

IMPACT OF ALKALINITY ON THE REMOVAL OF NATURAL ORGANIC MATTER FROM RAW WATERS BY ENHANCED COAGULATION

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ABSTRACT

Natural organic matter (NOM) in all soils, ground and surface waters cause negative effects in potable water quality (undesired colour, taste, odour, and bacterial re-growth in distribution systems). Numerous studies have also found that the reaction of NOM with oxidative chemicals during drinking water treatment processes can result to the formation of carcinogenic disinfection by-products (DBPs). Many countries including South Africa, have therefore established regulations to control and minimise NOM and its effects. Enhanced coagulation (EC), a multiple-objective chemical dosing strategy, offers a viable option for NOM removal, and this study explores its use for typical South African raw waters. A consistent and reproducible jar test procedure, simulating the actual coagulation and flocculation pre-treatment steps, was developed and used to investigate the treatability of NOM (measured as UV 254 nm) in all the source waters. Ferric chloride was used as the coagulant due to its extensive application in South Africa. Raw water samples representing the various water types found in the country were seasonally collected for investigation, thus corresponding to a year-long data collection period. Since the removal of NOM is linked to strict control of pH, the coagulant dosage for the jar tests aimed at specific pHs (pH 7.0, 6.0, 5.5, 5.0 and 4.5) with the use of titration curves. The response parameters for the tests were temperature, turbidity, pH and UV 254 nm. Algorithms of finding the optimum dosage for both turbidity and UV 254 nm removal were developed from jar tests and consistently applied to subsequent batch tests. The results of the study suggested that low-alkalinity waters are more amenable to coagulation than high-alkalinity waters. The results also led to the conclusion that the alkalinity and pH of a water are key factors influencing coagulation performance. The optimum pH for the waters fell within the range of 5.0 to 6.5.

Key Words: Alkalinity, enhanced coagulation, natural organic matter (NOM) and UV 254 nm.

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 (Freese et al, 2001).

Recently, the South African National Standards (SANS, 2011) have revised their drinking water quality standards. 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 (Qin et al, 2005). Furthermore, the presence of NOM is unfavourable in the water sector because it reacts with disinfectants to form disinfection by products (DBPs) which have been connected to carcinogenic diseases (Rizzo et al, 2005).

It is hypothesised that NOM has characteristics that vary distinctively depending on their origins, including the degradation of plant and microbial residues, soil, wastewater and agricultural returns (Eikebrokk et al, 2004; Mamba et al, 2009). NOM in water contains a heterotrophic mixture of humic substances and non-humic substances, where the humic fraction is said to be more aromatic, less soluble and of higher molecular weight than the non-humic fraction (Garcia and Moreno, 2009).

The US Environmental Protection Agency recognised enhanced coagulation (EC)/softening and granular activated carbon (GAC) as the best available methods to remove turbidity and NOM (Sulaymon, 2008). Enhanced coagulation, in particular, can be applied at most water treatment plants without extra capital expenditure (Yan et al, 2009). The removal of NOM from raw waters by EC is dependent on a variety of water properties including pH, alkalinity, coagulant type and dosage, and the fractions and amount of NOM. Coagulation, in general, effectively removes the humic and high molecular weight fractions of NOM (Uyak et al, 2006). However, the removal efficiency of NOM by coagulation 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 (e.g. ferric chloride and alum) and strict control of pH to attain a simultaneous removal of both particles and organic matter (Yu et al, 2007). The removal of these components in drinking water by coagulation is achieved via four primary mechanisms, namely enmeshment, adsorption, charge neutralisation and complexation.

Previous trials in South Africa (SA) met with mixed success. In a study on coloured waters with high SUVA values (i.e. mostly the humic fractions) and low alkalinity from the south-western coast, coagulation was effective at removing NOM. Other trial studies in SA, where SUVA values are typically lower (i.e. mostly the non-humic fractions), NOM removal was not as effective. At Umgeni Water, there was appreciable reduction in TOC, DOC and colour but not for micro-pollutants, taste and odour (Freese et al, 2001). Unpublished tests on the Highveld indicated very poor NOM removal. Moreover, the required coagulant dosage varied widely, up to seven times higher than the dosage required for turbidity removal. The success of EC clearly depends on the nature of the NOM and water characteristics, which reinforces the need for its systematic evaluation on the full range of raw waters.

