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Recovery of cooling tower blowdown water through reverse osmosis (RO): review of water parameters affecting membrane fouling and pretreatment schemes

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ABSTRACT

Desalination through reverse osmosis (RO) of cooling tower blowdown water streams has been increasing over the years. Recycling of cooling tower blowdown streams using RO has specific challenges in view of the fouling characteristics associated with water in open recirculating cooling systems. These include the propensity for algal blooms and microbiological growth, fouling potential of the chemicals used for treating the systems for scaling, corrosion, biofouling control, and cooling towers' ability to take in atmospheric debris, among other industry and location-specific challenges. Different pretreatment processes have been considered and implemented both in research and practical applications worldwide. This paper provides a review of different pretreatment technologies to address the specific challenges in recycling cooling tower blowdown.

Keywords: Cooling-tower blowdown; Reverse osmosis; Recycling; Membrane fouling; Pretreatment

1. Introduction

The cooling tower blowdown (CTBD) streams constitute a portion of the total wastewater generated in the industry, and treatment is applied holistically to the overall wastewater quality parameters. For industries like power plants, however, the CTBD streams represent a significant portion of the total water waste generated, and recycling these streams has the potential for proportionate water savings [1]. The chemical oxygen demand (COD) and biochemical oxygen demand (BOD) of CTBD streams are generally much lower than those found in wastewaters from specific wastes from, for example, textile, leather, food and beverage industries [2–4], so the primary challenge in recycling these streams is desalination because of the concentration effect of the cooling tower.

In recycling CTBD streams, as with other wastewater streams, the water to be recycled contains higher contaminant concentrations or additional concentrations that complicate further treatment due to, among other factors, potential for scaling due to increased hardness, alkalinity, sulfates, phosphates, and silica, fouling due to increased suspended solids concentrations or specific inorganic or organic foulants, and microbial growth from increased phosphate, ammonia and organics [5].

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2. Water quality characterization and challenges

Chemistry of the cooling water is largely dependent on the chemistry of the water used as make-up to the cooling water system, which varies from location to location. What is consistent, however, is that the cooling tower – through evaporation – concentrates the concentration of ions in the water. If there is no deposition or dissolution of any constituent, the cycles of concentration (or concentration ratio) of all the ions should ideally be the same [5]. Stratton and Lee [6] studied the water quality of 11 different cooling tower's make-up and blowdown streams treated with different chemicals and, as expected, found great variations in the chemical composition of the waters, that not only depended on the make-up water chemistry and the cycle of concentration but also on the chemicals used for treatment, specific contaminant pickup through air scrubbing, mutual chemical and chemical-biological interactions.

The cycle of concentration maintained for a cooling tower is important insofar as the concentrations of many of the physico-chemical properties of the CTBD streams. Other parameters like turbidity, total suspended solids (TSS), COD and total organic carbon (TOC) may vary not just with the concentration factor, but also with ambient conditions, chemical treatment program and specific operational parameters of the cooling water system.

The cycle of concentration is itself maintained by removing water from the cooling tower to prevent over-concentration of salts and insoluble airborne debris that may result in potential problems. Drivers for maintaining the cycles of concentration include saturation points of ionic species in water, primarily calcium, magnesium and alkalinity [7] and concentrations of aggressive constituents like sulfates and chlorides [8]. Concentrations of chlorides are especially important because Chlorine, commonly added as an oxidizing biocide to cooling towers, may lower the chloride tolerance of stainless steels to pitting in the cooling water system [9].

Irrespective of the driver, since a cooling tower cycles the concentration of the individual ions present in the water, the challenges for the treatment of the CTBD streams are compounded in the form of higher concentrations of the ions and subsequently their scaling and biofouling potential.

The passage of large amounts of air through the cooling towers results in appreciable amounts of airborne debris and dust to be taken into the water stream [10]. So, the cooling tower total suspended solids concentration and turbidities may not just be a concentrated version of the same in cooling tower make-up water, but additionally, represent the atmospheric debris taken into the system.

