

# Modelling Enhanced Alum Treatment of Southern Australian Raw Waters for Drinking Purposes

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**Abstract:** The feasibility of predicting enhanced alum treatment that maximises the removal of natural organic matter (NOM) from ground and surface waters for drinking purposes was investigated. Maximising NOM removal reduces the potential risks associated with disinfection by-product formation and improves the efficiency and stability of disinfectant use. Enhanced treatment can be seen as distinct from treatment based primarily on achieving aesthetically acceptable water quality, where removal of turbidity and colour is the key objective. Development of models for coagulant dose determination in the treatment of water for drinking purposes is based on factors such as the target water quality (anticipated customer and operator expectations) and on the costs and ease of analyses for parameters required in the models. In this study, data of readily obtainable parameters determined to be related to coagulant dosing, such as raw water pH, buffering capacity (alkalinity), turbidity and the concentration and character of NOM, were used in regression models to determine coagulant (alum) and pH adjustment reagent doses. The aim was to develop a generically applicable tool for prediction of alum and reagent doses for pH control for enhanced coagulation treatment. Data from laboratory based jar-tests of 6 southern Australian water sources, that varied in dissolved organic carbon (DOC) concentration, turbidity and alkalinity were used to derive a series of regression models for prediction of alum doses. Using these models, alum doses were then predicted for a further 25 water samples (ranging in DOC concentrations from about 4 to 14 mg/L). The removals of DOC using the predicted doses were similar to maximum removals for these waters. The results of modelled alum dosing for enhanced coagulation were also compared to those with alum dosing used to achieve aesthetically acceptable drinking water, where the criteria is for colour and turbidity removal. Alum doses for enhanced treatment were determined to be about 3 times higher which resulted in an average 30% more removal of UV@254 nm absorbing compounds.

**Keywords:** Enhanced coagulation; Alum treatment; Modelling; DOC; Water supply.

## 1. INTRODUCTION

Treatment of raw waters (surface and ground) for drinking purposes is based on ensuring that the water is safe and that it is aesthetically acceptable to consumers. For aesthetically acceptable water, both removal of colour and turbidity is generally required. The colour of water is mostly due to natural organic matter (NOM), which is usually determined as dissolved organic carbon (DOC) and in fewer cases, is due to high levels of iron in the water. Turbidity can be due to suspended clay particles, algae and particulate organic matter. Water treatment may focus on the removal of the above two water quality parameters.

In contrast, enhanced treatment, which generally involves the use of higher coagulant doses is used to maximise the removal of natural organic matter

from drinking water. This provides benefits by minimising the formation of disinfection by-products and maintaining the disinfectant in the distribution system. Natural organic matter (NOM) is a precursor for chlorinated organic compounds when water is disinfected with chlorine-based compounds. The resulting compounds may be of a health concern and may be more assimilable by micro-organisms in treated water in the distribution system. Enhanced coagulation using inorganic coagulants that are aluminium or iron-based form metal hydroxo complexes that neutralise the overall negative charge of the NOM. The formation of these complexes is pH dependant and consequently maximising removal of NOM from a drinking water involves treatment at a specific pH, dependant on the type of coagulant. Enhanced removal of dissolved organic carbon with alum

[Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> · 18 H<sub>2</sub>O] treatment at three pH levels was demonstrated by van Leeuwen et al. [1999a] and an example is shown in Figure 1. While addition of alum depresses pH, the pH can be manipulated independently of alum by addition of an alkali or acid.

The potential to model the treatment of water for drinking purposes has been shown by Bazer-Bachi et al. [1990], Ellis et al. [1991], Girou et al. [1992], Ratnaweera and Blom [1995] and van Leeuwen et al. [1999b]. Most of these models have been based on empirical relationships between various treated and/or raw water quality parameters and the coagulant dose required to achieve the desired water quality. Due to the wide variation in raw water quality from different sources together with different expectations in the treated water quality, models have tended to be site or region specific. Few studies have been reported in the literature to model enhanced treatment of drinking water supplies. Application of artificial neural networks for determination of coagulant doses in drinking water treatment have been reported by Adgar et al. [2000] and for enhanced coagulation by Stanley et al. [2000]. This paper describes a modelling approach for enhanced alum treatment of raw surface water, which is an extension of earlier work by van Leeuwen et al. [2001]. For the purpose of this work the doses are assumed to be practically suitable for water treatment plants that use sedimentation/filtration and enable maximum or near maximum NOM removal to be achieved.

