Performic acid (PFA): tests on an advanced primary effluent show promising disinfection performance

R. Gehr, D. Chen and M. Moreau

ABSTRACT

Performic acid, or PFA (CH_2O_3), is a well-known oxidizing agent and disinfectant in the medical field and food industry. It has recently become available on a commercial scale for potential use in wastewater disinfection. This study investigated its application to an advanced primary effluent which is recalcitrant to disinfection by UV and peracetic acid (PAA). Methods were developed for determining PFA concentrations in stock solutions as well as in residual concentrations in the wastewater. Batch and continuous-flow pilot studies showed a correlation between log fecal coliform removals and PFA doses. A PFA dose of approximately 3.4 mg/L and a contact time of 45 minutes could achieve 3-logs removal, and almost total disinfection could be achieved using a dose of 6 mg/L. The by-products of PFA addition are hydrogen peroxide and formic acid (CHOOH), neither of which is considered to be toxic to aquatic fauna at the doses required for disinfection.

Key words | advanced wastewater primary treatment, disinfection, performic acid

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INTRODUCTION

Performic acid, or PFA (CH_2O_3) is an oxidizing agent which is used in protein mapping to cleave disulfide bonds (Simpson 2007). It is also a well known disinfectant in the medical field and the food industry, due to its effectiveness against viruses, bacterial spores, microscopic fungi and mycobacteria, and because its degradation product – formic acid, FA - is acceptable as a food preservative (Bydzovska & Merka 1981). It is an unstable product which needs to be generated shortly before use, and can release a large amount of energy if not prepared and controlled carefully (Ripin *et al.* 2007). Recent patents have been granted which involve the preparation of PFA on a commercial scale using either FA and hydrogen peroxide (H_2O_2) plus a catalyst (Mattila & Aksela 2000) or FA, H_2O_2 and peracetic acid (PAA) (Pruess *et al.* 2001).

PFA is normally applied as a quaternary solution of PFA, H_2O, H_2O_2 and FA. Thus residuals following application would include all four compounds. For example, for a PFA dosage of 3 mg/L, using a 14% PFA solution, 6.3 mg/L of FA would also be added (Kemira, 2007). The degradation products include CO_2, O_2, and oxygen and hydroxyl radicals. None of these are considered toxic to aquatic life at doses which would be used for disinfection, and in fact tests with FA have yielded LC_{50} values of 46 – 175 mg/L for fish, 120 – 150 mg/L for Daphnia and 25 mg/L for algae (Kemira 2007).

To the best of our knowledge, although PAA has been tested and used at full-scale as a disinfectant for wastewater reuse (Simpson (2007); Koivunen & Heinonen-Tanski 2005), no published reports exist for a similar application for PFA. Bydzovska and Merka (1981) obtained over 5-log reductions of the Ø × 174 bacteriophage in water at PFA doses of 0.025 mL/L (~ 25 mg/L) after 5 minutes exposure, therefore it appeared reasonable that PFA might be successful against wastewater indicator bacteria, such as fecal coliforms (FC), at realistic doses and contact times. Primary wastewater effluents are difficult to disinfect to low target FC counts (such as 200 – 1,000 CFU/ 100 mL) due to their high organics and solids concentrations and their high FC counts. This is true when using UV radiation, as well as

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oxidizing chemicals such as PAA. PAA is successful only at relatively high doses (2 - 5 mg/L, depending on the target; Santoro *et al.* 2007). This renders its economics problematic in many cases. Accordingly, the purpose of this study was to assess the disinfection efficiency of PFA when applied to a primary effluent which had been treated by coagulation with various combinations of alum, ferric chloride and anionic polymer for suspended solids and phosphorus removal.

