

REMOVAL OF IRON AND MANGANESE FROM WATER WITH A HIGH ORGANIC CARBON LOADING. PART II: THE EFFECT OF VARIOUS ADSORBENTS AND NANOFILTRATION MEMBRANES

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Abstract. This paper describes the second part of an investigation into the removal of iron and manganese from water with a high dissolved organic carbon (DOC) loading. This investigation focused on the use of ferrichloride as coagulant in conjunction with hydrogen peroxide as an oxidant and different physical treatment processes, such as adsorption and nanofiltration, to reduce dissolved iron and manganese in water with a high DOC loading. It was found that nanofiltration employing H₂O₂ is the only treatment capable of producing drinking water within the set requirements of the treatment facility. Both fly ash and powdered activated carbon (PAC) used as adsorbents yielded a low percentage removal of DOC, while all the treatment methods evaluated accomplished high removals of the metallic ions Fe(II) and Mn(II). From the results a staggered treatment approach is recommended to obtain the best results at the lowest cost.

Keywords: dissolved organic carbon, fly ash, metal removal, nanofiltration, powdered activated carbon

1. Introduction

The first communique on this topic (Potgieter *et al.*, in press) outlines the process of water treatment at the plant when the water is withdrawn from the river. It has been found that it is difficult to remove Fe(II) and Mn(II) from water with a high DOC loading, especially when there are algal blooms present.

Stoebner and Rollag (1981) investigated the feasibility of using ozone (O₃) oxidation, followed by filtration, for the removal of iron (Fe) and manganese (Mn) and the removal of organic compounds from groundwater. It was found that Fe and Mn were almost totally oxidized in a very short time at a dosage of 4 mg/L O₃, and that Mn is apparently more difficult to oxidise than Fe. According to Mignot (1973), potassium permanganate (KMnO₄) or chlorine dioxide (ClO₂) gives equally good results, but requires longer contact times. The amount of organic compounds was also reduced significantly.

Tukkanen *et al.* (1994) conducted pilot scale experiments to evaluate the ability of ozonation, ozone/hydrogen peroxide (peroxone) treatment and nanofiltration to reduce levels of organic matter from purified and bank-filtered surface water rich in humic material. They found that ozonation and ozonation in conjunction with H_2O_2 removed 19 and 25% of the total organic content of the water, respectively.

Cipparone *et al.* (1997) found that the removal of organic carbon in a typical water source through ozonation alone generally increased with an increasing O_3 dosage. This correlates with the fact that chlorine (Cl_2) demand was directly related to the total organic carbon (TOC) concentration in the water, and therefore that any process that removes organic carbon from the water should decrease the Cl_2 demand. In an investigation conducted by Westerhoff *et al.* (1998), it was found that the reaction between natural organic materials (NOM) in water and O_3 depended on the source of the NOM and varied for the different fractions of the same NOM.

Van der Walt (1993) compared the effectiveness of peroxone as an oxidising agent with that of O_3 and H_2O_2 individually. In a sample of water spiked with phenol, it was found that oxidation by peroxone with a H_2O_2/O_3 ratio of 0.4 was more effective than normal ozonation at neutral and basic pH values (pH = 10), and that a lower O_3 dosage was required with peroxone than normal ozonation to achieve the same level of phenol destruction.

Theis and Singer (1974) investigated the oxidation of Fe(II) by oxygen (O_2) in the presence of dissolved organic species of humic origin and found that if large concentrations of organic matter were present, the complexation reaction with ferrous iron would compete with the oxidation reaction and slow it down significantly. Furthermore, the formation of the corresponding ferric complex with the organic matter would leave the resultant Fe(III) in an unstable state that could be reduced again by organic compounds. The fraction of ferrous iron complexed or oxidized depended on the pH, quantity and type of organic matter present.

The relationship between Fe(II) and DOC removal and type of oxidant used, is not a simple one. In various studies (Knocke *et al.*, 1992, 1994) it was found that the use of $KMnO_4$, hypochlorous acid (HOCl), ClO_2 and free Cl_2 were mostly ineffective in removing Fe(II) complexed by DOC, even at oxidant dosages much larger than the stoichiometric requirement for complete Fe(II) oxidation. Furthermore, in contrast to previous studies, it was found that the removal efficiency of Fe(II) decreased with an increase in the molecular weight of the DOC (Dennett *et al.*, 1996; Aguiar *et al.*, 1996). The type of DOC, contact time and the pH of the solution in which the treatments were attempted, were other factors that had a major influence on the Fe(II) removal efficiency. In the case of Mn, it was found that it was necessary to raise the pH to speed up the rate of oxidation (Van Duuren, 1997).

