

PRACTICAL GUIDELINES FOR ENHANCED COAGULATION USING UV₂₅₄

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Abstract

The negative effects of natural organic matter (NOM) in drinking water are well known and, where necessary, its removal is crucial. This is enforced by the increasingly stringent water regulations around the world. In South Africa, this regulation targets NOM in the form of total organic carbon (TOC), at a maximum of 10 mg/L. Enhanced coagulation (EC), a multiple-objective chemical dosing strategy, offers a viable method of NOM removal, and this study explored its use for typical South African raw waters. A consistent and reproducible jar test procedure was developed and applied to 19 widely different raw water samples collected from different locations and at different times of a year-long period. These samples consisted of a wide range of alkalinity, UV₂₅₄ and turbidity values. Three criteria were developed and applied to determine the best EC dosage for the optimal removal of UV₂₅₄ without compromising residual dissolved organic carbon (DOC) and turbidity. DOC was measured, prior to and after batch tests, to confirm removal similarities with UV₂₅₄ and compliance with national standards. The resultant percentage removals of UV₂₅₄ and DOC ranged between 56 to 96 % and 45 to 94 % respectively, irrespective of water source, period and coagulation dosage. The settled water residual turbidity values were less than 1.5 NTU. The costs for EC were found to be comparable to those for conventional coagulation in all cases.

Key words: Enhanced coagulation (EC), UV₂₅₄, Natural Organic Matter (NOM) and Turbidity.

1 INTRODUCTION

The primary objective of potable water treatment is to produce water that is clear without microbiological and physiochemical components which may pose health hazards to consumers. During the water treatment process train, chemicals are added with the desire to kill pathogens and remove turbidity. Despite the fact that South Africa is one of the most developed countries in Africa, it displays a mixture of First and Third world features as far as the treatment of potable water is concerned. The situation in the large cities resembles that of the First world, with high specific water consumption patterns, and the water supply to these areas is treated to international standards. However, in many of the rural areas, the situation is typical of Third world countries. There are low financial and technical skill resources, hence the need to treat water to suitable standards at relatively low costs, without using treatment methods and instruments that require high capital and high degree of expertise for sustained operation (1).

Recently, the South African National Standards (SANS, 2011) have revised their drinking water quality standards (2). They introduced a new regulation that calls for the control of total organic carbon (TOC), a surrogate parameter for natural organic matter (NOM). This compelled South African water treatment plants to add NOM on their list of components to be removed from the water. Moreover, NOM should indeed be removed from drinking water, as it gives the water body a brown colour and offensive odour which compromises the aesthetical quality of the water. It is also known to be the cause of microbial re-growth in water distribution systems and affects the stability and removal of inorganic particles, increasing the cost of treatment (3). Furthermore, the presence of NOM is unfavorable in the water sector because it reacts with disinfectants to form disinfection by-products (DBPs) which have been connected to carcinogenic diseases (4).

All surface water contains an appreciable concentration of NOM. Typical water treatment plants in South Africa rely nearly completely on surface water sources, which are often compromised due to high return flows and indirect re-use. Considering the often poor performance of wastewater treatment plants and the ever-changing and compromised raw water sources, an affordable and reliable treatment technique with a clear protocol must be developed for the production of good potable water even at smaller water treatment plants.

The US Environmental Protection Agency recognized enhanced coagulation (EC), softening and granular activated carbon (GAC) as the best available methods to remove turbidity and NOM (5). Enhanced coagulation, in particular, can be applied at most water treatment plants without extra capital expenditure (6). EC generally removes effectively the humic and high molecular weight fractions of NOM (7). However, the removal efficiency of NOM by EC is not consistent over time even at the same sampling point, suggesting that the bulk water properties and character of the NOM changes temporally. The process requires higher dosages of inorganic coagulants and strict control of pH to attain a simultaneous removal of both particles and organic matter (8). The removal of these components in drinking water by EC is achieved through charge neutralization, complexation and sweep floc coagulation (9,10,11).

This study seasonally evaluated the efficacy of EC for the removal of NOM from typical source waters of South Africa. This was to provide South African water treatment plants, particularly small water treatment plants, with a standard laboratory jar test protocol to remove organic compounds to "near-maximal" without pH control to simulate plant operations. A reproducible procedure and systematic criteria for picking the optimal

coagulation dosage for the removal of UV_{254} was developed. This protocol was then applied to all collected source waters to evaluate its consistency and reliability in removing dissolved organic carbon (DOC), UV_{254} and turbidity, and finally evaluate the cost of EC in comparison to that of conventional coagulation. The literature on coagulation reports either alum or ferric chloride as reference coagulants. In South Africa, ferric chloride is more commonly used than alum. In this study, therefore, ferric chloride was used as the reference coagulant.

