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Crossflow Microfiltration-Fouling Mechanisms Studies

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Abstract

Our objective has been to improve the commercial potential of a crossflow microfiltration process with lime softening of surface waters rich in humic and fulvic acids. These components complicate the filtration of $CaCO_3$ solids both in the filter cake layer and through direct interactions with the nylon membrane support surface. We characterized the humic/fulvic acid fouling and developed several strategies for alleviating the problem. Physical cleaning methods like crossflow and backflush alone are ineffective. We devised chemical pretreatment and chemical cleaning procedures which improve performance.

INTRODUCTION

A municipal water treatment plant used a crossflow microfiltration process to treat a hard surface water feed. The process used was lime-softening followed by crossflow microfiltration through tubular nylon-11 membranes to remove solids. The plant experienced excessive down time for chemical cleaning to reverse fouling. The response to chemical cleaning was not consistent, and the lifetime of the membrane was diminished through degradation by cleaning chemicals. We have elucidated the mechanisms for fouling and developed procedures for improving performance.

The commercial potential of membrane processes is often a strong function of fouling resistance and/or the ease with which fouling can be reversed through cleaning strategies. Membranes which work well in the laboratory with idealized feeds can fail in the field when ppm levels of unanticipated contaminants build up in the system and interact significantly with the polymer surface.

Surface waters from creeks and small rivers contain ppm levels of humic/fulvic acids. These water-soluble polymeric/colloidal organic materials complicate the filtration. These complications arise from differences in both size and chemistry between the organic and inorganic solids in the suspension/slurry.

EXPERIMENTAL

General

Metals determinations were made by atomic absorption spectrophotometry using a Perkin-Elmer Model 2380 instrument. The concentration of humic acid was estimated by measuring the absorbance at 320 nm ($\varepsilon = 0.0185\ \mathrm{L \cdot mg^{-1} cm^{-1}}$) using a Perkin-Elmer Model 552 spectrophotometer. These measurements were supplemented by total organic carbon determination by Rexnord, Inc. Zeta potentials were measured using a Model 1628 Zeta-Meter, and particle sizes were obtained by light scattering using either a Model 7991 or 7995 Leeds & Northrup Microtrac Analyzer. Unless otherwise stated, the porous tubes were nylon-11 tubes. The porosity of these tubes was determined by mercury intrusion using a Micromeritics Autopore 9200. Ozone was generated using a Welsbach ozone generator. Most experiments were made using an organic-rich standard solution (ORSS) containing 10 mg/L humic acid and 0.2 mg/L Magnifloc 990N. The humic acid (sodium salt) was purchased from Aldrich Chemical Co. (lot 1204 PE). No effort was made to remove the fulvic acid contaminant in this material. Magnifloc flocculants were obtained from American Cyanamid.

Filter Time Measurements

A nylon-66 0.45 μm filter (Rainin Instrument Co.) was clamped in a Millipore filter holder, and the time required to filter with suction 200 mL distilled water or treated solution was measured.

Isotherms

A standard solution of humic acid was adjusted to the desired pH, and 20 mL of this solution was placed in each of six 30 mL screw cap vials. To each of these was added a weighed small piece of nylon-11 porous tube (weight range 24.3 to 234.7 mg). These vials were allowed to stand at room temperature for 85 h. Samples were then removed from each vial and the absorbance at 320 nm was measured. Solution pH values were also obtained, and they showed no change from the original values.

Nylon Tube Dissolution

Nylon tubes were cut into 3 cm lengths and soaked in 100 mL of various cleaning solutions for 2 d with continuous agitation. The tube samples then were rinsed with distilled water and air dried. Five solutions of each sample were made at different concentrations in *m*-cresol, and the viscosity of each was measured using a Brookfield Model HATDCP viscometer. Intrinsic viscosities for each sample were obtained from the least-squares intercept of a plot of $\ln(\eta/\eta_0)/C$ vs C, where η and η_0 are the viscosities of the solution and solvent, respectively, and C is the nylon concentration.

Crossflow Filtration

Crossflow filtration performance was evaluated using 30 cm sections of porous tubing. The suspension to be filtered was pumped through the tube at 3.8×10^{-6} m^3/s (N_{re} = ~6000) and the filtrate flux was regulated at 4.7×10^{-4} m/s. Fresh feed was added to maintain volume in the recycle loop. A typical run was for 18 min with backflush every 6 min. Performance was monitored by measuring the trans-membrane pressure drop.

