



Colloidal fouling of RO membranes following MF/UF in the reclamation of municipal wastewater

Robert Y. Ning*, Thomas L. Troyer

*King Lee Technologies, 8949 Kenamar Drive, Bldg. 107, San Diego, CA 92121, USA
Tel. +1 (858) 693-4062; Fax: +1 (858) 693-4917; email: RNING@kingleetechnology.com*

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Abstract

Major municipal wastewater reclamation plants in California, USA, Singapore, and many built or planned for other regions of the world use the high pathogen reduction properties of microfiltration/ultrafiltration (MF/UF) membranes followed by reverse osmosis (RO) membranes. Operational experiences in these plants suggest that while MF and UF membranes encounter pore and cake fouling by colloidal particles (0.1 micron down to molecular sizes, ie. nanoparticles), a significant fraction of the smaller colloidal particles pass through the MF and UF membranes, and end up on RO membranes as cake-layer foulants. Autopsies, foulant analyses and cleaning studies performed on fouled RO membranes from the plants and pilot plants showed that colloidal natural organic matter, colloidal calcium phosphate and some times colloidal silicates are the main components. These colloidal particles have great affinity towards aggregation with each other. Due to incomplete removal by MF and even UF, fouling of RO membranes downstream becomes measurable by trend-charts of normalized values of permeate flow, differential pressure and salt passage. Normalized permeate flow is the most sensitive, and an early indicator of such fouling. In this paper we will provide some details of our studies and provide literature evidences that support the conclusion that calcium phosphate in foulants originated as nanoparticles in the wastewater.

Keywords: Municipal wastewater; Microfiltration; Ultrafiltration; Reverse osmosis; Colloidal fouling; Organic colloids; Colloidal calcium phosphate; Colloidal silica; Colloidal silicates; Nanoparticles

1. Introduction

The use of microfiltration (MF) or ultrafiltration (UF) as pretreatment to reverse osmosis (RO) membrane process offers the benefits of

additional high pathogen reduction credit as well as RO fouling mitigation for the treatment of secondary municipal wastewater. On this basis, major plants in California, USA, Singapore and Kuwait have been built and in operation with this design. Many major plants with this design will undoubtedly follow in China and elsewhere.

*Corresponding author.

Operating experiences in plants and pilot plants so far have shown [1] that colloidal fouling to varying degrees in both the first and second stages of ROs still occur despite MF or UF pretreatment. In the interest of fully controlling fouling of the RO membranes with antiscalants [2,3] and antifoulants [3], our efforts have been focused on differentiating between scaling and colloidal fouling [4] seen on the membranes [5,6], and developing methods for full control. While natural organic foulants and silica and silicates found on RO membranes can be presumed to arise from the coagulation and flocculation of colloidal organic and silicate particles that have passed through the MF/UF membranes upstream, the state in which calcium phosphate arrived in the RO system needs to be considered. If passage through the MF/UF pretreatment is in the form of dissolved calcium and orthophosphate ions, then deposition on the RO membrane would be by crystallization or scaling. Such a mechanism should be controllable by antiscalants. If passage through the MF/UF membrane is in the form of colloidal calcium phosphate particles, then antiscalants at low dosages would be relatively ineffective, requiring anticoagulant/dispersants [3].

Since we have found that antiscalants known to be very effective against calcium phosphate is relatively ineffective in controlling calcium phosphate deposition in the RO system, we have long suspected that calcium phosphate is passing through the MF/UF in the colloidal nanoparticulate [7] form, and coagulating with other colloidal particles in the MF/UF filtrate, giving rise to varying degrees of fouling in the RO system. Such depositions of calcium phosphate is easily cleaned by dissolving with acid cleaners. However, if calcium phosphate precipitates become extensively coated with organic foulants, RO membrane flux become increasingly difficult to recover by low pH and even very high pH cleaning. Report of similar fouling by calcium phosphate and organics in the full-scale plants in

UK and Spain [6], and Singapore [6,8] points to a general presence of colloidal (nanoparticles) of calcium phosphate in municipal wastewater around the world.

In this paper, we present the analysis of RO foulant from a severely fouled RO membrane, RO feedwater analysis from several municipal wastewaters relative to solubility product constant considerations for calcium phosphate and likelihood of presence of calcium phosphate in the colloidal form supported by the literature.

