Inorganic anion removal using micellar enhanced ultrafiltration (MEUF), modeling anion distribution and suggested improvements of MEUF: A review

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Abstract: Surfactants have been used often in environmental remediation strategies due to their special amphiphilic nature which alters surface and water interfacial properties. When the aqueous concentration of a cationic surfactant far exceeds the critical micelle concentration (CMC), a large concentration of cationic micelles will form in water. These micelles each consist of tens to hundreds of surfactant monomers, and collectively can be utilized as nano-sized ion exchangers to assist with ultrafiltration separation (i.e., removal) of anionic pollutants from natural waters or wastewaters. Target anionic pollutants include nitrate, phosphate, arsenate and chromate. However, most polluted waters contain a complex mixture of anions, with these different anions competing for the micellar pseudo-phase, thus potentially reducing the overall removal efficiency of the target anions. Further, loss of surfactant monomers through the membrane also reduces process efficiency as replenishment of surfactant over time is required. In this review, the existing research on inorganic anion removal by micellar enhanced ultrafiltration (MEUF) and similar processes

are summarized. Operating condition factors are discussed, including pressure, membrane pore size, surfactant-contaminant concentration ratios, and water chemistry conditions (i.e., pH, salinity). Because most micellar surfactant – anion interactions are through outer-sphere electrostatic association, emphases in this review are given to the measurement of selectivity coefficients used for identifying the affinity of anions to the micelles, which generally decreases in the order of: $\text{Fe(CN)}_6^{3-} > \text{CrO}_4^{2-} > \text{SO}_4^{2-} > \text{HAsO}_4^{2-} > \text{HPO}_4^{2-} > \text{NO}_3^- > \text{Cl}^- > \text{HCO}_3^- > \text{H}_2\text{AsO}_4^- > \text{H}_2\text{PO}_4^- > \text{F}^- > \text{IO}_3^-$; and to the development of a speciation model, based on these selectivity coefficients, for predicting anion distribution in micellar solutions. Ways to address improved process efficiency, as well as future challenges and opportunities, are also discussed.

Keywords: Micellar enhanced ultrafiltration (MEUF); Anions removal; Cationic surfactant; Ion exchange; Selectivity; Modeling

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1. Introduction

As a type of molecular structure with special amphiphilic properties, surfactants have been used to enhance environmental remediation processes [1-3], to improve oil production [4-6], to modify the surface of functional materials [7-10], to improve performance of membrane separation processes [11, 12], to assist with catalysis [13, 14], to solubilize non-polar compounds [15], and to assist with drug delivery [16, 17] for decades. Among these applications, surfactant micelle-assisted ultrafiltration separation processes (known as micellar enhanced ultrafiltration, MEUF) for contaminants removal from water has been studied for more than 30 years, ever since the 1980s when Scaemhorn first introduced the use of micelles as vesicles to effectively remove organic molecules from aqueous streams during ultrafiltration [18]. Since that time, the removal of cationic metals and removal of toxic organic pollutants by surfactant micelles across ultrafiltration membranes has been widely researched and reviewed [19-23]. As a result of the human activities, including industrial development, the discharge of many types of anionic contaminants into the environment has occurred, often causing severe water pollution issues. Commonly occurred inorganic anionic pollutants in the water environment include nutrients (e.g., nitrate and phosphate), metallic anions such as metal oxyanions (e.g., chromate and arsenate) and metal-anion complex (e.g. ferricyanide), and some other anions of concern (e.g. fluoride). Most of these anions pose a threat to human health due to their high toxicity or other health effects. High costs associated with their recovery from water, or simply difficulty in recovery from water often makes them problematic as pollutants. As a water treatment strategy to remove inorganic anions, MEUF has been studied; however, these studies collectively have not been critically reviewed. Many studies have been conducted to investigate the performance of MEUF for removal of various ions and how removal is

influenced by different operating and water quality parameters. However, of special concern are: (1) Competition from other anions in the water during MEUF, as naturally occurring bicarbonate (HCO_3^-) and sulfate (SO_4^{2-}) may greatly influence removal efficiency of target anions; and (2) loss of surfactant monomers across the membrane, as micelle self-assembly is a dynamic process with monomers always present in solution, basically at a concentration equal to the critical micelle concentration (CMC). Hence, in this review, the basic principle of MEUF are first summarized through an introduction to surfactants, micelles, and ultrafiltration separation assisted by micelles; then, literature that specifically focuses on inorganic anion removal using MEUF is summarized with respect to parameters that influence MEUF performance, including the relative affinities of common anions to cationic surfactant micelles, modeling anions distribution in a micellar solution, and improvement methods of solving the issue of the loss of surfactant monomers during MEUF.

2. Surfactant and micelle

Surfactants are a class of chemicals possessing both polar and nonpolar functional groups. The polar (i.e., hydrophilic) head group is typically either an ionic moiety (e.g., sulfate, benzenesulfonate, carboxylate, or quaternary ammonium salt), or a non-ionic moiety, such as a polyethoxylate group. The nonpolar (i.e., hydrophobic) “tail” group is typically a long chain (i.e., 10 to 20 carbon atoms) hydrocarbon, and may include two such tail groups, known as a Gemini-surfactant [24]. The amphiphilic nature makes surfactant molecules soluble to some degree in both aqueous and non-aqueous liquids. Surfactant molecules in the aqueous phase may diffuse and adsorb at the interface between two phases (water/air or water/oil), increasing the interfacial area and reducing the interfacial tension as shown in **Figure 1**, where cetyltrimethylammonium bromide (CTAB) and cetylpyridinium chloride (CPC) are representative surfactant examples (at 20 °C). From the

figure, it is clear that both CTAB and CPC decrease the water surface tension and increase solution conductivity as the concentration increases. Beyond a certain surfactant concentration, the decrease in surface tension (and increase in conductivity) attenuates significantly. This concentration value, referred to as the critical micelle concentration (CMC), is equal to the concentration of surfactant molecules in solution above which nano-sized aggregates (i.e., micelles) start to form spontaneously, and as the figure indicates, can be determined by measuring the surface tension or conductivity of aqueous surfactant solutions as a function of surfactant concentration (e.g., around 0.9 mM for both CTAB and CPC, as shown in **Figure 1**). From **Figure 1a**, at the monomer concentration at which micelles begin to form, addition of more surfactant results in negligible change in the surface tension; and from **Figure 1b**, once surfactant molecules form micelles, the counter-ions (i.e., ions of opposite charge from the surfactant) associate with the micellar pseudo-phase such that addition of more surfactant leads to an attenuated increase in conductivity. From a thermodynamic standpoint, micelle formation can be thought of similarly as a precipitation reaction. Both occur when the aqueous phase concentration reaches a specific value, and this value is affected by any factor that alters the aqueous phase activity of the surfactant, including temperature, pressure, and ionic strength. Variation of the CMC with temperature has been studied for different surfactants [25-27]. Generally, the CMC of ionic surfactants decreases to a minimum value with the increase of temperature and then increases, following a 'U-shaped' CMC versus temperature plot. The minimum CMC usually occurs between 0-40 °C (typically at room temperature) [28]. The formation of surfactant micelles is guided by thermodynamic rules, and the standard enthalpy can be derived by the van't Hoff equation [29, 30]. For example, Zieliński et al. [25] reported that the standard enthalpy of micelle formation of alkyltrimethylammonium bromides is zero at the minimum CMC, with a

positive or endothermic value on the lower temperature side and a negative or exothermic value on the higher temperature side. The entropy change of micelle formation is generally positive, due to the hydrophobic effect, and it is this which allows the free energy of micelle formation to be negative (i.e. a spontaneous process). Among surfactant species, the value of the CMC is a function of the head group size, the hydrophilicity of the head, the tail group length and branching, and the type and concentration of counter-ions present [24, 27].

Figure 1. Surfactant solution properties as a function of surfactant concentration at 20 °C:

(a) Solution surface tension; (b) Solution conductivity. [27]

The surfactant molecules in the micelles are in equilibrium with free surfactant molecules or ions in solution (monomers), with this concentration of water dissolved surfactant monomers in the solution equal to the CMC. At concentrations above the surfactant's CMC, colloidal-sized micelles will be present in the aqueous solution, and as the total concentration is increased, these added surfactant molecules all form micelles. In an aqueous solution, the hydrophobic tails form the organic core of the micelles, and the hydrophilic head groups are at the outer interface or surface in contact with the aqueous phase. In contrast, reversed micelles form in organic solvents. The shape of the micelles depends on the structure of the surfactant molecules, their concentration, and the

temperature and ionic strength of the solution, and even the flow conditions [31]. Micelles are commonly approximately spherical in shape, with other shapes, including elliptical, cylindrical, worm-shaped, and bilayer also possible [32, 33]. Typical spherical micelles are composed of 10 to 100 surfactant monomers, and the typical size is several nanometers in diameter, depending on the length of the surfactant molecules. As shown in **Figure 2**, most CTAB and CPC micelles range in size from 1 to 5 nm (hydrodynamic diameter) without other electrolytes present, as determined by dynamic light scattering (DLS), which emphasizes the particles with the highest number. If micelles are composed of ionic surfactants, the micelle aggregates can consist of tens to hundreds of monomers, and basically are nano-sized ion exchangers with hydrophilic ionic head groups on the surface of the micelles and hydrophobic central cores. Counter-ions in the aqueous solution ion-pair with the ionic surface of the surfactant micelles via electrostatic interaction, in most cases, such that this association can be treated as an aqueous phase ion exchange process.