The literature on coagulation reports either aluminium sulphate (alum) or ferric chloride as reference coagulants. In South Africa, ferric chloride is much more commonly used than alum. In this study, therefore, ferric chloride was used as the reference coagulant to evaluate and optimise coagulation for the removal of NOM in samples from various parts of the country.

MATERIALS AND METHODS

Sample collection and storage

Samples were collected from eight sites elected through a semi-random process based on the main surface water types encountered in SA. Five distinctively different raw water types were identified from the perspective of NOM removal, and a random selection was

made to ensure a representation of these water types, as well as a balanced spatial representation. These include:

(1) Water emanating from warmer areas with high population densities, with a fairly high NOM load.

(2) Oligotrophic water from Vaal Dam, a reservoir which supplies the largest water supply authority in the country. The NOM in this water type is characterised of surface water from a reasonably well protected Highveld catchment area with minimal return flows.

(3) Treated sewage effluents, which dominate the NOM character in many streams and rivers in SA during periods of low flow

(4) Eutrophic water from the Highveld, with typically high NOM loads. The eutrophication is being driven by large return flows and agricultural runoff.

(5). Coloured water from the south-western coast, very high in colour, humic and fulvic acid.

A total of 20 samples collected at these sites over a period of about a year, and representing four different seasons (1, 2, 3 and 4), are presented in this paper. The raw waters were collected into 25ℓ containers 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/experiment.

Determination of water quality parameters

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. The raw water colour was measured by an external lab and UV 254 nm absorbance (UV₂₅₄) was measured using an ULTROSPEC II: UV/Vis spectrophotometer (Model 80-2091-73, Biochrom, England) with 1 and 5 cm cuvette cells, after being filtered through non-sterile 33 mm MILLEX – HV MILLIPORE 0.45 µm filter units. Alkalinity (mg CaCO₃/L) and calcium hardness (mg Ca/L) were determined using protocols 403 and 311 C, respectively, outlined in standard methods (16th edition, 1985).

Coagulation pH and coagulant dose determination using jar tests

pH titration curves of raw waters using 0.1N and 0.02N hydrochloric acid (HCl), and the ferric chloride (FeCl₃·6H₂O) coagulant were determined. The stabilization of alkalinity was done by the addition of sodium carbonate (Na₂CO₃), and jar tests were performed on the above raw waters at ambient temperature without pH control, as described by Dlamini et al, 2011.

RESULTS AND DISCUSSIONS

Bulk raw water properties

The wide range of the water samples in terms of alkalinity, turbidity, pH and UV 254 nm are shown in Table 2. The pH and turbidity ranged from 5.0 to 9.0 and 0.4 to 88 NTU respectively. Generally, the M samples exhibited relatively high turbidity values while on the other extreme the W and P samples had low turbidity values. The alkalinity, which is the acid neutralizing power of the sample, also varied greatly from 3 to 152 mg/L (as CaCO₃). Much of these differences were due to urban, agricultural and geologic sources to the catchment area. However, in some cases e.g. the M samples, huge seasonal differences were observed for turbidity and alkalinity. In sample M3, the alkalinity was 67 mg/L CaCO₃ while in M2 it was 136 mg/L CaCO₃. The turbidity was 36 NTU in M3 whereas it was half this value (18NTU) in M2.

