

A METHODOLOGY FOR OPTIMISING THE REMOVAL OF CYANOBACTERIA CELLS FROM A BRAZILIAN EUTROPHIC WATER

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Abstract - This work is concerned with optimizing the performance of the coagulation process in terms of the removal of intact cyanobacteria cells and saxitoxins (STX). The evaluation has been carried out through bench-scale jar tests to construct coagulation diagrams for aluminium sulphate, polyaluminium chloride (PACl) and ferric chloride. The test water was taken from a eutrophic surface source, collected at the inlet to the water treatment plant that supplies Ponta Grossa City, Brazil, at a time of high algal activity corresponding to a total of 108833 cells/mL of cyanobacteria. By constructing the coagulation diagram for turbidity, the optimal dose-pH conditions were used in subsequent tests involving both coagulation and sand filtration. In these tests the benefits of adding a cationic synthetic polymer and powdered activated carbon (PAC) to the overall treatment were investigated. From the results of the tests, the optimal dosages and pH for each coagulant, polymer and PAC were obtained corresponding to the lowest concentrations of cyanobacteria cells, STX and turbidity.

Keywords: Alum; PACl; Ferric Chloride; Coagulation; Cyanobacteria; Saxitoxin.

INTRODUCTION

The quality and quantity of surface raw waters depend on the nature and use of the hydrographic basin and human activities can generate significant impacts on aquatic ecosystems, such as the acceleration of eutrophication processes. Eutrophication arises from the enrichment of aquatic ecosystems by nutrients, mainly nitrates and phosphates, which results in the rapid development of aquatic biological species, such as phytoplankton, in rivers, lakes and reservoirs. According to Azevedo and Brandão (2003) the main source of this enrichment has been identified as being the discharge of urban industrial and domestic effluents and from agriculture.

It has been widely reported (e.g., Bittencourt-Oliveira and Molica, 2003; Yamamoto and Nakahara, 2009) that one of the most common features of eutrophication is elevated algal concentrations and periodic blooms. Such intense algal development may be associated with the predominance of a few or even just one species, such as cyanobacteria (*Cyanophyceae*), which may form a dense layer of cells on the water surface, and their presence often leads to significant increases in the water treatment costs and health concerns related to the toxicity of intra-, and extra-cellular substances.

The development of algal blooms in surface waters can alter the treated water quality and cause operational problems in several treatment stages, for

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example with the filtration process. In this case a reduction in the filter run time and consequent increase in the use of filter backwash water leads to a decrease in the net water treatment plant (WTP) production. Other problems include increased coagulant use, greater sludge solids volumes, taste and odour, and chlorination byproduct formation. All these problems cause significant technical difficulties, raise the cost of water production and increase the need to monitor water quality more frequently and at more system points (Di Bernardo, 1995; Viana-Veronezi *et al.*, 2009; McDowall *et al.*, 2009).

In addition, some cyanobacteria genera have species with the potential to produce harmful toxins to humans, of which the most important are *Anabaena*, *Microcystis*, *Cylindrospermopsis*, *Synechocystis*, *Aphanizomenum*, *Lingbya*, *Oscillatoria*, *Phormidium* and *Schizothrix* (Azevedo and Brandão, 2003; Funari and Testai, 2008). The adverse health effects on humans of cyanotoxins can include hepatic problems (hepatotoxins), neurologic problems (neurotoxins), dermatitis (dermatotoxins), cytotoxic reactions (cytotoxins) and contact irritations (endotoxins) (Chorus & Bartram, 1999). The neurotoxins (anatoxin-a, homoanatoxin-a, anatoxin-a(s), saxitoxin and neosaxitoxin) act on the central nervous system, working as muscle blockers, and causing death by respiratory failure. The hepatotoxins include microcistins, nodularins and cilindrospermopsins, which produce symptoms such as weakness, paleness, cold extremities, breathlessness, vomiting and diarrhea, and can also cause death by respiratory failure, hepatic hemorrhage, and in some cases tumor apparition (Carmichael, 1994; Watanabe *et al.*, 1996; Porfirio *et al.*, 1999; Codd, 2000; Falconer, 2005).

In this study the test water originated from the Pitangui River, near to Ponta Grossa City, which was routinely monitored for cyanobacterial neurotoxins between 2001 and 2003 (Yunes *et al.*, 2003). Among six highly toxic neurotoxins identified was saxitoxin (STX), which is the toxin produced by the predominant cyanobacteria, *Cylindrospermopsis*, and the presence of STX has been confirmed by analyses carried out by SANEPAR (the local sanitation company).

The greatest human exposure route to cyanotoxins is believed to be via the water supply (WHO, 2006), and consequently the treatment of raw waters containing high cyanobacteria concentrations requires special care. If the treatment scheme and operating conditions are not optimized, then the removal of these toxins will be inefficient and there is evidence that populations supplied by surface waters that experience extensive algal blooms can be exposed to toxins at low levels for long periods (Lambert *et al.*, 1994). In particular, the treatment

scheme needs to avoid processes that cause the lysis of cyanobacterial cells thereby releasing toxins into solution. Thus, the use of oxidants, while enhancing the treatment and removal of cyanobacterial cells, may have the undesirable effect of disrupting cells and releasing cyanotoxins to the water (Newcombe and Nicholson, 2004).

The increasing degradation of the quality of water sources used for public water supply is causing many problems for WTP operators who need to modify their treatment processes in order to maintain drinking water quality. The study described in this paper is concerned with optimizing the coagulation process of water treatment to maximize the removal of cyanobacterial cells. The evaluation has been carried out through bench-scale jar tests to construct coagulation diagrams for the most commonly applied coagulant chemicals of aluminium sulphate (alum), polyaluminium chloride and ferric chloride, using water samples taken from a eutrophic surface source. The potential benefit of applying a cationic synthetic polymer and powdered activated carbon (PAC) has also been evaluated, and the corresponding removal of background STX has been determined.

MATERIALS AND METHODS

Bench-scale experiments were conducted using a modified jar test apparatus (Nova Ética, Brazil), which enabled the conventional treatment operations of rapid mix, mechanical flocculation, sedimentation (decantation) and filtration to be simulated. Details of the apparatus and methodology are described elsewhere (Di Bernardo *et al.*, 2002). Water samples used in the laboratory tests originated from the Pitangui River, downstream from an eutrophic reservoir, and were collected at the inlet to the water treatment plant (WTP) of the Ponta Grossa City/Brazil sanitation company (SANEPAR) prior to any chemical addition (before the Parshall unit). The WTP employs a conventional process scheme comprising coagulation, flocculation, decantation, filtration, disinfection, fluoride addition and pH adjustment. The samples were collected in December, 2007, during the Brazilian summer, and stored for less than a month in a closed 1000 L PVC reservoir located in a closed (not exposed to the sun) and ventilated room (room temperature 15°C to 25°C) at the WTP.