Figure 2. Micelle size distribution at surfactant concentrations of 5 mM [27].

3. Micellar enhanced ultrafiltration (MEUF)

As a semipermeable membrane, ultrafiltration (UF) membranes can be used to separate solutes and colloidal particles with high molecular weight (e.g., proteins, viruses) from those with low molecular weight (including the water molecules) by applying a pressure or concentration gradient. Ultrafiltration has been utilized widely in wastewater treatment and water reclamation due to the advantages of low energy consumption and high separation efficiency. The combination of surfactant micelles and UF is known as micellar enhanced ultrafiltration (MEUF), which has been considered as a promising water and wastewater treatment and resources recovery strategy [22]. The application of MEUF was first introduced in the 1980s [18, 34, 35], based on previous fundamental studies [36, 37]. This technology has been researched for decades and shown to be a viable separation process for removing various contaminants from water, including heavy metal species [38-42], dyes [43-45], and toxic organic compounds [18, 46, 47]. A schematic of the MEUF process (e.g., with a cationic surfactant) is shown in **Figure 3**. The basic principle of this strategy is that ionic pollutants with smaller sizes than the membrane pores are rejected by the UF membrane due to association with the larger surfactant micelles. Traditional ultrafiltration is ineffective at removing molecular and elemental ions and other low-molecular weight organic compounds (e.g., <1000 Da) since they can pass through the ultrafiltration membrane with the permeate. However, a UF membrane with an appropriate molecular weight cut-off (MWCO) can retain these species if they associate with the micelles, as the size of the micelles is larger than the pore diameter of the membrane. Therefore, the rejection of the nano-scale micelles by the membrane results in the removal of any ions associated with the surface of the micelles and also removal of any neutral organic molecules that are solubilized within the organic core of the micelles during the ultrafiltration process. The permeate that passes through the membrane can have greatly

reduced concentrations of these ions or molecules compared to the bulk solution retained by the membrane. A typical scheme of the experimental system for the MEUF process is shown in **Figure 4** [48]. The bulk solution is mixed with surfactant in the tank, followed by separation through the UF membrane under air pressure. The permeate with greatly reduced contaminants can be discharged, while the retentate is returned to the mixing tank. The back-flush device is used for membrane cleaning [49]. This process requires much lower pressures (i.e., energy input) compared to reverse osmosis (RO), yet can have relatively high performance in both the removal of contaminants and in the flow rate. Furthermore, because the surfactant micelles are present in the bulk aqueous phase, MEUF is a rapid process compared to heterogeneous treatment processes, such as ion exchange on a resin. However, continuous loss of surfactant monomers through UF membrane is an issue for this technology, since self-assembled surfactant micelles are in rapid equilibrium with monomers in the aqueous phase, the concentration of which is maintained at the CMC. These surfactant monomers pass through the UF membrane due to their smaller size compared to that of membrane pores, and may be considered as pollutants in the treated water. To minimize the effect of surfactant loss, a surfactant can be selected that minimizes loss and other negative effects, including those with low CMC values, large micelles, high solubilization, and those that are non-toxic or environmentally friendly. Selection of surfactant with low CMC values can reduce the free monomers in the permeate; larger micelles are beneficial for the application of UF membranes with larger pore sizes, thereby reducing energy input; a higher solubilization and lower Krafft temperature (the temperature at which the solubility equals the CMC at the same temperature, where the lower limit of micelle formation occurs) of the surfactant leads to more micelles being formed in the solution.

Considering that the surfactant used in MEUF may account for a large portion of the cost, the recovery of the surfactant is essential from an economical perspective. The surfactant monomer which passes through the UF membrane can be recovered from the permeate using a chemical method [50, 51]; while the recycle of the surfactant in the retentate can be achieved by changing temperature or pH, or through an ion exchange method [52-55].

Figure 3. The basic principle of surfactant micellar enhanced ultrafiltration.

Figure 4. A typical sketch of the MEUF experimental apparatus [48].

A key point of MEUF is that an appropriate membrane must be chosen to separate efficiently the surfactant micelles and contaminants from the water. The necessary

molecular weight cut-off (MWCO) or pore size of the membrane can be determined based on the surfactant micelle size. Using a membrane with a larger MWCO will cause loss of more surfactant, while using one with too low of a MWCO may require the input of more energy (i.e., higher operating pressure) or reduced flow. Because the typical size of surfactant micelles is several nanometers in diameter, UF membranes with MWCOs ranging from 3 to 10 kDa typically are used. Some studies do report the effective use of higher MWCO membranes (up to 100 kDa), as the gel layer formed on the membrane surface, due to concentration polarization, increases the rejected micelles and associated ions [56]. However, the adsorption or deposit of surfactant on the membrane surface, blockage by surfactant aggregates in pores, concentration polarization, and the formation of a gel layer or cake formation are all causes of membrane fouling and may reduce the fluid flux and increase the operating pressure [57, 58]. Indeed, fouling results in increased operational costs, due to increased energy demand, additional labor for maintenance, cleaning chemical costs, and shorter membrane life [59]. Commonly used UF membrane materials include cellulose, cellulose acetate, polyethersulfone (PES), polysulfone (PS), polyacrylonitrile (PAN), and ceramic materials. The MEUF process is usually performed under two configurations: dead-end filtration and cross-flow filtration (shown in **Figure 5** [60]). The former is a conventional form of filtration, mostly using flat sheet membranes in which the contaminants in solution are rejected by the membrane, and the filtrate is released at the bottom of (below) the membrane. This process can easily be operated in batch mode. For the cross-flow type, the feed flows parallel to the membrane surface, and is generally operated with continuous input and filtrate flow. Dead-end MEUF systems usually have higher removal efficiencies than cross-flow systems, while cross-flow filtration has been preferred in field applications because of the higher flow rates achieved by the higher

surface-area cross-flow filtration systems than by the flat-sheet dead-end filtration systems [20, 61].

Figure 5. Two operating configurations of MEUF [60].

4. Anionic contaminant removal using cationic surfactant micelles

4.1 Cationic surfactants used in MEUF

The positive charge of cationic surfactant micelles attracts anionic pollutants, whereas the hydrophobic core attracts nonpolar organic molecules through hydrophobic force. Numerous cationic surfactants are available, however only a few have been used in MEUF for anions removal due to commercial availability, cost, and chemical properties, such as the CMC value. **Table 1** provides a short list of some cationic surfactants that have been reported in the literature to be used for the removal/recovery of anions from water. The table indicates that an important class of cationic surfactants is the quaternary ammonium salts of different tail lengths, with the CMC value decreasing as the length of the hydrophobic tail group increases. For example, the CMC value of OTAB with an 18-carbon tail group is only 0.65 mM, much lower than that of DTAC (10 mM) with only 12 carbons in its tail. In addition, counter-ions with higher affinities for the micelle result in lower CMC values, e.g., Br^- displays a stronger electrostatic attraction than Cl^- to CTA^+ micelles [62], resulting in a lower CMC value for CTAB (0.92 mM) compared to that of CTAC (1.58 mM). A previous

study on n-alkylammonium salts indicates that CMC values increase through the sequence of counter-ions: $\text{NO}_3^- < \text{Br}^- < \text{Cl}^-$ [63]. Considering the cost and commercial availability, CTAB is the most widely used quaternary ammonium salt surfactant in practice. Another widely used surfactant is CPC, with a pyridinium head group and the same tail group as CTAB (the CMC is also similar to CTAB). Utilization of a surfactant with a low CMC value is beneficial as less surfactant is lost in the permeate during ultrafiltration. In particular, CTAB and CPC possess longer tail groups and lower CMC values comparing to the surfactant extensively used for cationic metals removal in MEUF, sodium dodecyl sulfate (SDS, 12 carbons in the tail group, with a CMC of 8.2 mM). Hence, fewer monomers are lost during anion removal using CTAB or CPC than during cation removal using SDS.