Table 1: Raw water characteristics

Sample ID	Alkalinity	UV 254 nm (m⁻¹)	Turbidity	pH
P1	3.3	31	0.8	6.2
P2	12	42	0.5	7.6
P3	3.0	76	3.4	5.7
P4	3.0	53	6.4	5.0
W1	54	11.1	1.2	8.1
W2	58	10.6	1.0	8.4
W3	58	11.2	0.9	8.7
W4	57	7.3	0.4	7.2
V1	59	20	74	7.9
V2	58	18	56	8.0
V3	53	30	88	8.1
V4	47	35	74	7.6
O1	93	15	1.5	8.2
O2	99	16	1.8	8.7
O3	88	15	2.6	8.5
O4	92	17	1.9	8.6
M1	152	16	6.5	9.0
M2	136	18	2.6	8.7

M3	67	36	85	7.8
M4	67	17	6.4	8.8

Garcia and Moreno (2006) observed a very good correlation for their raw water samples between DOC and UV 254 nm ($r^2 = 0.99$), and Bartles (1990) also observed the same coefficient of determination. This suggests that UV 254 can be used to estimate the concentration of DOC. Moreover, naturally occurring DOC contains benzenoid type components and aliphatic bonds that absorb UV radiation (Pernitsky 2003). In this study, UV 254 nm as surrogate parameter for NOM was used and they also varied greatly spatially ranging from 7.3 to 76 m^{-1} . The P samples, which were visibly coloured, had the highest UV values while the W samples, which were visibly clear had the lowest.

NOM and Enhanced Coagulation

The USEPA (1998), establishes TOC removal requirements based on the raw water TOC and alkalinity at the first step in the disinfection by-products (DBPs) regulation. The higher the amount of TOC in the raw water, the greater the TOC removal percentage by enhanced coagulation. They also found the TOC removals to be more difficult as the alkalinity increases, hence less TOC removal percentage is to be expected.

Figure 1 presents the UV 254 removal percentage by enhanced coagulation as a function of raw water UV 254 in the settled water. The optimum coagulant dosage used to reach the required level of UV 254 was between 6.7 and 51 mg/L of $FeCl_3 \cdot 6H_2O$. The same trend with UV 254 as the one described above was observed. The P raw water samples which had the highest UV 254 values also had the highest removal percentages (89, 79 and 72 %). At the other extreme, the W raw water samples which had very low UV values yielded very low percentage removals (21, 15 and 23 %).

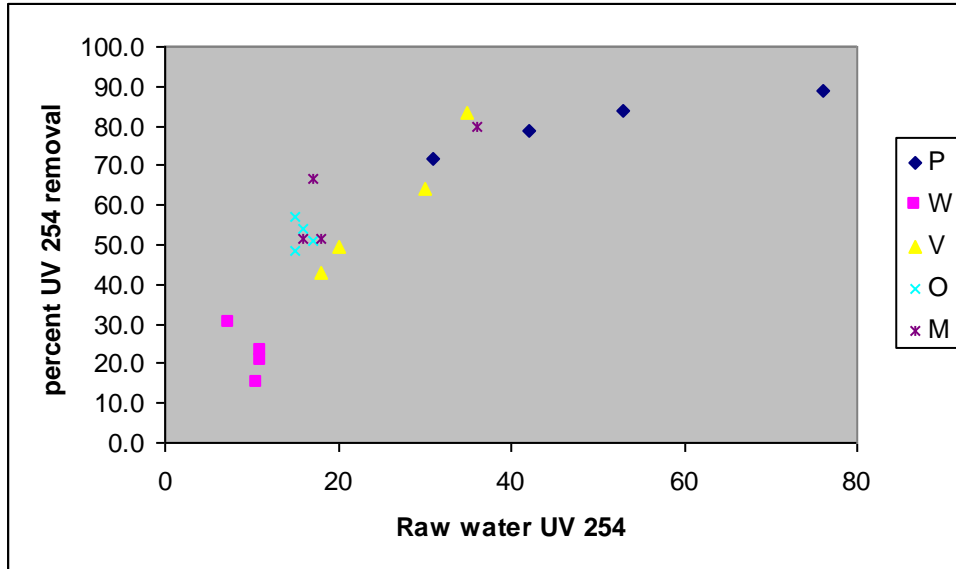


Figure 1: The relationship between raw UV 254 and its percentage removal.

As observed by the USEPA, the alkalinity of the samples seemed to have an influence on the removal percentage of UV 254, though the raw water UV values were not the same for all the samples (Figure 2). The P samples which had the lowest alkalinity, exhibited high removal percentages than the M1 and M2 samples which had the highest alkalinities. This trend was also observed in samples from the same source at different seasons. This was illustrated well by the M samples where the M3 and M4 samples had relatively high removal percentages due to their lower alkalinities. However, the influence of raw water UV seemed to have more effect than alkalinity in some samples i.e. the W samples. Though they had relatively low alkalinities, but they still had very low UV 254 removal percentages because they had very low raw water UV values.