From the discussion above, it seems that there might be advantages to first removing the DOC from the water before attempting to reduce the Fe(II) level. This may be accomplished by either precipitation with a cationic species, or by adsorption onto organic or inorganic solids, or by a combination of both. The

choice of coagulant for the removal of DOC and the Fe(II) complexed by it, will depend on a number of factors, such as the type and concentration of the DOC, pH and cost of coagulant. It can therefore be concluded that the best potential treatment for the solution of the problem will involve a combination of two or more processes.

This paper differs from most others in the literature that only investigated the use of coagulants and/or oxidants or nanofiltration, because it describes the results of the joint use of coagulants and an oxidant, coupled with physical processes such as adsorption/absorption onto various media and nanofiltration in an effort to remove Fe(II), Mn(II) and DOC from water from the Vaal River in South Africa. The rationale for using the specific choice of treatment, coagulant dosages and pH condition of the raw water grab samples, were given in the first paper of the series and will therefore not be repeated here.

2. Experimental Procedure

2.1. MATERIALS

Activated carbon is a well-known reagent for the removal of organic matter from water (Benefield *et al.*, 1982). It was therefore selected for this investigation to be used in conjunction with the coagulant ferrichloride (FeCl_3) and a polyelectrolyte coagulant aid S₃₈₃₅ (brand name). The raw water composition and the experimental procedures followed during this investigation have already been described in detail in the first paper on this investigation (Potgieter *et al.*, in press). The adsorbent was added during the slow stirring step and the solution was allowed to settle for 20 min before the supernatant was filtered and analysed. The fly ash used had a very low free lime content and did not affect the final pH of the treated samples.

2.2. INSTRUMENTAL ANALYSES

Both Fe and Mn were determined on a Unicam 939 AA, while DOC was measured on a Phoenix 8000 TOC analyzer. An indication of the NOM was obtained by measuring the UV absorption of each sample at 254 nm (UVA_{254}) on a Unicam 8625 UV-VIS spectrometer.

2.3. NANOFILTRATION EQUIPMENT

In the final instance three different nanofilter membranes were used to determine whether nanofiltration could be employed to remove the selected contaminants. Initially no pre-treatment was performed, then a coagulant FeCl_3 or an oxidant (H_2O_2) were used, and finally both together before filtering was done. A pressure of 19 bar was used throughout the nanofiltration process. The process was combined with filtration through Whatman No. 1 filter paper, in agreement with recommendations

TABLE I
Characteristics of the different nanofilter membranes used in this investigation

Membrane	Membrane type	Molecular mass cut-off (Da)	MgSO ₄ rejection (%)	Typical operating pressure (bar)	Maximum temperature (°C)	pH range	Flux (m ³ /m ² days)
NF 70 FilmTec™	Composite	200	95	5–20	50	3–9	3.2
NF 90 FilmTec™	Composite	200	95	5–20	25	3–9	2.6
D11 Membratex	Spiral wound	180	96	5–28	25	4–11	2.3

described in literature (Mulder, 1996). The characteristics of the different membranes used in this investigation are summarized in Table I. Samples were only run once through the different membranes, and no observations regarding fouling of the membranes, possible decreases in fluxes due to fouling or restoration of the fouled membranes were recorded.

3. Results and Discussion

The effectiveness of various physical treatment methods to remove the selected contaminants, namely Fe(II), Mn(II) and DOC, from the treated raw water, was investigated. Figure 1 schematically represents the results obtained when powdered activated carbon (PAC) was added in increasing dosages, in conjunction with varying FeCl₃ additions, in the presence of a constant concentration of coagulant aid to the water.