In this study, pH control, which is dependant on the raw water alkalinity, is also modelled in conjunction with the specific alum demand for DOC and turbidity removal.

## 2. MATERIALS AND METHODS

### 2.1 Determination of Water Quality Parameters

**Colour:** Colour, in Hazen units (HU) was determined by measuring the absorbance of a sample at 456 nm using UV/VIS spectrophotometer (Model 918, GBC, Australia). It was assumed that colour is primarily due to chromophores from higher molecular weight compounds or aggregates with a hydrophobic nature.

**Dissolved organic carbon (DOC) analysis:** DOC concentrations of filtered (0.45 µm) water samples 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:** A Hach ratio turbidimeter (Model 2100 AN, Co., USA) was used to measure turbidities of water samples, as nephelometric turbidity units (NTU).

**pH:** An Orion (Model 420A, MA. USA) pH meter was used.

### 2.2 Sample Collection

Water samples from drinking water reservoirs, ground water supply and from rivers in South Australia and Victoria were collected into 10L plastic containers and stored at approximately 4°C until jar tests were performed. Samples from six water sources (Hope Valley, Middle River, Moorabool, Mt Zero and Myponga reservoirs and Murray River, near Mannum, South Australia) varying in DOC concentration, alkalinity and turbidity were examined using complete jar tests, as previously described [van Leeuwen et al. 1999a]. Data from these experiments were used to generate models for alum dose prediction for enhanced coagulation. Acid titrations were performed on seven raw waters (Barossa, Lt Para, Moorabool, Mt Bold and Tod reservoirs and Murray and Torrens rivers). Jar tests were performed on Murray River water samples high in turbidity, alone and mixed with other natural waters to determine the alum demand exerted by the turbidity.

### 2.3 Alum Dose Determination by Jar Tests

The jar test procedure used is as described by van Leeuwen et al. [2001]. Jar tests were performed at ambient temperature.

### 2.4 pH Control of Water Samples

Reagents used for controlling the pH of water samples were (1) hydrochloric acid (HCl), 0.2 M, BDH grade, AnalaR® 35.4% (2) sodium hydroxide NaOH, APS AJAX, Finechem, Analytical Univar reagent, 0.2 M (3) alum as aluminium sulphate (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> · 18H<sub>2</sub>O), 20,000ppm solution.

## 3. RESULTS AND DISCUSSION

The optimum pH for treatment of raw water with alum is between 5 and 6 and this can be achieved by lowering the pH with an acidic solution. Alum coagulant is acidic and acts by both lowering the pH and allowing the formation of the positively charged hydroxo complexes that react with organic matter. The relationship between a standard acid solution (HCl, 0.2M) volume and alum dose to depress the pH to 5.5 for 13 southern Australian

raw waters is linear ( $r = 0.9962$ ) ie.

$$\text{Acid volume} = 0.0797 \times \text{alum doses} - 0.364. \quad (1)$$

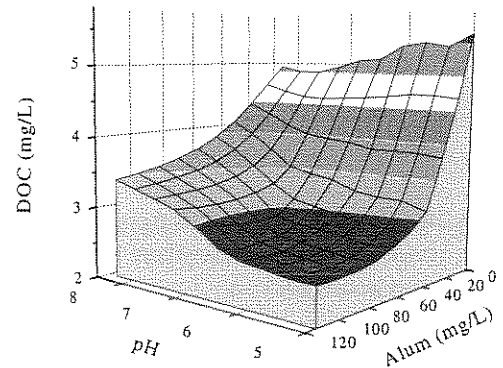
If alum alone were to be used for enhanced coagulation at a pH of about 5.5, the doses would often be much higher than industry acceptance for water treatment, based on coagulant cost. The objective for enhanced treatment is therefore to minimise the alum dose and use less expensive acids or alkali solutions to control the pH. Coagulant dosing for enhanced treatment may be partitioned to two functions; (1) for maximum removal of organics and (2) for achieving the target pH. The latter function of an inorganic acidic coagulant can be achieved using an acid or, if the buffering capacity of the water is low, an alkali reagent.