Table 1. Common cationic surfactants employed for anion removal

Surfactant name	Abbreviation	CMC (mM)	Molecule weight (g/mole)	Carbon number in the tail group	Chemical structure
Dodecyltrimethylammonium chloride	DTAC	10 [64]	263.89	12
Tetradecyltrimethylammonium bromide	TTAB	3.4 [65]	336.39	14
Cetyltrimethylammonium bromide	CTAB	0.92 [66]	364.45	16
Cetyltrimethylammonium chloride	CTAC	1.58 [67]	320.00	16
Octadecyldimethylammonium bromide	OTAB	0.65 [68]	392.5	18
Cetylpyridinium chloride	CPC	0.90 [66] 1.08 [69]	358.00	16
Octadecylamine acetate	ODA	0.90 [66]	329.05	18

4.2 Inorganic anion removal

MEUF has been shown to remove various inorganic anions including nitrate, phosphate, arsenate, chromate, and ferricyanide. When the aqueous concentration of a cationic surfactant far exceeds the CMC value, there will be a large number of positively charged micelles in the water which behave as an anion exchange nanomaterial. Aqueous phase anions with greater affinity for the charged micelles will replace the original counter-ions associated with the surfactant salt. Once associated with the micelle surface, they will be rejected by UF membranes. **Table 2** lists reported studies that have focused on anionic inorganic contaminant removal by cationic surfactant micelles across UF membranes. Often, removal efficiency for a specific anion has been examined as a function of surfactant type, water chemistry (e.g., pH and competing ions), and MEUF operating conditions including the concentration of the surfactant, membrane MWCO, and operating pressure. It can be seen from the table that CPC and CTAB have been used most widely in these studies. Overall, CPC has better removal efficiency for various anionic contaminants than CTAB, since the initial anion on CTAB is Br^- , which has a greater affinity for the micelles than Cl^- (in CPC). The MEUF removal performance usually depends on the concentration ratio of the surfactant to the contaminants, and not on the concentration of the contaminants themselves. Increasing surfactant concentration causes a higher removal of contaminants, since more exchange sites on the micelle surface are available for association of the target anions. On the other hand, increasing surfactant concentration also leads to a significant decrease in membrane flux because of the formation of a surfactant gel layer or cake on the

membrane surface. The effect of solution pH varies, and depends on the nature of the solute. Because the speciation of some metal and metalloid species, e.g., arsenic and chromium, changes with the pH of the solution, so the adjustment of pH can also influence MEUF performance. Considering the size of surfactant micelles, the MWCO of the UF membranes mostly ranges from 1 to 20 kDa, with pressures across the membrane ranging from 1 to 4 bar (0.1 to 0.4 MPa). Basically, a higher pressure causes a higher membrane flux. A lower MWCO leads to a greater removal of the contaminants, but also a lower permeate flux at a given pressure.

Table 2. Previous studies on anion removal by micelles with UF (MEUF)

Target Anions	Surfactants	MWCO	UF type	Membrane material	Pressure	Observed rejection	Parameters studied	Time	Ref.
NO ₃ ⁻	TTAB	1, 20 kDa	Dead-end	cellulose acetate	2 bar	64-96%	The effects of TTAB concentration and membrane MWCO; Mechanism and efficiency of the MEUF process.	1991	[65]
NO ₃ ⁻ and phosphate	CPC	3, 10 kDa	Dead-end	cellulose	2 bar	77-92% of NO ₃ ⁻ ; 83-95% of phosphate:	Individual anion and mixed anions removal by MEUF; The effect of membrane MWCO.	2003	[70]
phosphate	CPC	3, 10 kDa	Dead-end	cellulose acetate	2 bar	97%	The effects of pH, membrane MWCO, and concentration ratio of CPC to PO ₄ ³⁻ .	2004	[71]
NO ₃ ⁻ and phosphate	CPC	30, 10 kDa	Cross-flow	acrylonitrile	2 bar	>86% of NO ₃ ⁻ ; > 91% of phosphate	Individual anion and mixed anions removal by MEUF; The effects of CPC concentration and membrane MWCO on anions removal and flux change during the MEUF process.	2004	[60]
phosphate	CPC, CTAB, ODA, BC	10 kDa	Cross-flow	ceramic	1-5 bar	95%	Removal of PO ₄ ³⁻ from domestic wastewater; Effects of surfactant nature and concentration, pH value, temperature, and trans-membrane pressure on permeate flux and PO ₄ ³⁻ removal.	2009	[72]
phosphate	CPC, ODA	4, 30, 50 kDa	Dead-end	PES	0.1-0.2 Mpa (1-2 bar)	95%	The effects of surfactant type and concentration, membrane MWCO, and trans-membrane pressure; Flux change during the MEUF process.	2013	[73]
NO ₃ ⁻ and phosphate	CTAB	5, 10, 30 kDa	Dead-end	cellulose	0.1-0.2 Mpa (1-2 bar)	73-91% of NO ₃ ⁻ ; 11-34% of phosphate	The effects of surfactant concentration, membrane MWCO, and pressure on permeate flux trans-membrane pressure and removal.	2015	[74]
NO ₃ ⁻ and phosphate	CTAB, CPC	5 kDa	Dead-end	cellulose	60 psi (~4 bar)	84% of NO ₃ ⁻ ; 91% of phosphate	Determination of selectivity of common anions including NO ₃ ⁻ , H ₂ PO ₄ ⁻ , and HPO ₄ ²⁻ to CPC and CTAB; Prediction model for nutrients removal from water.	2017	[62]
phosphate	QACLE	1.2-1.4 kDa	Dialysis	/	Concentration gradient	22.1-66.7%	Competition of common anions to PO ₄ ³⁻ , and pH effect.	2018	[75]
As (V)	CPC	5, 10 kDa	Dead-end	Cellulose; PES	414 kPa (4.14 bar)	Up to 100%	The effects of membrane material, membrane MWCO, surfactant concentration, and pH on the removal.	2004	[76]
As (V)	CPC	5 kDa	Dead-end	PES	414 kPa (4.14 bar)	78.1-100%	The effects of co-occurring inorganic solutes and As concentrations on As removal and UF flux; Surfactant loss in permeate; As removal from well water.	2005	[77]
As (V)	CPC	Pore size 20-50 nm	Cross-flow	ceramic	185 kPa (1.85 bar)	~90%	The effects of membrane pore size, trans-membrane pressure, pH, surfactant concentration, and As concentration on permeate flux decline, As and CPC rejections.	2006	[78]

As (V)	CPC	100 kDa	Cross-flow	PES	1.85 kPa	93-98%	The effects of trans-membrane pressure, pH, CPC concentration, As concentration and ionic strength on permeate flux, As and CPC rejections.	2007	[56]
As (V)	CPC, CTAB, ODA, BC	3, 10 kDa	Dead-end	cellulose	200 kPa (2 bar)	96% for CPC; 94% for CTAB; 80% for ODA; 57% for BC	The effects of surfactant type, pH, co-occurring anions (NO_3^- and PO_4^{3-}), and membrane operation configurations on the removal.	2007	[66]
As (V)	CPC	10 kDa	Dead-end	cellulose	30 psi (~2 bar)	91% and 84%	Selectivity of As (V) to CPC micelles; The effects of CPC concentration, competing anions, and pH on the removal; Modeling As (V) distribution in different phases.	2018	[79]
As (V)	CTAB, CPC	pore size 27.18 nm	Dead-end	PAN	1 bar	Up to 100%	The effects of initial concentrations of As (V), surfactants, pH, membrane thickness, and co-existing anions on the removal of As, surfactant rejection, and permeate flux.	2019	[80]
As (V) and NO_3^-	CPC	/	Dead-end	PAN	/	96.9% of As (V); 90.5% of NO_3^-	The effects of surfactant concentration, solution pH, and trans-membrane pressure on the permeate flux, removal of As (V) and NO_3^- , and CPC rejection.	2019	[81]
As (V)	CPC	10 kDa	Cross-flow	PAN	1.5-2.5 bar	Up to 99%	Application of artificial neural network (ANN) to predict the optimum operational conditions, including time, pressure, molar ratio of CPC to As, concentration of As and pH of feed solution.	2020	[82]
CrO_4^{2-}	CTAC	5 kDa	Dead-end	cellulose acetate	414 kPa (4.14 bar)	>99.9%	Modeling CrO_4^{2-} binding with CPC with or without added NaCl via MEUF and dialysis.	1988	[83]
CrO_4^{2-}	CTAB	Pore size 0.2 μm	Cross-flow	cellulose acetate	150 kPa (1.5 bar)	Up to >95%	The effects of CTAB/chromate concentration ratio at a constant trans-membrane pressure and pH of the feed solution.	1997	[84]
CrO_4^{2-}	CPC, CTAB	10 kDa	tangential cell	PS	1-3 bar	Up to >99%	The effects of surfactant type, solution pH, and ionic strength on the removal.	2001	[85]
CrO_4^{2-} and NO_3^-	CPC	3, 10 kDa	Dead-end	cellulose	2 bar	80% of NO_3^- ; 98% of CrO_4^{2-}	The effects of molar ratio of surfactants to pollutants and the membrane MWCO.	2004	[86]
CrO_4^{2-} and NO_3^-	CPC	8 kDa	cross-flow	PES	2 bar	91% of NO_3^- ; >99% of CrO_4^{2-}	The effects of molar ratio of surfactants to pollutants on the removal.	2004	[87]
CrO_4^{2-}	CTAB, CPC	20 kDa	Dead-end	PS	400 kPa (4 bar)	99%; 80% with added NaCl	The effects of surfactant type and concentration, feed Cr concentration, salt concentration, solution pH, pressure and temperature.	2005	[88]
CrO_4^{2-}	CPC	10 kDa	Dead-end	PES	376, 580 and 716 kPa	Up to >95%	The effects of surfactant concentration, Cr concentration, and pressure on the removal.	2006	[89]