Additionally, cooling waters also have a high concentration of TOC, in part due to the natural organic matter (NOM) in the form of humic and fulvic substances in the make-up water, but also due to algal bloom conditions in the cooling water system, which may result in organic fouling [11]. Water quality parameters for different CTBD streams from the primary literature that studied cooling tower blowdown recycle are listed in Table 1.

Additionally, individual chemical constituents in the feed water stream that are not generally considered foulants per se, but – not only due to their presence in the feed water to the cooling towers, but also due to their concentration in the CTBD stream, and other chemicals added to the cooling tower for chemical treatment as discussed previously – impart the risk of scaling on the RO membranes include: calcium and magnesium hardness, barium, strontium, bicarbonates, sulfates, phosphates, silicate and fluoride.

The composition of CTBD streams is further complicated by chemicals used for treatment for corrosion and scale inhibition. Use of chromate, zinc, molybdate, polysilicate, azoles, polydiol, nitrates, orthophosphates, polyphosphates, phosphonates and nitrites as corrosion inhibitors for cooling towers open circuit has been documented – although, in practice, the treatment programs generally include a blend of multiple inhibitors for better performance. Common combinations include molybdate-silicate-azole-polydiol, phosphonate-phosphate-azole, and zinc phosphate-azole. Similarly, common scale inhibitors used for cooling towers include polyacrylates, polymethacrylates, polymaleics, phosphonates (AMP, HEDP, PBTC), chelates (EDTA, NTA), copolymers, terpolymers, and polyphosphates. Again, common treatment programs use blends of different chemicals, with a combination of phosphonates with a polymer among the most common ones [10]. From the perspective of subjecting the CTBD streams to RO, these chemicals bring new challenges.

Scale inhibitors, not just for the cooling tower treatment, but even for the RO membrane itself have been shown to exacerbate biofouling, and biofilm growth, on RO membranes, as with polyacrylates and phosphonates [24,25].

In order to control microbiological fouling in cooling towers, they are routinely treated with biocides. Different water treatment companies provide treatment for microbiological control through oxidizing and non-oxidizing biocides, with a combination of the two or more quite common.

From among the non-oxidizing biocides, the use of organobromine biocides (2-Bromo-4-hydroxy-acetophenone, bronopol, DBNPA), carbamates, guanides, glutaraldehydes, isothiazolines, quats, and polyquats, has been documented [26]. At least some RO membrane manufacturers have provided information of some non-oxidizing biocides that may be used for RO membrane preservation – suggesting compatibility and little or no risk of adverse consequences for the same – including DBNPA, isothiazolines [27–29], formaldehyde and glutaraldehyde, although with the caveat that the latter two may cause membrane flux reduction of 10%–50% for new elements [28].

From amongst oxidizing biocides, common ones include bromine, chlorine and chlorine dioxide [30,31]. The limited chlorine tolerance of the commonly used polyamide RO membranes is well documented [32–34]. Conversely, RO membranes are quite tolerant of chloramines [35].

Another class of treatment chemicals used in open cooling water recirculation systems is bio-dispersants (or biodetergents). Biodispersants are used to penetrate and loosen the matrices of biofilms in order to allow biocides to reach and inactivate microorganisms that may have been shielded by the biofilm. Common bio-dispersants include DTEA II (2-Decylthio ethanamine), dodecylamine acetate, polyquaternary amines [36]. Bio-dispersants have been reported to have caused appreciable fouling in ultrafiltration (UF) membranes when used to pretreat CTBD water for further desalination through RO [37].

A list of important recommended parameters for feed water for RO applications [27,38] is tabulated in Table 2. From the perspective of treating CTBD streams, individual parameters of concern are discussed below:

2.1. Turbidity

Cooling water turbidities generally exceed the 0.1 NTU threshold beyond which accelerated fouling is noted to be a potential cause for concern. From amongst the cooling towers from Table 1, the turbidity of the water is noted to be around 10 NTU, but as high as over 70 NTU. For turbidity values up to 30 NTU, single-stage, dual media filters followed by cartridge filters or ultrafiltration or microfiltration techniques may be sufficient, while for higher values, sedimentation is additionally being needed [38].