Four surface water samples (Table 1) were tested for DOC removals at three different pH levels over a range of alum doses. For these samples, the pH was controlled during coagulation. The alum doses applied can be directly related to the reduction of the DOC concentration and its character. The reductions were gradual and levelled off at higher doses until no further removal of DOC was evident. Alum doses were selected which resulted in maximum (Table 1- Trial 1) or near maximum removal of DOC (Table 1-Trial 2). The turbidities of these raw waters were very low and it was assumed that this parameter did not significantly influence the alum doses. In the first attempt to model enhanced treatment, alum doses that clearly provided enhanced coagulation (Table 1, Trial 1 doses) were correlated to the raw water colour and UV@254 absorbance. The following linear relationship was obtained:

$$\begin{aligned} \text{Enhanced Alum Dose 1 (EAD1)[mg/L]} \\ = 76 + 1.6 (\text{colour [Hazen units]} \times \\ \text{UV@254nm/cm}); \quad (2) \end{aligned}$$

From the above equation, alum doses for 15 waters were determined and tested for DOC removals. The doses ranged from ~ 80 to 140 mg/L and in all cases, removals were at or near maximum [van Leeuwen et al. 2001]. Although these doses may be practically acceptable for some waters, this equation resulted in an overestimation of alum doses for waters which had high UV absorbances and colour. Further, in the case where raw water has a low DOC concentration, the minimum dose would still be near 80 mg/L. Although this dose level would provide enhanced coagulation for waters with low DOC, it would probably be excessive in most cases. These high doses would also be unsuitable in water treatment plants where direct filtration is used. For the above reasons,

alternatives to EAD1 were trialed where predictions for alum doses were lower.



**Figure 1.** Dissolved organic carbon concentrations (mg/L) in Hope Valley water following treatment with alum at pH levels targeted at 5, 6 and 7.

**Table 1.** Key water samples used to determine the relationship between alum demand for enhanced coagulation and raw water parameters.

Source	Raw water		Alum (mg/L)	
	DOC	UV	Trial 1	Trial 2
Hope Valley	5.0	0.147	80	60
Mt Zero	9.0	0.265	100	80
Moorabool	6.9	0.178	80	70
Myponga	10.8	0.434	120	100

(DOC as mg/L; UV at 254 nm/cm); Trial 1: maximum DOC removal; Trial 2: near maximum DOC removal.

Lower alum doses (Table 1, Trial 2) that provided at or near maximum DOC removal were subsequently modelled, using linear and non-linear functions and different raw water quality parameters. The following parameters and functions were tested:

Using raw water colour and UV@254nm absorbance;

(a) where a fitted non-linear function passes at or near to the origin and the range extends to that of the available data; in this case raw water with a low DOC concentration would be determined as requiring a low alum dose (Figure 2).

$$\begin{aligned} \text{EAD2[mg/L]} = 0.016 + 92.4 \times [\text{UV@254nm/cm} \times \\ \log_{10}(\text{colour [HU]} \times 10)^{0.3559}], \text{ for UV@254nm/cm} \\ \times \log_{10}(\text{colour} \times 10) \leq 1.25. \quad (3) \end{aligned}$$

and,

(b) beyond the data range used for modelling, a linear function was applied to ensure a consistent alum dose rate per colour x UV absorbance unit, based on the available data.

$$EAD3[\text{mg/L}] = 50 + 41.4 \times [\text{UV@254nm/cm} \times \log_{10}(\text{colour}[\text{HU}] \times 10)], \text{ for } \text{UV@254nm/cm} \times \log_{10}(\text{colour}[\text{HU}] \times 10) > 1.25. \quad (4)$$

Using raw water UV@254nm absorbance alone to ensure a "security" minimal dose where the raw water colour is unusually low,

(c) as per (a) above, where

$$EAD4[\text{mg/L}] = 144.8 \times (\text{UV@254nm/cm})^{0.4426}, \text{ for } \text{UV@254nm/cm} \leq 0.434. \quad (5)$$

and,

(d) as per (b) above, where

$$EAD5[\text{mg/L}] = 43.9 + 131.1 \times \text{UV@254nm/cm}, \text{ for } \text{UV@254nm/cm} > 0.434. \quad (6)$$

The modelling approach taken for DOC removal, is to give precedence to the use of both the colour and UV@254nm parameters. However, where this dose is less than that determined by the UV@254nm parameter alone, the higher dose is then used.

The alum demand from raw water turbidity was estimated based on fine clay turbidity from a Murray River water sample. This was assumed to be of a natural turbidity type that would exert a relatively high alum demand.

