

## Analysis of a clariflocculation process with a photometric dispersion analyser (PDA2000)

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**Abstract** In this experimental study the clarification process of the drinking water treatment plant (WTP) of Florence (Italy) has been evaluated. At present, the most common way to optimise the clariflocculation process (best type and dosage of coagulants and mixing conditions) is the jar-test procedure which can give information about the final turbidity, and consequently the process efficiency, after a settling period in a batch procedure at laboratory-scale. An alternative method with a Photometric Dispersion Analyser (PDA2000) was recently introduced at the WTP to provide quick and continuous information (flocculation index, correlated with the flocs size) about the aggregation state of particles during a modified jar-test procedure. The PDA2000 was applied to a real suspension (namely Arno river water) providing useful data for the determination of best type and optimum dosage of coagulants. Furthermore a strong correlation between the removal efficiency of the turbidity and PDA a parameter derived from the PDA 2000 data (defined as the rate of the square root of the flocs size index and the maximum slope of the growing curve) was observed.

**Keywords** Coagulation; flocculation; flocs characteristics; jar-test; photometric dispersion analyser

### Introduction

The city of Florence (Italy) is supplied with drinking water from the Anconella treatment plant which draws water from the Arno river. The water varies greatly in composition and turbidity during the whole year (between 2.5 and 1,500 NTU). The WTP utilises pre-chlorination, coagulation-flocculation-sedimentation (by two traditional clariflocculator systems types Door and Pulsator), rapid sand filtration, ozonation and post chlorination. The plant supplies about 240,000 m<sup>3</sup> per day. Obviously the clariflocculation process is a step of fundamental importance for the final water quality. At present the well known jar-test procedure (Black, 1957) is used to optimise the clariflocculation process (best type and optimum dosage of coagulants and mixing conditions) and every day a medium of 14,000 kg of coagulants are used in the plant. The jar-test can give information on the final water quality after a sedimentation period in a batch procedure at laboratory-scale, but there is no comprehension of what happens during the destabilisation (coagulation) and floc formation (flocculation) phases.

As reported previously (Gregory, 1984) a simple flow-through optical monitoring technique gives detailed information on the growth and break-up of flocs in modified jar-test procedure and this technique can be easily used in parallel with the jar-test. For hetero-disperse suspensions, a Flocculation Index (FI) can be defined and it can be shown that larger value of FI imply larger flocs sizes (Rossi, 2000), although in practical systems detailed flocs size information cannot be derived. As the FI value can continuously acquired by a Photometric Dispersion Analyser (PDA2000), the coagulation-flocculation process can be monitored. The principle of the PDA2000 device has been presented by Gregory and Nelson (1986) and is based on the measurements of the fluctuation of the transmitted light through a suspension. The method has been successfully applied to kaolin suspensions, thus providing important data for the determination of the best type and

dosage of coagulants and mixing conditions (Gregory and Rossi, 2001). Therefore a useful comparison between the performance of different coagulants (growing rate and flocs sizes), which gives some insight into their mode of action, can be made. A PDA2000 was recently introduced at the Anconella plant to provide quick and continuous information about the aggregation state of particles during the jar-tests. In this case, the PDA2000 was applied to a real suspension, namely Arno river water.

## Experimental

### Materials

*Suspension.* Raw Arno river raw water was used. The first step was to characterise the suspension for its mineral composition with the Philips PW 1050/25 computer controlled powder diffractometer (Cu radiation). The analysis of the samples showed most of the material (about 75%) as clay (as the granular dimension is less than 2  $\mu\text{m}$ ), most of which is fillosilicate. The rest is lime (about 20%) as the granular dimension is bigger than 2  $\mu\text{m}$ . Our analyses (Table 1) were in good agreement with an earlier study (Bencini *et al.*, 1995) even if the river conditions were completely different when samples were taken. This means that the mineral concentration has a limited variability and hence the coagulant dosage depends on the total suspended solid (TSS), which in turn is highly variable, more than the variation in mineral composition.

As summarized in Table 2 the physical characteristics of water during the experimental period (July–September 2000) are variable especially in turbidity with a maximum peak at 40 NTU and a medium value of 23.7 NTU.

*Coagulants.* Five different types of coagulant were used (Table 3), all of them are commercial polyaluminium chloride (PACl) products from different companies. The solutions were used directly without prior dilution because it could have significant deleterious effects on the performance of the products.