2.2. Total organic carbon

The TOC and DOC (dissolved organic carbon) values in excess of 50 mg/L from Table 1 are indicative of severe algal bloom conditions. Table 1 also shows that TOC may be an important but underused parameter for characterizing CTBD streams. In any case, the values in Table 1 are well in excess of the 2.0 mg/L threshold from Table 2 and may entail the requirement for sedimentation in addition to conventional or membrane filtration [38]. The high TOC values may also have been contributed by synthetic organic carbon from the chemicals used for the treatment of the cooling tower. As noted previously, bio-dispersants used in the cooling tower have been noted to have caused fouling in UF membranes–these chemicals often are proprietary, and intermediate parameters like TOC is sometimes used to detect their presence in academia. In such cases, adsorption may also be considered as a pretreatment option [37].

2.3. Chemical oxygen demand

COD is another parameter generally used to quantify the number of organics in water. The organics can directly foul the RO membranes or indirectly be responsible for biofouling by promoting the growth of a biofilm on the membrane surface. RO membrane autopsies have identified either or both of organic fouling and biological fouling to be the leading modes of membrane fouling for surface waters and leading membrane elements even for groundwater [39,40].

COD of cooling water is generally expected to exceed the threshold values covered in Table 2 due to the presence of NOM, but the concentrations, and the associated risk of fouling, may further increase in case of leakages or contaminations [14]. In such cases, limits for oil and grease and/or THC (total hydrocarbon) will also become relevant.

2.4. Iron

From amongst the individual chemical constituents from Table 2, iron is important because it is often present in cooling water as a result of corrosion in the system. Total iron as high as 140 mg/L has been reported in open recirculating cooling water [16]. Limits are present for iron in both the reduced and the oxidized forms. Common removal techniques involve conventional filtration of iron in suspended oxidized form and oxidation-filtration of iron in dissolved reduced form. Under special conditions, specialized media may also be used for iron removal.

Iron, being a recognized feed water contaminant for seawaters with subsurface intake, is generally considered one of the main parameters in the selection of pretreatment schemes for RO applications. Badruzzaman et al. [41] consider media filtration, with specialized media like greensand for higher iron contents, to be sufficient for iron removal upstream of RO, but do note the risk of iron breakthrough to the RO membranes necessitating the conservative design of media filters.

2.5. Hardness and alkalinity

Role of hardness causing ions, primarily magnesium and calcium, along with alkalinity in causing scale are well understood. Indices like Langelier saturation index (LSI) or Ryznar stability index are functions of calcium hardness, total alkalinity, TDS, pH and temperature, and are used as much in cooling towers as in RO plants for evaluation of scaling potential of water. Common countermeasures include dosing of scale inhibitors and acid, and maintaining recovery and subsequently the concentration factor in the RO concentrates. An accepted target LSI value for RO concentrate is –0.2 without, and up to 2.5 with the use of scale inhibitors [42].

Scaling due to the presence and precipitation of other minerals like barium, strontium, sulfates and silicates is also possible for high recovery RO systems. The potential of these salts to precipitate as scale can be estimated by comparing the ion product of the salt in the RO concentrate with its solubility product. The development of simulation software of the saturation behavior of these salts has allowed convenient prediction of the potential of their saturation.

2.6. Phosphates

Phosphates are present in cooling towers generally as a result of the chemical treatment applied to control corrosion and scaling. Calcium phosphate scaling becomes a cause for concern if the relative concentrations of phosphates and calcium portend precipitation. However, even in low concentrations, phosphates are a cause of concern from the point of view of promoting microbiological growth even if present in concentrations lower than 1 mg/L [43,44].

In instances of CTBD recycling applications at full scale further covered in the next section of this paper, biofouling attributed to the presence of phosphate as a nutrient for promoting microbial activity has been noted to be a major operational concern necessitating the use of biocides as a mitigation measure [22,45]. Although phosphate removal is generally considered to be a subject of biological removal, different physico-chemical methods have also been studied. These include removal through ion-exchange, adsorption and coagulation–filtration [46].