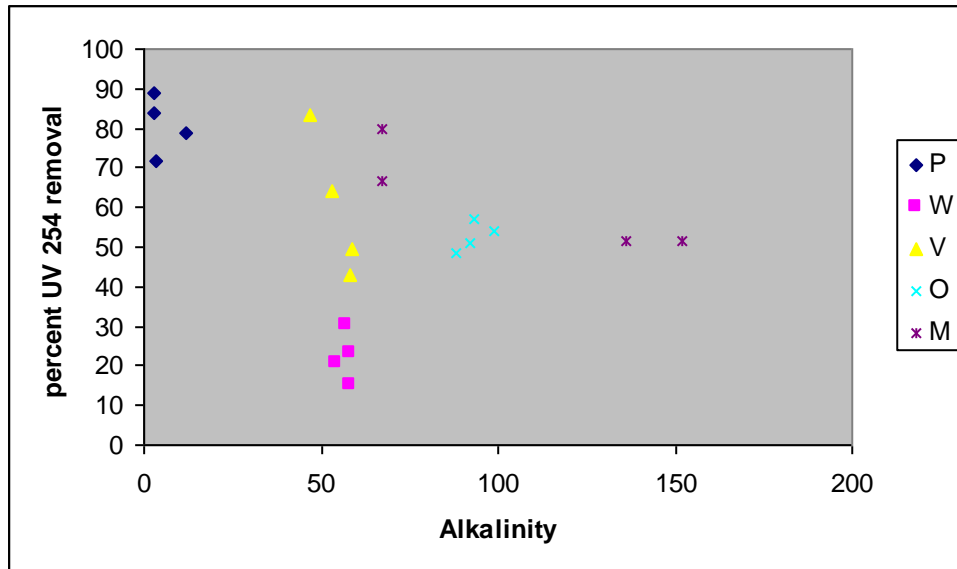


Figure 2: The effect of alkalinity on the removal of UV 254.

Alkalinity and Enhanced coagulation pH

The USEPA have also recognized the coagulation pH to be determined by the alkalinity. This could be explained by the fact that when metal coagulants are added in the raw water, they act as acids, and can depress the pH depending on the dosage and the water's buffering capacity. Hence, if the buffering pH is low, the target removal of NOM of coagulation pH will be reached sooner (with little addition of coagulant). Moreover, the removal of UV 254 is affected by the alkalinity because alkalinity also controls further the hydrolyzed species of metal coagulants during flocculation. When the alkalinity is high, the extent of the hydrolysis process and the formation of larger polymers occur further, causing more precipitation.

Many researchers have found the coagulation pH to be the parameter having greater effect on achieving optimal NOM removal by coagulation (Bell-Ajy et al, 2000; Qin et al, 2006; Sharp et al, 2005). Results from this study are in agreement with these findings, indicating that the coagulation pH, was the controlling factor for UV 254 removal rather than the coagulant dose for the varying alkalinity samples analyzed. As shown in Figure 3, the coagulation pH generally increased with increasing alkalinity for geologically and seasonally different samples. However, the raw water UV 254 still "dialed in" some effects to some extent. Based on the criteria used to judge optimum UV 254 removal, the dosages used resulted to a coagulation pH range of 5.1 and 6.5.

There are three mechanisms of NOM removal which are said to be most common in a ferric metal coagulant coagulation/sedimentation process i.e. charge neutralization, adsorption and entrapment (Qin et al, 2005; Vrijenhoek et al, 1998). In the pH range of between 5 and 6, the availability of positively charged species of $\text{Fe}(\text{OH})_2^+$ to react with the negatively charged NOM particles are thought to be maximal. Furthermore, at the pH range of about 5.5 and 6.5, the positively-charged Fe complexes satisfies the charge demand of the negatively charged NOM, and precipitates as $\text{Fe}(\text{OH})_{3(\text{am})}$ with removal of NOM either through co-precipitation of $\text{Fe-NOM}_{(\text{s})}$ or through adsorption of complexed Fe-NOM to $\text{Fe}(\text{OH})_{3(\text{am})}$ particles (Edzwald and Haarhoff, 2011). These pH results generally suggested that all three removal mechanisms were involved in removing the UV 254 absorbing species to comply with criteria.

