

# Modelling the Application of Inorganic Coagulants and pH Control Reagents for Removal of Organic Matter from Drinking Waters

**J. van Leeuwen<sup>a</sup>, M. Holmes<sup>b</sup>, C. Heidenreich<sup>b</sup>, R. Daly<sup>a</sup>,**

**I. Fisher<sup>c</sup>, G. Kastl<sup>c</sup>, A. Sathasivan<sup>c</sup> and D. Bursill<sup>a</sup>**

<sup>a</sup>Australian Water Quality Centre, SAWATER, <sup>b</sup>United Water International, <sup>c</sup>Sydney Water Corporation  
Co-operative Research Centre for Water Quality and Treatment, Salisbury, South Australia, 5108.

(john.vanleeuwen@sawater.com.au)

**Abstract:** Raw surface and ground waters used for drinking purposes can vary markedly in their chemical and biological composition. Inorganic content (such as salt, bicarbonate, clay and metal ions), organic content (natural organic matter and anthropogenic compounds, including pollutants) and micro-organisms present in raw water are key drivers for treatment processes that provide for safe and aesthetically acceptable drinking water. Conventional treatment at large scale water treatment plants (WTP) involves the use of inorganic coagulants to remove turbidity and colour, and more recently to maximise removal of organic compounds. The basis for the latter is to minimise the concentration of organics in treated water that leads to lower levels of disinfection by-products (post chlorination) and substrates for microbial growth in the water distribution system. Maximising removal of organic matter using inorganic coagulants is impacted by the character and concentration of the organics, the turbidity and alkalinity of the raw water. Removal of organics is also influenced by the type of coagulant used, its dose rate and the pH at which coagulation occurs. To date, few attempts have been made to model the relationships between raw water quality parameters and the use of coagulants and pH control reagents for removal of organics, colour and turbidity. In this paper, mathematical models are described that relate raw water quality parameters (ultraviolet light absorbing compounds, coloured compounds, turbidity and the pH buffering capacity of raw water) to dose rates of the coagulants, alum and ferric chloride, and pH control reagents. Also described are models that relate the concentration and character of organics in raw water to targeted percentage removal of organics. The aim of these models is to provide water treatment operators with a tool that enables prediction of chemical reagents and treatment conditions for selected removal of organics, based on raw water quality data.

**Keywords:** *Enhanced coagulation; Modelling; NOM, Water treatment.*

## 1. INTRODUCTION

Drinking water that is acceptable to the majority of consumers is clear (not turbid), colourless, has no unpleasant taste or odour, and is safe. In most cases, the quality of raw water from natural sources would not meet consumer acceptance, industry standards, water authority guidelines and statutory regulations for drinking water quality. In order to attain high quality drinking water a range of methods and treatment technologies have been developed including application of granular and powdered activated carbon, membrane filtration, coagulation-flocculation (with

sedimentation or dissolved air flotation) and filtration, ozonation and ion-exchange resins. In order to remove or destroy pathogens from drinking water, it is filtered and further treated with chemical disinfectants and/or UV irradiation. The most common water treatment process involves the use of metal based coagulants for removal of natural colour, turbidity and organic compounds. Turbidity can be caused by clay particles, algae or particulate organic matter and is typically efficiently removed by coagulation. In contrast, dissolved natural organic matter (DOM) comprises components that are

recalcitrant to removal by coagulation. Residual DOM in drinking water has been identified as a significant problem because it can act as a substrate for microbial growth in a distribution system and it reacts with chlorine based disinfectants forming by-products that may be of a health concern. For these reasons there is a strong interest in the water industry to maximise removal of organic compounds in drinking water.

The amount of DOM [measured as dissolved organic carbon (DOC)], removed by coagulation is affected by the dose and type of coagulant used and the pH at which coagulation occurs. At a given pH, the efficiency in removing DOC with increasing dose decreases from high to low or until no further removal is evident. For a given coagulant there is an optimum pH at which coagulation is most efficient for removal of organics. Natural DOC can be considered as comprising of two fractions in relation to a particular coagulant, (1) that which can be removed (coagulable) and (2) that which cannot be removed (recalcitrant).

Specified removal of organics to minimise disinfection by-products is a regulatory requirement in the USA, while water authorities in Britain and Europe are required to meet regulatory limits on disinfection by-products. The specific treatment of water using conventional processes to maximise removal of organics is referred to by the water industry as enhanced coagulation. In Australia, guidelines exist for levels of disinfection by-products in drinking water (NHMRC, 1996).