2.7. Silt density index (SDI)

Although limitations in the SDI test have been propounded and alternatives like the MFI (modified fouling

Table 1
Water quality parameters for different CTBD streams

Parameter	[11]	[12]	[13]	[14]	[15,16]	[17]	[18]	[19]	[20]	[21]	[22]	[23]
pH	7.5–8.0	8.5	7.9	6.7–7.2	8.55	8.4	8.5	7.9		8.8		9.2
Conductivity, µS/cm	3,944	7,132	3,620	2,928	1,500	1,581		1,920	5,010	2,790	3,617	3,710
M-alkalinity, mg/L as $CaCO_3$	54	254			356							
Sulfate, mg/L	1,109	2,341							880	407		503
Chloride, mg/L	549	399	500						766	336	417	712
Phosphate, mg/L	2	8.2	5.9				1.1	0.85				0.5
Nitrate, mg/L	88		86.7									19
Silica, mg/L		96	0.9	74.2	140	97.4	56			33		41
Calcium, mg/L as $CaCO_3$	1,093	578	1,204						635			455
Magnesium, mg/L as $CaCO_3$	251	116	259					43	470			423
Sodium, mg/L	332	1,158										
Potassium, mg/L	81	52										
Barium, µg/L			145									
Strontium, µg/L			1,500					1,230				
Zinc, mg/L								1.0				
TSS, mg/L	<15	32	12		10					25		26
Turbidity, NTU			7.3	73.6	7	9.6	9.9					
TDS, mg/L		4,749			1,342			893			2,315	2,676
TOC, mg/L	53				2							
DOC, mg/L			59.1									
COD, mg/L				181	3.5	79	3.5		115	12	32.2	
BOD, mg/L			1.4	8.75								

Table 2
Important recommended parameters for feed water for RO applications [27,38]

Parameter	Potential effect on RO membrane
Iron in reduced form (Fe^{2+})	Foulant if > 2.0 mg/L
Iron in oxidized form	Foulant if > 0.05 mg/L
Manganese	Foulant if > 0.02 mg/L
Aluminum	Foulant if > 0.1 mg/L
Copper	Potential membrane damage of > 0.05 mg/L
Turbidity	Accelerated fouling if > 0.1 NTU
Total suspended solids (TSS)	Accelerated fouling if > 1.0 mg/L
Silt density index (SDI)	Accelerated fouling if > 5
Total hydrocarbons	Foulant if > 0.02 mg/L
Oil and grease	Foulant if > 0.1 mg/L
Silica (colloidal)	Foulant if > 100 mg/L in concentrate
Total organic carbon (TOC)	Potential for accelerated fouling if > 2.0 mg/L
Assimilable organic carbon (AOC)	Potential for accelerated fouling if > 10.0 µg/L Ac-C
COD	Potential for accelerated fouling if > 10.0 mg/L
UV_{254}	Potential for accelerated fouling if > 0.5 cm^{-1}
Hydrogen sulfide	Odor and membrane fouling if > 0.1 mg/L
Ammonia	Membrane damage if bromide > 0.4 mg/L
Free chlorine	Membrane damage if > 0.01 mg/L
Oxidation reduction potential (ORP)	Membrane damage if > 250 mV

index) proposed, SDI remains one of the most commonly used indexes for measuring the fouling potential of water on RO membranes [47,48]. Since the test is considered to be applicable for low turbidity waters [49], the SDI value of the untreated CTBD streams is generally too high to properly quantify. Instead, the SDI of these streams after treatment through the different treatment schemes is compared against the threshold value of 5.0 as given in Table 2 and a preferred value of 3.0 or less.

SDI is generally thought of as a measure of suspended matter and colloids in water. Consequently, the unit process that is employed to reduce turbidity and TSS, will also have a positive influence on SDI.