2 MATERIALS AND METHODS

2.1 Site selection and sample collection

A total of 19 samples were collected at different locations enabling the representation of five distinctively different raw water types from the perspective of NOM removal. These water types included (i) oligotrophic water, (ii) water emanating from warmer areas with high population densities, and a fairly high NOM load, (iii) coloured water from the south-western coast, very high in colour, humic and fulvic acid, (iv) eutrophic water from the highveld, with typically high NOM loads, and (v) treated sewage effluents, which dominate the NOM character in many streams and rivers in South Africa during periods of low flow. The collection was made over a year-long period representing four different seasons. The raw waters were collected into 25 L cans before any pre-treatment, transported to the lab as quickly as possible and were stored in the dark at 4 °C to reduce biological activity until testing. The characteristics of the raw water varied widely as shown in Table 1.

Table 1: Raw water quality parameters

Sample ID	pH	Temperature (°C)	Turbidity (NTU)	Conductivity (mS/cm)	Alkalinity (mg/L CaCO ₃)	Calcium (mg/L Ca ⁺⁺)	UV ₂₅₄ (m ⁻¹)	DOC (mg/L)	SUVA (L·m ⁻¹ ·mg ⁻¹)
S1	-	26.0	3.3	0.10	3	5	69.5	12.0	5.8
S2	6.9	13.5	7.5	0.27	16	14	14.4	7.1	2.0
S3	-	26.2	-	0.28	19	11	11.2	6.9	1.7
S4	-	15.6	29.7	0.34	18	13	15.6	8.4	1.8
S5	7.7	21.1	90.8	-	58	17	15.1	8.0	1.9
S6	8.3	10.9	84.3	0.18	47	16	32.3	9.3	3.5
S7	7.5	15.9	1.9	0.46	93	50	12.9	5.8	2.2
S8	8.8	22.9	3.6	0.42	99	43	13.7	7.0	1.9
S9	9.6	26.0	3.6	0.51	88	39	12.5	6.7	1.9
S10	7.6	19.4	3.3	0.52	92	43	14.4	9.2	1.6
S11	8.1	12.4	1.8	0.42	121	41	13.0	5.9	2.3
S12	9.5	21.3	6.4	0.43	136	44	16.5	9.6	1.7
S13	7.8	21.2	3.6	0.39	97	38	21.5	8.1	2.7
S14	8.2	16.2	35.7	0.68	131	28	12.0	6.2	2.0
S15	8.2	19.6	52.1	0.56	129	29	14.4	7.2	2.0
S16	-	27.1	-	0.55	107	34	16.1	8.0	2.1
S17	-	-	-	-	152	74	13.3	6.1	2.2
S18	8.6	23.7	18.1	0.62	136	75	15.8	7.5	2.1
S19	8.1	25.7	114.0	0.27	67	31	33.5	10.0	3.4

2.2 Analytical methods

The pH, temperature (°C) and conductivity (mS/cm) were measured using a HANNA HI 98130 combo water proof pH, EC/TDS and temperature meter. Turbidity, in nephelometric turbidity units (NTU), was measured using a HACH 2100 turbidity meter. NOM in raw and treated water samples was determined by measuring DOC using a TOC analyzer (Teledyne Tekmar, TOC fusion). It was also indirectly determined by measuring UV_{254} using an ULTROSPEC II: UV/Vis spectrophotometer (Model 80-2091-73, Biochrom, England) with a 1 cm cuvette cell. Prior to analysis, all samples were passed through non-sterile 33 mm MILLEX-HV MILLIPORE, 0.45 µm filter units and acidified with concentrated H₃PO₄ solution to a pH less than 2. Alkalinity (mg CaCO₃/L) and calcium

hardness (mg Ca/L) were determined using protocols 403 and 311 C, respectively, outlined in standard methods (12).

