Optimized coagulation for the removal of Natural Organic Matter (NOM) from low alkalinity - hardness South African raw waters

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Abstract This example is to demonstrate the layout of the first page of a paper for *Water Science and Technology*. The authors' family names should be given in full; their forenames should be given as abbreviations. The title, authors' names and addresses should be indented 1.5 cm from the left-hand margin of the text area; the abstract is indented 1.5 cm from both margins. The abstract itself, set in 10 pt type like the authors' addresses, should start about 9 cm down from the top of the text area. It should be a single paragraph. Please do not make reference citations in the abstract and keep within the limit of 200 words. It is followed by your choice of up to six keywords, listed alphabetically and separated by semi-colons.
Keywords Abstract; author details; example; headings; layout; title page

INTRODUCTION

The primary objective of potable water treatment plants is to produce water that is clear, without microbiological and physiochemical components which may pose a health hazard to consumers. During the water treatment process train, chemicals are added in the desire to kill pathogens and remove turbidity. Recently, the South African National Standards (SANS, 2006) have developed and improved drinking water quality standards in an attempt to control water quality. Amongst these standards, as shown in Table 1, there is also a regulation that calls for the control of dissolved organic carbon (DOC), a surrogate parameter of natural organic matter (NOM). This compelled South African water treatment plants to add NOM on the list of components they wish to remove from the water.

Property	Recommended operational limit	Maximum allowable for limited duration	Consumption period, [a]maximum
Conductivity µS/m	< 150 000	150 000 – 370 000	7 years
pH	5.0 – 9.5	4.0 – 10.0	No limit
Turbidity NTU	< 1	1 – 5	No limit[d]
DOC mg/L C	< 10	10 - 70	No limit[e]
Calcium mg/L	< 150	150 - 300	7 years
Iron mg/L	< 0.2	200 - 2000	7 years[b]

Table 1. Quality of acceptable drinking water

[a] *Limits based on consumption of 2 L of water per day by a person of mass 70 kg over a period of 70 years*

[b] *The limits given are based on aesthetic aspects*

[d] *Process efficiency and risks associated with pathogens*

[e] *When DOC is deemed of natural origin, the consumption period can be extended*

It is hypothesised that natural organic matter 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 and 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). NOM should indeed be removed from drinking water as it gives the water body a brown colour and odour which compromises the aesthetical quality of the water. It is also known to be the cause of microbial regrowth 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).

The US Environmental Protection Agency recognised enhanced coagulation/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 using already available treatment processes (Yan et al, 2009). The

removal of NOM from raw waters by enhanced or optimised coagulation is dependant 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 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 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 from the south-western coast, coagulation was effective at removing NOM. Other trial studies in SA, where SUVA values are typically lower, 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. 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 enhanced coagulation clearly depends on the nature of the NOM, which reinforces the need for its systematic evaluation on the full range of raw waters.

MATERIALS AND METHODS

The literature on coagulation uses 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 low alkalinity samples from various parts of the country. It was prepared from reagent grade granular ferric chloride in the laboratory. As the ferric chloride solution is acidic and reacts with the

alkalinity to form ferric hydroxide flocs, each sample was first titrated to establish the dosing range of ferric chloride to keep the pH above pH 4.5. With the range established, a standard jar test was performed across the dosing range. From the results, an appropriate dosing concentration was established which would represent the "optimal" concentration to attain EC. A single sample was then dosed with the "optimal" concentration and the amount of NOM removal compared with the character of the raw water NOM from SUVA values.

Sample collection and storage

A total of 12 samples were collected at four treatment plants, Pletternbeg Bay (P) and Loerie (L) of the southern cape, Wiggins (W) of Umgeni water and Vereeniging (V), over a period of eight (July 2010 – February 2011) months, representing three different seasons (1, 2 and 3). The raw waters were collected into 25 L containers before any pre-treatment, transported to the lab as quick as possible and were stored in the dark at 4 ºC to reduce biological activity until testing/experiment.

Analytical methods

The pH, temperature (ºC) 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. Dissolved organic carbon (DOC) amounts in raw and treated water samples were determined indirectly by measuring UV_{254} absorbance using an ULTROSPEC II: UV/Vis spectrophotometer (Model 80-2091-73, Biochrom, England) with a 5 cm cuvette cell, after being filtered through non-sterile 33 mm MILLEX – HV MILLIPORE 0.45 µm filter units. Specific UV absorbance was used as an indicator of what fractions of natural organic matter dominate the DOC of the waters. It was calculated from UV_{254} (1/m) and DOC (mg/L) measurements as follows:

$$SUVA = \frac{UV_{254}(1/m)}{DOC(mg/L)}$$

Alkalinity (mg CaCO$_3$/L) and calcium hardness (mg Ca/L) were determined using protocols 403 and 311 C, respectively, as outlined in standard methods (16th edition, 1985).