Modelling of water treatment processes have been described by Bazer-Bachi et al. [1990], Ellis et al. [1991], Girou et al. [1992], Ratnaweera and Blom [1995] and van Leeuwen et al. [1999a]. These models are mostly based on empirical relationships between raw and treated water quality and treatment conditions required to achieve a target water quality. The emphasis for removal of organics is recent and models developed for and relating to this include Edwards [1997], Urfer et al. [1999], Baxter et al. [1999], Stanley et al. [2000] and van Leeuwen et al. [2001].

In this paper, feed-forward models are described that relate alum and ferric based coagulant doses to the quantity and character of organics matter present in raw water, measured as dissolved organic carbon. Coagulant doses are estimated either, as required for near maximum removal of

organics or for a selected percentage removal of coagulable organics, for a given pH.

## **2. MATERIALS AND METHODS**

### **2.1 Determination of Water Quality Parameters**

Colour: Colour (Col), in Hazen units (HU) was determined by measuring the absorbance at 456 nm using UV/VIS spectrophotometer (Model 918, GBC, Australia).

Dissolved organic carbon (DOC) analysis: DOC concentrations of water samples (filtered through 0.45  $\mu\text{m}$ ) were determined using a total carbon analyser (Model 820, Sievers Instruments Inc., USA) and indirectly by measuring the absorbance at 254 nm using a UV/VIS spectrophotometer (Model 918, GBC, Australia) with a 1 cm quartz cell.

Turbidity: Turbidity, in nephelometric turbidity units (NTU), was measured using a Hach ratio turbidimeter (Model 2100 AN, Co., USA).

pH: Orion (Model 420A, MA. USA) and WTW pH 340i meters were used.

### **2.2 Samples**

Samples were collected from various water sources in South Australia, Victoria, New South Wales and Queensland, including Baroon Dam, Upper Avon Dam, Happy Valley, Hope Valley, Middle River, Moorabool, Mt Zero and Myponga reservoirs and the Murray and Hawkesbury-Nepean rivers. These waters varied in DOC concentration, alkalinity and turbidity.

### **2.3 Coagulant Dose Determination Using Jar Tests and Pilot Plant studies.**

Jar tests were performed on the above waters at ambient temperature, as previously described [van Leeuwen et al. 1999b]. Jar tests were also performed on Murray River water samples (high in turbidity) mixed with other natural waters (low in turbidity) to determine the alum and ferric chloride demand exerted by the turbidity. Pilot plant studies were performed as previously described (van Leeuwen et al. 2003).

The coagulants, alum as aluminium sulphate ( $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ) and ferric chloride ( $\text{FeCl}_3$ ) were used in jar tests and in pilot plant studies.

## 2.4 pH Control of Water Samples

Curves of pH titrations of raw waters using coagulants and sulphuric acid were determined as previously described (van Leeuwen et al. 2001).

Reagents used for controlling the pH of water samples were (1) hydrochloric acid (HCl), BDH grade, AnalaR® 35.4% (2) sodium hydroxide NaOH, APS AJAX, Finechem, Analytical Univar reagent (3) sulphuric acid (BDH AnalaR® 98%)

## 3. RESULTS AND DISCUSSION

Coagulant dose selection using jar tests and pilot plant studies is based on achieving criteria (organisational; guideline and/or regulatory) for treated water quality. This may include minimising (a) colour and turbidity (b) residual DOC and (c) particle counts. Coagulant dose rates can be selected which minimise residual organics in treated water. An example is shown in Figure 1. For this water, alum dose rates higher than ~ 85mg/L would be ineffective for further removal of DOC while lower doses might be used if higher residual DOC concentrations are tolerable.

For all the waters tested, there was an initial high level of DOC removal with increasing alum dose followed by a lowering in efficiency. This trend can be explained by the different types of organics that comprise NOM. High molecular weight hydrophobic compounds are readily removed by coagulation-flocculation while small molecular weight hydrophilics are recalcitrant to this type of treatment. Generally, organics that cause natural waters to be coloured brown are humic in nature and large in molecular weight and therefore, are readily removed by inorganic coagulants.

The results of jar tests of individual waters were modelled to relate residual DOC with the alum dose applied, where treatment was performed at a set pH. The following is a general model fit of this data:

$$\text{DOC (residual in treated water)} = A_1 + B_1 \exp(-C_1 \times \text{alum}) \quad (1)$$

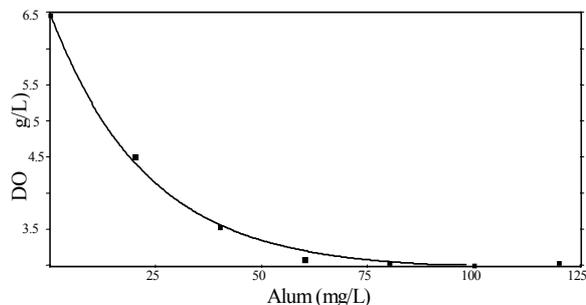
where  $A_1$ ,  $B_1$  and  $C_1$  are constants for any one water, coagulant demand from turbidity was minimal and alum is the dose in mg/L.