The SUVA gives an indication of the aromaticity of the NOM and also the amount of humic substances relative to non-humic substances of the water samples. It may also give an insight on the treatability of water by coagulation (13). The SUVA was expressed as a ratio of UV_{254} (m^{-1}) and DOC (mg/L) values as illustrated in the equation 1.

$$SUVA \left(\frac{L}{m \cdot mg} \right) = \frac{UV_{254} (m^{-1})}{DOC \left(\frac{mg}{L} \right)} \quad [1]$$

2.3 Jar and batch tests

Jar and batch tests were done as outlined by Dlamini et al (14).

3 RESULTS AND DISCUSSION

3.1 Removal of UV_{254} , DOC and turbidity

Simple analytical techniques, including the single wavelength UV_{254} measurement and colour (UV_{456}) are instrumental in monitoring the NOM content of water, and are widely accepted by water treatment operators as parameters to assess the performance of water treatment plants. The measurement of these parameters is quick, and enables easy characterization of samples, and the spectrophotometers for both laboratory and field instruments are widely available and affordable (15). UV_{254} measurements, in particular, provide a quick and precise indication of the organic carbon content of raw and treated water (16).

Generally, treated water UV_{254} of 2.3 to 3.3 m^{-1} correspond to treated water TOC or DOC of 1.5 to 2.0 mg/L respectively (11). Garcia and Moreno (17), also investigated the relationship between treated water DOC and UV_{254} and found a good correlation ($R^2 = 0.99$). Chow et al (18), found good correlations between DOC and UV_{254} for both raw and treated waters ($R^2 = 0.94$ and 0.92 respectively), indicating that the treated water UV_{254} could also be used to predict the treated water DOC.

Figure 1 a) shows the amount of residual UV_{254} after EC. Generally, all the residual UV_{254} values were lower than 6 m^{-1} . Most of the residual UV_{254} values in our tests, however, were higher than the 3.3 m^{-1} level that is achieved by full-scale water plants operating with optimum coagulation dosing and pH conditions for both particles (turbidity) and TOC (prior to chlorine or oxidant addition) in the United States, as shown by Edzwald and Kaminski (19). This could be because of the differences in the nature of the waters experienced by the two countries, the differences in the EC criteria employed and, perhaps, the fact that in this study the pH was not controlled (16). An extrapolation using literature findings predicts corresponding residual DOC values lower than about 3.5 mg/L in our tests.