All jar test experiments were carried out with the water temperature maintained at 20±1°C. Turbidity and pH measurements were conducted using a 2100 Turbidimeter (HACH) and pH meter APA-200 (Meter), respectively, and aluminium and iron

concentrations were measured using a DR 890 (HACH) spectrophotometer.

Cyanobacteria populations were analysed qualitatively (identification) by use of a binocular optical microscope (NIKON, eclipse TS100) and quantified as cell density (cells/mL) by the Utermöhl method (Utermöhl, 1931). The determination of saxitoxin (STX) concentration was by high-performance liquid chromatography (HPLC, VARIAN ProStar), using the method of Oshima (1995) (post-column with Pickering reactor), with a fluorescence detector (ProStar 363) with detection at 390 nm and excitation at 330 nm (detection limit of 1 µg/L).

The remaining analyses and characterization of the test water were undertaken at SANEPAR laboratories following standard methods (Standard Methods, 2005).

For the jar tests the coagulation pH was controlled by the addition of either sodium hydroxide (0.1 N) or hydrochloric acid (0.1 N). The coagulants used were the following commercial products: aluminium sulphate or alum, as $\text{Al}_2(\text{SO}_4)_3 \times 14.3\text{H}_2\text{O}$ liquid (7.64% of Al_2O_3), the same as that dosed at the SANEPAR Ponta Grossa/Brazil WTP; polyaluminium chloride (PACl), as liquid (11.26% of Al_2O_3), the same as that dosed at the SANEPAR Imbituva/Brazil WTP; ferric chloride, as $\text{FeCl}_3 \times 6\text{H}_2\text{O}$ liquid (39.1% FeCl_3), courtesy of Chemical Products Guaçu company, Brazil. Stock solutions of the coagulants were prepared at a concentration of 4 g/L.

The rapid mix, flocculation and decantation conditions used for the jar tests and to construct the coagulation diagrams are shown in Table 1.

Table 1: Jar Test Conditions.

Parameter	Value
Rapid mix time (T_{mr})	10 s
Rapid mix average velocity gradient (G_{mr})	600 s^{-1}
Flocculation time (T_f)	20 min
Flocculation average velocity gradient (G_f)	20 s^{-1}
Settling velocity (V_s)	$V_{s1} = 3.0$ cm/min
	$V_{s2} = 1.5$ cm/min
	$V_{s3} = 0.5$ cm/min

The coagulation diagrams were constructed according to the approach used by Amirtharajah and Mills (1982), for the three settling velocities presented in Table 1 and for the three coagulants included in this study. The curves in the diagrams were built as groups (conjuncts), where the curves delimit the area corresponding to the coagulant dosage and coagulation pH that has a turbidity less than, or equal to, that indicated by the curve. With these diagrams, an optimal point ('selected point') can be selected for each coagulant corresponding to a

specific dose and pH giving the minimum turbidity. Turbidity was chosen as the measure of treatment performance because it is a rapid and convenient measurement, in contrast with the quantitative analysis (i.e., counting the cells), and represents the overall presence of solid particles in suspension (silt, clay, silica, colloids), colloidal organic matter and microscopic organisms and algae, the latter being the principal contaminant of interest in this study. Since turbidity is an indirect measurement of these impurities (AWWA, 1999) conditions giving rise to a minimum turbidity were assumed to be those corresponding to a maximum treatment performance. In the coagulation diagrams shown in Figures 1-9 the notation SP means 'selected point', and NC means 'not collected'.

Having established the 'selected point' for each coagulant, subsequent tests were carried out to examine the additional benefits of adding a synthetic cationic polymer (Magnafloc LT225, Gross 25, 10 KGS, polyacrylamide; the same that is used at the Ponta Grossa WTP) in terms of treated water turbidity and cyanobacteria removal. In these tests the cationic polymer was prepared as a 0.5 g/L stock solution and added to the jar test flasks (2 L) in the middle of the flocculation period (the same as is done at the WTP).

For each coagulant at its 'selected point' and optimal cationic polymer dose, the additional benefits of pre-dosing powdered activated carbon (PAC) (Brascarbo, CarboActiv K800, Brazil, vegetable origin, physical process of activation, sludge number_{min} = 800 mg/g, alkaline pH, apparent density 0.20-0.75 g/cm^3 , total ash_{max} = 12%, moisture_{max} = 8%, mesh_{min}, that pass, # 100 = 99%, # 200 = 95%, # 325 = 90%; also the same that is used at the Ponta Grossa WTP) was evaluated, again in terms of treated water turbidity and cyanobacteria removal. In these tests the PAC was prepared as a 5 g/L stock solution and dosed to the jar test flasks at the selected concentration 15 min before the coagulant addition, under mixing conditions equivalent to a velocity gradient of 125 s^{-1} .

For these tests with polymer and PAC, the experimental procedure included a filtration step after the jar test traditional procedure to simulate the conventional treatment being used at the Ponta Grossa WTP. The filtration step employed a filter column coupled immediately downstream of the jar test flask. The filter column was a 19 mm internal diameter acrylic tube which contained sand as the filter medium (15 cm depth). The effective, minimum and maximum size of the sand was 0.45, 0.33 and 1.37 mm respectively, and the uniformity coefficient was 1.60. The filtration average flow rate

was 16 mL/min (corresponding to a filtration rate of $80 \text{ m}^3/\text{m}^2\cdot\text{d}$) and the filtered water was collected 20 min after the decantation time corresponding to a settling velocity of 1.5 cm/min. It was necessary to filter during 20 min to renew the water inside the filters, since the backwash water is from the tap.

With each coagulation/filtration test the concentrations of residual aluminium or iron, algae (cyanobacteria) and STX in the filtered water were determined.