RESULTS AND DISCUSSION

Crossflow filtration involves pumping the suspension to be filtered parallel to the filtration barrier. This high velocity flow across the surface erodes the entrapped solids layer as it forms, minimizing resistance to filtrate flow. Operating in this mode allows for continuous filtration with high flux rates and a low pressure drop. In addition to crossflow, periodic backflush serves to disrupt the cake layer and help maintain flux rates. Figure 1 shows our process flow scheme.

Our filtration barrier is porous nylon-11 tubing (8 mm o.d., 6 mm i.d.). The tubes are 60–70% porous with a narrow, isotropic pore size distribution centered at 2 μm. For well-behaved systems, we can produce high quality filtrate at 4.7×10^{-4} m/s (1000 GFD) with a trans-membrane pressure drop of only 20 to 35 kPa. When the membrane fouls, this pressure drop increases dramatically and eventually the flux cannot be maintained at the desired level.

The solids to be filtered in this application are generated by lime softening. $Ca(OH)_2$ is added to the feed water to precipitate divalent cations by the following general reaction:

$$Ca(OH)_2(s) + Ca(HCO_3)_2(aq) \rightarrow 2CaCO_3(s) + 2H_2O(l) \qquad (1)$$

The size distribution of particles to be filtered will depend on the kinetics of nucleation and growth of $CaCO_3$ solids in the reactor. At optimal water softening pH (10.2), we find the average particle size is

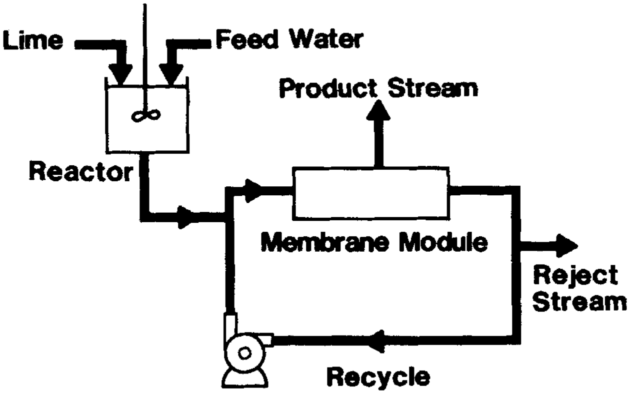

FIG. 1. Flow diagram of the crossflow microfiltration process

approximately 25 μm with very few solids small enough to create pore plugging problems (<2 μm).

Under these conditions the mechanism for filtration is particle entrapment at the membrane surface. For smaller size distributions, some particles can intrude into the membrane which then acts as a depth filter. However, even in this case we find that most of the separation is still accomplished at the surface. The thin solids layer or dynamic membrane which forms at the surface is sufficient to capture most solids which are smaller than 2 μm.

We identified humic/fulvic acids as the principal dynamic membrane foulants. These components are concentrated in the dynamic membrane and play an important role in the deterioration of process performance. They pack into the solids layer, substantially decreasing permeability. Furthermore, they adhere to the nylon-11 surface, diminishing the efficiency of hydraulic cleaning procedures like crossflow and backflush. During acid cleaning, this adhesion is even more pronounced.

Humic and fulvic acids are naturally occurring organic polymers which normally comprise one-third to one-half (*1–4*) of the dissolved organic carbon in natural waters. Presumed to be products from the biological decay of plants, these darkly colored materials are highly soluble in water. They differ only in that humic acid is sparingly soluble in aqueous acid, while fulvic acid is soluble. Structurally, humic acid is a polymer (*1*) of molecular weight 20,000–50,000, which is both highly unsaturated (C/H 10–17) and highly oxygenated (30–48%). Titration and degradation studies (*4*) have shown that the principal functional groups in these acids are alcohols (including phenols), ethers, quinones, and aromatic carboxylic acids with smaller amounts of amino acids and carbohydrates. This dense functionalization is responsible for the high chelation ability of this material (base exchange capacity (*1*), 4–6 meq/g).

PROCESS FOULING MECHANISMS

Figure 2 shows performance curves for two filtration runs of suspensions with differing pH. The suspensions differ only in the amount of $Ca(OH)_2$ added. At high pH (11.5), the trans-membrane pressure drop is on-scale and backflush every 6 min is very effective in restoring this pressure to the starting value. At lower pH (10.8), the pressure drop rises precipitously until it is offscale at about 4 min. With this run the backflush is ineffective; there is no restoration of low trans-membrane pressure. We have seen repeatedly that this small change in pH is sufficient to make a large difference in process performance.