METHODS

Unless otherwise mentioned, all analytical measurements followed conventional procedures in *Standard Methods* (APHA *et al.* 1998). Colour was measured by spectrophotometer at 585 nm to approximate the yellow colour of the wastewater samples. NH_3 and H_2S were measured by commercial test kits from Hagen and Hach, respectively. ORP was measured by means of a platinum electrode. Fecal coliforms were measured by *Standard Methods* method 9222 D (Membrane Filter Procedure). Coliphages were measured by Method 1602 of the US EPA, Enterococci by Method 1600 (mEI) of the US EPA (both available on the US EPA web site), and *Clostridium perfringens* by means of a modified m-CP medium (Armon & Payment 1988).

Batch tests

Batch tests were conducted in 1L jars at room temperature (~22 °C) on composite effluent samples from a physico-chemical wastewater treatment plant. Each test used a combination of doses (blank, 0.5, 1, 2, 4 mg/L) and contact times (5, 10, 20, 30 minutes). Each combination was repeated at least three times in random sequence on different days.

Pilot tests

The pilot plant was designed by Kemira Water Solutions Canada and installed at the same treatment plant from which the batch samples were obtained. The pilot plant comprised three parts: PFA preparation and storage unit (including preparation pump, reactors, emergency alarm, flushing system, cooling system), PFA injection system (include peristaltic pump and inline mixer) and PFA contact tanks. These consisted of two identical stainless steel tanks, each with 8 baffles to encourage plug flow, in series to give nominal contact times of 45 minutes and 90 minutes respectively at 50 L/min flow rate. Test samples were taken at the ends of the first and second contact tanks.

PFA preparation; addition of PFA and tracer to the wastewater

PFA was prepared in batches for both the batch tests and the continuous-flow pilot plant. For the latter, fresh batches of PFA were prepared each day and stored in a fridge, from which the PFA was added continuously via in-line mixer to the wastewater flow by peristaltic pump prior to the contact tanks. The doses ranged from 1 to 6 mg/L. A tracer study was conducted using a salt solution (30 g/L) which was prepared and injected as a pulse of 15 L.

Hydrogen peroxide (35 mL, 50 Wt%, Sigma-Aldrich) was added to a 50-mL volumetric flask; this was topped up with deionized water to 50 mL to dilute the hydrogen peroxide to 35 Wt% as required. Formic acid (50 mL, 85 WT%, Univar) was added to a 100-mL Erlenmeyer flask, followed by 4.7 mL concentrated (95–98 Wt %) sulphuric acid as a catalyst. A water bath was used to keep the mixture temperature below 20 °C. The hydrogen peroxide solution prepared in step 1 was slowly added to the formic acid prepared in step 2 in the water bath. The mixture was maintained at 20 °C for 90 minutes, following which the PFA solution was ready for use. This solution prepared according to the above procedure is approximately 9 Wt% of PFA, and has a density of 1.18 g/cm^3. Proportionally larger volumes of the reagents were used with the pilot plant when necessary.

PFA concentration measurements

Indirect method - ABTS-HRP colourimetric assay

For quality control, it was essential to measure the concentrations of the initial PFA, residual PFA after the contact time, and final PFA to confirm effective quenching. The literature is sparse concerning methodologies for measuring PFA residual

concentrations as well as quenching practice. Wagner *et al.* (2002) have developed a method for PAA using an ABTS-HRP colourimetric assay; it was adapted and found in the current study to be suitable for PFA as well. When PFA is added to the assay solution, ABTS (2,2″-azino-bis[3-ethylbenzothiazoline-6-sulfonic acid] diammonium salt) is oxidized to its radical cation ($ABTS^{+}$) by PFA and H_2O_2 in the solution, due to the catalytic function of horseradish peroxidase (HRP) at pH 6.0. The amount of $ABTS^{+}$ oxidized is expressed in terms of absorbance at 405 nm measured by spectrophotometer (Model 8453 diode array spectrophotometer, Hewlett-Packard Co., Palo Alto, California) after 6 minutes of PFA addition. The total assay volume is 2.4 mL. The assay mixture consists of 0.2 mL of 20 mM ABTS of 98% purity from Sigma Chemical Co., St. Louis, MO. (in pH 6.0 phosphate buffer solution) and 0.2 mL of HRP (Sigma Chemical Co., St. Louis, MO., USA), 0.5 mg/mL in pH 6 phosphate buffer solution. The remaining 2.0 mL is composed of the phosphate buffer and the sample. The sample volume was varied from 0.2 to 1.6 mL. Prior to testing, a calibration curve for PFA was constructed. As shown in Figure 1, which is a typical calibration curve obtained during the study, the equation in the figure is the calibration equation used to calculate the initial, residual and after-quenching concentrations of PFA.