### Equipment

*Apparatus.* A jar test device was used in this study. With this unit, 100 rpm fast mixing for one minute, 40 rpm slow stirring for 10 minutes, and 20 minutes sedimentation time (when the final turbidity had to be measured) were used. The vessel was a 1,000 ml Pyrex beaker,

**Table 1** Mineral analysis of the suspension: our result compared to Bencini and Malesani (1995)

Clay mineral	Our analysis (%)	Bencini and Malesani (1995) (%)
Vermiculite	25	30 $\pm$ 4
Illite-montmorillonite	20	18 $\pm$ 4
Clorite-vermiculite	15	9 $\pm$ 3
Clorite	15	11 $\pm$ 2
Kaolin	15	17 $\pm$ 3
Illite	10	15 $\pm$ 3

**Table 2** Suspensions characteristics

	Temp. (°C)	pH	Turb. (NTU)
No samples	50	50	50
Max	28.3	8.44	40
Min	19.5	7.58	9.5
Mean	24.2	7.97	23.7
Stand. Dev.	7.1	0.21	8.4

**Table 3** Coagulants characteristics

Name	pH	Density [kg/dm <sup>3</sup> ]	Al <sub>2</sub> O <sub>3</sub> [%wt]	OH <sup>-</sup> [%]	Cl <sup>-</sup> /SO <sub>4</sub> <sup>2-</sup>
A	2.3	1.23	9.25	63.5	2.98
B	2.8	1.24	10.2	66	43.3
C	2.35	1.19	10.1	40.5	
D	2.06	1.24	10.17	71	7.3
E	2.3	1.2	10.5	38.5	22

with a rectangular stirrer blade (750 mm × 250 mm), positioned 50 mm above the base of the beaker. For the flocculation monitoring a Photometric Dispersion Analyser (PDA 2000, Rank Bros Ltd, Cambridge, UK) was used. The flocculating suspension was conveyed through a PVC tube by a peristaltic pump at a rate of 0.5 L/min. As the obtained floc sizes were out of range, the PVC tube supplied by the Rank Bros had to be replaced with a larger diameter tube and the PDA settings had to be adjusted. The sample continuously passed through the PDA detector and the monitoring was carried out directly through the transparent tubing. The results were recorded in terms of Flocculation Index (FI). The output from the PDA was converted to digital form and the data stored in a personal computer spreadsheet for subsequent analysis (see Figure 1). For the turbidity measurements a Hach 2100N Turbidimeter was used.

#### Procedure

The suspensions were used both for jar-tests and PDA2000 experiments. Two litres of test suspension was placed in two different flocculation beakers (1 litre each) and both stirred at the same speed: 1 minute at 100 rpm, 10 min at 40 rpm. In the jar-test vessel, the final turbidity and therefore the removal efficiency was measured after 20 minutes with no stirring to allow the suspension to settle. In the other vessel sample was pumped at about 0.5 L/min through the tubing and the FI value was monitored by the PDA2000 device (Figure 1). After allowing time for steady readings to be established, coagulant at the required dosage (the WTP dosage was chosen as reference) was added to both vessels. Readings were taken every second and the results stored in a computer for subsequent spreadsheet analysis. This procedure allowed us to obtain the aggregation rate ( $G$ , which is the maximum slope of the growing curve) and an index of the floc size ( $B$ , see below) obtained under the same conditions as those used for the jar-tests experiments. A total of 50 tests were carried out under specific conditions such as different types and dosage of coagulants.

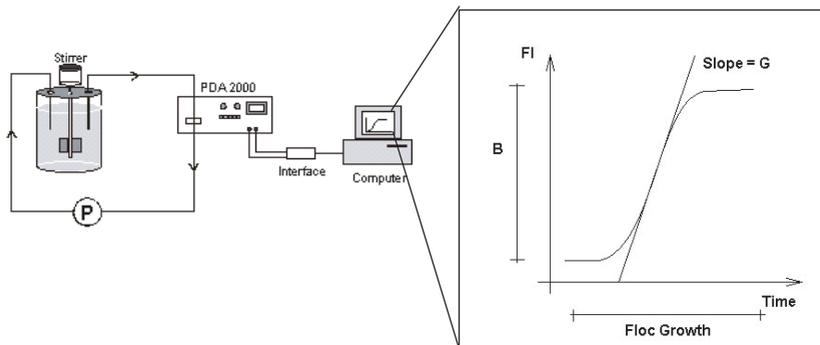
## Results and discussion

#### Curve fitting

All the curves (FI-time) obtained during the experimentation can be fitted empirically to a simple mathematical form such as the sigmoid curve:

$$FI = a + \frac{B}{1 + \exp\left(-\frac{t-c}{d}\right)} \quad (1)$$

where the flocculation index (FI) at time  $t$  depends on the empirical parameters  $a, B, c$  and  $d$ . The value of  $a$  reflects the initial FI value, before the flocculation starts. As the initial particle size can be assumed the same for all tests this parameter is negligible in this work. The value  $B$  is related to the ultimate floc size as shown in Figure 1,  $c$  is the time at which the curve reaches the maximum slope and  $d$  is related to the rate of increase. There is no fundamental justification for fitting experimental data to the sigmoid curve, but it provides



**Figure 1** Flocculation test arrangements with a typical flocs growing curve

a convenient means of analysing the results. Using curve fitting routine, it is possible to find best fit values for all the parameters, and the maximum slope ( $G$ ) of the curve can also be derived.