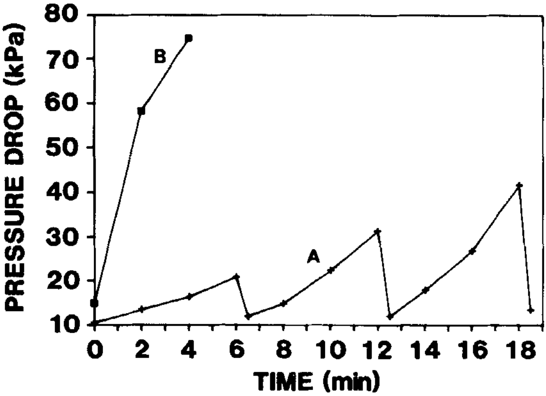

FIG. 2. Pressure drop across filtration tube during a run (backflushed every 6 min). (A) Run at pH 11.5 (B) Run at pH 10.8

Other evidence suggests that this sensitivity to pH is due to the way in which humic acid responds to pH. Figure 3 is a plot of UV absorbance (320 nm) vs pH for our organic-rich standard solution (ORSS). At extremes of pH, both low and high, we see evidence of brown precipitate and a corresponding decrease in absorbance, suggesting that the humic acid drops out of solution. At intermediate pH, the humate salts remain soluble. We have used NaOH as well as $Ca(OH)_2$ to adjust pH and find that there is some counterion effect. The calcium system precipitates at

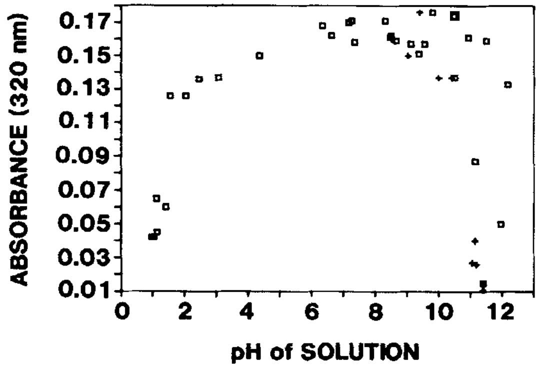

FIG. 3. Absorbance of ORSS as a function of pH. (□) pH adjusted with NaOH/HCl. (+) pH adjusted with CaO.

lower pH; this is probably a consequence of incorporation of the organic material with the forming $CaCO_3$ particles and/or formation of insoluble calcium-humate complexes. However, regardless of counterion, there is a sharp drop in absorbance in the same pH range where we observe a change in the process performance. It appears that good performance correlates with "precipitated" rather than soluble humate salts.

Figure 4, Curve A, shows the effect of pH on the zeta potential of the suspended solids. The inflection in this curve occurs in the same critical pH region as the deterioration in filtration performance. At low pH we have a significant negative potential which approaches zero as pH increases. Zeta potential is often a good indicator of stability in solid-liquid systems. Solids with zeta potential near zero experience less electrostatic repulsion and therefore tend to aggregate more easily, forming flocs which settle rapidly. With higher absolute zeta potential, particulates experience a substantial repulsion and cannot form aggregates.

Photographs (Fig. 5) of the interior surface of used tubes illustrate the fate of the organic material at different pH values. A brown film develops on the membrane surface when the process has been run at low pH. At high pH there is less evidence of dark material adhering to the membrane. Clearly, the solubility of humic material is pH sensitive, and this has a bearing on crossflow filtration performance.

Under our experimental conditions, the average size of $CaCO_3$ solids generated in the lime-softening reaction is generally larger than the 2-μm pore opening in the nylon porous tubes. As long as this is true, there will

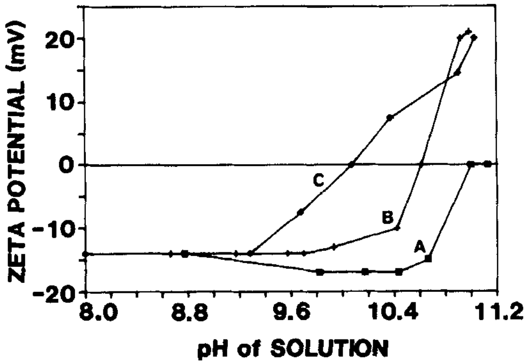

FIG. 4. Effect of pH on zeta potential. (A) ORSS treated with $Ca(OH)_2$ only. (B) ORSS treated with ozone, then $Ca(OH)_2$. (C) ORSS treated with $Ca(OH)_2$, then ozone. All ozonated solutions were treated for 5 min.

