk liquid membrane system. A simple mass transfer model predicts the permeation rate in the bulk liquid membrane. The permeation process in an emulsion liquid membrane appears to be controlled by the aqueous boundary layer resistance and diffusion in the emulsion globule. This is perhaps the demonstration of the liquid membrane as an effective technique for selective extraction of CPC from fermentation broth of Cephalosporium acremonium [62].
3.5 Reference

19. Mingzhe D., Qiang L. and Aifen Li, Society of Core Analysts held in Calgary, Canada, 10-12 September (2007).