Direct analytical method for PFA

Because the PFA solution prepared on site is a mixture containing H_2O_2, and the HRP enzyme can utilize both PFA and H_2O_2 to oxidize ABTS to ABTS +, the ABTS-HRP assay cannot distinguish between these two species, hence before constructing a standard curve, it was essential to obtain an accurate PFA concentration. An analytical method developed by Kemira Chemicals was used, as described below. This method is unsuitable for wastewater matrices due to colour interferences.

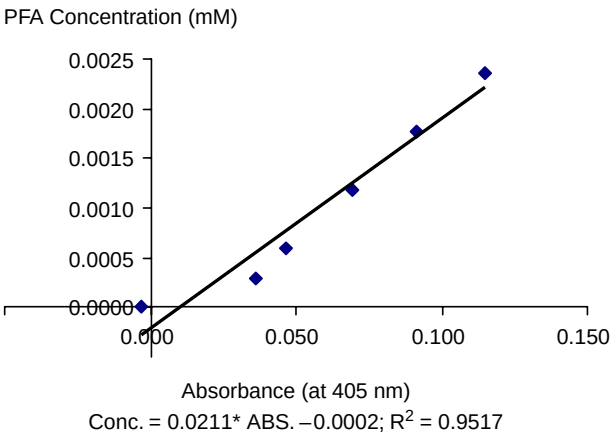

Figure 1 | Typical PFA concentration calibration curve.

Determination of the hydrogen peroxide concentration

100–200 mg of the performic acid sample is accurately weighed into the titration vessel containing 10 mL of 5% H_2SO_4 solution. One piece of ice is added to maintain the temperature of the aliquot solution under 10 °C. 40 mL of 5% H_2SO_4 solution and three drops of ferroin indicator (Merck 109193) are added and the sample is titrated with 0.1 N ammonium cerium sulphate from orange to light blue.

The hydrogen peroxide (H_2O_2) concentration is calculated as follows:

$$H_2O_2(\mathrm{Wt}\%) = \frac{V_1 \times N_1 \times t_1 \times E_1 \times 100\%}{m_1} \quad (1)$$

where:

t_1 = titer of 0.1 N $(NH_4)_4Ce(SO_4)_4$ solution
m_1 = weight of the performic acid sample (mg)
V_1 = consumption of the 0.1 N $(NH_4)_4Ce(SO_4)_4$ solution (mL)
E_1 = equivalent weight of H_2O_2 (17)
N_1 = actual normality of the 0.1 N $(NH_4)_4Ce(SO_4)_4$ solution

Determination of the performic acid concentration

5 mL of a 10% potassium iodide (KI) solution (Merck 105043), three drops of a 3% ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}$) solution (Merck 101182) and 1 mL of a 1% starch solution (Merck 101252) were added to the aliquot solution, from which PFA was titrated. The liberated iodine was titrated with a 0.1 N $Na_2S_2O_3$ solution from dark brown to orange.