Reagents

Hydrochloric acid (HCl) 0.1N and 0.02N were used for alkalinity titrations. Standard EDTA (0.01M), Eriochrome Blue Black R indicator (stable form) and sodium hydroxide (NaOH), 1N and 8N were used for the calcium titration. The metal coagulant used was ferric chloride (FeCl$_3$·6H$_2$O), due to its extensive use in South African water treatment plants. Standardized sodium carbonate (Na$_2$CO$_3$) was used to increase the alkalinity of the extremely low alkalinity samples.

Jar test procedure

Prior to jar testing, all the water samples were brought to ambient temperature. An FC6S jar test apparatus (VELP SCIENTIFICA) was used for coagulation and flocculation experiments in 1 L beakers containing 900 mL samples of water. Two mixing speeds were used, namely a rapid mix of 200 rpm for 2 minutes, followed by flocculation/slow mix of 30 rpm for 10 minutes, followed by 30 minutes settling time. 50 ml aliquots of sample were extracted from each beaker from the centre of the jar using 50 ml pipettes with a 90° bend at the tip. The remaining samples in the 1 L beakers were measured for temperature, pH and conductivity. The extracted 50 ml aliquots were measured for turbidity and UV$_{254}$ absorbance after being passed through the 0.45 µm filter units.

Determination of coagulation pH and coagulant dose for optimized coagulation

The determination of coagulation pHs for the jar tests was arbitrary and were chosen to be 7.0, 6.0, 5.5, 5.0 and 4.5, with the first jar acting as a control, i.e. no coagulant added and, therefore, the pH remaining unaltered. Since the alkalinity of the waters used in this study was low (less than 60 mg CaCO$_3$/L), the waters had low or no buffering capacity at all. Na$_2$CO$_3$ was, therefore, used to augment the buffering capacity of the waters. STASOFT4 (a tool for designing, modelling and controlling water treatment processes involving carbonate chemistry) was used to predict the amount of Na$_2$CO$_3$ standard

solution to be added in the raw water sample to reach an alkalinity of at least 60 mg $CaCO_3$/L alkalinity. This tool was also used to predict the amount of 100% hydrochloric acid (HCl) to be subsequently added to the mixture of raw water and Na_2CO_3 standard solution to reach the pH corresponding with the target alkalinities of 7.0, 6.0, 5.5, 5.0 and 4.5. Conversions of 100% HCl acid to 0.1N HCl were made to get corresponding amounts, which were then converted to equivalent amounts of $FeCl_3 \cdot 6H_2O$.

Many preliminary experiments in the lab with different South African raw waters (apart from the ones mentioned here) were made to establish the relationship between a standard acid solution (0.1N HCl) volume and $FeCl_3 \cdot 6H_2O$ dose to depress the pH to 4.5. For waters with alkalinity close to 60 mg $CaCO_3$/L, an alkalinity titration curve was used to predict the coagulant dosages that would depress the pHs to the target values.

RESULTS AND DISCUSSIONS

Water characteristics

Table 2.   Raw water quality characteristics

Sample ID	pH	Alkalinity (mg/L)	Calcium (mg/L)	UV$_{254}$ (1/m)	DOC (mg/L)	SUVA (L/mg·m)	Turbidity (NTU)
P 2		3.3	5.1				0.8
P 3		12.0	5.6				0.5
P 4		3.0	4.8				3.4
L 2		15.6	13.6				3.0
L 3	N/A	N/A	N/A	N/A	N/A	N/A	N/A
L 4		18.5	11.2				1.3
W 2		54.4	25.6				1.2
W 3		58.0	16.0				1.0
W 4		58.3	16.8				0.89
V 2		58.9	21.6				74.4
V 3		57.8	16.8				56.3