In this study the alum demand from turbidity (TD) was estimated as follows:  $\text{TD}[\text{mg/L}] = K \times \text{Turbidity}(\text{NTU})$ , where  $K = 0.4775$ .

Ten water samples were treated at pH 5.5 with alum determined using the above algorithms and constants and acid/alkali addition. Of these, eight had moderate to high alkalinity which were also treated with very high alum doses (~160 to 380 mg/L) to depress the natural raw water pH to 5.5. These high alum doses result in maximum or near maximum removal of DOC [van Leeuwen et al. 2001]. The residuals of UV absorbances of waters treated with the model predicted doses were similar to those treated with the very high doses (Table 2), indicating that near maximum removal of organics had occurred. In order to achieve a target pH for enhanced coagulation, either an acid or a further alum dose needs to be added with the alum dose already determined by equations 2 to 5. If the pH

has been lowered below the target value an alkali would need to be added for pH control.

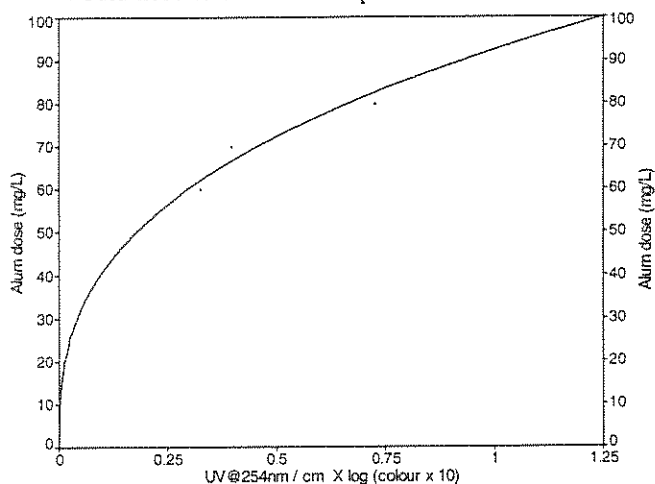


Figure 2. Model fit of UV@ 254 nm/cm x colour (HU) data of four key waters versus Trial 2 alum doses (see Table 1).

The dose response curve for acid addition to raw water with pH change is not linear. An example of this curve is shown in Figure 3.

Table 2. Residual UV@254 absorbance of treated water after model determined and maximum alum treatments.

Source	UV@254nm cm <sup>-1</sup>		
	Raw water	at max. removal	at model dose
1. Barossa Res.	0.274	0.067	0.075
2. Hope Valley R.	0.238	0.059	0.065
3. Lt Para Res.	0.151	0.045	0.050
4. Middle River	0.665	0.070	0.074
5. Moorabool Res.	0.297	n.a.	0.078
6. Mt Bold Res.	0.311	0.070	0.074
7. Murray River	0.258	0.058	0.056
8. Torrens River	0.205	0.052	0.058
9. Tod Res.	0.342	0.103	0.138
10. Sth Para Res.	0.332	0.080	0.087

n.a. Not available.

The dose response curve of standard acid addition (HCl, 0.2 M, mL) to the resultant pH is dependant on the buffering capacity or alkalinity of the raw water and can be described by the following function,

$$\text{Standard Acid Volume}(\text{mL}) = \frac{K}{K + B/[1 + (\text{pH}/Q)^2]} \quad (7)$$

where B is a variable related to the buffering capacity of the raw water and K, Q and Z are constants. For a series of 7 raw water samples from South Australia, these were determined as follows:  
 $K=-0.73$ ,  $Q=6.44$  and  $Z=14.49$ . ( $r^2 > 0.99$ ).

The B variable being directly related to buffering capacity of the water or alkalinity, can also be correlated to either the total alum or total acid dose to depress the natural raw water pH to 5.5.