Cr (VI) and Cr(III)	Rhamnolipid (JBR425)	10 kDa	Cross-flow	PS	/	Up to 96.2%	A type of bio-surfactant was used; The effects of initial concentration of Cr, pH, and surfactant concentration on the removal.	2014	[90]
CrO ₄ ²⁻	QACLE	5 kDa	Dead-end	cellulose	60 psi (~4bar)	95.9%	Selectivity of CrO ₄ ²⁻ to QACLE micelles; The effect of surfactant concentration.	2017	[27]
Fe(CN) ₆ ³⁻ and NO ₃ ⁻	CPC	3, 10 kDa	Dead-end	cellulose	2 bar	>99.9% of Fe(CN) ₆ ³⁻ and 78% of NO ₃ ⁻ at molar ratio of 1:1:10 (CPC)	Competing of Fe(CN) ₆ ³⁻ and NO ₃ ⁻ ; The effect of surfactant to pollutants concentration ratio.	2003	[91]
Fe(CN) ₆ ³⁻ and CrO ₄ ²⁻	ODA	3, 10 kDa	Dead-end	cellulose	2 bar	98% of Fe(CN) ₆ ³⁻ and >99.9% of CrO ₄ ²⁻ at molar ratio of 1:1:6 (ODA)	Competing of Fe(CN) ₆ ³⁻ and CrO ₄ ²⁻ ; The effect of surfactant to pollutants concentration ratio.	2003	[92]
Fe(CN) ₆ ³⁻	CPC	10 kDa	Dead-end	cellulose	4 bar	Up to 99.9%	The effects of surfactant and ferricyanide concentration ratio on the removal.	2005	[93]
PdCl ₄ ²⁻	DTAC	3 kDa	Dead-end	cellulose	300 kPa (3 bar)	>95%	The effects of surfactant concentration and solution pH on the removal.	2008	[64]
ClO ⁻	CTAB	/	Cross-flow	Self-made PES with TiO ₂	/	75%	The effects of various parameters including operating time, trans-membrane pressure, CTAB concentration, pH of feed solution, and feed chlorine concentration on the MEUF process performance.	2017	[94]
F ⁻	CPC, ODA	4, 5 kDa	Dead-end	PES; cellulose	0.2 MPa (2 bar)	Up to 90% for CPC; up to 74% for ODA	The effects of surfactant type, F ⁻ concentration, surfactant concentration, and salt concentration on the MEUF process performance.	2018	[95]

4.2.1 Nutrients removal

Phosphorus and nitrogen are essential nutrients for living organisms and play important roles in growth (i.e., synthesis of proteins, DNA, and RNA) and energy supply (i.e., energy transfer through adenosine triphosphate) of organisms [96]. However, the extensive use of phosphorus and nitrogenous compounds in industrial and agriculture activities often cause discharge of excess nutrients into natural waterbodies, which often results in eutrophication [96, 97]. Effluent from municipal wastewater treatment plants and discharge from agricultural practices often contains high concentrations of phosphorus and nitrate that accelerates the rate of eutrophication [98, 99]. Therefore, nutrient pollution control is critical to prevent eutrophication in many waterbodies, including major waterbodies such as Lake Erie in North America, and Lake Taihu in Eastern China. Nitrate and (poly- or ortho-) phosphate are the most common nutrients in natural waters. Researchers have focused on the removal of anionic nutrient species using cationic surfactant micelle assisted UF. Morel *et al.* [65] investigated NO_3^- removal using TTAB with UF (MWCO of 1 or 20 kDa), and reported that removal increased with an increase in surfactant concentration, and decreased with increasing MWCO. The MEUF efficiency was found to not depend on the initial nitrate concentration in the feed water, but was a function of the surfactant/nitrate concentration ratio, with up to 91% of NO_3^- removed using a TTAB/ NO_3^- concentration ratio of 5 across a 1 kDa membrane. It was postulated that TTAB monomers adsorbed onto the UF membrane played an important role in the separation process. Baek *et al.* [71] reported that phosphate removal during MEUF with CPC highly depended on pH because of the difference in o-phosphate species (H_2PO_4^- , HPO_4^{2-}) concentrations as a function of solution pH. At low pH (< 7), removal was lower than at the high pH (> 7), because at low pH the monovalent phosphate species dominated. Camarillo *et al.* [72] employed ODA and CPC during MEUF to

remove phosphate ions from treated domestic wastewaters, and found MEUF was able to achieve phosphate rejection > 99% at the optimal surfactant dosage. Beak *et al.* [70] and Kim *et al.* [60] studied mixed nutrient removal using MEUF. They observed both nitrate and phosphate were removed with high efficiency when a certain CPC concentration was applied, yet the permeate flux was reduced with increasing addition of CPC due to the gel layer formed on the surface of the membrane. Chen and Jafvert [62] investigated relative association affinities of common anions, including nitrate and phosphate, towards micelles formed with two common surfactants (CPC and CTAB) and developed a model to predict anions removal. They reported that up to 84% and 91% of NO_3^- and $\text{HPO}_4^{2-}/\text{H}_2\text{PO}_4^{2-}$ respectively, were removed from natural surface water and nutrient-enriched water using MEUF (MWCO of 5 kDa), and removal was not as efficient using CTAB compared to CPC at the same molar concentrations due to the higher affinity of Br^- for the micelles.

4.2.2 Arsenic (V) removal

Arsenic (As) in drinking water and food can seriously impact human health and environmental quality due to its bioaccumulation, high toxicity and carcinogenicity [100]. Arsenate (As (V)) ions are generally the dominant inorganic arsenic species occurring in water under oxidizing conditions; Arsenite (As (III)) is the dominant species under reducing (anoxic) conditions. As (III) has a higher toxicity and is more difficult to eliminate from water than As (V), but is easily converted to As (V) by oxidation. Arsenate is a triprotic acid, so its speciation depends on pH. H_2AsO_4^- and HAsO_4^{2-} ($pK_a = 6.98$) are the dominant anions in the pH range of 6 – 9, which is the typical pH range of surface waters and groundwater [79]. Gecol *et al.* [76] investigated As (V) removal using UF membrane with and without CPC at varying pH values. They found the As removal and permeate flux depend on the membrane material, membrane MWCO, and water pH. Arsenic (V) removal of 100% was achieved at As

concentrations of 22 and 43 $\mu\text{g/L}$ using a 5 kDa PES membrane at pH 5.5, and with a 10 kDa membrane at pH of 8. Iqbal *et al.* [66] compared the removal of As (V) using four types of surfactants, including CPC, CTAB, ODA, and BC, and the results indicated CPC shows the highest removal efficiency, CTAB has a slightly lower removal efficiency, whereas BC has the lowest removal efficiency, largely due to its high CMC value. Removal was influenced by pH and competing anion concentration (NO_3^- and o-phosphate). They also compared cross-flow and dead-end configurations, and the results indicated the decline in flux during cross-flow filtration was less than during dead-end filtration, but with comparable As removal.

Ergican *et al.* [77] investigated As (V) removal from well water by MEUF with CPC, with co-occurring inorganic solutes, including HCO_3^- , HPO_4^{2-} , H_4SiO_4 , and SO_4^{2-} at pH 8. They report arsenic (at 0 to 105 $\mu\text{g/L}$ in the feed water) removal significantly increased to between 78.1% to 100% with addition of 10 mM CPC to the feed water, and indicated removal was dependent on the concentrations of arsenic and co-occurring inorganic solutes in the feed water. Beolchini *et al.* [56, 78] reported that membranes with large pore sizes (ceramic membrane with pore sizes of 20 to 50 nm, and 100 kDa PES membranes) allow treatment of As-bearing solutions at high flux even when using low surfactant concentrations (1 to 3 mM). They observed surfactant leakage in the permeate at concentrations below the CMC, indicating a potential effect of the concentration polarization layer. Chen *et al.* [79] investigated the relative selectivity of As (V) at different pH values, indicating the relative affinity sequence for binding of monovalent anions to CPC micelles as: $\text{NO}_3^- > \text{Cl}^- > \text{HCO}_3^- > \text{H}_2\text{AsO}_4^-$; and for divalent anions as: $\text{SO}_4^{2-} > \text{HAsO}_4^{2-}$. Based on selectivity coefficients and mass balance equations, a model was developed to predict As (V) distribution in the aqueous and the micellar phases. Bahmani *et al.* [80, 81] reported that micelles composed of CPC resulted in higher arsenic removal (91.7%) compared to CTAB

micelles (83.7%), and an increasing removal of both As (V) and NO_3^- as the CPC concentration was increased, however with an associated decrease in permeate flux. Because of the acid-base chemistry of As(V), relative removal of NO_3^- *versus* As(V) is highly pH dependent, however under optimal conditions (CPC concentration = 5 mM, pH = 7 to 8, Pressure = 1 bar), in a mixed solution more than 90% of both As(V) and NO_3^- can be removed by MEUF.