The performic acid concentration is calculated as follows:

$$\mathrm{HCOOOH}(Wt\%) = \frac{V_2 \times N_2 \times t_2 \times E_2 \times 100\%}{m_2} \quad (2)$$

where:

t_2 = titer of 0.1 N $Na_2S_2O_3$ solution
m_2 = weight of the performic acid sample (mg)

V_2 = consumption of the 0.1 N $Na_2S_2O_3$ solution (mL)
E_2 = equivalent weight of *HCOOOH* (62/2 = 31)
N_2 = actual normality of the 0.1 N $Na_2S_2O_3$ solution

PFA quenching

The performic acid/hydrogen peroxide residual was quenched with sodium thiosulfate at 150 mg/L and catalase (Sigma Chemical Co., St. Louis, MO.) at 50 mg/L. It has been observed that the addition of catalase before sodium thiosulfate was not effective in eliminating hydrogen peroxide (Wagner *et al.* 2002).

RESULTS AND DISCUSSION

Characteristics of the wastewater samples are shown in Table 1.

The PFA stock solution was found to be reasonably stable at 20 °C over $2\frac{1}{2}$ hours; actual concentrations and doses were within 10% of the nominal values, and the quenching procedure described above left no residuals of either H_2O_2 or PFA.

Batch tests

Concentration x time (Ct) values ranging from 2.5 to 120 mg-min/L were tested. As can be seen in Figure 2, the minimum mean log removal of fecal coliforms is 2.70, which is at 0.5 mg/L PFA for 5 minutes contact time (Ct = 2.5 mg-min/L). At 4 mg/L PFA and 10 minutes contact time (40 mg-min/L), the fecal coliforms in the treated sample were below detection levels (equivalent to > 6-log reduction).

The PFA solution is a mixture containing H_2O_2, water, formic acid, and performic acid. For comparison purposes, two additional blank tests were conducted to evaluate the disinfection efficiency of the components of PFA: first, a hydrogen peroxide blank solution was prepared exactly as for the preparation of PFA, but replacing formic acid with deionized water. Second, a formic acid blank solution was prepared exactly as for the procedure for PFA, but instead of adding hydrogen peroxide to form PFA, deionized water was used. The same volume of blank solution as for a PFA

Table 1 | Characteristics of wastewater samples

Test & dates	Coagulant	COD (mg/L)	H_2S (mg/L)	N_0^* ($\times 10^{-3}$)	pH	SS (mg/L)	Temp (°C)	Turb. (NTU)	UVT* (%)
Batch, Apr & May, 2006	100% $FeCl_3$ to 15% $FeCl_3$ + 85% alum	37–238 Mean 110	N/A	70–1,110 Mean 550	7.4–8.1 Mean 7.6	10–100 Mean 25	25	N/A	9.6–63.3 Mean 33.8
Pilot, Aug – Oct, 2006	30% $FeCl_3$ + 30% alum to 70% $FeCl_3$ to 30% alum	77–179 Mean 126	0–1.7 Mean 0.64	50–8,000 Mean 1,700	5.9–7.9 Mean 7.06	16–72 Mean 25	10–26 Mean 21	4.5–51.1 Mean 12.8	8.3–76.9 Mean 26
Pilot, Nov, 2006	0–40% $FeCl_3$ and 60 – 100% alum	77–143 Mean 108	0	110–1,000 Mean 400	6.9–7.4 Mean 7.1	14–33 Mean 26	12–15 Mean 14	6.4–50.2 Mean 12.7	3.1–51.7 Mean 31.6

*N_0 = initial fecal coliform count (CFU/100 mL); UVT = UV transmission.