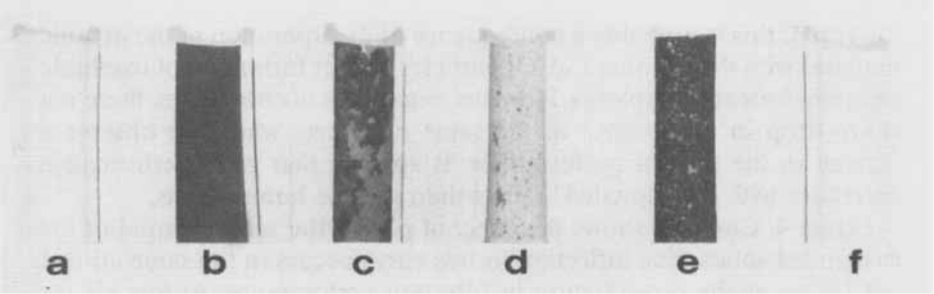

FIG. 5. Interiors of filtration tubes. (a) Unused tube. (b) Tube after filtration of ORSS/CaO mixture, pH 10.8. (c) pH 11.1. (d) pH 11.5. (e) Tube after cleaning with 0.1 *M* HCl. (f) Tube after filtration of ozone pretreated ORSS/CaO, pH 10.8.

be few processing difficulties caused by pore plugging. We have also identified conditions where the $CaCO_3$ size distribution shifts to smaller diameter, potentially fouling the porous substructure.

Figure 6 shows particle size distributions for solids generated with $Ca(OH)_2$ in ORSS. At high pH (~11.0) there is a significant increase in the number of particles which are small enough to plug the 2-μm pores. The process could deteriorate by a clogging of the nylon porous substructure. But, since we observed failure in the pH range where the inorganic particle size is increasing rather than decreasing, we conclude that fouling is more likely coupled to the fate of the humic acids.

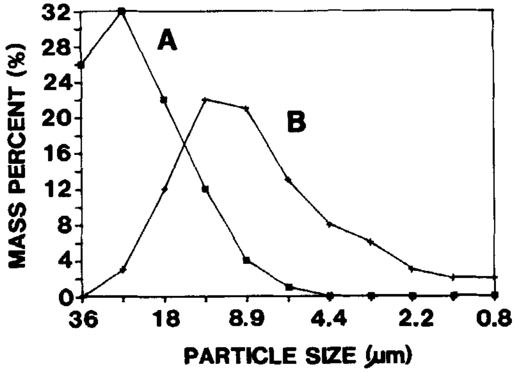

FIG. 6. Particle size profiles of calcium carbonate/ORSS mixtures. (A) pH 10. (B) pH 11.

Fouling during Tube Cleaning

Since progressive fouling of the porous nylon tubes occurs even under the best process conditions, it was necessary to clean the tubes periodically. The standard procedure was backflushing the module with pH 1 hydrochloric acid for a fixed period of time, supplemented when necessary with a prewashing rinse with 1% aqueous sodium hypochlorite solution.

Acid cleaning is highly effective in removing the inorganic portion of the dynamic membrane, which accounts for the majority of the solids by weight. Conversion of insoluble calcium carbonate and iron oxides to the chlorides (Eqs. 2 and 3), which are more water soluble, allows them to be flushed from the system. However, the acid cleaning does not remove the accumulated humates which were sorbed on these solids. Figure 5 shows that tubes fouled with humate-containing water, then cleaned with acid, retain the brown stain of the organic material.

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O \quad (2)$$

$$Fe(OH)_3 + 3HCl \rightarrow FeCl_3 + 3H_2O \quad (3)$$

$$M_n^{+x}Hum^{-xn} + xnHCl \rightarrow H_{xn}Hum + nMCl_x \quad (4)$$

where M is any cation.

Filtration experiments using nylon-66 filter disks confirmed these observations. When a disk was fouled with calcium carbonate/humate solids, then cleaned with acid, the flux through the disk increased briefly, then decreased to zero. Once the flux had been allowed to decrease, even reversing the flow through the disk could not restore the flux. The fouling was irreversible. The acid treatment resulted in the dissolution of 85% by weight of the solids, but the color of the filtrate was unchanged, indicating that little of the humic acids had been removed.