4.2.3 Chromium (VI) removal

Electroplating industries, leather tanning facilities, metal finishing industries, and nuclear power plants are heavy users of chromium salts and generate effluents containing chromium (Cr) ions. The stable oxidation states of Cr are Cr (III) and Cr (VI) in the natural environment. Whereas Cr(III) is an essential element for living beings, playing an important role in carbohydrate metabolism, Cr(VI) becomes carcinogenic under long exposure times, and shows 100 to 1000 folds higher toxicity than Cr (III) [101, 102]. Cr (VI) is the thermodynamically stable oxidation state in oxygen-rich environments, often present as chromate (CrO_4^{2-}) or dichromate ($\text{Cr}_2\text{O}_7^{2-}$) in aqueous solutions. Considering the toxicity of Cr (VI), the US Environmental Protection Agency (EPA) determined the allowable amount of dischargeable Cr(VI) to surface water at below 50 $\mu\text{g/L}$ [103]. Pollution of soil and groundwater by Cr (VI) is often a challenging environmental issue. Cr (VI) removal using MEUF has been studied widely since the 1980s and research results indicate high Cr (VI) removal due to the high affinity of divalent Cr (VI) species to cationic surfactant micelles under natural water conditions. Christian *et al.* [83] investigated CrO_4^{2-} equilibrium exchange with Cl^- on CPC micelles across UF and dialysis membranes. The experimental results showed that very large selectivity for CrO_4^{2-} was obtained, even in the presence of 0.05 to 0.10 M NaCl, with CrO_4^{2-} permeate concentrations less than 0.1% compared to the original water

concentration. Research results have shown that MEUF with CPC or CTAB can result in > 99% removal of CrO_4^{2-} under optimal conditions of pressure, pH, feed chromate and surfactant concentration. The rejection rate depends on ionic strength and pH, with added NaCl reducing Cr (VI) rejection. However, even in the presence of 100 mM NaCl, between 82 to 88% rejection still was achieved [85, 88]. Similar to As (V), the rejection rate of chromate is highly dependent on the pH of the feed solution as Cr (VI) is present at different charges (i.e., valences) depending on pH [88]. Beak and Yang [86, 87] investigated the simultaneous removal of Cr (VI) and NO_3^- , and have shown a larger affinity for CrO_4^{2-} compared to NO_3^- for CPC micelles is due to the higher valence. Hence, at equal concentrations, nitrate removal is inhibited by the co-existence of chromate; however, with the proper surfactant/pollutant concentration ratio, both pollutants can be effectively removed (e.g., at a molar ratio of 1:1:10 (chromate: nitrate: surfactant), rejection of nitrate and chromate reached 80% and 98%, respectively). Recently, some new types of surfactants have been employed for Cr (V) removal by MEUF. Abbasi-Garravand and Mulligan [90] applied a type of bio-surfactant (rhamnolipid, JBR 425) during MEUF for the removal of Cr (V) and Cr (III), and the results showed a maximum reduction in hexavalent chromium of 98.7% at an initial concentration of 10 mg/L at pH 6, and with a JBR 425 concentration of 2% (vol/vol). Chen *et al.* [27, 75] synthesized a new surfactant (QACLE) using conjugated linoleic acid and a quaternary ammonium salt, and showed that QACLE and CTAB both have higher selectivity for CrO_4^{2-} over most common anions (e.g., SO_4^{2-} , Cl^- , NO_3^- , and HCO_3^-) found in the natural waters. Up to 95.9% removal of CrO_4^{2-} was achieved using 5 mM QACLE self-assemble micelles.

4.2.4 Cyanide removal

Cyanide contains a triple bond between single carbon and nitrogen atoms, and since the pK_a of hydrogen cyanide (HCN) is approximately 9.2, it exists in water predominately as the

anionic species, CN^- , at near neutral pH values. The most common source of cyanide contamination is former gas manufacturing sites. Yet, cyanide contamination is also associated with electroplating factories, gold mine tailings, road salt storage facilities, and other source of contamination [104]. Cyanide in groundwater in the presence of iron is tightly complexed to form ferricyanide or ferrocyanide. Ferricyanide ($\text{Fe}(\text{CN})_6^{3-}$) is an anthropogenic contaminant in soil and groundwater. Beak and Yang [93] reported high cyanide removal (up to 99%) at a molar ratio of CPC to $\text{Fe}(\text{CN})_6^{3-}$ of 3:1, at a $\text{Fe}(\text{CN})_6^{3-}$ concentration of 1 mM, without competition from co-occurring anions. Beak *et al.* [91, 92] also studied simultaneous removal of several anions by MEUF, including $\text{Fe}(\text{CN})_6^{3-}$, and have found that ferricyanide ions are more easily associated to the surfactant micelles than chromate or nitrate; however, simultaneous removal of chromate and nitrate can be achieved by increasing the surfactant concentration. Additional research reported the order of anion affinity to the cationic micelles decreases in the order: $\text{Fe}(\text{CN})_6^{3-} > \text{CrO}_4^{2-} > \text{NO}_3^-$, with affinity clearly associated with ion charge (i.e., valence) [105].

4.2.5 Other anion removal

MEUF also has been studied to remove other inorganic anions from water. Ghezzi *et al.* [64] investigated removal of the precious metal, palladium (II) from water using DTAC, which exists predominately as PdCl_4^{2-} in moderately saline water. The results indicated addition of DTAC at concentrations above the CMC results in Pd (II) removal exceeding 95%; interestingly, the addition of a strong electrolyte (e.g., MgCl_2) was useful in expelling the metal complex from the micelles, presumably due to competition from Cl^- ions. Rahmati *et al.* [94] investigated the potential to use MEUF for the removal of free active chlorine (FAC) from synthetic wastewater using a polyethersulfone/titania (PES/ TiO_2) nano-composite membrane with assistance from CTAB. The results showed that the FAC rejection efficiency

could be increased by increasing the nanoparticle concentration and by decreasing of pH and the feed chlorine concentration. It was shown that UF with PES/TiO₂ nano-composite membranes had moderate retention of FAC under acidic conditions (pH of 2 to 4), with rejection of about 75.0%. Grzegorzek and Majewska-Nowak [95] applied MEUF for fluoride (F⁻) removal from aqueous solutions; the results indicated that for a F⁻ concentration of 10 mg/L, and a high surfactant concentration (3 times the CMC), a F⁻ ion concentration in the permeate, below the permissible level for drinking water, could be achieved. The presence of NaCl in the aqueous solution resulted in a significant reduction of F⁻ removal due to competition from Cl⁻ for the micellar surface.

5. Ion exchange on surfactant micelles

Based on the results reported by previous researchers, MEUF conditions often can be controlled to achieve an optimum removal of target contaminants. Such operating conditions include: increasing the surfactant concentration, decreasing the membrane MWCO, and adjusting the trans-membrane pressure. Yet, co-occurring (competing) anions in the water adversely affect target anion removal during MEUF, and the competition from non-target anions often cannot be eliminated or neglected, as association is generally due to weak electrostatic (outer-sphere) association, rather than specific (inter-sphere) complexation (coordination). Indeed, wastewater and natural waters contain various anions of significant concentration, including HCO₃⁻, NO₃⁻, SO₄²⁻, Cl⁻, and HPO₄²⁻/H₂PO₄⁻, making removal efficiency a complex function of water ion composition, including hydrogen ion concentration. The surfactant micelles, however, can be treated as nano-sized ion exchange materials within the continuous aqueous phase, and the anions in the water form electrostatic bonds with the ionic surface of surfactant micelles, such that the distribution of

anions between the micelle pseudo-phase and the surrounding continuous water phase depends on their relative affinity for the micelles and the total concentration of each ion in solution. Once the relative affinity (or selectivity) of each anion is known, this (thermodynamic) information can be used (alone with knowledge of the total concentration of each ion) to determine the distribution of all ions in solution; hence, the removal efficiency for each anion can be predicted via model calculation.

5.1 Selectivity coefficients of anions for cationic surfactant micelles

As nano-sized colloidal particles with electrical charge, ionic surfactant micelle association with counter-ions can be described by a triple-layer model [106, 107], shown in **Figure 6**. Surfactant molecules are the first layer, and the hydrated counter-ions closely associated with the surface of the micelle are considered the Stern layer (second layer). The diffuse layer (third layer) is between the Stern layer and the continuous solution phase, with a decrease in the electrical potential occurring through this layer, with also a decrease in the concentration of counter-ions also occurring within this layer. At the continuous phase boundary, the charge of the surfactant ions in the micelles is balanced by the charge of the counter-ions in the Stern and diffuse layers. Since ion association is often only through electrostatic interactions (i.e., outer-sphere complexation), it is not possible to distinguish the amount of surface charge that has been neutralized by Stern layer ions versus diffuse layer ions. Indeed, the distinction between these layers for outer-sphere complexation is simply a modeling exercise.

Figure 6. A triple-layer model for ions associated with a charged micelle surface [79].

Ion exchange models for resins have been reported widely [108-111], with the basic theory for ion exchange first developed by Helmholtz in 1879 [112]. To design a model for ion exchange, the equilibrium relationships for ions distributing between the resin and the solution phase need to be quantitatively and accurately captured. There are analogies between the interactions of counter-ions with ionic surfactant micelles and with ion exchange resins.

Fan *et al.* [113] and Miller [114] considered the micelle surface to have discrete exchange sites and defined the exchange of Na^+ with Ca^{2+} on anionic micelles through the following ion exchange-like equilibrium equation with equilibrium constant β ,

$$\beta = \frac{X_{Ca} [Na^+]_f^n}{X_{Na}^n [Ca^{2+}]_f} \quad (1)$$

where X_{Ca} and X_{Na} are the fractions of Ca^{2+} and Na^+ (in units of equivalence) in the micellar phase (per equivalent of surfactant), respectively; where the subscript f denotes free aqueous solution ion molar concentrations; and n ($= 2$) is the substitution ratio of Ca^{2+} to Na^+ on the micellar surface. With this equation, complete charge neutralization of the micelle is assumed ($X_{Ca} + X_{Na} = 1$), and essentially the micelle and associating ions are considered as a double layer (as opposed to a triple layer model with separate Stern and diffuse layers).