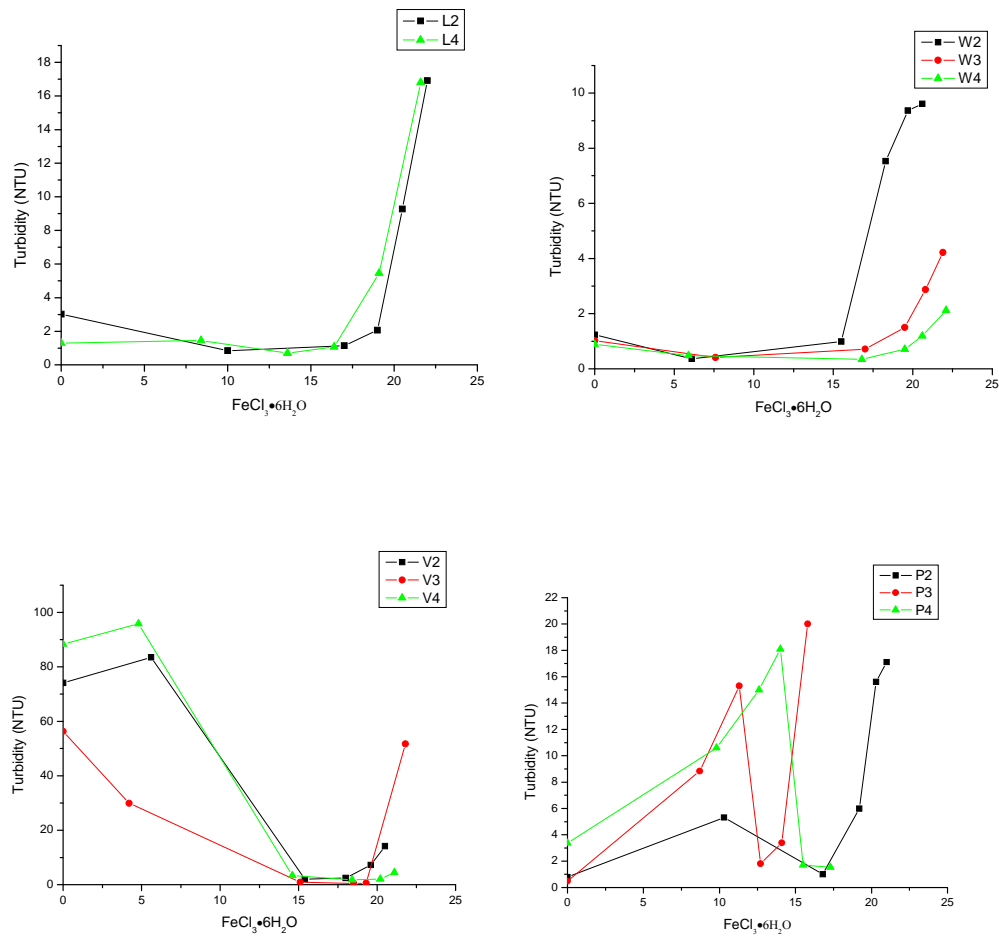| **V 4**	52.8	15.2	88.3

N/A: Not available

Effects of coagulant dose on turbidity

Figure 1.   Effects of dosage on residual turbidity.

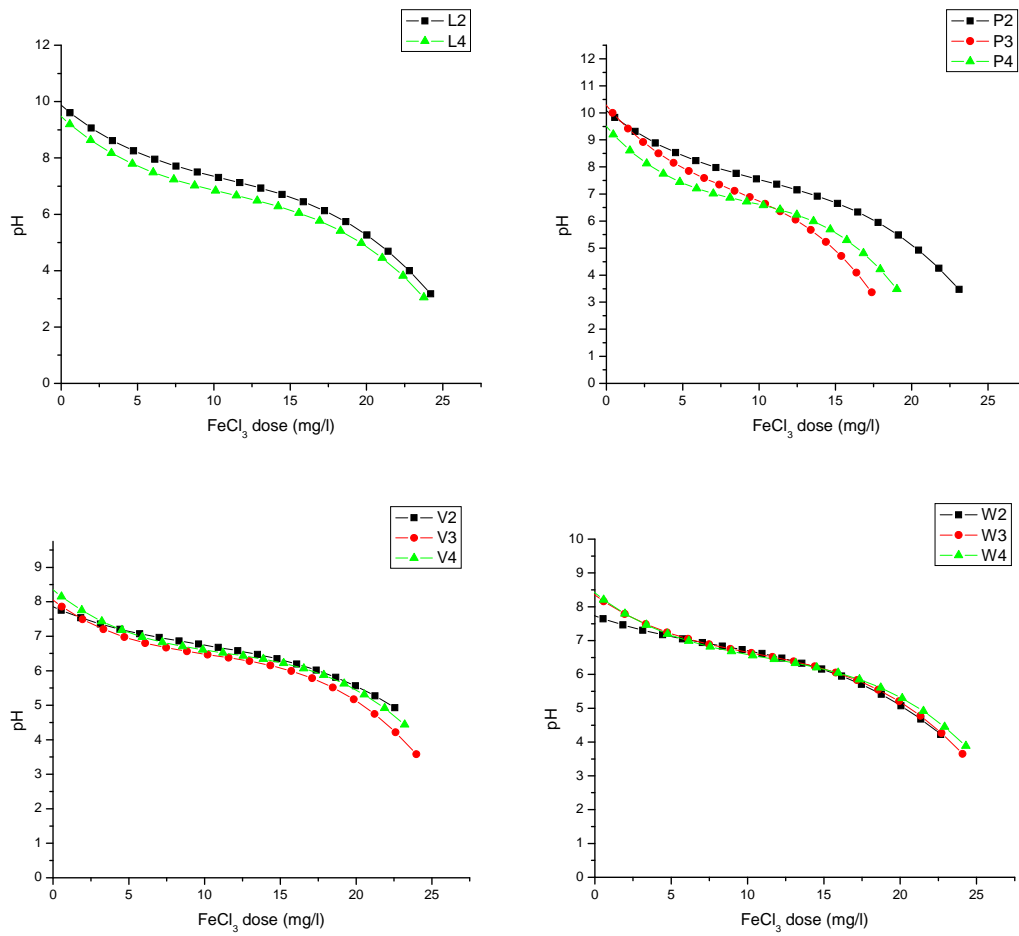*Effects of coagulant dose on pH and UV$_{254}$*