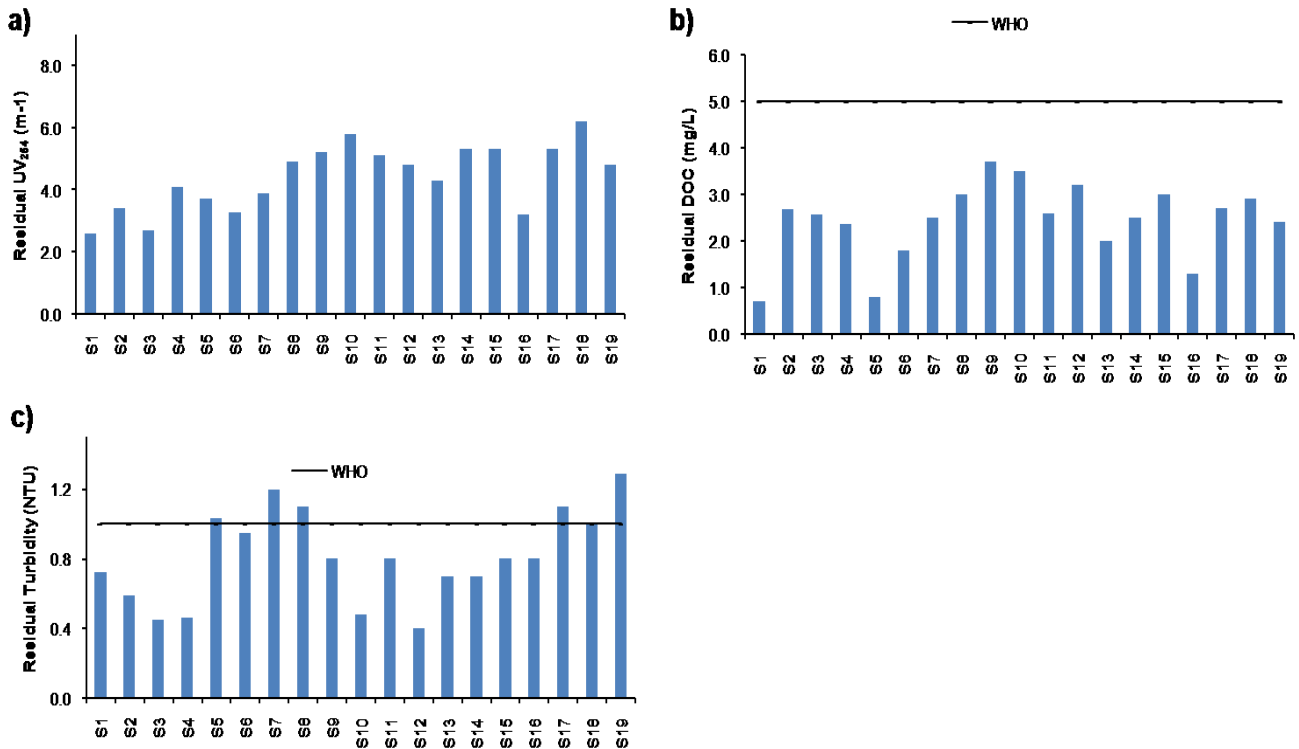


Figure 1: Residual amounts of parameters in comparison with WHO standards
 a) Residual UV₂₅₄ b) Residual DOC c) Residual NTU

South African water plants can achieve the WHO DOC limit of 5 mg/L and the high SANS 241 limit of 10 mg/L (2,20). As shown in Figure 1 b), the residual DOC values closely matched those from theoretical extrapolations, which were below 4 mg/L. Though the removal percentage of UV₂₅₄ was generally higher than that of DOC, the removal efficiencies were still comparable judging from the reasonably high correlation ($R^2 = 0.733$) as shown in Figure 2.

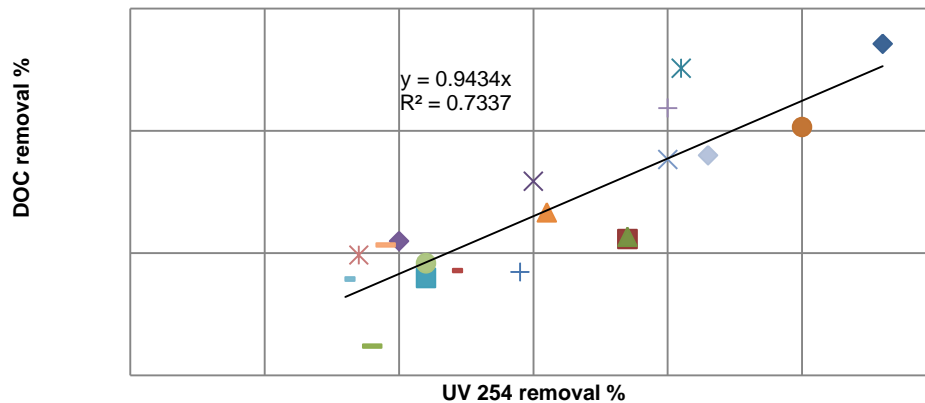


Figure 2: Correlation between DOC and UV₂₅₄ removal percentages

The coagulation experiments did not only remove UV₂₅₄ and DOC with appreciable percentages (up to 96 and 94 % respectively), they also exhibited high efficiencies for turbidity removal. Though there are optimum coagulation conditions for turbidity removal, these coagulation experiments which were optimized for UV₂₅₄ removal were also able to reduce the turbidity to values below 1.5 NTU as shown in Figure 1 c). For most samples, the turbidity was reduced to levels at or below the WHO (and SANS 241) limits. In the other samples with residual turbidity greater than 1.0 NTU, the values were still sufficiently low to be removed further by filtration units. Thus, simply meeting the performance criteria for EC may not be the only motivating factor if optimized coagulation for NOM (UV₂₅₄ and/or DOC) removal can still obtain low turbidity values.

3.2 Effectiveness of enhanced coagulation in the removal of NOM

Generally, the waters analyzed in this study had high NOM removal percentages as illustrated in Figure 2. The amenability of a sample to EC was measured by the ratio of the effectively removed amount of UV₂₅₄ and DOC per coagulant dose at the EC condition. Comparisons in the removal rates of the two parameters showed similar trends as shown in Figure 3 a). The product of the two ratios gave the removal rate of "NOM" (the combined removal rates of UV₂₅₄ and DOC) per coagulant dose at the EC condition. This ratio revealed that low-alkalinity waters (≈ 60 mg/L CaCO₃ just before EC) were more amenable to EC than high-alkalinity waters as shown in Figure 3 b). This means that 1 mg/L of ferric dose removed more NOM (of the effectively removed parameters) in the low-alkalinity than in the high-alkalinity waters, with S1 being the most amenable and S7 the least amenable. The EC conditions in this study were primarily a function of coagulant dosage without the control of pH to simulate plant conditions. Alkalinity was therefore the main parameter influencing amenability because it was by far the main parameter controlling coagulant dosage. This was in agreement with USEPA findings (21).