A feature of the relationship between residual DOC and alum dose is that at a certain level of

dosing near maximum removal of organics occurs for a particular coagulation pH. Hence, provided that a 'high enough' dose is always chosen then near maximum removal of organics should be attained. However, opposing pressure to the application of high coagulant doses is the financial cost this imposes. Practical coagulant dose selection at a large-scale water treatment facility is balanced by the need to remove organics to minimise disinfection by-products and the costs of chemical use. Therefore, coagulant dose rates may be selected which result in near maximum removal of DOC or some target removal.

From the fitted curves of jar test data, alum doses were selected where (a) a reduction of 0.15 mg DOC per 10 mg alum had occurred (gradient = -0.015) and (b) resulted in selected percentage removals (90 to 50%) of coagulable organics, at a particular pH. The gradient chosen was arbitrary but represented an area of the curve where further reduction of DOC with higher alum doses was minimal. Other gradients may be selected. In determining the relationship between raw water DOC and alum dose for a specific level of removal, a range of waters that had minimal turbidity were selected. This was done to ensure that turbidity did not impact significantly on the coagulant dose rate determined. These alum dose rates were then plotted against the raw water UV absorbance (at 254nm) alone and UV absorbance with colour [UV x log (Col x 10), Figure 2]. UV absorbance at 254nm and colour are used by the drinking water industry as an indirect measure of the concentration and character of DOM. They are easily applied and inexpensive methods that indicate the amount organics that can be removed by coagulation, ie high-molecular weight hydrophobic compounds.

In this study coagulant dose rate was modelled in relation to both UV with colour and UV alone. For prediction of coagulant requirements from these models, the higher of the two is used.

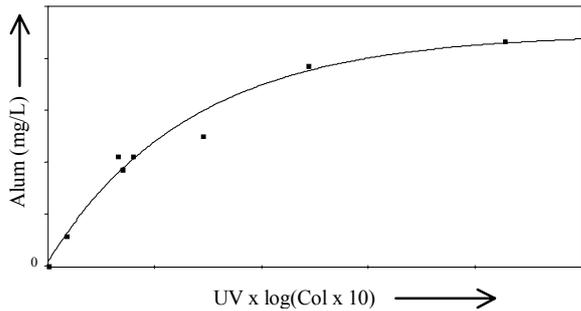


**Figure 1:** Results of a jar test performed on Moorabool Reservoir water using alum with the pH controlled at pH 5.

A model fit of data that relates alum dose to achieve a  $\Delta\text{DOC} / \Delta\text{Alum}$  of  $-0.015$  with the raw water UV absorbance at 254nm and colour (Figure 2), is as follows:

$$\text{Alum} = A_{2c} + B_{2c} (1 - \exp(-C_{2c} \times \text{UVCol})) \quad (2)$$

where UVCol is  $\text{UV} \times \log(\text{colour} \times 10)$ , colour is in Hazen units and  $A_{2c}$ ,  $B_{2c}$  and  $C_{2c}$  are constants.



**Figure 2:** Relationship between raw water UV absorbance (254nm) and colour (456nm) with alum dose at a gradient of  $-0.015$  for  $\Delta\text{DOC} / \Delta\text{Alum}$ .

For a selected percentage removal of coagulable DOC (between 90% and 50%) using alum, the following general model was determined:

$$\text{Alum} = A_{2v} + B_{2v} (1 - \exp(-C_{2v} \times \text{UVCol})) \quad (3)$$

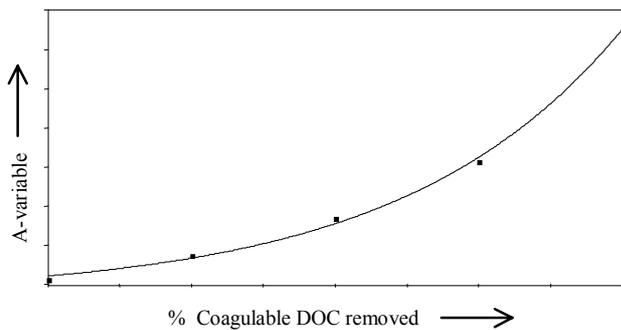
where  $A_{2v}$ ,  $B_{2v}$  and  $C_{2v}$  are variables for percentage (P) reductions, each modelled as follows:

$$A_{2v} = D_1 + E_1 \exp(-P/F_1) \quad (4)$$

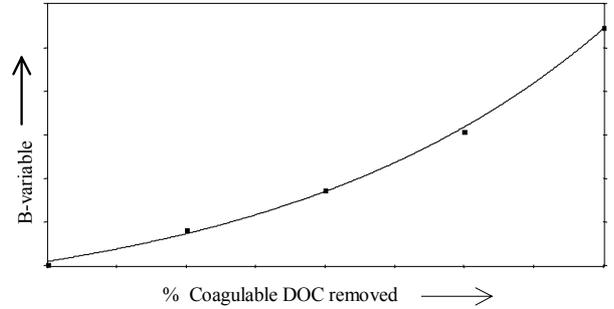
$$B_{2v} = D_2 + E_2 \exp(-P/F_2) \quad (5)$$

$$C_{2v} = D_3 + P \times E_3 \quad (6)$$

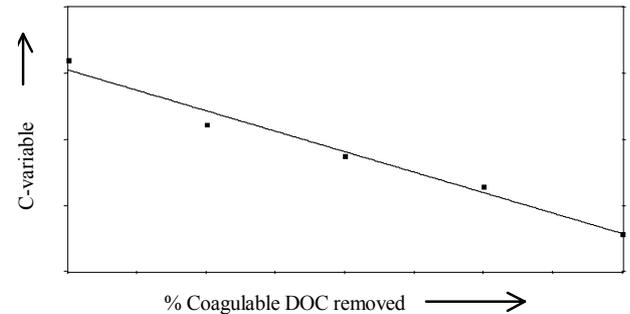
where  $D_1$ ,  $E_1$ ,  $F_1$ ,  $D_2$ ,  $E_2$ ,  $F_2$ ,  $D_3$  and  $E_3$  are constants and P is the percentage of coagulable organics (figures 3 to 5).



**Figure 3.** Relationship between the percentage removed of coagulable DOC and the variable  $A_{2v}$ .



**Figure 4.** Relationship between the percentage removed of coagulable DOC and the variable  $B_{2v}$ .



**Figure 5.** Relationship between the percentage removed of coagulable DOC and the variable  $C_{2v}$ .

Using UV absorbance at 254nm alone as a measure of coagulable organics in raw water,

$$\text{Alum dose (at } \Delta\text{DOC} / \Delta\text{Alum} = -0.015) = A_{3c} + B_{3c} (1 - \exp(-C_{3c} \times \text{UV})) \quad (7)$$

where  $A_{3c}$ ,  $B_{3c}$  and  $C_{3c}$  are constants,

and for a percentage removal of coagulable DOC (between 90% and 50%) using alum,

$$\text{Alum} = A_{3v} + B_{3v} (1 - \exp(-C_{3v} \times \text{UV})) \quad (8)$$

where  $A_{3v}$ ,  $B_{3v}$  and  $C_{3v}$  are variables for percentage reductions, each modelled as follows:

$$A_{3v} = D_4 + E_4 \exp(-P/F_4) \quad (9)$$

$$B_{3v} = D_5 + E_5 \exp(-P/F_5) \quad (10)$$

$$\text{and } C_{3v} = D_6 + P \times E_6 \quad (11)$$

where  $D_4$ ,  $E_4$ ,  $F_4$ ,  $D_5$ ,  $E_5$ ,  $F_5$ ,  $D_6$  and  $E_6$  are constants and  $P$  is the percentage of coagulable organics.

Similar models were fitted to data from jar tests performed on waters using ferric chloride as coagulant.

Using UV absorbance at 254nm and colour of raw water as a measure of coagulable DOC, a model fit of ferric chloride dose (mg/L,  $\text{FeCl}_3$ ) to achieve a gradient of  $-0.015$  for  $\Delta\text{DOC} / \Delta \text{FeCl}_3$  was determined as follows:

$$\text{FeCl}_3 = A_{4c} + B_{4c}/(1 + \exp(-(UVC_{ol} - C_{4c})/G_{4c})) \quad (12)$$

where  $A_{4c}$ ,  $B_{4c}$  and  $C_{4c}$  and  $G_{4c}$  are constants.

For removal of a selected percentage of coagulable DOC (between 90% and 50%) using ferric chloride,

$$\text{FeCl}_3 = B_{4v} (1 - \exp(-C_{4v} \times UVC_{ol})) \quad (13)$$

where  $B_{4v}$  and  $C_{4v}$  are variables for percentage reductions, each is modelled as follows:

$$B_{4v} = D_7 + E_7 \exp(-P/F_7) \quad (14)$$

$$C_{4v} = D_8 + E_8/P^2 \quad (15)$$

where  $D_7$ ,  $E_7$ ,  $F_7$ ,  $D_8$  and  $E_8$  constants and  $P$  is the percentage of coagulable organics.