3. Treatment schemes

3.1. Constructed wetlands

Phosphate removal is already well-established through biological processes. Wagner et al. [50] have further reviewed the use of constructed wetlands (CW) to treat CTBD streams in view of the adverse fouling potential of the treatment chemicals used in cooling towers for downstream membrane processes. Among the different removal mechanisms at work in CWs, they noted the CWs ability to remove some biocides like glutaraldehyde in limited concentrations through biodegradation, other biocides (DBNPA and bronopol) and scale and corrosion inhibitors (polycarboxylates, phosphonates, and benzotriazole) through photodegradation, scale and corrosion inhibitors (phosphates, phosphonates, zinc, and benzotriazole) and surfactants through adsorption and corrosion inhibitors (zinc and benzotriazole) through plant uptake. However, polycarboxylates, from commonly used scale inhibitors are noted to be resistant to biodegradation. They separately demonstrated removal of some of these chemicals, corrosion inhibitor benzotriazole, in a pilot CW setup [51], and continue to stress the need for removal of the chemicals used in cooling water treatment prior to desalination [52].

3.2. Coagulation-settling/filtration

Among other technologies, Löwenberg et al. [13] studied the pretreatment of CTBD water in terms of DOC concentration and its removal. In amongst the coagulation-settling results, although up to 50% DOC reduction was documented using $FeCl_3$ as the coagulant, the supernatant turbidity was reported to be higher than that of the untreated CTBD. This was attributed to the aggregation of hydroxylated iron from the coagulant and organic matter which was not able to settle potentially due to the presence of scale inhibitors present in the CTBD stream.

Farahani et al. [14] investigated 21 different coagulants on CTBD water from an oil refinery through jar-testing and found polyaluminum chloride (PACl) to be the most effective coagulant. In the subsequent lab trial, the feed water was passed, after coagulant and co-coagulant dosing, through a lamella clarifier, two-stage single media filters – sand with a grain size in the range of 1.0–1.6 mm (uniformity co-efficient of 1.5) and granular activated carbon (GAC) with a mesh size of 10 × 30 – and a cartridge filter. With this treatment scheme and a 50 mg/L PACl dose, along with 0.5 mg/l anionic polyacrylamide as a co-coagulant, optimum results were found at pH below 6.5, with turbidity reduction of up to 99% (73.6 NTU in feed water; 0.61 NTU in filtrate), COD reduction of around 20% (181 mg/L in feed water; 145 mg/L in filtrate) and SDI_{15} reduction from 6.57 to 2.22. Permeate flux across the downstream RO membrane showed up to a 33% improvement over untreated water stabilized flux. The study did not specify a surface hydraulic loading rate for the media filters. Moreover, no observations on media fouling were documented.

Additionally, the carryover of residual coagulant and its impact on downstream RO membranes is also an important factor. Appreciable carryover, as well as membrane fouling through aluminum salts, have been reported [53]. For aluminum-based coagulants, investigation through SEM and energy dispersive X-ray spectroscopy of fouling on the RO membranes for a pilot test revealed the presence of silica and phosphorous, suggesting an incidence of fouling through aluminum silicate and phosphorous from phosphonate-based scale-inhibitor with aluminum [54]. Since the pilot test was carried out at low recoveries (14%–15%), fouling would have occurred at or near influent water concentrations, rather than concentrated water concentrations. Mitigation of aluminum fouling through chemical addition – chelating agents, including EDTA and citrate – has been investigated, but with limited efficacy in the presence of other scale inhibiting chemicals [55], and a more feasible option may be to limit aluminum carryover to 50 μg/L [56].

For iron-based coagulants, an appreciable decrease in RO membrane salt rejection has been observed due to iron carryover [54]. However, whether dosed as a coagulant or present in the original CTBD stream, iron is recognized as a foulant at low concentrations (2 mg/L in reduced form and 50 μg/L in an oxidized form) [38].