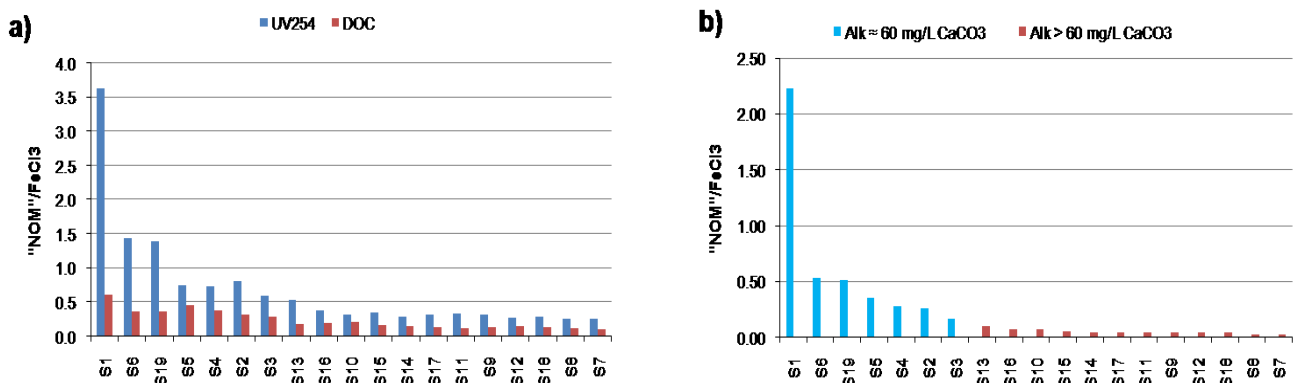


Figure 3: Amenability of samples for the removal of NOM using ferric chloride a) Removal ratio of UV₂₅₄/FeCl₃ and DOC/FeCl₃ b) Removal ratio of (UV₂₅₄×DOC)/FeCl₃².

3.3 Cost evaluation

The aim of this study was also to estimate the economic benefits of EC over conventional coagulation, with results presented for 19 samples. However, only the chemical costs for pre-treating 1 m³ of water to the required levels were evaluated, because of the hypothesis that water treatment plants will need to change only the dosing of the chemicals for EC. The chemicals included a base (Ca(OH)₂) for both raising the alkalinity in the low-alkalinity samples before EC and stabilizing the treated water, and a coagulant (FeCl₃·6H₂O).

The quotation for the chemicals' unit prices (without VAT) was made from a regular supplier in SA (Protea Chemicals (PTY) Ltd) on the 8th of November 2011, and is shown in Table 2.

Table 2: Unit Prices for Chemicals

Chemical	Price (ZAR/kg)
Calcium Hydroxide (Ca(OH) ₂)	ZAR2.51
Ferric Chloride (FeCl ₃ ·6H ₂ O)	ZAR5.16

In general, the chemical amount appeared to be equal to or a little more for enhanced coagulation as compared to conventional coagulation, which is in agreement with the general assumption as shown in Figure 4 a) and b). In some cases, though, mostly the high-alkalinity waters (i.e. S14, S15, S16 and S18), the amount of chemicals for EC were about twice that required for conventional coagulation. However, sample S11 showed a different trend since the amount of EC chemicals were about half that needed for conventional coagulation.

In all the cases, the cost of EC was less than ZAR0.17 more than conventional coagulation as illustrated in Figure 4 c) and d). The EC cost for the S11 sample was ZAR0.18 less than that of conventional coagulation. However, judging from the costs for treating 1 m³ of water presented in this manuscript, the average cost of EC was found to be ZAR0.22 ± 0.10, and ZAR0.16 ± 0.09 for conventional coagulation. For the EC amenable low-alkalinity samples, as illustrated in Figure 3 b), the cost for EC was ZAR0.19 ± 23 % relative standard deviation. This showed that EC does not really cost much as compared to conventional coagulation; hence, it could be employed as a cost-effective NOM removal strategy in the South African water industry.