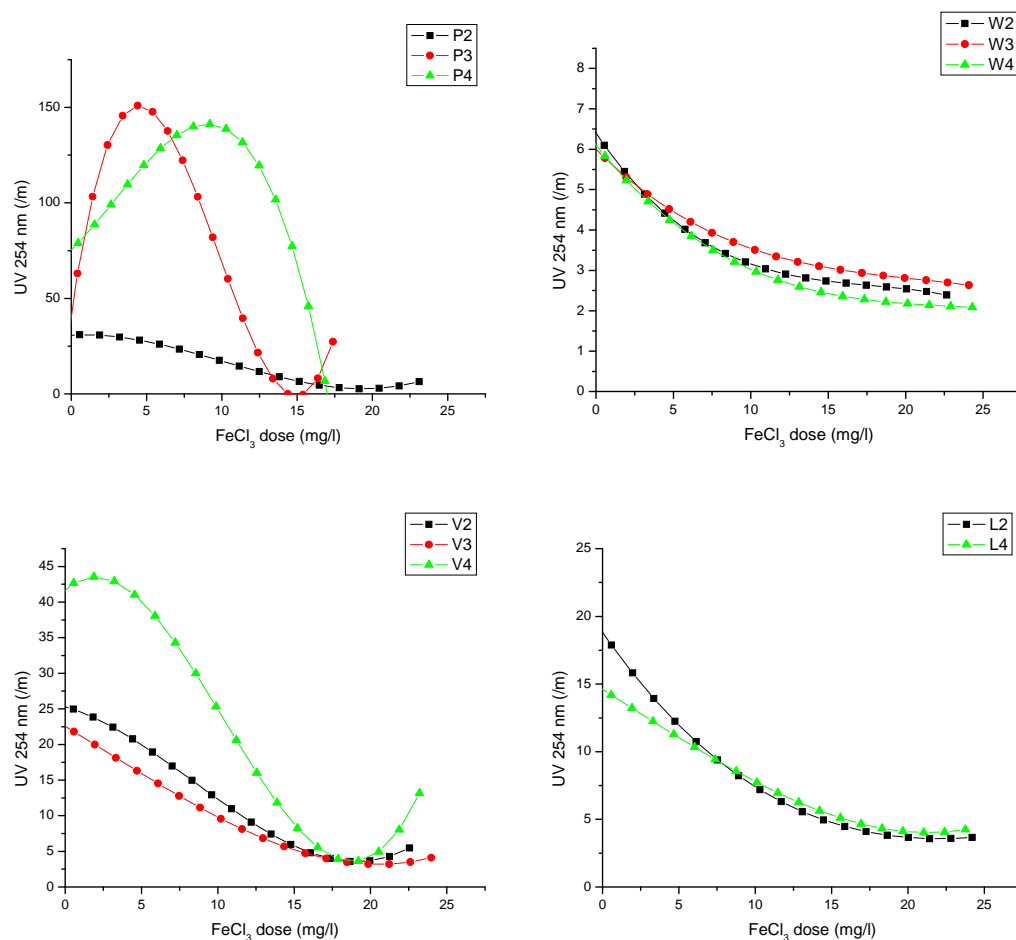**Figure 2.** Dose response curve of ferric chloride Vs pH of raw waters.

Figure 3. Effects of dosage on the removal of natural organic matter (NOM).

Optimized coagulation for the removal of turbidity and natural organic matter (NOM)

Table 3. Removal of NOM surrogate parameters after optimized coagulation.

Sample ID	Optimum dose (mg/L)	pH	UV$_{254}$ removal percentage	DOC removal percentage	Turbidity (NTU) at optimum dose
P 2	17.0				
P 3	13.6				
P 4	16.6				
L 2	12.3				
.L 3	N/A	N/A	N/A	N/A	N/A
L 4	15.9				

W 2	7.9
W 3	6.7
W 4	8.6
V 2	14.7
V 3	14.0
V 4	16.3

CONCLUSIONS

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