Frick et al. [17] investigated different combinations of coagulation–filtration as pretreatment for RO for CTBD from a petrochemical plant on a bench scale. They found PACl to be the most effective coagulant from amongst PACl, alum and ferric chloride. They also observed that although coagulation-settling using PACl and a commercial anionic polyelectrolyte as flocculent did improve the supernatant turbidity (6.6–12.5 NTU in feed; 0.65–0.85 NTU in the supernatant), COD (74.8–83.2 mg/L in feed; 38–52 mg/L in the supernatant) and silica (84.9–109.9 mg/L in feed; 45.5–53.5 mg/L in the supernatant), no appreciable improvement in SDI values was found. The addition of a filtration step improved the performance of turbidity (6.6–12.5 NTU in the feed; 0.29–0.37 NTU in filtrate), COD (74.8–83.2 mg/L in feed; 34.7–50.3 mg/L in filtrate), silica (84.9–109.9 mg/L in feed; 39.6–42.4 mg/L in filtrate) and SDI_5 (16 in feed; 5.5 in filtrate) reduction. It is further noted that the coagulant dosages in this study were an order of magnitude higher than those of other studies using PACl. Although no explanation for this has been offered, it is possible that the presence of phosphonates necessitated higher consumption of the coagulant in view of the detrimental effect of the common phosphonates on coagulation [57].

Wang et al. [19] investigated different coagulants in treating CTBD stream before media filtration, and also found PACl to be an effective coagulant along with polymer flocculant (cationic polyacrylamide) in reducing turbidities to less than 1 NTU and SDI to less than 5.

Although the focus of study of Altman et al. [58] was on the reduction of water usage through side-stream membrane (nanofiltration) filtration for a cooling tower, they observed silica fouling of the membranes fed with water pretreated through a set of filtration steps (sand filter > GAC filter > 50 μm cartridge filter > 1 μm cartridge filter). Based on a higher feed-interstage than interstage-concentrate differential pressure, fouling can be assessed to have been caused by colloidal silica and suggests a limitation of the media and cartridge filters in preventing colloidal silica carryover.

3.3. Powdered activated carbon (PAC) adsorption

As opposed to applications of GAC, which involves the use of the activated carbon in granular form loaded in beds similar to that of media filters, PAC has a much smaller particle size, allowing it to be dosed into the feed water to allow adsorption within the water stream prior to removal through sedimentation or filtration, while some studies have also noted it to be more effective at organics removal than GAC due to a higher surface area resulting from smaller particle size [59]. Different configurations and modes of application of PAC with UF have been studied as a method that uses the PAC to remove organics through adsorption, improves membrane performance by forming a porous cake layer on the UF membrane surface, a phenomenon which also reduced irreversible fouling [60].

PAC adsorption has been found to be capable of reducing DOC concentrations to a minor extent, with a preference towards low molecular weight (LMW) organic substances. When succeeded by UF, however, the results–discussed in succeeding sections – were found to be better than tests for UF alone and UF preceded by coagulation. Furthermore, with a PAC dose of 20 mg/L, specific DOC adsorption in the range of 0.06–0.17 mg DOC/mg PAC was reported which was comparable that in wastewater treatment plant effluent, indicating a generally high organic load in CTBD streams and corresponding affinity for adsorption onto PAC [13,61].

Frick et al. [17] also considered GAC sorption in their experiments, but noted no improvement in the filtrate quality in terms of turbidity and silica removal. They did, however, observe a further 50% reduction in COD values than when the water was passed through sand filters after coagulation only.

3.4. Ultrafiltration

Study of Farahani et al. [14] on ultrafiltration as a pretreatment to RO showed performance comparable to their tests for coagulation–sedimentation–filtration, with a turbidity reduction of 98% (73.6 NTU in feed water; 1.55 NTU in filtrate), COD reduction of 17% (181 mg/L in feed water; 151 mg/L in filtrate) and SDI reduction from 6.57 to 2.07. Permeate flux across the downstream RO membrane showed up to a 33% improvement over untreated water stabilized flux. Additionally, the permeate flux of the UF membrane itself receded over time suggesting a requirement for suitable pretreatment for the UF membrane as well.