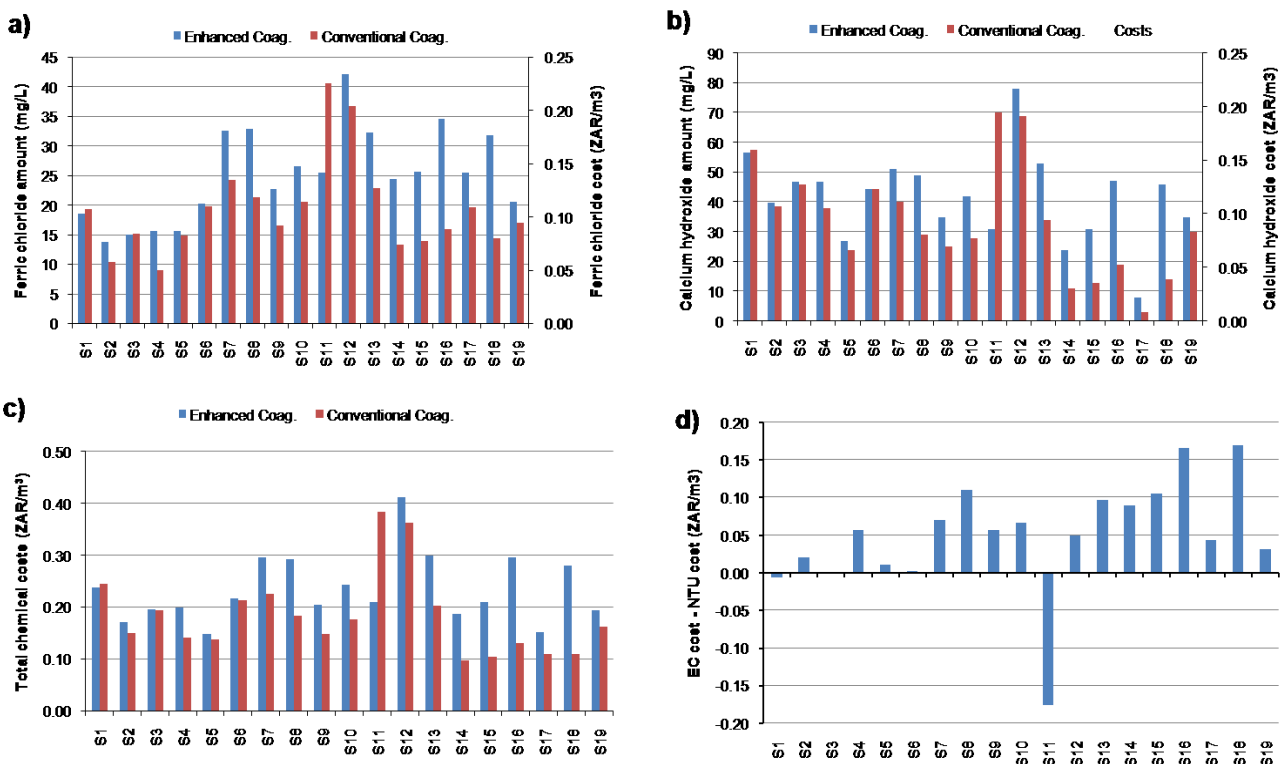


Figure 4: Evaluation of chemical costs for conventional and enhanced coagulation a) Cost of ferric chloride b) Cost of calcium hydroxide c) Cost of total chemicals used d) Difference in costs between conventional and enhanced coagulation.

4 CONCLUSIONS

The treatability of NOM, as UV_{254} , by the EC technique was evaluated using 19 different raw waters of South Africa collected over a year-long period. The use of UV-based EC gave similar trends in the removal of both UV_{254} and DOC. UV_{254} was reduced to levels below 6 m^{-1} and DOC was reduced to levels below the SANS (10 mg/L) and WHO (5 mg/L) levels. Moreover, turbidity was dropped to levels ($< 1.5\text{ NTU}$) low enough for removal by subsequent treatment steps in the water treatment train. It was also observed that the EC amenability of the samples decreased with increasing alkalinity. The costs of EC were found to be comparable to those for conventional coagulation. In some cases, the difference in costs was more imaginary than real. Generally, EC costed a little ($< 23\%$) more than conventional coagulation; hence, it could be employed as a cost-effective NOM removal strategy.

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