RESULTS AND DISCUSSION

During the period of the laboratory tests, the water samples had the following quality characteristics: pH = 7.4 ± 0.1 ; apparent colour = 146 ± 43 Hu (H - Hazen unit); turbidity = 11.9 ± 0.5 NTU (nephelometric turbidity unit). These analyses were done every day during the period of tests. The water temperature during all experiments was adjusted to $20 \pm 1^\circ\text{C}$. The water was also characterized immediately after its collection by the SANEPAR laboratories, and the following additional characteristics were obtained: aluminium = 0.241 mg/L ; total dissolved solids = 80 mg/L ; *Aphanizomenon* sp = 903 cells/mL ; *Cylindrospermopsis* sp = 106148 cells/mL ; *Oscillatoriales* sp = 1782 cells/mL . Thus, the sum of cyanobacteria present in the water samples was 108833 cells/mL , consisting predominantly of *Cylindrospermopsis* sp. Equivalent STX concentration was below the method detection limit ($1 \mu\text{g/L}$).

According to classical scientific interpretations, there are two predominant mechanisms of metal ion coagulation, these being 'charge neutralisation' and 'sweep flocculation', with the former occurring at low pH conditions (eg. pH 5-6) with the coagulant in its cationic form (eg. $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_3^+$), and the latter at higher pH (> 6.5) and higher doses where the coagulant precipitates as metal hydroxide (Duan and Gregory, 2003). Between these conditions coagulation may occur by a combination of mechanisms involving colloid charge destabilization, adsorption to floc surfaces, and incorporation within amorphous precipitates. Depending on the nature of the water and the colloid properties the coagulation performance will vary considerably. The results of the jar test study with alum are shown in Figures 1-3 where the residual turbidities for different equivalent settling velocities are summarized for a range of alum dose ($1.3 - 4.1 \text{ mgAl/L}$) and pH ($4.4 - 7.2$). It is evident that the best results (lowest turbidity) were achieved with dosages of commercial product exceeding 60 mg/L and coagulation pH values between 5.4 and 6.9. It is also

clear that, when the pH is outside this range, there is a significant increase in the turbidity, and for lower coagulant dosages ($< 60 \text{ mg/L}$) the turbidity is also greater, indicating that these dosages were insufficient to destabilize, or otherwise coagulate, the water impurities.

From the results presented in Figures 1-3, an optimal dose-pH was selected based on achieving a minimum residual turbidity and without the need to adjust pH by the addition of either alkali or acid. For this water the optimal dose-pH for alum was 2.83 mgAl/L (commercial alum dosage of 70 mg/L) and pH 6.19.

The results of the jar test study with PACl are shown in Figures 4-6. In comparison with the alum results, it can be seen that satisfactory results were achieved with lower equivalent coagulant dosages (as Al), and with a greater coagulation pH range of between 5.9 and 7.8.

For this water the optimal dose-pH for PACl (selected point), based on the results shown in Figures 4-6 and without any pH adjustment by hydroxide or acid addition, was 2.09 mgAl/L (commercial PACl dosage of 35 mg/L) and pH 6.80. Thus, PACl appears to offer considerable advantages over alum as a coagulant since the equivalent aluminium dose is approximately 26% lower, the pH reduction due to the coagulant is 50% less, and the gravimetric dosage of commercial coagulant is 35 mg/L instead of 70 mg/L (hence lower chemical dosing and storage costs in practice). In addition, the lower coagulant dose with PACl compared to alum is expected to give rise to a lower sludge production at the WTP.

The results of the jar tests with ferric chloride are shown in Figures 7-9. It is evident that, for the whole range of ferric chloride doses tested, 35 to 100 mg/L as commercial product, the results in relation to turbidity removal were satisfactory. For this dose range the corresponding coagulation pH range was between 4.8 and 7.7, which was a greater range than that found with PACl. Such a broad pH range is advantageous practically since it provides WTW operators with greater flexibility in order to optimize the treatment process for multiple contaminant removal objectives, and unavoidable variations in pH during treatment should not cause significant changes in coagulation performance. For this water the optimal dose-pH for ferric chloride (selected point), based on the results shown in Figures 7-9 and without any pH adjustment by hydroxide or acid addition, was 7.41 mgFe/L (commercial ferric chloride dosage of 55 mg/L) and pH 6.22.

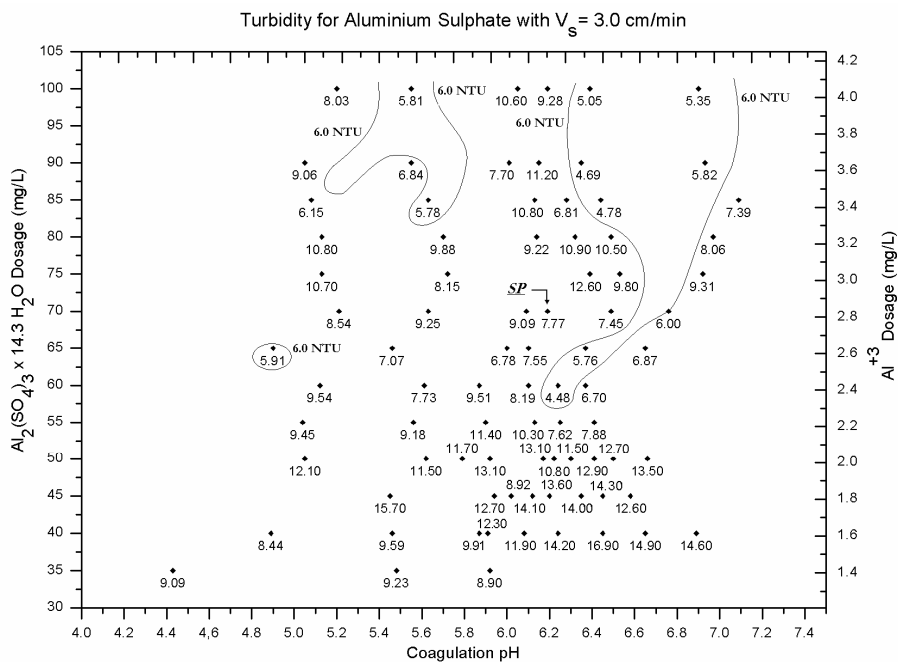


Figure 1: Alum dose – pH coagulation diagram for residual turbidity (NTU) at an equivalent settling velocity of 3.0 cm/min (concentration units on left hand scale show dose of commercial product). Note: SP = Selected point.