The study of Löwenberg et al. [13] on UF also showed a significant reduction in CTBD water turbidity, but negligible performance in reducing DOC. This was attributed to the size of the organic matter in CTBD potentially being lower than the UF membrane pore size (<20 nm). They also encountered repeated fouling on the membrane, and in view of the previous observation concluded that suspended solids and colloids may be responsible for the fouling. They also concluded that UF as a stand-alone pretreatment for RO may be insufficient with a 60% reduction in downstream RO permeate flux in 5 d. Flux decline for UF preceded by PAC dosing was, in comparison, less than 50%. Considering the portion of the DOC reduction through PAC–primarily LMW range – and the presence of bio-dispersant within the CTBD stream of the comparable molecular weight range, the appreciable influence of biodispersant on membrane fouling was identified. In their experiments with coagulation–ultrafiltration, they did not find a significant improvement in the reduction in membrane fouling. Moreover, the RO membrane fouling through residual iron was also observed.

An investigation by Zhang et al. [15] in using UF to treat CTBD from a coal-fired power plant involved pilot testing two UF membranes in inside-out and outside-in operational modes. The UF modules were fed with CTBD water after passing through a disk filter, the porosity of which, as well as details of inline coagulant dosing, were not documented. The UF membranes removed roughly 35%–50% of the COD (3–4.8 mg/L in feed; 1.5–3.0 mg/L in filtrate) and consistently reduced turbidity to less than 0.3 NTU (from 5.0–23.0 NTU in the feed). The UF membranes also removed around 60% of the orthophosphate (0.5–2.0 mg/L in feed; 0.2–0.7 mg/L in filtrate) and a major portion of total iron and colloidal silica. The UF filtrate SDI was consistently below 2.5. Performance of downstream RO in terms of transmembrane pressure (TMP) and permeate flux of both types of membranes were comparable–both were, however, backwashed at different frequencies.

Zhang et al. [18] also studied outside-in UF membranes in a pilot test for recycling CTBD in terms of turbidity, COD, total iron, colloidal silica, copper and SDI reduction. The UF module was fed with CTBD water after passing through a 50 μm disk filter and dosed with PACl and PAM (polyacrylamide) among other chemical additives. They documented total iron reduction of around 70% (47–197 mg/L in feed; 15–44 mg/L in filtrate), colloidal silica reduction of 65% (14–109 mg/L in feed; 1.2–32 mg/L in filtrate), COD reduction of 40% (2.9–4.8 mg/L in feed; 1.4–4.0 mg/L in filtrate), phosphate reduction of 55% (0.7–2.0 mg/L in feed; 0.2–0.8 mg/L in filtrate) and negligible copper reduction, along with a consistent SDI less than 3.0.

COD reduction of over 65%, and as high as 85%, was reported by in another pilot study by Jinpo et al. [62] using outside-in UF with a 150 μm disk prefiltration. They also reported UF filtrate turbidity and SDI values consistently below 1 NTU and 2.0 respectively.

Chunxia and Lin compared the increase in TMP of a downstream nanofiltration membrane as a measure of residual fouling potential for UF preceded by media filtration and coagulation–sedimentation and found the latter to be more effective in limiting the increase in the nanofiltration TMP [20].

Experience at full-scale plants recycling CTBD streams supports the sufficiency of UF in meeting filtrate SDI values typically below 3.0, and exclusively below 5.0, but note its limitation in rejecting organics, with only a third of the organics in terms of COD removed at the Gaojing Power Plant in China. The CTBD recycling plant at this facility otherwise allowed recovery of 370 m^3/hr of CTBD water into high purity boiler feed water with a pretreatment scheme of media filter > disk filter > ultrafiltration upstream of the RO units [21]. Furthermore, Ying identified the propensity of the UF membrane system at this facility itself to foul, and the phenomenon was attributed to biofouling, and the use of biocides successfully mitigated the extent of fouling [45].

For another full-scale facility recovering 450 m^3/hr of CTBD water through coagulation–sedimentation > ultrafiltration upstream of the RO, Qi et al. [22] also identified organic/biological fouling as a major impediment to the stable operation of the UF, and used lime treatment to reduce the COD of the CTBD by over 50% upstream of the UF, which further allowed the UF to reduce the effluent COD to around 10 mg/L from an initial value of over 40 mg/L.