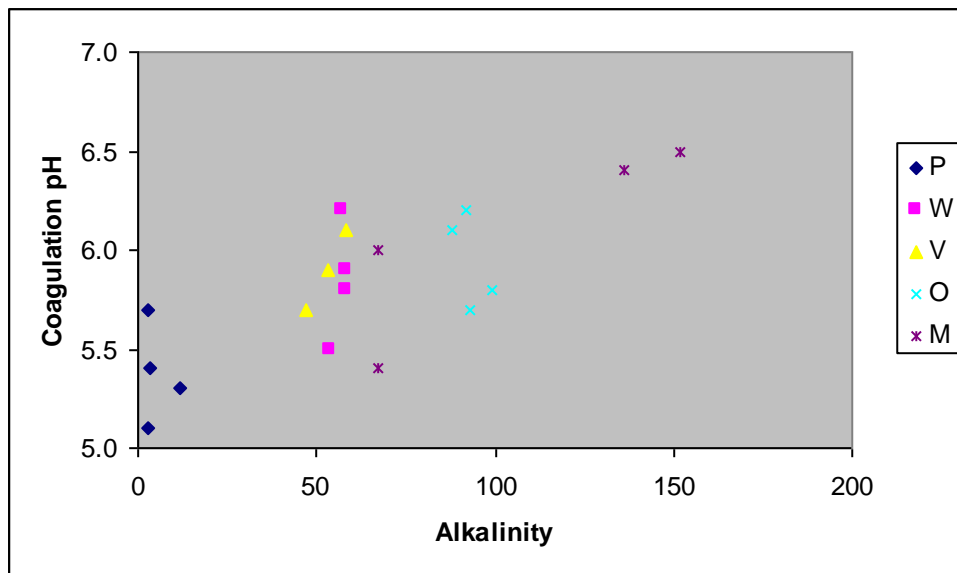


Figure 3: The effect of alkalinity on coagulation pH

Residual UV 254 and Turbidity on Settled Water

UV 254 is instrumental in identifying the aromatic content of water, it can therefore be used as a surrogate parameter for monitoring organic matter and disinfection by-products formation potential (Yan et al, 2009), the seasonal coagulation of the typical South African water treatment plants are set with the parameter UV 254. The measurement of this parameter is quick, easy to operate and is suitable for routine monitoring at a water treatment plant. Figure 4 shows the amount of residual UV 254 after enhanced coagulation. Generally, all the residual UV values were lower than 9 m^{-1} except V1, V2 and V3 samples where they were slightly greater than 10 m^{-1} .