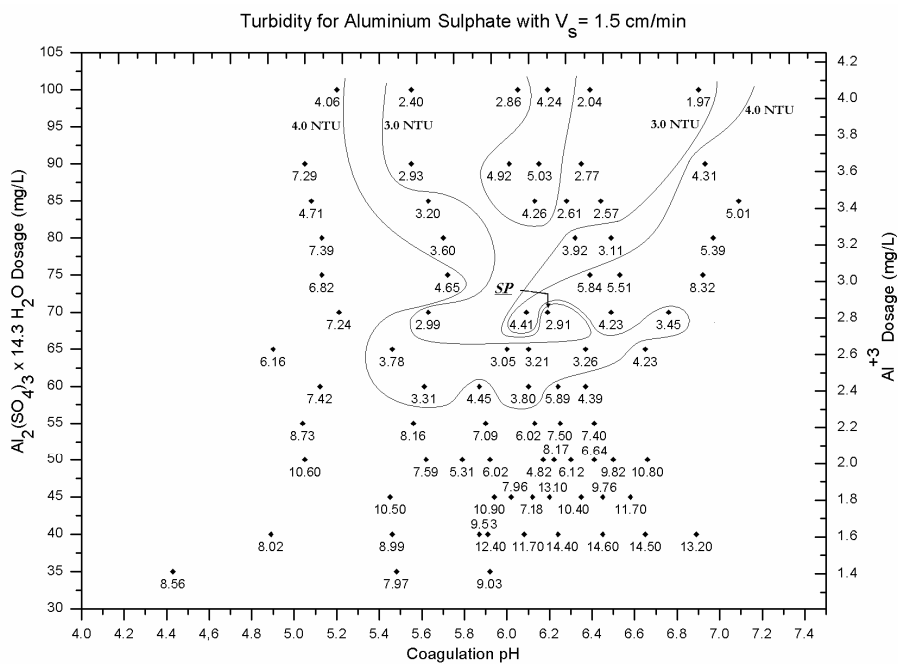


Figure 2: Alum dose – pH coagulation diagram for residual turbidity (NTU) at an equivalent settling velocity of 1.5 cm/min (concentration units on left hand scale show dose of commercial product).

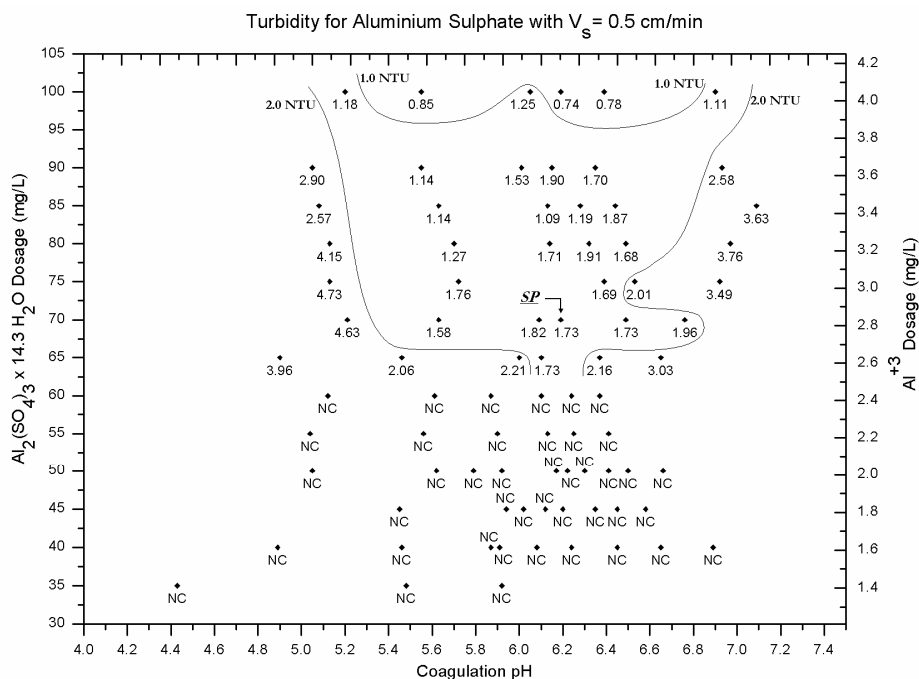


Figure 3: Alum dose – pH coagulation diagram for residual turbidity (NTU) at an equivalent settling velocity of 0.5 cm/min (concentration units on left hand scale show dose of commercial product). Note: NC = Not collected.

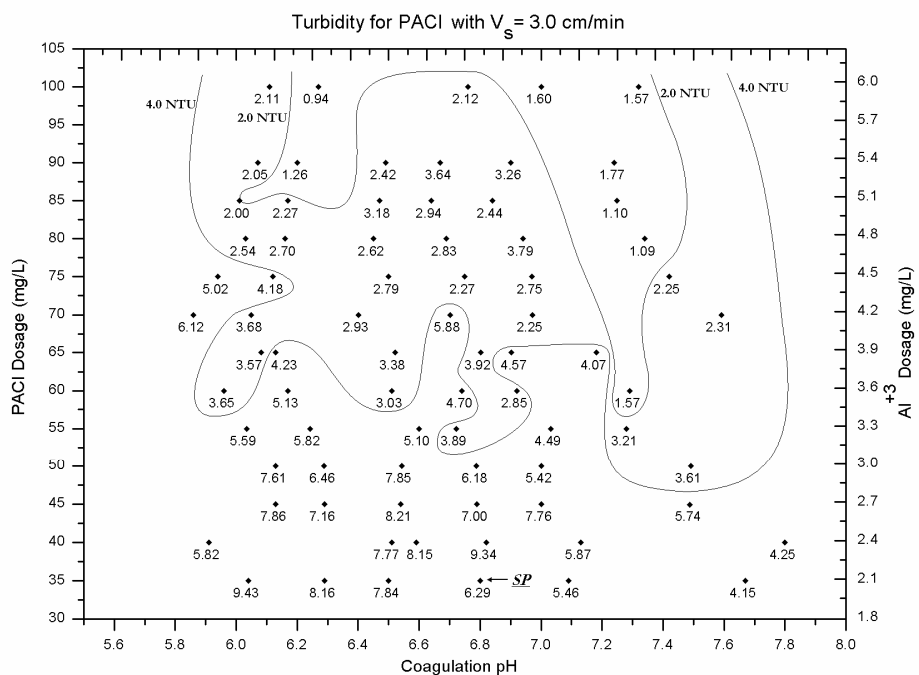


Figure 4: PACl dose – pH coagulation diagram for residual turbidity (NTU) at an equivalent settling velocity of 3.0 cm/min (concentration units on left hand scale show dose of commercial product).