One algorithm for estimation of the B variable based on the data of seven waters, is as follows:

$$B = 1.91 + 0.7756 \times (\text{Std Acid Vol. to lower the raw water pH to 5.5})^{1.1036} \quad (r^2=0.994). \quad (8)$$

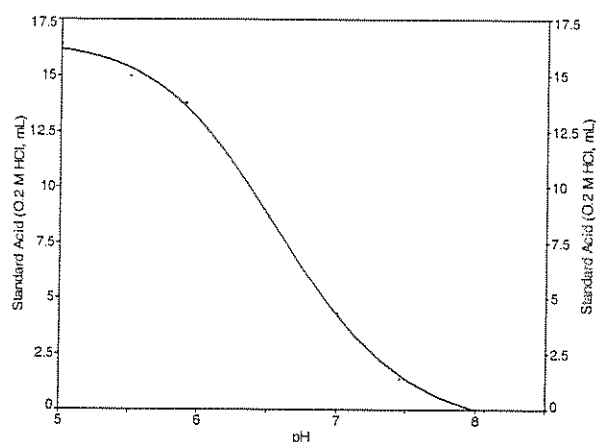
From a standard titration using alum or a standard acid solution to say pH 5.5, the above variable can be estimated and applied for acid/alkali determination for pH control during coagulant dosing. Model determined acid additions for attainment of various target pH levels are shown in Table 3.

From the total acid volume (TA) requirements to achieve a target pH and from the alum dose required for maximising DOC and turbidity removal (ADT), the additional acid or alkali (DpH) for target pH achievement can be determined. This is done by converting the alum dose (ADT) to an equivalent standard acid volume (ESA) and subtracting this from the TA, ie.

$$ESA = 0.357 + \text{Alum dose} \times 0.0778, \text{ and} \quad (9)$$

$$DpH = TA - ESA. \quad (10)$$

From the above, the requirements for enhanced coagulation with alum for southern Australian waters may be estimated. These being the alum dose for maximum or near maximum DOC and



**Figure 3.** Dose response curve of a standard acid addition versus pH of a raw water sample from Little Para Reservoir, South Australia.

turbidity removal and the acid or alkali requirements for attainment of the target pH at which coagulation is to occur. Alkali addition is required where the raw water buffering capacity is insufficient in relation to the acidity of the ADT, causing the pH to be lowered below the target value. This can be readily estimated from the excess of alum acidity in relation to the target pH. The modelling of alum treatment for the attainment of aesthetically acceptable drinking water from southern Australian waters has been previously reported (van Leeuwen et al. 1999b). In that study alum treatment was based on colour and turbidity removal but not DOC reduction. For samples from 14 different waters sources of that study, the mean removal of UV@254nm absorbance was 43% (S.D. 17.6%). With enhanced treatment of this study, using EAD2-EAD4, the mean removal for nine waters was 73% (S.D. 7.5%).

**Table 3.** Model and actual standard acid volumes (HCl, 0.2M, mL) for lowering the pH of seven raw waters.

Water source	7-M	7-A	6.5-M	6.5-A	6-M	6-A	5.5-M	5.5-A
Barossa Res.	2.8	3.3	6.5	7.4	10.7	11.2	13.4	13.4
Lt Para Res.	3.3	4.3	7.4	8.7	12.0	13.0	15.0	15.0
Moorabool Res.	0.9	0.8	2.6	2.2	4.5	4.4	5.7	5.6
Mt Bold Res.	3.2	2.7	7.3	6.9	11.9	11.9	14.9	14.9
Murray R.	3.6	3.1	8.1	7.8	13.2	12.9	16.4	16.4
Tod Res.	7.4	6.9	15.7	14.4	25.2	23.6	31.3	30.2
Torrens R.	3.9	3.9	8.6	8.4	14.0	13.6	17.4	17.3

M, model and A, actual.

The maximum removals of these nine waters were determined to be 76% (S.D. 5.7%). Alum doses applied in the earlier study were on average, about 3 times less than in the present study.

The use of models for determination of coagulant doses may be more readily adopted by larger water treatment plants supplying drinking water to urban populations. These plants would have the capital infrastructure for analytical equipment needed to measure the data required for dose prediction. Benefits could include; rapid determination of treatment requirements for minimising the residual organic content, reduction in disinfection by-product formation and better maintenance of disinfectants in the distribution system.

#### 4. CONCLUSIONS

The results of this study indicate that the models can be used to determine coagulant and pH control reagent doses for enhanced coagulation. This modelling approach is based on readily obtainable raw water quality parameters that should enable application at water treatment facilities. The benefits of adoption of modelling for enhanced coagulation may include rapid determination of alum and pH adjustment reagents, rapid response to raw water quality changes and reduced reliance on labour intensive and time consuming jar tests.

#### 5. ACKNOWLEDGEMENTS

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