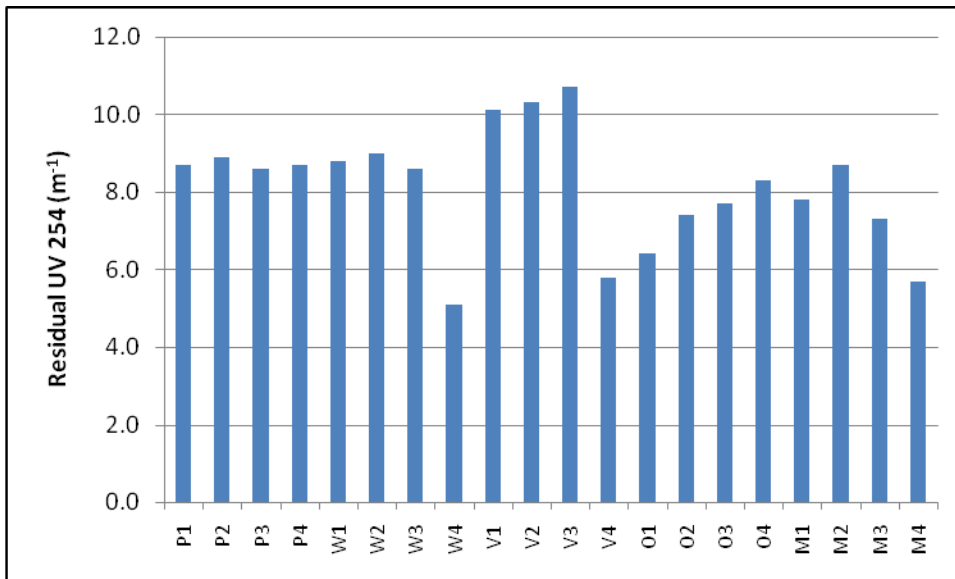


Figure 1: Effect of optimized coagulation on UV 254 nm.

The coagulation experiments did not only remove UV 254 with appreciable percentages, they also exhibited high efficiencies for turbidity removal. Though there are also optimum coagulation conditions for turbidity removal, but these coagulation experiments which were optimized for UV removal were able to reduce the turbidity to values below 1.5 NTU, except for the M3 sample where it was 2.3 NTU (Figure 5). However, all these values are sufficiently low to be removed further by filtration units. Thus, simply meeting the performance criteria for enhanced coagulation may not be the only motivating factor if optimized coagulation for UV removal can still obtain low turbidity values.

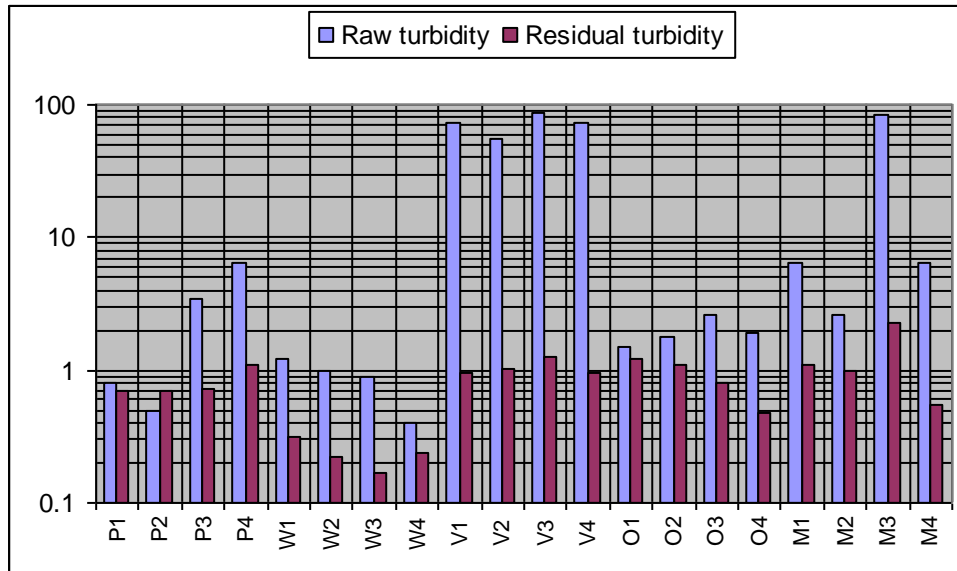


Figure 2: The effect of optimized coagulation for UV 254 on turbidity.

Summary and Conclusions

This study analyzed a wide spectrum of natural waters in terms of alkalinity, UV 254 and turbidity for enhanced coagulation. A series of jar tests were performed in all samples, and the effect of alkalinity on the removal of UV 254 were assessed. The removal percentage of UV 254 was found to be primarily a function of the raw water value. Nevertheless, the alkalinity also affects enhanced coagulation by controlling the coagulant dose and the resultant coagulation pH. Based on the criteria used to judge optimum UV 254 removal, the dosages (for all samples) used resulted to a coagulation pH range of 5.1 and 6.5. The possible mechanisms involved for the removal of NOM are charge neutralization, adsorption and entrapment. The coagulation experiments did not only remove UV 254 with appreciable percentages, they also exhibited high efficiencies for turbidity removal.

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