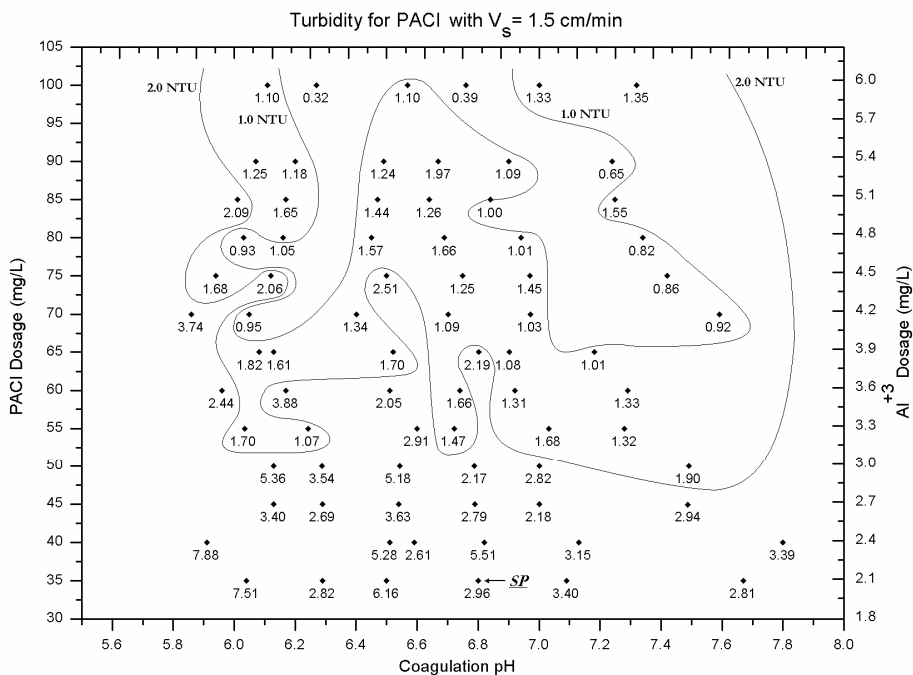


Figure 5: PACl dose – pH coagulation diagram for residual turbidity (NTU) at an equivalent settling velocity of 1.5 cm/min (concentration units on left hand scale show dose of commercial product).

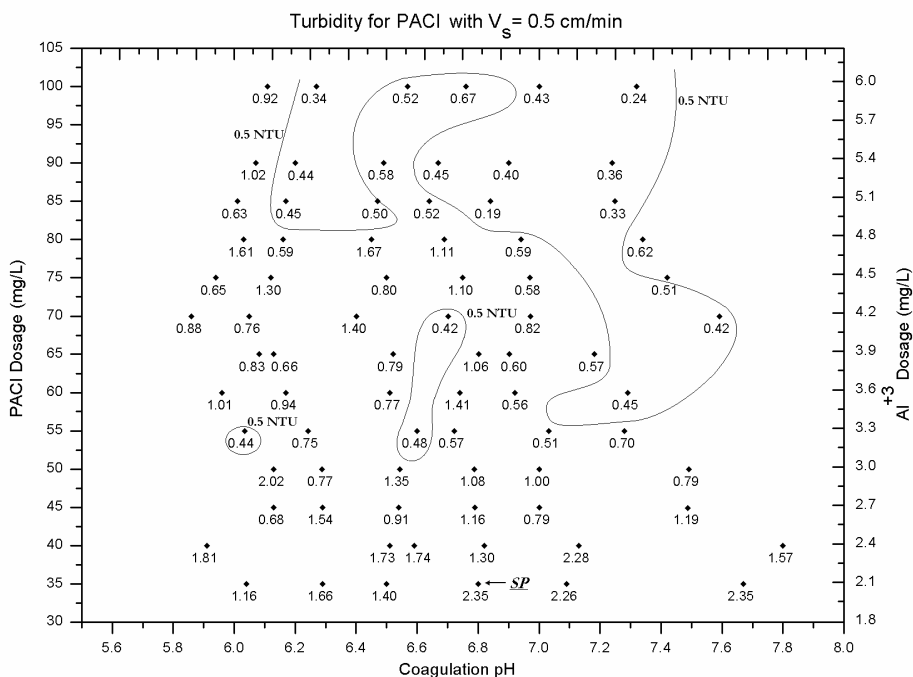


Figure 6: PACl dose – pH coagulation diagram for residual turbidity (NTU) at an equivalent settling velocity of 0.5 cm/min (concentration units on left hand scale show dose of commercial product).

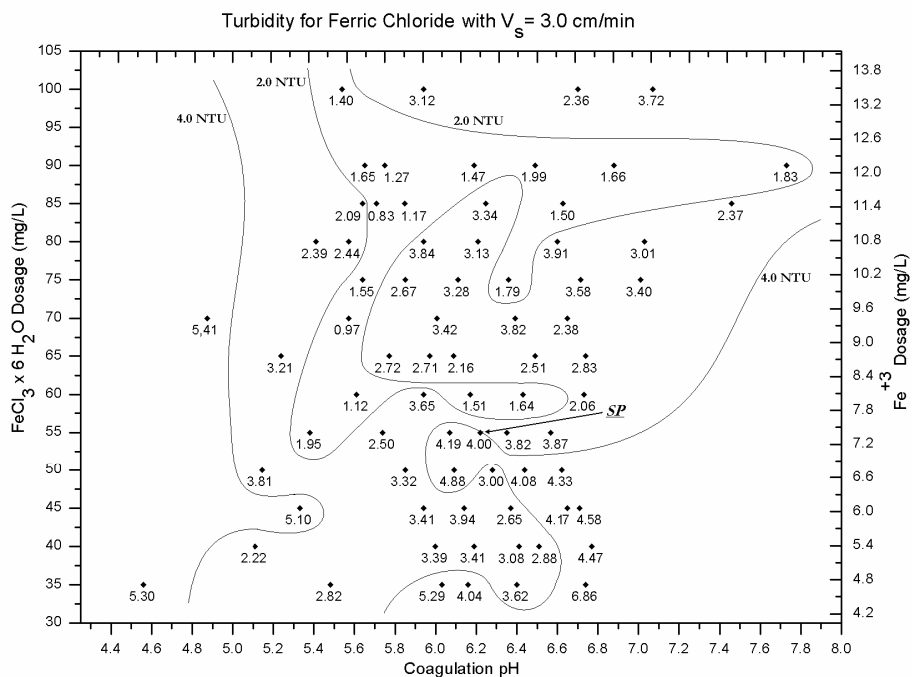


Figure 7: Ferric chloride dose – pH coagulation diagram for residual turbidity (NTU) at an equivalent settling velocity of 3.0 cm/min (concentration units on left hand scale show dose of commercial product).