The residual humic acid fouls the tube by forming an impermeable skin attached to the tube. This skin was isolated by soaking a fouled acid-cleaned tube in *m*-cresol, which dissolved the nylon tube, leaving behind a semitransparent cylinder of dark brown material. We believe that surface interactions play a role in this skin formation. When a filter made of a lower surface energy (*5*) polymer like polyethylene (28 mJ/m^2) was used in place of nylon-11 (33 mJ/m^2), no skin formed because humic acid clumping occurred at the surface.

Humic acids, while highly soluble in neutral or basic solution, are much less soluble (*1*) in acid. Figure 3 shows the abrupt reduction in solution color in the pH 1-2 region. Most of this reduction in color is due to precipitation of the humic acids, though some may be from changes in extinction coefficients (*2*). Protonation of the various phenolate and carboxylate anions suppresses the surface charge and allows aggregation to occur. Acidification first frees the organic material sorbed on the inorganic particles which make up the dynamic membrane, then reprecipitates it in more concentrated form on the tube.

This new solid, formed by the reduction in pH, is less tractable. Allowed to stand, solutions which originally appear homogeneous form large fragile flocs. Concentration polarization normally leads to an increase in the effective concentrations of solids near a filter surface. Particle size measurements of the concentrated acidic solutions show that the solids are highly polydisperse, with sizes ranging from at least 36 μm to less than 0.5 μm. This observation is confirmed by centrifugation of the solution at 2300 rpm, which is expected to remove solids > 2 μm. Essentially all solids were removed from solution.

The cohesive interactions responsible for flocculation are accompanied by adhesive interactions with the tube material. Figure 7 shows the results of an isotherm sorption experiment at pH 2.0. The affinity of the humic acid for nylon-11 resulted in removal of the former from solution even under nonfiltration conditions. We reason that hydrogen bonding between the amide linkages in the nylon and the phenols and carboxylic acids in the humic acid is sufficient to promote sorption in this low pH region. Similar experiments at higher pH showed no sorption.

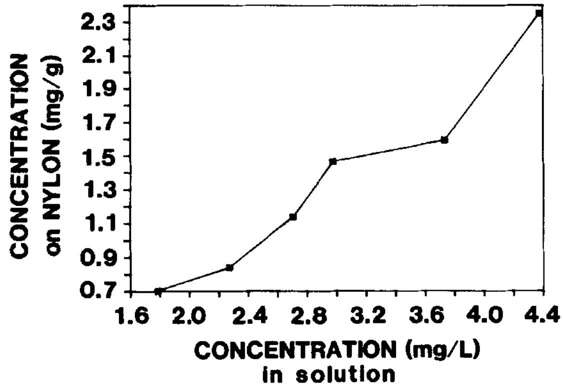

FIG. 7. Isotherm for sorption of humic acid on nylon tubes at pH 2.0.

Treating the humic acid fouled tubes with sodium hypochlorite before acid washing alleviates the fouling problem. This treatment allowed the subsequent acid wash to effectively remove the remaining solids, and restored good filtration. When cleaned with hypochlorite alone, the color of both the tube and the cleaning solution decreased but filtration performance was not restored. The calcium carbonate solids are not soluble in this solution and remained on the tube.

Cleaning with hypochlorite proved, however, to be an unworkable solution. Tubes cleaned with this reagent soon became brittle and cracked. Experiments showed that the burst strength of nylon tubes is decreased by hypochlorite. We also observed reductions in the intrinsic viscosity of cresol solutions of the nylon from treated tubes, indicating that molecular weight changes had occurred in the nylon. These changes were aggravated if the hypochlorite solutions used were acidic, but changes occurred even under basic conditions. We devised cleaning methods using surfactants. Dilute solutions of any of a number of surfactants solubilized the humic acid.

Pretreatment of Feed Water Alleviates Fouling

The most effective way to extend the period between chemical cleanings was to pretreat the feed waters. Two strategies resulted in good filtration performance and slow foulant build-up: oxidative treatment and addition of coagulants or flocculants.

Oxidative treatment. Oxidative purification of the feed water is best carried out with ozone. In trials in which the water was treated with increasing doses of sodium hypochlorite, hydrogen peroxide, chlorine dioxide, or ozone, only ozone changed the filterability of our standard humate solution at reasonable dosages. Ozone is the most powerful of these oxidants with a reduction potential of 1.24 V under alkaline conditions (*6*). Previous investigations have shown that humates are relatively impervious to oxidation (*7*) and react even with ozone reluctantly.