Using UV absorbance at 254nm of raw water only as a measure of coagulable DOC, a model fit of  $\text{FeCl}_3$  dose to achieve a gradient of  $-0.015$  for  $\Delta\text{DOC} / \Delta \text{FeCl}_3$  is as follows:

$$\text{FeCl}_3 = A_{5c} + B_{5c}/(1 + \exp(-(UV - C_{5c})/G_{5c})) \quad (16)$$

where  $A_{5c}$ ,  $B_{5c}$  and  $C_{5c}$  and  $G_{5c}$  are constants.

For selected percentage removal of coagulable DOC (between 90% and 50%) using ferric chloride,

$$\text{FeCl}_3 = B_{5v} (1 - \exp(-C_{5v} \times UV)) \quad (17)$$

where  $B_{5v}$  and  $C_{5v}$  are variables for  $P$  reductions, each is modelled as follows:

$$B_{5v} = D_9 + E_9 \exp(-P/F_9) \quad (18)$$

$$C_{5v} = D_{10} + E_{10}/P^2 \quad (19)$$

where  $D_9$ ,  $E_9$ ,  $F_9$ ,  $D_{10}$  and  $E_{10}$  are constants and percentage is the percentage of coagulable organics.

Estimation of coagulant doses for removal of a selected percentage of DOC using models 3, 8, 13 and 17 requires some caution due to the changes in the gradient of the curve that relates DOC removal with coagulant dose. The gradient of the curve progressively becomes steeper going from near maximum to 50% removal where the change in dose leads to greater removal of DOC. Increases in error are likely to occur when applying such models for lower percentage DOC removals. Further, coagulant dosing is based only on an indirect measure of organics with the aim of enabling feed-forward prediction. It involves no prior calibration of DOC removal with coagulant dose.

Maximising removal of organics from treated water is dependant on the type of coagulant used and the pH at which coagulation occurs. The general curve of Figure 1 describes the removal of DOC using alum with the pH maintained at a constant level. For each coagulant there is an optimum pH, and above and below this, lower levels of DOC removal results.

Both alum and ferric chloride are coagulants that lower the pH of water during treatment. Therefore, if the pH after coagulant dosing is not the selected pH either the dose rate may be changed or addition of an acid or alkali is required. In order to predict the change in pH with coagulant dosing and the additional acid or alkali for a selected pH, the buffering capacity or alkalinity of raw water needs to be determined. From this the pH titration curve of raw water can be predicted, as previously reported (van Leeuwen et al. 2001).

One model that relates the amount of acid ( $A_c$ ) required to achieve a selected pH ( $SpH$ , between  $\sim 5.5$  and 7) with the raw water buffering capacity is as follows:

$$A_c = K + B/[1 + (SpH/Q)^Z] \quad (20)$$

where  $K$ ,  $Q$  and  $Z$  are constants and  $B$  is a variable related to the buffering capacity or alkalinity of the raw water.  $B$  can be estimated from equations that relate it to the amount of a standard acid required to lower the raw water pH to 5.5 or the alkalinity of raw water as  $\text{CaCO}_3$  or bicarbonate. From knowledge of a coagulant's acidity and the raw water pH titration curve, the shift in pH with coagulant dosing can be estimated. Further requirements of acid or alkali to attain a target pH can then be estimated.

The above models were developed on the basis that input variables are easily, rapidly and cheaply determined. They are feed-forward generic models from which coagulant dose rates and pH control reagents can be rapidly estimated. However, their practical application should be on the basis of validation of predictions through site specific testing. Adjustment of models may be warranted to make them site specific and with incorporation of feed-back parameters (of treated water quality) to further optimise treatment conditions.

#### 4. CONCLUSIONS

Models can be developed that relate coagulant dose to the concentration and character of organics present in natural raw waters. These models can be specific for coagulant type, where the dose is selected either for maximising removal of organics or for a pre-determined percentage removal (90-50%). However, because the modelling approach is solely feed forward, its reliance on indirect DOC measurements and the kinetics of removal of NOM with coagulant dosing, higher errors are likely to be encountered when predicting doses for a selected percentage removal of organics. Acid and alkali addition for pH control, essential for enhanced coagulation, can also be modelled based on the alkalinity of the raw water.

#### 5. ACKNOWLEDGEMENTS

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