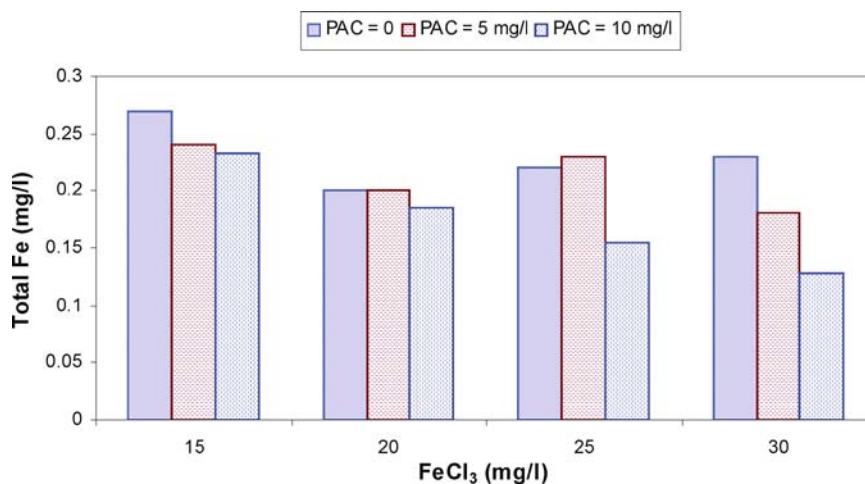


Figure 1. The effect of varying PAC additions on Fe removal in the presence of varying FeCl₃ coagulant concentrations and coagulant aid (S₃₈₃₅, 2 mg/L) (pH: 7.5–8.4).

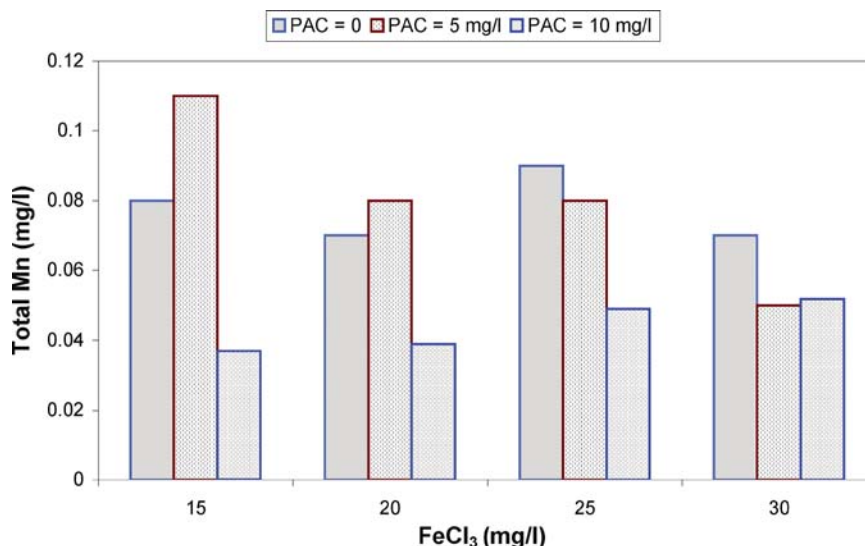


Figure 2. The effect of varying PAC additions on Mn removal in the presence of varying FeCl₃ coagulant concentrations and coagulant aid (S₃₈₃₅, 2 mg/L) (pH: 7.5–8.4).

Additions of FeCl₃ and S₃₈₃₅ alone did not result in any significant removal of the Fe(II). Neither did a further addition of 5 mg/L PAC improve the situation. However, when 10 mg/L of PAC was used in the treatment process, a steady decrease in the residual amount of Fe(II) was observed with increasing FeCl₃ dosages and approximately 50% of the original Fe(II) was eventually removed during the treatment process, using a FeCl₃ dosage of 30 mg/L. For Mn(II) removal the effective dosage of PAC required to increase the removal of the metal ion, was also 10 mg/L. The difference in effectiveness between 5 and 10 mg/L PAC dosages to remove Mn(II) at the maximum coagulant addition of 30 mg/L FeCl₃, was minimal (see Figure 2).

Figure 3 shows a substantial reduction in DOC levels of the treated samples once PAC was added. Although some DOC removal could be achieved by using only FeCl₃ and S₃₈₃₅, a significant reduction was only observed after the addition of PAC. There was not a great deal of difference between the effectiveness of the two PAC dosages in decreasing the levels of DOC and the 5 and 10 mg/L concentrations showed no significant difference in results obtained at all levels of FeCl₃.