We found that reaction of lime-treated humic acid solutions with ozone led to improved filtration (Table 1), but that a deterioration in filtration time was noted when no solids were formed. When the humate solution had been treated with lime, performance improved and rapidly reached a plateau after a consumption of 1-2 mg ozone/mg humic acid. This level of ozone is insufficient to completely oxidize the organic material (as evidenced by monitoring UV absorbance at 320 nm), but previously has been noted (*8*) as being sufficient to cause some reduction

TABLE 1
Effect of Ozone Treatment Time on Filtration

Treatment time (s)	Filter time ratio[a]	Zeta potential (mV)
0	7.1	−18
20	2.7	−16
30	1.9	−14
40	2.0	−16
60	1.4	−11
120	1.6	−5
180	1.5	0
300	1.6	0
600	1.4	7

[a] $\text{Filter time ratio} = \dfrac{\text{time to filter treated solution}}{\text{time to filter distilled } H_2O}.$

in molecular weight. The improvement must therefore be due to an alteration of the properties of the filtered solid particles.

Zeta potential measurements allow some perspective on the mechanism of this improvement. Figure 4, Curves B and C, shows the relationship between zeta potential and pH as a function of ozone treatment and treatment order. Ozonation of the humate solution results in a decrease in the pH at which the curve breaks toward zero surface charge, and thus the pH at which easy filtration will be observed. The effect of treatment order may be that when lime treatment precedes ozonation, only the humates sorbed on the surfaces of lime particles need to be oxidized. One major ozone-sensitive functionality in the humic acid structure is the phenol, and since ozonation will replace (*9*) this group with a carboxylic acid having a lower pK_a, we interpret this shift in zeta potential curves to be due to an alteration in the titration curve.

Treatment with ozone also caused a decrease in particle size (Fig. 8). This effect is counterintuitive with respect to the zeta potential measurements since lower zeta potentials ought to lead to greater aggregation. The smaller, more hydrophilic humic acid polymer chains may be less able to adhere to the growing carbonate particles during the lime-softening step, thus decreasing their size. Alternatively, the more numerous smaller polymer moieties may increase the number of nucleation sites available when the carbonate particles begin to grow.

Treatment with coagulants and flocculants. We investigated two types of chemical treatment to promote floc formation, cationic polymers, and ferric sulfate. Table 2 shows the response of our suspensions to treat-

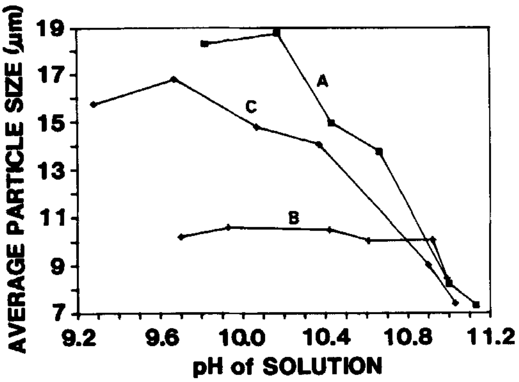

FIG. 8. Effect of ozone on particle size. (A) ORSS treated with $Ca(OH)_2$. (B) ORSS treated with ozone, then $Ca(OH)_2$. (C) ORSS treated with $Ca(OH)_2$, then ozone.

ments with cationic polymers. Magnifloc 572C, 573C, and 587C are polyquaternary amines and differ from each other only in molecular weight (572C < 573C < 587C). ORSS at pH 11.3 exhibits a low zeta potential (0 to +5 mV) and filters well relative to the sample with pH 10.3, which exhibits a large negative zeta potential (−15 to −20 mV). Addition

TABLE 2
Filter Time Ratio[a] and Zeta Potential for Lime-Treated ORSS with Cationic Flocculants

Flocculant	Flocculant concentrations (ppm)	pH = 10.3		pH = 11.3	
		Filter time ratio	Zeta potential (mV)	Filter time ratio	Zeta potential (mV)
572C	0	8.0	−15	2.5	+5
572C	12.5	1.5	+6	2.7	+13
572C	37.5	1.7	+10	3.8	—
572C	62.5	2.2	+10	2.8	+22
573C	0	5.9	−19	2.4	+0
573C	12.5	1.9	+10	2.1	+20
573C	37.5	9.3	+18	2.7	—
573C	62.5	6.9	+22	2.9	+25
589C	0	6.3	−20	2.2	0
589C	12.5	2.0	+6	1.9	+21
589C	37.5	7.1	+23	2.6	+28
589C	62.5	7.0	+26	3.2	+33

[a] Defined in Table 1.

of cationic polymer in the low pH case neutralizes the negative charge, promoting flocculation and improving filtration. Further addition of polymer increases the colloidal surface charge past zero to high positive values, decreasing the tendency to flocculate and inhibiting filtration.