2. Early encounter

Since 1975 until the recent shutdown for plant reconstruction, Water Factory 21 in Orange County, CA, had famously treated 15 million gallons per day (mgd) of secondary municipal wastewater using lime-softening followed by RO.

Table 1
Composition of RO foulant resulting from MF pretreatment

Gravimetric assays (absolute % by weight):	
Carbon	6.83
Hydrogen	1.87
Nitrogen	0.64
Ash	80.47
Scanning electron microscope–energy dispersive X-ray (relative weight % excluding carbon, oxygen and nitrogen):	
Calcium	53
Phosphorous	33
Magnesium	3.6
Iron	2.6
Sulfur	2.0
Sodium	2.0
Silicon	1.1
Chloride	0.7
Magnanese	0.6
Aluminum	0.6
Potassium	0.2

As a supplier of antiscalant and cleaning chemical support to the plant, we were familiar with the low antiscalant requirements of the RO. Fouling was limited to a low level of colloidal organics. In supporting the process development efforts at the plant for substituting lime-softening with MF as pretreatment to RO, there was noticeable fouling of the pilot RO that was not very responsive to antiscalants [9]. A foulant was obtained from the membrane surface during an autopsy of a severely fouled element from the pilot RO. After washing and drying, analyses of the composition of the dry foulant (Table 1) showed that it contained 20% by weight of organic matter and 80% of inorganic salts which was primarily calcium phosphate. We recognized then that calcium phosphate is extremely insoluble at neutral to high pH, and that it has to be dealt with in the new process since phosphate in the old process is removed by lime-softening.

3. Properties of calcium phosphate

Phosphate is the only oxidation state of phosphorous element in soils [10], plants and animals. Due to its low abundance in nature, it is highly conserved as the main component of bones and teeth and bound as metabolites and in genes of cells. It is not surprising that calcium phosphate is the most insoluble of calcium salts with a molar solubility product of 2×10^{-33} , far lower than that of all scales commonly encountered in RO systems.

Fine particles of highly insoluble calcium phosphate have been extensively used as adsorbent and chromatography media in the separation of proteins [11] in aqueous solutions on analytical and preparative scale. When aqueous solutions of calcium chloride and tribasic sodium phosphate are mixed, calcium phosphate precipitates in a gelatinous form. When calcium chloride solution is slowly mixed with dibasic sodium phosphate, brushite, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, is formed. When

brushite is boiled with sodium hydroxide, it is converted to hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. All three forms of calcium phosphate have been used as stationary phase adsorbents for the separation of proteins and biological materials. Hydroxyapatite is the main inorganic constituent of bones and teeth, and as such is extensively studied for hard tissue repair applications such as implant coatings and bone substitutes.

4. Calcium phosphate in the colloidal form

Both in nature and industrial processes, calcium phosphate usually aggregate in amorphous colloidal forms. In milk, colloidal calcium phosphate is present in the form of amorphous nanometer-sized clusters throughout the matrix of casein micelle [12], and is a parameter in the processing of cheese [13].

The mineral component of bone and teeth consists of hydroxyapatite in poorly crystalline or nearly amorphous forms [14]. Extensive methods [15] are available to produce biological prototypes of modified hydroxyapatite in nanocrystalline forms by chemical precipitation, spray drying, hydrothermal treatment, sol-gel approach, precipitation from complex solutions, wet chemical methods incorporating a freeze drying step, mechanochemical synthesis and electrodeposition, in the presence of biological polymers or molecules of interest. An injectable calcium phosphate-based paste that can conform to and interdigitate with host bone offered for stabilizing fractured bone within a short time [16] illustrates the adhesive power of such nanocrystalline particles. Such aggregations, adhesions between colloidal particles and precipitations from water that results, appears to us to be examples of the colloidal fouling mechanism occurring in our membrane process for the municipal wastewater.