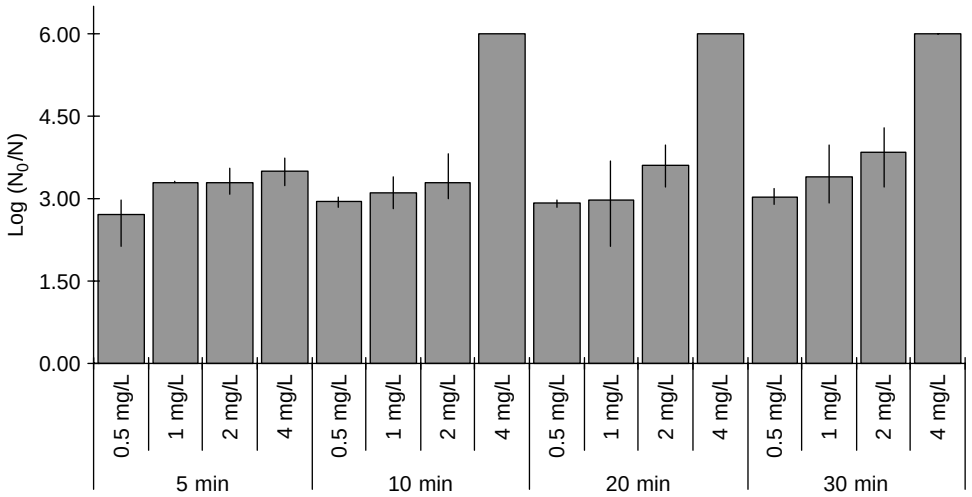

Figure 2 | Batch test disinfection results (log reductions). Bars indicate range (max. and min.)

dose of 1.2 mg/L was added to samples for 5 minute contact times. Results are shown in Figure 3. Both blanks showed slight growth (negative log removal), whereas PFA at 1.2 mg/L for 5 minutes contact showed more than 3 logs removal of fecal coliforms. This demonstrates that PFA, alone or in combination with H_2O_2, is the component in the solution which is responsible for disinfection.

The product of disinfectant concentration (C, mg/L) and contact time (t, min.) is a common design parameter for chemical disinfection. This parameter is based on the concept that dose and contact time have the same impact on disinfection performance, hence a change in one may be compensated for by a change in the opposite direction by the other. Alternatively, if one or other parameter has a greater or lesser influence, this is accounted for by a power factor, for example, using $C^{0.8}t$ instead of Ct.

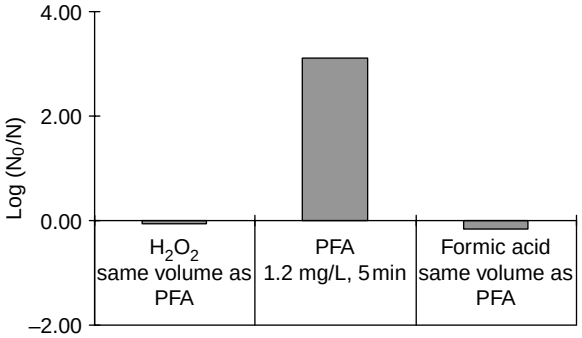

Figure 3 | Comparison of PFA disinfection efficiency and blanks.

Various combinations of Ct were tested, and the combination shown above in Figure 4, i.e. Ct with no power factor, gave the highest coefficient of regression (R^2). This value is very low (0.2618), indicating a poor relationship between N_0/N and Ct, and this is evident in the scatter of the data about the trend line. A probable explanation for this behaviour lies in the unsteady nature of "C" itself. The concentration used in the figure was the *applied* concentration, whereas the concentration which should be used is the *integrated residual* concentration. In this case, the residual concentration would have to be monitored continually over the contact period, and a mean or median value taken which would be more reflective of the action of the disinfectant over the entire course of the contact period. Alternatively, more sophisticated models could be applied which would account for changes in both C and N_0/N over time (Santoro *et al.* 2007). Such data were not available for this study, and it would be advisable to collect them in future work with PFA.