The second absorbent used, was fly ash. The fly ash used originated as a waste product from a coal-fired power station nearby. It mainly comprised an alumina-silicate glass structure and had a low (<0.4%) free lime (CaO) content. The curves depicted in Figure 4 indicate that there is a decrease in the amount of Fe(II) remaining in the treated solution after an increased contact time with various dosages of fly ash used in conjunction with 30 mg/L of FeCl₃ and 2 mg/L of coagulant aid S₃₈₃₅ from an initial value of more than 0.5 mg/L. An increase in the amount of

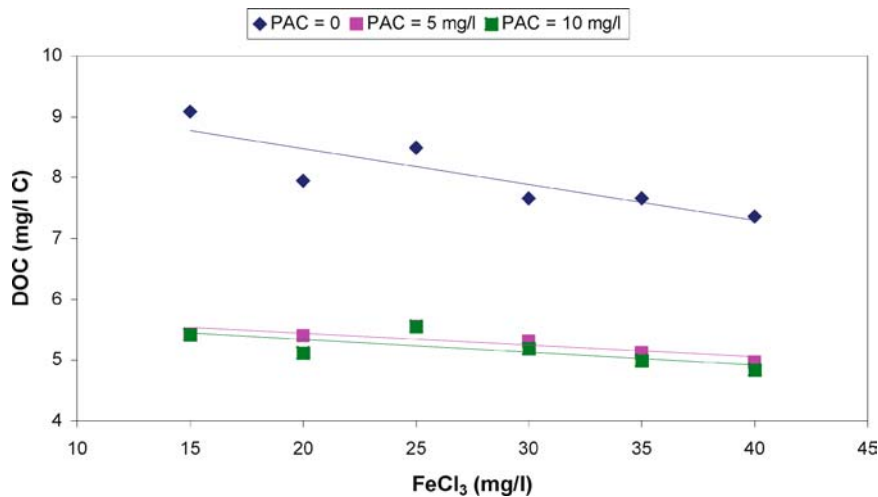


Figure 3. The effect of varying PAC additions on DOC removal in the presence of varying FeCl₃ coagulant concentrations and coagulant aid (S₃₈₃₅, 2 mg/L) (pH: 7.5–8.4).

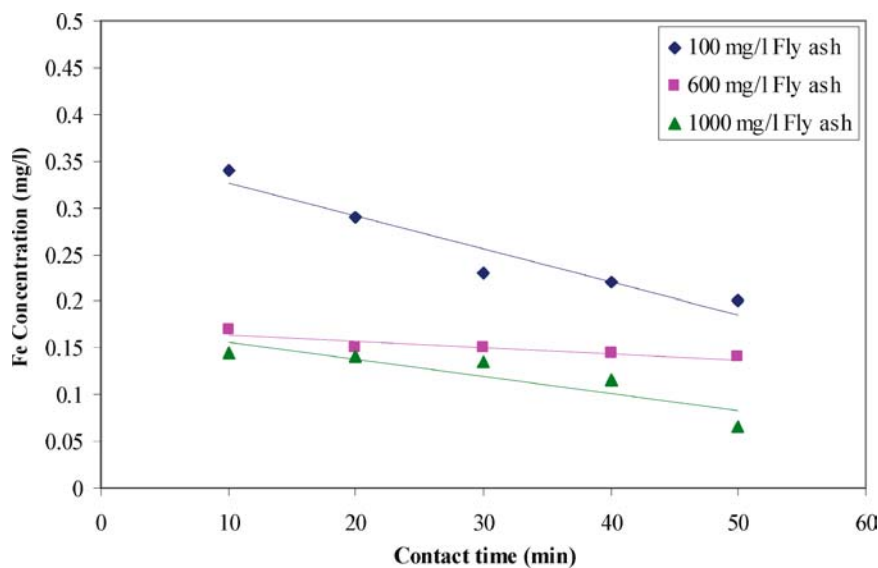


Figure 4. The effect of varying fly ash additions on Fe removal in the presence of 30 mg/L FeCl₃ coagulant and 2 mg/L coagulant aid S₃₈₃₅ (pH: 7.5–8.4).

fly ash used, results in a lowering of the amount of Fe(II) remaining in the final solution.