Chen and Jafvert [62, 75] have invoked a simple ion exchange model to describe anion exchange on the micelle surface, with the activity coefficients captured within the overall selectivity coefficients. Since it is assumed that the positive charge of each micelle is completely neutralized by associating anions, association of each ion is measured relative to the initial ion contained within the surfactant salt. The initial anions contained in the surfactant salt (e.g. Br⁻ or Cl⁻) exchange with an anion added to the aqueous phase at micellar surfaces as represented by **eq 2**,

where *A* and *B* represent the two different anions; α and β refer to the valences of the anions *A* and *B*, respectively; and the subscripts *mic* and *aq* refer to micellar pseudo-phase and continuous aqueous phase, respectively. At equilibrium, the ion exchange equilibrium constant (selectivity coefficient) is defined as follows,

$$K_{sel} = \frac{[A^{\alpha-}]_{aq}^{\beta} [B^{\beta-}]_{mic}^{\alpha}}{[A^{\alpha-}]_{mic}^{\beta} [B^{\beta-}]_{aq}^{\alpha}} \quad (3)$$

Where $[i]_{aq}$ refers to the molar concentrations of the anions expressed in mol/L in the aqueous phase; and $[i]_{mic}$ refers to the molar fraction of anions expressed in mol/mol surfactant in the micellar phase. Molar fractions in the micellar phase are easily determined by UF separation experiments using either UF dialysis tubing or UF flat sheet membranes.

Based on the simple ion exchange model, the selectivity coefficients on aqueous micelles composed of either cetyltrimethylammonium (CTA⁺) bromide or cetylpyridinium (CP⁺) chloride towards many environmentally relevant anions, including IO₃⁻, F⁻, Cl⁻, HCO₃⁻, NO₂⁻, Br⁻, NO₃⁻, H₂PO₄⁻, HPO₄²⁻, SO₄²⁻, and CrO₄²⁻ were investigated in a series of UF experiments. Chen *et al.* [79] also studied the affinity of As (V) species at different pH values, and compared removal relative to NO₃⁻, SO₄²⁻, and HCO₃⁻. Using the same ion exchange

model, anion affinities for QACLE (quaternary ammonium hydroxypropyl conjugated linoleic acid ester) surfactant micelles or QASE (quaternary ammonium stearic acid ester) nanoparticles were investigated also using dialysis equilibrium experiments. Generally, a higher valence on the anion lead to a greater affinity for the micelle or nanoparticle; with the affinity decreasing as the hydrated radii of the anions increased among same-valence ions. **Table 3** shows common selectivity coefficients (**equation 3**) on surfactant micelles with respect to Cl^- . Because the selectivity coefficients only slightly vary among the different surfactant micelles for a given anion, the similarity of the affinities to each micelle is obvious. According to the previous studies concerning $\text{Fe}(\text{CN})_6^{3-}$ and some other anions (including CrO_4^{2-}), the overall affinity of anions to CTA^+ or CP^+ surfactant micelles is expected to decrease in the following order: $\text{Fe}(\text{CN})_6^{3-} > \text{CrO}_4^{2-} > \text{SO}_4^{2-} > \text{HAsO}_4^{2-} > \text{HPO}_4^{2-} > \text{NO}_3^- > \text{Cl}^- > \text{HCO}_3^- > \text{H}_2\text{AsO}_4^- > \text{H}_2\text{PO}_4^- > \text{F}^- > \text{IO}_3^-$.

Table 3. Selectivity coefficients (K_{sel}) for surfactant micelles with respect to Cl^- [27, 62, 75, 79]

Anions	CPC	CTAB [†]	QACLE
IO_3^-	/	0.45	/
F^-	0.31	0.47	0.49
H_2PO_4^-	0.32	0.47	0.53
$\text{H}_2\text{AsO}_4^{4-}$	0.55	/	/
HCO_3^-	0.60	0.70	0.89
Cl^-	1	1	1
NO_2^-	1.27	1.43	1.20
Br^-	2.57	2.13	1.65
NO_3^-	2.73	2.70	1.93
$\text{HPO}_4^{2-\ddagger}$	0.030	0.026	0.035
HAsO_4^{2-}	0.047	/	/
$\text{SO}_4^{2-\ddagger}$	0.071	0.069	0.128
$\text{CrO}_4^{2-\ddagger}$	/	0.196	0.368

[†] Measured from ion exchange with Br^- and then calculated relative to Cl^-

[‡] unit of L/mol

5.2 Anion distribution model in a micellar solution

Once the equilibrium coefficient of an anion in the micellar solution is obtained via experimentation, a model composed of mass action (i.e., ion exchange), mass balance, and charge balance equations, can be developed to predict anion distribution and anion removal during MEUF. Christian *et al.* [83] first reported an equilibrium model to predict chromate distribution on CPC micelles, and the results showed a good correlation with ultrafiltration and equilibrium dialysis results. A similar method was reported for use in predicting the binding of arsenic anions to cationic micelles [115]. However, these studies focused on single anion system. A model that accounted for multi-ion distribution between the aqueous and micellar (or polymer) phase has been developed and verified in previous studies which can be used to predict target ion removal during UF [62, 79, 116, 117]. The model was constructed based on all necessary mass action equations (i.e., selectivity coefficient equations), mass balance equations (i.e., on micellar surfactant and total ionic species concentrations), and any necessary acid-base reaction equations (i.e., to determine speciation of phosphate, arsenic, and/or chromate). The set of equations for calculating anion distribution in a micellar solution are listed in **Table 4** (using CPC as the example surfactant), consistent with previous literature [79]. The total concentration of each anion in water is determined prior to the addition of a known concentration of surfactant into the water, $[A_i^{n-}]_{\text{total}}$, except for chloride, which is the sum of the initial Cl^- concentration in the water and the chloride added with the surfactant salt. The pH of the sample is that measured after surfactant addition in order to properly calculate any anion concentration affected by acid dissociation, including As (V), Cr (VI), and phosphate species. In the model,

unknown values (to be determined) are the concentrations of anions in the aqueous and micellar phases, i.e., $[A_i^{n-}]_{aq}$ and $[A_i^{n-}]_{mic}$. Micellar surfactant concentration (M) can be determined by knowing or measuring the CMC value, or at significantly high surfactant concentrations, can be assumed to equal the total concentration of surfactant added if the CMC is quite low. Because charge balance is assumed for each micelle, the total equivalent fraction of anions in the micellar pseudo-phase equals 1 (i.e., the same as the micellar surfactant concentration). Based on the selectivity coefficients of anions obtain from UF or dialysis experiments (discussed in Section 5.1), the equations of the model can be solved using “Solver” in Microsoft Excel to iteratively minimize the sum of squared errors on all mass balance equations by adjusting initial guesses on all unknown concentrations. This is accomplished by subtracting the left-hand-side of each mass balance equation from its respective right-hand-side, dividing by the left-hand side (to obtain a fractional error), and squaring the numerical result. These squared fractional errors are added to obtain the sum of squared errors, which when minimized by adjusting all unknown values results in the calculated ion distribution.

Table 4. Equations for calculating anion distribution in a micellar solution

	$[Cl^-]_{total} = [CPC]_{total} + [Cl^-]_{initial}$
Mass balance	$[A_i^{n-}]_{total} = [A_i^{n-}]_{aq} + [A_i^{n-}]_{mic} * M^+$ $\sum_i n[A_i^{n-}]_{mic} = 1$
CMC calculation [‡]	$M = [CPC]_{total} - CMC$ $\ln CMC = a \ln [Q]_{aq} + b$ $[Q]_{aq} = \sum_i [A_i^{n-}]_{aq}$

Mass action	$K_{sel}^{A_i^{n-}} = \frac{[Cl^-]_{aq}^n [A_i^{n-}]_{mic}}{[Cl^-]_{mic}^n [A_i^{n-}]_{aq}}$
Species	$pH = -\log[H^+]$
dependence on pH	$K_a = \frac{[H^+][A_i^{2-}]}{[A_i^-]}$

[†] A_i refers to each anion i in the system, including Cl^- , Br^- , F^- , NO_2^- , NO_3^- , HCO_3^- , SO_4^{2-} , As, Cr and P, while mass balance equations for those species depended on pH are listed for the total mass. For example, $[As]_{total} = [H_2AsO_4^-]_{aq} + [H_2AsO_4^-]_{mic} * M + [HAsO_4^{2-}]_{aq} + [HAsO_4^{2-}]_{mic} * M$

[‡] If the CMC of surfactant is quite low, the value of the CMC in the equations can be assumed to be negligible.