At higher pH, the beneficial effect of cationic polymer is not so evident. In this case the surface charge is already nearly neutral and the system tends to flocculate even without the extra component. Addition of the polymer causes the surface charge to rise, interfering with flocculation and efficient filtration.

Table 3 shows results from a series of experiments testing the effect of $Fe_2(SO_4)_3$ in lime-treated ORSS at pH ~10.3 and 11. The independent variables are amount of $Fe_2(SO_4)_3$, amount of $Ca(OH)_2$, and order of addition. Either $Ca(OH)_2$ or $Fe_2(SO_4)_3$ was added to ORSS, and the resulting suspension was stirred for 20 min. The other component was then added, and stirring was continued for an additional 20 min. Then we determined filter time ratios, particle size distributions, and zeta potentials.

The zeta potential approaches zero as the pH increases, while average particle size decreases with increasing pH. There is a clear improvement in filtration performance with $Fe_2(SO_4)_3$ addition. This effect is more pronounced at lower pH than at higher pH. There appears to be a good correlation between zeta potential and filter time ratio.

TABLE 3

ORSS Treated with Lime and Ferric Sulfate: Effect on Filter Time Ratio,[a] Zeta Potential, and Average Particle Size

pH	Ferric sulfate (ppm)	Order of addition	Filter time ratio	Zeta potential (mV)	Average particle size (μm)
10.3	10	Ca 1st	1.2	−5	13.3
10.3	5	Ca 1st	1.1	−12	19.9
10.3	10	Ca 2nd	1.0	0	11.7
10.2	5	Ca 2nd	1.4	−14	16.9
10.3	0	Ca only	14.4	−14	23.5
11.0	10	Ca 1st	1.7	+9	10.7
11.0	5	Ca 1st	1.7	0	8.7
11.1	10	Ca 2nd	1.5	+6	7.8
11.1	5	Ca 2nd	1.9	0	8.9
11.0	0	Ca only	1.9	0	9.6

[a] Defined in Table 1.

Systems which aggregate readily should settle rapidly. Figure 9 shows settling behavior for several systems. Here, we report the position of the interface between turbid and transparent regions of the fluid as solids settle in a graduated cylinder. For ORSS at pH = 11.4 (zeta potential (z.p.) ≅ 0), this process is very slow. At pH = 10.2 (z.p. ≅ −15 mV), the solids settle at a moderate rate with no clear interface. At pH = 10.3 with 10 ppm of $Fe_2(SO_4)_3$ (z.p. = 0), the system settles very rapidly. Thus, zeta potential is not a reliable predictor of settling behavior.

In a crossflow filtration, zeta potential again is not a good predictor of performance. Figure 10 shows the results of several runs from the crossflow test unit with stainless steel tubes (2 μm pores). We used stainless steel tubes to avoid effects associated with the use of nylon. In Fig. 10 we see three runs at essentially the same pH (Curves A, B, and C) with very different responses. Curves A and B are both examples of poor performance. The pressure drop increases quickly and is not restored by backflush. The treatment for Curve A was simply lime. The treatment for curve B was lime and 12.5 ppm of cationic polymer (572C). Thus, the polymer was effective in improving a dead-end filtration, but had very little impact during the crossflow experiment. Curve C shows the effect of $Fe_2(SO_4)_3$ treatment at the same pH. This run is a dramatic improvement over Curves A and B. Curve D represents a run with lime only, but at higher pH.

Curves B, C, and D represent three systems, all with zeta potential near zero but having a wide variation in processibility during crossflow

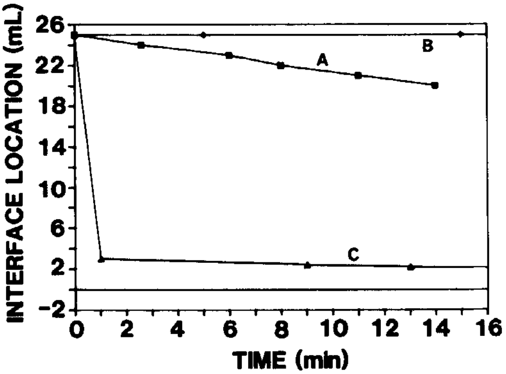

FIG. 9. Sedimentation rates of ORSS solutions. (A) ORSS treated with $Ca(OH)_2$, pH 10.2. (B) ORSS treated with $Ca(OH)_2$, pH 11.4. (C) ORSS treated with $Ca(OH)_2$ and $Fe_2(SO_4)_3$, pH 10.3.