A similar pattern is observed in Figure 5, in which the removal of Mn(II) is graphically represented. The residual amount of Mn(II) decreases with an increase in contact time of the solution with the fly ash, and increasing the fly ash dosage

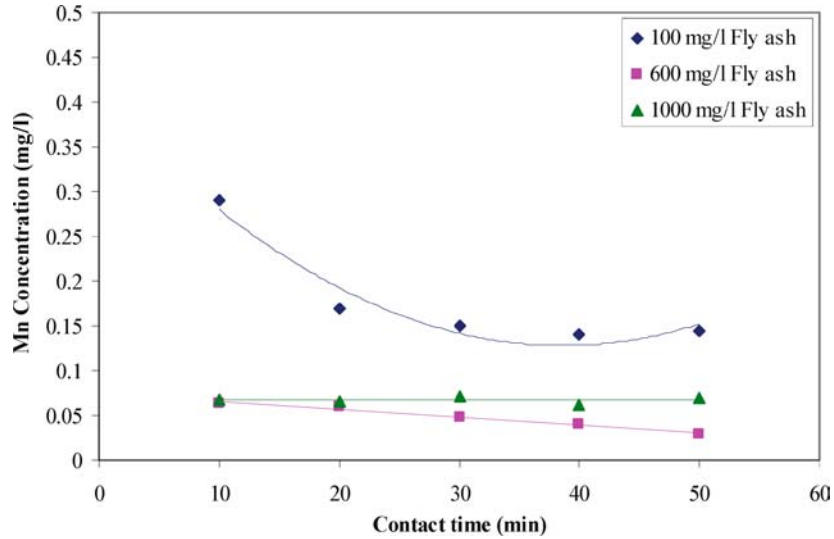


Figure 5. The effect of varying fly ash additions on Mn removal in the presence of 30 mg/L FeCl_3 coagulant and 2 mg/L coagulant aid S_{3835} (pH: 7.5–8.4).

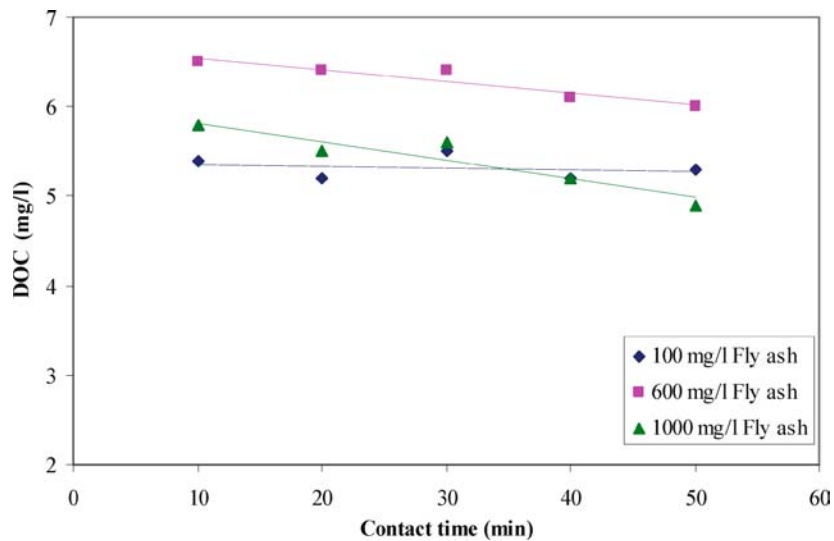


Figure 6. The effect of varying fly ash additions on DOC removal in the presence of 30 mg/L FeCl_3 coagulant and 2 mg/L coagulant aid S_{3835} (pH: 7.5–8.4).

increases the effectiveness of the treatment. The fly ash is even successful in lowering the DOC concentration, as can be seen from the results schematically represented in Figure 6. However, a fairly large dosage of fly ash is required to achieve this and the degree of reduction of this contaminant (DOC) is much less than in the case of both the Fe(II) and Mn(II) removal.

TABLE II
Contaminant concentrations after treatment by nanofiltration

Filter type	Treatment	Feed concentration of contaminants (mg/L)			Permeate concentration of contaminants (mg/L)		
		Fe(II)	Mn(II)	DOC	Fe(II)	Mn(II)	DOC
NF 70	None	2.96	0.29	8.3	0.21	0.10	2.4
	FeCl ₃	3.22	0.24	6.6	0.14	0.08	1.4
	H ₂ O ₂	2.71	0.15	6.4	0.07	0.05	2.2
	FeCl ₃ and H ₂ O ₂	3.52	0.17	5.6	0.13	0.12	3.9
NF 90	None	2.96	0.29	8.3	0.11	0.14	2.3
	FeCl ₃	3.22	0.24	6.6	0.11	0.09	4.1
	H ₂ O ₂	2.71	0.15	6.4	0.18	0.10	2.0
	FeCl ₃ and H ₂ O ₂	3.52	0.17	5.6	0.17	0.09	4.0
D 11	None	2.96	0.29	8.3	0.21	0.10	2.4
	FeCl ₃	3.22	0.24	6.6	0.10	0.07	1.6
	H ₂ O ₂	2.71	0.15	6.4	0.18	0.13	6.3
	FeCl ₃ and H ₂ O ₂	3.52	0.17	5.6	0.14	0.12	5.0
Recommended value in final water		–	–	–	0.10	0.05	10.0