Figure 7 shows the iterative least squares scheme that can be used to solve the set of simultaneous algebraic equation (modified from the literature) [62], where o-phosphate removal using CPC micelles is taken as the example, with the co-occurring anions of Cl^- , F^- , Br^- , NO_3^- , HCO_3^- , and SO_4^{2-} , and where the CMC is neglected (i.e., assumed negligible relative to the total surfactant concentration). To solve the system of simultaneous algebraic equations, first, the value of $[H]^+$ is directly calculated from the pH value; because the CMC is assumed to be low in comparison to the total surfactant concentration, the value of M is set equal to the total surfactant concentration; and finally, the total Cl^- concentration is set equal to the sum of the concentration of CPC and any chloride initially present in the water. For this example case, there are 16 unknown values which are the aqueous and micellar anion concentrations. There are also 16 equations, which include the mass balance and mass action equations, which can be used to solve the unknown values. To further simplify the calculations (as shown in **Figure 7**), all species are calculated through an iterative process by making reasonable initial guesses on three species: $[Cl^-]_{aq}$, $[SO_4^{2-}]_{aq}$, and $[H_2PO_4^-]_{mic}$. With a guess on $[Cl^-]_{aq}$, the value of $[Cl^-]_{mic}$ is calculated, and from these two values, the aqueous

and micellar concentrations of all monovalent anions are calculated (F^- , HCO_3^- , Br^- and NO_3^-).

With a guess on $[SO_4^{2-}]_{aq}$, the value of $[SO_4^{2-}]_{mic}$ is calculated. With a guess on $[H_2PO_4^-]_{mic}$, the value of $[H_2PO_4^-]_{aq}$ is calculated; the acid dissociation constant for $H_2PO_4^-$ is used to calculate $[HPO_4^{2-}]_{aq}$, and from this value, the divalent phosphate on the micelles ($[HPO_4^{2-}]_{mic}$) is calculated. Based on the three guessed values, the model is simplified to three mass balance equations on phosphate, sulfate, and the total charge balance on the micelle phase.

Therefore the normalized squares errors (between the right-hand-side and the left-hand-side of these three mass balance equations) are calculated, and added together to provide a sum of squared errors (SSE). The calculations are performed in Microsoft Excel, such that the built-in minimization algorithm “Solver” can be used to iteratively minimize the sum of squared errors by adjusting the initial guesses on $[Cl^-]_{aq}$, $[SO_4^{2-}]_{aq}$, and $[H_2PO_4^-]_{mic}$. Because Solver often assumes low values are negligible or close to zero, it is important to minimize errors on fractional (or percent) squared errors, and initial guesses to be adjusted should be the negative logarithms of concentrations (i.e., guess $p[Cl^-] = 3$, and then immediately calculating $[Cl^-] = 0.001$ M, such that the value of 3 is adjusted during iterations rather than 0.001, as 0.001 may be sufficiently close to zero to discontinue the iterative process).

The model has been demonstrated to accurately converge to the anticipated solution under real MEUF conditions using both artificial and natural surface waters. **Figure 8a**, for example, shows predicted and experimental nutrient removal (NO_3^- and PO_4^{3-}) using CTAB and CPC, where the removal is defined by $1 - \frac{\text{permeate concentration}}{\text{feed concentration}}$. The results show there is no significant difference between the model-calculated and

experimentally-measured values. **Figure 8b** indicates good agreement between predicted and experimental aqueous concentrations of various anions in a cross-linked surfactant micelle solution after equilibrium during UF and dialysis processes. **Figure 8c** shows the increase in As (V) removal as the concentration of CPC increased, and with good prediction of this increase by the model in an artificial mixed-ion solution.

Figure 7. Calculation method for anion distribution in the aqueous and micellar phases (modified base on the literature).

Figure 8. Model prediction for anion removal during MEUF: (a) Relationship between calculated and measured anion rejection fractions for the natural and nutrient-enriched waters with 5 to 10 mM CPC and CTAB [62]; (b) Relationship between measured aqueous concentrations and model predicted values in cross-linked QACLE solution (solid and open symbols are results from dialysis and UF experiments, respectively) [75]; (c) As (V) removal by CPC from artificial water samples with other anions present in solution [79].

6. Suggested improvements in MEUF

Surfactant micelles self-assemble, and if ion exchange occurs across a membrane, where the external water phase is flowing, significant loss of surfactant monomers (at a concentration equal to the CMC) will occur over time through the UF membrane to an unacceptable level, and these surfactant monomers at concentrations up tens of milligrams per liter will be new organic pollutants in the permeate. For example, Baek *et al.* [70] have reported on monomeric CPC concentrations in the permeate at 0.7 to 0.75 mM when they used a membrane with a MWCO between 3 to 10 kDa. In experiments conducted by Kim *et al.* [60], they reported that 1 to 3% of the CPC passed through the membrane, and they found the permeate CPC concentration increased as the MWCO of the membrane increasing. Several approaches have been investigated to resolve this issue, including applying mixed surfactants to decrease the CMC [118], utilizing adsorption methods on the permeate to remove the surfactant in the permeate [119], synthesizing cross-linked micelles [116], and using surfactant and polymer mixture, which forms colloidal aggregates [120]. A list of suggested improvements of MEUF is shown in **Table 5**.

Table 5. Suggested improvement methods for MEUF

Improvement method	Example cases	Ref.
Mixed surfactant micelles	Simultaneous removal of trichloroethylene and Cr (VI) by MEUF with mixed micelles composed of CPC and Tween 80.	[69]
	Removal of Cr (VI) using mixed surfactants (Tween-80 or Triton X-100 and CTAB) during MEUF.	[121]
	Treatment of MEUF permeate with 1 g/L powdered activated carbon, with more than 98% removal of the surfactant.	[66]
Combination of MEUF and adsorption	Removal of Cr(VI) using CTAB and powdered activated carbon (PAC) together during cross-flow microfiltration, with CTAB and chromate rejections of 91% and 97.2%.	[122]
	Removal of Cr (VI) by MEUF followed by activated carbon fiber treatment to remove CPC in the permeate, leaving only 0.29 mg/L CPC in the permeate.	[123]

Application of cross-linked micelles	A quaternary ammonium hydroxypropyl conjugated linoleic acid ester cationic surfactant (QACLE) was synthesized and cross-linked by UV-light in the presence of a photo-initiator. The cross-linked micelles have been used for chromate and phosphate removal across UF and dialysis membranes, without monomer loss.	[27, 75]
Polymer-surfactant aggregates (PSAs)	Removals up to 99% $\text{Fe}(\text{CN})_6^{3-}$ and 80% CrO_4^{2-} were observed using PSAs consist of PAA and MTAB filtered through a 20 μm coarse filter. The overall recycle process has shown that up to 94% of both CrO_4^{2-} and the PAA-MTAB were recovered and were able to be reused, respectively, upon addition of NaOH and H_2SO_4 at optimal dosages.	[124] [125]

6.1 Mixed surfactant micelles

As described above, the CMC value varies among surfactants as a function of molecular structure, with variation in head group size and charge, overall hydrophilicity of the head group, tail group length, and the hydrophobicity of tail group. Although ionic surfactants are suitable for removal of oppositely charged ions from aqueous solution by MEUF, the CMC of ionic surfactants is often rather large. Non-ionic surfactants normally have much lower CMC values [126], but cannot attract ions. The addition of a small amount of a non-ionic surfactant results in the formation of “mixed micelles” composed of non-ionic and ionic surfactants with an overall lower CMC value compared to the pure ionic surfactant system, due to reduced electrostatic repulsion of charged cationic head groups [127]. As a result, the residual surfactant monomers in the permeate decrease markedly. Lee *et al.* [69] have reported on simultaneous removal of trichloroethylene and chromate by MEUF with mixed micelles composed of CPC and Tween 80 surfactants. Tween 80 decreased the CMC of the surfactant mixture to below 0.2 mM when the Tween 80 mole fraction was 0.2. In order to decrease the CMC, Bielska and Szymanowski [128] studied mixtures of sodium dodecyl sulfate (SDS) added with an oxy-ethylated coconut fatty acid methyl ester to recover methylene blue from wastewater. The introduction of the non-ionic surfactant reduced the

CMC from 8.3 mM (of pure SDS in water) to 2.0 mM, at a mixture ratio of SDS to non-ionic surfactant of 4:1. Nura *et al.* [121] reported an effective removal of Cr(VI) by using mixed surfactants (non-ionic and cationic) during MEUF, with removal of chromate (20 mg/L) measured at 93% to 97% using 1.2 mM CTAB + Tween-80 or, CTAB + Triton X-100, respectively, at constant surfactant molar ratios of 0.1:1 (non-ionic : cationic). However, residual surfactant monomers remained in the UF permeate, and with increasing concentration of the non-ionic surfactant, the surface charge density of the micelles decreases, negatively influencing the removal efficiency of the target anions.