#### Different dosage

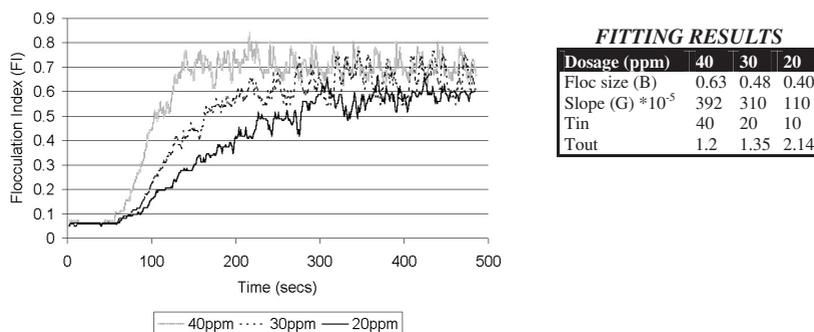
Figure 2 shows a typical case of different dosage of the same type of coagulant. The stirring conditions were the same in all the experiments. In all cases an increase of the PACl dosage gives a higher rate of increase in the FI value (slope of the curve,  $G$ ), and greater values of FI (larger floc size). As the dosage of the coagulant is increased both the effects are less pronounced (see next).

#### Different coagulants

As shown in Figure 3 different coagulants (type A,B,C,D,E, see Table 3) can be compared. By dosing the same quantity of coagulant under the same initial conditions, the effect on variation of floc size ( $B$ ) and growth rate ( $G$ ) were compared.

Growth rate and floc size were determined by the sigmoid fitting for each curve obtained during the experimentation. Hence the medium value of each parameter for single reagents was determined (Figure 4). With this kind of suspension reagent B and D obtain bigger flocs whereas reagent B and A permit a faster growth rate. The medium values of the PDA2000 parameters for coagulants C and E are evidently lower. This does not necessarily mean that coagulants C and E are less effective.

For a better understanding of the results obtained from the fitting, the values of the each parameter were plotted against the dosage for single coagulant, and log-curves were used to



**Figure 2** Changes of Flocculation Index by different dosage of coagulant type A and the relative fitting results

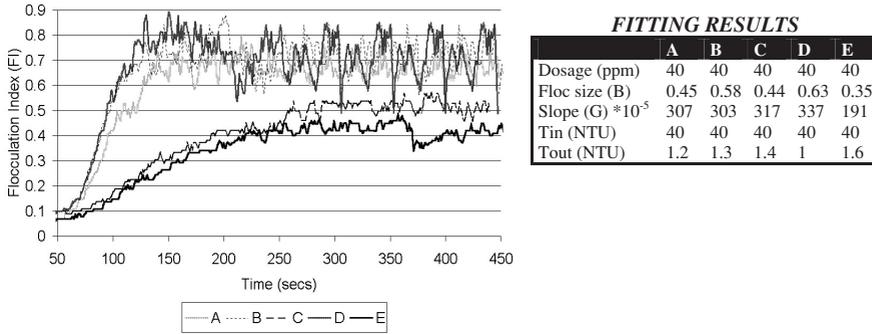


Figure 3 Effect of different coagulants under the same conditions of dosage (40 ppm) and of water quality