Study of Wanbing on a full-scale CTBD recycling facility used coagulation–sedimentation followed by multimedia filtration upstream of the UF. They reported a coagulant dose on the order of 50–60 mg/L along with a coagulant aid of 0.50–0.75 mg/L to be optimum for turbidity removal. Furthermore, even with multiple unit processes upstream of the UF, they also noted biofouling to be incident on the UF membranes and made us of biocides to alleviate the extent of fouling [23].

3.5. Microfiltration (MF)

Yin et al. [63] applied MF to treat CTBD stream after a stage of coagulation–sedimentation. They reported consistent turbidity reduction from 6–10 NTU in the influent to less than 1 NTU and effluent SDI values consistently below 3. In short term filtration runs, they were able to recover the TMP totally through regular backwashing.

The study of Zhang et al. [18] provided a comparison of UF membranes to MF (0.1 μm pore size) membranes. MF performance was slightly worse off, but largely comparable to UF, with total iron reduction of around 70% (47–197 mg/L in feed; 19–48 mg/L in filtrate), colloidal silica reduction of 45% (9.6–70.4 mg/L in feed; 1.2–32 mg/L in filtrate), COD reduction of 38% (2.9–4.8 mg/L in feed; 1.5–3.5 mg/L in filtrate), phosphate reduction of 56% (0.7–2.0 mg/L in feed; 0.1–0.8 mg/L in filtrate) and negligible copper reduction, along with a consistent SDI less than 3.0. They also noted that the addition of PACl and PAM did not result in a significant improvement of permeate quality.

Wang et al. [64] investigated MF and UF as pretreatment for RO for a pharmaceutical industry CTBD stream. For both trials, the CTBD water was prefiltered through a sand filter. The addition of coagulants or other chemical conditioners was not documented. They found that MF, operating in a cross-flow mode, was able to consistently maintain filtrate turbidity less than 0.2 NTU for feed turbidity of 2–12 NTU. Although they found comparable results for the UF membranes, they concluded MF to be more feasible on commercial grounds.

4. Conclusion

Characterization of CTBD water has been carried out based on physical parameters like turbidity, which seem a very reasonable choice given that membrane manufacturers have generally provided threshold limits. COD and TOC have also been used as indicators of organic fouling. Other parameters that have not been the focus of characterization, but have a profound effect on membrane processes include iron, phosphate, and concentrations of otherwise omnipresent ions that although may not directly affect the treatment performance, become precursors for scaling for high recovery desalination plants.

In most of the pilot tests carried out for evaluation of pretreatment schemes for feed the CTBD recycle water to RO unit, it is observed that feed water characterization has generally ignored the chemical treatment program and impact of residual chemicals on the pretreatment performance as well as fouling on RO membranes and pretreatment equipment. This may primarily be due to the fact that most industries tend to use proprietary chemicals where the exact composition of the treatment chemicals are withheld by the suppliers as trade secrets. In any case, the detrimental effect of these chemicals warrants further studies focusing on their removal.

Biological processes have recently been considered for the removal of chemicals in the CTBD streams. Even so, multiple installations on full scale suggest that physico-chemical processes are sufficient as unit processes for CTBD water pretreatment for RO.

From among the prefiltration schemes, ultrafiltration has been a popular choice as pretreatment for RO for the CTBD streams. Additionally, in all full-scale facilities covered in this paper, pretreatment for ultrafiltration was provided and is especially advisable if the cooling tower chemical treatment program includes specific chemicals – like bio-dispersants – that may cause repeated and/or irreversible fouling in the UF membranes themselves.

Microfiltration has not been a popular choice, but a comparison of MF with UF suggests that MF may be an equivalent or even a better alternative to UF. In the selection of the level of filtration, however, it is strongly felt that the particle size distribution of the suspended solids in water has been ignored, and warrants inclusion among parameters of characterization in future studies.

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