Pilot tests

For the tracer studies, the calculated mean detention time of the first contact tank was 47.8 minutes and that of the combined first and second tanks was 90.8 minutes. To evaluate the flow type, T_{90}/T_{10} was calculated, where T_{90} and T_{10} are the times of passage of 90% and 10% of the tracer, respectively. T_{90}/T_{10} for the first contact tank is 2.42,

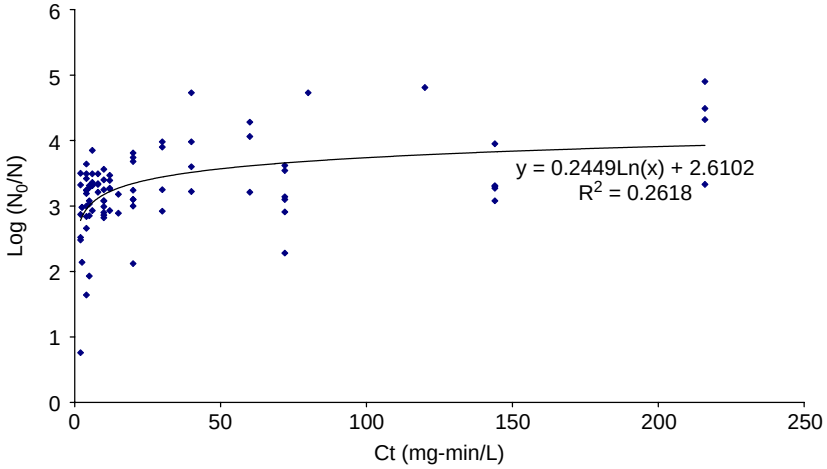

Figure 4 | Batch test disinfection results (log reductions) vs Ct.

and T_{90}/T_{10} for the second tank is 2.01, which indicates that both tanks are functioning at close to plug flow conditions (Droste, 1997).

The ORP of the treated (PFA dose of 5.6 mg/L) and untreated wastewaters was measured at intervals of 0, 45, and 90 min. in batch tests, as well as for samples from the first and the second contact tanks. ORP increased significantly immediately after injecting the PFA. The elevated ORP remained virtually unchanged throughout the entire process. ORP could possibly be used on-line for PFA dosage control.

Disinfection results are shown in Figure 5 below. From the average results, as well as the maximum and minimum removals, to achieve 2–3 log removals of FC, the practical dosage of PFA is between 2 to 4 mg/L, and 45 min. contact time is sufficient to achieve the target removal efficiency.

Figure 6 shows a 7-day moving average of the PFA dose, the initial FC count and the log FC removal, for a 1-month period, using a contact time of 45 minutes. Although the initial FC count varies over a range close to 1 log, the log FC removal follows reasonably closely the PFA dose. This is also illustrated by the correlation line in Figure 7. Therefore if, for example, a target count of 1,000 CFU/100 mL is desired for this wastewater effluent, and the influent FC count were 10^6 CFU/100 mL, a PFA dose of 3.4 mg/L would likely achieve the objective.

The disinfection of enterococcus, coliphage and *Clostridium* microorganisms was also evaluated. Samples

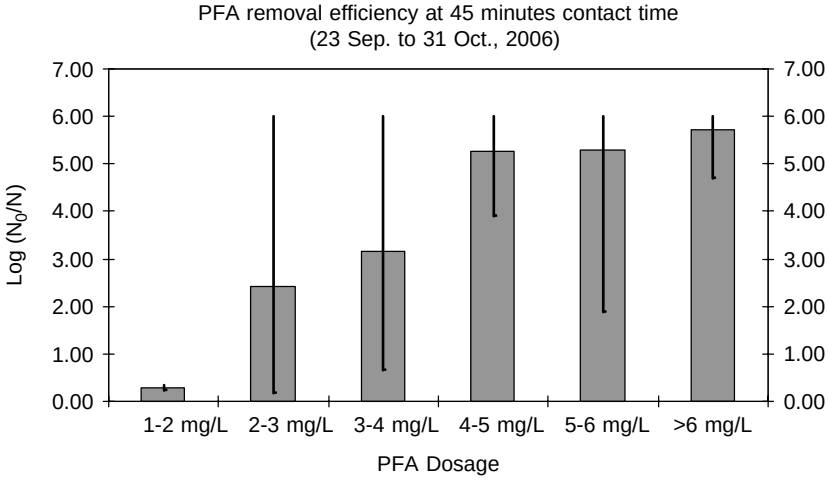

Figure 5 | Dose–response results (average and range) for fecal coliform inactivation by PFA.