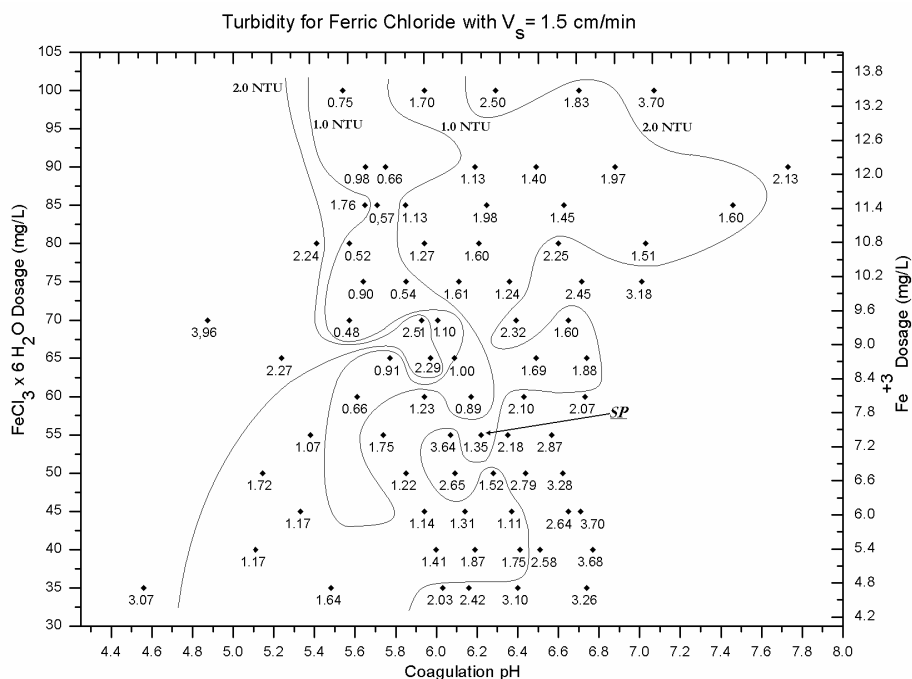


Figure 8: Ferric chloride dose – pH coagulation diagram for residual turbidity (NTU) at an equivalent settling velocity of 1.5 cm/min (concentration units on left hand scale show dose of commercial product).

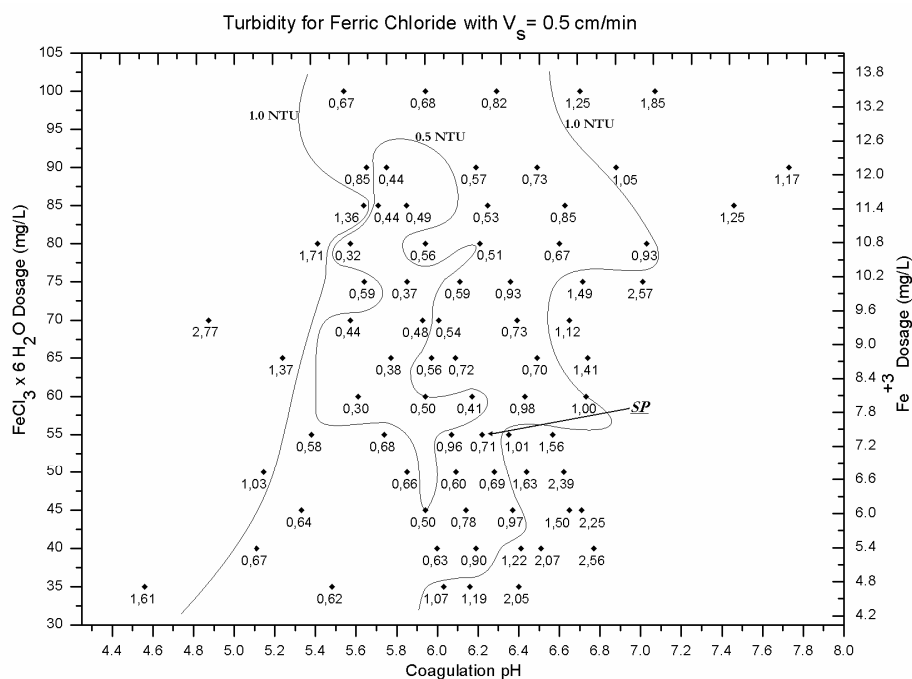


Figure 9: Ferric chloride dose – pH coagulation diagram for residual turbidity (NTU) at an equivalent settling velocity of 0.5 cm/min (concentration units on left hand scale show dose of commercial product).

By comparison of the selected/optimal Al and Fe dosages for the three coagulants it is clear that in gravimetric terms the Fe dosage was approximately 2.6 times the Al dosage with alum (viz. 7.4 mgFe/L and 2.8 mgAl/L), and 3.5 times the Al dosage with PACl (viz. 7.4 mgFe/L and 2.1 mgAl/L). In molar terms the corresponding dose ratios were 1.26:1 Fe:Al (alum), and 1.71:1 Fe:Al (PACl). Thus, under these conditions the aluminium coagulants were more dose-efficient than the ferric chloride, and PACl was more dose-efficient than alum. However, the residual turbidity was lower with ferric chloride compared to the aluminium coagulants, suggesting a greater treatment performance with the iron coagulant, while alum and PACl were similar in their performance. In contrast, Jun *et al.* (2001) reported that alum was more effective in algal removal (based on *Synedra* spp.) than PACl and ferric chloride from the results of jar tests with samples from a Korean WTW source water. Such differences are to be expected given that the predominant coagulation mechanism for a particular coagulant and type of water will be determined by the actual dose applied and resulting pH of the solution. In the tests reported here, the predominant mechanism is believed to be

sweep coagulation, with the formation of the metal hydroxide, $\text{Al}(\text{OH})_3$ or $\text{Fe}(\text{OH})_3$, leading to flocs of a size and density capable of settling relatively rapidly. As expected, the extent of floc settling was dependent on the settling time (with the lowest V_s presenting the lowest residual turbidity, as it is shown in Figures 1-9) and a residual turbidity of < 3 NTU was achieved at an equivalent settling velocity of 0.9 m/h.