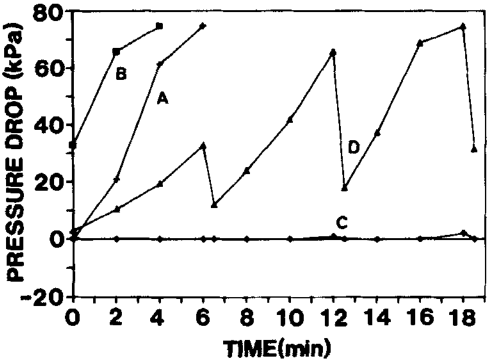

FIG. 10. Pressure drop across filtration tube during a run (backflush every 6 min). (A) ORSS treated with CaO, pH 10.1. (B) ORSS treated with Magnifloc 572C and CaO, pH 10.2. (C) ORSS treated with $Fe_2(SO_4)_3$ and CaO, pH 10.2. (D) ORSS treated with $Ca(OH)_2$, pH 11.1.

filtration. This is probably due, in part, to variations in floc stability under shear. It is a rule of thumb in filtration processes that flocculated systems are more readily separated than systems of independent particles. When concentrated at a surface, preflocculated solids pack in a more irregular fashion, thus creating extra voids and ultimately a more permeable filter cake. In contrast to quiescent systems in which the presence or absence of flocs is an important issue, in our high shear, crossflow environment, floc formation is not easily accomplished. Furthermore, once formed, flocs are unlikely to be stable structures. The forces which bind these aggregates are relatively weak. Too much turbulence during treatment with flocculating chemicals is known to be deleterious (*10*).

We promoted floc formation by the addition of cationic polymers and ferric sulfate. Polymers are believed to facilitate aggregate growth by a bridging mechanism. The opposite charge causes the polymer to complex with a particle. The high molecular weight allows this molecule to extend into the fluid and capture more than one particle, thus creating flocs. These links can be tenuous. If an aggregate is destroyed, the polymer can wrap around one particle irreversibly and lose its effectiveness as a flocculant, sometimes restabilizing the suspension.

Ferric sulfate works as a coagulant, neutralizing the charged surface. When charge is neutralized, aggregation can take place by van der Waals interactions. This type of floc is also unstable to shear, but the process is more likely to be reversible. Broken aggregates can reform in low energy regions of a turbulent system.

CONCLUSIONS

We have found several mechanisms by which deterioration can occur in a process to treat a hard surface water feed using lime softening followed by crossflow microfiltration. Some mechanisms operate during the filtration and reflect characteristics of the dynamic membrane of solids. Other mechanisms operate during cleaning of the tubes and reflect either irreversible fouling of the nylon tubes by an impermeable skin of organic material or degradation of the porous tubes.

An ideal filter cake contains a monodisperse system of particles, which tend to flocculate and form a loose, very porous solids matrix. Humic acids in surface waters are small colloids (<1 μm). The $CaCO_3$ solids formed during water softening can be much larger (5–30 μm). At optimal lime softening pH ($\sim$10.2), this system consists of large inorganic particles and small organic particles, which do not flocculate due to their common surface change.

There are several strategies for improving performance. Increasing pH precipitates humic material and promotes flocculation. Adding an agent like $Fe_2(SO_4)_3$ also promotes flocculation. Oxidation with ozone degrades humic acid and influences its characteristic charge in such a way as to promote flocculation. Whatever the treatment, a good dynamic membrane develops when the colloidal organic material is incorporated into or onto larger particles and the bimodal character of the size distribution is destroyed.

Successful membrane cleaning relies on preventing precipitation of humic acid solids while the solids on which they are sorbed are dissolved. Either oxidation or addition of a surfactant can accomplish this. However, choice of the appropriate cleaning strategy must include consideration of the stability of the filter to the cleaning agent.

In general, membranes are prone to fouling. These studies have shown that fouling occurs by a variety of mechanisms. Therefore, careful analysis of the interactions between all feed components and the membrane surface is an essential step prior to the implementation of a membrane process.

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