The results obtained when using PAC and fly ash as adsorbents, confirm the deduction that can be made from the literature reports quoted in the introduction, namely that the removal of Fe(II) and Mn(II) will improve if the DOC is removed first, and justify the approach adopted in this investigation.

The results obtained with the various treatments and subsequent nanofiltration are summarized in Table II.

The results summarized in Table II indicate the following.

- i. That NF 70 gave the best Mn(II) removal of all three nanofilters evaluated.
- ii. That only NF 70 met the required treatment limits set for all three contaminants, provided that the feed water is pre-treated with H₂O₂. None of the other treatments or treatment combinations, nor the different nanofilter types, could meet all the requirements set.
- iii. In all the cases evaluated, the FeCl₃ used alone was fairly successful in causing a major decrease in the DOC concentration if it was followed by nanofiltration.
- iv. Neither the pre-treatment with H₂O₂ nor the combined H₂O₂ and FeCl₃ treatment, followed by nanofiltration with the D11 filter, was very successful in reducing the DOC concentration.
- v. The additional treatment of the raw water with FeCl₃, H₂O₂ and FeCl₃ and H₂O₂ was only effective in improving the removal of the selected contaminants when the NF 70 nanofilter was used. In the case of both the other filters these

TABLE III
Summary of contaminant removals with different treatment configurations

Methods	Treatment conditions	Lowest levels of contaminants obtained (mg/L)			Best % removal compared with initial concentration		
		Fe(II)	Mn(II)	DOC	Fe(II)	Mn(II)	DOC
PAC adsorption	30 mg/L FeCl ₃ /2 mg/L S ₃₈₃₅ /10 mg/L PAC	0.13	0.03		82	96	
	15 mg/L FeCl ₃ /2 mg/L S ₃₈₃₅ /5 mg/L PAC			5.1			43
Fly ash absorption	1000 mg/L FA/30 mg/L FeCl ₃ & S ₃₈₃₅	0.14			96		
	600 mg/L FA/30 mg/L FeCl ₃ & S ₃₈₃₅		0.06			71	
	1000 mg/L FA/30 mg/L FeCl ₃ & S ₃₈₃₅			4.9			30
Nanofiltration	NF 70/500 mg/L H ₂ O ₂	0.07	0.05		98	82	
	NF 70/15 mg/L FeCl ₃			1.4			83

further additions of treatment chemicals just seem to decrease the removal of contaminants compared to the untreated water filtered through the nanofilters.
vi. It seems that overall the NF 70 nanofilter delivered the most desirable and best performance.

The best performances and removals that could be achieved during this campaign with all three treatment configurations, are summarized in Table III.

4. Conclusions

From this phase of the investigation the following conclusions can be made.

- (1) Nanofiltration used in conjunction with H₂O₂ oxidation is the only treatment of the three evaluated that is capable of delivering water complying with the recommended limits set for all three contaminants (compare Table III, Potgieter *et al.*, in press). This is in agreement with results from the first part of the investigation and literature reports that no single treatment method alone is sufficient to yield water of the desired quality.
- (2) Both adsorption methods yielded a low percentage removal of DOC. However, provided that the DOC concentration in the raw water is not too high, it can render a treated solution with the DOC concentration below the required threshold value.
- (3) All three physical treatment methods accomplished high removals of the metallic ions Fe(II) and Mn(II).
- (4) Fly ash displayed a remarkable removal of all the contaminants when used in conjunction with a coagulant and coagulant aid.

- (5) Considering the costs of the various treatment options, it is recommended that fly ash together with FeCl_3 and the polyelectrolyte coagulant aid be used as a pre-treatment stage at the plant, and that nanofiltration just be employed as a final polishing step, should the concentrations of the three contaminants in question exceed the recommended values.

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