Having established the 'selected point' for each coagulant, subsequent tests were carried out to examine the additional benefits of adding a synthetic cationic polymer in terms of treated water turbidity and cyanobacteria removal, after both coagulation/settling and filtration, and the results are summarized in Tables 2-4. Some minor changes in the coagulation pH were believed to be caused by the effects of water storage on water quality and because of PAC and polymer addition.

Table 2 shows that for alum a polymer dosage of 0.4 mg/L was not enough to achieve total cyanobacteria removal after filtration. With greater polymer doses (0.6, 0.8 and 1.0 mg/L) the cyanobacteria removal was complete and the turbidity of the filtered water systematically decreased with increasing polymer dose, even

though the turbidity of the coagulated water increased slightly with polymer dose. Since the use of polymer adds to the cost of water treatment, a 'practical' optimal polymer dose can be taken to be 0.6 mg/L since this achieved the principal treatment objective of a complete removal of cyanobacteria and a satisfactory filtered water turbidity; greater polymer doses produced only minor improvements in filtered water turbidity.

Table 3 shows that for PACl the 0.4 mg/L polymer dosage was not enough for total cyanobacteria removal after filtration. A higher dose of 0.6 mg/L was sufficient to achieve a complete removal of cells and a low level of filtered water turbidity. Increasing the polymer dose to 0.8 and 1.0 mg/L did not achieve a greater filtered water quality, so the practical optimal polymer dosage for PACl was 0.6 mg/L.

Table 4 shows that with ferric chloride the 0.4 mg/L polymer dosage, as for the other coagulants, was not enough to achieve total cyanobacteria removal after filtration. While polymer doses of 0.6 and 0.8 mg/L both achieved a complete removal of cells, the lowest filtered water turbidity was with the latter dose, so the practical optimal polymer dosage was chosen to be 0.8 mg/L.

For each coagulant at its 'selected point' and 'practical' optimal cationic polymer dose, the additional benefits of pre-dosing powdered activated

carbon (PAC) were evaluated, again in terms of treated water turbidity and cyanobacteria removal. Table 5 concerns the use of alum as the primary coagulant and shows that, with increasing PAC dosage from 5-20 mg/L, there was a systematic decrease in the filtered water turbidity and cyanobacteria cell concentration. A PAC dosage of 20 mg/L was clearly the optimal dose since it achieved a complete removal of cyanobacteria cells and the lowest filtered water turbidity.

With PACl as the primary coagulant, the results summarized in Table 6 show a similar behavior to that for alum, whereby the quality of the filtered water improves with increasing PAC dosage. In this case a PAC dose of 10 mg/L is sufficient to achieve complete removal of cyanobacterial cells, but higher PAC doses also achieved lower filtered water turbidities. In this case the practical optimal PAC dosage was 15 mg/L.

With ferric chloride as the principal coagulant, Table 7 shows that each of the PAC doses employed was sufficient to achieve complete cyanobacteria removal. Increasing the PAC dose between 5 and 20 mg/L gave lower filtered water turbidities, and at 20 mg/L PAC the filtered water turbidity was 0.32 NTU. In selecting a 'practical' optimal dose, the results suggest that 15 mg/L would be sufficient to achieve final water quality objectives and avoid the greater cost of dosing at 20 mg/L.

Table 2: Variation of filtered water quality (residual turbidity and cyanobacteria concentration) with cationic polymer dosage for alum.

Al ₂ (SO ₄) ₃ x 14.3 H ₂ O Dosage (mg/L)	Polymer Dosage (mg/L)	Coagulation pH	Settled Water		Filtered Water		
			Turbidity (NTU)		pH	Turbidity (NTU)	Cyanobacteria (cells/mL)
			3.0 cm/min	1.5 cm/min			
70	0.4	6.64	0.64	0.59	7.19	0.56	36
70	0.6	6.59	0.66	0.67	7.14	0.51	0
70	0.8	6.53	0.71	0.87	7.20	0.49	0
70	1.0	6.50	0.76	0.73	7.19	0.33	0

Table 3: Variation of filtered water quality (residual turbidity and cyanobacteria concentration) with cationic polymer dosage for PACl coagulant.

PACl Dosage (mg/L)	Polymer Dosage (mg/L)	Coagulation pH	Settled Water		Filtered Water		
			Turbidity (NTU)		pH	Turbidity (NTU)	Cyanobacteria (cells/mL)
			3.0 cm/min	1.5 cm/min			
35	0.4	7.00	0.50	0.46	7.41	0.32	48
35	0.6	7.07	0.55	0.63	7.48	0.35	0
35	0.8	7.05	0.74	0.49	7.28	0.58	24
35	1.0	7.08	0.61	0.66	7.47	0.42	0

Table 4: Variation of filtered water quality (residual turbidity and cyanobacteria concentration) with cationic polymer dosage for FeCl₃ coagulant.

FeCl ₃ x 6 H ₂ O Dosage (mg/L)	Polymer Dosage (mg/L)	Coagulation pH	Settled Water		Filtered Water		
			Turbidity (NTU)		pH	Turbidity (NTU)	Cyanobacteria (cells/mL)
			3.0 cm/min	1.5 cm/min			
55	0.4	6.71	1.28	1.14	7.23	0.41	48
55	0.6	6.67	1.87	1.33	7.17	0.48	0
55	0.8	6.76	1.76	1.49	7.13	0.31	0
55	1.0	6.68	1.71	1.61	7.10	0.32	36

Table 5: Variation of filtered water quality (residual turbidity and cyanobacteria concentration) with PAC dosage for alum.

Al ₂ (SO ₄) ₃ x 14.3 H ₂ O Dosage (mg/L)	Polymer Dosage (mg/L)	PAC Dosage (mg/L)	Coag pH	Settled Water		Filtered Water		
				Turbidity (NTU)		pH	Turbidity (NTU)	Cyanobacteria (cells/mL)
				3.0 cm/min	1.5 cm/min			
70	0.6	5	6.62	0.78	0.64	7.24	0.51	154
70	0.6	10	6.58	0.83	0.65	7.23	0.49	59
70	0.6	15	6.67	0.67	0.62	7.24	0.35	24
70	0.6	20	6.59	0.61	0.67	7.18	0.35	0

Table 6: Variation of filtered water quality (residual turbidity and cyanobacteria concentration) with PAC dosage for PACl coagulant.