6.2 Activated carbon adsorption combined with MEUF

Regarding adsorption methods to remove the surfactant in the permeate, activated carbon has been shown to efficiently remove surfactant monomers from the permeate and is of widespread use among the adsorption materials in wastewater treatment practices [129]. Therefore, activated carbon adsorption could be used as a supplementary technology for controlling secondary pollution by the surfactants during MEUF [130]. In order to lower the concentration of the surfactant in the permeate during arsenate removal using MEUF, Iqbal *et al.* [66] treated the permeate with 1 g/L powdered activated carbon before discharging to the environment, and more than 98% of the surfactant was removed by the PAC. Basar *et al.* [122] investigated the removal of chromate using CTAB and powdered activated carbon (PAC) together during cross-flow microfiltration, and the study showed that CTAB and chromate rejections of 91% and 97.2% were achieved, respectively, under conditions of 0.5 g PAC/L, 5 mM CTAB, and 0.2 mM chromate, with a 120-minute processing time. Bade *et al.* [123] used MEUF to remove chromate followed by activated carbon fiber treatment to remove CPC in the permeate (at the molar ratio of chromate to CPC of 1:5),

with 98.6% of the chromate removed across the membrane, and 99.9 % of the CPC removed by the activated carbon, leaving only 0.29 mg/L CPC in the permeate. Use of activated carbon, however, is expensive leading to much higher costs for overall water treatment.

6.3 Cross-linking of surfactant micelles

If the monomers within the micelles can be cross-linked, the new nano-sized colloid will be stable in suspension and loss of monomers across the membrane will not occur. A schematic of cross-linking surfactant micelles through reacting surfactants that contain double bonds is shown in **Figure 9**. Indeed, in recent years various new types of polymerizable amphiphilic molecules have been synthesized [131-134] and used in a variety of application, including for transport and release of pharmaceuticals [135, 136], as molecular templates [137], for making membranes for molecular-size based separations [138], and so on. Some researchers [139-141] have focused on environmental remediation by nano-sized polymerized amphiphilic molecules. Stable cross-linked micelles have the potential to be used to recover ions from water or wastewater when combined with UF or dialysis processes [116]. Chen *et al.* [27, 75] have synthesized a new quaternary ammonium hydroxypropyl conjugated linoleic acid ester cationic surfactant (QACLE) via reaction between conjugated linoleic acid (CLA) and (2,3-epoxypropyl)- trimethylammonium chloride (ETAC). QACLE has a similar quaternary ammonium head group structure as CTAB, but with conjugated double bonds in the tail group, making cross-linking possible under certain conditions. Because of the longer tail group, QACLE has a lower CMC value and large micellar size than those of CPC and CTAB. The selectivity coefficients of the QACLE micelles towards common anions in natural water are similar to those of CPC and CTAB. When present in aqueous micellar form, QACLE was cross-linked by UV-light in the presence of a

photo-initiator, forming stable nanoparticles with high anion exchange capacity. After cross-linking, the surfactant will not be lost continuously during membrane separation processes as shown in **Figure 9** where dialysis of both cross-linked and non-cross-linked (CPC) surfactant micelles is shown. The cross-linked micelles (or nanoparticles) have been used for chromate and phosphate removal across UF and dialysis membranes.

Figure 9. Cross-linked surfactant micelles: Schematic of cross-linking (left) with initiator and UV light; Dialysis of CPC micelles (left image), and QASE nanoparticles (right) with $K_2S_2O_4$ added to both the internal and external solution after 24 h (right photo) [75].

6.4 Surfactant-polymer aggregate enhanced membrane separation

Similar to surfactant micelle, water soluble polyelectrolyte can be used to improve membrane separation performance [142, 143]. Based on studies of surfactant and polyelectrolyte systems, a novel heavy metal treatment process that uses polymer-surfactant aggregation has been developed, and has been shown to offer a promising approach to removal and recovery of valuable metal ions from water and wastewater [144-147]. This approach allows for the use of larger pore size membranes, such as microfiltration or coarse filtration membranes, because the size of the self-assembled “aggregates” is enlarged by addition of the polymer. Also, because the monomer concentration in the continuous water phase is lower than the typical CMC, reduced loss of material occurs during operation. Advantages include low operational costs, high treatment

rate, and operational stability. The process uses oppositely charged polymer (or polyelectrolyte) and cationic surfactant to form aggregates referred to as polymer–surfactant aggregates (PSAs) held together by purely electrostatic interactions. Because the aggregates differ from pure surfactant micelles, the activity of monomers (hence, the concentration) in the aqueous phase is lower than the CMC value of micelles composed of the same surfactant. PSAs formed by an anionic polymer and a cationic surfactant also have been developed for the removal and recovery of metallic anions (shown in **Figure 10**). Shen *et al.* [124] reported that anionic polymers, such as poly(sodium 4-styrenesulfonate) (PSS) or poly(acrylic acid) (PAA), can form a back-bone structure onto which cationic surfactants, such as MTAB, can form micelle-like aggregates. This results in larger flocculated aggregates with the ability to remove anions from solutions. The removals up to 99% $\text{Fe}(\text{CN})_6^{3-}$ (initially at 0.1 mM) and 80% CrO_4^{2-} (0.2 mM) were observed using PSAs consist of PAA and MTAB filtered through a 20 μm coarse filter. Research found that use of PSAs is effective for metallic anion removal over a pH range 4.5 to 6 and a temperature range of 5 to 50 °C. Furthermore, both salt and organic contaminants do not significantly interfere with anion removal. In addition, it was observed that using a cationic surfactant with a longer tail group facilitated the formation of PSAs and the removal of metallic anions [148]. Further research found adjustment of pH can result in greater recover the metallic anions from the flocculated PSAs into a concentrated solution, essentially recovering the polymer and surfactant for re-use. Results on the overall recycle process have shown that up to 94% of both CrO_4^{2-} and the PAA-MTAB were recovered and were able to be reused, respectively, upon addition of NaOH and H_2SO_4 at optimal dosages [125].

Figure 10. Removal of metallic anions from dilute aqueous solutions by polymer–surfactant aggregates [124].

7. Challenges and future opportunities of MEUF

As shown in this review, MEUF is a promising strategy for the removal of anionic pollutants from aqueous solutions, with the advantages of high removal efficiency, low energy input, and rapid reaction. The state-of-the-art studies of MEUF have often focused on bench-scale MEUF tests. While there are some attempts at using MEUF for anion, metal or organic removal from real domestic and industrial wastewaters [72, 149-151], the process has not been adopted as a standard water treatment technique as of yet, and there is no reported industrial-scale water treatment plant applying MEUF. Some improvements have been employed to reduce the loss of surfactant monomers or to eliminate secondary pollution, as discussed in the above section; nevertheless, industrial scalability of this technique seems reasonable and can be positively expected if some key challenges can be properly overcome or addressed.

Without the reuse of surfactants, the MEUF operation will be costly and un-sustainable, because of the required continuous input of fresh surfactants to each batch of the feed solution. The increasing trend of efficiently recycling surfactants, valuable organics, and heavy metals from the MEUF retentate is inevitable. Although some studies have reported

the recovery and recycle of surfactant, the required processes are still complicated. Purkait *et al.* [50, 51] reported a two-step chemical process to recover CPC from permeate and retentate, i.e., the precipitation of CPC using potassium iodide in the solution, followed by the addition of cupric chloride to recover CPC. Schwarze *et al.* [54] reported the recycle of surfactants by a temperature variation and using the cloud point phenomenon. However, studies on the efficient recycling of surfactants are still rare, especially for large-scale application. Thus, more attention should be paid to the feasible, economic and effective surfactant recovery strategies for industrial recyclability. Membrane flux is another key aspect for industrial applications. Although many factors, including operating pressure, solute concentration, membrane MWCO and surface area, and temperature may affect the flux, membrane fouling caused by surfactants will reduce the flux and membrane life markedly. Fouling-resistant UF membranes with minimum surfactant adsorption and efficient membrane cleaning methods are both therefore needed.

8. Conclusions

Surfactants have been studied extensively for the field of environmental remediation. Surfactant micelles have been used to enhance ultrafiltration separation performance for pollutants removal, with this process known as micellar enhance ultrafiltration (MEUF). When the concentration of ionic surfactants far exceeds the critical micellar concentration (CMC), a large concentration of micelles, consisting of tens to hundreds of monomers, will form in water as nano-sized ion exchanger. Assisted by ultrafiltration separation, pollutants associating with the micelles can be removed from natural waters or wastewaters. Metal cation removal using MEUF has been studied extensively and is well-reviewed in the literature. This review has focused on the removal of anions using MEUF. Anions of

significance include nutrient species (nitrate and o-phosphate), arsenic chromium species, cyanide, and other anions (e.g., F^- and metal complexes). Factors that influence MEUF performance include operating conditions (i.e., operating pressure, membrane pore size, pH, competing ion concentrations), and the properties of the specific surfactant used during separation (i.e., chain length, CMC, head group). Because different anions compete for association with the micellar phase, relative affinity (i.e., selectivity) for the micellar phase in multi-ion systems was reviewed. Based on anion selectivity coefficients and the associated mass action and mass balance equations, a simple model has been presented that can quantitatively predict anion distribution and recovery during micellar-enhanced ultrafiltration processes. Because loss of surfactant monomers during MEUF is an issue, ways of reducing this loss have been summarized, including: the application of mixed surfactant micelles to reduce the CMC, the combination of MEUF with activated carbon adsorption, the use of cross-linked micelles, and the combination of polymers with the surfactants to generate aggregates of larger size, also resulting in lower aqueous phase surfactant monomer concentrations. We expect that over the next few decades, these technologies will be more commonly adapted in industrial and environmental applications to remove anionic contaminants from aqueous water streams.

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