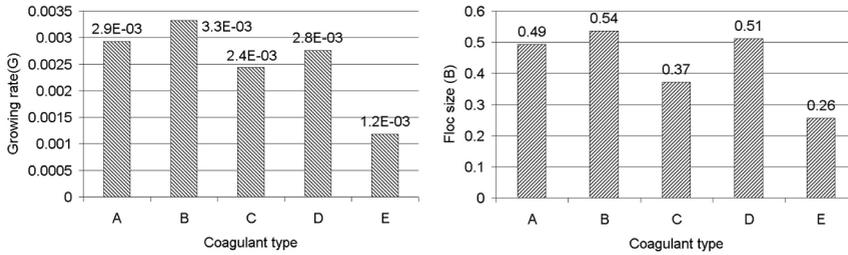


Figure 4 Medium value of growing rate and the floc size parameters

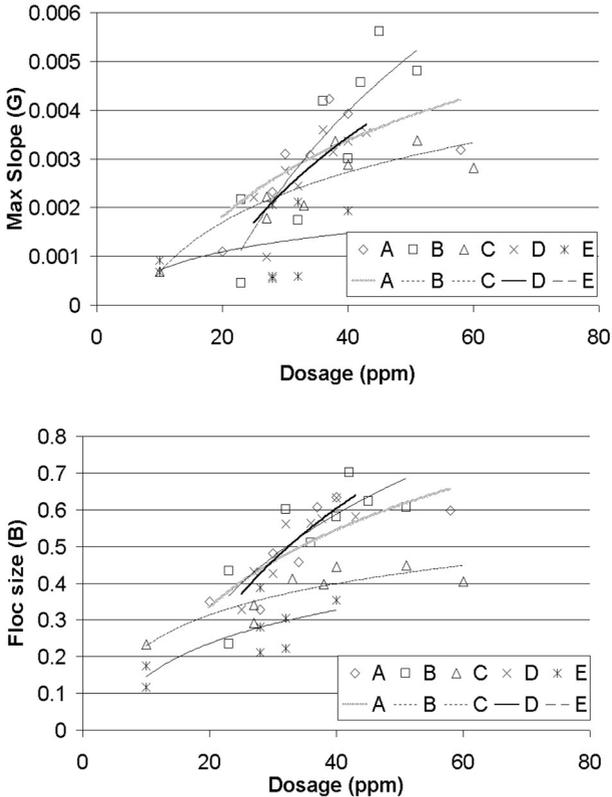


Figure 5 Growing rate and floc size parameters plotted against the reagent dosage

describe the trends. Some conclusions can be drawn. There is a clear distinction in two different groups: a group of coagulants that have a higher concentration of  $\text{OH}^-$  ions (A,B, and D) which allow bigger flocs and higher growth rate, and a group (C and E) that, even for high dosage, is not able to form flocs as big as the others. Then, as the dosage of the coagulant is increased, both the effects are less pronounced. Such properties could be helpful in determining the optimal dosage for every single coagulant. This result, obtained with a real suspension, confirms the conclusions made in previous work where a laboratory kaolin suspension was used (Gregory and Rossi, 2001).

#### Jar test and PDA2000 results comparison

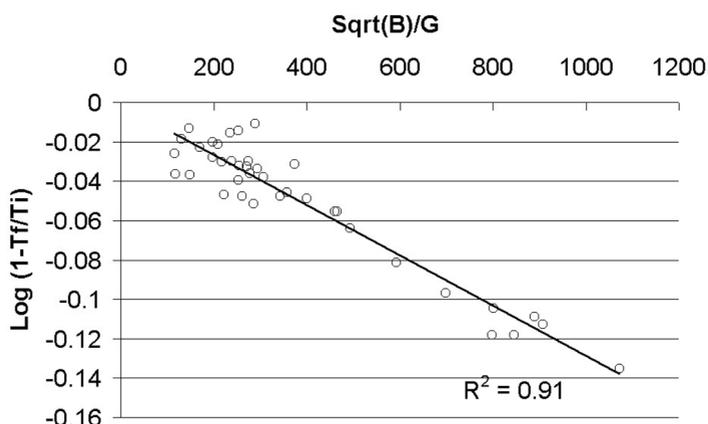
Results of jar tests, in terms of efficiency of removal turbidity, and the characteristics of flocs, in terms of growth rate and floc size, were then compared. A parameter that reassume the PDA2000 was defined as the rate of the square root of  $B$  (floc dimension) and the growth rate ( $G$ ). Of course there should be a correlation also between the floc size and the growth rate as bigger flocs are often coupled with a faster growth rate. Anyway a very good correlation was found between the square root of  $(B)/G$  and the log removal efficiency as shown in Figure 6.

Afterwards as the ratio value decreases (smaller flocs and faster growth rate) a better clarification process was obtained.

#### Conclusions

The following conclusions can be drawn from the results and analyses above.

1. The dosage and type of coagulant used for the process is not dependent on the mineral characteristics of the suspension but rather on the variability in the TSS (total solid suspension) concentration.
2. The application of the PDA2000 gives good results when real suspensions are used due to the non-dependence of their optical properties. However, as the size of the flocs obtained was out of range, the setting of the instrument had to be adjusted.
3. A strong correlation between the logarithmic of the removal efficiency of the turbidity and the ratio between the square root of  $B$  and  $G$  ( $\sqrt{B/G}$ ) was observed. This result was obtained with different initial suspensions, different types and dosages of coagulant and varying mixing parameters. As the ratio value decreases (smaller flocs and faster growth) a better clarification process was obtained. In the case of the Anconella treatment plant, this meant that the flocculation process had to be carried out with a strong stirring rate and that a coagulant with a fast growing rate had to be employed.



**Figure 6** Correlation between the logarithmic of the turbidity removal and the parameter  $\sqrt{B/G}$

4. The time for obtaining parameters from the PDA2000 analyses is less than that when jar-tests are used; in particular, the time to find optimal parameters can be reduced to one twentieth compared with a traditional jar-test.

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