PACl Dosage (mg/L)	Polymer Dosage (mg/L)	PAC Dosage (mg/L)	Coag pH	Settled Water		Filtered Water		
				Turbidity (NTU)		pH	Turbidity (NTU)	Cyanobacteria (cells/mL)
				3.0 cm/min	1.5 cm/min			
35	0.6	5	7.11	0.64	0.77	7.36	0.40	36
35	0.6	10	7.16	0.66	0.75	7.55	0.41	0
35	0.6	15	7.17	0.55	0.56	7.64	0.26	0
35	0.6	20	7.22	0.56	0.60	7.60	0.28	0

Table 7: Variation of filtered water quality (residual turbidity and cyanobacteria concentration) with PAC dosage for FeCl₃ coagulant.

FeCl ₃ x 6 H ₂ O Dosage (mg/L)	Polymer Dosage (mg/L)	PAC Dosage (mg/L)	Coag pH	Settled Water		Filtered Water		
				Turbidity (NTU)		pH	Turbidity (NTU)	Cyanobacteria (cells/mL)
				3.0 cm/min	1.5 cm/min			
55	0.8	5	6.72	1.67	1.59	7.23	0.49	0
55	0.8	10	6.70	1.72	1.60	7.19	0.54	0
55	0.8	15	6.83	1.57	1.51	7.32	0.40	0
55	0.8	20	6.75	1.50	1.60	7.26	0.32	0

Finally, for each primary coagulant at its optimal dose and pH, and optimal polymer and PAC dosage as indicated in Tables 5-7, for all tested coagulants, jar test-filtration experiments were carried out to determine the residual aluminium or iron and STX concentration in the filtered water (and at the same time the reproducibility of the experiments). The results obtained were as follows: cyanobacterial cells were not found in the filtered water in all cases;

0.019 mg/L of aluminium with alum as coagulant; 0.006 mg/L of aluminium with PACl as coagulant; residual iron was below the method detection limit of iron (< 0.01mgFe/L) with ferric chloride as coagulant; equivalent STX concentrations were below the method detection limit in all cases.

The treatment performance in these tests can be compared to those of Orr *et al.* (2004) who studied alternative treatment methods to remove saxitoxins,

specifically: granular activated carbon (GAC) (15 min contact time – approximately the same contact time as the PAC applied in this research); ozone; ozone + GAC; hydrogen peroxide + ozone. The findings of the tests were that only GAC treatment (with or without ozone) was able to achieve STX-equivalents below 3 $\mu\text{g/L}$, and the lowest concentration obtained with GAC alone was 1 $\mu\text{g/L}$. These results and those reported in this paper indicate clearly that activated carbon is a treatment step that must be included in a WTP when STX is present in the raw water.

Overall, the experimental methodology undertaken in this study, in which the dose-pH coagulation diagram was constructed on the basis of residual turbidity (a rapid and non-expensive test parameter), has been demonstrated to be effective and useful in assisting WTP operators to identify quickly the optimal treatment conditions to match changes in raw water quality. In particular, the methodology minimizes the number of samples that need to undergo cyanobacteria quantification and cyanotoxin analysis, which are expensive and time-consuming measurements.

CONCLUSIONS

This paper has described an experimental methodology for optimising the coagulation conditions, with the co-addition of a cationic polymer and PAC, to achieve the greatest removal of cyanobacteria cells and saxitoxins. Coagulation diagrams of coagulant dose versus pH have been constructed from jar test experiments in terms of settled turbidity for aluminium sulphate, polyaluminium chloride and ferric chloride. With these tests settled turbidity was used as a surrogate for the removal of cyanobacteria cells. Optimal dose-pH conditions, or 'selected points', have been identified for each coagulant with the objective of avoiding the need to adjust pH by the addition of either acid or alkali.

For the water used in this study PACI appears to offer considerable advantages over alum as a coagulant since the equivalent aluminium dose was approximately 26% lower, the pH reduction due to the coagulant was 50% less, and the gravimetric dosage of commercial coagulant was 35 mg/L instead of 70 mg/L (hence lower chemical dosing and storage costs in practice). In addition, the lower coagulant dose with PACI compared to alum is expected to give rise to a lower sludge production at

the WTP. Ferric chloride was found to give satisfactory results in relation to turbidity removal over a wide coagulation pH range (4.8 - 7.7), which was greater than that found with PACI. Such a broad pH range is advantageous practically since it provides WTW operators with greater flexibility in order to optimize the treatment process for multiple contaminant removal objectives, and unavoidable variations in pH during treatment should not cause significant changes in coagulation performance.

By comparison of the selected/optimal Al and Fe dosages for the three coagulants, it is clear that in gravimetric terms the Fe dosage was approximately 2.6 times the Al dosage with alum and 3.5 times the Al dosage with PACI. In molar terms the corresponding dose ratios were 1.26:1 Fe:Al (alum), and 1.71:1 Fe:Al (PACI). Thus, under these conditions the aluminium coagulants were more dose-efficient than the ferric chloride, and PACI was more dose-efficient than alum. However, the residual turbidity was lower with ferric chloride compared to the aluminium coagulants, suggesting a greater treatment performance with the iron coagulant, while alum and PACI were similar in their performance.

The optimal dose-pH conditions for each coagulant were used in subsequent tests involving both coagulation and sand filtration to simulate conventional treatment and the benefits of adding a cationic synthetic polymer and powdered activated carbon (PAC) to the overall treatment were investigated. From the results of the tests, the optimal dosages and pH for each commercial coagulant, polymer and PAC were obtained, corresponding to the lowest concentrations of cyanobacteria cells, STX and turbidity. In all cases, under the optimal conditions, the treated water was found to meet Brazilian and European drinking water standards in relation to the key parameters under study, these being turbidity, cyanobacteria, saxitoxins, and residual aluminium or iron concentration.

In conclusion, the experimental methodology undertaken in this study, in which the dose-pH coagulation diagram was constructed by jar testing on the basis of residual turbidity (a rapid and inexpensive test parameter), has been demonstrated to be effective and useful in assisting WTP operators to select the most appropriate coagulant and identify quickly the optimal treatment conditions to match changes in raw water quality. In particular, the methodology minimizes the number of samples that need to undergo cyanobacteria quantification and cyanotoxin analysis, which are expensive and time-consuming measurements.

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NOMENCLATURE

alum	aluminium sulphate
GAC	granular activated carbon
N	normal
NC	not collected
NTU	nephelometric turbidity unit
PAC	powdered activated carbon
PACl	polyaluminium chloride
SANEPAR	Parana Sanitation Company
SP	selected point
STX	saxitoxins
Hu	Hazen unit
V_s	settling velocity
WTP	Water Treatment Plant

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