Since phosphate is a limiting nutrient in soils for plants and natural waters for microorganisms, a large body of literature exists for the monitoring

Table 2

Some calcium, phosphate and pH values for RO feed water in recent public tenders for antiscalant

Plant/location	Date	Calcium, mg/l	Phosphate, mg/l	pH	
Bedok, Singapore	Feb. 2005	43–51	9–37	5.8–6.8	
Seletar, Singapore	Jan. 2005	15–40	9–37	4.6–8.0	
Kranji, Singapore	Jan. 2005	20–40	77–123	6.0–7.5	
Water Factory 21, CA, USA	Jun. 2005	60–89	0.6–7.0	<7.9–8.0	
	Sept. 1996	71–174	4.6–7.0	5.5	
West Basin, CA, USA	May 2000; Oct. 2001				
		Trains 1 and 2	42–92	—	5.8–6.0
		Train 3	38–64	4.2–8.8	6.3

of the movements of colloidal phosphates in the environment, and is recognized to be poorly understood [17–19].

In medical research, calcium phosphate solubility product and the maintenance of target serum calcium and phosphate concentrations with treatments has gained much attention [20–22]. In end-stage renal disease patients, dramatic cardiovascular mortality is connected with disturbances in calcium and phosphate homeostasis, and calcification of soft tissues. Normally serum concentration of calcium ion is 40–60 mg/L and phosphate (by molybdate colorimetric assay) is 25–45 mg/L. It is pointed out [20] that even at normal levels, serum calcium and phosphate concentrations exceed their molar solubility product in an aqueous solution by many orders of magnitude (water: 2.1×10^{-33} vs extracellular body fluid: 1.8×10^{-6}). This raises the question of whether the physiological concentrations are “metastable” or supersaturated with respect to calcium phosphate precipitation, or whether much of calcium and phosphate are bound in a colloidal polynuclear form. The extensive indirect evidence in the literature and kinetic physical chemical studies [23] points to the latter. In parallel to these developments, nanoparticles of calcium phosphate have been shown to be an attractive adjuvant when co-injected with parenteral vac-

ines, and allergens for desensitization, while producing minimal local irritation [24–26].

To assess the likelihood of the presence of colloidal calcium phosphate in municipal RO feedwaters following MF/UF pretreatment, we provide in Table 2 some calcium, phosphate and pH values for RO feed water presented to antiscalant providers in public tenders. Since phosphoric acid has pKa values of 2.16, 7.21 and 12.32, and the least soluble calcium phosphate salt results from the presence of the tribasic orthophosphate ion, the pH of the feedwater is a critical parameter, and is included for comparison. All indications in the colloidal calcium phosphate literature show that nanoparticle concentrations increase or decrease in the pH range of 5–7, a range amazingly coincidental with the complexities of phosphate transport, utilization and control in biological and environmental aqueous systems. It follows naturally that in controlling fouling of both MF/UF and RO membranes by municipal wastewaters, we need to deal with calcium phosphate both in the ionic and in the particulate forms. The wide ranges of values for the critical parameters presented in Table 2 calls for an investigation of colloidal calcium phosphate concentration profile in each plant process, especially where membrane fouling is experienced, and optimal pH control is uncertain.

4. Conclusion

Colloidal fouling of RO membranes following MF/UF pretreatment poses a serious challenge to economical and reliable operation of large membrane plants around the world for treatment of municipal wastewater. Colloidal calcium phosphate is being recognized as a major factor together with natural organic and other colloidal matter in observed coagulation and deposition on the membranes. We are providing documentation on the presence of calcium phosphate in RO foulants as a characteristic of the membrane process in treating municipal wastewater. A review of the literature on the occurrence and synthesis of nanoparticulate calcium phosphate shows that its presence in municipal wastewater before and after MF/UF as well as RO is an important process parameter. To optimize process control and avoiding membrane fouling, our efforts are now focused on differentiating between ionic and colloidal phosphate and developing a practical method for quantitation.

Question about the molecular sizes of nanoparticulate calcium phosphate vs pore sizes of MF/UF membranes is one we believe will be addressed by us and others in years to come. One can expect clouds of nanoparticulate (colloidal) calcium phosphate to form in a spectrum of particle sizes that are unstable in RO feedwater and concentrate due to continued growth through crystallization process if antiscalant actions are insufficient, and through aggregation with other colloidal sized particles through surface interactions. The new research emphasis these days on nanotechnology has brought a host of methods to bear on measurements, characterization and process control. Measurement of pore size distributions and characteristics on MF/UF membranes presents another applied research frontier. Eventual full control of colloidal fouling of both MF/UF and RO membranes awaits advancement in the mentioned research fields.

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