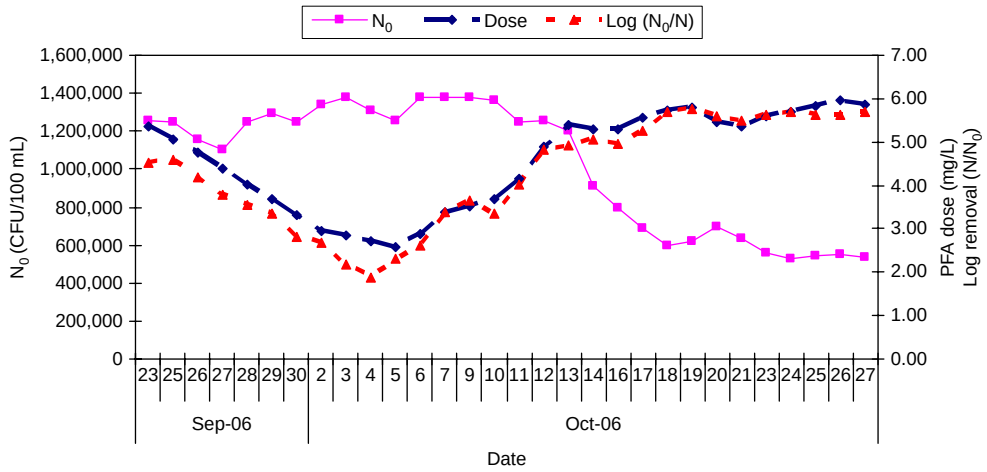

Figure 6 | Seven-day moving average of disinfection performance.

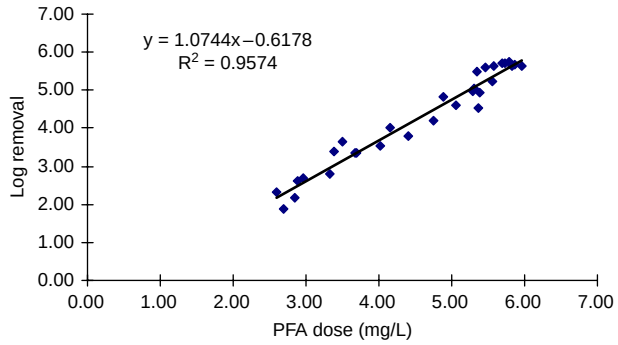

Figure 7 | Correlation of dose–response data, Sept and Oct, 2006.

were taken three days per week; PFA was quenched after 90 min. contact time in the pilot plant. Removals of enterococcus of 4 −6 log could be achieved at 5 to 6 mg/L PFA. However, for coliphage and *Clostridium*, only 1 to 2 log could be removed at the same dose.

CONCLUSIONS AND RECOMMENDATIONS

PFA, a new disinfection method for wastewater, can achieve high log removals of indicator organisms at practical doses. In this study on a physicochemical wastewater effluent, 2 to 4 mg/L PFA at 45 min. contact time could achieve 2 to 3 logs removal of fecal coliforms during the summer and fall months. Further developments on the efficiency of PFA production and application in a continuous-flow system will likely improve this performance. The PFA had no effect on the wastewater's natural colour, and it increased the ORP. By-product formation and toxicity to fauna is unknown at this stage; it is recognised that carboxylic acid (formic acid) and hydrogen peroxide would be discharged with the effluent together with any performic acid residuals. Clearly the effects of these two aspects of disinfection practice, i.e. by-product formation and toxicity, need to be taken into account when contemplating full-scale applications of PFA, and further research is necessary. Safety issues will also enter any full-scale, continuous-flow design applications, as PFA needs to be generated continuously and maintained below 20 °C.

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